

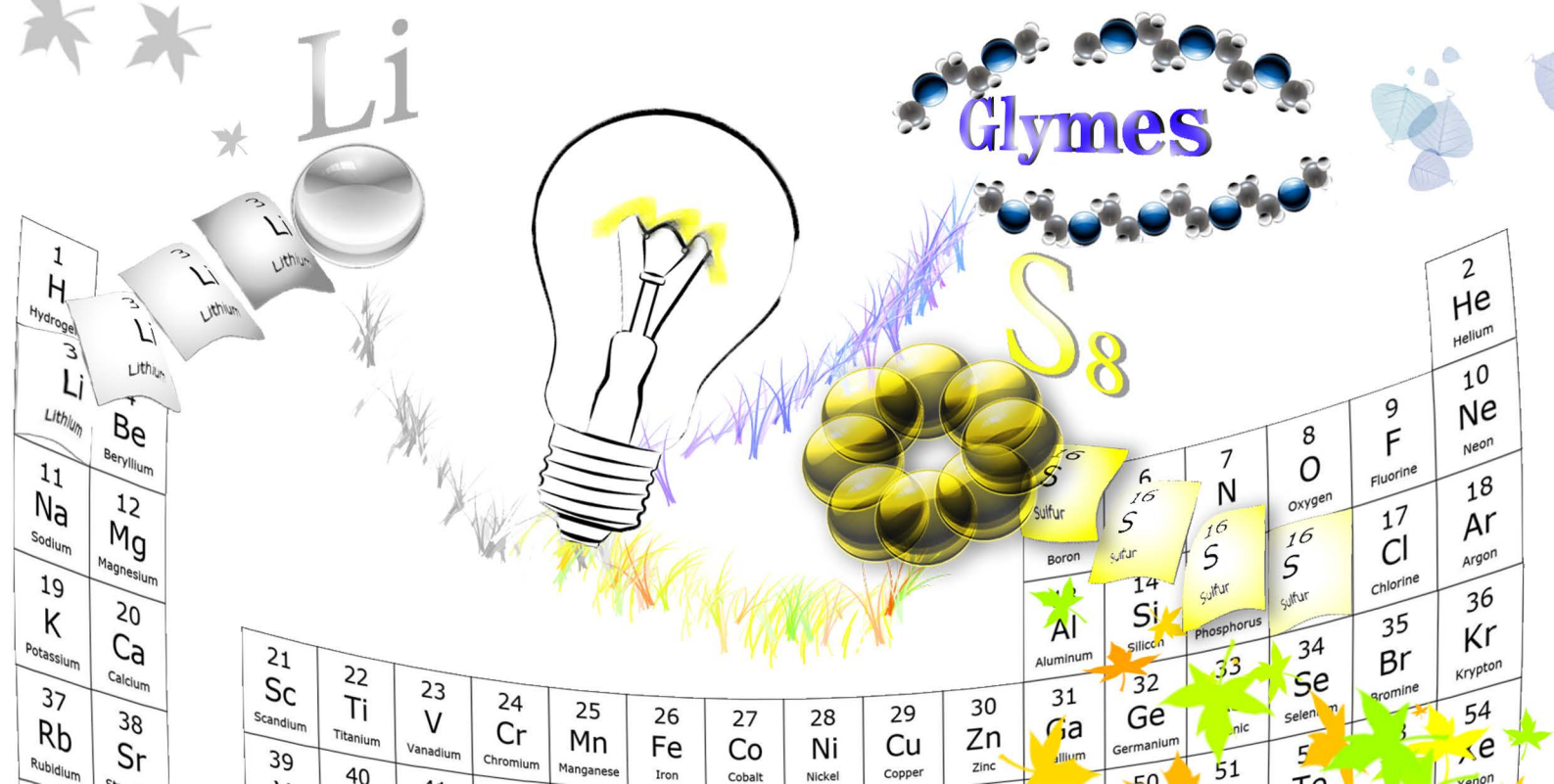
Glyme Electrolytes for the New Generation of Energy Storage Devices



Candidate: **Lorenzo Carbone**

Doctor of Philosophy in
Mathematical Models for Engineering, Electromagnetics and Nanosciences
curriculum "Materials Science"
Sapienza University of Rome
Department of Basic and Applied Science for Engineering
2017 cycle XXX

Thesis Supervisor: Professor Jusef Hassoun
Ph.D. course Coordinator: Professor Paola Loreti
Curriculum Supervisor: Professor Carlo Mariani



Index

Introduction	1
Lithium Batteries	1
Lithium Sulfur Processes	2
Electrolytes	4
Aim of the thesis	6
Experimental Pathway	6
 Glymes characterization	 8
¹⁷ O NMR study	9
¹⁷ O Experiment summary	9
DMC as Reference	9
Electrolytes Spectra	10
Salt and Solvent Interaction	11
Glymes N _(O) /N _(Li+) Ratio	13
 Glymes in Li/S cell	 15
Moving to battery application	15
Experiment Summary	15
Glymes-LiCF ₃ SO ₃ Properties	15
Shuttle Effect in Li-S Cell	19
Glymes Self Diffusion Activation Energy	20
LiNO ₃ Addition	20

LiNO₃ characterization **22**

LiNO₃ Effect **23**

Experiment Summary **23**

PEG500 LiCF₃SO₃ Properties **23**

LiNO₃ Free **25**

LiNO₃ Added Solution **26**

LiNO₃ effect - overview **27**

LiNO₃ Added Electrolyte a Deep Investigation **27**

TREGDME LiCF₃SO₃ Properties **28**

Bare and LiNO₃ added Solution Comparison **31**

LiNO₃ Voltammetry Study **34**

TREGDME-LiNO₃ Galvanostatic Cycling **36**

LiNO₃ passivation layer over LFP electrode **38**

Chapter Overview **38**

LiNO₃-Glymes electrolytes toward better performances **39**

Nonflammable Glyme **40**

Olivine Cathode for ether based electrolyte **42**

TEGDME LiCF₃SO₃ LiNO₃ Properties **43**

TEGDME Electrolyte and High Rate Cathodes **44**

Glymes and High Rate, Overview **48**

Glymes and Lithium Sulfur Battery

Carbon Composites for Sulfur

Cathode Characterization

Electrochemical processes

Galvanostatic Performances

Optimizing the Li/S Cell

Experiment summary

DEGDME LiTFSI Properties

LiNO₃ Addition to DEGDME LiTFSI

Morphology and Structure of the active material

Cyclic voltammetry study

Tuning the sulfur loading

Galvanostatic performances

Optimizing the Li/S overview

Glymes, Prospect & Future

PEO Membrane and Li/S cell

PEO LiTriflate Properties

Cathode- TGA & Morphology

Cathode with TEGDME

Cathode with PEO-LiTriflate solid electrolyte

From S and PEO-Membrane to Li₂S and PEO-Binder	72
The Li ₂ S-C-PEO electrode	73
Structural and morphological study	74
DOL-DME-LiF ₃ SO ₃ Properties	74
LiNO ₃ -addition to the electrolyte	75
Electrochemical process of Li ₂ S-C-PEO electrode	76
Cycling performances of Li ₂ S-C-PEO electrode	79
Glyme Electrolytes and Sodium	81
Sodium Glymes Properties	82
Sodium and Glymes in Sulfur Cell	86
Glyme electrolyte and Lithium Oxygen battery	88
TEGDME-LiTFSI Properties	89
TEGDME-LiTFSI in Li/O ₂ Cell	91
Comparison overview	95
Electrolyte	96
Lithium Cells	101
Conclusion	105
Acknowledgement	106
List of Articles	107
References	109
Experimental Section	126

Introduction

Lithium Batteries

The lithium-ion battery, nowadays the most popular and efficient energy storage system, has almost achieved the maximum performance expected from its theoretical potentiality, i.e., an energy density of about 250 Wh kg⁻¹. However, this value may be insufficient for emerging applications such as all-electric vehicles, which requires high energy storage in order to extend the driving range of the car between charges². Among the various systems proposed to match this challenging target, lithium sulfur and lithium air batteries represent the most promising solutions. These emerging systems, suitable for achieving an energy density higher than 400 Wh kg⁻¹, have the additional bonuses of low expected cost and modest environmental impact³. Recent progress has led to satisfactory performances with particular relevance for lithium sulfur battery, while much efforts are still required to make these promising systems suitable for practical application. Room temperature lithium-sulfur battery based on organic electrolytes of practical interest has been developed only recently by replacing carbonate-based electrolytes, i.e., not-suitable media for the electrochemical reaction of sulfur with lithium, by new classes of solutions.⁴ The new electrolytes, mainly based on ether chains⁵, glymes⁶, polyethylene oxide⁶ and solid, glass-type media⁷, have triggered a remarkable improvement of Li/S battery. However, additional efforts have been needed during the last years

to address various problems affecting the cell, such as the short cycle life, cell polarization⁸ and the shuttle reactions due the dissolution of polysulfide intermediates in the electrolyte during cell operation⁹. Indeed, the polysulfide shuttle effect is a central challenge in the development of a stable system. This phenomenon is an electrochemical short-circuit due to the migration of the polysulfide species between the electrodes along the charge processes, leading to active material loss, a critical reduction of coulombic efficiency and a fast capacity fading.¹⁰ These issues have been recently mitigated and remarkably addressed by tuning the sulfur cathode morphology^{11,12}, chemical nature¹³, the electrolyte composition¹⁴ and characteristics, as well as by setting-up a proper cell configuration¹⁵. These efforts have led to lithium sulfur cell of remarkable performances, comparable to lithium-ion battery, with the additional bonus of the high energy density, thus suggesting this system well suitable for employment in the emerging applications¹⁶. The clear understating of the lithium-sulfur electrochemistry is needed to toward the issues and challenges of this promising innovation, hence a briefly overview of the lithium sulfur electrochemical processes from recent literature as well as a clarification on the use of a new class of electrolytes for this emerging system is following presented.

Lithium Sulfur Processes

Lithium-sulfur electrochemical reaction proceeds at about 2.1V vs. Li^+/Li by the formation of various intermediates of a general formula of Li_2S_x , where x ranges from 8 to 2.^{17,18} The overall process, i.e., $16\text{Li} + \text{S}_8 \leftrightarrow 8\text{Li}_2\text{S}$, delivers a specific capacity of about 1700 mAh g^{-1} as referred to the pure sulfur mass which is reflected into a theoretical energy density as high as 3600 Wh kg^{-1} .¹⁹ However, the intermediate species, i.e. polysulfides, are extremely soluble in organic liquids and they may leading to battery failure.¹⁰ A direct identification and quantification of the reaction species formed during discharge/charge cyclin of the lithium-sulfur battery may be performed by *in-situ* ^7Li NMR technique which provides real time, semi-quantitative information related to the

temporal evolution of lithium polysulfide allotropes.²⁰ Figure 1(A-C)²⁰ reports the study of a cylindrical micro-battery used to probe the transient electrochemical and chemical reactions occurring during the cycling of a Li-S system. The in-situ experiments provide information about the reaction sequences and reveal a reaction pathway composed of mixed species rather than discrete step-by-step reactions. The large line shifts and line broadening noted suggest a complex chemical environment, and potentially the important role of intermediate species. In particular, the study reveals that the polysulfide redox reactions involve charged free radicals as intermediate species that are difficult to detect in ex situ NMR studies²¹. Additionally, the study uncovers information about the ^7Li chemical environments during the electrochemical and parasitic reactions on the Li metal anode²². For the an-

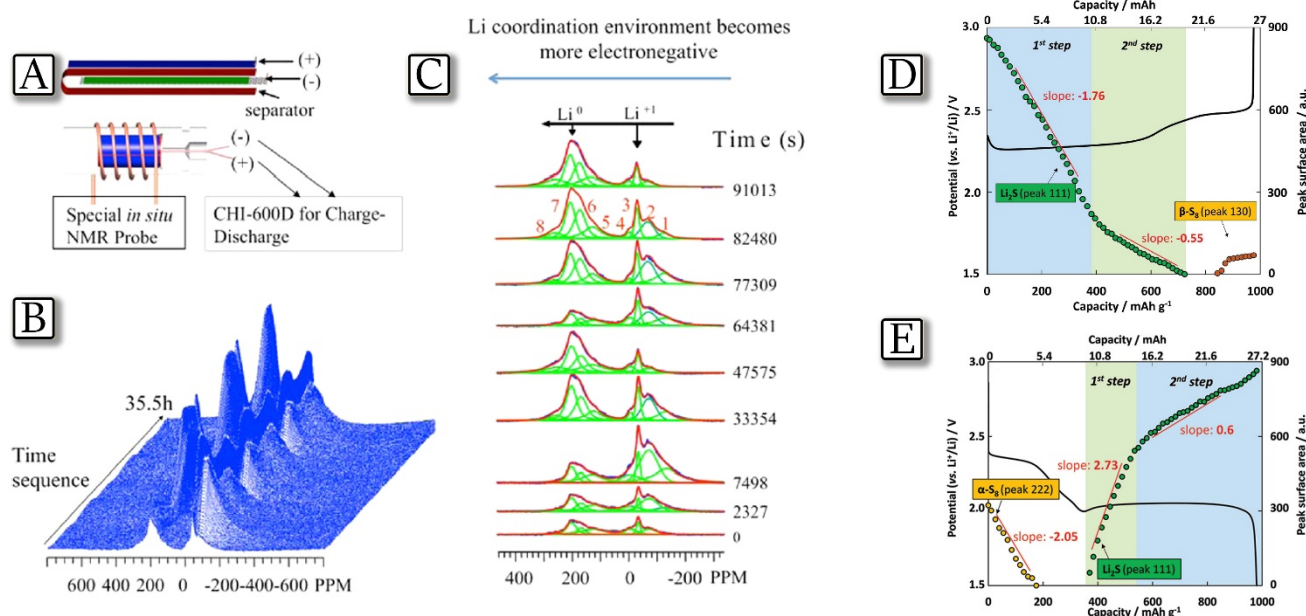


Figure 1 In situ NMR probe and the acquired spectra as a function of discharge/charge time. (A) Cylindrical micro-battery, fitted into the in-situ NMR probe. (B) Stacked plot of the in situ ^7Li NMR spectra in a functioning Li-S cell vs time during discharge/charge. (C) Major peaks of interest within the range of -260 to 300 ppm extracted at different times by fitting the spectra.²⁰ (D) Investigation of the Li_2S consumption during the charge process and (E) Proposed mechanism for $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ formation upon discharge. Integrated surface area of (111) reflection as a function of capacity, superimposed with the experimentally obtained galvanostatic cycling profile.²³

ode side, the continuous evolution of the Li microstructure, SEI accumulation, and polysulfide contamination are simultaneously captured by ^7Li in situ NMR, which are correlated with the Li-S cell degradation mechanisms. A quantitative evaluation of Li_2S formation and consumption upon cycling may be also performed by means of XRD as reported in Figure 1(D-E)²³. The figure, obtained from a pouch Li/S cell using nonwoven carbon sheet as a current collector and relatively high sulfur loading, with a controlled electrolyte amount, shows the expected voltage profile, and charge/discharge capacities of 980 and 976 mAhg^{-1} , respectively. The corresponding XRD pattern evolution indicates that, as the discharge proceeds the peak intensities of the elemental orthorhombic $\alpha\text{-S}_8$ linearly decrease as a function of capacity. They vanish at the end of the first discharge plateau, proving

a complete reduction of sulfur. This linear evolution can be associated with a one-step electrochemical process, based on the reduction reaction of S_8 to S_8^{2-} . Indeed, a twostep process occurs, where crystalline Li_2S is initially formed alone²⁴. Afterward, the specificity of the reduction reaction clearly decreases due to the complete coverage of the available conductive surface. The number of electrons exchanged is coherent with the formation of intermediate species such as Li_2S_2 . During the lower discharge plateau, 24% of S_4^{2-} is involved in the formation of Li_2S whereas 72% of S_4^{2-} is assumed to be converted into Li_2S_2 . During the following charge, Li_2S is converted into a soluble polysulfide species in a two-step oxidation process, however, in a different reaction pathway as during discharge. The discharge/charge pathways of Li/S cell may be also directly observed by monitoring

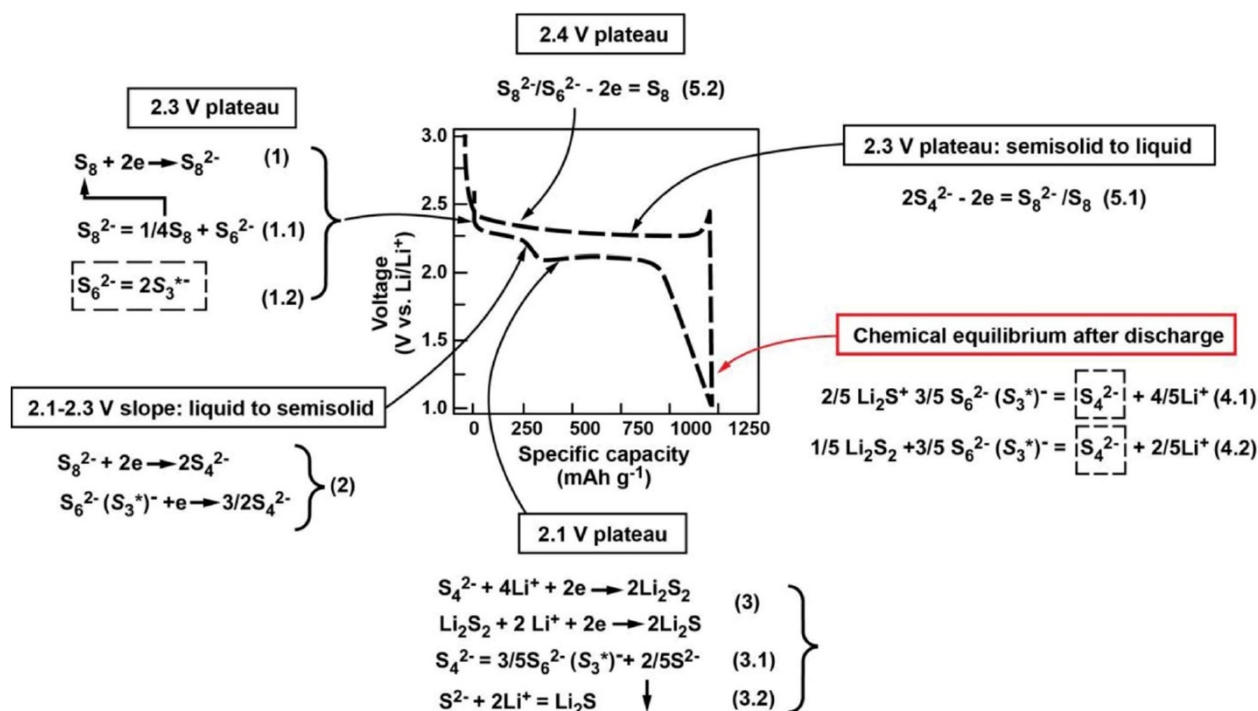


Figure 2 Proposed reaction mechanism for Li-S batteries during cycling. The equilibria between S_6^{2-} and $\text{s}^{*-}3$ always exists and shifts at different potentials. S_6^{2-} prefers to stay at relatively high potential (> 2.1 V) while $\text{s}^{*-}3$ is the preferred form at low potential (≤ 2.1 V). Different reaction pathways are suggested for discharge and charge processes. The Li-S cell was tested at C/5 rate between 1 V and 3 V in typical button cells.

the sulfur radicals using in situ electron paramagnetic resonance (EPR) technique²⁵. Figure 2²⁵ reveals that the chemical and electrochemical reactions in Li-S cell are driving each other to proceed through sulfur radicals, leading to two completely different reaction pathways during discharge and charge. The different reaction pathways for the discharge and charge processes of Li-S battery match with their voltage profiles and help to describe the origin of the high over potential of pure Li₂S. In situ EPR identifies S₃^{•-} throughout the whole cycling, thus indicating the temporal equilibrium among different polysulfides instead of producing a single polysulfide component at each different potential. The EPR study also suggests that the electrolyte selection for Li-S system should consider the reactivity of sulfur radicals to enable the long-term cycling stability of the cells²⁶.

Electrolytes

In its most common design, a lithium battery employs a carbonate-based liquid electrolyte, a metal-oxide cathode in combination with a highly electropositive lithium metal anode, thus allowing a correspondingly high energy density.²⁷ However, the large-scale deployment and acceptance of this powerful system has been hindered by safety issues associated with dendrite formation during cell charge, leading to internal short circuit, heat generation and flammability or, in rare cases, explosion.²⁸ This relevant inconvenient has been mitigated by the introduction of the lithium-ion battery, i.e., a system in which the lithium metal is replaced by a graphite intercalation anode.²⁹ However, this battery revealed a lower energy density with respect to lithium metal-based one, due to the

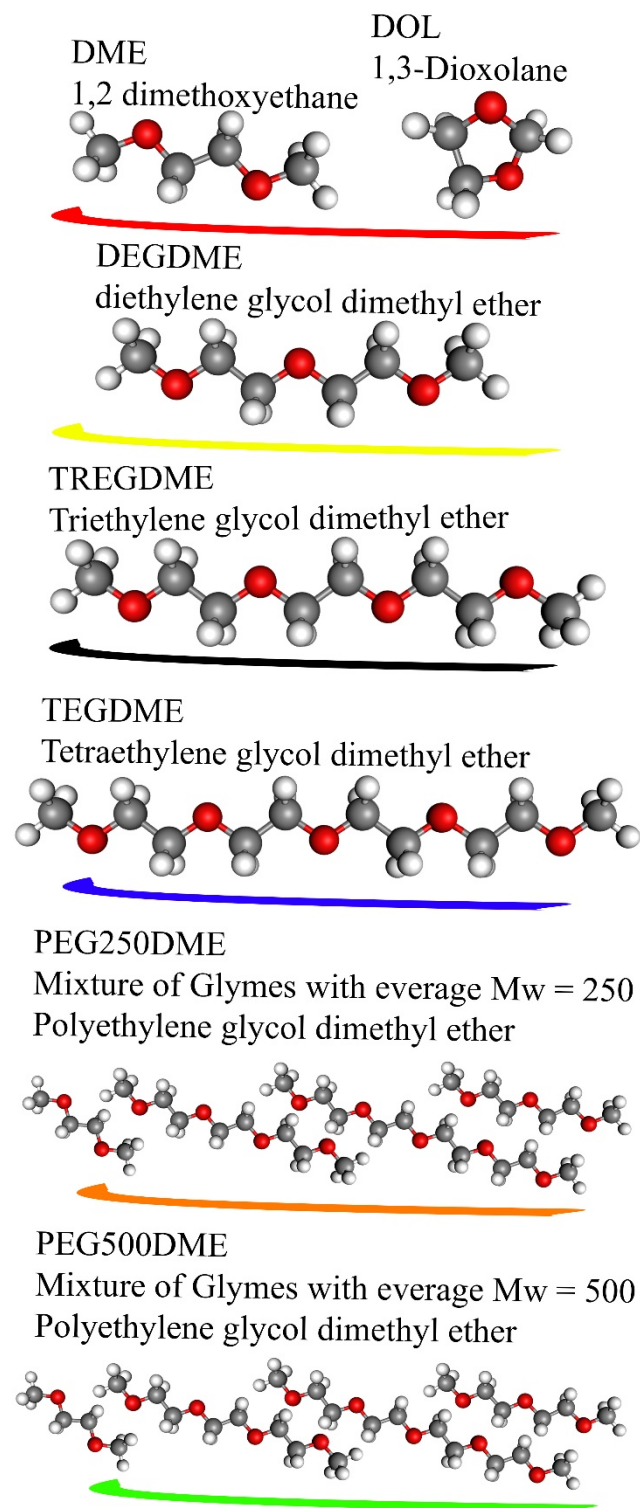


Table 1 Scheme of the ether based electrolyte employed in the exposed experiments. Red balls = oxygens, grey balls = carbon and white balls = hydrogen.

higher working potential of graphite (0.2V instead of 0V vs. Li/Li+) and to the lower specific capacity (372 mAh g⁻¹ instead of 3800 mAh g⁻¹, respectively). As previously reported, increased energy at the cathode side has been achieved by developing efficient lithium-sulfur batteries.³⁰⁻³² Indeed, the

improvement of sulfur-based electrodes, characterized by capacity largely exceeding the value associated with the common cathodes triggered renewed interest on the lithium metal anode.^{33,34} The use of polymer electrolyte, such as PEO (polyethylene oxide), can allow a safe use of the lithium metal anode, however only at temperature exceeding 70°C.^{35,36} The addition of ceramics to the polymer electrolyte revealed increased performances in terms of conductivity and lithium transference number at the lower temperatures, however further improvements are still required in order to allow proper operation of these electrolytes at room temperature³⁷. A valid alternative to solid PEO polymer, advantageously showing suitable room temperature conductivity and comparable safety content, is represented by end-capped ethers, based on $-(\text{OCH}_2\text{CH}_2)_n-$ groups of short chain configuration, such as ethylene glycol dimethyl ether as shown in Table 1^{5,38,39}. Despite their promise in terms of suitable characteristics for application in lithium ion battery^{40,41}, such as high solvation ability for salt dissociation, as well as high electron donation ability and relatively strong Lewis basicity due to the lone pair of oxygen atoms in their structures these ethers still suffer from issues related to the stability of lithium metal-electrolyte interphase, leading to resistance increase, cell polarization⁴², uncontrolled dendritic lithium growth²² as well as electrolyte decomposition in lithium sulfur batteries⁴³. However these issues, can be efficiently suppressed by the formation of a stable and uniform solid electrolyte interphase layer⁴⁴. Several film-forming additives have been proposed to improve the anode interphase in organic electrolytes, such as vinylene carbonate (VC)⁴⁵ and fluoroethylene

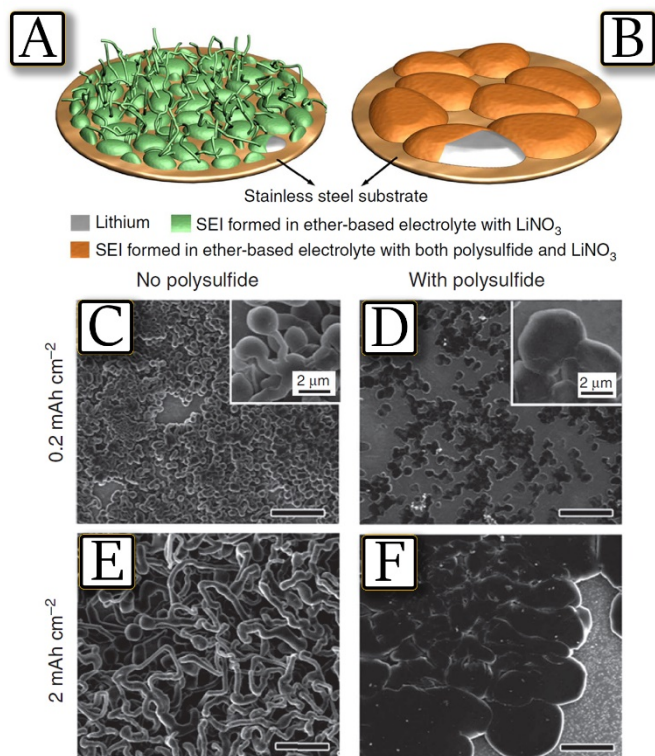


Figure 3 Schematic illustration showing the morphology difference of lithium deposited on the stainless-steel substrate in the two electrolytes (both contain lithium nitrate), but (A) without lithium polysulfide (B) containing lithium polysulfide. SEM images of lithium metal deposited onto bare stainless steel substrate (the edge region of the whole deposition area) in the electrolyte (C, E) with the addition of only LiNO₃ (1 wt%) and (D, F) with the addition of both Li₂S₈ (0.18M) and LiNO₃ (1 wt%) at a current density of 2mA cm⁻² and deposition capacities of 0.2 and 2mAh cm⁻², respectively. Scale bars, 20 μm.

carbonate (FEC)⁴⁶. However, these additives revealed suitable properties mainly in carbonate-based solvents. Among the various additives, lithium nitrate (LiNO₃) evidenced the most favorable effect in ether-based electrolyte, and, in particular, in cells using lithium metal anode^{43,47,48}. However the synergetic effect of both lithium polysulfide and lithium nitrate as additives in ether-based electrolyte⁴⁹ may overcome stability issues performing a stable solid electrolyte interface. Indeed, Figure 3(A)⁴⁹ schematizes how lithium dendrite growth can be effectively suppressed via manipulating the chemical reactions of lithium, lithium polysulfide and LiNO₃. By controlling the concentration of polysulfide and LiNO₃ in the electrolyte, a stable

and uniform SEI can be formed on the lithium surface, which greatly minimizes electrolyte decomposition and prevents dendrite growth^{48,50}. The observations, made at the edge regions of the deposition area where dendrite growth is most exaggerated due to the absence of physical constraint, revealed no lithium dendrites formation at practical currents and Coulombic efficiency and cycle life of the lithium metal cells significantly improved.

Aim of the thesis

The increasing demand of portable energy in terms of cycle life for electronic devices such as smartphones, tablets and computers or the high stability required for medical application and the high energy density for smart energy grids and electrified transport require a breakthrough in performance, lower cost, safety and environmental compatibility. Indeed, the conventional energy storage devices are characterized by limited specific capacity and energy density due to the intrinsically properties of the cathodic active materials *i.e.* LiCoO₂ with specific capacity of 150 mAhg⁻¹ and a theoretical energy density of 550 Wh kg⁻¹. Therefore, the deep investigation and optimization of new classes of electrodes proposed in this work of thesis, may shed light on the possible candidates for a new generation of energy storage devices characterized by high energy and environmental compatibility. Furthermore, one of main topic of this work is the study of new classes of electrolytes characterized by low flammability and high ion mobility properties in order to ensure high performances and safety level.

Experimental pathway

In this scenario, my work focused on the preparation and characterization of ether based electrolytes and a deep investigation of the LiNO₃ effects in order to make a suitable electrolyte for lithium batteries. Moreover, the synthesis and characterization of sulfur cathodes and cell optimization, were a crucial aspect of my work reflecting further innovation such as solid-state sulfur battery, sodium-sulfur battery and finally lithium-air battery. The characterization of two series of glyme-based electrolytes, with lithiumtrifluoromethanesulfonate (LiTriflate) or lithium-bis-(trifluoromethanesulfonyl)-imide (LiTFSI) in six glymes was performed by natural abundance oxygen-17 (¹⁷O) NMR spectroscopy to obtain an overview on the ion-solvent and ion-interaction properties of the electrolyte.⁵¹ Successively, the glymes-LiTriflate series was used in lithium-sulfur battery in order to obtain a performances comparison through electrolytes and cells characterization. The tests revealed the presence of the shuttle effect by using glymes with short chain such as DME, DOL:DME mixture and DEGDME.⁴ The problem was solved by adding LiNO₃ salt to the solution and a further study was performed to understand the LiNO₃ effect. Initially, the activation and the relevant stabilization effect of the LiNO₃ salt was evaluated in a lithium metal cell⁵² using a commercial cathode, the lithium iron phosphate LiFePO₄ (the full characterization and study of the olivine cathodes materials is beyond the scope of this work and will not be reported in the further paragraphs) the PEG500DME-LiTriflate-LiNO₃ was used as electrolyte. The battery delivered a stable capacity of 150mAhg⁻¹ with a flat working voltage of 3.5 V, thus leading to a theoretical energy density referred to the cathode of

520 Wh kg⁻¹. The promising results triggered the interest on glymes electrolyte as suitable media for higher voltage cathode with faster current rate. Therefore, a deep investigation on bare electrolyte and LiNO₃ added solution was performed in terms of thermal and rheological characteristics, transport properties of the dissolved species by self-diffusion coefficients, lithium transference numbers, ionic conductivity, ion association degree and electrochemical impedance spectroscopy. Furthermore, the formation of a stable interfaces at the electrodes surface in Li/LiCF₃SO₃-LiNO₃-TREGDME/LiFePO₄ cell was clearly evidenced by cyclic voltammetry, impedance spectroscopy, and ex situ scanning electron microscopy.⁵³ Finally, the nonflammable TEGDME with LiTriflate and LiNO₃ was tested in a lithium metal cell with LiFePO₄ cathode at high current rate and within LiMn_{0.5}Fe_{0.5}PO₄ cathode. The Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cell operates at 3.5 V with capacity ranging from 150 mAh g⁻¹ at C/10 to 110 mAh g⁻¹ at 2C, while the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFe_{0.5}Mn_{0.5}PO₄ cell performs following two plateaus at 4.1 V and 3.5 V with capacity ranging from 160 mAh g⁻¹ at C/10 to 75 mAh g⁻¹ at 2C.⁵⁴ Hence, the results demonstrated the suitability of ether based electrolytes for high performances lithium battery such as the lithium sulphur system. Therefore, a comparison of carbon composite high energy carbon sulfur cathode was performed in order to optimize the carbon morphology. Carbon of various natures, namely, graphite,

mesocarbon microbeads, and multi-walled carbon nanotubes, were characterized in terms of SEM and XRD, cyclic voltammetry and galvanostatic cycling in lithium cells. The best lithium-sulfur composite achieves a capacity higher than 500 mAhg⁻¹ over 140 cycles with no sign of dendrite formation or failure.⁵⁵ However, a further optimization of this system was performed and the lithium/sulfur cell using the S-MWCNTs composite coated on a carbon cloth and the DEGDME-LiTFSI-LiNO₃ electrolyte Li/S cell was studied by advantageously increasing the sulfur loading. The cell with optimized active mass loading, shows satisfactory rate capability, and a very stable specific capacity of about 1000 mAhg⁻¹ delivered with coulombic efficiency approaching 100%. The outstanding properties of the electrolyte, its low-flammability, the simple synthesis procedure of the cathode as well as the remarkable performance of the cell suggest the configuration adopted as viable solution for high energy, safe and low-cost lithium sulfur battery. In the end, will be presented a prospect of the near future innovation such as the use of solid electrolyte system applied to lithium sulfur cell by using poly ethylene oxide PEO,⁹ the performances of a sodium-sulfur cell⁵⁶ and finally, a lithium-air battery prototype with glyme electrolytes. All the tests were performed at least two times in order to obtain a clear and reproducible data.

Glymes characterization

The following paragraphs report the natural abundance ^{17}O NMR study to probe the lithium ion solvation behavior of electrolytes based on the series of glyme solvents of various ether chain length, beginning from the monomeric units DME, to polyethylene glycol dimethyl ethers with molecular weight 500 (PEG500), containing LiTriflate or LiTFSI. The NMR study is carried out in order to better understand the behavior of these two different salts in various glyme-based electrolytes, by charactering the chemical shift and the linewidth of oxygen-17 nucleus in both salt anions, solvents, and in the corresponding solutions. Successively, will be presented a comparison of the LiTriflate glymes series investigated in terms of thermal properties by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry), transport properties focusing on ion conductivity evaluated by impedance spectroscopy and lithium transference number calculated by the self-diffusion coefficients obtained by PFG-NMR measurements. Furthermore, the self-diffusion activation energy of the ether based electrolyte were presented and discussed. The study of the lithium/electrolyte interface in static and dynamic condition were performed by EIS and galvanostatic tests respectively. The electrochemical window stability was defined by linear sweep voltammetry. Finally, the glymes electrolyte were evaluated in lithium sulfur cell with a sulfur carbon composite cathode material prepared by using the high energy ball milling.



¹⁷O NMR study

¹⁷O Experiment summary

The lithium solvation behavior of the ether based electrolyte DME, DEGDME, TREGDME, TEGDME, PEG250 and PEG500 with lithium trifluoromethanesulfonate (LiTriflate) or lithium-bis-(trifluoromethanesulfonyl)-imide (LiTFSI) was characterized using natural abundance oxygen-17 (¹⁷O) NMR spectroscopy. The effect of salt addition on chemical shift is observed by comparing the ¹⁷O NMR spectra of electrolytes and their corresponding neat solvents. The study reveals a more pronounced effect of the salt addition on the chemical shift of ether oxygens in respect to terminal oxygens of glymes, thus suggesting a preferential coordination of Li⁺ with the ether oxygens. The ¹⁷O NMR data indicate a limited chemical shift changes of longer glymes with respect to the shorter ones due to the increased number of ether oxygens coordinating each Li⁺ in the electrolytes. In addition, the trend of anion oxygen chemical shift, particularly for Triflate⁻ anion, suggests an effect of the chain length on the ion association degree. In summary, the results illustrate the sensitivity of ¹⁷O NMR to subtle changes in the ion-solvent and ion-ion interactions.

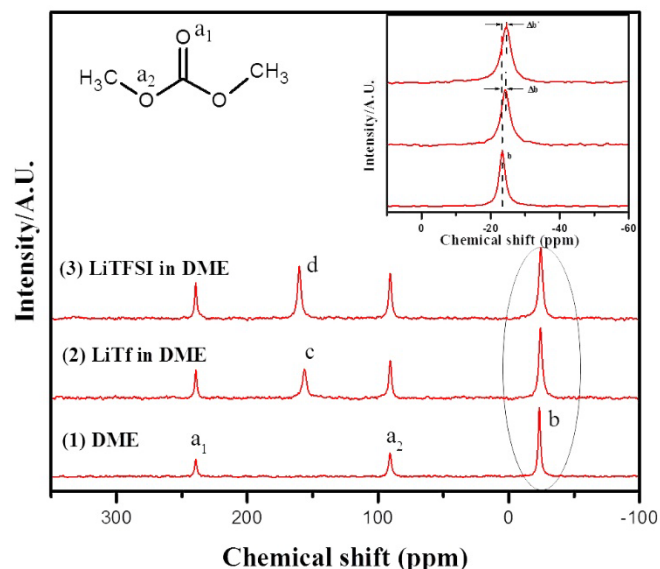


Figure 4 ¹⁷O NMR spectra of DME electrolyte with DMC reference addition. (1. DME neat solvent; 2. LiTriflate in DME; 3. LiTFSI in DME) – (a₁-a₂) DMC oxygen (b) DME oxygen, (c) LiTf oxygen, (d) LiTFSI oxygen

DMC as Reference

Figure 4 shows the ¹⁷O NMR spectra of 1 m LiTriflate solution and 1 m LiTFSI solution in DME mixture, along with the corresponding neat DME solvent in the absence of lithium salt. The DMC reference shows two ¹⁷O resonances located at 239.4 ppm (carbonyl ¹⁷O, a₁) and 90.5 ppm (methoxy ¹⁷O, a₂) respectively, i.e., in convenient positions since not overlapping the resonances of Triflate⁻, TFSI⁻ and glyme solvents. The addition of LiTriflate salt and LiTFSI salt leads to further ¹⁷O resonances observed at around 156.3 ppm and 160 ppm, respectively, in the DME solutions. Methoxy ¹⁷O resonances of DME experience an upfield shift by adding the LiTriflate and LiTFSI salts, as will be discussed later. It is noteworthy that the relative

Experimental section: Sample preparation

All reagents were purchased from Sigma Aldrich. Electrolyte solutions were prepared by dissolving 1 mol of LiTf or LiTFSI in 1 kg of either in DME, DEGDME, TREGDME, TEGDME, PEG250, or PEG500. The neat solvents without salts as standards were also set aside for comparison. All solvents were dried under molecular sieves (5Å) for several days until the water content was under 10 ppm, as verified by 831 Karl Fisher Coulometer METROHM. All the salts were dried under vacuum for 24 hours at 100°C before solution preparation.

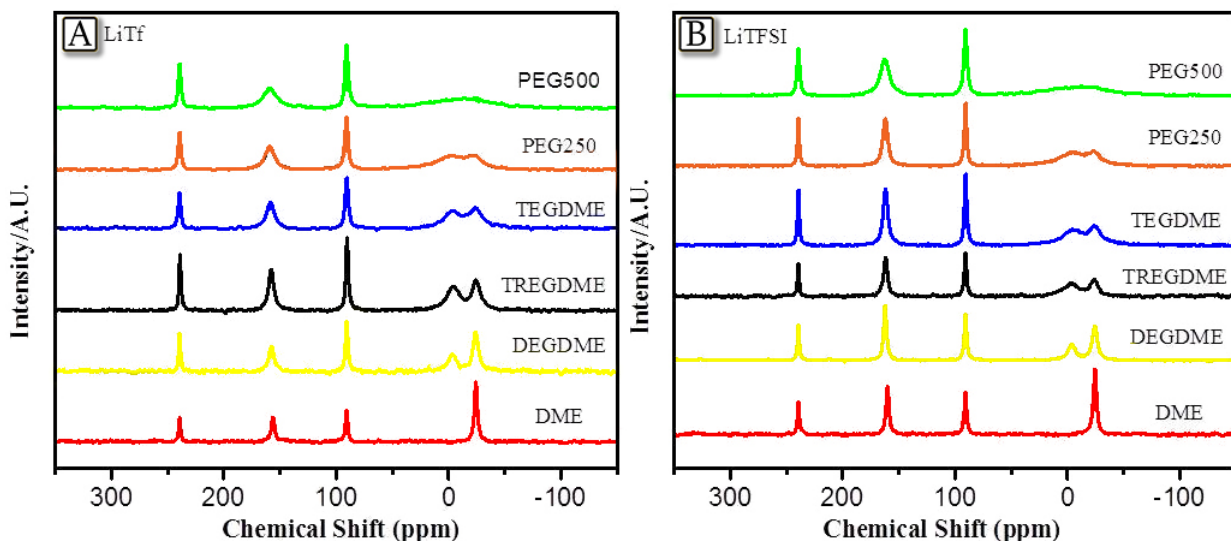


Figure 5 ^{17}O NMR spectra of all electrolytes (a. LiTf series; b. LiTFSI series).

signal intensities of ^{17}O in DMC and glyme electrolytes directly depends on the amount of sample in the NMR reference tube and insert.

Electrolytes Spectra

^{17}O NMR experiments were performed on LiTri-flate and LiTFSI electrolyte solutions with various glymes differing by chain length. Stacked ^{17}O NMR spectra are displayed in Fig.5 (a) for LiTri-flate series and Fig.5 (b) for LiTFSI series, respectively. The ^{17}O resonances of glyme oxygen are located between 0 ppm and -25 ppm. Besides DME,

in which there is only one ^{17}O nucleus environment, the ^{17}O NMR spectra of longer chain glymes (DEGDME to PEG500) show two ^{17}O resonances. The more positive resonance is the average ^{17}O nuclear chemical shift of the oxygen located in the middle of the glyme chain, which is defined as R- ^{17}O -R' group, while the more negative chemical shift is associated to the oxygen nucleus at the terminal, i.e., ^{17}O -CH₃. The linewidth of ether ^{17}O increases from short chain glyme to long chain glyme, as indeed expected by the large increase of the oxygen atoms content, becoming particularly

Experimental section: NMR Characterization

For ^{17}O NMR characterization, the chemical shift reference dimethyl carbonate (DMC) was placed in a 4 mm borosilicate tube which was inserted into a 5 mm NMR borosilicate tube containing the electrolyte solution or neat solvent. This coaxial arrangement yields convenient a reference spectrum while preventing contact between the reference and the sample. All sample handling procedures were performed in an Ar-filled glovebox, and inserts and outer tubes were all sealed under Ar. The ^{17}O NMR experiments were acquired on a 400 SB Bruker Avance III spectrometer with a broadband probe working at ^{17}O frequency of 54.25 MHz. All experiments were performed at 60°C in order to improve spectra resolution and each spectrum was collected between 32k to 128k scans for good Signal/Noise ratio. The average number of (OCH₂CH₂)- units (n) in PEG250 (M.W. 250 g/mol) and PEG500 (M.W. 500 g/mol) molecule, with formula CH₃(CH₂CH₂O)_nOCH₃, has been estimated as n ≈ 4.6 and 10.3, respectively, by using Eq. 1:

$$(2 + 2n) * 12.011 \frac{\text{g}}{\text{mol}} + (6 + 4n) * 1.008 \frac{\text{g}}{\text{mol}} + (n + 1) * 15.999 \frac{\text{g}}{\text{mol}} = M_{\text{ave}} \quad (1)$$

Where M_{ave} is the average of molecular weight of PEG250 or PEG500. $(N_{(\text{O})})$ to $\text{Li}^+ (N_{(\text{Li}^+)})$ molecular ratio in chain of solvent for both LiTf and LiTFSI electrolyte series has been calculated by using Eq.2:

$$\frac{N_{(\text{O})}}{N_{(\text{Li}^+)}} = \frac{\frac{1000\text{g}}{M_{\text{ave}}} * N_{(\text{O})}}{n_{\text{Li}^+}} \quad (2)$$

the salt concentration is 1 mol kg⁻¹; n_{Li^+} is 1 mol; m_{elec} is 1 kg, and $N_{(\text{O})}$ is n+1. $N_{(\text{Oxygen in R-O-R'})}$ always equal to $N_{(\text{O})}^{-2}$.

severe in PEG500 electrolyte, and making it difficult to resolve in the two ^{17}O resonances. The interaction between salt and solvent may be another source of glyme ^{17}O NMR line broadening, due to the reduction of the solvent molecular mobility (i.e., the same phenomenon that leads to an increase of the macroscopic viscosity). The linewidth data are listed in Table.2. Fig.6 shows a detailed comparison of ^{17}O resonance corresponding to the glyme oxygen of electrolytes prepared using each solvent with either LiTriflate and LiTFSI salts, along with that of the pure solvent, magnified in the low chemical shift region. The figure remarks the above-mentioned line broadening by adding the Li salt in the glyme compared to neat solvent. The smallest solvent molecule (DME) and corresponding electrolytes show a very clear, relatively sharp ^{17}O resonance. Increasing the ether chain length from DEGDME to PEG500 leads to signal bordering, however neat solvents still show two clear ^{17}O resonances, even in the case of the glyme with largest molecular mass (PEG500). All ^{17}O NMR resonance position data are listed in Table 3.

Salt and Solvent Interaction

The comparison of ^{17}O NMR chemical shift between each electrolyte and its corresponding pure solvent, plotted in Fig. 7, may actually quantify the interaction between the solvent and the salt, that is

most likely dominated by the Li^+ ions. However, the aforementioned broadness of ^{17}O linewidths in PEG500 electrolyte solution leads to excessive uncertainty in determining its chemical shift and limits the data of Fig. 7 to PEG250 glyme. The bar diagrams of Fig. 7 reveal much larger signal shift of the R-O-R' group in respect to -O-CH₃ group by adding the LiTriflate and LiTFSI salts into the glyme solvents, while the ^{17}O chemical shifts of glymes exhibit a decreasing trend in both -O-CH₃ and R-O-R' group by increasing the chain length. Local electron density dominates the shielding of a specific nucleus. To investigate the behavior of oxygen nucleus a series of aliphatic ethers with variable chain length was studied by measuring the chemical shift of ^{17}O nuclei and calculating the net (nuclear minus electronic) charges on the nucleus⁵⁷. An evaluation of the atomic net charge q_o of oxygen has been performed by increasing the electron-releasing ability of the substituents, thus enhancing the electron withdrawal of oxygen due to its electron enrichment. The linear correlation between ^{17}O NMR chemical shift (δ_o)^{58–60} and net charge variation (Δq_o)⁶¹ may be performed by an extensive geometry and exponent optimization for various ethers, such as dimethyl-, diethyl-, and diisopropyl-ethers.⁵⁷ The correction between Δq_o and chemical shift δ_o is reported in equation (3):

$$\Delta q_o = -0.267\Delta\delta_o \quad (3)$$

Table 2 ^{17}O NMR linewidth data of pure solvents and electrolytes.

Solvent name	Linewidth of ^{17}O in R-O-R' group(Hz)			Linewidth of ^{17}O in O-CH ₃ group(Hz)			Linewidth of ^{17}O in LiTf(Hz)	Linewidth of ^{17}O in LiTFSI (Hz)
	pure solvent	LiTf Electrolytes	LiTFSI Electrolytes	pure solvent	LiTf Electrolytes	LiTFSI Electrolytes		
DME				2.1	3.0	3.2	4.1	2.8
DEGDME	4.8	7.4	7.7	2.9	5.0	4.8	5.2	3.0
TREGDME	6.8	11.8	12.1	3.9	8.6	6.8	5.8	3.7
TEGDME	8.4	13.9	17.1	4.6	11.2	12.0	6.6	5.5
PEG250	11.5	25.8	22.6	5.9	13.8	13.8	7.4	6.2
PEG500	22.6	45.3	33.9	7.7	23.6	23.3	13.0	8.9

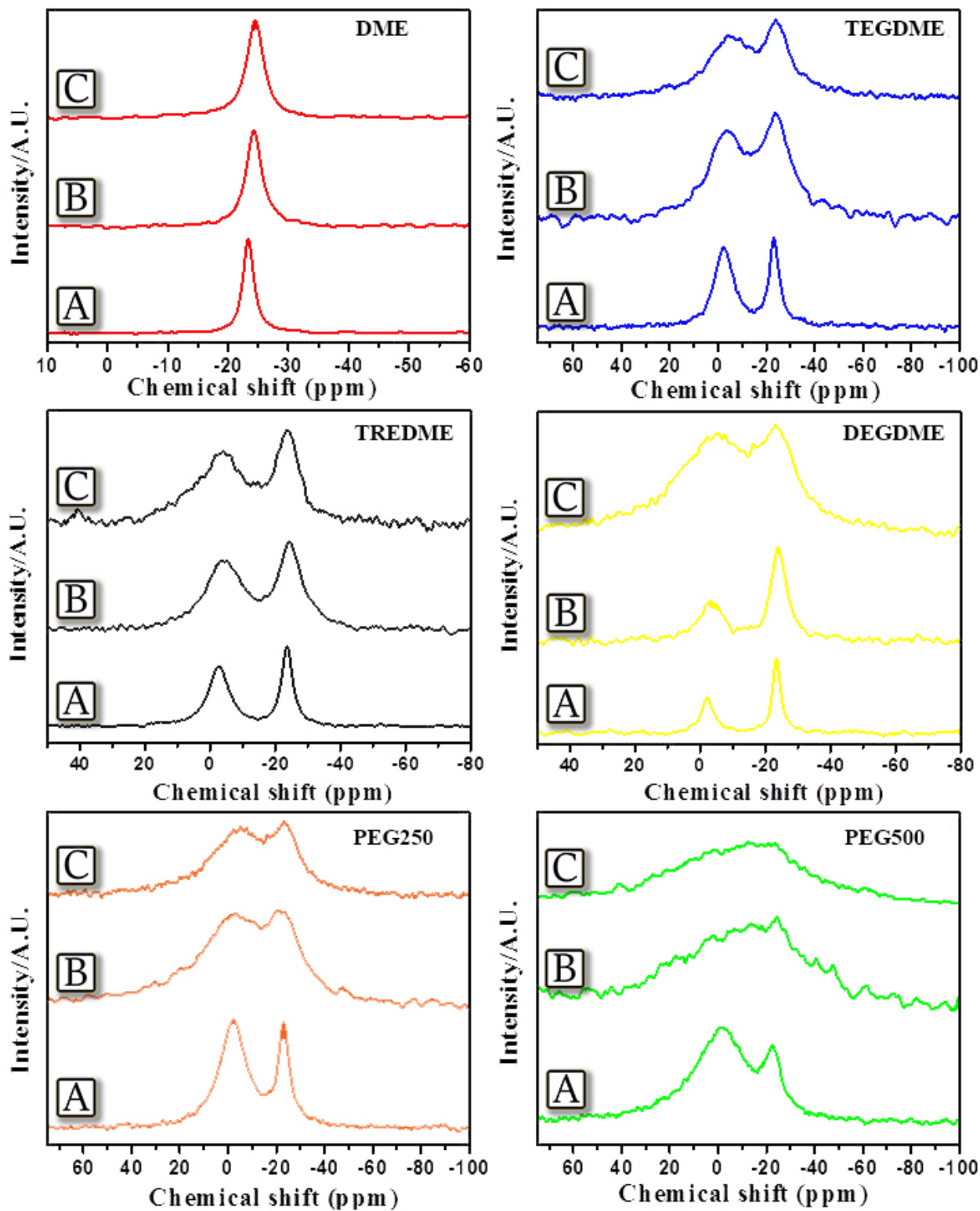


Figure 6 ^{17}O NMR resonances of the glymes (A. solvents; B. LiTriflate electrolytes; C. LiTFSI electrolytes)

Table 3 ^{17}O NMR chemical shift of pure solvents and electrolytes.

Solvent name	Chemical shift of ^{17}O in R-O-R' group(Hz)			Chemical shift of ^{17}O in O-CH ₃ group(Hz)			Chemical shift of ^{17}O in LiTf (Hz)	Chemical shift of ^{17}O in LiTFSI (Hz)
	pure solvent	LiTf Electrolytes	LiTFSI Electrolytes	pure solvent	LiTf Electrolytes	LiTFSI Electrolytes		
DME				-23.4	-24.3	-24.6	156.3	160.1
DEGDME	-2.2	-3.7	-3.9	-23.5	-23.9	-24.1	157.7	162.4
TREDME	-2.6	-3.6	-4.1	-23.5	-23.7	-23.9	158.3	161.8
TEGDME	-2.5	-3.3	-3.9	-23.2	-23.5	-23.6	158.6	162.0
PEG250	-2.7	-3.3	-3.9	-23.4	-23.6	-23.6	159.0	162.4
PEG500	-1.6	-1.8	-0.5	-22.6	-23.1	-23.0	159.6	162.5

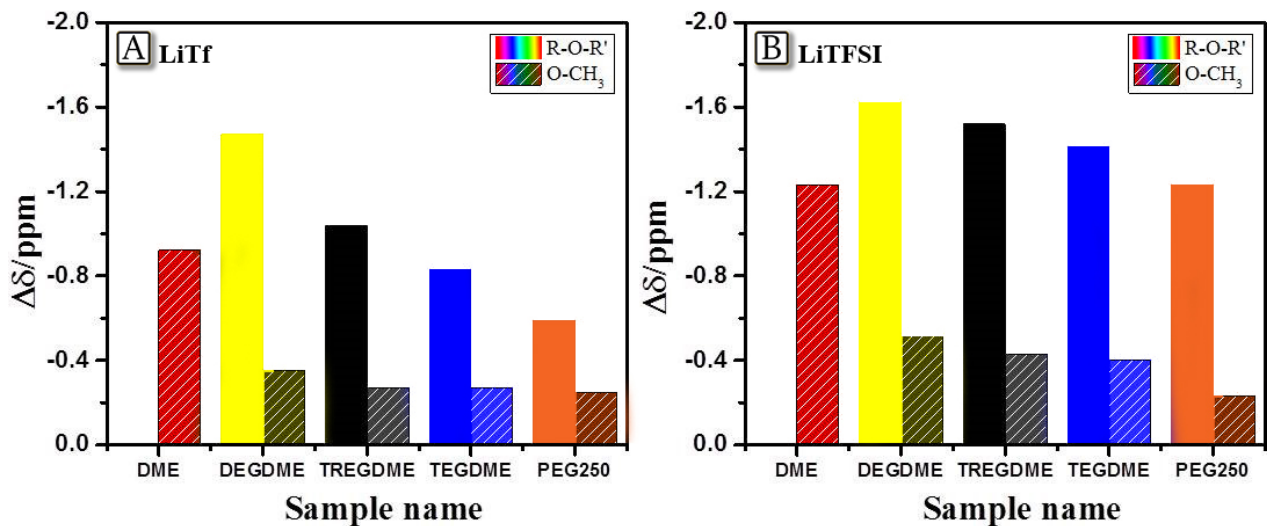


Figure 7 Chemical shift difference of ^{17}O resonance of glyme between Li salt solution and pure solvent ($\Delta\delta = \delta_{\text{electrolyte}} - \delta_{\text{solvent}}$).

charge at the oxygen atom leads to a downfield ^{17}O NMR shift, which contradicts the common held view, suggesting an upfield shift by electron density increase.⁶² The ^{17}O chemical shift of the glyme-based electrolytes studied herein moves upfield upon lithium salt addition, i.e., by decreasing the net charge of the oxygen due to the electron withdrawal effect of Li^+ , thus in complete agreement with Eq. 3.⁵⁷ Accordingly, the salt addition induces a larger chemical shift change on the downfield shifted, more polar and electron richer chain oxygen (R-O-R') in respect to the terminal oxygen (-O-CH₃), since the former represents the preferred site for hosting Li^+ cations⁶³. Fig.7 also reveals a decreasing trend of the ^{17}O chemical shift of both in -O-CH₃ and in R-O-R' group by increasing the ether chain length.

Glymes $N_{(\text{O})}/N_{(\text{Li}^+)}$ Ratio

Fig.8 reports the calculated $N_{(\text{O})}$ to $N_{(\text{Li}^+)}$ molar ratio in the glyme-based electrolytes (see experimental section for details), and exhibits a slightly increasing $N_{(\text{O})}/N_{(\text{Li}^+)}$ by chain length increase. Hence, glymes of longer chain have an increased number

of oxygen atom per Li^+ ion, and a relevant ratio of lithium ion preferential sites R-O-R' in respect to -O-CH₃. Consequently, the individual oxygen in R-O-R' becomes less associated with the Li^+ in the longer glymes, and its chemical shift less affected by the presence of the salt. Accordingly, the increase of $N_{(\text{O})}/N_{(\text{Li}^+)}$ ratio from diglyme, TREGDME, TEGDME to PEG250 (Fig.5) changes the chemical shift of the corresponding electrolyte by -1.5, -1.0, -0.8 and -0.6 ppm (LiTriflate series), and by -1.6, -1.5, -1.4 and -1.2 ppm (LiTFSI series), respectively (see Table 2). In summary, the lower ratio of lithium solvating R-O-R' groups in the

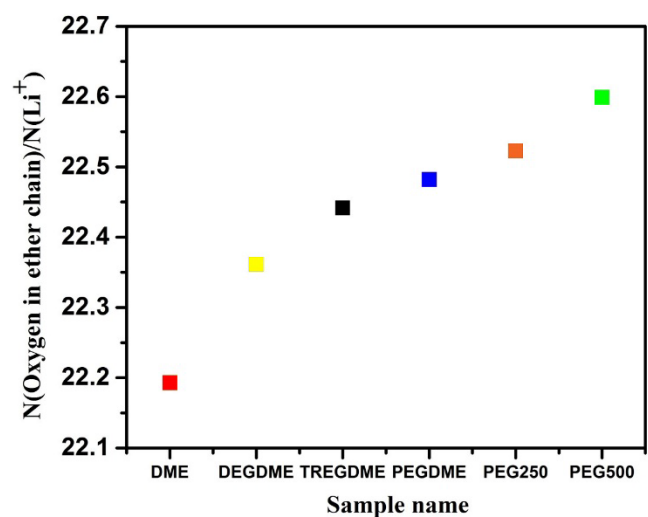


Figure 8 Ratio of the number of oxygen in ether chain to Li^+ .

shorter chain glyme electrolyte (smaller $N_{(O)}/N_{(Li+)}$ in Fig. 8) induces a stronger shielding effect and corresponding ether chain oxygen chemical shift change. Furthermore, oxygen in both R-O-R' group and methoxy group in LiTFSI series exhibits a larger shift in respect to LiTriflate series, as most likely ascribed to the higher dissociation degree of the LiTFSI salt. Indeed, TFSI⁻ ions are less located in the first coordination shell of the Li⁺ in respect to Triflate⁻, thereby allowing a stronger interaction between Li⁺ and oxygen in the glymes. The ¹⁷O chemical shifts of Triflate⁻ and TFSI⁻ plotted as a function of glyme chain length in Fig. 9, show a slightly increasing trend by glyme chain length increase. This behavior can be explained by taking into account the electron density of the oxygen in the anion. The exceptional cation solvation in the glymes, often results in poorly solvated or even naked active anions.⁶ In contrast, the NMR measurements reported in figure 9 indicate a change of anion environment from the observed downfield shift by increasing chain length. It has been reported that lithium cations preferentially interact with the SO₃ group rather than CF₃ group in LiTriflate containing electrolytes.⁶⁴ The positive Li⁺ ions attract electrons from oxygen atoms in Triflate⁻ group by association, thereby inducing a downfield shift. Accordingly, the ¹⁷O NMR results of Fig. 9 suggest enhanced Li-Triflate association degree by chain length increase. This result is consistent with the literature data⁶⁵ suggesting the ion pairs as the predominant species instead of 'free' ions and aggregates, and indicating an increase of ion pairs concentration by increasing the chain length in glymes with $n=1\sim4$. Similar increasing trend however with a minor extent, except for the DME solution, may be observed for the ¹⁷O chemical shift in TFSI⁻.

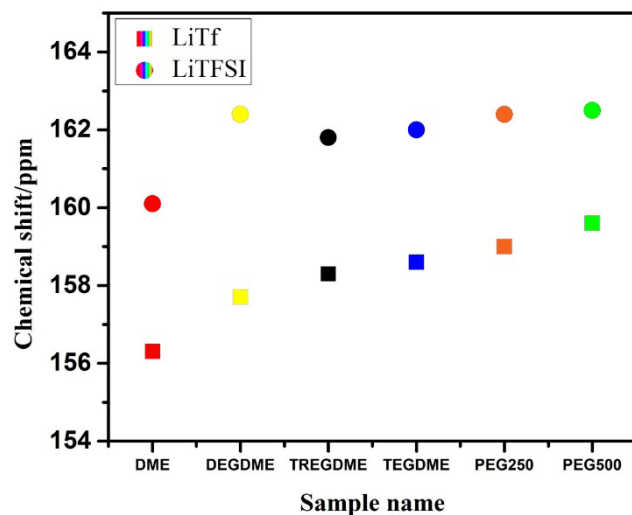


Figure 9 ¹⁷O chemical shift of the anion in the different electrolytes.

The sensitivity of natural abundance ¹⁷O NMR technique for investigating the lithium ion solvation behavior was confirmed by comparing the chemical shift of the glyme oxygen in electrolytes with those of corresponding neat solvents. This unique method can directly observe the specific oxygen atom coordinating sites associated to the lithium ion solvation sheath, and probe the dependence of cation-solvent interaction on the glyme chain length. The results suggest stronger interaction for the ether oxygens with higher electron density in respect to terminal oxygens. In addition, the data indicate decreasing oxygen shielding effect on Li⁺ by increasing chain length due to a more relevant competition of the oxygen atoms for Li⁺ solvation. The downfield shift of anion oxygen in the electrolytes suggests that longer chain length favors the association of cation and anion.

Glymes in Li/S cell

Moving to battery application

The electrolytes proposed differ by concepts, design, and materials, as well as the effect of their chemical and physical characteristics on the lithium ion. The use of the electrolyte should be studied and optimized in order to obtain the best result for the needed application. The attention now is focused on the species mobility within glyme-based electrolytes and its effects on the polysulfide shuttle reactions.

Experiment Summary

The electrolytes, considered as suitable media for lithium-sulfur battery, are characterized in terms of thermal properties (TGA, DSC), lithium ion conductivity, lithium interface stability, lithium-transfer number, cyclic voltammetry and self-diffusion coefficient measured by NMR analysis. Furthermore, the electrolytes are characterized in lithium cell using a sulfur-carbon composite cathode by Galvanostatic charge-discharge tests. The results clearly evidence the influence of the chain length on the species mobility within the electrolytes that is directly reflected into a different behavior in lithium sulfur cell.

Experimental section: Cathode preparation

The cathode material was based on elemental sulfur and mesophase micro bead (MCMB) carbon, in a weight ratio of 1:1. Before mixing with MCMB, the sulfur was melted at 135°C. The mixture was stirred for 3 hours at 135°C and then cooled down to room temperature. A stainless-steel jar was used to hold and mechanically treat the sample by high-energy ball milling system (Retsch Mill MM400) with a frequency of 15 Hz for a total time of 2 hours, using a milling time of 30 minutes, rest period of 15 minutes and repeating the above procedure four times. The electrodes were prepared by mixing the carbon-sulfur composite, super P carbon (Timcal) and polyvinylidene difluoride (PVDF) binder in 80:10:10 mass ratio in N-methylpyrrolidone (NMP) solution. The slurry was casted on aluminum foil by Doctor Blade, punched as disks and then vacuum-dried at 50°C for 24 h before assembling the cells in argon filled glove box.

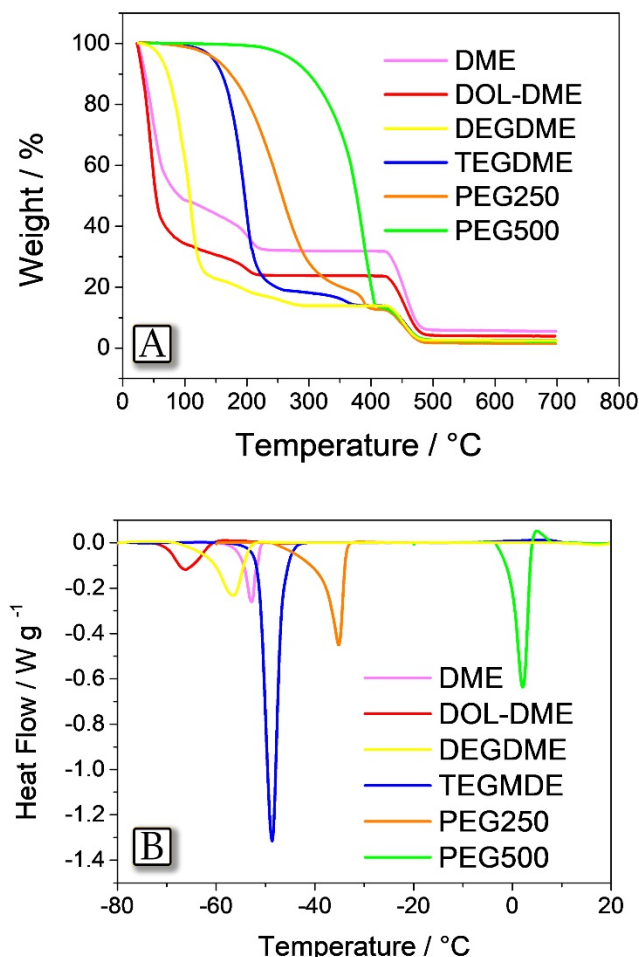


Figure 10 (A) Thermo-gravimetric analysis (TGA) profiles of the ether-based electrolytes performed from 25 °C to 700°C at 10°C/min heating rate, under nitrogen flow. (B) Differential Scanning Calorimetry (DSC) profiles of the ether-based electrolytes cooled from 20 °C to -80°C at 5°C/min, under argon atmosphere

The results may effectively contribute to the progress of an efficient, high energy lithium-sulfur battery.

Glymes- LiCF_3SO_3 Properties

Thermo-gravimetric analysis (TGA) was performed in order to detect the stability of the various ether-based electrolytes at elevated temperature.

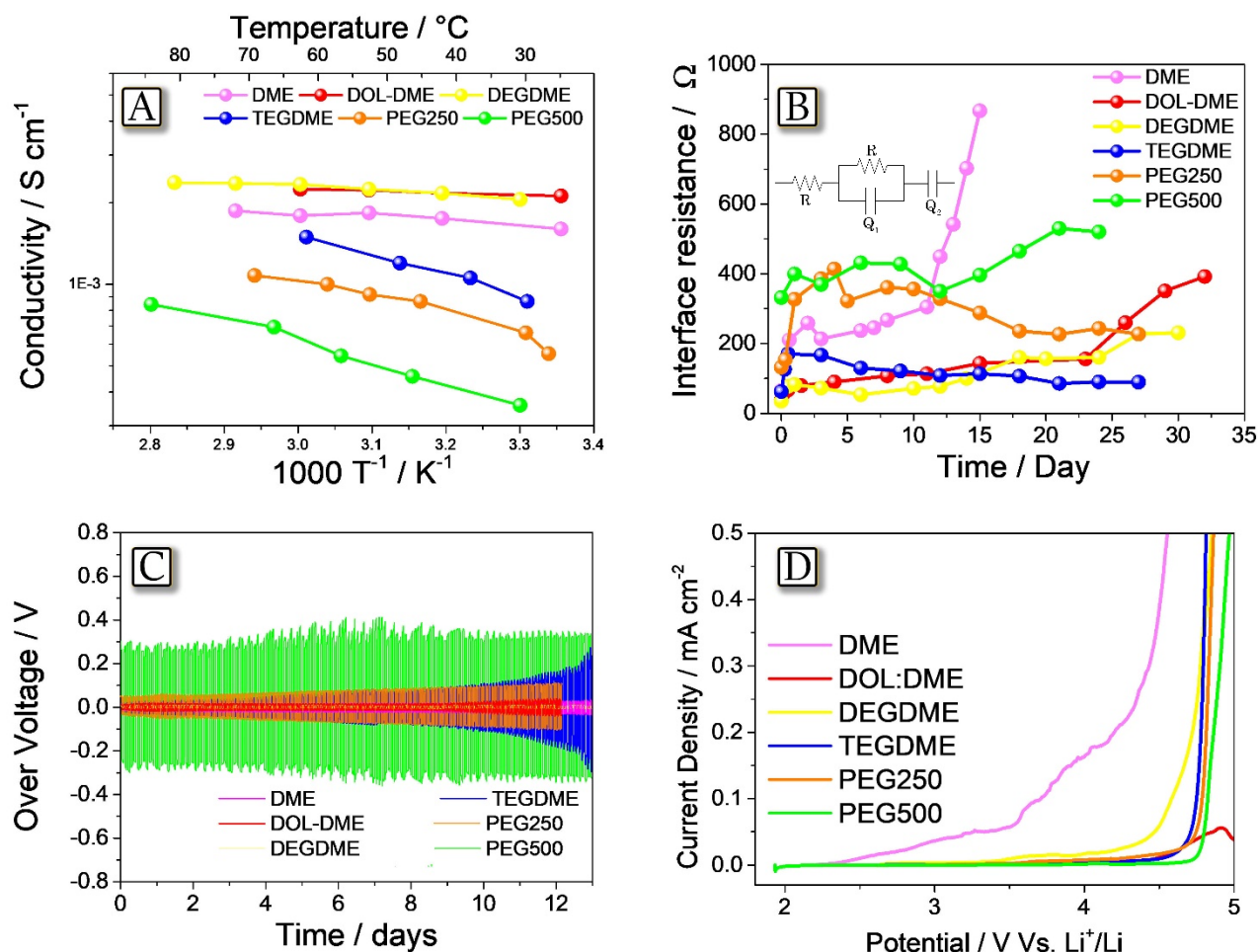


Figure 11(A) Conductivity Arrhenius plots of the ether-based electrolytes performed by ranging the temperature from 30 °C to 80 °C. The measurements have been performed in coin-cell, using electrochemical impedance spectroscopy with signal amplitude of 10 mV within 500 MHz-100Hz frequency range. (B) Time evolution at room temperature of the lithium-electrolyte interface resistance performed in Swagelok-type, Li/Li symmetrical cell using electrochemical impedance spectroscopy with signal amplitude of 10 mV within 500 MHz-100 mHz frequency range. (C) Voltage vs. time profile of lithium deposition/stripping galvanostatic test performed applying a 0.1 mA current to symmetrical Li/electrolyte/Li cell. (D) Current vs. potential profile of the linear sweep voltammetry (LSV) performed using the Li/electrolyte/SP cell within the OCV-5.0 V vs. Li/Li⁺ range at 0.1 mV s⁻¹ at room temperature employed for the determination of the electrochemical stability window of the electrolyte.

The DSC and, in particular, the TGA measurement are considered as an indication of the upper and lower temperature limits where the electrolytes maintain their characteristics. Therefore, we used this information as a suggested temperature range suitable for stable working of the cell. Figure 10A, reporting the TGA traces, demonstrates that the electrolytes based on both DME and DOL-DME

are characterized by thermal stability limited to temperatures lower than 50°C, while DEG-based one reveals a slightly higher stability, i.e. extended up to 70°C. In contrast, TEG-based electrolyte shows a thermal stability exceeding 200°C that is further increased for PEG500-based one up to a temperature as high as 350°C. As indeed expected, the above results reflect a thermal stability enhanced by the increasing the ether-chain length, i.e.

Experimental section: Electrolyte preparation

Before mixing, the solvents were dried for several days under molecular sieves until the water content was below 10 ppm as determined by 831 Karl Fisher Coulometer – METROHM. The electrolyte solutions were prepared by dissolving lithium trifluoromethanesulfonate (LiCF₃SO₃, i.e. lithium triflate) in 1 mol kg⁻¹ ratio in an argon filled glove-box. Lithium nitrate was then added to the solution in a 0.4 molar ratio

DOL-DME < DEG < PEG250 < PEG500, thus suggesting a higher safety content of the long-chain, ether-based electrolytes in view of the possible application in lithium batteries. The DSC measurements performed within the electrolyte crystallization region, and reported in figure 10B, indicate a lower freezing point for DME and DOL-DME-based electrolytes, i.e. of about -53°C and -68°C , respectively, in respect to TEGDME and PEG250-based electrolytes that show the still very low freezing points of -49°C and -34°C , respectively. PEG500-based electrolyte freezes at about 5°C , thus suggesting possible issues associated with its use at the lower temperatures. Figure 11A, reporting the conductivity Arrhenius plots of the selected electrolytes, shows conductivity values suitable for lithium battery applications for all the samples in the studied temperature range. Indeed, the room temperature conductivity decreases from about $2 \cdot 10^{-3} \text{ S cm}^{-1}$ for DME, DOL:DME and DEGDME-based electrolytes to about $1 \cdot 10^{-3}$ for TEGDME, $7 \cdot 10^{-4}$ for PEG250 and down to $4 \cdot 10^{-4} \text{ S cm}^{-1}$ for PEG500-based one, thus suggesting increasing conductivity by decreasing the ether-chain length. However, DME and DEGDME show a different trend, most likely due to an additional effect

of the solvent dielectric constant that is predominant at the low viscosity values. Indeed, DME has a lower viscosity as well as a lower dielectric constant than DEGDME (i.e., 0.46 mPa.s and 5.5 for DME and 1.03 mPa.s and 5.8 for DEGDME).⁶⁶ This is reflected by a slightly lower conductivity of the former with respect to the latter. Furthermore, a slight and linear increase of the conductivity, in particular for the electrolyte based on PEG500, is observed by raising the temperature as expected by solvent viscosity decrease. The time evolution of the lithium interface resistance of the symmetrical lithium cells using the studied electrolytes reported in figure 11B reveals a stable lithium-electrolyte interface, with relatively low resistance ranging from 100 Ohm for DOL:DME, DEGDME and TEGDME-based solutions to 400 Ohm for PEG250 and PEG500-based ones. However, the cell using DME-based electrolyte shows a continuous increase of the interface resistance due to possible evaporation over time, thus excluding its possible use as the electrolyte solvent for lithium battery applications, while DME-DOL combination appears a still suitable solution. DEGDME and TEGDME-based solutions show lower resistance values and excellent stability over time, thus suggesting these electrolytes as the preferred ones for

Experimental section: Electrolyte Characterization Part 1

The thermal characterization was performed by **thermo-gravimetric analysis TGA** (Mettler Toledo TGA/SDTA851) and by **differential scanning calorimetry DSC** (Mettler Toledo DSC821). TGA was performed by raising the temperature from 25°C to 700°C , with a heat rate of $10^{\circ}\text{C}/\text{min}$. DSC was performed by cooling from 25°C to -80°C at $-5^{\circ}\text{C}/\text{min}$. **Conductivity tests** were performed by using 2032 coin cells including stainless steel symmetrical electrodes and Teflon O-ring separator with a constant and known size in order to ensure a fixed cell constant. **Electrochemical impedance spectroscopy (EIS)** was performed by using a Biological VMP3 with 10mV-signal amplitude, within 500 MHz-100 Hz frequency range. The interface resistance has been calculated by Non-linear least-squares (NLLSQ) fit of the impedance spectra, carried out by using a Boukamp software product. An R(RQ)nQ equivalent circuit (shown in the figure inset) was used for the Nyquist plot analysis, where R represents a resistance and Q a constant-phase element (CPE). The Chi-square (χ^2), a parameter used to evaluate the fitting quality, was below 10^{-4} .^{235,236} The electrochemical stability window was studied by **linear sweep voltammetry (LSV)** at a scan rate of 0.1 mV s^{-1} , in a three electrodes lithium cell using a Biological VMP3. The configuration cell has lithium metal as counter and reference electrode and super P on aluminum as working electrode in the OCV- 5.0V Vs Li/Li⁺ range at room temperature. **Lithium stripping/deposition** galvanostatic test was performed by applying a 0.1 mA cm^{-2} current to Li/Li symmetrical cell, using a MACCOR Series 4000 Battery Test System (Maccor Inc.).

application in lithium cell. The lithium stripping-deposition voltage profiles shown in figure 11C evidence a very limited overvoltage, i.e. to about 10 mV, for DME and DEGDME-based electrolytes (pink and yellow curves, respectively) with an increase of the value by increasing the chain length to about 300 mV for PEG500-based electrolyte (green curve) at room temperature, which is most likely associated to the increased charge transfer resistance at the lithium interphase. Furthermore, minor changes in the polarization value, in particular for TEGDME-based electrolyte, is observed over time due to the expected growth and following consolidation of the solid electrolyte interphase (SEI) film at the lithium surface upon lithium stripping-deposition.^{38,67} In line with the results already observed by time evolution test of the Li-interface resistance (see Fig. 11B), the lithium deposition-stripping test of suggests DEGDME as preferred electrolyte solvent for application in lithium battery. The linear sweep voltammetry (LSV) in Lithium/carbon cells reported in figure 11D exhibits the same trend for DEGDME, TEGDME, PEG250 and PEG500, with electrochemical stability extended up to 4.5V. In spite of the onset of decomposition of DME and DEGDME-based electrolytes at 2.3V and 2.5V, respectively, the electrolyte obtained by their combination shows rather higher stability, i.e. extended up 4.0V. This test, in addition to the pre-

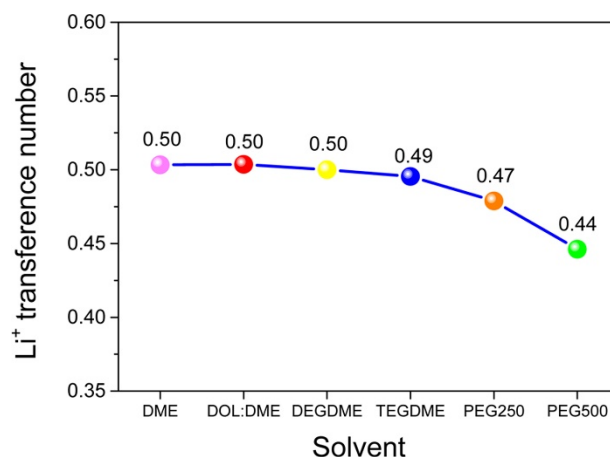


Figure 12 Lithium transference number of the ether-based electrolytes at room temperature. The values have been obtained as the ratio of the self-diffusion coefficient of Li⁺ with respect to that of overall charge carriers, i.e. Li⁺ and CF₃SO₃⁻ measured at 25°C by NMR

vious ones (see Fig. 11 A, B and C), suggest possible interactions between the two co-solvents, i.e. DOL and DME, leading to a mixed phase with slightly different electrochemical properties with respect to the single solvent. Lithium transference number plays a key role in optimizing the behavior of the electrolyte in Li-cell. This important parameter is here determined by using the ionic self-diffusion coefficients as determined by NMR (see experimental section for details) and reported in Figure 12.^{68–70} Indeed, the figure shows a decrease of the lithium transference by increasing the ether-chain length from DME to PEG500-based electrolyte. The observed decrease of the lithium transference number may be most likely ascribed to the expected kinetic limits hindering the solvated-ions mobility by increasing the ether-chain length.⁷¹

Experimental section: Electrolyte Characterization Part 2

Temperature dependence of the self-diffusion coefficient for ¹H, ¹⁹F, and ⁷Li nuclei was measured on a Bruker 400 Avance III NMR spectrometer using a double stimulated echo pulse sequence to suppress convection effects.²²⁴ Gradient pulses, of sine shape with duration $\delta = 2-5$ ms and strength $g = 0-45$ G/cm, were applied with a diffusion delay of $\Delta = 80-800$ ms within a temperature ranging 20°C and 70°C, in steps of 10°C. The self-diffusion activation energies were estimated by the Arrhenius plot linear slope of the corresponding self-diffusion coefficients measured at various temperatures. The room temperature lithium transference number (t^+), corresponding to the fraction of current carried out by the lithium ions, was determined as the ratio of the self-diffusion coefficient of Li⁺ with respect to overall charge carriers, i.e. Li⁺ (⁷Li nuclei) and CF₃SO₃⁻ (¹⁹F nuclei) measured at 25°C. This method does not take into account the effects of ion association and is therefore used only as guide to comparative behavior in electrolytes

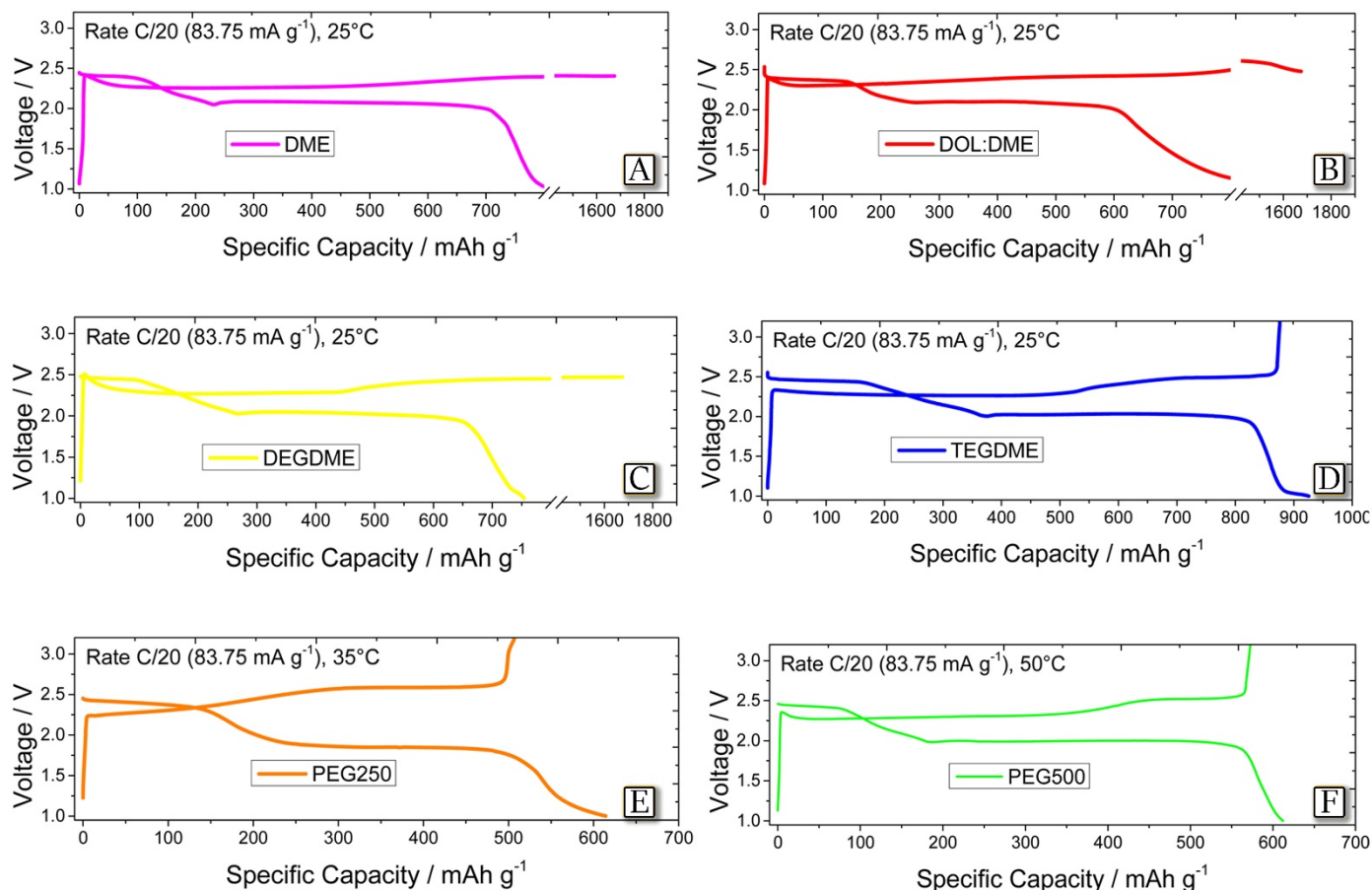


Figure 13 Voltage profile of the lithium sulfur cells using the various electrolytes, i.e. (A) DME-1m LiCF_3SO_3 @ 25°C, (B) DEGDME-1m LiCF_3SO_3 @ 25°C, (C) DOL:DME-1m LiCF_3SO_3 @ 25°C (D) TEGDME 1m LiCF_3SO_3 @ 25°C, (E) PEG250-1m LiCF_3SO_3 @ 35°C and (F) PEG500-1m LiCF_3SO_3 @ 50°C. The galvanostatic charge-discharge cycle is performed at a current rate of C/20 (83.75 mA g^{-1}) within 1.2–3.2 V voltage.

Shuttle Effect in Li-S Cell

Figure 13 shows the voltage profiles of the first galvanostatic charge-discharge cycle of the various electrolytes in a lithium-sulfur cell. The figure evidences a remarkable polysulfide-shuttle effect for the cells using short-chain glymes,⁷² i.e. DME (A), DEGDME (B) and DOL:DME (C), characterized by conventional discharge process and by continuous charging, until cell failure.⁷³ Instead, the cells using TEGDME (D), PEG250 (E) and PEG500 (F) reveal very limited, or complete absence of polysulfide-shuttle reaction during the first cycle, with a typical trend associated with the Li-sulfur process.²⁵ However, the performance of the sulfur cell

using TEGDME, characterized by a capacity of about 900 mAh g^{-1} and limited polarization, may be approached only by raising the temperature up to 35°C and 50°C for the cell using PEG250 and PEG500, respectively. This behavior may be ascribed to the lower conductivity and higher viscosity of the long-chain glymes at room temperature, and consequent high activation energy required for the motion of the various electrolyte constituents, in particular at the electrode-electrolyte interface. Furthermore, the cell using TEGDME shows higher capacity than that using DEGDME, despite the lower viscosity of the latter. This aspect may be reasonably attributed to the lower resistance observed in figure 11B for the Li-TEGDME interface

Experimental section: Cathode Characterization

Cycling tests were performed using a Maccor instrument at a C/20 current rate ($1\text{C} = 1675 \text{ mA g}^{-1}$ based on the sulfur weight), within 1 V – 3.2 V limit.

with respect to Li-DEGDME, however further study is required to fully clarify this trend.

Glymes Self Diffusion Activation Energy

Figure 14 reports the self-diffusion activation energies of the various species within the electrolyte obtained by Arrhenius plot linear-slope determination of the self-diffusion coefficient for ^1H , ^{19}F , and ^7Li nuclei measured by NMR (see experimental section for details). The ^{19}F (Fig. 14A) and ^7Li (Fig. 14B) self-diffusion activation energies are ascribed to the LiCF_3SO_3 salt ions moving within the selected solvent, while the ^1H activation energy (Fig. 14C) is associated to the ether-segment diffusion.

The figure shows that the short-chain glymes are generally characterized by lower activation energy in comparison to the long chain ethers. Indeed, DOL and DME-based electrolytes reveal very low activation energy both of the salt and of the ether-chains, i.e. ranging from 5 to 10 kJ mol^{-1} , hence a higher mobility in respect to PEG-based electrolytes, characterized by an activation energy ranging from 25 to about 30 kJ mol^{-1} . DEGDME and TEGDME-based solutions exhibit intermediate values, i.e. ranging from 15 to 20 kJ mol^{-1} . The similarity in values and activation energy trends between the ions and the host molecules is consistent with the highly cooperative ion transport mechanism known to occur in ether-based solvents. The above reported data are in line with the remarkable shuttle reaction observed in figure 13 (A, B and C) for lithium sulfur cells using electrolyte based on short-chain glymes, in which the high mobility of salt ions and solvents allows an easy pathway for polysulfide migration from cathode to anode, and consequent direct reaction. Instead, long-chain

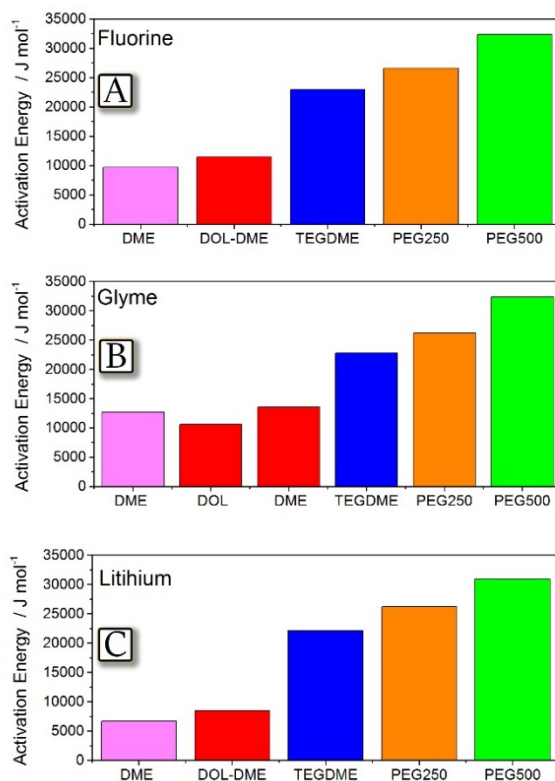


Figure 14 Comparison of self-diffusion activation energy for ^{19}F (A), ^7Li (B) and ^1H (C) nuclei. The NMR measurements were performed using gradient pulses, of rectangular shape with duration $\delta = 2\text{--}5$ ms, strength $g = 0\text{--}45$ G/cm applied on each side of 180° pulse with a separation of $\Delta = 80\text{--}800$ ms

glymes partially inhibit the above process that is almost absent during the first charge-discharge of the corresponding Li-S cells (see Fig. 13 D, E and F).

LiNO₃ Addition

The above polysulfide shuttle effect in short-chain glymes may be efficiently mitigated by protecting the lithium electrode surface, such as by adding lithium nitrate (LiNO_3) salt to the electrolyte solution.^{22,74} Accordingly, Figure 15 reporting the voltage profile of the cells using DME (A), DOL:DME (B) and DEGDME (C) solutions, with added LiNO_3 , clearly evidences the reduction of the polysulfide shuttle-effect, and the corresponding increase of the cell efficiency during the galvanostatic charge-discharge cycle. Furthermore, the figure shows an over discharge at about 1 V, attributed

to the LiNO_3 reduction, and expected to significantly buffer the lithium polysulfide shuttle reaction. The figure shows the typical profile expected for the Li-S reaction and a relatively limited polarization. These data, in addition to the previous experimental evidences, suggest DEGDME- LiCF_3SO_3 with added LiNO_3 solution is a suitable medium for application in lithium-sulfur cell. Therefore, DEGDME- LiCF_3SO_3 - LiNO_3 solution has been employed as the electrolyte in Li/S cell, of coin-configuration, galvanostatically cycled for several times at C/20 rate, i.e., a low current in order to evaluate possible shuttle process that is, in general, magnified at the lower C-rates. The results reported in Figure 16, reported in terms of voltage profile (A) and corresponding cycling behavior (B), confirm the mitigation of this side reaction by showing a coulombic efficiency higher than 90%. The figure reveals an initial capacity of about 900 mAh g^{-1} , due to the reversible Li-S reaction, that decreases and then stabilizes at about 750 mAh g^{-1} due to polysulfide dissolution until final solution saturation. The above saturation, with consequent buffer-effect by mass action of the dissolved polysulfide, i.e. avoiding further cathode loss and leading to capacity stabilization, is allowed by the use of a separator soaked by a very low electrolyte amount, i.e. about $10\text{--}15 \mu\text{l}$. Taking

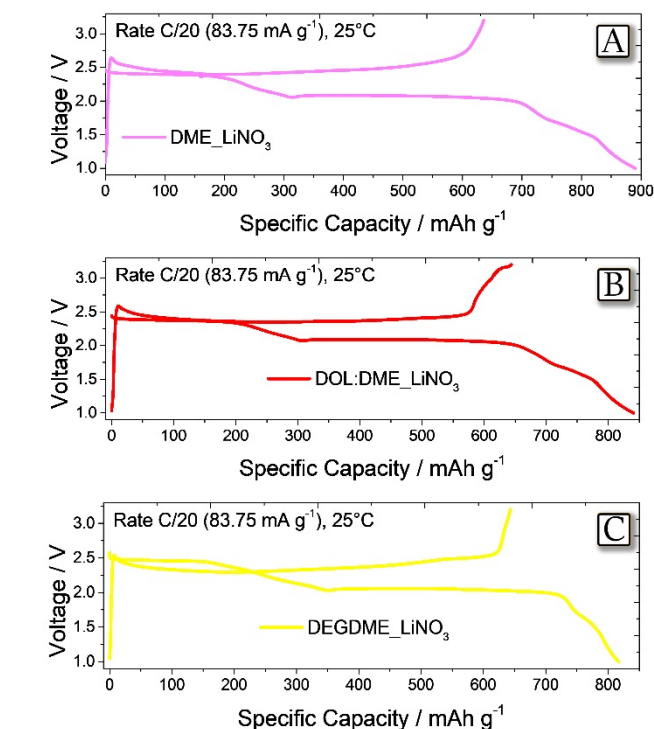
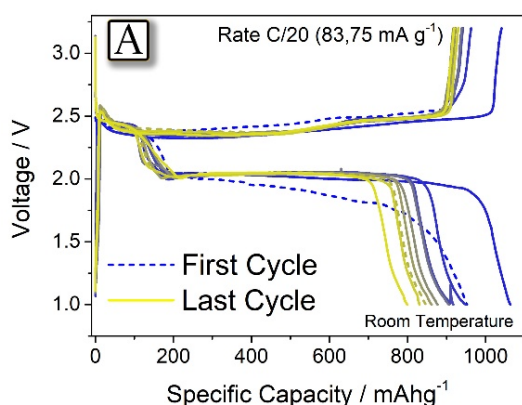


Figure 15 Voltage profiles of the galvanostatic charge-discharge cycle of lithium sulfur cells using DME-1m LiCF_3SO_3 (A) and DOL:DME-1m LiCF_3SO_3 (B) and DEGDME-1m LiCF_3SO_3 (C) electrolytes added by 0.4m LiNO_3 as lithium polysulfide shuttle protecting-agent. Current rate C/20 = 83.75 mA g^{-1} , voltage range 1.2–3.2 V. Room temperature.

into account a specific capacity of about 750 mAh g^{-1} and a working voltage of 2V, the theoretical energy of the cell may be calculated to be of the order of 1500 Wh kg^{-1} that may reflect, considering side and inactive cell components, a practical energy as high as 500 Wh kg^{-1} and, finally, of 250 Wh kg^{-1} considering also the carbon content of the sulfur electrode employed for the tests (i.e., S:C, 1:1 weight ratio)

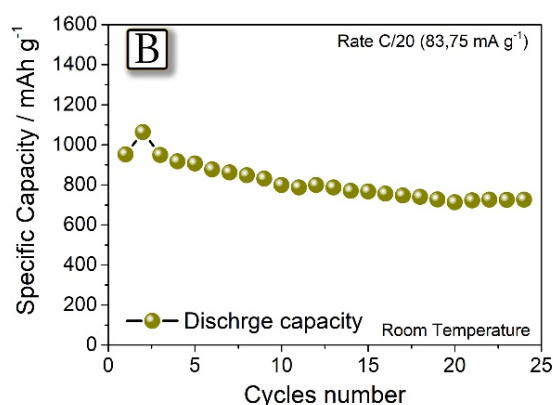
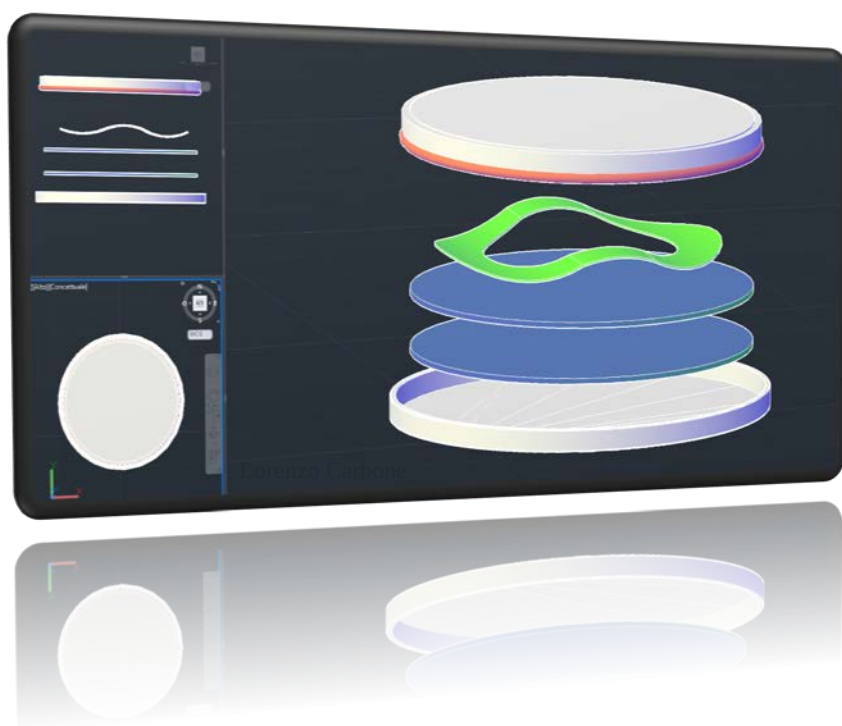


Figure 16 Galvanostatic behavior of a Li/DEGDME- LiCF_3SO_3 - LiNO_3 /S-C coin-cell reported in terms of voltage profile (A) and corresponding cycling behavior (B). Current rate C/20 = 83.75 mA g^{-1} , voltage range 1.2–3.2 V. Room temperature.

LiNO₃ characterization

The beneficial effect of LiNO₃ was widely investigated in lithium-sulfur batteries using glyme-based electrolytes. Indeed, LiNO₃ can protect the lithium electrode surface from parasitic reactions by forming a passivation film, which avoids the polysulfide shuttle phenomenon, i.e., the lithium metal corrosion by polysulfide species dissolved in the electrolyte solution.^{72,75} Such protective solid electrolyte interphase (SEI) starts growing immediately upon Li-S cell assembly, by precipitation of Li_xNO_y and Li_xSO_y species blocking the electron transfer from lithium metal to the polysulfides dissolved in the solution and ensuring at the same time Li⁺ conduction.²² Thus, LiNO₃ ensures stable cycling of Li-S cells by formation of a suitable SEI on the anode. However, the irreversible reduction of NO₃⁻ anions on the cathode side at potentials lower than 1.8 V vs. Li⁺/Li leads to (i) limited electrode kinetics likely due to precipitation of reduction products on the cathode surface, and (ii) nitrate consumption. In particular, XPS measurements revealed polymerization products over the cathode, which have been related in literature to possible nucleophilic attack of the solvent molecules by O²⁻ formed during reduction of nitrate to nitrite species.^{43,50,76} This peculiar behavior of electrochemical stabilization needs further investigations, which is therefore one of the aims of the further paragraphs.



Scheme of the 2032-coin cell. stainless steel current collector in blue, the spring in green. Teflon ring in red and in light grey the body of the cell in stainless steel

LiNO₃ Effect

Experiment Summary

Polyethylene glycol dimethyl ether (Mw 500) dissolving lithium trifluoromethanesulfonate (LiCF₃SO₃) salt was selected due to his higher electrochemical stability window in respect to others glymes. Voltammetry and galvanostatic tests reveal significant enhancement of the electrolyte characteristics, in terms of cycling life and chemical stability, by the addition of lithium nitrate (LiNO₃) to the solution. Furthermore, PFG NMR measurements suggest the applicability of the electrolyte in battery in terms of ionic conductivity, lithium transference number, ionic-association degree and self-diffusion coefficient. Accordingly, the electrolyte is employed in a lithium battery using lithium iron phosphate as the selected cathode. The battery delivers a stable capacity of 150 mAh g⁻¹ and flat working voltage of 3.5V, thus leading to a theoretical energy density of 520 Wh kg⁻¹. This battery is considered a suitable energy storage system for advanced applications requiring both high safety and high energy density.

PEG500 LiCF₃SO₃ Properties

The suitability of the PEG500DME-LiCF₃SO₃ electrolyte in terms of ion mobility for application in battery has been verified both by PFG NMR and

by electrochemical method. Figure 17 A reports the self-diffusion coefficient of ⁷Li, ¹⁹F and ¹H within the electrolyte, as obtained by NMR measurement (the ¹H NMR results will not be discussed further here, but they are mostly reflective of solution viscosity). The figure evidences that lithium, i.e. the smallest particle in the solution, is characterized by the lowest values of diffusion coefficient due to a high solvation degree in view of its high charge density. Furthermore, the figure reveals the expected increase of the diffusion coefficient of the various species by increasing the temperature. The diffusion coefficient of the cation (D_{Li}) and of the anion (D_{CF₃SO₃}) at the various temperatures, represented by D_{Li} (LiCF₃SO₃) and D_F (LiCF₃SO₃) in Figure 17A, respectively, are used to determine the electrolyte ionic conductivity following the Nernst-Einstein formula, (see equation (4) in the *experimental section: electrolyte characterization* of this paragraph). Figure 17B reports the comparison between the conductivity values determined by NMR and directly measured by electrochemical impedance spectroscopy (EIS). The figure reveals a conductivity at 30°C of nearly 10⁻³ S cm⁻¹, i.e., a satisfactory value suitable for battery application. However, the plots reveal a discrepancy between the value directly measured by EIS and that determined by employing the diffusion coefficient, i.e., the latter higher in respect to the former. Indeed, PFG NMR reveals the movement of all the species

Experimental section: Electrolyte and Cathode Preparation

Poly ethylene glycol dimethyl ether (Sigma Aldrich, average MW 500, indicated by the acronym PEG500DME) was dried under molecular sieves (5Å) for several days until the water content was under 10 ppm as determined by Karl Fisher instrument (Metrohm). Lithium-trifluoromethanesulfonate (LiCF₃SO₃ Sigma Aldrich) and lithium-nitrate (LiNO₃, Sigma Aldrich) were dried at 100°C under vacuum for 24 hours. The electrolyte solution was prepared by dissolving 1 mol of LiCF₃SO₃ in 1 kg of PEG500DME. A second solution of the same composition of the previous was added by 0.4 mol of LiNO₃. The cathode was prepared by dispersing an homogeneous slurry of LiFePO₄,⁸⁰ super P carbon conductor (Timcal) and polyvinylidenedifluoride (PVDF, Solvay) binder in 80:10:10 mass ratio in N-methylpyrrolidone (NMP, Aldrich). The cathode film was cast onto aluminum foil by doctor Blade, dried at 70°C, disk-punched and finally dried under vacuum at 100°C for 3 hours.

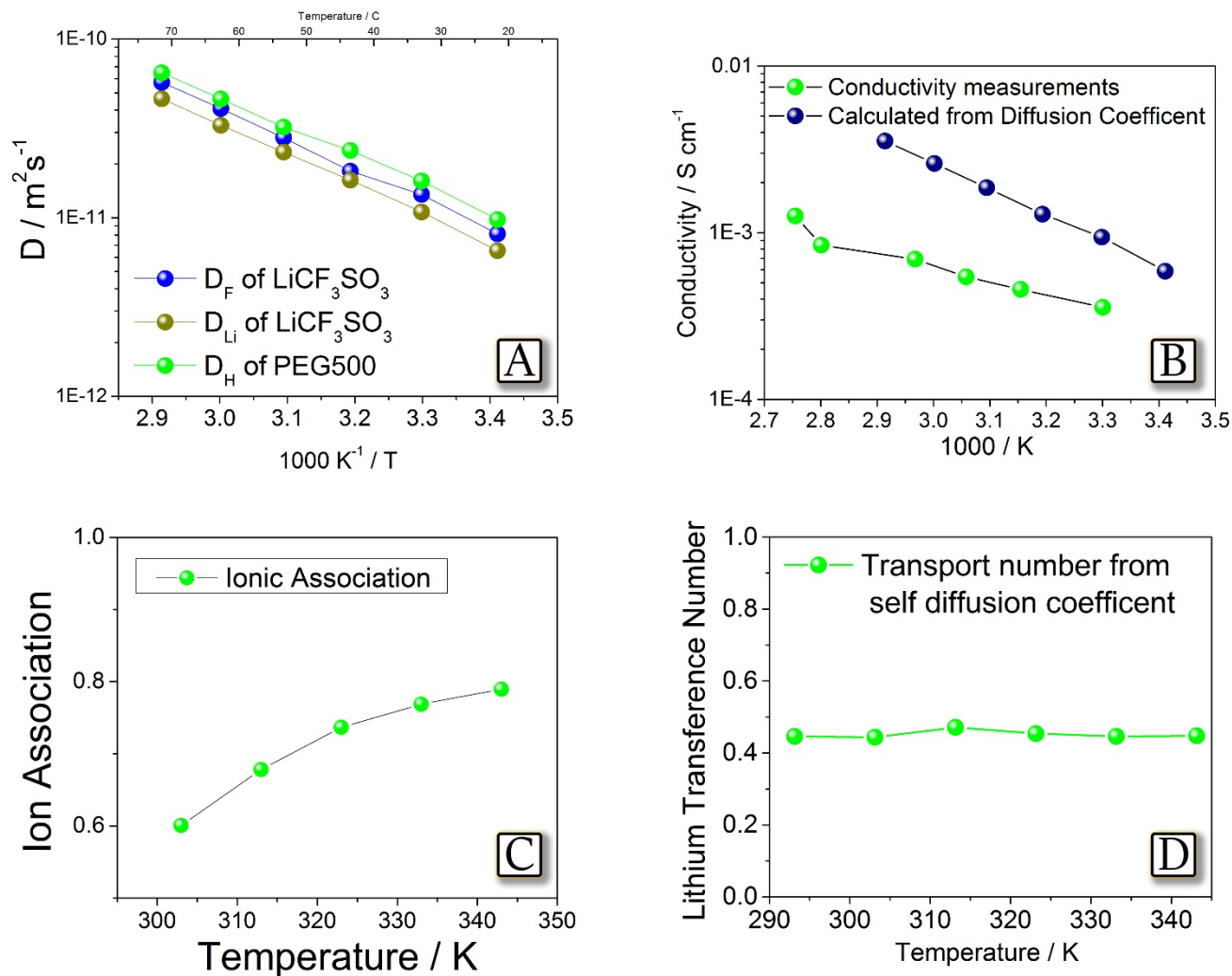


Figure 17 A) Self-diffusion coefficient (D) of ^7Li , ^{19}F and ^1H within the PEG500DME-LiCF₃SO₃ electrolyte determined by pulse field gradient NMR. B) Comparison between the conductivity values determined by using ions self-diffusion coefficients (equation 4) and measured directly by electrochemical impedance spectroscopy (EIS). C) Ionic association degree (α) trend at various temperatures calculated by (equation 5). D) Lithium transference number (t^+) trend determined at various temperatures (using equation 6). Temperature range 20°C-90°C. For equations (4), (5) and (6) see experimental section in the next page.

within the electrolyte solution, including single ions, neutral ionic pairs, couples and multiple associated ions. On the other hand, impedance spectroscopy records only the movement ascribed to the single charge carriers. This is a well-known and widely reported phenomena in both liquid and PEO-based solid electrolytes.^{63,77,78}. Accordingly, the ratio between the two values may be employed to determine the ionic association degree (α) using

equation (2) reported in the experimental section. Figure 1(c), reporting the trend of α , reveals an increase of the ionic association by increasing the temperature as most likely ascribed to possible recombination of the various ions into couple pairs or higher multiplet. This effect is in part due to the decreasing dielectric constant and hence decreasing solvating power of the polyether host at elevated

Experimental section: Cathode Characterization

Cyclic voltammetry was carried out by using a three-electrodes cell equipped by lithium metal counter and reference electrode and a Super P coated on copper working electrode. The measurement was performed by a 10 mV s^{-1} scan rate, within 0.01V and 3V potential window using a Biological VMP3 instrument. Swagelok, T-type lithium cells using lithium iron phosphate (LiFePO₄) cathode and PEG500DMEDME-based electrolyte soaked in a Whatman® glass fiber separator, were galvanostatically characterized at C/5 rate ($1\text{C} = 170 \text{ mA g}^{-1}$) using MACCOR Series 4000 Battery Test System (Maccor Inc.).

temperature.⁷⁹ Li-transference number has been determined by NMR at the various temperatures and reported in Figure 17D, in order to evaluate the charge fraction carried by lithium ions. The figure shows a stable value of about 0.45 in the whole temperature range that is considered a suitably high value allowing the use of the electrolyte in lithium ion batteries.

LiNO₃ Free

In order to verify the suitability of the electrolyte for lithium battery application, a Li/PEG500DME-1M LiCF₃SO₃/LiFePO₄ cell was assembled and cycled. Figure 18, reporting the voltage profile (A) and corresponding cycling behavior (B), reveals an initial cycle characterized by a typical profile centered at about 3.5V, a low charge-discharge polarization, a high efficiency and a specific capacity of about 150 mAh g⁻¹, i.e., of about 90% of the theoretical value. However, the following cycles evidence a remarkable polarization increase (Fig.18A) leading to efficiency decrease, noise, capacity fading and final cell failure (Fig.18B). These issues are attributed to an unstable solid electrolyte interphase (SEI) film at the lithium surface, or to a very poor stability of the latter. It has been reported that the

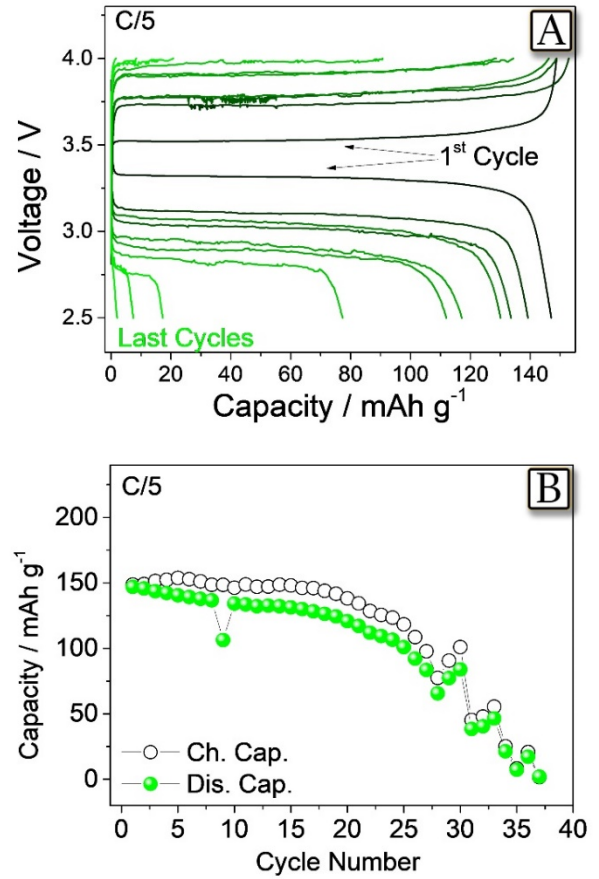


Figure 18 . A) Voltage profiles and B) cycling behavior of the Li/PEG500DME, 1m LiCF₃SO₃/LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mA g⁻¹) within 2.5V and 4V voltage range. Room temperature (25°C)

addition of lithium nitrate (LiNO₃) to the electrolyte as film-forming agent may represent a suitable solution to increase the lithium cell performance.^{47,48} Indeed, LiNO₃ may decompose at about 1.5V to form a stable SEI layer protecting the lithium surface and preventing cell degradation.

Experimental section: Electrolyte Characterization

Self-diffusion coefficient was measured by using a Bruker 400 Avance III NMR spectrometer operating by double-stimulated echo pulse sequence in order to suppress convection effects [28]. The measurements were performed by within temperature ranging from 20°C to 70°C, collecting the signal each 10 °C, by gradient pulses of sine-shape with duration $\delta = 2-5$ ms, strength $g = 0-45$ G/cm and diffusion delay of $\Delta = 80-800$ ms. The electrolyte conductivity (δ) was calculated by using the diffusion coefficient of the anion and the cation along with the Nernst-Einstein equation (4): $\delta = \frac{F^2[C]}{RT} (D_{Li} + D_{CF_3SO_3})$

where F is the Faraday constant (96485 Coulomb), $[C]$ is the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the selected temperature value, D_{Li} and $D_{CF_3SO_3}$ are the self-diffusion coefficient Li⁺ cation and CF₃SO₃⁻ anion, respectively, measured by NMR technique. The ionic conductivity was also directly determined within temperature ranging from 20°C to 90°C by electrochemical impedance spectroscopy (EIS) in symmetric stainless steel/electrolyte/stainless steel 2032 coin cell. The cell was equipped by Teflon separator in order to fix the cell thickness, and the impedance spectroscopy was performed in a 100 mHz - 100 kHz frequency range with a signal amplitude of 10 mV using Biological VMP3 instrument. The ion association degree (α) was determined by using equation (5): $\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right)$ where δ_{EIS} and δ_{NMR} are the conductivity values measured by EIS and calculated by equation (4), respectively. The cation transference number (t^+), corresponding to the fraction of current carried out by the lithium ions, was calculated by using equation (6): $t^+ = \frac{D_{Li}}{D_{Li} + D_{CF_3SO_3}} =$

LiNO₃ Added Solution

Accordingly, PEG500DME-LiCF₃SO₃ solution has been augmented by the addition of LiNO₃ salt and characterized by voltammetry in order to detect its decomposition potential. Figure 19 reports the cyclic voltammetry of the bare PEG500DME-based electrolyte (blue line) and the corresponding solution containing LiNO₃ (green line) in a lithium cell using a carbon working electrode. The potential profiles show a huge peak around 0.5V mainly due to the reductive degradation of the PEG500DME for the bare electrolyte, and the expected additional peak at around 1.5V for the LiNO₃ containing one that is expected to form the above mentioned protective layer.⁴³ The voltammetry test suggests a discharge voltage lower than 1.5V in order to allow LiNO₃ decomposition with production of a passivation film preventing cell deterioration. Accordingly, we assembled a Li/PEG500DME, 1M LiCF₃SO₃, 0.4M LiNO₃/LiFePO₄ cell and performed a first discharge lowering the voltage down to 1V in order to allow the LiNO₃ decomposition, while the following cycles were performed within a typical voltage

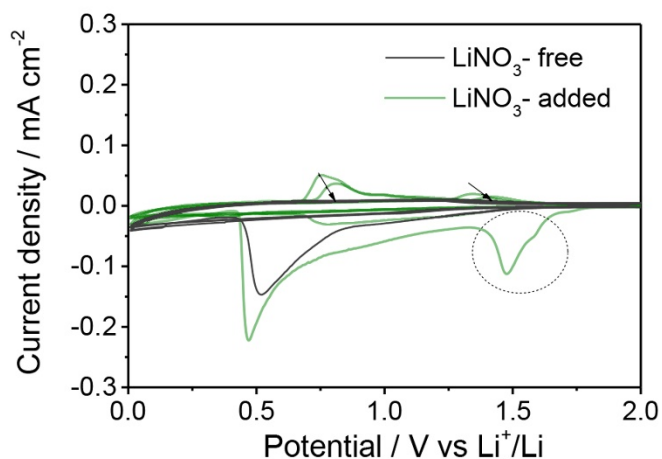


Figure 19 Cyclic voltammetry trends of the bare PED500DME, 1m LiCF₃SO₃ electrolyte (blue line) and the corresponding solution added by 0.4m LiNO₃ (green line) in a lithium cell using a carbon working electrode. Scan rate 0.1 mV s⁻¹, potential limits 0.01V-2V. Room temperature (25°C)

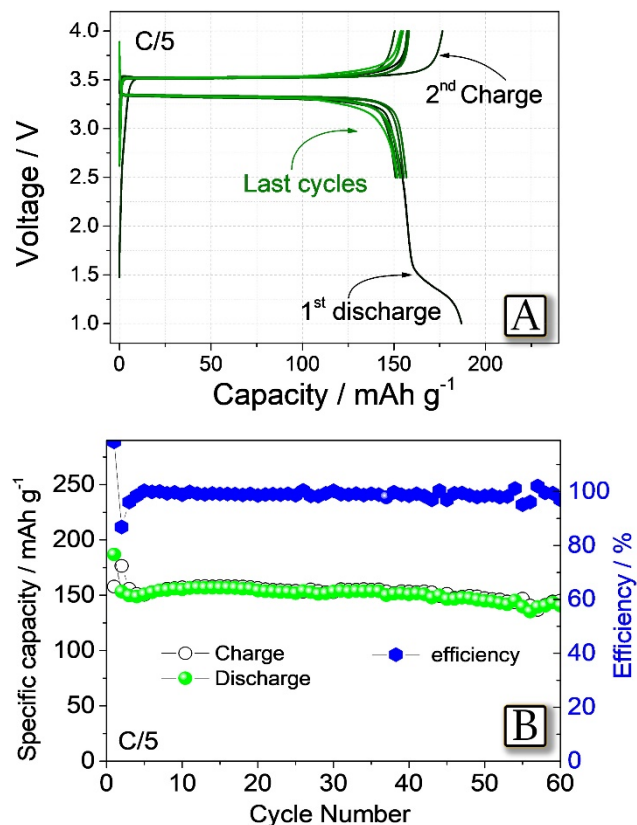


Figure 20 A) Voltage profiles and B) cycling behavior of the Li/PEG500DME, 1m LiCF₃SO₃, 0.4LiNO₃/LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mA g⁻¹). First cycle performed within 1V and 4V and following cycles within 2.5V and 4V voltage range. Room temperature (25°C)

range, i.e. 2.5V to 4V. Figure 20, reporting the voltage profiles (a) and the cycling behavior (b) of the lithium cell, shows a greatly enhanced behavior in terms of low polarization and cycling stability. During the first cycle, the cell reveals the expected decomposition starting at about 1.5V and a following charge characterized by a specific capacity of about 170 mAh g⁻¹, comprised of irreversible reactions such as minor electrolyte oxidation and structural reorganization of the LiFePO₄ electrode.⁸⁰ During the following cycles, the cell reveals a working voltage of about 3.5V, very limited polarization and a specific capacity of about 150 mAh g⁻¹ that is 90% of the theoretical value (Fig. 20A). Furthermore, the cell shows an efficiency approaching 100% and a very stable cycling trend (Fig. 20B), thus confirming the effective role of the film formed by LiNO₃ in protecting the cell from side reactions and allowing optimized cycling.

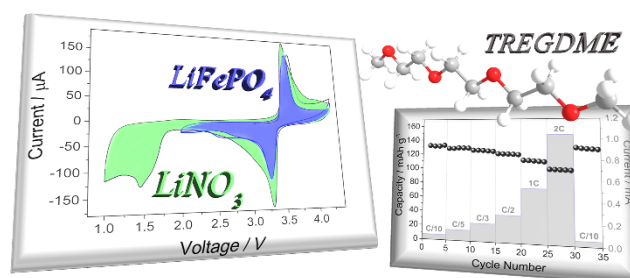
LiNO₃ effect - overview

The results demonstrated the suitability of a polyethylene glycol dimethyl ether (PEGDME)-based electrolyte for application in an efficient lithium battery. NMR and electrochemical tests revealed that the electrolyte has a conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ and a lithium transference number of 0.45, i.e. proper values for optimized cell performances. The addition of a lithium nitrate salt (LiNO_3) allowed the formation of a stable SEI film protecting the lithium metal and avoiding further electrolyte decomposition. Indeed, the lithium battery employing the modified electrolyte has shown high performances in terms of delivered capacity, efficiency and stability. The cell delivered a capacity of 150 mAh g^{-1} at a working voltage of 3.5 V, thus leading to a theoretical energy density of 525 Wh kg^{-1} . We believe that the data here reported may allow a safe use of lithium metal in efficient, high energy lithium batteries

LiNO₃ Added Electrolyte a Deep Investigation

For the first time, we presented that LiNO_3 allows the use of glyme- LiCF_3SO_3 -based electrolytes in lithium metal batteries with olivine cathodes. However, this peculiar behavior needed further investigation. Therefore, the full study of an electrolyte solution formed by dissolving lithium triflate (LiCF_3SO_3) in new end-capped glyme, i.e., triethylene glycol dimethyl ether (TREGDME, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$) is presented. TREGDME is characterized by a lower viscosity, thus higher conductivity, with respect to previously studied glyme. Thermogravimetric

analysis (TGA), differential scanning calorimetry (DSC), viscosity analysis, as well as pulse field gradient nuclear magnetic resonance (PFG NMR) and electrochemical impedance spectroscopy (EIS), are employed to determine thermal and rheological properties, the mobility of the dissolved species and the electrochemical characteristics of the electrolyte, respectively. The paragraph reports a deep investigation of the self-diffusion coefficient, ionic conductivity, lithium transference number, and ionic association degree and suggests the solution as suitable electrolyte medium in a lithium metal cell using a LiFePO_4 cathode prepared in our laboratory.⁸¹ Particular care is devoted to the study of both LiNO_3 addition effects and the electrochemical activation procedure before cell cycling, which ensure the formation of a stable electrode/electrolyte interface over anode and cathode. The study of the electrode/electrolyte interface is carried out by lithium stripping/deposition, voltammetry, electrochemical impedance spectroscopy (EIS), as well as by ex situ scanning electrode microscopy (SEM). Accordingly, the formation of the SEI at the electrodes surface promoted by the condition adopted in this work represents a key parameter allowing proper operation of the lithium cell. The $\text{Li}/\text{LiCF}_3\text{SO}_3\text{-TREGDME-LiNO}_3/\text{LiFePO}_4$ battery is studied by galvanostatic cycling at several current rates, revealing suitable performances.



TREGDME LiCF₃SO₃ *Properties*

TREG-LiCF₃SO₃ is investigated by TGA and DSC for determining key parameters for battery application, such as thermal characteristics and freezing point. Fig. 21a, reporting TGA under nitrogen flow, reveals weight loss starting at about 75 °C, likely due to evaporation of TREGDME, which represents a first indication of the upper operating temperature of the electrolyte.⁸² A further massive weight loss is observed above 200 °C. This could be related to the boiling of TREGDME (which falls in the 224 – 227 °C range). Then, weight losses at higher temperatures reveal salt decomposition.⁴ The inset in figure 21A compares the TGA profiles of pristine TREGDME black, TREG- LiCF₃SO₃ grey, and TREG- LiCF₃SO₃-LiNO₃ green. The pure solvent exhibits a weight loss beginning at 60 °C due to evaporation promoted by the N₂ flow, followed by a further weight loss above 200 °C indicating the boiling point. TREG-LiCF₃SO₃ and TREG- LiCF₃SO₃-LiNO₃ exhibit a similar trend upon heating and a higher thermal stability than pristine TREGDME. Fig.21B shows the DSC cooling profile of TREG- LiCF₃SO₃ from room temperature to –90 °C, performed in order to determine the freezing point of the electrolyte. The curve reveals an exothermic crystallization peak at –60 °C which suggests the lowest temperature suitable for the application of the electrolyte in lithium cell. In summary, the thermal properties revealed by Fig. 21 suggests a possible operating range extending from –60 °C to 75 °C, which exceeds that one of conventional carbonate-based electrolytes.⁸³ Fig. 21C reports the viscosity profile of TREG- LiCF₃SO₃ studied within temperature ranging from

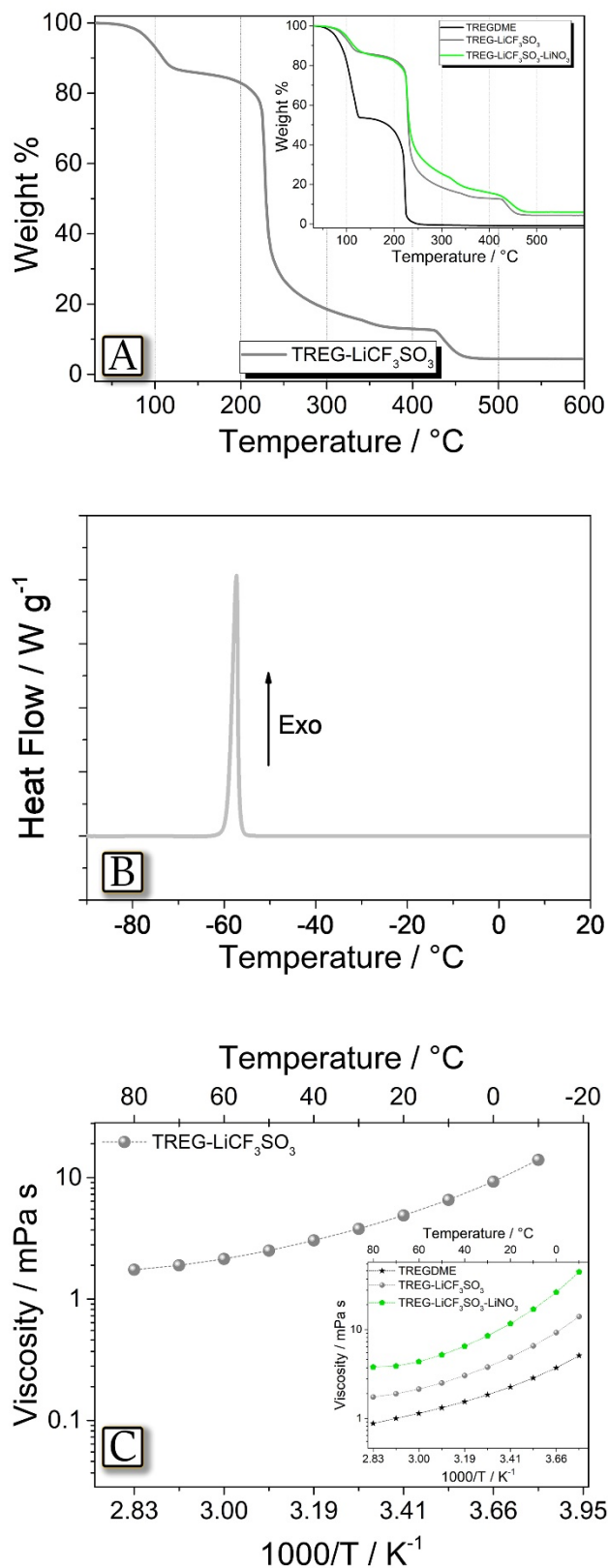


Figure 21 Thermal properties of TREG-LiCF₃SO₃ as studied by (A) thermogravimetric analysis (TGA) under nitrogen purge (40 mL min⁻¹) at 10 °C min⁻¹ heating rate from room temperature to 600 °C and (B) differential scanning calorimetry (DSC) under Ar atmosphere at 5 °C min⁻¹ cooling rate from 20 °C to –90 °C. (C) Viscosity vs. temperature of TREG-LiCF₃SO₃ performed by applying constant shear rates and collecting data every 10 °C after 15 minutes of thermal stabilization; temperature range from –10 °C to 80 °C. (in the inset the comparison between TREG solvent black, electrolyte grey and LiNO₃ added solution green)

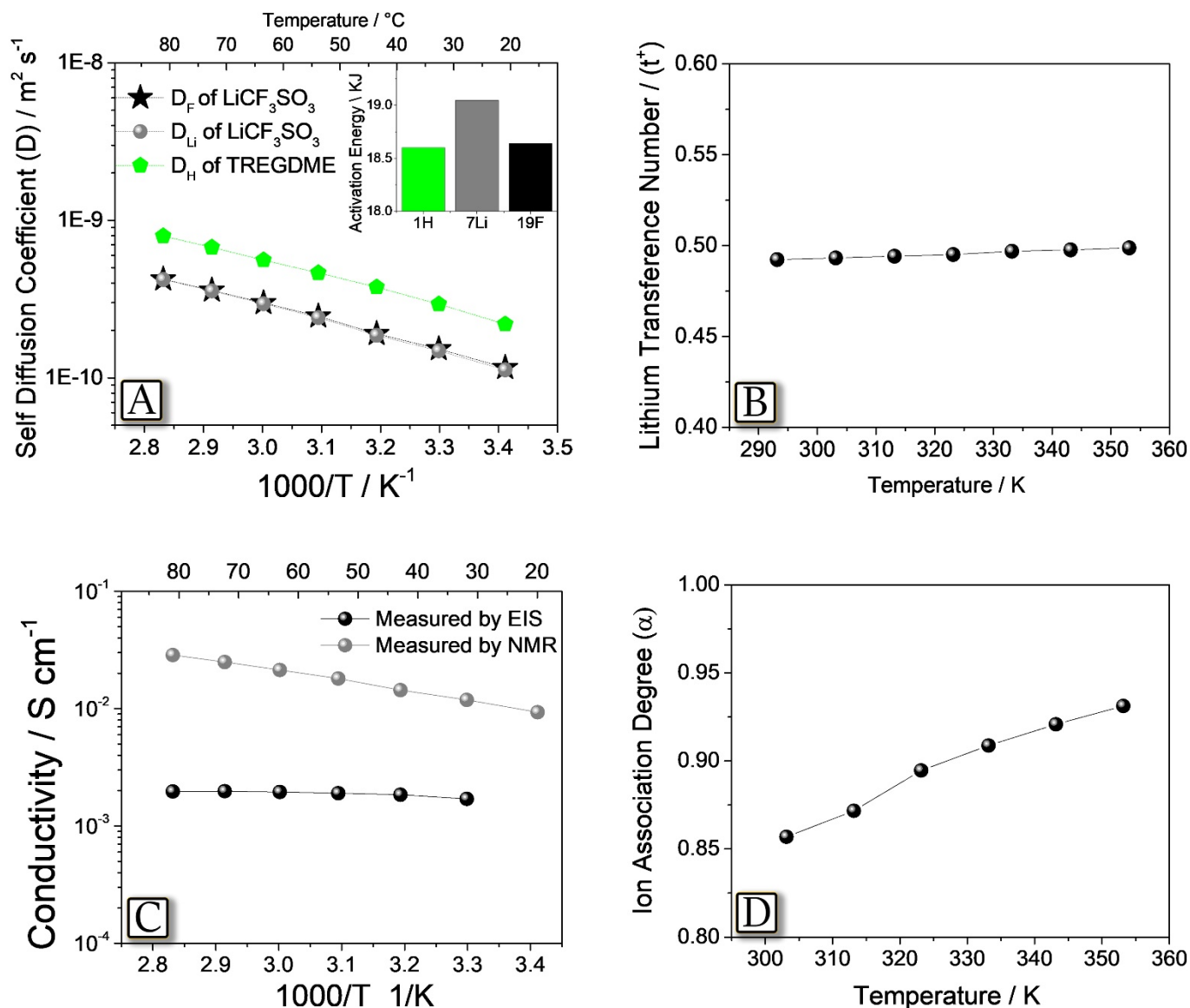


Figure 22 (A) Self-diffusion coefficient of the ^1H , ^{19}F , and ^7Li nuclei of TREG- LiCF_3SO_3 (see the experimental section for sample acronym) as determined by PFG NMR in the 20 – 80 °C temperature range; figure inset: self-diffusion activation energies for each nucleus (^1H , ^{19}F , and ^7Li) extrapolated from the self-diffusion coefficient in the Arrhenius plot. (B) Lithium transference number calculated from the self-diffusion coefficient data by equation (2) within the 20 – 80 °C temperature range. (C) Ionic conductivity obtained by EIS (black line) and calculated from the self-diffusion coefficient data by equation (3) within the 20 – 80 °C temperature range. (D) Ion association degree between Li^+ cation and CF_3SO_3^- anion calculated by using equation (4) from the ionic conductivity data obtained by EIS and PFG NMR.

–10 °C to 80 °C. The figure reveals the expected decreasing trend by raising temperature. The TREG- LiCF_3SO_3 electrolyte has viscosity of about 5 mPa s at 20 °C, which is consider suitable value for battery application. Viscosity measurements on

TREGDME solvent and TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3$ electrolyte have been also carried out to evaluate the changes due to salt addition. The inset of figure 21C shows that the viscosity increases in the whole range of temperature due to addition of LiCF_3SO_3

Experimental section: Electrolyte Preparation

Triethylene glycol dimethyl ether (TREGDME, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$, Sigma-Aldrich) was dried under molecular sieves (5Å) until the water content was below 10 ppm, as determined by using the Karl Fischer titration instrument (831 Karl Fisher Coulometer, Metrohm). Lithium trifluoromethanesulfonate (lithium triflate, LiCF_3SO_3 , Sigma-Aldrich) and lithium nitrate (LiNO_3 , Sigma-Aldrich) were dried overnight under vacuum at 80 °C before use. The electrolyte was prepared by dissolving LiCF_3SO_3 in TREGDME in 1 mol kg^{-1} concentration with respect to the solvent (solution indicated by the acronym TREG- LiCF_3SO_3). A second electrolyte solution was prepared by dissolving LiCF_3SO_3 and LiNO_3 in TREGDME; both salts were used in 1 mol kg^{-1} concentration with respect to the solvent (solution indicated by the acronym TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3$). The electrolyte preparation was carried out in an argon-filled glovebox with moisture and oxygen content lower than 1 ppm.

and LiNO₃, with values at 20 °C of 2.3 and 11.7 mPa s for TREGDME and TREG-LiCF₃SO₃-LiNO₃, respectively. The transport properties of TREG-LiCF₃SO₃ were investigated by coupling PFG NMR and EIS in the temperature range from 20 °C to 80 °C, i.e., the typical window for battery applications. Fig. 22 shows the results in terms of self-diffusion coefficient (Fig. 22A), lithium transference number (Fig. 22B), conductivity (Fig. 22C), and ion association degree (Fig. 22D). The PFG NMR of ¹H, ⁷Li and ¹⁹F nuclei indicates the same increasing trend of self-diffusion coefficient of TREGDME solvent, Li⁺ and CF₃SO₃⁻ salt ions, respectively, with increasing temperature (Fig. 22A); however, the TREGDME chains exhibit higher mobility in the whole temperature range with respect to the ion species, which show similar

value of the coefficients. The activation energies related to the self-diffusion process, reported in inset of Fig. 22A, are comparable for TREGDME chains and anions, while the small lithium ion shows a slightly higher activation energy, however within the experimental error of the test (see *experimental section: electrolyte characterization* of this paragraph). On the other hand, a higher activation energy for lithium ions may be reasonably expected by the strong interaction with the other species promoted by its high charge density. The lithium transference number (*t*⁺) was calculated by equation (6) as the amount of charge carried by lithium cations with respect to the total charge and reported in Fig. 22B. The figure shows a *t*⁺ value of about 0.5 within the whole temperature range, which may be

Experimental section: Electrolyte Characterization part 1

The thermal properties of TREG-LiCF₃SO₃ were evaluated by **differential scanning calorimetry (DSC)**. The samples were put in a sealed Al crucible in an argon-filled glovebox for DSC; the measurement was performed from 20 °C to -90 °C with a cooling rate of 5 °C min⁻¹. **Thermogravimetric analyses (TGA)** of TREGDME, TREG-LiCF₃SO₃, and TREG-LiCF₃SO₃-LiNO₃ were carried out by using a TG209 F1 Libra, Netzsch, instrument. The samples were heated at a rate of 10 °C min⁻¹ from room temperature to 600 °C under a nitrogen purge (40 mL min⁻¹). The samples were hermetically sealed inside a dry room (dew point < -70 °C) in aluminum pans, which were punched under nitrogen atmosphere just before the measurement. **The viscosity** of TREGDME, TREG-LiCF₃SO₃, and TREG-LiCF₃SO₃-LiNO₃ was evaluated at various temperatures in a dry room (dew point < -70 °C) through an Anton-Paar Physica MCR102 rheometer, by applying constant shear rates and using a Peltier system for cooling/heating. The measurements were performed every 10 °C upon sample heating after 15 min of equilibration at constant temperature. **The self-diffusion coefficients** of TREG-LiCF₃SO₃ for the ¹H, ¹⁹F and ⁷Li nuclei were investigated with a Bruker 400 Advance III NMR spectrometer. Screw-cap gas-tight NMR tubes were used. The measurements were carried out using a double stimulated echo sequence with pulsed field gradients (PFG) in order to suppress convection; data were collected every 10 °C from 20 °C to 80 °C for each nucleus. Gradient pulse duration (δ) of 1.4 – 4 ms, diffusion delay (Δ) of 200 – 400 ms, and a gradient pulse strength increased linearly in 32 steps from 1 to 45 G cm⁻¹ were used. A longitudinal eddy-current delay (LED) of 5 ms was used to avoid eddy current effects. error on the self-diffusion coefficient is about 3-5%.⁶¹ **Ionic conductivity** was measured by impedance spectroscopy (EIS) using 10 mV signal amplitude in the 100 kHz – 100 mHz frequency range through a VSP (Biologic) instrument. The measurements were performed every 10 °C from 30 °C to 80 °C on symmetrical stainless steel/electrolyte/stainless steel 2032-coin cell, using a Teflon ring (thickness = 500 μ m) as the separator in order to fix the cell constant. The conductivity values obtained by EIS were compared with those calculated using the self-diffusion coefficient (δ_{NMR}) through the Nernst-Einstein eq.

$$(4): \delta = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3})$$

where δ_{NMR} is the conductivity determined by the NMR, *F* is the Faraday constant (96485 C), [*C*] is the concentration of the salt in the electrolyte (mol cm⁻³), *R* is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), *T* is the temperature (K), *D*_{Li} and *D*_{CF₃SO₃} are the corresponding self-diffusion coefficient. The **ion association degree** was derived from equation

$$(5): \alpha = \left(1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}}\right)$$

where α is the ion association degree, δ_{NMR} and δ_{EIS} are the conductivity by PFG NMR and EIS, respectively. The **lithium transference number** was obtained by the following equation

$$(6): t^+ = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3}}$$

where *t*⁺ is the transference number of the cation, *D*_{Li} is the self-diffusion coefficient of lithium, and *D*_{CF₃SO₃} is the self-diffusion coefficient of the CF₃SO₃⁻ anion. **Lithium stripping-deposition** tests were carried out on TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ solutions using Swagelok-type symmetrical cell with a Whatman® separator, by applying constant current of 0.1 mA cm⁻¹ with step duration of 1 h through a Maccor 4000 series Battery Test System.

considered a suitable value for lithium battery application. The ionic conductivity of the electrolyte was calculated from the self-diffusion coefficient data estimated from PFG NMR by applying the equation (4) and is compared with the data measured by EIS in Fig. 22C. Remarkably, the two methods provide conductivity values having difference of about one order of magnitude, as already reported in the previous paragraph.^{52,78,84} Indeed, is noteworthy to remind again that this discrepancy is due to the differences between the two techniques: PFG NMR overestimates the ionic conductivity since it reveals the motion of all selected atoms within the electrolyte, i.e., single ions, ionic couples, and multiple associated ions, while EIS indicates the actual ionic conductivity ascribed to the net charge flow.^{52,78,84} In fact, this high degree of ionic association is at least partially responsible for the observation that the apparent Li^+ transference numbers are close to 0.5. Indeed, the conductivity measured by EIS has a stable value of about $1.9 \times 10^{-3} \text{ S cm}^{-1}$ within the whole temperature range, which well matches the battery application requirements, while the conductivity derived from self-diffusion coefficient exhibit slightly increasing

trend, with a value of the order of $10^{-2} \text{ S cm}^{-1}$. According to the above discussion, the conductivity data were used to calculate the ion association degree (Fig. 22D) by applying the equation (5). The slight increase of the association degree with increasing temperature reflects free ions recombination in pairs or complexes, which leads to a lower number of charge carriers at higher temperature. This phenomenon, already reported in literature for ether-based electrolytes, has been attributed to a solvent dielectric constant drop due to temperature increase, which causes a decrease of the glyme solvation power.⁵² Despite increased ion association degree, the stable values of the actual ionic conductivity measured by EIS (Fig. 22C) is attributed to a simultaneous solvent viscosity decrease at the higher temperature, leading to a better mobility of the charge carriers.

Bare and LiNO_3 added Solution Comparison

The previous chapter underlined the stability of lithium cell using insertion electrode and long chain glyme electrolyte. The issues may be strongly mitigated by the addition of LiNO_3 to the

Experimental section: Electrolyte Characterization part 2

The **anodic stability** of TREG- LiCF_3SO_3 and TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3$ was investigated by linear sweep voltammetry at 0.1 mV s^{-1} on Swagelok-type 3-electrodes cells with lithium metal for the counter and reference electrodes, and carbon-coated on aluminum foil as working electrode. Carbon-coated Al electrode allows determination of the actual electrochemical anodic stability window, which may be underestimated with Ni or Pt working electrodes. The same cell configuration, was used for **cyclic voltammetry** measurements; the working electrode reasonably reproduces the electrolyte behavior on composite cathodes, usually formed by active material, conductive carbon and polymer binder. The tests were performed on TREG- LiCF_3SO_3 and TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3$ to evaluate electrolyte behavior and the effect of LiNO_3 addition, at a scan rate of 0.1 mV s^{-1} within the 1 – 4.3 V vs. Li^+/Li potential range for the first cycle, and within the 2 – 4.3 V vs. Li^+/Li potential range for the subsequent cycles. Further voltammetry experiments were carried out employing LFP (on aluminum support) as the working electrode, with a scan rate of 0.1 mV s^{-1} within the 1 – 4.3 V vs. Li^+/Li potential range for the first cycle, and within the 2 – 4.3 V vs. Li^+/Li potential range for the subsequent cycles. The voltammetry measurements were performed through a VersaSTAT MC Princeton Applied Research – AMETEK potentiostat. The **lithium/electrolyte interfacial stability** of TREG- LiCF_3SO_3 and TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3$ were evaluated by performing EIS tests on symmetrical lithium/electrolyte/lithium Swagelok-type cells with a Whatman® separator, using 10 mV signal amplitude in the 500 kHz – 200 mHz frequency range through a VersaSTAT MC Princeton Applied Research – AMETEK potentiostat. The impedance spectra were analyzed by nonlinear least-square (NLLS) fit using the Boukamp software;^{62,63} the fit reliability was confirmed by chi-square (χ^2) values lower than 10^{-4} . The equivalent circuit (shown in the inset of the figure) adopted for the Nyquist plot was $R_a(R_iQ_i)$ or $R_a[(R_iQ_i)(RW)]$, where R represents a resistance and Q a constant phase element (CPE) and W a finite length diffusion element for non-blocking electrodes.

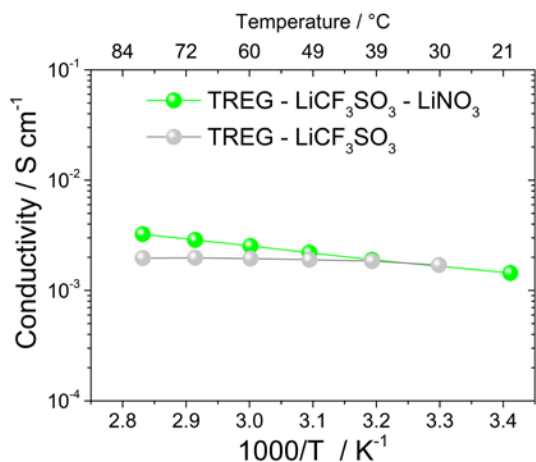


Figure 23 Ionic conductivity TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ obtained by EIS, collecting data every 10 °C from 20 °C to 80 °C.

electrolyte, despite negligible change of the thermal characteristic and viscosity increase (Fig. 22). Furthermore, the LiNO₃ addition partially affect the ionic conductivity of the solution. Indeed, Fig. 23 reveals for both TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ ionic conductivity of the order of 10⁻³ S cm⁻¹ within the investigated temperature range. However, the effect of LiNO₃ addition is further studied by galvanostatic measurements, impedance spectroscopy and voltammetry. Fig. 24 shows a comparison of the electrochemical features of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ in terms of lithium/electrolyte interface stability throughout lithium deposition/dissolution by galvanostatic cycling (Fig. 24A), anodic stability window (Fig. 24B), and lithium/electrolyte interface resistance trend upon storage of Li/Li symmetrical cell (Fig. 24C). Fig. 24A reveals for TREG-LiCF₃SO₃ a remarkable overvoltage increases over six days of cycling, which indicates poor stability of lithium metal anode in the pristine electrolyte. On the other hand, the LiNO₃ addition stabilizes the lithium/electrolyte interface; indeed, the TREG-LiCF₃SO₃-LiNO₃ cell maintains a polarization as low as 20 mV for up to 12 days of cycles. LiNO₃ has a beneficial effect on the anodic stability too, as

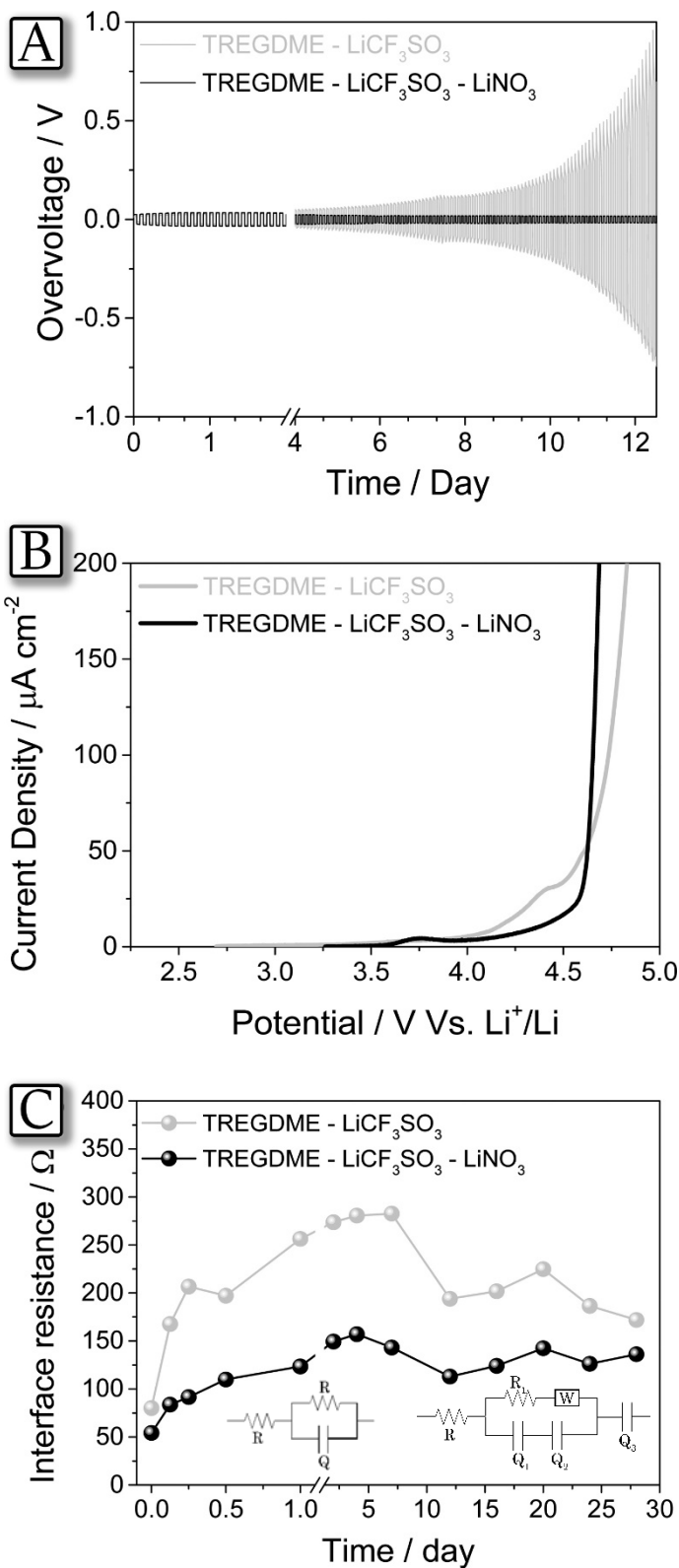


Figure 24 (A) Lithium stripping/deposition test of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ (see the experimental section for sample acronyms) in symmetrical Li/Li cell at constant current of 0.1 mA cm⁻²; voltage limit: +1 V and -1 V; step time: 1 hour each. (B) Anodic stability window of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ (see the experimental section for sample acronyms) as determined by linear sweep voltammetry of three-electrode cells at 0.1 mV s⁻¹ scan rate (carbon-coated Al disk working electrode, Li metal counter and reference electrodes, respectively). (C) Interface resistance of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ (see the experimental section for sample acronyms) as calculated by NLLS of EIS tests on Li/Li symmetrical cells throughout storage.

shown by the linear sweep voltammetries of Fig. 24B. TREG-LiCF₃SO₃ exhibits a current onset of about 5 $\mu\text{A cm}^{-2}$ at 3.55 V vs. Li⁺/Li and undergoes further oxidation above 4 V vs. Li⁺/Li, as revealed by rising current at higher potential. Meanwhile, TREG-LiCF₃SO₃-LiNO₃ shows a current peak at about 3.72 V vs. Li⁺/Li, likely associated with LiNO₃, and only minor decomposition processes below 4.5 V vs. Li⁺/Li, followed by remarkable current increasing at 4.6 V vs. Li⁺/Li. Therefore, the anodic stability of the electrolyte well matches the application in a lithium battery using LFP cathode characterized by working voltage of 3.45 V vs. Li⁺/Li (see following paragraphs).⁸⁵ The stability of the lithium/electrolyte interface under static condition, i.e., the chemical stability, is investigated by EIS tests carried out during 28 days of storage in symmetrical Li/Li cell without current flowing. The impedance data of Fig 25 have been analyzed by NLLS fit, in order to evaluate the lithium/electrolyte interface resistance; the related results are shown in Fig. 24C. The interface resistance of TREG-LiCF₃SO₃ quickly grows to 260 Ω during the first day upon SEI formation⁸⁶ and slightly increases up to 280 Ω throughout the following days. After 10 days of storage, the cell exhibits an interface resistance drop to about 200 Ω , attributed to partial dissolution/degradation of the passivation

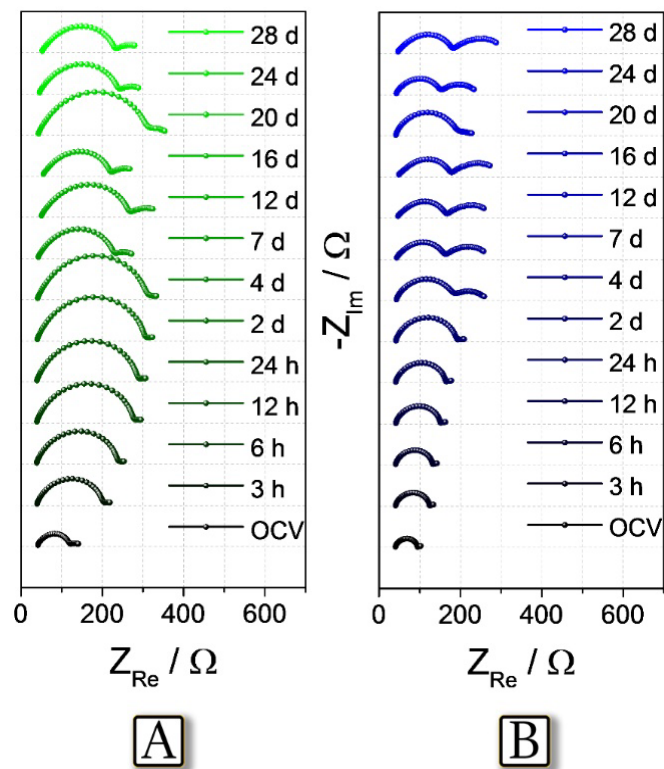


Figure 25 Nyquist plots related to EIS measurements performed during storage of Li/Li symmetrical cells using (A) TREG-LiCF₃SO₃ and (B) TREG-LiCF₃SO₃-LiNO₃

layer,⁸⁷ and further interface stabilization. On the other hand, TREG-LiCF₃SO₃-LiNO₃ reveals stable lithium/electrolyte interface upon storage, after initial increase due to SEI formation,⁸⁶ which is reflected into interface resistance values ranging between 110 Ω and 160 Ω . In summary, LiNO₃ addition to the glyme-based solution has beneficial effects on the lithium/electrolyte interface, since it promotes the formation of a stable SEI layer. This phenomenon has been widely investigated for Li-S batteries.^{43,47,48,50,88} Furthermore, Fig. 25 shows the Nyquist plots related to EIS measurements of the

Experimental section: Cathode Preparation

The LiFePO₄ (LFP) powder was synthesized by solvothermal treatment and following high-temperature annealing in inert atmosphere, as reported in our paper.⁸¹ The cathode film was prepared mixing the active material, poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP copolymer, Kynar Flex 2801) as binder, and Super P Carbon (Timcal) as conductive additive in the ratio 80:10:10% w/w in Tetrahydrofuran (THF, Sigma-Aldrich). The slurry thus obtained was casted on either aluminum foil or carbon cloth current collector by doctor blade. The carbon cloth support was used for cycling test at constant current rate, while the aluminum support was used for cyclic voltammetry and rate capability tests. The carbon cloth electrode supports may enhance the electrochemical performances of olivine cathode materials synthesized in our laboratory, particularly in terms cycling stability. This phenomenon is likely related to the improved electric contact between active material particles and current collector as well as to the higher electrode contact area of carbon cloth with respect to Al foil. Therefore, we used the carbon cloth for cycling test at a constant rate. Beside cycle life, cyclic voltammetry and rate capability tests were performed in order to detect the electrochemical processes due to LiFePO₄ and LiNO₃, hence we considered the aluminum support as the most suitable current collector for evaluation. The electrode films were dried overnight under vacuum at 110 °C, cut in the form of 10 mm diameter disks, and brought in an argon-filled glovebox before cell assembling. The electrodes had mass loading of about 4 mg cm⁻².

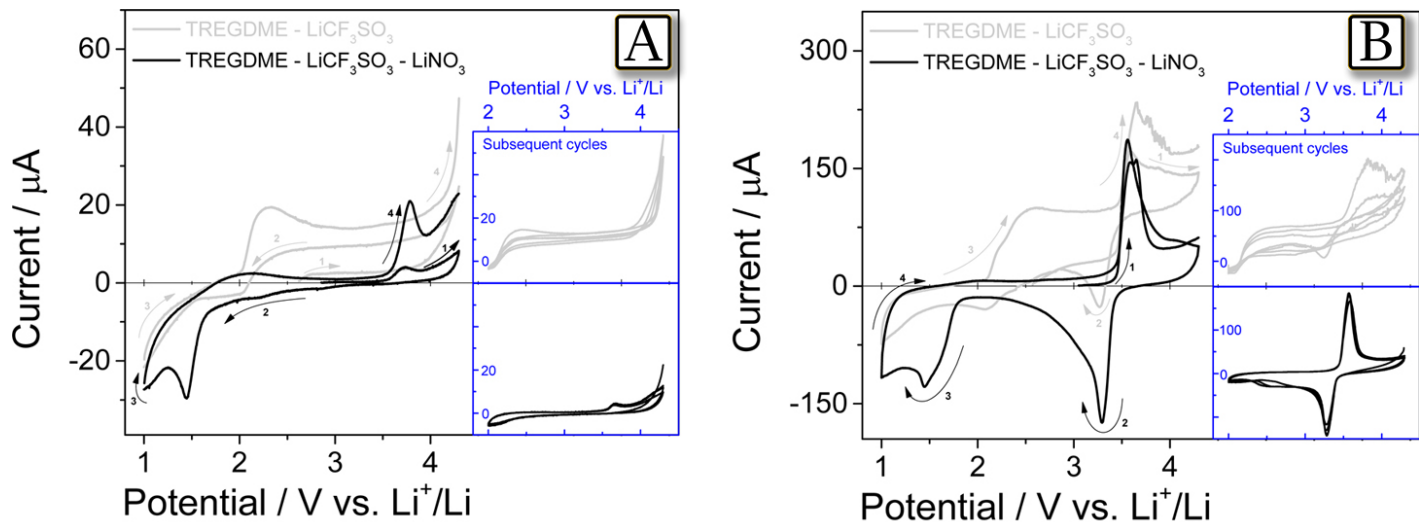


Figure 26 Cyclic voltammetry of TREG-LiCF₃SO₃ (grey line) and TREG-LiCF₃SO₃-LiNO₃ (black line, see the experimental section for sample acronyms) used in three-electrode cells with Li metal as counter and reference electrodes; (A) carbon-coated Al disk working electrode and (B) LFP working electrode; scan rate: 0.1 mV s⁻¹; potential range: 1 – 4.3 V vs. Li⁺/Li for the first cycle, 2 – 4.3 V vs. Li⁺/Li for the subsequent cycles; first cycles in the main figure; subsequent cycles in inset.

cells using TREG-LiCF₃SO₃ (Fig. 25A) and TREG-LiCF₃SO₃-LiNO₃ (Fig. 25B). Both panels reveal impedance responses characterized by a high-medium frequency semicircle due to the SEI over the electrode surface.⁸⁹ In addition, after 4 days of storage, the cell using TREG-LiCF₃SO₃-LiNO₃ exhibits a low frequency response attributed to the finite-length Warburg-type^{90,91}. Despite this aspect exceeds the scope of this study, which focused on the passivation film properties, it may be considered as a different feature of the SEI owing to the LiNO₃ addition.

LiNO₃ Voltammetry Study

The electrochemical activation technique consisting in potential decrease down to 1 V vs. Li⁺/Li to reduce LiNO₃ at the working electrode allowed the efficient use of a polyethylene glycol dimethyl ether PEGDME-LiCF₃SO₃ solution added by LiNO₃ as the electrolyte in lithium cell using insertion cathodes. This intriguing behavior is herein further investigated for TREGDME-based electrolyte by cyclic voltammetry of lithium cells using carbon (Fig. 26A) and LFP (Fig. 26B) working

electrodes. The voltammetry of Fig. 24A clearly reveals for the TREG-LiCF₃SO₃ electrolyte (light gray line) a positive current flow of about 15 μA within the 2 – 4.3 V vs. Li⁺/Li potential range after the first charge, both during oxidation and during reduction scans. This undesired current flow may be attributed to parasitic decomposition processes of the pristine electrolyte at the carbon electrode. Furthermore, a current drift is observed by lowering the potential to 1 V vs. Li⁺/Li during the first reduction, which is attributed to further electrolyte reductive decomposition at the working electrode⁸³ as well as to possible lithium arrangement within carbon. Oxidative positive current is also observed by the subsequent cycles, performed by limiting the potential cutoff to 2 V vs. Li⁺/Li (inset of Fig. 26A). Instead, the voltammetry of TREG-LiCF₃SO₃-LiNO₃ shows a different trend owing to the LiNO₃ addition. The test reveals the small oxidation peak at 3.72 V vs. Li⁺/Li, already observed in Fig. 26B, during the first anodic scan, and a narrow peak at 1.5 V vs. Li⁺/Li during the first cathodic scan, ascribed to the electro-reduction of LiNO₃ at the working electrode.^{22,50} During the second anodic

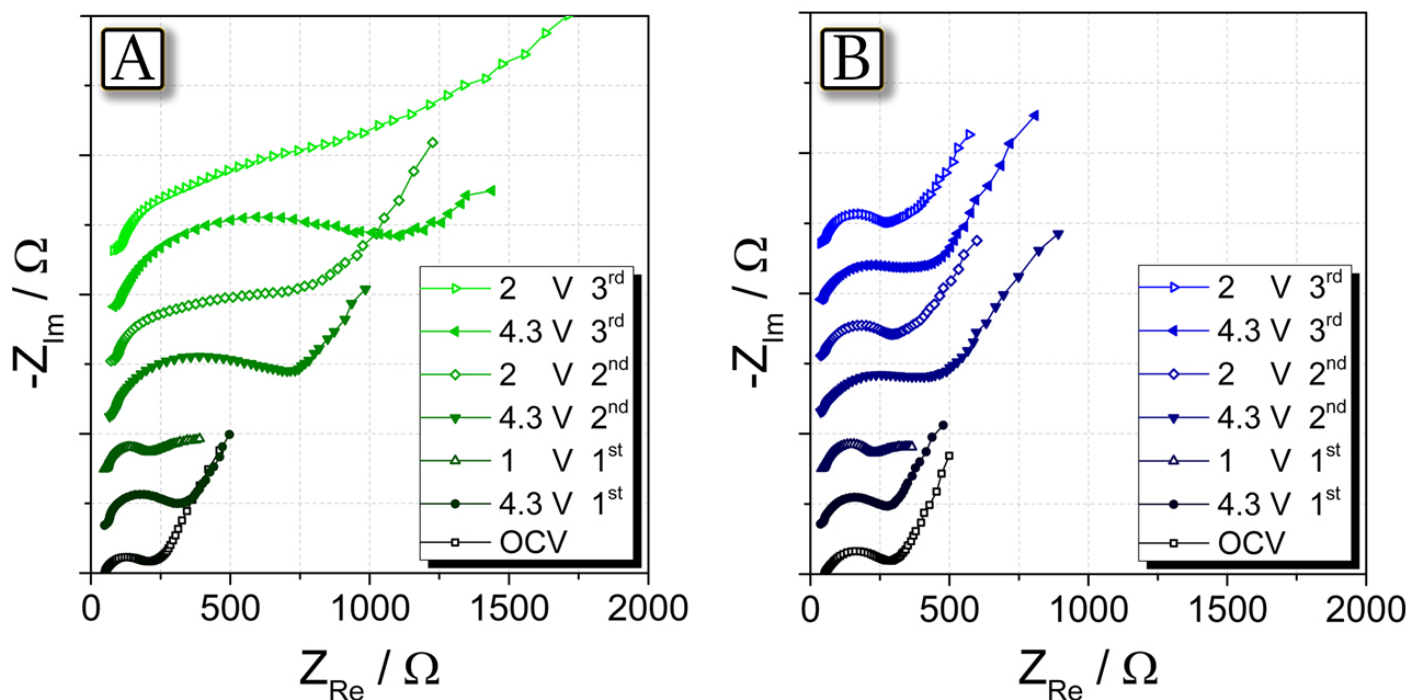


Figure 27 Nyquist plots related to EIS measurements carried out on three-electrode cells using LFP working electrode and lithium metal counter and reference electrodes; tests performed at the open circuit voltage (OCV) and at the end of each voltammetry cycle shown in Fig. 4. Cells using (a) TREG-LiCF₃SO₃ and (b) TREG-LiCF₃SO₃-LiNO₃ (see the experimental section of the manuscript for sample acronyms).

scan the peak at 3.72 V vs. Li⁺/Li increases, and drops by subsequent cycles (inset of Fig. 26A). The peak at 3.72 V vs. Li⁺/Li, missing in the cyclic voltammetry of the pristine TREG-LiCF₃SO₃, may be associated to LiNO₃ indeed. Furthermore, the absence of undesired positive current flow for cell using TREG-LiCF₃SO₃-LiNO₃ indicates that LiNO₃ addition actually mitigates the parasitic processes due to electrolyte oxidation, thus suggesting this solution as suitable electrolyte for application in lithium cell using LFP. This aspect is confirmed by Fig. 26B, reporting the cyclic voltammetry in Li/LFP cell of bare (light gray) and LiNO₃-added (black) electrolytes. The cell using TREG-LiCF₃SO₃ shows noisy voltammetry profiles and

shift toward positive currents due to electrolyte decomposition, as already observed for the cell using the carbon electrode (compare Fig. 26A and 26B). Furthermore, the continuous electrolyte electro-oxidation at the LFP working electrode during cycles progressively leads to additional issues such as peak broadening, remarkable increase of the charge-discharge polarization, and final cell failure (inset of Fig. 26B). The voltammetry of the Li/TREG-LiCF₃SO₃-LiNO₃/LFP cell shows a different trend characterized during the first cycle by narrow peaks centered at 3.45 V vs. Li⁺/Li due to the Fe³⁺/Fe²⁺ redox reaction within the olivine structure,⁸⁵ in addition to the previously discussed reduction peak at about 1.5 V vs. Li⁺/Li attributed to LiNO₃.^{22,50} The subsequent cycles overlap and

Experimental section: Cathode Characterization

Galvanostatic cycling tests were performed through a Maccor 4000 series Battery Test System on Li/TREG-LiCF₃SO₃-LiNO₃/LFP Swagelok-type two-electrode cells with a Whatman® separator. The cells were electrochemically activated by 4 galvanostatic cycles at C/5 rate (1C = 170 mAhg⁻¹); the first discharge was performed by decreasing the voltage below 2 V and limiting the time to 5.15 h, in order to form a stable solid electrolyte interphase (SEI) layer at the electrode surface. The subsequent cycles were performed within the 2 – 4 V voltage range at C/5 rate for test at single current, and at C/10, C/5, C/3, C/2, 1C, and 2C for rate capability test (1C = 170 mAhg⁻¹). SEM Zeiss EVO 40 with a thermionic electron gun equipped by LaB₆ crystal was employed to study the morphology of the electrodes at various cycling stages.

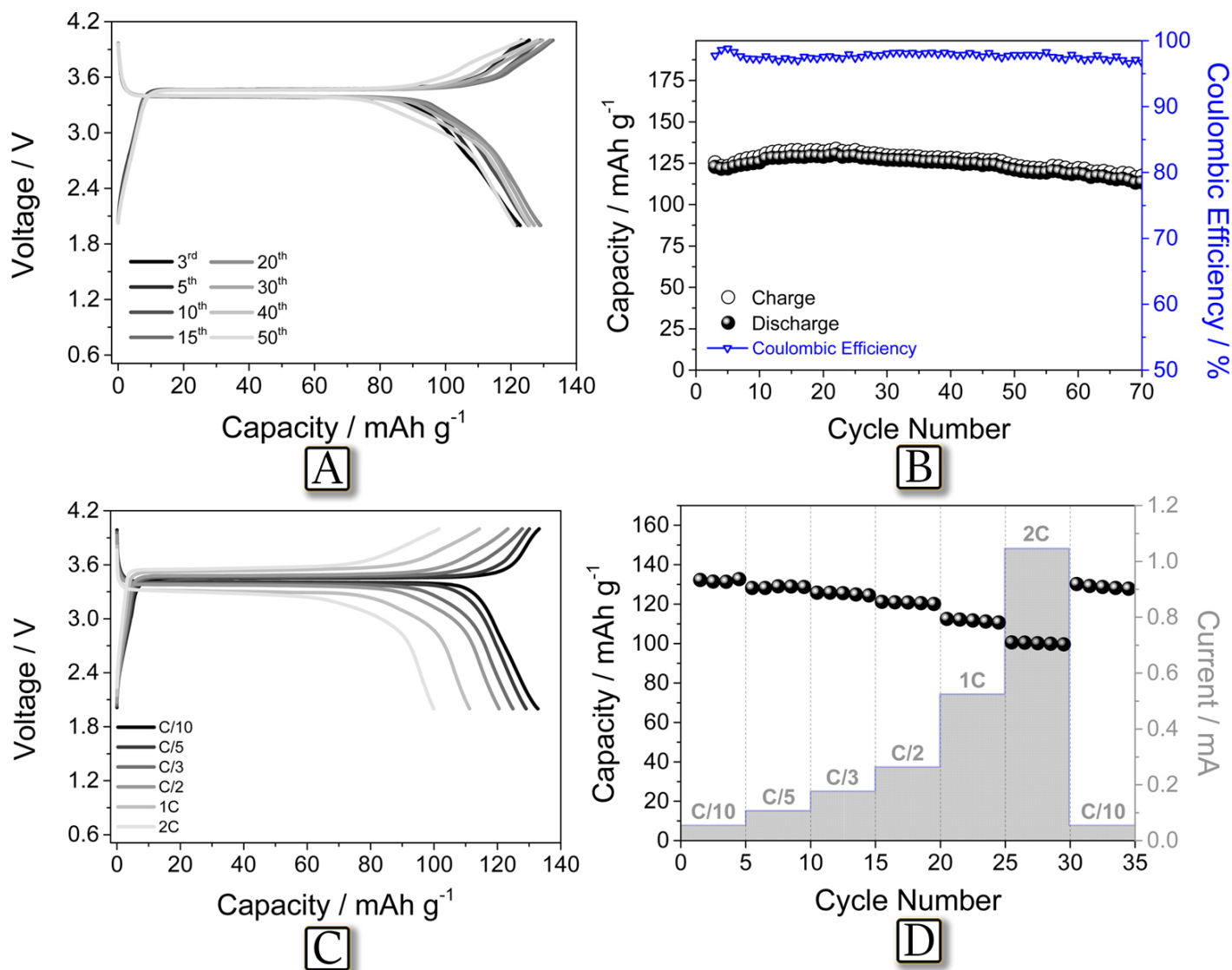


Figure 28 Galvanostatic cycling at C/5 rate ($1C = 170 \text{ mA g}^{-1}$) in terms of (A) voltage profile and (B) cycling behavior of a Li/TREG-LiCF₃SO₃-LiNO₃/LFP cell within 2 – 4 V voltage range. Rate capability test at C/10, C/5, C/3, C/2, 1C, 2C rates ($1C = 170 \text{ mA g}^{-1}$) in terms of (C) voltage profile and (D) cycling behavior of a Li/TREG-LiCF₃SO₃-LiNO₃/LFP cell within 2 – 4 V voltage range

the electrochemical process proceeds reversibly with limited polarization, following the typical profile associated with lithium (de-)insertion within LiFePO₄ (inset of Fig. 26B). Fig. 27 reports the Nyquist plots of the EIS tests performed throughout the voltammetry experiments. In particular, impedance spectra have been taken at open circuit voltage (OCV) and at the voltammetry cutoffs, i.e., at 4.3 V vs. Li⁺/Li at the end of charge as well as at 1 V vs. Li⁺/Li (first cycle) and at 2 V vs. Li⁺/Li (subsequent cycles) at the end of discharge. Fig. 25A reveals remarkable increase of the LFP/TREG-LiCF₃SO₃ interface resistance after three voltammetry cycles. On the other hand, Fig. 25B reveals

for the LFP/TREG-LiCF₃SO₃-LiNO₃ interface a stable resistance after the first activation, which is reflected into the above discussed stability of the voltammetry profiles of Fig. 25B. This behavior suggests formation of a suitable LFP/electrolyte interface during the first voltammetry scan using the solution added by the LiNO₃.

TREGDME-LiNO₃ *Galvanostatic Cycling*

The electrochemical results of Figs. 25, 26 and 27 suggest LiNO₃ as effective stabilizing agent for al-

lowing proper operation of the lithium metal battery using LFP and TREGDME-based electrolyte. In particular, the lithium plating/stripping and cyclic voltammetry tests of Figs. 25A and 26 clearly reveal fast failure of the cells without LiNO_3 , which might be attributed to poor stability of the electrode/electrolyte at both anode and cathode sides. Accordingly, the previous chapter reported the comparison of the galvanostatic cycling behavior of two Li/LiFePO_4 cells using glyme-based electrolyte with and without LiNO_3 . The paragraph revealed remarkable increase of cell polarization, electrolyte decomposition and high irreversible capacity upon cycling of the cell without LiNO_3 , which led to capacity fading from 150 mAh g^{-1} in the first cycle to a value as low as 0 mAh g^{-1} after only 37 cycles. Therefore, basing on the voltammetry tests reported herein as well as on the previous results may be confirmed the stabilizing effects of LiNO_3 addition to the electrolyte on the galvanostatic cycling trend of $\text{Li/TREG-LiCF}_3\text{SO}_3\text{-LiNO}_3\text{/LFP}$ cells (Fig. 28). An electrochemical activation procedure of the cell for galvanostatic cycling, first proposed in the previous paragraph and herein further optimized, has been performed and shown in Fig. 29. The figure indicates a plateau at about 1.7 V related to the LiNO_3 reduction, according to the CV results shown in Fig. 26, and a 2nd charge plateau with capacity exceeding the theoretical value for LFP (170 mAh g^{-1}), partially attributed to electrolyte irreversible reaction occurring at about 3.5 V , which overlaps the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox reaction. It is noteworthy that the actual composition of the electrolyte solution reasonably changes due to the significant consumption of LiNO_3 in the electrochemical activation process. However, the 1 mol kg^{-1} concentration of lithium

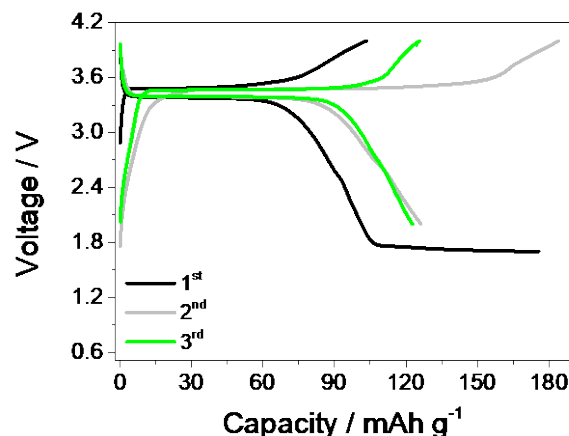


Figure 29 Three electrochemical activation cycles of a $\text{Li/TREG-LiCF}_3\text{SO}_3\text{-LiNO}_3\text{/LFP}$ cell cycled at $C/5$ rate ($1C = 170 \text{ mAh g}^{-1}$); first discharge performed by decreasing the voltage below 2 V and limiting the time to 5.15 h ; subsequent cycles within the $2 - 4 \text{ V}$ voltage range; $C/5$ rate for test at ($1C = 170 \text{ mAh g}^{-1}$).

nitrate ensures suitable cell operation after the activation process. Indeed, this process leads to formation of stable electrode/electrolyte interface, as confirmed by EIS in Fig. 27, as well as by galvanostatic tests of the $\text{Li/TREG-LiCF}_3\text{SO}_3\text{-LiNO}_3\text{/LFP}$ cell performed at $C/5$ rate ($1C = 170 \text{ mA g}^{-1}$) and reported in Fig. 28 in terms of voltage profile (A) and cycling trend (B). Fig. 28A reveals a flat voltage plateau centered at 3.45 V , according to the two-phase reaction of LiFePO_4 ,⁸⁵ with polarization as low as 0.05 V . The cell stably delivers reversible capacity of about 125 mAh g^{-1} , upon capacity increase during the first 10 cycles owing to structural stabilization of the olivine cathode and electrode wetting.^{81,83} However, the electrolyte formulation and the electrochemical activation procedure of the $\text{Li/TREG-LiCF}_3\text{SO}_3\text{-LiNO}_3\text{/LFP}$ cell herein proposed do not completely avoid a slight capacity fading after 70 cycles and a coulombic efficiency limited to 98%. These issues, likely related to electrolyte side reaction, require additional work aimed at optimizing the electrolyte composition and improving the electrode/electrolyte stability, in order to further enhance the cell performances. An additional $\text{Li/TREG-LiCF}_3\text{SO}_3\text{-LiNO}_3\text{/LFP}$ cell

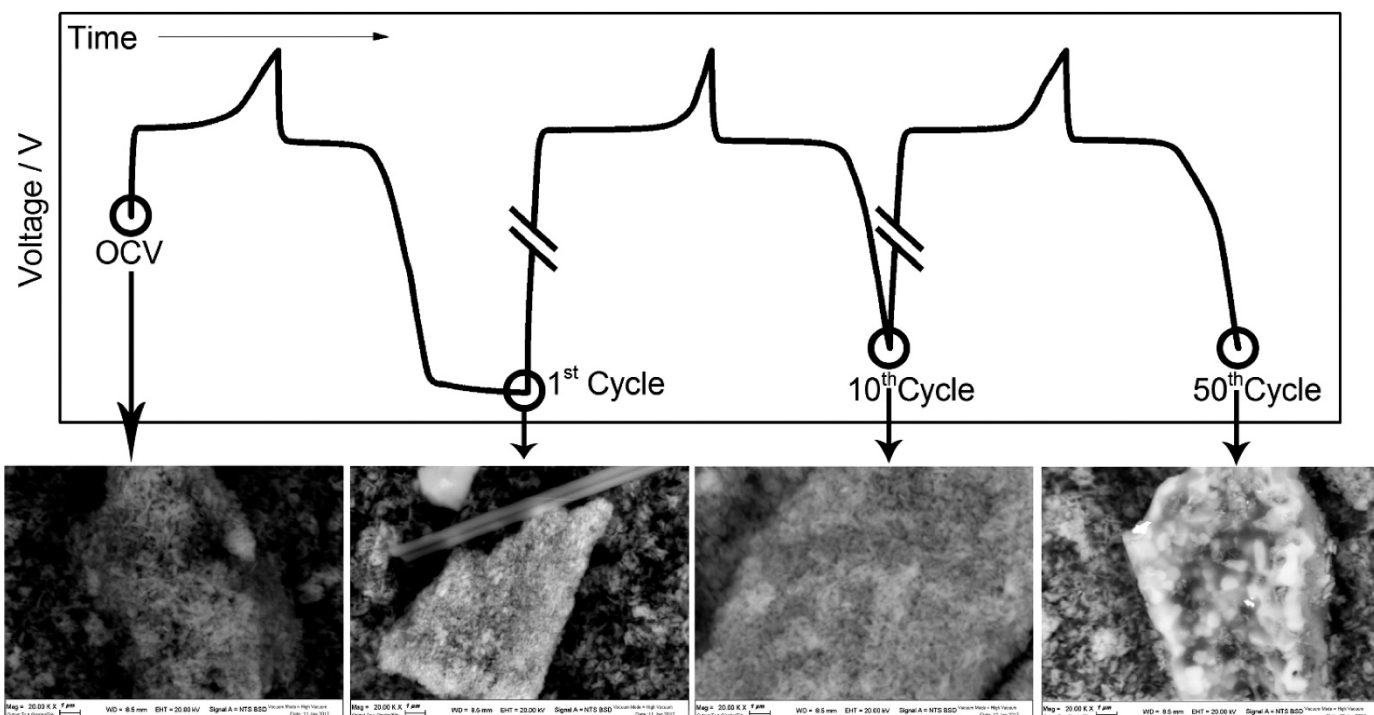


Figure 30 *Ex situ* SEM images of LiFePO₄ electrodes recovered by Li/TREG-LiCF₃SO₃-LiNO₃/LFP cells at the OCV (just after cell assembling and stabilization) and after the first, the 10th, and the 50th galvanostatic cycles. First discharge performed by decreasing the voltage below 2 V at C/5 rate and limiting the time to 5.15 h; subsequent cycles within the 2 – 4 V voltage range at C/5 rate (1C = 170 mAhg⁻¹).

has been tested by galvanostatic cycling at several current rates, as shown by Fig. 28C, D. The voltage profiles of Fig. 28C reveal flat reversible plateaus with minor polarization increase due to current rise to 2C rate (1C = 170 mAh g⁻¹). The cell delivers reversible capacities of 133, 129, 125, 120, 112 and 100 mAh g⁻¹ at C/10, C/5, C/3, C/2, 1C, and 2C (1C = 170 mA g⁻¹), respectively. These performances clearly evidence the suitability of the electrolyte in lithium metal batteries by formation of a stable solid electrolyte interphase. LiNO₃ passivation layer over LFP electrode. Beside the formation of stable SEI at the lithium surface by the addition of LiNO₃, already demonstrated by several literature works,^{43,48,50,75} the electrochemical tests suggest the formation of a suitable layer over the LFP electrode during cell operation (see Fig. 26B discussion). This aspect is further investigated by *ex situ* SEM on LFP electrodes recovered from Li/TREG-LiCF₃SO₃-LiNO₃/LFP cells. LFP electrodes have been recovered at the OCV (just after

cell assembling and stabilization), after the first discharge, at the 10th discharge, and the 50th cycles of galvanostatic test (Fig. 30). The experiments clearly reveal a film growth during cell operation. It is worth noting that this film allows the Li⁺ transport at the cathode and ensures stable cathode/electrolyte interface and reversible cycling, as shown by the EIS and galvanostatic tests of Figs. 28 and 29, respectively.

Chapter Overview

The results demonstrate very promising features suitable for lithium metal battery application and wide operating temperature range. The TREGDME-LiCF₃SO₃ solution has an ionic conductivity of 10⁻³ S cm⁻¹, lithium transference number of about 0.5, and association degree ranging from 0.85 to 0.95 with increasing temperature due to the formation of ion-ion couples. Furthermore, the LiNO₃ addition to the electrolyte formulation

played crucial role in determining the electrodes/electrolyte interfacial and electrochemical stability. The study demonstrated that an electrochemical activation procedure promoting the LiNO_3 reaction may allow full operation of the $\text{Li/TREGDME-LiCF}_3\text{SO}_3\text{-LiNO}_3/\text{LiFePO}_4$ cell. The battery revealed stable galvanostatic cycling, with polarization as low as 0.05 V cell, coulombic efficiency higher than 98% and reversible capacity ranging between 133 mAh g^{-1} at C/10 and 100 mAh g^{-1} at 2C rates at about 3.5 V. Accordingly, the estimated theoretical energy density of the system is about 460 Wh kg^{-1} . This value might lead to a practical energy density of the order of 150 Wh kg^{-1} in a lithium-ion battery using conventional carbon-based anodes. However, the use of lithium metal anode, allowed by the low flammability of glyme-based electrolytes, may increase the energy density of the battery to an estimated value of the order of 200 Wh kg^{-1} .

LiNO₃-Glymes electrolytes toward better performances

Glymes based electrolyte have revealed appealing properties reflecting in good transport properties and stability by the use of a film forming agent. Moreover, the glymes electrolyte are not flammable, thus suggesting their suitability with olivine materials with working voltage below 4.5 V vs. Li^+/Li ^{85,92} such as Fe and Mn which are characterized by remarkable stability of the polyanionic framework ^{93,94}. In the previous paragraph the use of LiFePO_4 cathode material with glymes electrolyte was already presented, however a further investigation in terms of current rate and

operative working voltage is needed. Therefore, the electrochemical study of $\text{LiFe}_{1-\alpha}\text{Mn}_\alpha\text{PO}_4$ olivines in glyme-based solutions is expected to effectively contribute to the development of rechargeable lithium cells. Several synthetic approaches have been studied in order to achieve olivine cathodes with controlled morphology and proper particle size for ensuring efficient electrochemical process with limited electrolyte decomposition ^{95–102}. The use of alternative electrolytes designed for lithium metal cell, such as those basing on end-capped glyme solvents, may lead to a narrow voltage window with respect to conventional carbonate-based solutions ⁵². This choice reasonably requires further careful morphology optimization of the $\text{LiFe}_{1-\alpha}\text{Mn}_\alpha\text{PO}_4$ cathode. Indeed the particle size plays a crucial role for allowing fast Li^+ insertion/de-insertion at the high rates and contemporary ensures limited parasitic processes at low current ^{103,104}. Accordingly, morphologically optimized LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ olivine materials ¹⁰⁵ are employed in lithium metal cells using a solution of lithium triflate (LiCF_3SO_3) in tetra ethylene glycol dimethyl ether (TEGDME) as electrolyte. This particular electrolyte formulation has already shown suitable characteristics in terms of thermal properties, and electrochemical stability window ⁴. However, prior to use in cell, the electrolyte was studied by pulse field gradient nuclear magnetic resonance (pfg-NMR) for the determination of conductivity value, ionic association degree and lithium transference number. Additional, *ad hoc* designed test demonstrate herein a complete non-flammability of this promising electrolyte. The morphology and atomic composition of the olivine cathodes are studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive

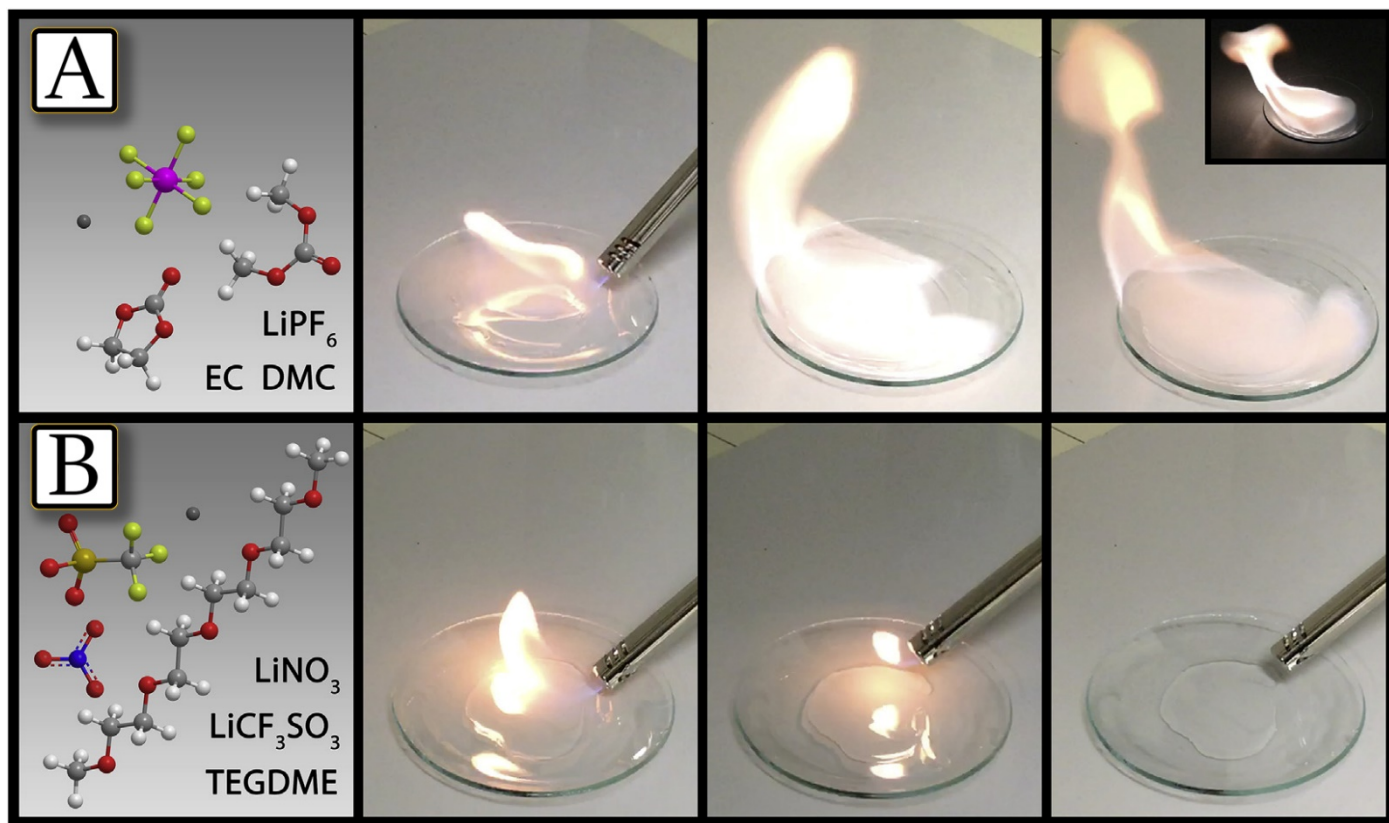


Figure 31 Flammability tests carried out on (A, top panels) conventional 1 M LiPF_6 in EC:DMC 1:1 w/w and (B, bottom panels) 1 mol kg^{-1} LiCF_3SO_3 , 1 mol kg^{-1} LiNO_3 in TEGDME

X-ray spectroscopy (EDS). Hence, the electrochemical performances of the $\text{Li}/\text{LiCF}_3\text{SO}_3\text{-TEGDME}/\text{LiFe}_{1-\alpha}\text{Mn}_\alpha\text{PO}_4$ ($\alpha = 0, 0.5$) cells are evaluated by galvanostatic cycling at several current rates. To the best of my knowledge, the results herein reported demonstrate for the first time the applicability of $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}$ with LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ cathodes and lithium metal anode.

Nonflammable Glyme

The employment of glyme and olivine electrode may actually hinder the safety issues related to the use of lithium metal anode, owing to the high thermal stability of both electrolyte⁴ and cathode⁹⁴. A relevant proof of the electrolyte suitability even under hazardous conditions is represented by the flammability test in reported in Fig. 31, carried out on the $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}$ solution and, for comparison, on conventional carbonate-based

electrolyte. Fig.31A shows that flame exposure leads to fast ignition of the conventional $\text{LiPF}_6\text{-EC-DMC}$ electrolyte, followed by combustion up to almost full electrolyte consumption. Instead, the $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}$ solution shows a remarkable stability and a complete absence of fire evolution, even towards prolonged flame exposure, as confirmed by Fig. 31B. The flash points of TEGDME, EC, and DMC may account for the observed enhanced stability of the proposed electrolyte with respect to standard carbonate-based solutions. Indeed, despite the flash point of TEGDME is 141 °C, which is slightly lower than that of EC (143 °C), the volatile DMC has a flash point as low as 16 °C. Therefore, 1:1 mixtures of EC and DMC, allowing proper ion conduction and commonly used in lithium-ion batteries, suffers by flammability issue mainly due to low flash point of DMC¹⁰⁶. On the other hand, the $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}$ solution is stable upon flame exposure

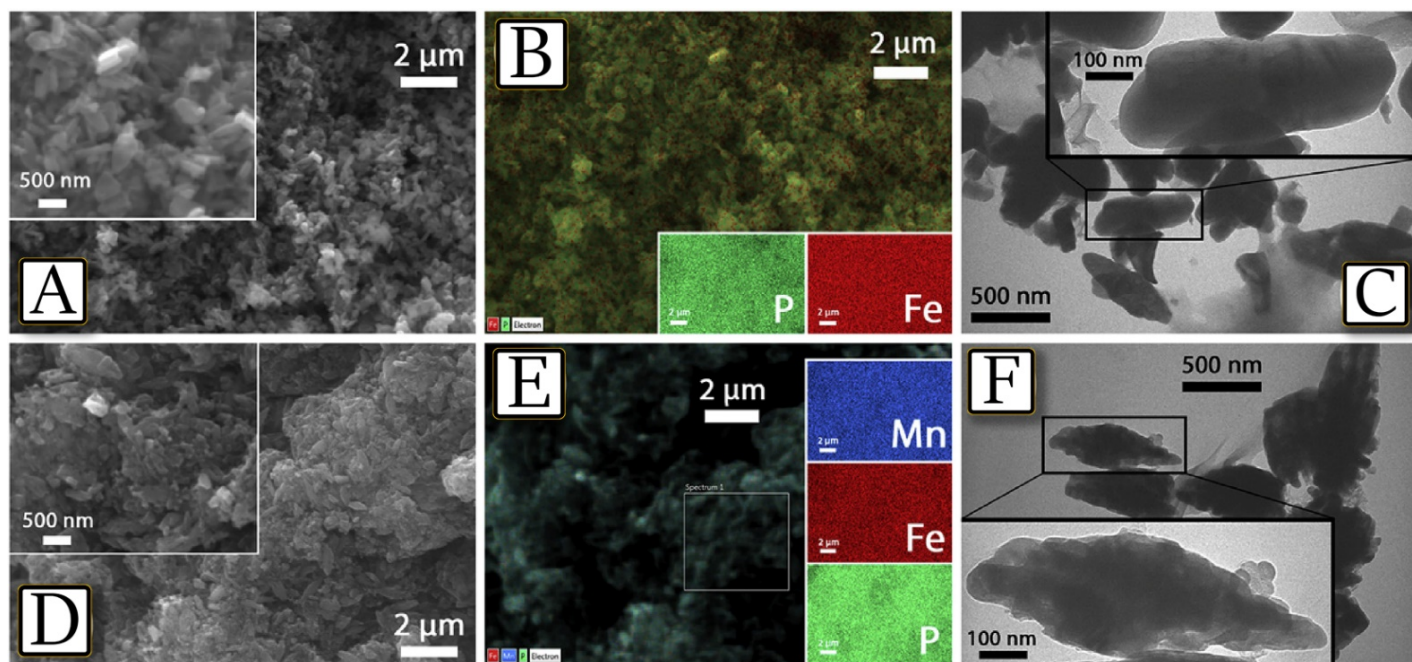


Figure 32 Electron microscopy analyses of (top, A-C) LiFePO_4 and (bottom, D-F) $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ in terms of: (A,D) SEM images (magnification in inset); (B,E) SEM-EDS maps of (blue) Mn, (red) Fe, and (green) P over the sample powders (overlapped maps in the main panel; single maps in inset); (C,F) TEM images (magnification in inset).

by the experimental setup adopted in this work, as shown by Fig 31, due to the relatively high flash point of TEGDME. Despite the non-flammability of the electrolyte in its pristine state, i.e., prior to cell assembly, possible formation of new side species during cycling that may alter the flammability of the whole system, i.e., the battery composed of electrodes, electrolytes as well as decomposition products. The evaluation of such a complex system requires *ad hoc* extended study, including cell nailing and heating tests, as well as calorimetric,

thermo-gravimetric and chemical detection techniques, e.g. as mass spectroscopy, upon cell operation such as that reported in literature for polymer cell¹⁰⁷. This study exceeds the aim of the present work; however, we may reasonably expect the non-flammability of the pristine glyme-based electrolyte (Fig. 31B) to remarkably increase the safety level of the cell with respect to the flammable carbonate-based electrolyte reported in Fig. 31A.

Experimental section: Cathode Preparation

C-coated LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ powders (C content of about 5 wt. %) with olivine structure were synthesized by using a solvothermal pathway followed by high-temperature annealing in Ar atmosphere as previously reported^{94,105}. Sample morphology was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were acquired by using a Zeiss EVO 40 microscope, equipped with a LaB_6 thermo-ionic electron gun. The atomic composition of the samples was studied by SEM-energy dispersive X-ray spectroscopy (EDS), by using a X-ACT, Cambridge Instruments analyzer. TEM images were taken by a Zeiss EM 910 microscope, equipped with a tungsten thermo-ionic electron gun operating at 100 kV. The samples were suspended in water, sonicated, and deposited onto a Formvar® support film applied to Cu grid for TEM. The cathode slurries were prepared by mixing active material (LiFePO_4 , $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$), poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP copolymer, Kynar Flex 2801) binder, and Super P Carbon (Timcal) conductive additive in the ratio 80:10:10% w/w. Tetrahydrofuran (THF, Sigma-Aldrich) was used as solvent for the electrode slurries. The slurries were de-posited on carbon-cloth current collector by doctor blade, casted, dried overnight under vacuum at 110 °C, and cut in the form of 10 mm diameter disks. The electrode mass loading was about 4 mg cm^{-2} . Additional LiFePO_4 electrodes were prepared using Al foil, in order to evaluate the effect of the current collector. T-type cells were assembled in Ar-filled glovebox by stacking cathode, glass fiber separator (Whatman) soaked in the electrolyte solution ($\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}$), and lithium metal an-ode. Benchmark electrolyte solution, i.e., 1 M LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) 1:1 w/w, was used for flammability tests and Li/ LiFePO_4 reference cells. The cell case had three stainless steel cylinders as current collectors and polypropylene holder; the cell was sealed by polypropylene screws. The flammability tests were carried out on the electrolytes just taken out from the glovebox.

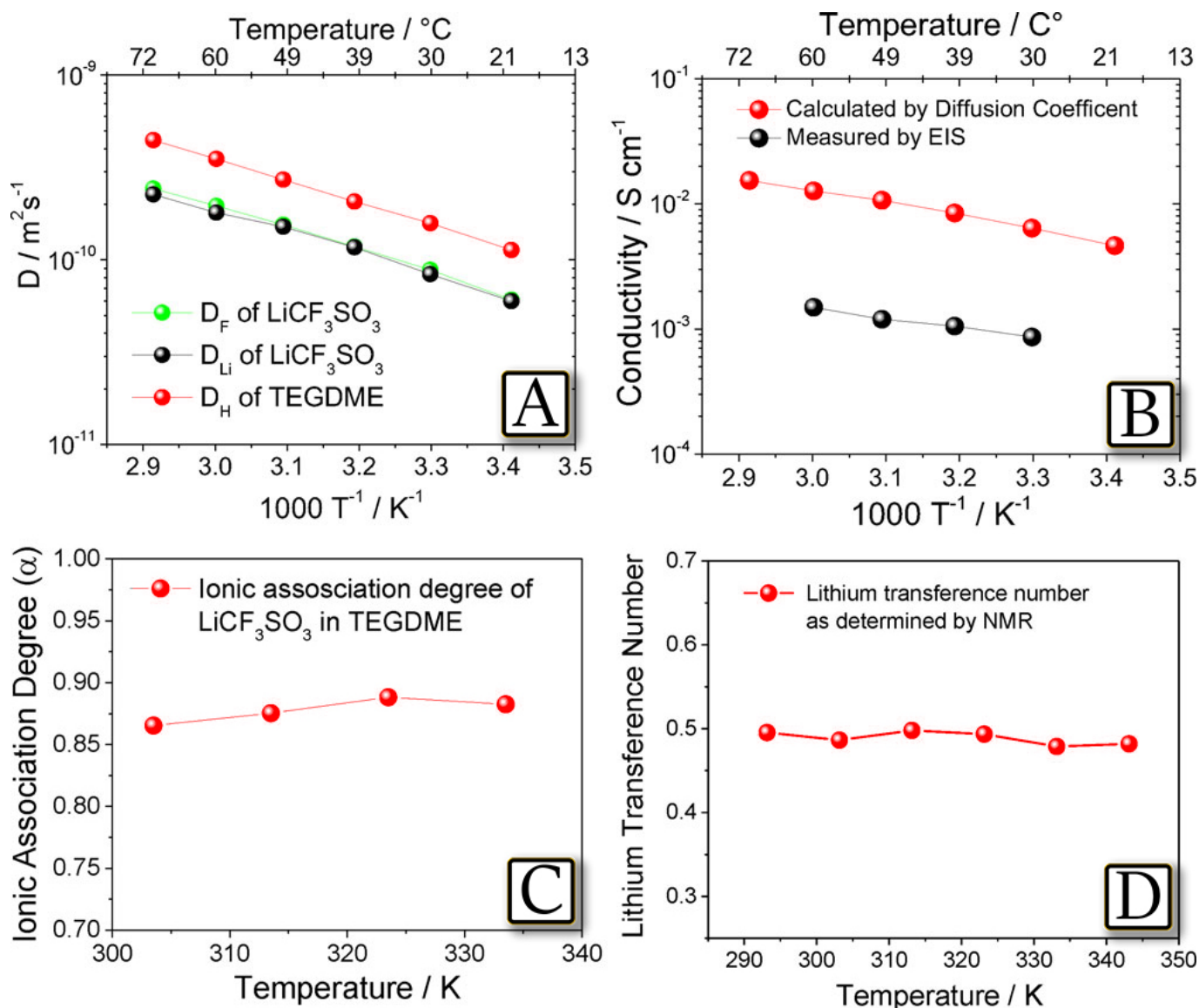


Figure 33 Self-Diffusion coefficients of Li (D_{Li}) and F (D_F) in LiCF_3SO_3 salt, and of H (D_H) in TEGDME solvent. (B) Comparison of conductivity values directly obtained by EIS and calculated by NMR data (see experimental section for details). (C) Ionic association of lithium LiCF_3SO_3 . (D) lithium transference number calculated by NMR data (see experimental section for details). All measurements were performed in a 20 °C – 70°C temperature range.

Olivine Cathode for ether based electrolyte

LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ cathodes have been prepared by a simple solvothermal synthesis optimized in our laboratory, which leads to crystalline $\text{LiFe}_{1-\alpha}\text{Mn}_{\alpha}\text{PO}_4$ powders able to operate reversibly in lithium and lithium-ion cells^{94,105}. Further careful characterization of the LiFePO_4 (Fig. 32A-C)

and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (Fig. 32D-F) materials has been carried out by SEM (panels A, D), SEM-EDS (panels B, E), and TEM (panels C, F) considering the expected influence of sample morphology in controlling the electrochemical behavior of the electrode in glyme-based lithium cell. Fig. 32A, B reveals that the LiFePO_4 sample is homogeneously formed by sub-micrometric platelet-like particles, having uniform distribution of Fe and P in the 1:1

Experimental section: Electrolyte Preparation

The electrolyte solution was prepared in Ar-filled glovebox by dissolving lithium trifluoromethanesulfonate (lithium triflate, LiCF_3SO_3 , Sigma-Aldrich) and lithium nitrate (LiNO_3 , Sigma-Aldrich) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich) solvent; both salts were used in 1 mol kg^{-1} concentration with respect to the solvent. Prior to electrolyte preparation, the salts were dried under vacuum at 100 °C for 24 h and TEGDME was dried under molecular sieves. The final water content in TEGDME was below 10 ppm by Karl Fisher titration (831 Karl Fisher Coulometer, Metrohm).

atomic ratio. The LiFePO_4 particles have elongated shape with maximum size of about 500 nm, as further shown by TEM (Fig. 32C). The $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ material has comparable morphology, characterized by diamond-shaped platelets with maximum size of about 500 nm (see SEM of Fig. 32D and TEM of Fig. 32F). The EDS analysis reveals homogeneous distribution of Mn, Fe, and P over the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ grains, and quantification confirms sample stoichiometry. The particle size shown in Fig. 32 is considered suitable both for allowing a fast Li^+ transport through the one-dimensional olivine channels, and for limiting the decomposition of LiCF_3SO_3 -TEGDME-based solution during cell operation. Indeed, particle size reduction down to few tens of nanometers significantly enhances the electrochemical performances of $\text{LiFe}_{1-a}\text{Mn}_a\text{PO}_4$ cathodes, particularly at the higher Mn contents^{92,104,108}, however it contemporary favors electrolyte decomposition, interfacial resistance increase, and cell failure due to the deterioration of the electrode/electrolyte interface^{103,104}. This aspect appears particularly relevant in view of the narrow oxidative stability windows of TEGDME- LiCF_3SO_3 solution (i.e., 4.5 V vs. Li^+/Li)⁴ with respect to conventional LiPF_6 -carbonate electrolytes (above 4.7 V vs. Li^+/Li)¹⁰⁹.

TEGDME LiCF₃SO₃ LiNO₃ Properties

Therefore, was selected these cathode materials, characterized by sub-micrometric particles, for

study in LiCF_3SO_3 - LiNO_3 -TEGDME electrolyte. Figure 33 reports the TEGDME- LiCF_3SO_3 characteristics as determined by combining NMR and impedance spectroscopy. The ^1H , ^7Li and ^{19}F nuclei self-diffusion coefficients determined by NMR increase with increasing temperature over the investigated temperature range (Fig. 33A), as indeed expected for glyme based electrolytes for application in lithium battery.⁴ Lithium cation as well as CF_3SO_3^- anion, i.e., the charge carriers in the solution, exhibit similar self-diffusion coefficients (D_{Li} and D_{F} , respectively) with value lower than that corresponding to TEGDME (D_{H}) due to their substantial solvation shell. Electrolyte conductivity may be calculated by the Nernst-Einstein equation (4) using the self-diffusion coefficients (δ_{NMR}) and measured by EIS (δ_{EIS}). Fig. 33B, reporting the comparison between δ_{NMR} and δ_{EIS} , reveals the same increasing trend with increasing temperature, however with values differing by one order of magnitude, i.e., of the order of $10^{-3} \text{ S cm}^{-1}$ for δ_{EIS} and $10^{-2} \text{ S cm}^{-1}$ for δ_{NMR} , due to the different nature of the two techniques as already discussed in previous chapters.^{68,110} Accordingly, the combination of δ_{NMR} and δ_{EIS} in equation (5) leads to the ionic association degree (α) over the explored temperature range reported in Fig. 33C, with a stable value of about 0.87, in line with the values observed for similar glyme-based electrolytes.^{52,111} It is noteworthy that carbonate base electrolytes, such as EC:DMC, LiPF_6 (namely commercial LP30), have a room temperature conductivity of about $5 \cdot 10^{-3} \text{ S cm}^{-1}$,

Experimental section: Cathode Characterization

Rate capability tests on two-electrodes lithium cells were performed by galvanostatic cycling at C/10, C/5, C/3, C/2, 1C, and 2C rates ($1\text{C} = 170 \text{ mAh g}^{-1}$), within the 2 – 4 V and 2 – 4.3 V voltage ranges for LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, respectively. **Galvanostatic cycling** tests using a single current rate were performed at C/5, C/3, and 2C rates. All the cells using glyme-based electrolyte were activated by 4 galvanostatic cycles at C/5 rate; the first discharge was performed by decreasing the voltage below 2 V and limiting the time to 5.15 h, according to a previously reported procedure suitable for the formation of a stable SEI layer at the electrode surface, see Fig. 29. All the cycling tests were carried out at room temperature through a Maccor 4000 series Battery Test System.

^{29,109} while our solution has, at the same temperature a conductivity of 2×10^{-3} . The conductivity values, slightly lower than those expected for carbonate based electrolytes ^{69,112,113}, are considered suitable for lithium cell application; however, they might partially limit the rate capability of the cell using LiFePO₄ at the lower temperatures. Nevertheless, the ion association still allows our electrolyte to have an ion conductivity value well suitable for lithium battery application. Figure 33D, reporting the lithium transference number calculated by using the self-diffusion coefficients of Li-cation (D_{Li}) and CF₃SO₃-anion (D_F) determined by NMR and equation (6), reveals a stable value of about 0.5 in the whole temperature range, considered a suitable value for electrolyte application in lithium batteries.⁶⁹ This method does not take into account the effects of ion association and is therefore used only as guide to comparative behavior in electrolytes.^{4,52} Furthermore, the TEGDME–LiCF₃SO₃ electrolyte has been herein added by LiNO₃ as film forming agent that allows a further stabilization of the SEI at the electrodes surface, as reported previously.⁵² Accordingly, the cycling tests herein reported have

been carried out after performing 3 activation cycles reported in Fig 29 The TEGDME-based electrolyte herein proposed has thermal stability ranging from – 49 °C to 200 °C and ionic conductivity of about 1×10^{-3} S cm⁻¹ at room temperature ⁴; therefore, it is expected to ensure suitable performances in Li/LiFePO₄ cell at higher current rates and lower temperatures than PEG500DME of the previous chapter. The high-rate performances have been herein demonstrated up to 2C rate (1C = 170 mAh g⁻¹) for Li/LiFePO₄ and Li/LiMn_{0.5}Fe_{0.5}PO₄ cells, as following reported.

TEGDME Electrolyte and High Rate Olivine Cathodes

Rate capability of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cell has been evaluated by galvanostatic cycling at several current rates, as shown in Fig. 34. The voltage profiles (Fig. 34A) reveal plateaus centered at about 3.45 V, which indicate reversible two-phase reaction of LiFePO₄ ⁸⁵. The cell exhibits flat voltage profiles and low polarization (about 0.05 V) at slow rates; as expected, the rise of C-rate to 2C (1C = 170 mA g⁻¹) produces slope of the voltage profile, polarization increase,

Experimental section: Electrolyte Characterization

The TEGDME–LiCF₃SO₃ 1 mol kg⁻¹ electrolyte was characterized by a Bruker 400 Avance III NMR spectrometer in order to determine **self-diffusion coefficients** of ¹H, ⁷Li and ¹⁹F nuclei using PFG double-stimulated echo sequence to suppress convection effects.²²⁴ The gradient pulse widths were 4-5 ms, gradient strength g was varied from 0-45 G/cm and diffusion delay Δ of 500-800 ms was employed. Measurements were made each 10°C from 20°C to 70°C. The Nernst-Einstein equation (4) was used to calculate the **electrolyte conductivity** (δ_{NMR}) from Li⁺ cation and CF₃SO₃⁻ anion self-diffusion coefficients:

$$\delta_{NMR} = \frac{F^2 [C]}{RT} (D_{Li^+} + D_{CF_3SO_3^-}) \quad (4)$$

Where F is the Faraday constant (96485 C), $[C]$ is the salt concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature (K) and D_{Li^+} and $D_{CF_3SO_3^-}$ are the self-diffusion coefficient of lithium cation and triflate anion respectively. The electrolyte conductivity was also measured by electrochemical **impedance spectroscopy (EIS)** in symmetric stainless steel/electrolyte/stainless steel 2032-coin cell, with an O-ring Teflon separator to keep the volume of the cell constant. VSP (Biologic) instrument was used to perform the measurements in a 100 mHz – 100 kHz frequency range with signal amplitude of 10 mV, acquiring data from 30°C to 60°C each 10°C. The equation (5) was used to calculate the **ion association degree** (α):

$$\alpha = (1 - \frac{\delta_{EIS}}{\delta_{NMR}}) \quad (5)$$

Where δ_{EIS} is the conductivity value obtained from EIS measures and δ_{NMR} is the conductivity from equation (4). The **lithium transference number** (t^+) can also be calculated from the self-diffusion coefficients according to equation (6):

$$t^+ = \frac{D_{Li^+}}{D_{Li^+} + D_{CF_3SO_3^-}} \quad (6)$$

where D_{Li^+} and $D_{CF_3SO_3^-}$ are the self diffusion coefficient of the lithium cation and the triflate anion respectively.

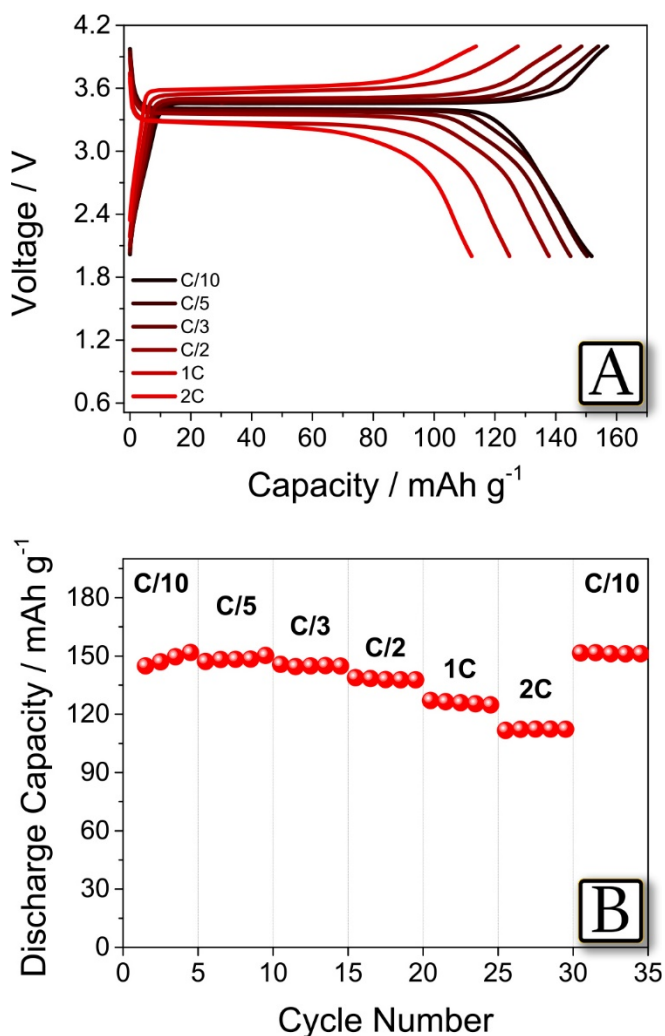


Figure 34 Rate capability test of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cell in terms of (A) voltage profiles and (B) cycling behavior, performed by galvanostatic cycling at C/10, C/5, C/3, C/2, 1C, and 2C rates (1C = 170 mAh g⁻¹) within the 2 – 4 V voltage range; test performed after electrochemical activation of the cell (see Fig. 29); room temperature (25 °C).

and lower capacity. Indeed, the cell delivers reversible capacity of 152, 150, 145, 138, 125, and 112 mAh g⁻¹ at C/10, C/5, C/3, C/2, 1C, and 2C (1C = 170 mA g⁻¹), respectively (see Fig. 34B). These results demonstrate the full suitability of the LiCF₃SO₃-LiNO₃-TEGDME electrolyte in lithium cells that use LiFePO₄ cathode. This cathode has been widely investigated over the last few years, leading to its current commercial use in cells¹¹⁴. In particular, recent literature works^{115–118} reported LiFePO₄ powders prepared by solvothermal pathways characterized by excellent electrochemical performances in standard carbonate-based electrolyte. Hence, cycling results of lithium cells using

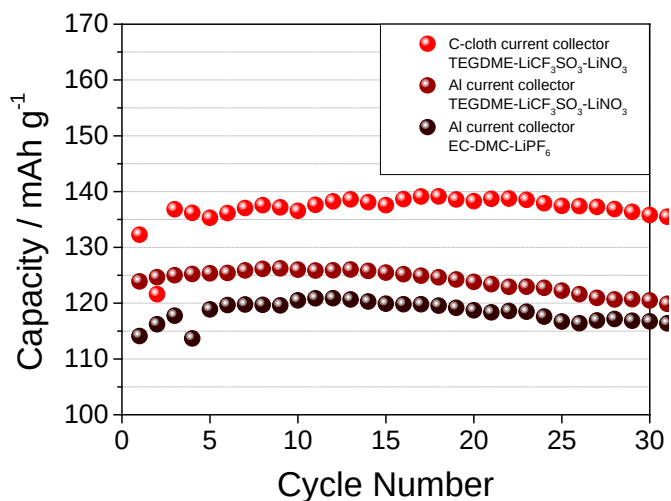


Figure 35 Galvanostatic cycling tests at C/3 rate (1C = 170 mAh g⁻¹) of Li/LiFePO₄ cells using either 1 M LiPF₆ in EC:DMC 1:1 w/w or 1 mol kg⁻¹ LiCF₃SO₃, 1 mol kg⁻¹ LiNO₃ in TEGDME as electrolyte; 2 – 4 V voltage range; LiFePO₄ on either Al or carbon-cloth current collector; tests using TEGDME-based electrolyte performed after electrochemical activation of the cell (see Fig. 29); temperature = 25 °C.

LiCF₃SO₃-LiNO₃-TEGDME and a common carbonate-based electrolyte are compared with the LiFePO₄ sample synthesized in our laboratory^{94,105} in Fig. 35. Cycling performances at C/3 rate (1C = 170 mAh g⁻¹) of LiFePO₄ in 1 M LiPF₆ EC:DMC 1:1 w/w standard electrolyte and in the new LiCF₃SO₃-LiNO₃-TEGDME formulation are reported in Fig. 35. The cell using standard carbonate-based electrolyte delivers reversible capacity of 114 mAh g⁻¹ at the 1st cycle, which increases to 121 mAh g⁻¹ after 10 cycles due to cathode structural reorganization already observed for similar olivine materials^{94,101,105}; at the 30th cycle the capacity slight decreases to 117 mAh g⁻¹, i.e., 103 % and 97 % with respect to the 1st cycle and 10th cycle values, respectively. The glyme-based electrolyte ensures capacity of 124 mAh g⁻¹ and 126 mAh g⁻¹ at the 1st and 10th cycles, respectively; at the 30th cycle the capacity is 120 mAh g⁻¹, i.e., 97 % and 95 % with respect to the 1st cycle and 10th cycle

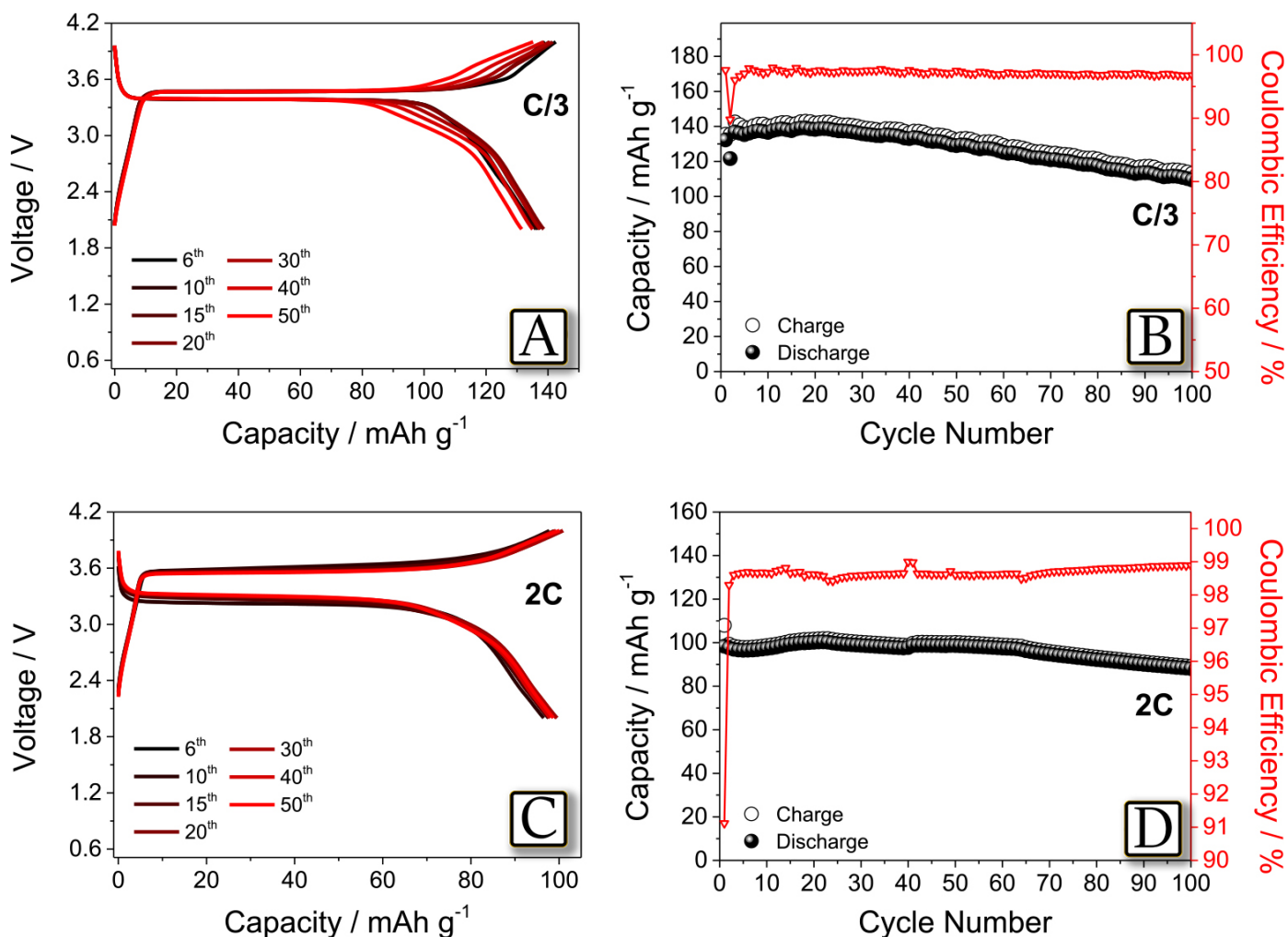


Figure 36 Galvanostatic tests of Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cells in terms of (A,C) voltage profiles and (B,D) cycling behavior within the 2 – 4 V voltage range at two C-rates: (A,B) C/3, and (C,D) 2C rates (1C = 170 mAh g⁻¹); test performed after electrochemical activation of the cell (see Fig. 29); room temperature (25 °C).

values, respectively. Therefore, these results further demonstrate the applicability of TEGDME-based electrolyte in Li/LiFePO₄ cell: indeed, the cells employing TEGDME-based electrolyte exhibit comparable electrochemical behavior with higher capacity with respect to the conventional carbonate-based electrolyte. This observation has been confirmed by several tests in lithium cell. However, the cell using glyme suffers more capacity fading, which may be ascribed to not fully optimized LiFePO₄/electrolyte interface. This issue could be addressed by further tuning of the electrochemical activation procedure, which is expected to improve the SEI films attributed to nitrate reaction⁵². It is noteworthy that the first attempts to employ LiCF₃SO₃-glyme solutions in lithium cells

with insertion cathodes revealed very poor electrochemical stability, which has been remarkably improved by LiNO₃ addition, as shown by Fig. 35. The figure also reveals the beneficial effect on the cell performances of C-cloth support with respect to standard Al foil as well. In particular, we have compared the cycling behavior at C/3 rate (1C = 170 mAh g⁻¹) of two Li/ LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cells only differing in the current collector. Fig. 35 clearly shows a capacity improvement due to C-cloth from 126 mAh g⁻¹ to 139 mAh g⁻¹, which is likely related to the higher surface area of the electrode support with respect to Al disk. This particular current collector morphology enhances the electric contact between olivine parti-

cles and current collector and increases the effective cathode/electrolyte interface. Fig. 36 shows the galvanostatic cycling performances of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cell at C/3 (panels A, B) and 2C rates (panels C, D; 1C = 170 mA g⁻¹) upon 100 cycles. The Li/LiFePO₄ cell cycled at C/3 rate exhibits flat plateaus with limited polarization, which slight evolve throughout cycling. This phenomenon may be related to irreversible processes leading to coulombic efficiency of 97%, and it is reflected into capacity fading from about 140 mAh g⁻¹ at the first cycles to 110 mAh g⁻¹ at the 100th cycle (see Fig. 36B). Low coulombic efficiency values and capacity fading are likely attributed to a not fully optimized LiFePO₄/electrolyte interface, as well as to the reactive lithium metal interface and the adopted T-cell configuration, which is commonly used for short-time cycling. Higher efficiency values, i.e., of about 99%, are obtained by rising the C-rate to 2C, thus allowing enhanced cycling stability with reversible capacity of 100 mAh g⁻¹ (Fig. 36D) and expected cell polarization increases (Fig. 36C). The improvement of stability at high C-rate is likely related to decreased magnitude of parasitic reactions at the electrode/electrolyte interface. Fig. 37 reports a rate capability test of the LiMn_{0.5}Fe_{0.5}PO₄ cathode in the LiCF₃SO₃-LiNO₃-TEGDME electrolyte. The voltage profiles (Fig. 37A) clearly evidence the electrochemical fingerprints of the Fe³⁺/Fe²⁺⁸⁵ and Mn³⁺/Mn²⁺⁹² couples at the various rates. Fig. 37B shows reversible capacity values of 166, 148, 130, 120, 99, and 73 mAh g⁻¹ at C/10, C/5, C/3, C/2, 1C, and 2C (1C = 170 mA g⁻¹), respectively. It is noteworthy that the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cell exhibits lower performance at high rates with respect to the

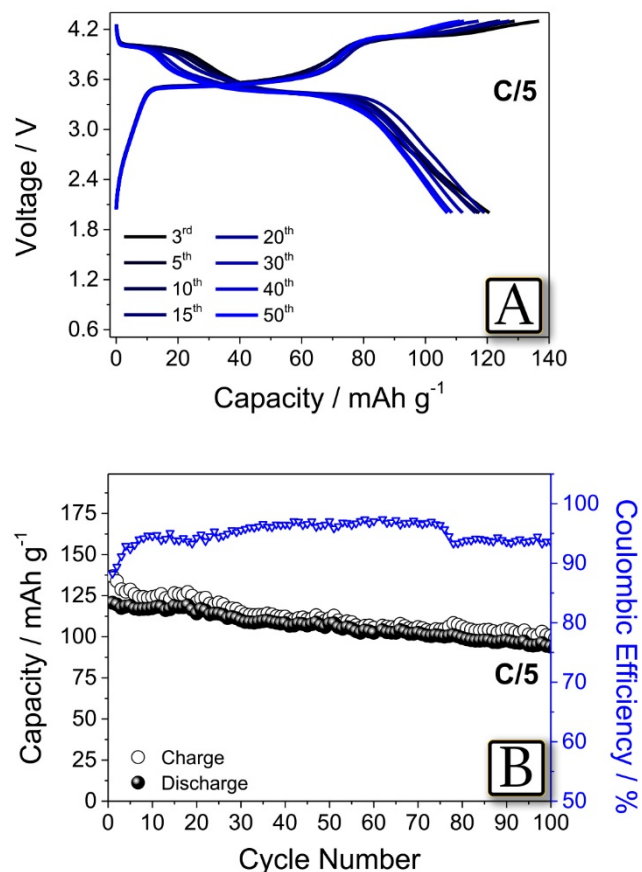


Figure 37 Rate capability test of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cell in terms of (A) voltage profiles and (B) cycling behavior, performed by galvanostatic cycling at C/10, C/5, C/3, C/2, 1C, and 2C rates (1C = 170 mAh g⁻¹) within the 2 – 4.3 V voltage range; test performed after electrochemical activation of the cell Fig. 29; room temperature (25 °C).

cell using LiFePO₄ (compare Fig. 34 and Fig. 37), owing to the well-known kinetic hindrance to Li⁺ insertion/deinsertion of LiFe_{1- α} Mn _{α} PO₄ phases¹⁰⁵. The rate capability test of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cell suggests the system particularly suitable for application at the lower currents. Therefore, we have studied the galvanostatic performances over 100 cycles using C/5 rate (1C = 170 mA g⁻¹). Fig. 38 demonstrates reversible operation of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cell, with relatively stable voltage profile upon cycling (Fig. 38A) and reversible capacity of about 125 mAh g⁻¹. However, the cell exhibits coulombic efficiency values of about 95% and capacity fading to 94 mAh g⁻¹ at

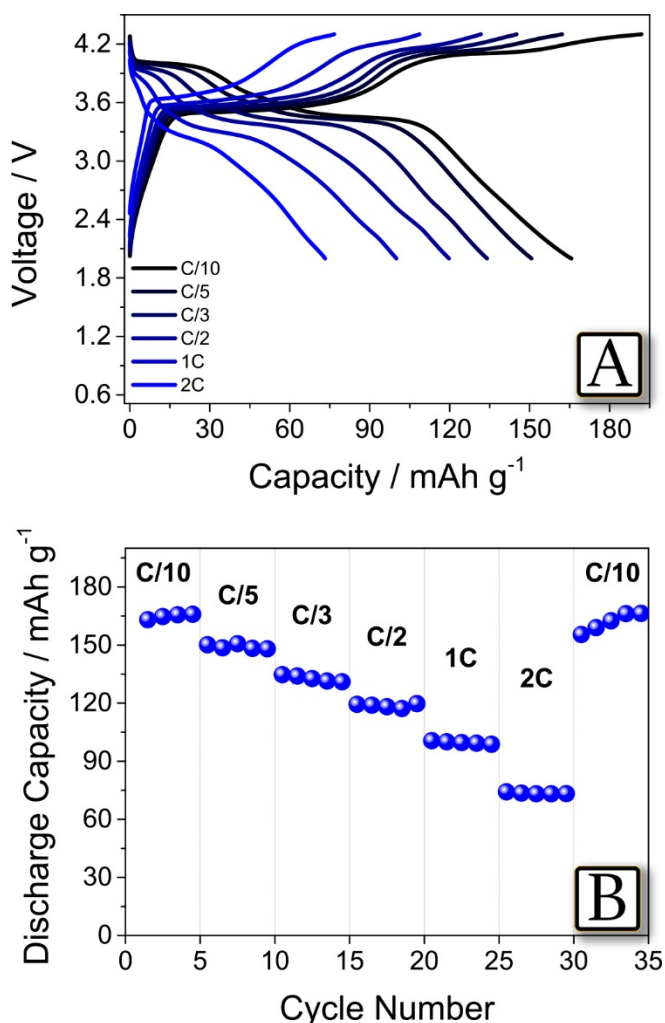


Figure 38 Galvanostatic cycling tests of Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cells in terms of (A) voltage profiles and (B) cycling behavior at C/5 rate (1C = 170 mAh g⁻¹) within the 2 – 4.3 V voltage range; test performed after electrochemical activation of the cell (see Fig. 29); temperature = 25 °C.

the 100th cycle, i.e., a cycling performance less remarkable than that one of the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ cell. As already reported in Fig. 37 discussion, we partially attribute this drawback to not fully optimized cathode/electrolyte interface. Furthermore, the higher working voltage of LiMn_{0.5}Fe_{0.5}PO₄ with respect to LiFePO₄ may account for the observed cell performance. Indeed, the higher voltage cutoff used for the Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cell allows proper operation at the Mn³⁺/Mn²⁺ potential, but contemporary induces a concomitant electrolyte

decomposition. Accordingly, the previous chapter revealed that the electrolyte undergoes oxidation at about 4.5 V vs. Li⁺/Li⁰, which is close to the voltage cutoff used herein. In addition, comparison of Fig. 37 and Fig. 38 reveals higher capacity values at the higher currents with respect to the galvanostatic cycling at single rate, similarly to the trend observed for the lithium cell using LiFePO₄ by comparing Fig. 34 and Fig. 36.

Glymes and High Rate, Overview

The last chapter revealed a possible strategy to employ high energy lithium metal in safe and high energy rechargeable batteries. LiFePO₄ and LiMn_{0.5}Fe_{0.5}PO₄ olivine cathodes were studied in lithium cells with a glyme-based electrolyte solution having composition 1 mol kg⁻¹ LiCF₃SO₃, 1 mol kg⁻¹ LiNO₃ in TEGDME. Flammability tests demonstrated the electrolyte stability under hazardous conditions, thus suggesting possible applicability in combination with lithium metal anode. Scanning and transmission electron microscopies, as well as X-ray energy dispersive analysis of the olivine powders, evidenced sub micrometrical particles with homogenous atomic distribution. This morphology allowed proper operation of the lithium cell using TEGDME-based electrolyte, as demonstrated by galvanostatic cycling tests. Li/LiCF₃SO₃-LiNO₃-TEGDME/LiFePO₄ and Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ cells exhibit promising rate performances and stable cycling trends, thus actually suggesting the suitability of the proposed combination as promising energy storage systems.

Glymes and Lithium Sulfur Battery

In the previous chapters a deep investigation of the LiNO_3 stabilizing agent was presented. The film forming agent addition to ether based electrolytes increases the lithium/electrolyte interface formation improving the stability and the battery operations. Moreover, the transport properties of the bare electrolyte are slightly affected from the LiNO_3 addition, due to its sacrificial rule on the electrodes surface. These promising results confirm the suitability of ether based electrolyte with LiNO_3 for the use in high energy storage devices such as lithium sulfur battery. Indeed, the next chapters focus on the preparation, synthesis and characterization of carbon composite cathode materials. The low conductivity of sulfur, which significantly depresses the delivered capacity and the rate capability of the cell,¹¹⁹ is mitigated by infiltrating sulfur into several kinds of carbonaceous materials, such as graphite layers,¹²⁰ amorphous carbon,¹²¹ carbon nano-tubes¹²², nano-sheets¹²³ and hierarchical-structure carbons¹²⁴. This strategy led to great improvement of the cycling stability, electron and ion conductivity and, consequently, the rate capability and the cycle life of sulfur cathodes in lithium cells.^{41,125,126} However, most of the studies reporting sulfur composites,^{127,128} mainly basing on carbons,^{31,121,129} involved complex procedures for the active material preparation which may actually lead to a rapid increase of the economic impact of the cell. Instead, this study proposes a simple syntactical pathway, involving bare commercial carbons, sulfur and mechanical milling, thus allowing a remarkable decrease of the composite material cost. The S/C active materials presented is obtained by high energy ball milling of carbons and molten sulfur, is then studied in terms of structure, morphology and electrochemical process. The electrodes are employed in Li/S cells revealing a performance clearly influenced by the morphology of the carbons over 140 galvanostatic charge/discharge cycles. Furthermore, the optimization of the cathode with higher performances is reported, revealing outstanding performances, very stable specific capacity of about 1000 mAh g^{-1} delivered with coulombic efficiency approaching 100%.

Scheme of the 2032-coin cell. Every coin cell is sealed at the same pressure by a crimping machine. The Teflon ring avoid the electrodes contact to prevent the short circuit and seals the coin cell from the external environment.



Carbon Composites for Sulfur

A comparative study of sulfur composites using carbon of various natures, namely graphite, mesophase micro bead carbon (MCMB) and multi walled carbon nanotubes (MWCNTs), is performed in lithium battery design and evaluation. Morphological and structural analyses, by means of scanning electron microscopy (SEM) and X-ray diffraction with cycling voltammetry and galvanostatic cycling in lithium cells are employed for materials characterization. Tetra ethylene glycol dimethyl ether (TEGDME) dissolving lithium trifluoromethanesulfonate (LiCF_3SO_3) is considered the preferred electrolyte (the electrolyte was already investigated in the previous chapter and will not be further discussed). The lithium sulfur following reported achieves a capacity higher than 500 mAh g^{-1} over 140 cycles with no sign of dendrite formation or failure. This performance is considered sufficiently suitable for the development of high energy lithium battery, in particular considering the expected safety of the cells employing a non-flammable glyme electrolyte instead of conventional carbonate-based one.

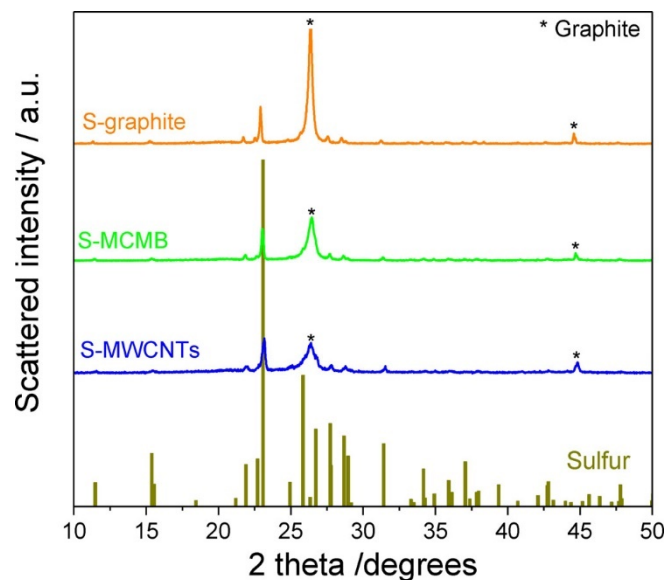


Figure 39 Comparison of the X-ray diffraction (XRD) patterns of the various S-C electrode samples performed using diffractometer equipped by Cu $K\alpha$ source and a graphite monochromator, in the $2\theta/\theta$ scanning mode.

Cathode Characterization

The structure of the electrode materials, i.e., S-Graphite, S-MCMB and S-CNTs, is detected by means of XRD and reported in Figure 39 (A, B and C, respectively). The diffraction patterns reveal the characteristic peaks ascribed to the orthorhombic sulfur S_8 (Ref. JCPDS 85-0799) and broad reflections of the hexagonal carbon lattice (Ref. JCPDS-751621), thus suggesting that the high energy ball milling treatment is not sufficient for complete

Experimental section: Cathode and electrolyte Preparation

The **active materials** were prepared by mixing elemental sulfur and either mesophase micro bead carbon (MCMB), graphite or multi walled carbon nanotubes (CNTs), by Sigma Aldrich. Elemental sulfur was melted at 135°C , added to the selected carbon powder in a 2:3 weight ratio, and subsequently stirred for 3 hours until homogenous mixture was obtained. The mixture was subsequently cooled down to room temperature, refined by mortar and high energy ball milling four times for 15 min with a frequency of 15 Hz and 30 min of rest between steps, using a Retsch Mill MM400. For electrode preparation the active material powders, i.e., S-Graphite, S-MCMB and S-CNTs, were mixed together with polyvinylidene difluoride (PVdF, Solvay Solef) binder in an 85:15 weight ratio, and dispersed in N-methylpyrrolidone (NMP) solution. The resulting slurries were stirred for 1 hour, casted on aluminum foil by Doctor Blade technique with a wet thickness of $300 \mu\text{m}$ and dried for 3 hours at 60°C under air. Before cell assembly in the glove box, the electrodes were disk punched and vacuum dried overnight at 60°C . The cells were filled by $30 \mu\text{l}$ of electrolyte and by an overall amount of sulfur of about 2 mg, thus leading to an electrolyte-to-sulfur ratio of 15 ml/g . The loading of sulfur into electrode surface was of 1.3 mg cm^{-2} : taking into account the delivered specific capacity of about 600 mAh g^{-1} , the surface capacity may be calculated to be of 0.8 mAh cm^{-2} . This capacity is of the same order of magnitude with respect to the one delivered by common batteries, such as those using LiFePO_4 and LiCoO_2 , which is of about 1 mAh cm^{-2} (taking into account a mass loading of about $5\text{--}6 \text{ mg cm}^{-2}$ and delivered capacity of about 150 mAh g^{-1}). The **electrolyte** was prepared by dissolving 1 mole of lithium trifluoromethanesulfonate salt (LiCF_3SO_3 , Sigma Aldrich) in 1 kg of tetra ethylene glycol dimethyl ether (TEGDME, Sigma Aldrich). Before mixing in argon filled glove box, TEGDME was dried by molecular sieves until the water content was lower than 10 ppm (determined by Karl Fischer titration instrument Metrohm) and the LiCF_3SO_3 was dried under vacuum at 80°C for 24 hours.

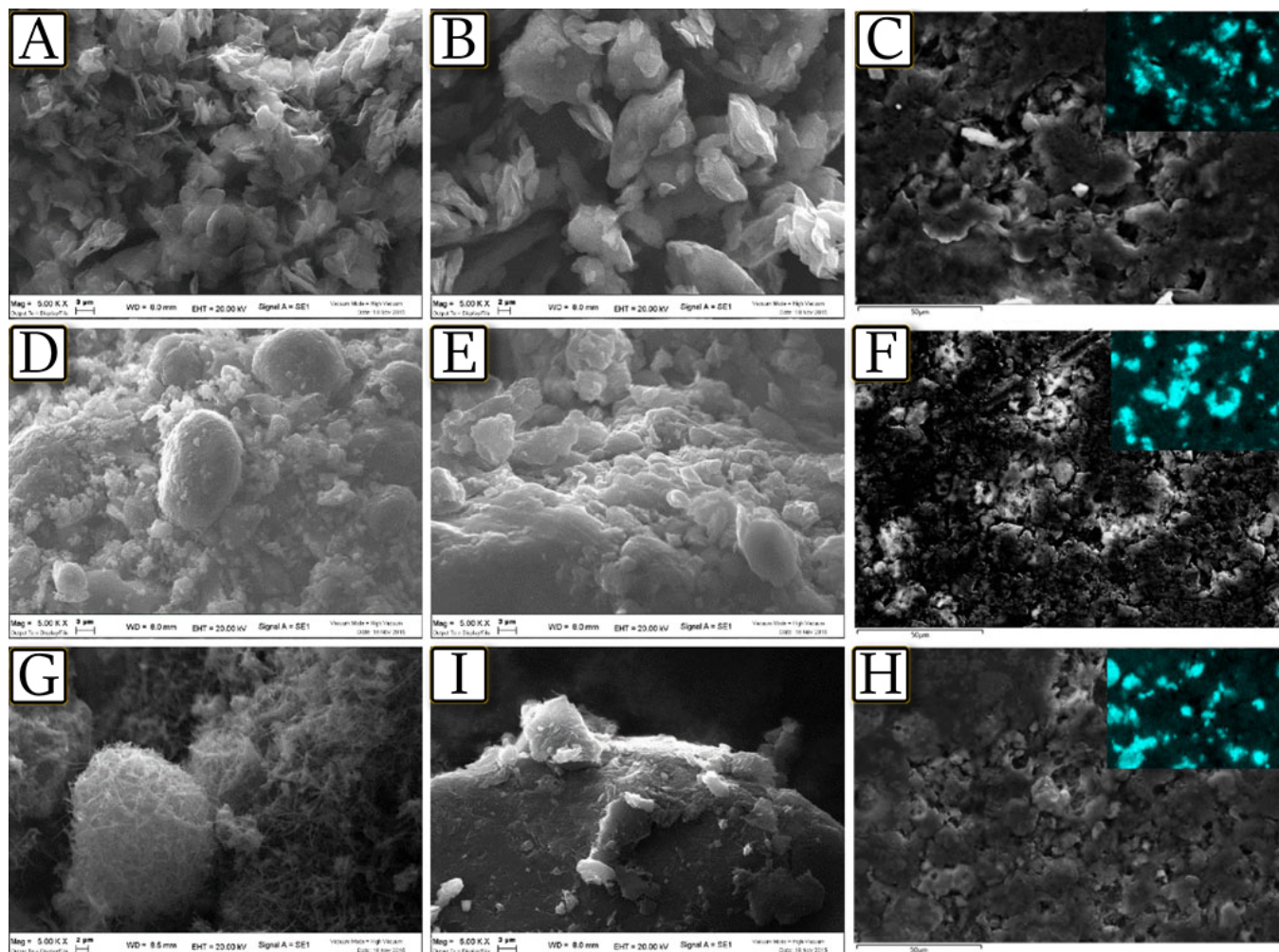


Figure 40 SEM images of the active material powders before and after high energy ball milling treatment, (A)-(B) S-Graphite, (D)-(E) S-MCMB, (G)-(H) S-CNTs. SEM Images of the electrodes and corresponding sulfur EDX mapping (insert) (C) S-Graphite, (F) S-MCMB, (I) S-CNTs

sample amorphization. In addition, Figure 39 suggests the lower crystallinity for CNT-S sample, while the higher one for the Graphite-S sample. The presence of amorphous phase is expected to improve the composite electrode conductivity and enhance the sulfur retention, thus resulting in increased rate capability and stability during cycling in lithium cell.¹⁹ Figure 40 reports the morphology of the electrodes as imaged by SEM, before and after the high energy mechanical treatment. The pris-

tine S-Graphite sample (Fig. 40A) shows the micrometric lamellar shape characteristic of natural graphite, which vanishes after mechanical treatment to form micrometric S-C carbon aggregates (Fig. 40B). Similarly, the pristine S-MCMB displays the granular, sphere-like morphology of MCMB (Fig. 40D) and S-CNTs reveals the agglomerated nano-tubes morphologies of CNTs (Fig. 40G), that are modified by milling with formation of composites in which sulfur and the cor-

Experimental section: Cathode Characterization

The active materials structure was characterized by X-ray diffraction by a XRD Bruker instruments using Cu K α source and a graphite monochromator, in the $2\theta/\theta$ scanning mode. Scanning electron microscope (SEM) Zeiss EVO 40, using thermionic electron gun equipped with LaB₆ crystal, was employed to study the samples morphology. Cycle voltammetry in three electrode T-cell configuration, using lithium metal as counter and reference electrode, was carried out in a 1 V – 3 V potential range, with a current scan of 0.05 mV s⁻¹ by a VersaSTAT MC, Princeton Applied Research. Galvanostatic cycling of Sulfur-Carbon electrodes was performed using a MACCOR Series 4000 Battery Test System in a 2032-coin cell, with lithium metal anode and a Whatman[®] glass fiber separator soaked with TEGDME–LiCF₃SO₃ electrolyte, at C/5 current rate (1C = 1675 mAh g⁻¹) in the voltage range of 1.8V - 2.7V.

responding carbon are intimately mixed and aggregated (Fig. 40E and Fig. 40H, respectively). This morphology, in which carbon and sulfur are homogeneously distributed within micrometric aggregates, may actually simultaneously ensure electrode stability, rate capability and reduced electrolyte decomposition, compared to the case of dispersed nanoparticles.¹³⁰ Furthermore the Fig. 40C, Fig 40F and Fig. 40I, showing respectively the morphology of the S-Graphite, S-MCMB and S-CNT electrodes with the EDX mapping in inserts, reveal uniform distribution of the sulfur on the electrodes surface.

Electrochemical processes

The electrochemical processes of the sulfur-carbon composites are investigated by cycling voltammetry and reported in Figure 41. The CV of the S-Graphite electrode (Fig. 41A) evolves following the multiple-peaks profile associated to the electrochemical process of sulfur with lithium.¹⁷ Accordingly, during the first discharge elemental sulfur initially reacts to form Li_2S_8 (peak at 2.5 V vs. Li/Li^+), while the formation of shorter chain lithium polysulfide takes place at lower potentials (i.e., peaks at 2.1 V and 1.9 V vs Li/Li^+).¹³¹ During the reverse anodic scan (oxidation) the CV profile shows only an intense merged peak at about 2.4 V vs. Li/Li^+ , in which the delithiation reaction occurs. The second CV cycle of S-Graphite electrode shows limited changes, including slight shift and intensity reduction of the peaks mainly due to minor electrode dissolution and possible structural reorganization.¹³² The CV profile of S-MCMB electrode (Fig. 41B) reveals during cathodic scan the reduction peak at 2.5 V vs. Li/Li^+ related to the long chain polysulfide formation, while the two peaks

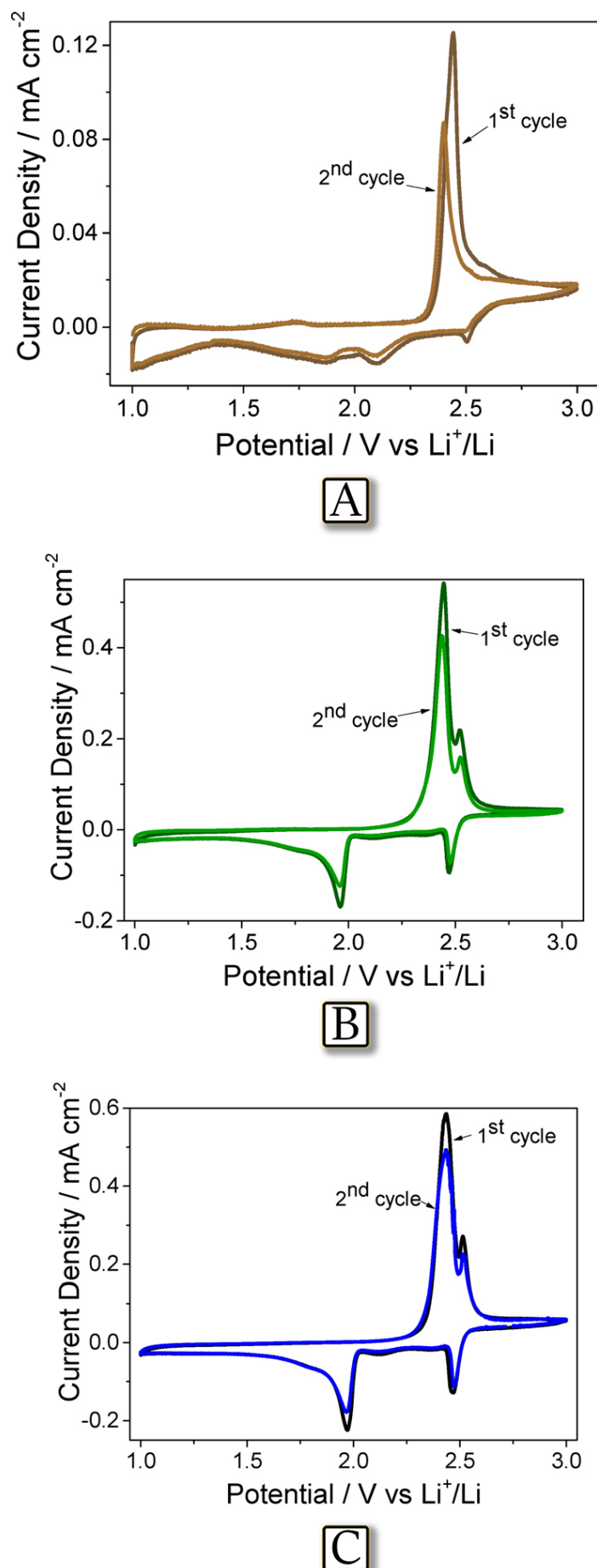


Figure 41 Cycling Voltammetry profiles of (A) S-graphite, (B) S-MCMB carbon and (C) S-CNTs electrodes in lithium cells. Measurements performed in three-electrode configuration cell, with a 0.05 mV/s scan rate, in a 1 V – 3 V potential range. The electrolyte used for the CV tests at the room temperature (25 °C) was TEGDME– LiCF_3SO_3 1mol kg^{-1} .

observed for S–Graphite are here merged into one, more intense and centered at about 2 V vs. Li/Li^+ (compare Fig. 41A and Fig. 41B). A further difference between the two electrodes is shown by the subsequent anodic scan, evidencing for S–MCMB two oxidation peaks centered at 2.4 V and 2.6 V vs. Li/Li^+ instead of the one already observed for S–Graphite. The second CV cycle of the S–MCMB shows a slight profile change, observed also for S–Graphite, however with a minor ratio. Figure 41C, reporting the CV profile of the S–CNTs electrode, highlights a trend very similar to the one observed for S–MCMB, with a slightly improved profile retention between first and second cycle. The similar CV shape of S–MCMB and S–CNT observed in Figure 41 may be justified by the similar crystallinity of the two electrodes revealed by Figure 39, while the higher crystallinity of the S–Graphite, favoring the formation of polysulfides of different length,^{133,134} may account for its different CV trend.

Galvanostatic Performances

Figure 42 displays the galvanostatic behavior of the various electrodes in Li/S cells using TEGDME– LiCF_3SO_3 as the electrolyte media. Interestingly, all the cells reveal a stable trend upon prolonged cycling, thus accounting for the practical interest of the synthetic pathway used for electrode preparation. Furthermore, the cycling tests evidence differences in the voltage shape and magnitude between the electrodes and exhibit an activation trend at the beginning of the test. The first cycle shows for all cells a limited discharge which is followed by a higher charge capacity may be due to a partial self-discharge of the soluble sulfur¹³⁵. The activation trend during the subsequent 20 cycles, can be asso-

ciated with kinetic effects at the electrode electrolyte interface and progressive electrode wetting with the electrolyte.¹³⁶ Accordingly, several literature works^{137,138} have attributed effects such as a low initial capacity, the anomalous discharge profile during the first cycle, as well as the increase of the capacity by cycling to a progressive electrode surface wetting. This phenomenon allows electrolyte flooding into the internal part of porous electrodes, such as those studied in our work, which progressively becomes electrochemically active by the contact with the electrolyte. The relatively low electrolyte amount used herein (i.e., 30 μl) may actually lead to activation cycles ascribed to the above mentioned wetting issue. However, the low electrolyte amount positively affects the cell stability by limiting the polysulfide production.¹³⁷ Furthermore, Figure. 42 suggest that the extent of the activation process is directly affected by the electrode structure, crystallinity and morphology (see XRD and SEM in Figs. 39 and 40, respectively). S–Graphite (Fig. 42A) shows a steady state specific capacity of about 400 mAh g^{-1} (0.52 mAh cm^{-2}), a coulombic efficiency exceeding 95% and a voltage profile (Fig. 42B) reflecting the Li/S electrochemical process. However, the electrode exhibits a substantial charge/discharge polarization, thus accounting for the low capacity achieved in lithium cell. The S–MCMB electrode reveals an enhanced performance (Fig. 42C), with a steady state specific capacity approaching 500 mAh g^{-1} (0.65 mAh cm^{-2}) and a voltage profile (Fig. 42D) characterized by a lower polarization with respect to S–Graphite. However, the cell shows a rapid decrease of the efficiency from about 95% to 80% by the final stage of the cycling test, thus suggesting a partial disso-

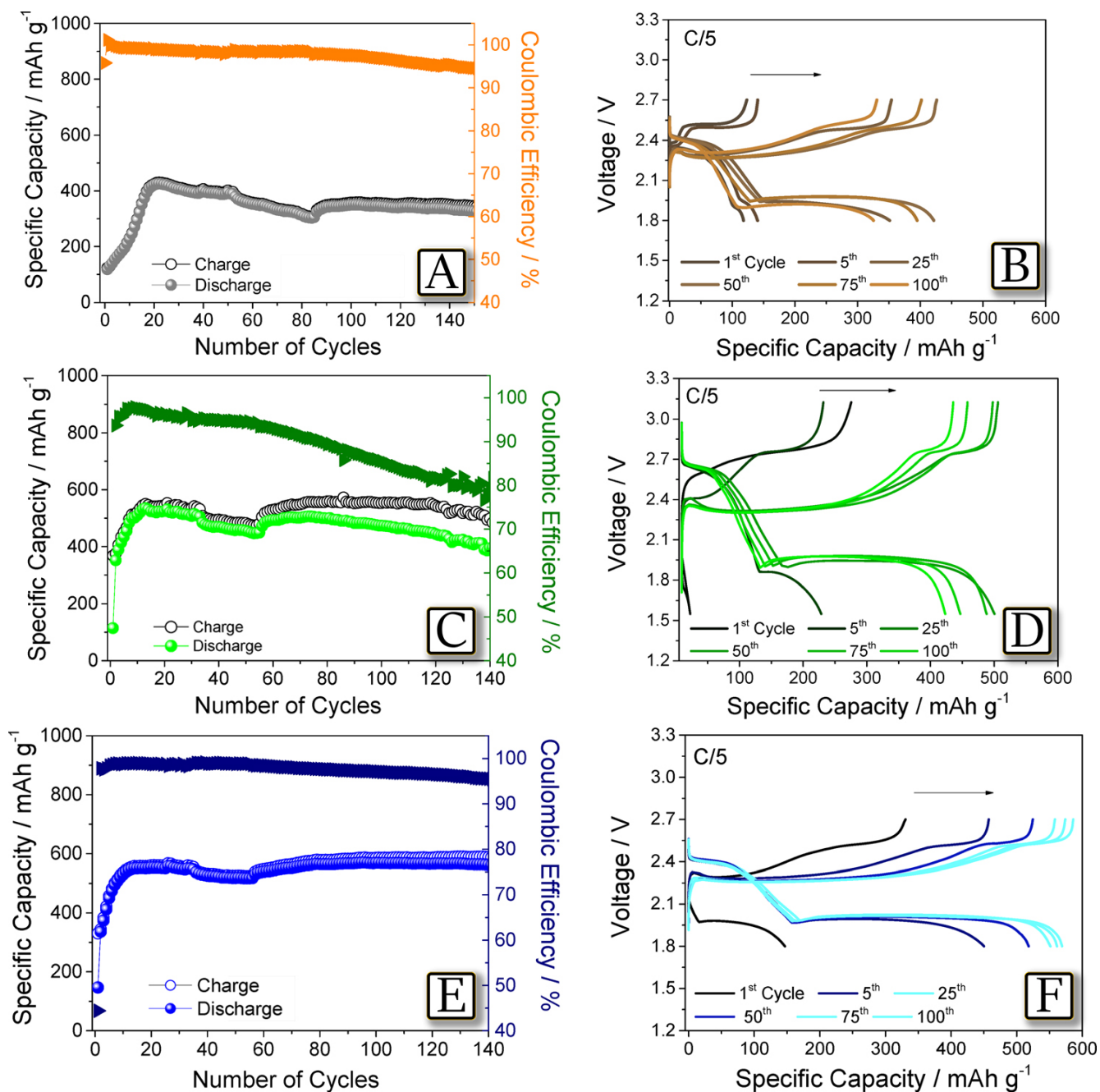


Figure 42 Galvanostatic performances in terms of cycling trend and voltage profiles, respectively, of (A)-(B) S-graphite, (C)-(D) S-MCMB and (E)-(F) S-CNTs electrodes in lithium cells. Measurements performed in 2032 coin-cell using a 1.8 V – 2.7V voltage range at a current rate of C/5 (335 mA g⁻¹). Electrolyte: TEGDME–LiCF₃SO₃ 1mol kg⁻¹. Room temperature.

lution of the S-MCMB electrode by prolonged cycling, leading to shuttle effect and consequently decreased efficiency.¹⁰ The best performance is achieved by S-CNTs electrode, with a very stable cycling trend, and a steady state capacity approaching 600 mAh g⁻¹ (0.8 mAh cm⁻²) (Fig. 42E). Furthermore, the S-CNTs shows the lowest charge-discharge polarization (Fig. 42F), a working voltage centered at about 2.1 V and a stable efficiency of about 95%, thus suggesting this material as the

most promising candidate for application in advanced, high energy Li/S cell. Therefore, the polarization observed for the cells herein studied can be likely ascribed to the nature of the materials employed for the cathode preparation and to the electrode/electrolyte interface, rather than the electrolyte conductivity and transference number that may allow limited polarization. Nevertheless, the very limited material cost and the simple synthetic pathway of the electrodes may account for a slightly lower energy density due to the cell polarization.

Optimizing the Li/S Cell

The study demonstrated differences in the electrochemical behavior of the S-C composites due to differing reaction kinetics directly affected by the electrode structure and morphology. Among the various materials, the S-CNTs electrode has shown the most promising performance by revealing a very stable capacity approaching 600 mAh g^{-1} (0.8 mAh cm^{-2}), delivered at an average working voltage of 2.1 V and leading to an energy density as high as 1260 Wh kg^{-1} . Certainly, a further increase of the practical capacity, coulombic efficiency and stability during cycles is required. Therefore, further improvements of the cell are investigated by tuning the sulfur mass loading in the cathode and employing alternative separators to physically trap the polysulfides on the cathode side.^{139–141} Moreover, the high energy ball milling treatment was avoided from the active material preparation pathway in order to obtain a high order morphology. The electrolyte based on DEGDME solvent, LiTFSI salt, and LiNO_3 additive was used advantageously combining the high safety level of the glyme, and a high conductivity expected by the low viscosity and the high solvating ability of the short-chain DEGDME. The studied Li/S cell reveals high safety content and significant performances; hence it is proposed for promoting a sustainable scaling-up of an efficient high energy storage system.

Experiment summary

The electrolyte with low-flammability, based on diethylene glycol dimethyl ether (DEGDME) dissolving lithium bis-trifluoromethane sulfonimide (LiTFSI), and lithium nitrate (LiNO_3), designed for application in lithium sulfur battery is presented. Ionic mobility, self-diffusion coefficients and lithium transport number of the electrolyte are obtained by nuclear magnetic resonance (NMR) and conductivity values by electrochemical impedance spectroscopy (EIS). Combining these two methods also yields the degree of ion association. Further properties, such as electrolyte/lithium interface stability, both under dynamic and static condition, lithium stripping/deposition ability, and electrochemical stability window, are determined by voltammetry and EIS. All the tests suggest particular suitability of the electrolyte for lithium metal battery, due to conductivity higher than $10^{-2} \text{ S cm}^{-1}$, lithium transport number of 0.5, electrochemical stability extending from 0V to 4.6V, and excellent compatibility with lithium metal, while a direct test indicates the low-flammability of the electrolyte. A composite cathode is prepared by simply melting elemental sulfur into multi walled carbon nanotubes (MWCNTs), and characterized in terms of structure and morphology by X-ray diffraction and electron microscopy, respectively. The tests show for the material a spherical flakes morphology in which the nanotubes protect the crystalline sulfur from excessive dissolution, and create the optimal

Experimental Section: Electrolyte Preparation

Diethylene glycol dimethyl ether ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}$) (Sigma-Aldrich), denoted hereafter by DEGDME, was dried before use with molecular sieves (5 Å) until the water content was below 10 ppm as measured by 831 Karl Fischer Coulometer (Metrohm). Lithium bis-trifluoromethanesulfonimide ($\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)_2$, LiTFSI) and lithium nitrate (LiNO_3), from Sigma-Aldrich, were separately dried under vacuum overnight at 80 °C. All the samples were subsequently handled in argon filled glove box, with oxygen and moisture content lower than 1 ppm. LiTFSI was dissolved in DEGDME by a salt to solvent ratio of 1 mol kg^{-1} to obtain the electrolyte (indicated by DEGDME-LiTFSI). The electrolyte for battery application (DEGDME-LiTFSI- LiNO_3) was prepared by dissolving LiNO_3 (film forming sacrificial additive with salt to solvent ratio of 1 mol kg^{-1}) and LiTFSI (ions conductor with salt to solvent ratio 1 mol kg^{-1}) in DEGDME.

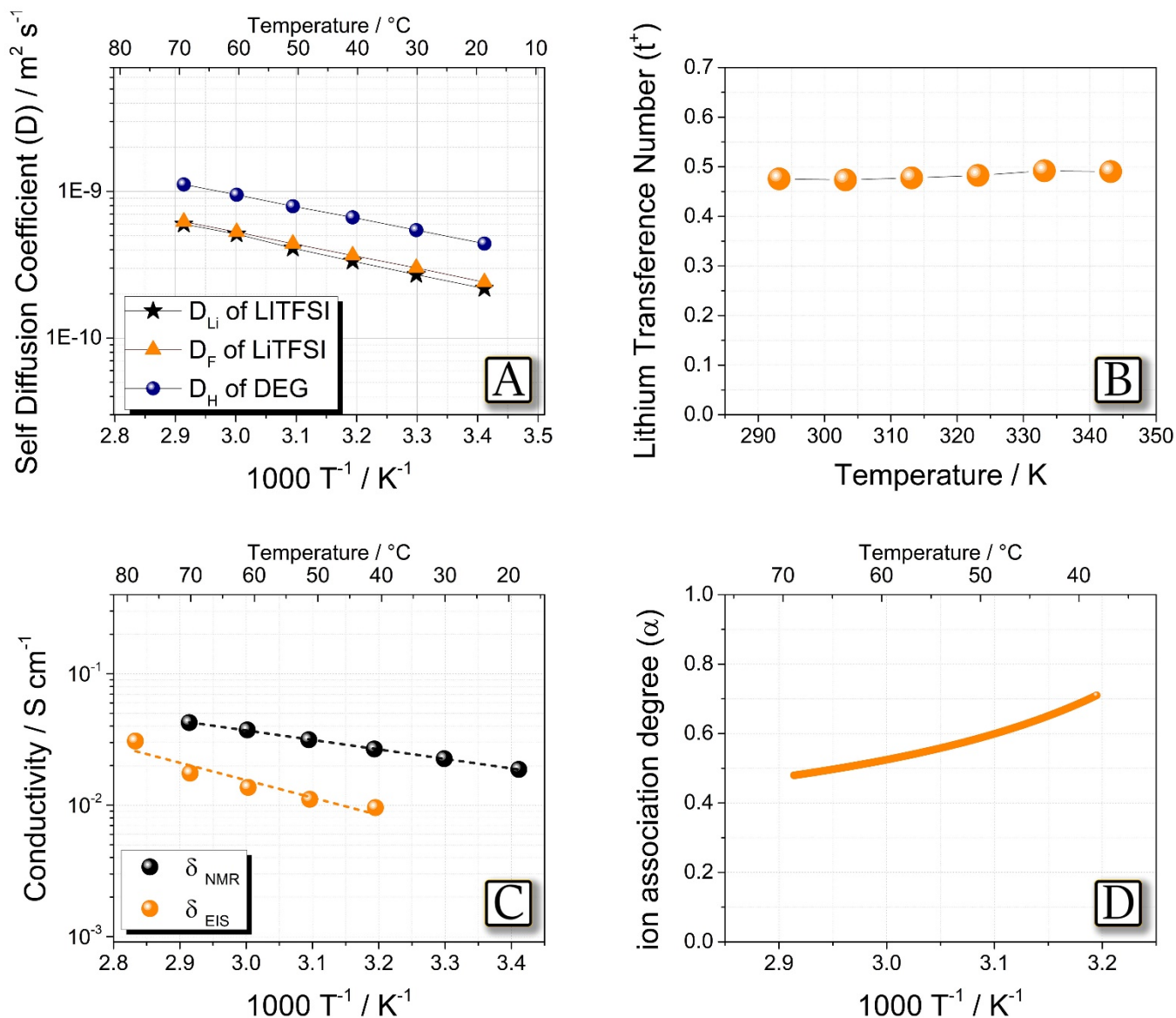


Figure 43 (A) Self-diffusion coefficient of ⁷Li, ¹⁹F and ¹H in the DEGDME-LiTFSI electrolyte (1mol kg⁻¹) determined by PFG NMR. (B) Conductivity Arrhenius plots of the DEGDME-LiTFSI electrolyte performed using electrochemical impedance spectroscopy (EIS) by heating and cooling the sample in the temperature range between 40°C and 80 °C in a coin-cell, with signal amplitude of 10 mV within 500 MHz– 100 Hz frequency range. (C) lithium transport number (t⁺) calculated from the self-diffusion coefficient values using equation (2), and (D) ion association degree (α) determined by equation (3) using the conductivity values determined by EIS (δ_{EIS}) and the values obtained from the self-diffusion coefficient (δ_{NMR}) by Nernst Einstein equation (4).

host for allowing the proper cell operation. The electrochemical tests of the lithium/sulfur cell using the S-MWCNTs composite coated on a carbon cloth and the DEGDME-LiTFSI-LiNO₃ electrolyte show highly reversible process with fast kinetic, suggested by a lithium diffusion coefficient in the cathode ranging from about 10⁻¹² at the charged state to about 10⁻¹⁰ cm² s⁻¹ at the discharged one, calculated by the Randles-Sevcik equation using voltammetry at increasing scan rate. The Li/S cell is studied by advantageously increasing the sulfur

loading, and shows a capacity ranging from 1300 mAh g⁻¹ to 900 mAh g⁻¹, depending on the cycling current and the active material loading, a theoretical energy density ranging from 2600 to 1800 Wh kg⁻¹ and a practical energy higher than 400 Wh kg⁻¹. A cell with optimized active mass loading using shows satisfactory rate capability, and a very stable specific capacity of about 1000 mAh g⁻¹ delivered with coulombic efficiency approaching 100%. The outstanding properties of the electrolyte, its low-flammability, the simple synthesis procedure of the

cathode as well as the remarkable performance of the cell suggest the configuration herein adopted as viable solution for high energy, safe and low-cost lithium sulfur battery.

DEGDME LiTFSI Properties

Ions and solvent molecules mobility represents a key factor in determining the electrolyte characteristics for application in the energy storage devices. A very suitable protocol for determining such an important parameter has been developed in the previous studies by combining NMR and EIS measurements, and adopted in this chapter for the study of the new LiTFSI-DEGDME electrolyte (Figure 43). It is worth mentioning that LiNO₃ is not considered by this protocol since it is added as a sacrificial film forming agent for passivating the lithium metal which is consumed by the initial cycling stages and, therefore, excluded from ion conduction mechanism.^{22,50} Figure 43A shows the self-diffusion coefficient of the ¹H, ¹⁹F, and ⁷Li nuclei in the electrolyte, determined between 20°C and 70 °C. All the coefficients increase with increasing

temperature, however the glyme chain shows higher mobility (D_H) in the whole range with respect to the ions nuclei as indeed observed other ether based electrolytes,¹⁴² while lithium and anion (D_{Li} and D_F, respectively) show similar mobility. The lithium transport number, calculated by eq. 6 (experimental section) and reported in Figure 43B reveals a value ranging from 0.47 at 20°C to 0.49 at 70 °C, which is expected to ensure a fast charge transfer at the electrode/electrolyte interface in lithium battery. It is important to point out that the apparent transport number value close to 0.5 is at least partly a consequence of ion association, which results in correlated motion with similar cation and anion diffusion coefficients. However as will be discussed next, these electrolytes exhibit markedly less ion association than glymes with other salts.⁴⁸ Nonetheless, NMR-determined Li⁺ transport numbers in electrolytes as disparate as high molecular weight PEO and liquid carbonates are more typically around 0.2 – 0.3. Notably, the ionic conductivity in the current system shows a practical value as high as 10⁻² S cm⁻¹ as measured by EIS (δ_{EIS} in

Experimental Section: Electrolyte Characterization

The **self-diffusion coefficient** of the ¹H, ¹⁹F, and ⁷Li nuclei in the DEGDME-LiTFSI electrolyte were measured by a Bruker 400 Advance III NMR spectrometer within screw-cap gastight NMR tubes in order to overcome possible evaporation along the temperature scan from 20°C to 70°C. The data were collected every 10 °C for each nucleus using a double-stimulated echo sequence with pulse field gradients (PFG) to suppress convection. The gradient pulse strength was increased linearly in 32 steps from 1 to 45 G cm⁻¹, the gradient pulse duration (δ) was of 1.4 – 4 ms with a diffusion delay (Δ) of 200 – 400 ms. Eddy current effects were avoided by using a longitudinal eddy-current delay (LED) of 5 ms. The error on the self-diffusion coefficient is about 3-5%.²²⁵ **Ion conductivity** was calculated from the self-diffusion coefficients by the Nernst-Einstein equation

$$\text{eq. 4: } \delta_{\text{NMR}} = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3})$$

where δ_{NMR} is the conductivity determined by the NMR, F is the Faraday constant (96485 C), [C] is the concentration of the salt in the electrolyte (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature (K), D_{Li} and D_{LiTFSI} are the corresponding self-diffusion coefficients. Ion conductivity was also measured by electrochemical **impedance spectroscopy (EIS)** using a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. A symmetrical stainless steel/ stainless steel 2032 coin-cell with a Teflon ring separator was used to ensure a fixed cell constant during the measurements. The data were collected every 10°C by heating and cooling the cell within 40°C - 80°C temperature range using a signal amplitude of 10 mV and in a 0.1 Hz-0.5 MHz frequency range. The conductivity values determined by NMR (δ_{NMR}) and measured by EIS (δ_{EIS}) were used to obtain the **ion association degree** (α) of the LiTFSI salt by

$$\text{eq. 5: } \alpha = (1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}})$$

The **lithium transport** (t⁺) number was calculated from the self-diffusion coefficient by

$$\text{eq. 6: } t^+ = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{LiTFSI}}}$$

where D_{Li} is the self-diffusion coefficient of lithium, and D_{LiTFSI} is the self-diffusion coefficient of the TFSI anion [N(SO₂CF₃)₂⁻].

Figure 43C) which is very suitable for high rate applications. The conductivity observed for the DEGDME-LiTFSI electrolyte is much higher than that observed for other glyme solutions reported previously,⁵⁴ and comparable to DOL/DME-based electrolyte, which is the one commonly used in lithium-sulfur battery.¹⁴³ The apparent conductivity of the electrolyte calculated by eq. 4 using the NMR self-diffusion coefficients of the ions (δ_{NMR} in Figure 43C), may be combined in eq. 5 with the practical value of the conductivity determined by EIS (δ_{EIS} in Figure 43C) for the evaluation of the ion association degree (α) which is reported in Figure 43D. The figure reveals relatively low ion association for the DEGDME-LiTFSI electrolyte with respect to solutions based on LiCF_3SO_3 salt which confirms the higher dissociation ability of LiTFSI with respect to LiCF_3SO_3 .^{51,52,54,142} This important characteristic is ascribed to the interaction between salt and solvent which is temperature-dependent: an increasing interaction between solvent molecules and salt ions hinders the ion association and promotes the free ions in the solution. Indeed, DEGDME-LiTFSI electrolyte shows the decrease of α from 0.7 at 40°C to 0.45 at 70°C in Figure 43D. This presents a very interesting contrast with previous studies involving LiCF_3SO_3 ^{43,44,47} as the electrolyte salt, in which it was found that ion association actually increases with increasing temperature

due the decreasing solvating ability of the elevated temperature solvent with a salt that is more prone to ion pairing.

LiNO₃ Addition to DEGDME LiTFSI

As already mentioned in the previous paragraphs, the addition of LiNO_3 to the electrolyte has a crucial role in allowing its use in Li/S cell.¹⁴⁴ Therefore, we have studied the chemical stability of the interface between DEGDME-LiTFSI- LiNO_3 solution and lithium, as well as the electrochemical stability windows of the electrolyte (Figure 44). The galvanostatic lithium stripping/deposition in symmetrical cell reported in Figure 44A reveals an average overvoltage of 0.02 V after 12 days, slightly changing during the initial stages of the test and finally stabilizing due to chemical formation, partial dissolution and consolidation of a solid electrolyte interphase (SEI) film.⁴⁸ A similar trend is observed over time for the interface chemical stability detected by impedance spectroscopy in Figure 44B (corresponding Nyquist plots in inset). The test evidences an initial fluctuation of the resistance from 250 to 700 Ω , and a final drift to 500 Ω as the SEI is formed and stabilized.⁷⁶ The DEGDME-LiTFSI- LiNO_3 electrolyte is further studied by voltammetry, both in the cathodic region (CV in Figure 44C)

Experimental Section: *Electrolyte Characterization*

Lithium/stripping deposition test was carried out in a symmetrical lithium/lithium 2032-coin cell using a current of 0.1 mA cm^{-2} with a step time of 1 hour at 23 °C, the test was performed by a MACCOR 4000 series Battery Test System. The electrochemical **anodic stability widow** was evaluated by linear sweep voltammetry (LSV) using a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat, with scan rate of 0.1 mV s^{-1} within OCV and 5V vs Li/Li^+ with a three electrode Swagelok T-cell equipped with lithium metal reference and counter electrodes, and a Super P carbon coated on carbon cloth working electrode. The same cell configuration and instrument were used to study the cathodic electrochemical stability of the electrolytes by **cyclic voltammetry (CV)**. The CV was performed with a scan rate of 0.1 mV s^{-1} in a 0 - 2 V vs Li/Li^+ potential range. The **lithium/electrolyte interface** chemical stability was evaluated by electrochemical impedance spectroscopy in a symmetrical lithium/lithium 2032-coin cell, acquiring with a VersaSTAT MC Princeton Applied Research-AMETEK the impedance spectra every day, using 10 mV signal amplitude in a 0.1 Hz - 0.5 MHz frequency range. The impedance spectra were analyzed by non-linear least squares fit (NLLSQ) using a Boukamp software.^{235,236} Only fitting results with a chi-square (χ^2) lower than 10^{-4} were accepted. The equivalent circuit (shown in the inset of the figure) adopted for the Nyquist plot was $R_a(R_iQ_i)$ where R represents a resistance and Q a constant phase element (CPE). **Flammability tests** was performed on the DEGDME-LiTFSI- LiNO_3 electrolyte by direct ignition of the solution

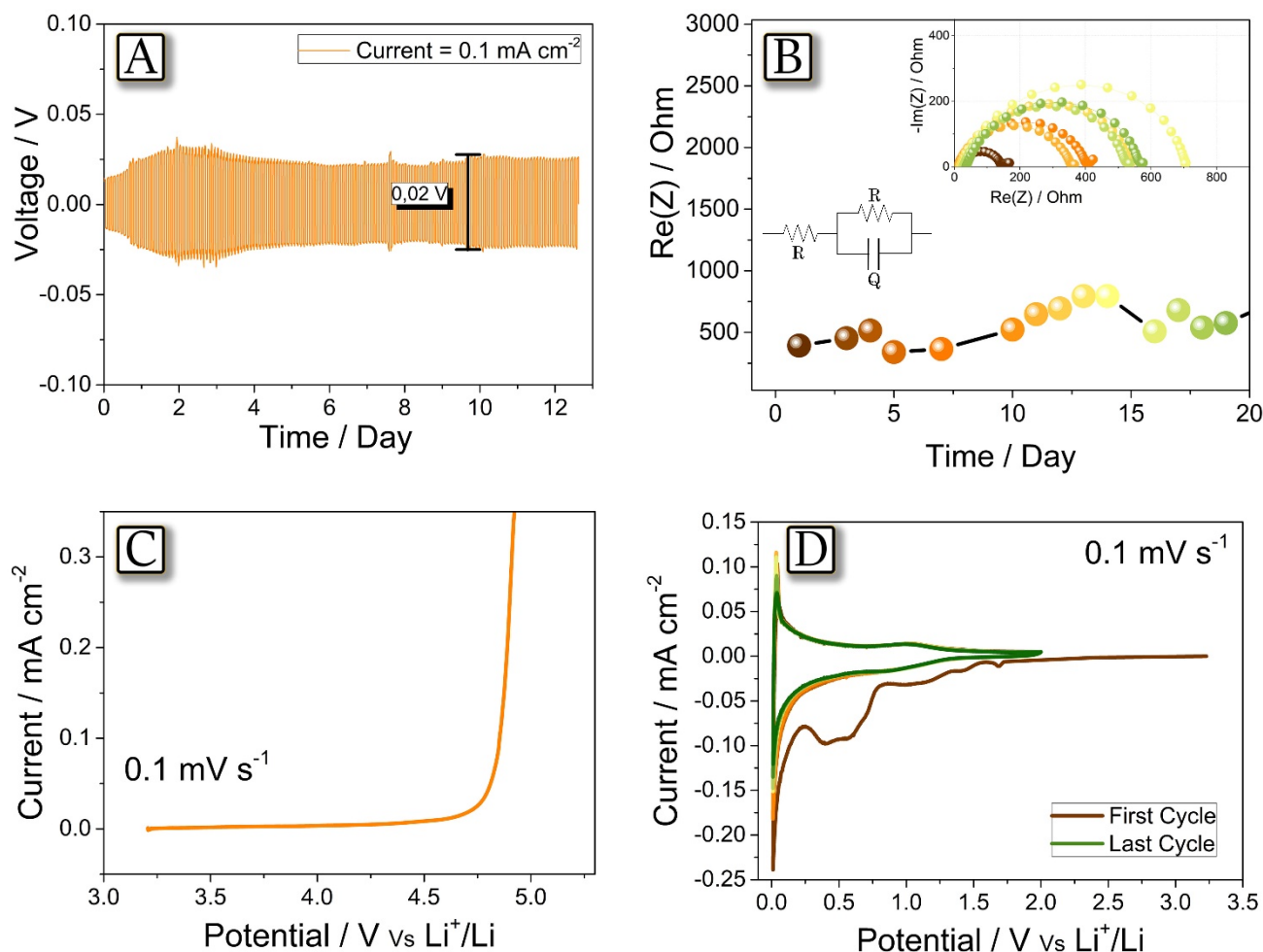


Figure 44 (A) Voltage versus time profile of lithium deposition/stripping galvanostatic test performed by applying a 0.1 mA cm^{-2} current to symmetrical Li/DEGDME-LiTFSI/Li cell. (B) Time evolution at 23°C of the lithium/electrolyte interface resistance performed in symmetrical Li/DEGDME-LiTFSI/Li cell using electrochemical impedance spectroscopy with signal amplitude of 10 mV within 500 MHz–100 mHz frequency range. (D) Cyclic voltammetry (CV) using potential limits of 0.01 V - 2 V and (C) linear sweep voltammetry (LSV) of the DEGDME-LiTFSI electrolyte in a tree electrode cell using a carbon coated on Cu and Al substrate, respectively, as the working electrode and lithium metal as counter and reference electrode. Scan rate 0.1 mV s^{-1} . Temperature 23°C .

and in the anodic one (LSV in Figure 44D). The first CV cycle in Figure 44C exhibits irreversible peaks at 1.5 V and 0.8 V vs Li^+/Li , due to reduction of the electrolyte and electrochemical formation of the SEI, while the subsequent cycles reveal the reversible lithium insertion/de-insertion into amorphous Super-P carbon at about 1V and 0.1 V vs Li^+/Li , as well as possible lithium deposition/stripping at very low potentials (i.e., at about 0 V vs

Li^+/Li),¹⁴⁵ without any further side reaction. The LSV of Figure 44D indicates for the electrolyte an anodic stability extended above 4.6V vs Li^+/Li , which is a suitable range for application in several lithium battery configurations, including the Li/S one which operates at about 2.1-2.4 V.¹³⁴ Beside high conductivity, chemical and electrochemical stability, another suitable characteristic of the electrolyte, particularly attractive for a safe application

Experimental Section: Cathode Preparation

The S-carbon powder was prepared by melting elemental sulfur (Sigma-Aldrich) at 135°C and mixing with multi-walled carbon nanotubes MWCNTs (from Sigma-Aldrich) by a 60:40 S to C weight ratio. The sample was stirred 3 hours under heating at 135°C in order to obtain a homogeneous mixture, cooled down to room temperature and refined by mortar. The electrode slurry was prepared by mixing the S-MWCNTs-S powder, Super P Carbon conductive additive (Timcal) and polyvinylidene difluoride binder (PVdF; Solvay Solef) binder in 80:10:10 weight ratio, using N-methylpyrrolidone (NMP) as solvent. The slurry was cast onto carbon cloth support (GDL ELAT) by the Doctor Blade method with a wet thickness varying from 300 μm to 600 μm , in order to obtain various sulfur loadings. The electrode foils were punched into 10 mm and 16 mm disks, dried for 48 hours at 60°C under vacuum before assembling the cell in the argon filled glovebox with oxygen and water content lower than 1 ppm. The sulfur loading of the final electrodes was 2, 2.5, 3 and 4 mg cm^{-2}

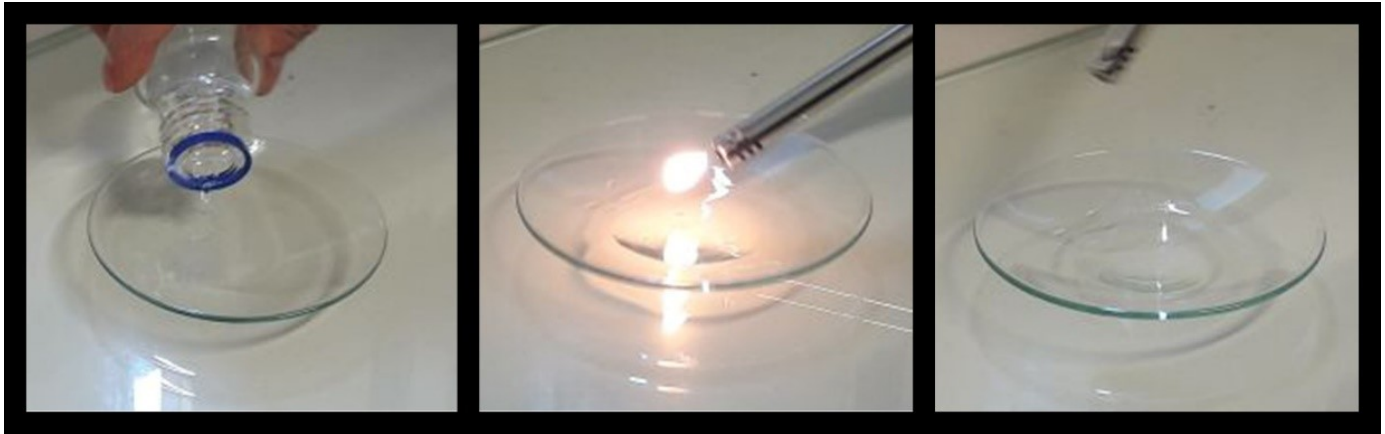


Figure 45 Flammability tests performed by direct ignition of a DEGDME LiTFSI LiNO₃ electrolyte sample in standard room environment.

in high energy lithium metal cells, is represented by its very low flammability observed in Fig. 45 which evidences no fire evolution by a direct ignition test.

Morphology and Structure of the active material

The DEGDME-LiTFSI-LiNO₃ electrolyte is subsequently studied in a Li/S cell using a cathode prepared by melting S and mixing with MWCNTs (see experimental section), i.e., a simple technique leading to a crystalline material (XRD in Figure 4A) in which the orthorhombic sulfur S₈ (PDF # 85-0799)

and the hexagonal MWCNTs are intimately mixed. Pristine tubes of carbon (SEM in Figure 46B) with micrometric length (4 μm) and nanometric diameter (10-30 nm) surround the sulfur to form a spherical-shape composite with a size of about 10-25 μm (SEM in Figure 46C). Indeed, the EDX mapping in Figure 46D indicates that the S-MWCNTs sample is characterized by the presence of sulfur mainly in the core and MWCNTs in the shell with homogeneous distribution. This spherical-like, core-shell morphology enables a very important characteristic which may allow efficient ion and electron conduction into the electrode, hence satisfactory rate capa-

Experimental Section: Cathode Characterization

Bruker instrument **x-ray** diffractometer equipped with a Cu Kα source and a graphite monochromator in the 2θ/θ scanning mode was used to evaluate the structure of the sulfur-carbon electrode. The morphology of the sample was studied by a **scanning electron microscopy** (SEM, Zeiss EVO 40) with a thermionic electron gun equipped with LaB₆ crystal and by energy dispersive x-ray spectrometry (SEM-EDX) by a X-ACT Cambridge Instruments analyzer. **Cyclic voltammetry** of S-MWCNTs working electrode with a sulfur loading of 3 mg cm⁻² was performed in a three-electrode cell with lithium metal as reference and counter electrode using the DEGDME-LiTFSI-LiNO₃ as the electrolyte. The test was performed with a scan rate of 0.1 mV s⁻¹ in a 1.8 V - 2.8 V potential range. A second cyclic voltammetry test in the above reported potential range was carried using the same cell configuration at various scan rates (i.e., 0.1, 0.2, 0.3, 0.4 and 0.5 mV s⁻¹) in order to evaluate the Li⁺ diffusion coefficients (D) within the cathode material by the **Randles-Sevcik equation** (Eq. 7):^{152,237}

$$I_p = 0.4463 z F A C \sqrt{\frac{z F v D}{RT}}$$

where I_p is the peak current value (A), z is the number of exchanged electrons for the taken peak, F is the Faraday constant (96485 C mol⁻¹), A is the electrode geometric area (cm²), C is the Li⁺ concentration in the active material (mol cm⁻³), v is the scan rate (V s⁻¹), R is the gas constant (J K⁻¹ mol⁻¹), and T is the used temperature (K). The **CV tests** were performed at 23°C by a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. **Galvanostatic cycling** tests of the electrodes with various sulfur loadings (2 mg, 2.5, 3 and 4 mg cm⁻²) were carried out at the current rate of C/3, while the electrode with a sulfur mass loading of 4 mg cm⁻² required a current of C/8 for significant cycling (1C = 1675 mAhg⁻¹), in a 1.9V – 2.8V voltage range. A **cycling test** at various c-rates (i.e., C/10, C/8, C/5, C/3, C/2 and 1C) was performed using an electrode with 3 mg cm⁻² sulfur loading in a 1.9 V – 2.8 V voltage range. Cycling tests prolonged over 100 cycles were performed at C/3 in a 1.9 V – 2.8 V voltage range and at 1C in a 1.8 V – 2.8 V voltage range, using an electrode with 3 mg cm⁻² sulfur loading. All the galvanostatic tests were performed by a MAC-COR 4000 series Battery Test System using a 3032-coin cells (electrode geometric surface 1.54 cm²) filled by 50 μl of the DEGDME-LiTFSI-LiNO₃ electrolyte at 23°C. Cells were cycled following 3 hours of rest at the OCV.

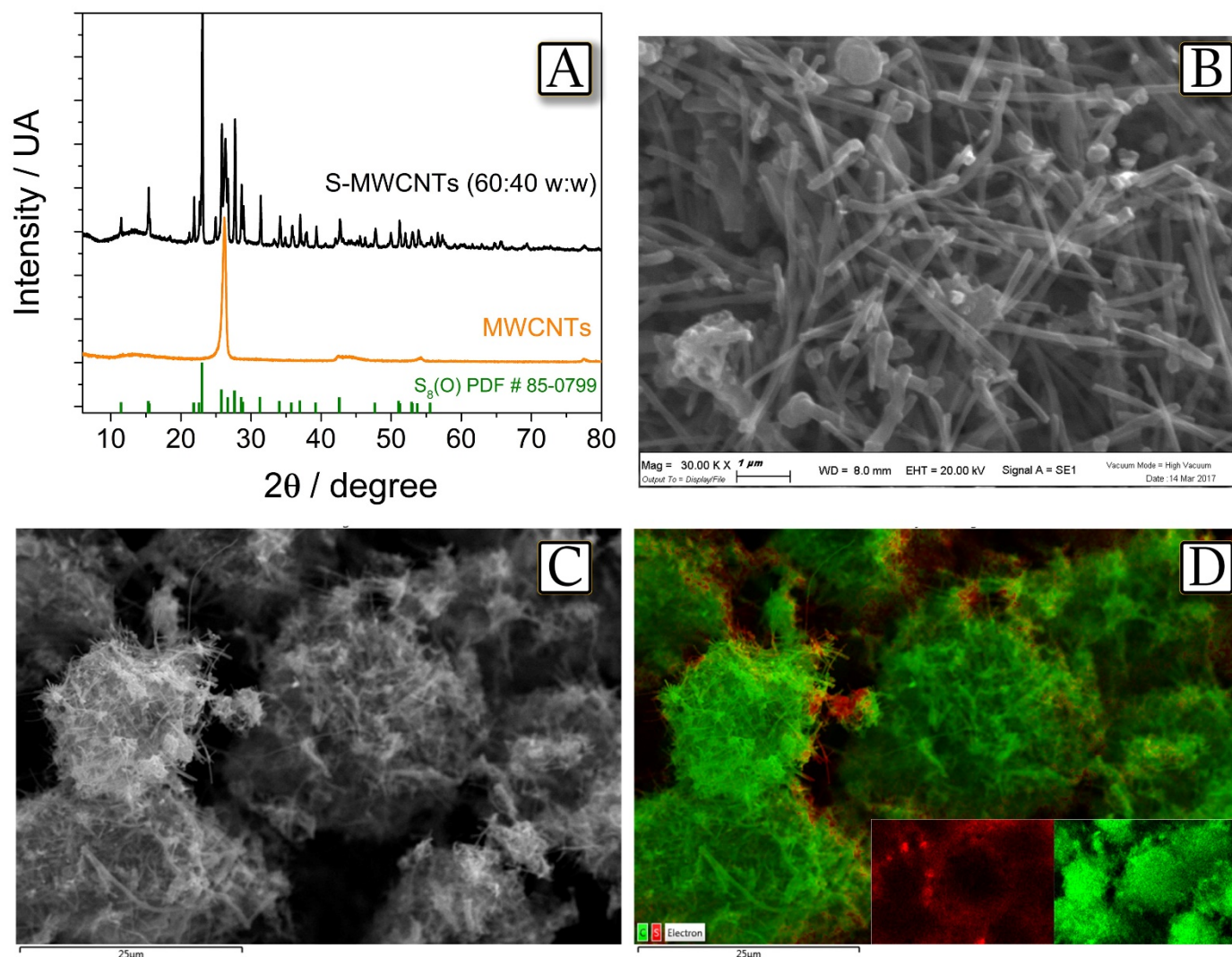


Figure 46(A) X-ray diffraction patterns (XRD) of the S-MWCNTs composite. (B) Scanning electron microscopy (SEM) image of the pristine MWCNTs powder. (C) SEM image and (D) corresponding energy dispersive x-ray spectroscopy (EDX) mapping the S-MWCNTs composite. Carbon and sulfur are depicted by green and red color, respectively, in the EDX map.

bility, in particular considering the insulating character of sulfur⁸. Furthermore, a homogeneous distribution of MWCNTs at the particles shell may partially prevent the active material loss caused by soluble polysulfides formation during the electrochemical process.⁷² Fig.47 reports the SEM images of the carbon cloth used instead of aluminum as the electrode support in the Li/DEGDME-LiTFSI LiNO₃/S-MWCNTs cell. It is worth mentioning that the use of a porous carbon cloth represents a viable strategy to efficiently host possible dissolved species at the cathode/electrolyte interface, avoid their migration through the cell, thus improving the cell cycling stability. Another relevant characteristic of the material is represented by a

straightforward synthetic pathway which allows easy and low cost preparation, thus leading to the reduction of the cost of the battery.¹⁴⁶

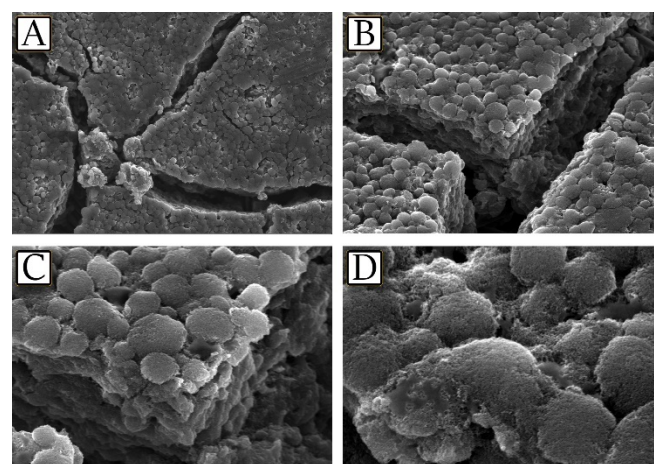


Figure 47 Scanning electron microscopy (SEM) images of the carbon cloth, GDL ELAT, at different magnification. (A) 500X, (B) 1000X, (C) 2500X, (D) 5000X.

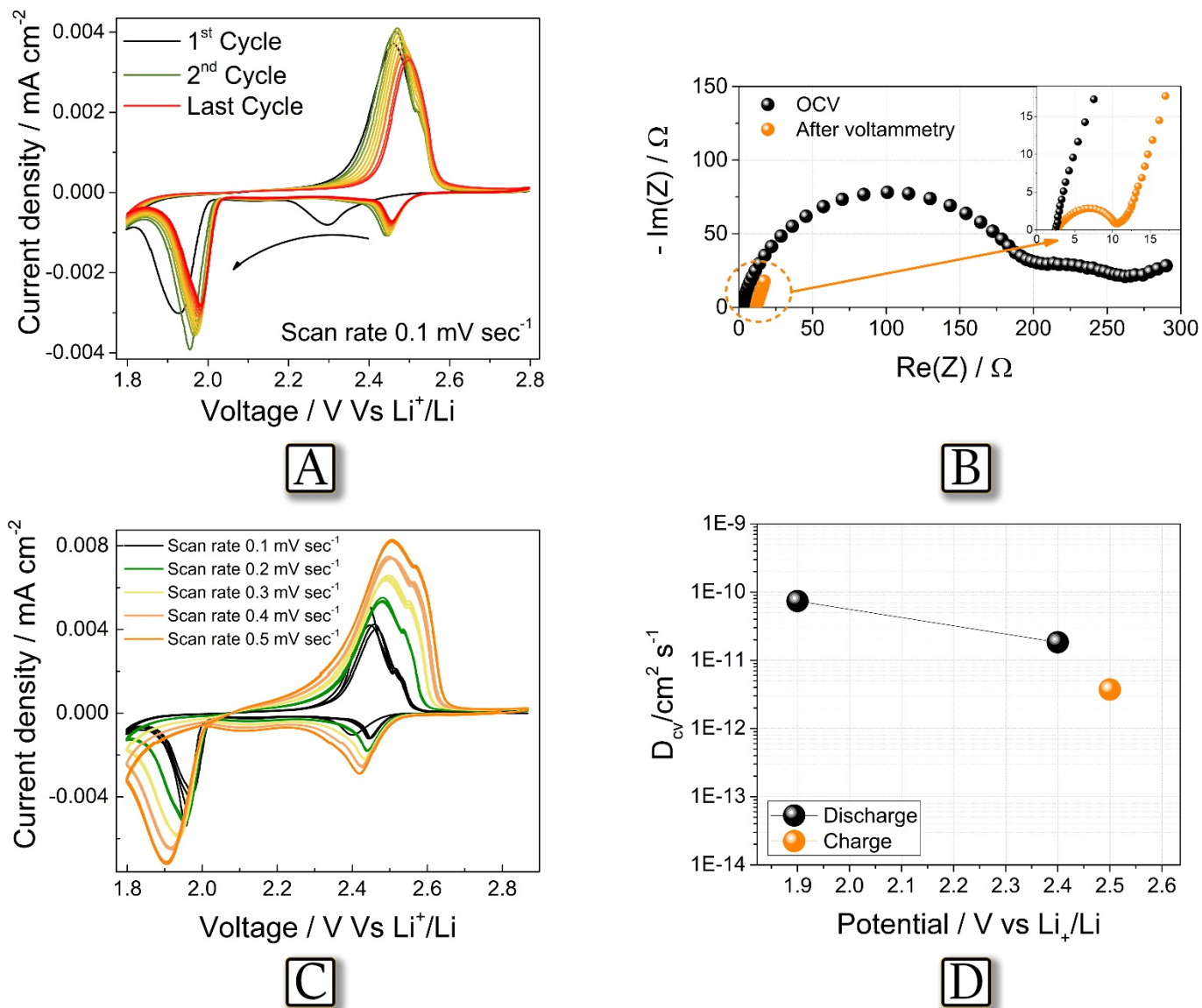


Figure 48 (A) Cyclic Voltammetry (CV) tests of the S-MWCNTs working electrode in three-electrode using lithium metal as reference and counter electrode and the DEGDME-LiTFSI-LiNO₃ electrolyte performed in a potential range of 1.8 V - 2.9 V with a scan rate of 0.1 mV s^{-1} , and (B) impedance spectra of the cell before and after the CV test. (C) CV test performed in the same potential window by increasing the scan rate every three by 0.1 mV s^{-1} from 0.1 mV s^{-1} to 0.5 mV s^{-1} , and (D) Lithium ion diffusion coefficient calculated from the above CV tests by using the peak intensity (I_p), the scan rate (v) and the Randles-Sevcik equation (5). See experimental section for equation.

Cyclic voltammetry study

The CV profiles of the Li/DEGDME-LiTFSI LiNO₃/S-MWCNTs cell at a constant scan rate (0.1 mV s^{-1}) reported in Figure 48A exhibit during the first cycle (black line) the characteristic shape ascribed to the electrochemical process of lithium and sulfur,¹³⁴ with formation of long chain polysulfides (i.e., Li₂S₈, Li₂S₆) at 2.3 V vs. Li⁺/Li and of short-chain species (i.e., Li₂S₄, Li₂S₂, Li₂S) at 1.9 V vs. Li⁺/Li in the cathodic scan,²⁰ which are oxidized

back by a merged double peak centered at about 2.4 V vs. Li⁺/Li due to the multi-electron charge reaction during anodic scan.²¹ The subsequent cycle (dark green line) reveals an increase of the reduction potentials to 2.4 and 2 V vs. Li⁺/Li, i.e., a decrease of the cell polarization, as well as an increase of the peaks intensity which may be likely ascribed to the decrease of the electrode resistance by the diffusion of the lithium ions into the material and the formation of lithiated species¹⁴⁷. This trend is well justified by Figure 48B which displays the Nyquist

plots of the impedance spectroscopy tests performed before and after the CV cycles. Indeed, the figure shows a remarkable decrease of the cell impedance from about $250\ \Omega$ at the OCV to about $10\ \Omega$ after the CV cycles. This process suggests the use of activation cycles and proper voltage cutoff tuning for suitable cycling of the cell, even at higher C-rates as will be shown hereafter. However, the CV cycles of Figure 48A evidence a slight reduction of the peak intensity by cycling after the second cycle, thus suggesting partial dissolution of the electrode by formation of polysulfides. The lithium diffusion into the electrode is further investigated by CV by increasing the scan rate (Figure 48C), using the Randles-Sevcik equation (eq. 7)^{105,148–151} according to which the peak current (I_p) is proportional to the square root of the scan rate, with a slope that depends on the lithium diffusion coefficient (D_{CV})¹⁵². Considering the overall process of the lithium with sulfur, summarized by $2\text{Li} + \text{S} \rightleftharpoons \text{Li}_2\text{S}$, in order to simplify the determination of D_{CV} we have attributed one electron to each reduction peak, and two electrons to the oxidation merged peak, despite the complex multiple step reaction mechanism.²⁰ This assumption allows the determination of the Li^+ -diffusion coefficient at the various states of charge (Figure 48D), i.e., at about 2.5 V vs Li^+/Li during charge, 2.4 V vs Li^+/Li during discharge and 1.9 V vs Li^+/Li during discharge (corresponding linear fit in Fig. 49. Figure 48D shows the expected increase of the Li^+ -diffusion coefficient, hence of the electrode ion conductivity, by the ongoing of the lithiation, from about $3.7 \times 10^{-12}\ \text{cm}^2\ \text{s}^{-1}$ at the charged (de-lithiated) state at 2.5 V vs Li^+/Li , to about $1.7 \times 10^{-11}\ \text{cm}^2\ \text{s}^{-1}$ and $7.3 \times 10^{-11}\ \text{cm}^2\ \text{s}^{-1}$ at the discharged (lithiated) state at 2.4 V and 1.9 V vs Li^+/Li , respectively, which is in full

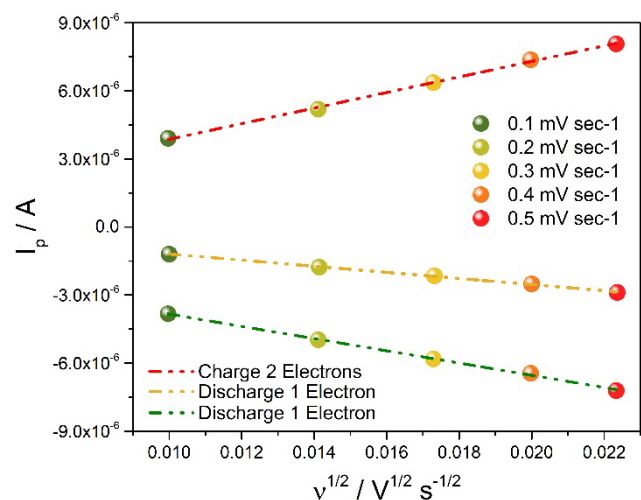
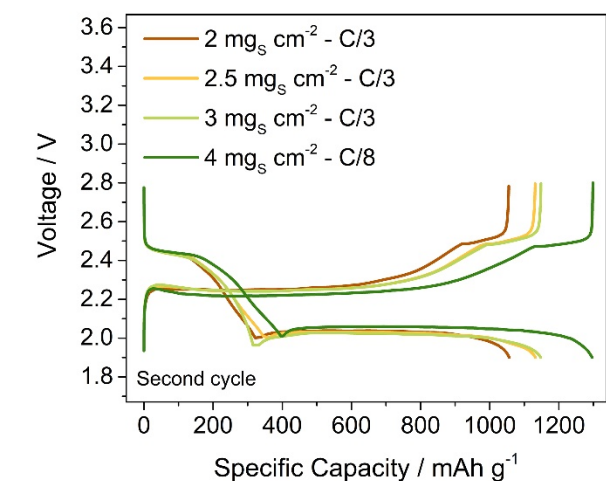


Figure 49 Peak current (I_p) linear fit vs. square root of the scan rate ($v^{1/2}$) of the cyclic voltammetry reported in figure 48C of Li/DEGDME-LiTFSI $\text{LiNO}_3/\text{S-MWCNTs}$ cell, at 2.5 V vs Li^+/Li during charge involving 2 electrons (red line), 2.4 V vs Li^+/Li during discharge involving 1 electron (yellow line) and 1.9 V vs Li^+/Li during discharge involving 1 electron (green line)

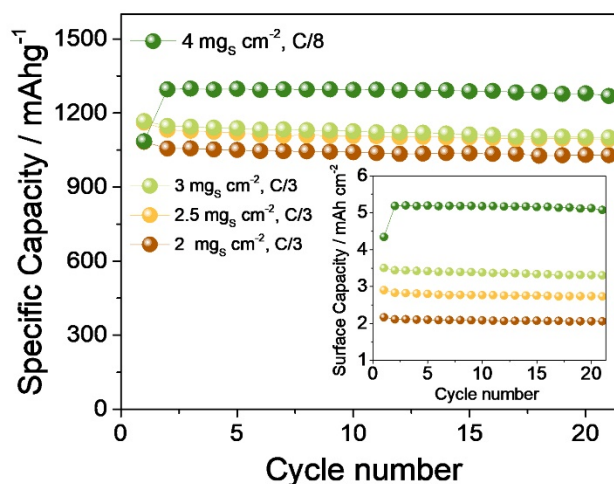
agreement with the impedance decrease observed in Figure 48B.

Tuning the sulfur loading

An important parameter affecting the cell performance, particularly during galvanostatic cycling, is represented by the sulfur loading of the electrode.¹⁵³ Fig. 50 reports the cycling trends of the Li/DEGDME-LiTFSI $\text{LiNO}_3/\text{S-MWCNTs}$ cells with a sulfur content increasing from 2 to $4\ \text{mg cm}^{-2}$ in the 1.9 V – 2.8 V range. The voltage profile of Figure 50A shows a capacity of about $1100\ \text{mAh g}^{-1}$ (66% of the theoretical value) for the cell with sulfur loading of $2\ \text{mg cm}^{-2}$ at C/3 rate, which increases at the same c-rate to about $1200\ \text{mAh g}^{-1}$ (72% of the theoretical value) for the cells using electrodes with a sulfur loading of 2.5 and $3\ \text{mg cm}^{-2}$, most likely due to an optimal ratio between MWCNTs and S promoting efficient lithium ions conduction.¹³⁷ It is worth mentioning that the cell with sulfur loading of $4\ \text{mg cm}^{-2}$ requires a lower C-rate (C/8 instead of C/3) for allowing suitable operation with a capacity of $1300\ \text{mAh g}^{-1}$ (78% of



A



B

Figure 50 (A) Voltage profile and (B) cycling trends of a Li/S 2032-coin cells using the DEGDME-LiTFSI-LiNO₃ electrolyte and S-MWCNTs electrodes with increasing sulfur loading. The cycling rate is C/3 for the cells with sulfur loading of 2, 2.5 and 3 mg cm⁻², and C/8 for the cell with sulfur loading of 4 mg cm⁻² (1C = 1675 mA g⁻¹). Voltage limits 1.9 V - 2.8 V. Temperature 23°C. The figure inset shows the corresponding surface capacity (mAh cm⁻²) calculated with respect to the geometric area of the electrodes.

the theoretical value), due to excessive polarization at the higher C-rates. Indeed, 1C current remarkably increases from 3.4 mA cm⁻² for electrode loading of 2 mg cm⁻² to about 7 mA cm⁻² for electrode loading of 4 mg cm⁻², which may actually lead to cell polarization due to several factors, including insufficient electrode and electrolyte conductivity.¹⁵⁴ Despite the lower c-rate, the cycling tests in Figure 50B and inset evidence a remarkable in-

crease of the practical capacity, i.e., the value normalized by the electrode geometric area, from 2, 3 and 3.5 mAh cm⁻² for the cell employing a sulfur loading of 2, 2.5 and 3 mg cm⁻², respectively, to 5.3 mAh cm⁻² for the cell using a sulfur loading of 4 mg cm⁻², which represents a very suitable characteristic for the employment of the materials in scaled-up lithium-sulfur cell.

Galvanostatic performances

The cycling ability of the Li/DEGDME-LiTFSI LiNO₃/S-MWCNTs cell is evaluated by galvanostatic cycling performed at various currents as well as at a constant c-rate, using an electrode with a sulfur loading of about 3 mg cm⁻² (Figure 51). The cycling trend (Figure 51A) and voltage profiles (Figure 51B) of the rate capability test performed by increasing the current within 1.9 V and 2.8 V reveal a remarkable performance, with a delivered capacity ranging from 1200 mAh g⁻¹ at C/10 to about 850 mAh g⁻¹ at C/2 (1C = 1675 mA g⁻¹), and limited charge/discharge polarization. At the higher c-rate (1C), the figure evidences a continuous increase of the capacity from 350 to about 500 mAh g⁻¹, and an initially high polarization subsequently decreasing by the 3 cycles of the test. This behavior may be justified by the cell resistance decrease and the Li⁺-diffusion coefficient increase upon cycling, already observed in Figure 48 by EIS and CV, respectively. The cycling test performed at a constant rate of C/3 reported in Figure 51C, and the corresponding voltage profiles in Figure 51D, show an initial capacity of about 1100 mAh g⁻¹ delivered with an efficiency approaching 100% and very low polarization. The figure evidences a capacity decrease and a final stabilization at about 900 mAh g⁻¹ over 120 cycles, as

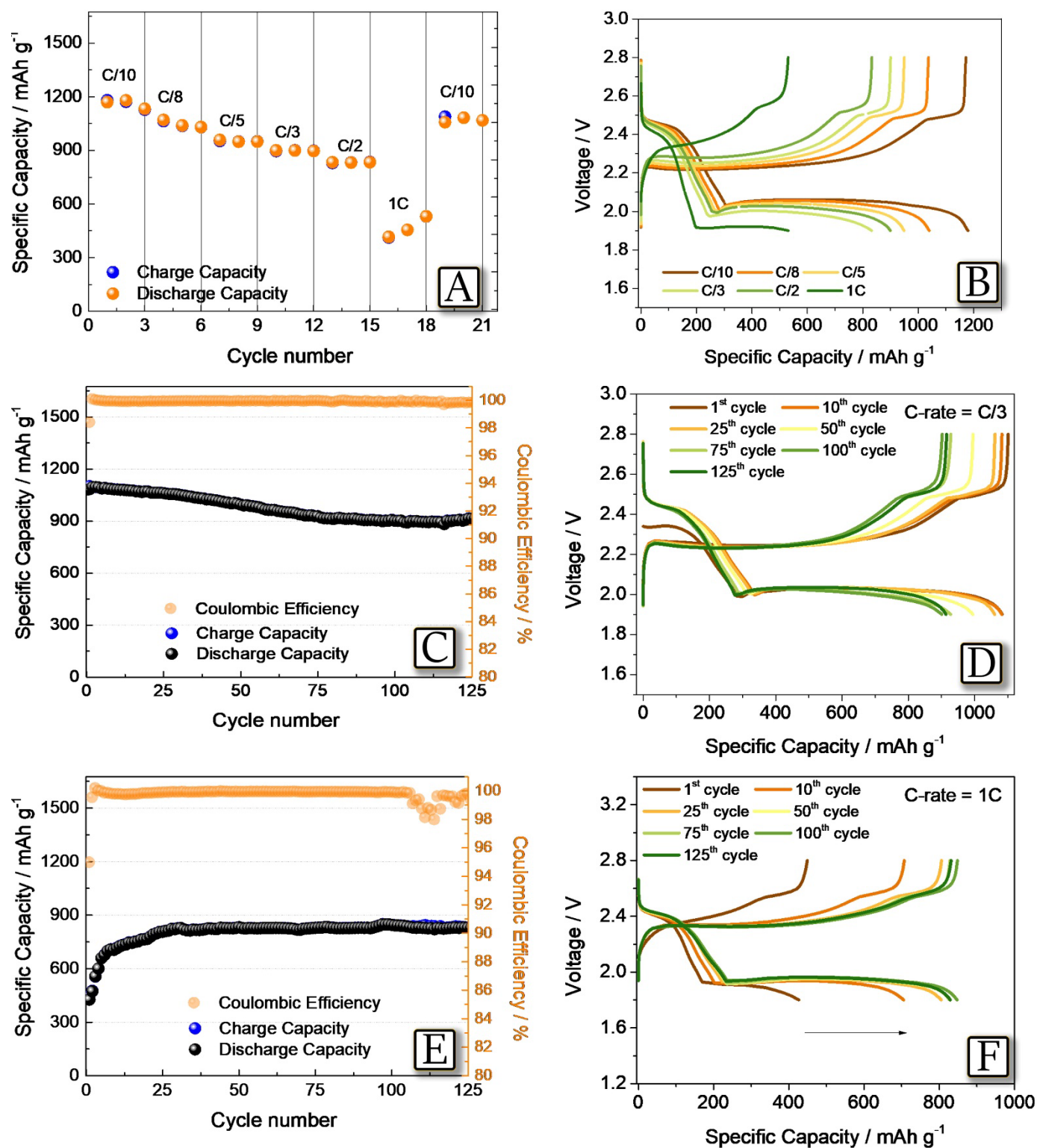


Figure 51(A) Rate capability cycling behavior performed at C/10, C/8, C/5, C/3, C/2 and 1C ($1\text{C} = 1675\text{ mA g}^{-1}$), and (B) corresponding voltage profiles of a Li/S 2032-coin cell using the DEGDME-LiTFSI- LiNO_3 electrolyte and S-MWCNTs electrode. Prolonged cycling behavior and voltage profile of selected cycles of a Li/S 2032-coin cell using the DEGDME-LiTFSI- LiNO_3 electrolyte and S-MWCNTs electrode at a c-rate of C/3 (C, D) and 1C (E, F), respectively. Sulfur loading 3 mg cm^{-2} . Voltage limits $1.9\text{ V} - 2.8\text{ V}$ at C/3 and $1.8\text{ V} - 2.8\text{ V}$ at 1C. Temperature 23°C .

most likely due to slight electrode dissolution already observed by the CV test in Figure 48A. Interestingly, the cycling test at 1C reported in figure 51E reveals the electrode activation mentioned during the discussion of the rate capability test, with a

capacity increasing by the initial 25 cycles from 350 mAh g^{-1} to the remarkable value 890 mAh g^{-1} , which remains very stable over the whole test. A further proof of the reduction of the cell resistance by cycling is given by the voltage profiles of the

same cell reported in Figure 51F, which show a notable decrease of the cell polarization from the first to the last cycle of the test which is in line with the EIS measurement observed in Figure 48B.

Optimizing the Li/S overview

A DEGDME-LiTFSI electrolyte with added LiNO_3 is proposed as suitable solution for use in efficient and high-performance Li/S cell, in combination with an electrode formed by combining sulfur and MWCNTs. The battery exploits suitable characteristics of the electrolyte such as high conductivity (of about of $10^{-2} \text{ S cm}^{-1}$), low ion association degree, an apparent lithium transport number of 0.5, as well as a relevant chemical and electrochemical stability. Furthermore, an optimized morphology of the electrode, consisting of spherical shape particles in which the MWCNTs shell coats the sulfur core, and the use of a suitable carbon cloth as the support, allow the cell to achieve a maximum capacity of 1300 mAh g^{-1} using a loading as high as 4 mg cm^{-2} , which is reflected into a practical areal capacity higher than 5 mAh cm^{-2} . Interestingly, the electrode material shows an increase of the lithium diffusion coefficient from $3.7 \cdot 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ to $7.3 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ by lithiation process, as revealed by CV at various scan rates, which leads to a remarkable decrease of the cell resistance measured by EIS. This phenomenon is particularly relevant for cells cycling at the higher c-rates (1C) which undergo an activation process characterized an increase of the delivered capacity and a decrease of the polarization. Hence, the Li/S cell herein studied

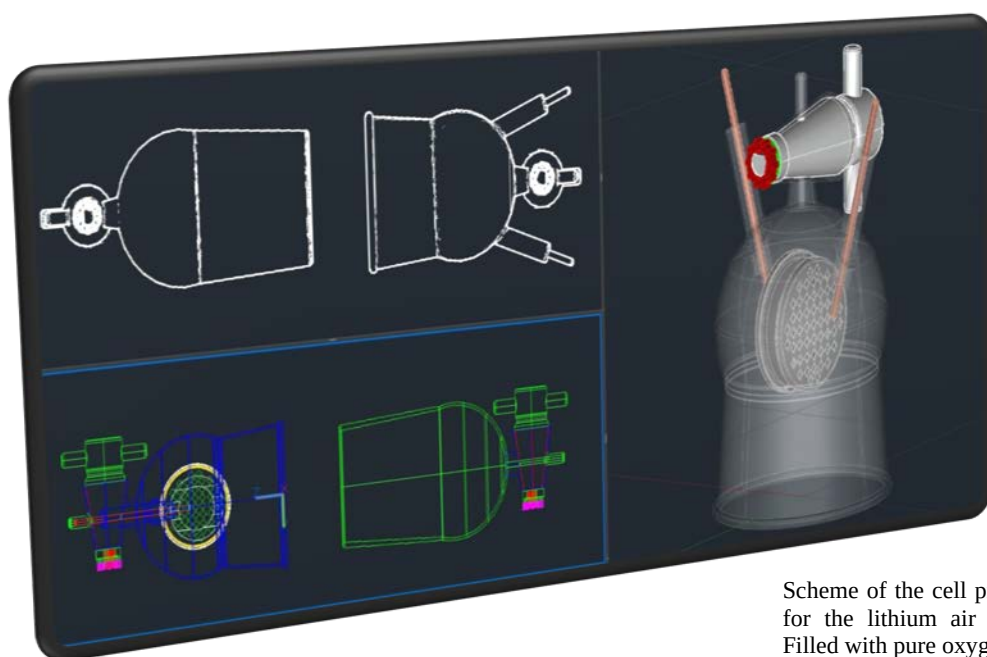
delivers a specific capacity exceeding 900 mAh g^{-1} with a coulombic efficiency approaching 100% for over 120 cycles. Considering a working voltage of 2 V and the above capacity, we may calculate for the battery a theoretical energy density of 1800 Wh kg^{-1} which may be reflected into a practical energy over 400 Wh kg^{-1} , i.e., a value much higher than that of the 200 Wh kg^{-1} ascribed to the most diffused commercial lithium ion battery.³ This characteristic, the relevant safety content of the electrolyte and the low expected cost of the employed materials suggest the cell as a high energy storage system for next generation applications, such as EVs.



Scheme of the 2032-coin cell.
Pink cathode, azure separator and green anode.

Glymes, Prospect & Future

Lithium battery application has consistently broadened over the last few decades and nowadays ranges from advanced portable electronics to electrified transport and smart energy grids. The acceptance and deployment of this appealing energy storage system on a global scale presently require a breakthrough in performance, improved safety and relevant environmental compatibility.¹⁵⁵ In this scenario the exploitation of new systems such as the use of polymer or solid electrolytes to enhance the safety level of the cell, the use of sodium instead lithium to overcome the limitation of lithium resources in our planet or the optimization of the lithium-air battery to obtain high energy system are required. The ether based electrolytes, as previously described, revealed promising characteristics in terms of ionic conductivity, transport properties and stability with lithium metal. Moreover, they are suitable for a wide range of systems, reflecting in the most convincing solution to forward the major challenge of the recent years. Therefore, the further paragraphs will discuss the use of glyme electrolytes in innovative systems. Will be presented a safety and high energy battery configuration, by coupling sulfur cathodes and ether based polymer electrolyte, to avoid lithium dendrite formation¹⁵⁶ and overcome the lithium shuttle effect. Furthermore, an alternative sulfur cathode performed by Li_2S and PEO is deeply investigated by EIS and the performances are discussed in lithium metal cell with DOL:DME-LiTriflate- LiNO_3 electrolyte. An innovative environmental friendly prototype adopting sodium instead lithium will be proposed employing sulfur-carbon composite cathode material and focusing on the characterization of the glyme electrolytes behavior coupled with sodium salt. Finally, lithium air battery with glyme electrolyte exploiting outstanding performances will be discuss. The results underline the suitability of these new generation of electrolytes as valid candidate for the new generation of energy storage devices



Scheme of the cell prototype used for the lithium air battery tests. Filled with pure oxygen. The holes on the coin cell allow the oxygen reactions on the cathode surface

Lithium-Sulfur Cell with Polyethylene Oxide (PEO) Solid Electrolyte

Polymer configuration, mainly basing on polyethylene oxide (PEO) in which lithium salts are dissolved, may have additional bonuses such as an increased safety content due to the absence of volatile components and a limited cost³⁶. Taking in mind these aspects, in particular safety and cost, following is presented a polymer cell using high energy lithium metal anode, sulfur carbon composite cathode and polyethylene oxide (PEO)-lithium trifluoromethanesulfonate (LiCF_3SO_3) electrolyte. The limited cost of the raw materials, i.e., S and PEO, as well as the very simple synthetic procedures involving planetary ball milling (S-C cathode) and solvent casting (PEO-based electrolyte), are expected to reflect into remarkable reduction of the economical-impact of the proposed battery. Furthermore, the high energy of the Li/S cell and safety of the polymer configuration represent additional bonuses of the system. The thermal properties of the membrane are determined by differential scanning calorimetry (DSC), while its suitability for application in lithium battery is verified by checking the interface stability within static condition and under current flow by

meaning of electrochemical impedance spectroscopy (EIS). The conductivity measurement has shown values approaching $10^{-3} \text{ S cm}^{-1}$ above 80°C that is considered the proper temperature for cell operation. The S-C cathode has been characterized by thermogravimetric analysis (TGA) and scanning electron microscope (SEM) and following verified as the active materials in lithium metal cells at different current rate in a bare glyme-based liquid electrolyte. The S-C material, revealing a maximum capacity as high as 700 mAh g^{-1} in liquid electrolyte, is finally employed within the polymer configuration in a lithium sulfur battery operating at 80°C . The polymer cell, characterized by expected low cost due to the simple preparation techniques, delivers a capacity of 450 mAh g^{-1} at a voltage of about 2V, hence a theoretical energy density of 900 Wh kg^{-1} that may reflect into a high practical value, suitable for advanced energy storage applications.

PEO LiTriflate Properties

Prior to cell application, the suitability of the polymer electrolyte has been investigated in terms of thermal characteristics, ion-conductivity as well as by checking the interphase stability. Fig. 52A, reporting the Arrhenius plots of the PEO-electrolyte, exhibits a conductivity value higher than $10^{-4} \text{ S cm}^{-1}$ only at temperature exceeding $60\text{--}70^\circ\text{C}$. This is in line with the DSC analysis of Fig. 52B that suggests

Experimental part: Electrolyte Preparation

Poly ethylene oxide (PEO) with molecular weight of 600KDa (0.6M) and lithium trifluoromethanesulfonate (lithium triflate, LiCF_3SO_3) from Sigma-Aldrich, were used to prepare electrolyte membrane by solvent casting method. Acetonitrile from Sigma-Aldrich was used as solvent and dried several days under molecular sieves until the water content was under 10 ppm as determined by 831-Karl Fisher Coulometer (METROHM) while lithium triflate was dried at 80°C under vacuum for 2 days. PEO powder, salt and acetonitrile were then mixed to and stirred until homogeneous slurry is obtained. The salt concentration, considered as the molar ratio between the ethylene oxide (EO) oxygen of and the lithium in the salt (LiCF_3SO_3), was O:Li = 20:1. The mixture was cast onto a flat glass plate by Doctor-Blade and dried under vacuum at 80°C for 3 hours. The membranes thus obtained had a thickness of 100 μm and was cut into disks of 18 mm of diameter. All the procedures involved in solid polymer electrolyte preparation were carried out in the Argon filled glove box with oxygen water content lower then 10 ppm. A 1M tetra ethyleneglycol dimethylether-lithium trifluoromethan sulfonate (TEGDME- LiCF_3SO_3) containing 5% w:w of dissolved Li_2S_8 was used as the reference liquid electrolyte for preliminary tests of the cathode material

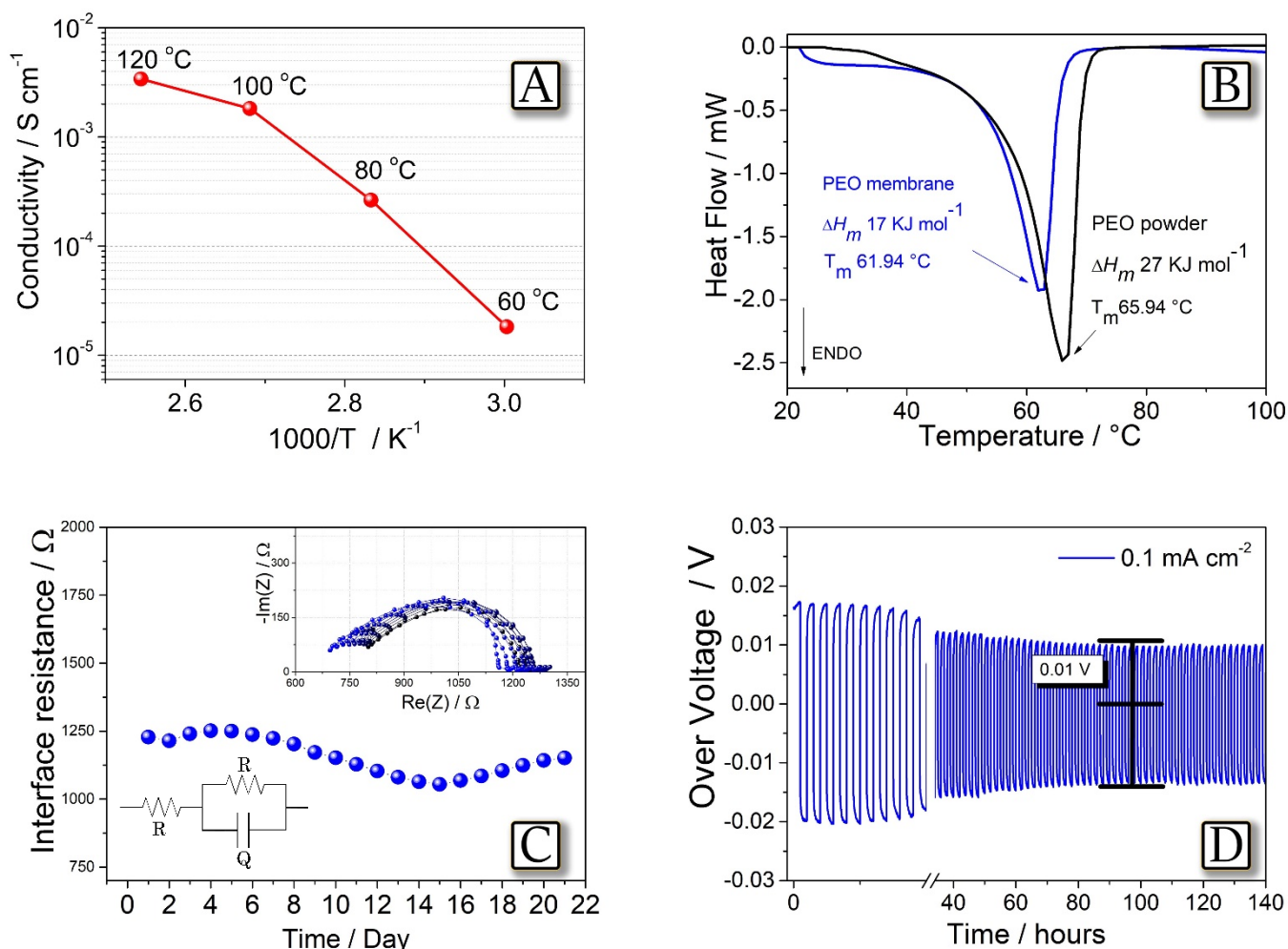


Figure 52 (A) Conductivity Arrhenius plot of the PEO-electrolyte. The impedance spectroscopy was carried out using a signal amplitude of 10 mV in a 1MHz - 0.1Hz frequency range. The data was collected every 10°C, from 60°C to 120°C. (B) Differential scanning calorimetry (DSC) of the PEO-electrolyte in argon atmosphere performed by heating the sample from 20°C to 100°C at 5°C min⁻¹. (C) Time evolution of the lithium interface resistance of the PEO-electrolyte an, in the insert, the corresponding Nyquist impedance plots carried out within 1MHz-0.1 Hz frequency range using 10mV signal amplitude. Temperature 80°C. (D) Over voltage profile of the galvanostatic stripping-deposition test in a symmetric Li/PEO-electrolyte/Li symmetrical cell at the current rate of 0.1 mA cm⁻².

membrane melting around 62°C, i.e., a process allowing ion conduction. Furthermore, the figure evidences that melting process occurs at a lower temperature value in respect to the pure PEO ($T_m = 66^\circ\text{C}$) with a corresponding melting enthalpy (ΔH_m) decreasing from 27 kJ mol⁻¹ to 17 kJ mol⁻¹ by LiCF₃SO₃ salt addition due to its plasticizing effect. Fig. 52C reports the time evolution of the lithium interface resistance in a Li/PEO-electrolyte/Li

symmetrical cell and, in the insert, the corresponding Nyquist impedance plots at 80°C. The measurement shows a slight increase of the cell impedance from 1200 to 1250 Ω upon the first days of measurement due to a solid electrolyte interface (SEI) film formation¹⁵⁷. Upon 22 days of measurement the impedance decreases, slightly fluctuates and finally stabilizes at about 1100 Ω due to initial dissolution, consolidation and final stabilization of the

Experimental part: Cathode Preparation

Elemental sulphur and mesophase micro bead (MCMB) carbon were mixed into 1:1 weight ratio at 130°C under stirring for 3 hours. The mixture was cooled down at room temperature and ground into fine particles by mortar. The powder was then planetary ball-milled for 54 minutes in overall, using milling steps of 5 min and 2 minutes of rest at a speed rate of 300 Rpm. The obtained sulfur-carbon active material was dispersed together with super P carbon (Timcal) and polyvinylidenedifluoride (PVdF) binder in a 80:10:10 weight ratio in N-methylpyrrolidone (NMP) and stirred for 3 hours. The resulting slurry was cast by Doctor-Blade onto aluminum foil and punched as 14-mm disks. The electrodes were dried under vacuum at 50 °C for 24 hours and transferred to Argon filled glove-box for cell assembling.

SEI layer¹⁵⁸. This test, evidencing a good stability of the Li/electrolyte interface, is fully in agreement with the galvanostatic profile of the lithium stripping/deposition test of a cell with the same symmetrical configuration, showing an overvoltage during cycles limited to about 10 mV (Fig. 52D). In summary, these tests suggest the electrolyte well suitable for application in lithium polymer cell at temperature exceeding 70°C.

Cathode- TGA & Morphology

Following electrolyte characterization, the sulfur-carbon composite (S-MCMB) cathode is investigated by thermogravimetric analysis (TGA) under nitrogen and scanning electron microscopy (SEM). The TGA profile (Fig. 53A) reveals an overall sulfur content of about 38% on the electrode film, that is composed by S-MCMB, PVdF binder and SP-carbon conductor, while the corresponding differential profile (in insert) shows sulfur evaporation at 275°C, and PVdF thermal degradation at about 460°C. The remaining mass, of about 55%, corresponds to MCMB, super P and carbon resulting by PVdF degradation. It can be noticed that the S content observed by TGA (38%) slightly differs from that expected by preparation method (i.e., 40%, see experimental section) as mostly ascribed to some sulfur loss during powder preparation by ball milling (S/MCMB 1:1, w:w) or electrode film casting

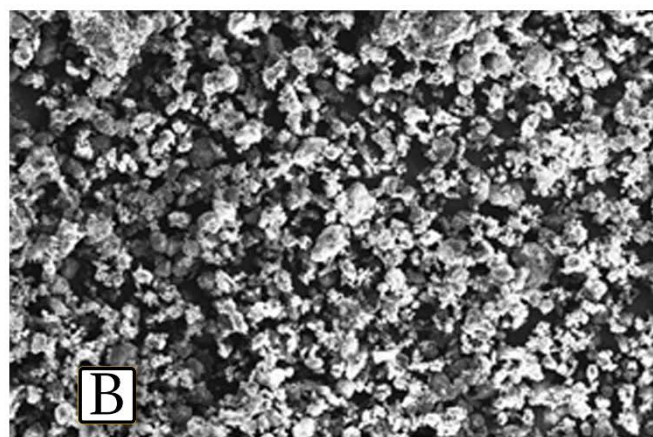
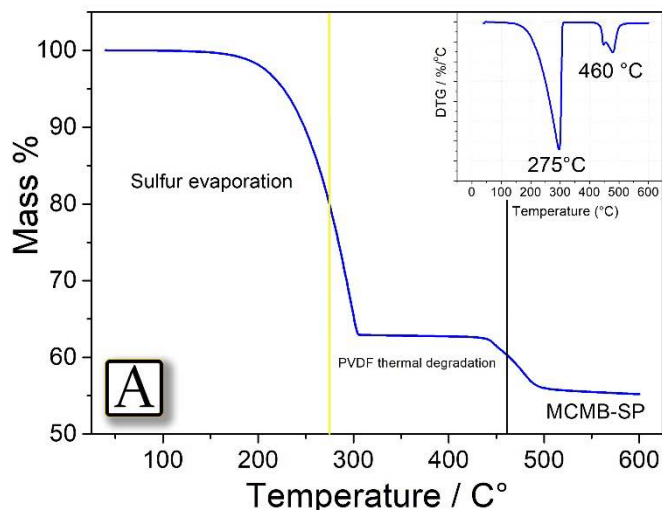


Figure 53 (A) Thermogravimetric analysis (TGA) profile and (B) scanning electron microscopy (SEM) image of sulfur-carbon electrode composed by active material, super P and PVdF (80:10:10 weight ratio). TGA heating rate of 10°C min⁻¹, from 25°C to 600°C in nitrogen atmosphere.

(S-MCMB/PVdF/SP 80:10:10, w:w). Furthermore, the SEM image of Fig. 53B reveals that the electrode surface is characterized by a very uniform distribution of micrometrical particles that is expected to positively reflect the electrode-electrolyte interface in lithium sulfur cell¹⁵⁹.

Experimental part: Electrolyte Characterization

Conductivity tests were performed with 2032 coin cells in a symmetrical stainless steel current collector configuration using a Teflon O-ring separator to keep fixed the cell constant. The electrochemical impedance spectroscopy (EIS) tests were performed by VSP (Biologic), setting the signal amplitude at 10mV and using 0.1 Hz – 1 MHz as frequency range. The temperature range considered for the analyses was from 60° to 120°C collecting data each 20°C. The same instrument and frequency range reported for conductivity study were used for the lithium interface stability study. The latter was carried out in a symmetrical Li/PEO electrolyte/Li 2032-coin cell hold at an operating temperature of 80°C. Nonlinear least-squares (NLLSQ) fit of the impedance Nyquist plots was used to determinate the interface resistance by employing a Boukamp software and R(RQ)_nQ equivalent circuit (R = resistance, Q= constant phase element) as shown in the inset of the figure. In order to ensure high quality, only fitting characterized by a chi-square (χ^2) parameter lower than 10⁻⁴ has been considered²³⁶²³⁸. Differential scanning calorimetry DSC (Mettler Toledo DSC821) was performed by heating up electrolyte sample, sealed in crucibles under argon atmosphere in the Glove-Box, from 20°C to 200°C at 5°C min⁻¹ rate. Thermogravimetric analysis TGA (Mettler Toledo TGA/SDTA851) was performed by heating the sample from room temperature to 600°C at 10°C min⁻¹ rate under nitrogen flow.

Cathode with TEGDME

The S-MCMB electrode has been preliminarily studied in a lithium-sulfur cell using a TEGDME-based electrolyte (see experimental section for details)¹⁶⁰. Fig. 54 shows voltage profiles (A) and the corresponding cycling trend (B) of the above-mentioned cell characterized at a c-rate increasing from C/10 to C/3 (1C = 1676 mA g⁻¹). During the first discharge at C/10 the cell delivers a capacity of about 1000 mAh g⁻¹, i.e., 60% of the theoretical value, that is reversed during following charge into a capacity of about 800 mAh g⁻¹, with a coulombic efficiency of 80%, a working voltage centered at about 2.1V reflecting the Li/S electrochemical process and a limited charge/discharge polarization¹³⁴. The relatively low coulombic efficiency of the first cycle is ascribed to the formation of a solid electrolyte interface (SEI) layer at the electrodes surface during the first discharge that is expected to be more relevant at the lower c-rates¹⁵⁹. During the following cycles (Fig. 54B) the cell delivers a stable capacity of about 750 mAh g⁻¹ with no signs of decay by operation. This trend is considered very promising, particularly in view of the relatively simple method used for S-MCMB electrode preparation and thus the expected modest economic impact of the resulting Li/S. However, at c-rates raising to C/5 and C/3, the cell shows increased polarization (Fig. 54A) and reversible capacity decreasing to about 400 mAh g⁻¹ and 180 mAh g⁻¹, respectively, in addition to some activation with capacity

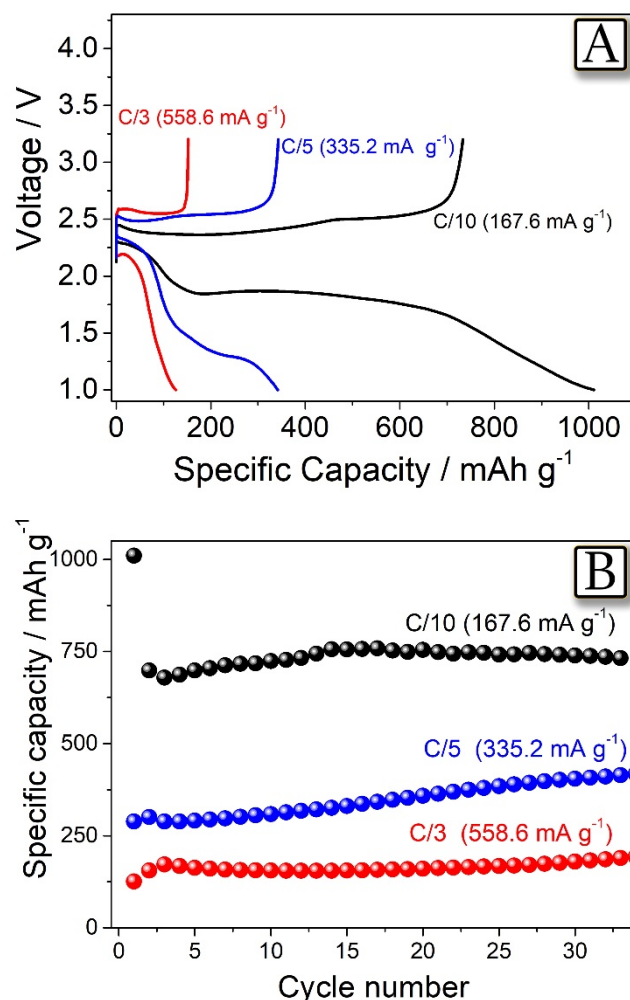


Figure 54 (A) Voltage profiles and (B) corresponding cycling trend of the sulfur-carbon composite electrode in lithium cells using the liquid TEGDME-electrolyte. The current rate varied from C/3 to C/5 and to C/10 (1C = 1676 mA g⁻¹) within a voltage range of 1V-3.2V. Room temperature (80°C)

increase during cycling (Fig. 54B) due to kinetic limits affecting the electrode-electrolyte interface at the higher currents (e.g., C/5)¹⁵⁹.

Cathode with PEO-LiTriflate solid electrolyte

The results of Fig. 54 indicate the S-MCMB electrode as suitable material for application in a lithium sulfur polymer cell in combination with the

Experimental part: Cathode Characterization

Galvanostatic test applying a 0.1 mA cm⁻² current to Li/Li symmetrical cell was carried out to determine the lithium stripping-deposition ability by using a MACCOR Series 4000 Battery Test System (Maccor Inc.). The first screening of S-C composite cathode in lithium cell was performed using a liquid electrolyte (See electrolyte preparation section) within 1V – 3.2V voltage range at room temperature, with a current rate ranging from C/10 (167.6 mA g⁻¹), to C/5 (335.2 mA g⁻¹), and to C/3 (558.6 mA g⁻¹). The galvanostatic cycling of S-C composite cathode in polymer configuration lithium cell was carried out at 80 °C with 1.2V-3V voltage range at a current rate of C/20 (83.85 mA g⁻¹), using a MACCOR Series 4000 Battery Test System (Maccor Inc.). All the galvanostatic tests of the Li-S cells were performed by using a MACCOR Series 4000 Battery Test System (Maccor Inc.).

From S and PEO-Membrane to Li₂S and PEO-Binder

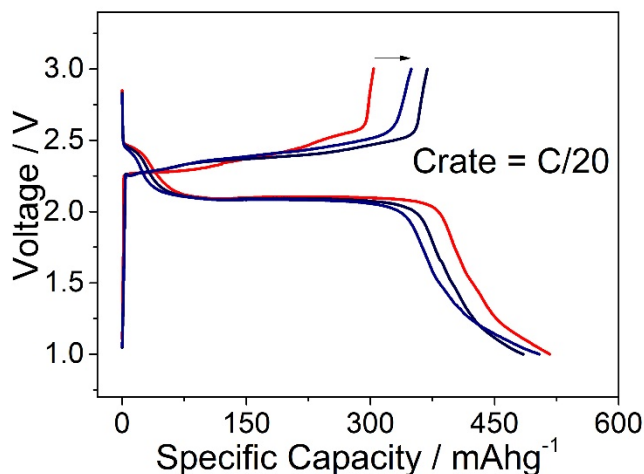


Figure 55 Voltage profile of the lithium polymer cell using the sulfur carbon electrode and the PEO-electrolyte developed in this work, galvanostatically cycled at 80°C within 1.2V and 3V at a current rate of C/20 (83.85 mA g⁻¹).

PEO-electrolyte above characterized (see Fig. 52). Indeed, Figure 55 reports the galvanostatic cycling voltage profile of the Li/PEO-electrolyte/S-MCMB cell carried out at 80 °C in order to ensure suitable electrolyte conductivity and at a current rate of C/20. During the first discharge the cell shows a capacity of about 520 mAh g⁻¹, while the subsequent charge is limited to about 300 mAh g⁻¹, thus resulting in an efficiency limited to about 60%. During the following cycles the efficiency increases and the delivered capacity stabilizes to about 450 mAh g⁻¹. This trend may be ascribed to film formation at the electrodes surface during the first charge-discharge cycle and possible kinetic limits associated with polymer electrolyte-electrode wetting¹³⁶. Furthermore, the cell shows a voltage profile centered at about 2.1V and characterized by remarkably low polarization. The lower capacity of this cell in respect to the one using the liquid electrolyte (compare with Fig. 54) is associated with its polymer nature.

A valid approach in order to obtain higher performance is the use of polymeric binders such as PEO. Indeed, it has been demonstrated to be beneficial for both the Li⁺ diffusivity and for the electrode mechanical stability upon cycling.^{161,162} Furthermore slurry-less, nano Li₂S cathode Graphene Oxide Paper cathode has been recently demonstrated to stably deliver capacities as high as 600 mAh g⁻¹ even at high cycling rates (i.e. 5C), using LiNO₃ and Li₂S⁻ added electrolyte.¹⁶³ Polysulfide dissolution has been physically and chemically limited by confining the Li₂S active particles within carbonaceous and polymeric matrixes¹⁶⁴ and by replacing conventional electrolytes with polymeric, solid state^{165,166} and polysulfide saturated solutions.^{7,167} The Li₂S electrode operates in lithium cell following the electrochemical process characterized by a theoretical specific capacity extending up to 1166 mAh g⁻¹, delivered at about 2.1V with a resulting theoretical energy density as high as 2500 Wh kg⁻¹ as referred to the cathode mass.¹⁶⁸ However, Li₂S suffers from poor electronic and ionic conductivity and consistent volume changes upon cycling that severely limit its cell performances. Moreover, the dissolution within the electrolyte of the polysulfide species, leads to active material loss and shuttle reactions strongly limiting the cell cycle life. A novel Li₂S-C composite electrode, including polyethylene oxide (PEO) binder and a lithium trifluoromethanesulfonate (LiCF₃SO₃) salt in its composition, is here originally reported. The new electrode configuration is expected to enhance the diffusivity

of Li^+ ions within the insulating Li_2S active particles, thus improving the electrode mechanical stability upon cycling and limiting polysulfides dissolution during cell operation. Moreover, the electrode film here disclosed is easily prepared by using Li_2S -C-(PEO)₂₀ LiCF_3SO_3 mixed powders and 1,3 dioxolane (DOL) solvent, that is a further advantage in view of large-scale applications. The cathode is characterized in a lithium metal cell, using bare and LiNO_3 added, 1m LiCF_3SO_3 , DOL:DME electrolyte. A detailed NMR study of the electrolyte diffusion properties demonstrated the full applicability of the solution in advanced lithium battery. Furthermore, the features of the Li_2S electrochemical process, including the highly polarized first cycle and the trend leading to a polarization decrease during following cycles, are studied by combining galvanostatic cycling tests, electrochemical impedance spectroscopy and ex-situ XRD measurements. The proposed electrode/electrolyte formulation, employing economically and environmentally sustainable materials, is herein suggested as a suitable candidate for application in enhanced energy density and environmentally friendly batteries.

The Li_2S -C-PEO electrode

A Li_2S -C-(PEO)₂₀ LiCF_3SO_3 composite electrode (Li_2S -C-PEO) easily prepared by doctor-blade

casting a dispersion of soft milled (PEO)₂₀ LiCF_3SO_3 - Li_2S - Super P carbon mixture in 1,3 dioxolane (DOL) in Ar filled glove box. Polyethylene oxide (PEO) is to date one of the most used binder materials in sulfur and Li_2S -based electrodes.¹⁵⁵ PEO is employed as ionic conductor in the composite electrode in order to ensure intimate contact between the insulating Li_2S active materials and the carbonaceous electronic conductors. Moreover, this binder provides a connection between the electrode components and the current collector upon cycling. Chain entangled PEO binder provides a conductive network for Li^+ diffusion within the electrode and ensures electrode integrity upon cycling by minimizing Li_2S or S phase segregation and stabilizing the carbon network. As reported in literature,¹⁶¹ high viscosity PEO binder may reasonably suppress active material loss upon cycling and reduce the dissolution rate of polysulfides within the electrode-electrolyte interphase, thus enhancing the electrode cycling efficiency and stability.¹⁶⁹ Furthermore, the use of PEO binders enhances the electrode mechanical properties in terms of homogeneity and surface porosity, which translate into high electrode kinetics. Super P carbon is employed as conductive agent within the insulating Li_2S active particles.¹⁷⁰

Experimental part: *Cathode and Electrolyte Preparation*

Dry Polyethylene Oxide (PEO, Mw 600000 Da, Sigma Aldrich), LiCF_3SO_3 (>99.9% Sigma Aldrich), in a EO: LiCF_3SO_3 molecular ratio of 20:1 ($\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$), Li_2S (>99.9% Sigma Aldrich) and Super P carbon (Timcal) powders were mixed under Ar atmosphere in a $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$: Li_2S :Super P weight ratio of 30:35:35. The mixture was subjected to soft, glass-ball milling under Argon atmosphere for 24 hours. The cathode, hereafter referred to as Li_2S -C-PEO was prepared by doctor-blade casting on Al foil a slurry obtained by dispersing the soft milled ($\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$ - Li_2S - Super P carbon mixture in 1,3 dioxolane (DOL, Sigma Aldrich) in Ar filled glove box. The electrode mass loading was 1.5 mg cm^{-2} . The electrolyte solutions were prepared by dispersing LiCF_3SO_3 (>99.9% Sigma Aldrich) powder in a 1:1 wt mixture of 1,3 dioxolane (DOL, Sigma Aldrich), 1,2 dimethoxyethane (DME, Sigma Aldrich), with 1 mol/kg (1m) triflate concentration. LiNO_3 additive (1m) was subsequently added to the solution. 1-2 dimethoxyethane (DME Sigma Aldrich) and 1,3-dioxolane (DOL, Sigma Aldrich) herein reported as DOL-DME were dried under molecular sieves separately until the water content was lower than 10 ppm of water. Karl Fischer titration instrument (Metrohm) to control the water content was used. Before electrolyte preparation, both LiCF_3SO_3 and LiNO_3 salts were dried under vacuum at 100°C .

Structural and morphological study

The morphology of the Li₂S-C-PEO (Figure 56) is probed by scanning electron microscopy (SEM). The micrographs, collected at increasing magnification, evidence the dispersion of Li₂S active material (crystals) within the (PEO)₂₀ LiCF₃SO₃-carbon amorphous matrix. The figure reveals the formation of micrometric Li₂S aggregates exhibiting a characteristic high active surface and lamellar morphology. The good dispersion of the insulating Li₂S active material within carbon and binder is expected to enhance the electrode electronic conductivity and Li⁺ diffusivity, and to improve the mechanical stability by buffering the electrode structural changes upon charge and discharge.

DOL-DME-LiF₃SO₃ Properties

The DOL-DME-LiF₃SO₃ electrolyte suitability for application in battery has been investigated by NMR. Accordingly, Figure 57 reports the characteristics of the electrolyte in terms of self-diffusion coefficient (A), lithium transference number (B),

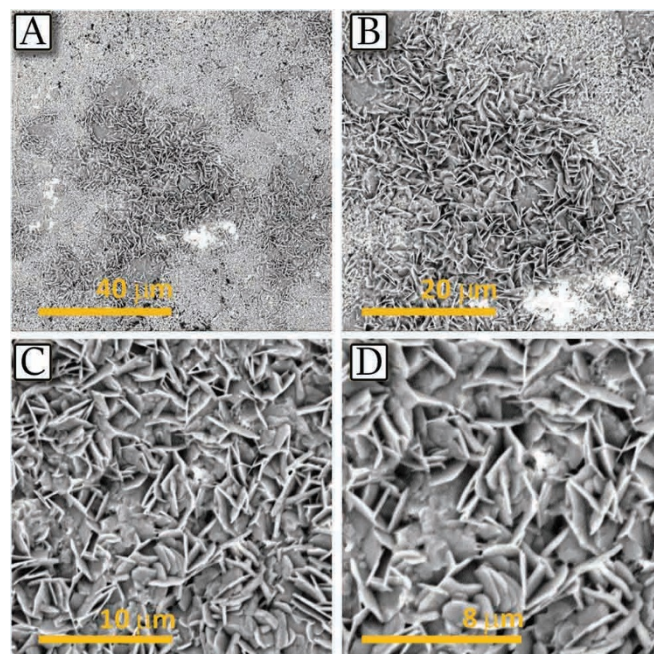


Figure 56 SEM micrographs of the pristine Li₂S-C-PEO electrode.

conductivity (C) and ionic association degree (D), obtained at various temperatures. Fig. 57A reveals a diffusivity of the Li⁺ cation and CF₃SO₃⁻ anion of about 10⁻⁹ m² s⁻¹ while, at the same conditions, the DOL and DME solvents show a higher mobility, i.e., of about 3×10⁻⁹ m² s⁻¹, most reasonably due to the hindrance effect of the solvation shell. Moreover, Fig. 57A shows lower self-diffusion coefficient for DME compared to DOL, thus suggesting a higher interaction of the DME with the charged species that may be ascribed also to viscosity effects. The lithium transference number reported in

Experimental part: Cathode Characterization

The **electrochemical tests** were performed on coin cells assembled in Ar filled dry box using Celgard separators. The cell were assembled using the Li₂S-C-PEO cathode and a 1 m LiCF₃SO₃, DOL:DME 1:1 v/v electrolyte, to which 1 m LiNO₃ was added as a film-forming agent, in order to avoid shuttle reaction (evidenced by a cycling test performed by using a LiNO₃-free electrolyte). About 30 μl of electrolyte solution were used for the cell assembly. A Maccor Series 4000 Battery Test System was used for the **galvanostatic cycling** tests, within the voltage limits 1.4–3.7 V and 1.9–2.7 V during the first and subsequent cycles, respectively, at a C/5 C-rate (1C = 1166 mA g⁻¹). **Electrochemical Impedance Spectroscopy (EIS)** tests were performed by applying 10mV AC amplitude signal to the cells within the 1MHz – 0.1 Hz frequency range. The equivalent circuit (shown in the figure inset) used for the analysis of the impedance data is R_e(RQ)_{PF}(R_{CT}Q_{DL})Q, where R_e is the electrolyte resistance, the (RQ)_{PF} elements are associated to the passivation of the electrode surface, R_{CT} and Q_{DL} describe the charge transfer and double layer capacitance associated to the cathode lithiation/delithiation, respectively, and Q is related to Li⁺ diffusion within the electrode. A VSP (Biologic) was used for the EIS measurements upon cycling. The EIS responses were analysed by using the Boukamp program. All the electrochemical tests were run at 40°C. **Ex-situ XRD** measurements were performed on the electrode at different stages of charge/discharge by using a Rigaku D-Max Ultima + diffractometer, with Cu Kα source and a graphite monochromator, in 2θ/θ scanning mode. The electrodes were collected from the cell in Ar-filled glove box, washed with DME, and sealed in plastic-bags into the XRD-sample holder in order to avoid the change of the electrode structure by contact with air. The electrode morphology was investigated by means of **Scanning Electron Microscopy**, using a Phenom-FEI instrument. The electrode was then transferred into the instrument under argon, and subjected to fast vacuum upon introduction into SEM-sample holder, in order to avoid excessive contact with atmosphere.

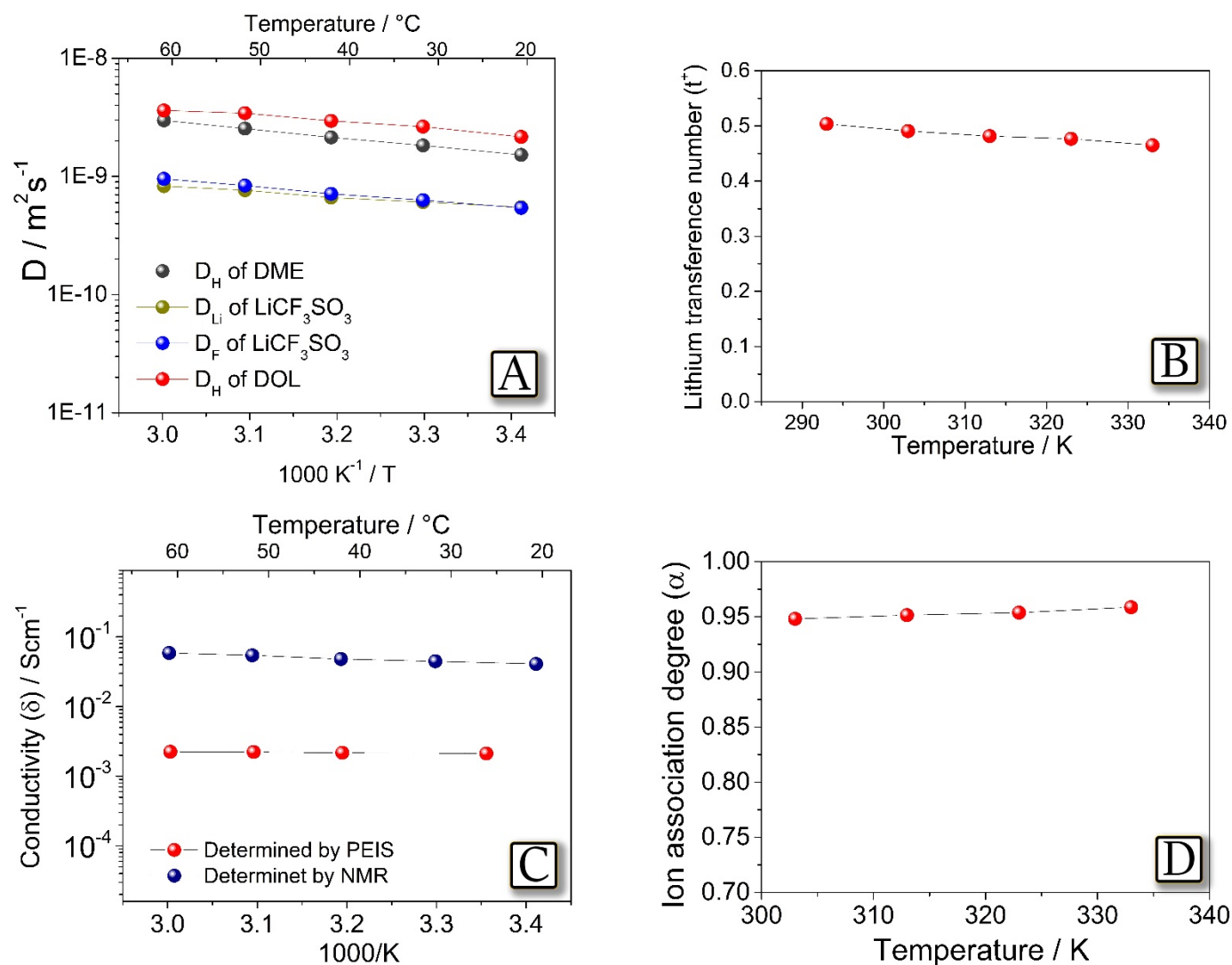


Figure 57 Self-diffusion coefficient (A), transference number (B), conductivity (C) and ionic association (d) of 1m LiCF₃SO₃, DOL:DME 1:1 v liquid electrolyte at increasing temperatures as determined by NMR measurements (see experimental section for details). Temperature range: 293 K - 333 K.

Fig. 57B (calculated following equation (6)) shows a value of about 0.5, sufficiently high for battery application, in the whole investigated temperature range. Fig. 57C displays the conductivity values calculated by using the self-diffusion coefficients (following the Nernst-Einstein equation (4)) and, for comparison, the values measured by electrochemical impedance spectroscopy. The conductivities determined by the two techniques exhibit similar trend, a value higher than 10⁻³ S cm⁻¹ in the explored temperature range, however, with a different order of magnitude. This discrepancy is attributed to a substantial difference between the two techniques already discussed in the previous chap-

ters. Accordingly, the ion association degree (α) determined by the comparison of the conductivity values determined using EIS and NMR, following equation (5), results of about 0.95 (Fig. 57D).

Lithium metal passivation by LiNO₃-addition to the electrolyte

Despite the full suitability of the DOL:DME-LiCF₃SO₃ for battery in terms of ion transport properties and conductivity, as previously described, that sulfur electrode suffers by severe shuttle effect in this electrolyte that may be prevented only by adding a sacrificial film forming agent, i.e.,

LiNO₃. This issue affects also the cell using the electrode here prepared, as indeed demonstrated by Figure 58, reporting in comparison the voltage profile of the first galvanostatic charge-discharge cycle of the Li₂S-C-PEO cathode in lithium half-cell using LiNO₃-free (red line) and LiNO₃-added (black line) electrolytes. The figure evidences for the cell using LiNO₃-free electrolyte (red line) the typical profile of Li/S process affected by severe shuttle reaction resulting in a noisy, decomposition-like charge and very limited discharge. Instead, the cell using the LiNO₃-added electrolyte (black line) reveals the charge-discharge curve typically observed during the first cycle of Li₂S electrode in lithium cells using liquid electrolyte,¹⁷¹ with reversible capacity of about 1000 mAh g⁻¹, without significant signs of shuttle reaction.

Characteristics of the electrochemical process of Li₂S-C-PEO electrode

Further insights into the Li₂S-C-PEO electrochemical process using the selected, LiNO₃-added electrolyte are given by combining cycling test, X-Ray Diffraction (XRD) and Electrochemical Impedance Spectroscopy (EIS) measurements, displayed in Figures 59A, B and 4C-H, respectively. The first de-lithiation step of the Li₂S-C-PEO cathode (dark-

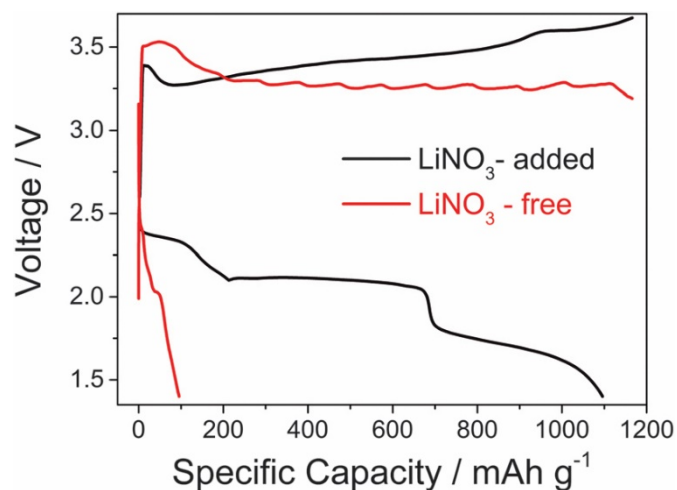


Figure 58 Voltage profile of the first galvanostatic charge-discharge cycle of the Li₂S-C-PEO cathode in lithium half-cell, cycled at C/5 (1C=1166 mA g⁻¹ referred to Li₂S mass) using LiNO₃-free (red line) and LiNO₃-added (black line), 1 m LiCF₃SO₃, DOL:DME 1:1v electrolyte. Voltage range 1.4 V – 3.7 V. Temperature: 40°C. The specific capacity.

red line in Fig. 59A) proceeds by an activation process characterized by high polarization extending up to about 3.5 V that is ascribed to the Li₂-xS polysulfide phase nucleation, according to the reaction: $\text{Li}_2\text{S} \rightarrow \text{Li}_{2-x}\text{S} + x\text{Li}^+ + x\text{e}^-$. The barrier extension is not only due to the high charge transfer activation energy of the lithium at the Li₂S surface, but also to contributions from other kinetic factors, including limited Li-ion diffusivity and low electronic conductivity of the electrode.¹⁷¹ The series of sequential steps between 3.27V and 3.5V during first charge are ascribed to the formation of short chain (Li_2S_y , $2 \leq y \leq 4$) and long chain (Li_2S_y , $4 \leq y \leq 8$) polysulfide intermediates.^{72,172}

Experimental part: Electrolyte Characterization

A Bruker 400 Avance III NMR spectrometer was used to measure self-diffusion coefficients with a pulse field gradient double-stimulated echo sequence. The data were acquired each 10°C from 20 to 60 C°, using a diffusion delay of 80-250 ms between the gradient pulses of strength of 0-45 G/cm and duration of 1-2.5 ms. The Nernst-Einstein equation (4) was used to calculate conductivity values from the self-diffusion coefficient following indicated by. $\delta_{\text{NMR}} = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3})$

where F is the Faraday constant (96485 Coulomb), [C] represents the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature value, D_{Li} and D_{CF₃SO₃} are the self-diffusion coefficients of the Li⁺ cation and CF₃SO₃⁻ anion, respectively. The electrochemical impedance spectroscopy to obtain conductivity values of the electrolyte was carried out in a 2032 coin cell, stainless steel current collectors and a Teflon ring as a separator were used to keep the cell constant fixed. The measurements were carried out with a signal amplitude of 10 mV in a frequency range from 100 mHz to 100 KHz using a biological VSP instrument. The ion association was calculated following the equation (5): $\alpha = \left(1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}}\right)$

where δ_{EIS} and δ_{NMR} are the conductivity measured by EIS and calculated by equation (1), respectively. The lithium transference number (t^+) was calculated from the equation (6). $t^+ = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3}}$

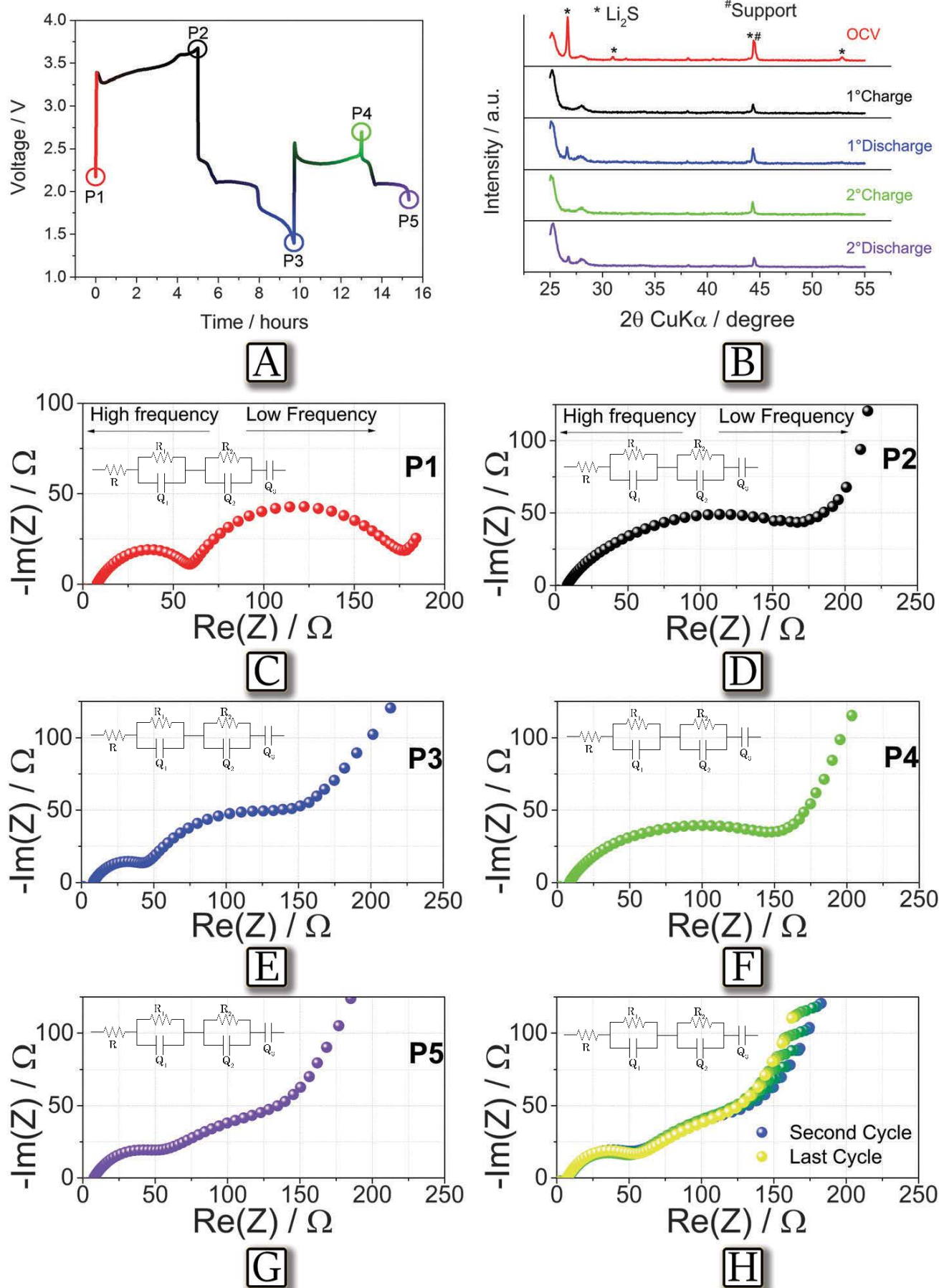


Figure 59 First and second cycles voltage profiles of the Li_2S -C-PEO cathode cycled in lithium half-cell using 1 m LiCF_3SO_3 , 1 m LiNO_3 , DOL:DME 1:1 v electrolyte (A). Corresponding ex-situ electrode XRD patterns (marked by circles in the voltage profile) at various charge and discharge steps (B). Corresponding Nyquist plots of the cell (marked by circles in the voltage profile) at the OCV (C) and after full charge and discharge in the first two cycles (D, F and E, G, respectively). The evolution of the cell EIS response upon 50 cycles (H). Temperature: 40°C. Voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles). Cycling rate C/5 (1C=1166 mA g^{-1} referred to Li_2S mass).

The plateau centered at about 3.6 V in the Li_2S composite cathode voltage signature may be reasonably ascribed to oxidative parasitic reactions of species formed from reductive processes of the LiNO_3 additive in contact with metallic lithium during the cell assembly, i.e. before starting the cycling test. This process represents a chemical reduction of LiNO_3 . Besides, when the cell is discharged up to low voltages (below 1.6 V), the electrochemical reduction of LiNO_3 occurs and a passivation film is formed on the electrode surface which suppresses polysulphides shuttle phenomena. Moreover, the extra capacity gained at voltages higher than 3.5 V may be reasonably ascribed to poor contact between the Li_2S active material and the carbon electronic conductor. The first discharge profile (dark-blue line in Fig. 59A) reveals the two main plateaus centered at about 2.37 and 2.12 V, typical of sulfur lithiation process, as well as an additional plateau between 1.8V and 1.4 V due to the electrochemical reductive decomposition of LiNO_3 additive, precipitation at the lithium surface of the formed species and final consolidation of the passivation film that is expected to enhance the cell Coulombic efficiency.^{7,167} Following the first cycle, the reaction proceeds with very low polarization, thus suggesting a decrease of the resistivity of the active material by the ongoing of the electrochemical process. The evolution of the XRD patterns of the Li_2S -C-PEO electrode performed at different cycling stages of the lithium cell (i.e., corresponding to the circle marks P1-P5 in Fig. 59A) is reported in Fig. 59B. The figure reveals that the characteristic signals of Li_2S phase (JCPDS#772145), centered at about 27, 3, 44 and 53 degrees, disappear upon full charge and then reappear, even if with lower intensity due to electrode

amorphization, after full discharge, thus confirming the reversibility of the Li_2S redox process. The reflection of Li_2S centered at about 44 degrees is not taken into account because of the overlapping electrode current collector signal. Figs. 59(C-G) report the impedance Nyquist plots of the lithium cell using the Li_2S -C-PEO electrode at various states of charge (corresponding to the circle marks P1 to P5 in the voltage profile of Fig. 59A), while Fig. 59H reveals the evolution of the impedance plots of the same cell, collected at the discharged states, during the subsequent cycles (following the two reported in Fig. 59A). It can be noticed that the electrolyte resistance R_e , i.e., the highest frequency intercept of the Nyquist plots in Fig. 59, is about $8\ \Omega$, without significant variation upon cycling. At the OCV (Fig. 59C, corresponding to P1 in the voltage profile of Fig. 59A), two well defined, high and low frequency semi-circles are detectable, corresponding to the formation of a passivation film on the electrode surface and to the charge transfer at the electrode/electrolyte interface, respectively. Upon de-lithiation by charge (Fig. 59D, corresponding to P2), the EIS response shows a broad and depressed semicircle, most likely from convolution of the two semicircles discussed above, while at the fully discharged states (Fig. 59E, corresponding to P3) two distinct semicircles are again detected. Following, Fig. 59F, G and H show the same EIS trend previously illustrated, characterized by two semicircles at the discharged state merged into one during charge. This trend is ascribed to the different electrode kinetics for S (charged state) and Li_2S (discharged state). In particular, the charge transference (represented by the second semicircles) is favored by the presence of S (charged states) compared to the more insulating Li_2S (discharged

state), thus allowing the second, low frequency semicircle to shift to higher frequencies (faster kinetics) and overlap the first semicircle corresponding to the passivation film. The NLLSQ analysis of the impedance responses reported in Table 1 (see experimental section for details) reveals changes, i.e. decrease and increase, of the passivation film resistance and capacitance values upon charge and discharge that can be reasonably associated to progressive dissolution and re-formation with final consolidation of the film. Similar behavior is observed by the charge transfer process, however with a decreasing resistance trend. Indeed, Table 4 shows that the cell has OCV resistance values of about 54Ω and 108Ω , for passivation film (RPF) and charge transfer (RCT), and final values of about 53Ω and 66Ω , respectively. These data indicate a stable SEI film and an enhanced charge transference in subsequent cycles, thus accounting for the decrease of the cell polarization upon charge-discharge process and confirming the optimized electrode configuration. The suitability of the system is further suggested by the Nyquist plots during the first ten cycles reported in Fig. 59H, again suggesting stable electrode kinetics and electrode/electrolyte interface for the Li₂S-C-PEO cathode in lithium cell.

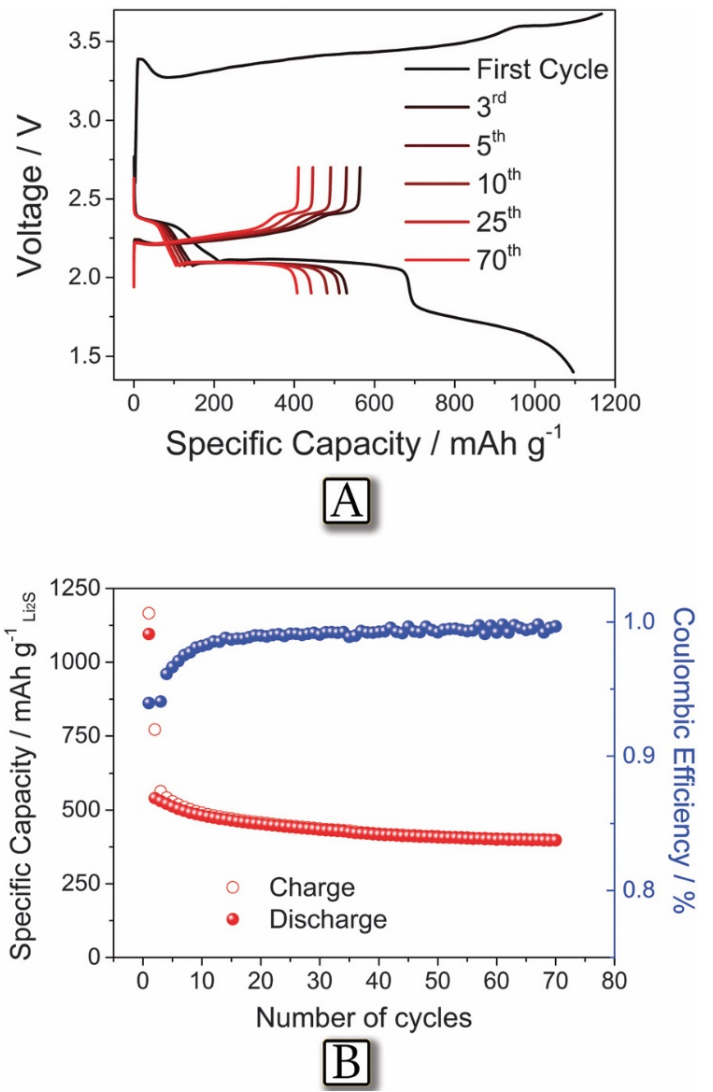


Figure 60 Galvanostatic cycling voltage profiles (A) and specific capacity versus cycle number plot (B) of the Li/1m LiCF₃SO₃, 1m LiNO₃, DOL:DME 1:1 v:v/Li₂S-C-PEO cell. The Coulombic efficiency versus cycle number plot is displayed in blue. Temperature: 40°C. Voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles). Cycling rate C/5 (1C=1166 mA g⁻¹ referred to Li₂S mass)

	R_e/Ω	R_{PF}/Ω	Q_{PF}/F	R_{CT}/Ω	Q_{DL}/F	Q/F
OCV	7.98 ± 0.05	54.13 ± 0.51	$(2.13 \pm 0.1) \times 10^{-5}$	108.17 ± 3.81	$(6.70 \pm 0.27) \times 10^{-4}$	$(7.19 \pm 1.43) \times 10^{-2}$
P1	7.86 ± 0.02	36.61 ± 5.91	$(8.21 \pm 0.27) \times 10^{-5}$	135.51 ± 8.61	$(10.54 \pm 0.03) \times 10^{-4}$	$(2.25 \pm 0.07) \times 10^{-3}$
P2	8.33 ± 0.07	39.49 ± 0.61	$(3.05 \pm 0.2) \times 10^{-5}$	84.44 ± 2.91	$(2.46 \pm 0.14) \times 10^{-4}$	$(3.98 \pm 0.03) \times 10^{-3}$
P3	8.30 ± 0.09	90.29 ± 12.50	$(6.83 \pm 0.38) \times 10^{-5}$	61.09 ± 13.60	$(2.21 \pm 0.3) \times 10^{-4}$	$(2.35 \pm 0.01) \times 10^{-3}$
P4	7.95 ± 0.06	52.62 ± 1.03	$(3.67 \pm 0.15) \times 10^{-5}$	75.41 ± 3.32	$(4.62 \pm 0.27) \times 10^{-4}$	$(2.85 \pm 0.01) \times 10^{-3}$
P5	8.12 ± 0.10	53.52 ± 1.49	$(3.63 \pm 0.27) \times 10^{-5}$	66.21 ± 4.46	$(4.13 \pm 0.43) \times 10^{-4}$	$(2.85 \pm 0.02) \times 10^{-3}$

Table 4 Electrolyte resistance R_e , Passivation film resistance R_{PF} and capacitance Q_{PF} , Charge Transfer resistance R_{CT} , Double Layer capacitance Q_{DL} and Li⁺ diffusion capacitance Q values obtained by NNLSQ fitting of the impedance responses of the lithium cell reported in Figure 59, using the Li₂S-C-PEO electrode at the OCV (P1) and upon the first two charge-discharge cycles (P2-P5)

Cycling performances of $\text{Li}_2\text{S-C-PEO}$ electrode in lithium cell

Figure 60 reports the galvanostatic performances at C/5 rate at 40 °C, in terms of voltage profile (A) and cycling behavior (B), of the lithium cell using the $\text{Li}_2\text{S-C-PEO}$ electrode. The electrode is reversibly charged and discharged to about 70 cycles and shows, after the first activation cycle, two main characteristic redox plateaus at about 2.25 and 2.42 V in charge and at 2.37 and 2.10 V in discharge (Fig. 60A). The voltage hysteresis rapidly decreases from about 1.4 V during the first cycle to a stable value of 0.2 V in the following ones, due to the kinetic improvement upon cycling discussed in Fig. 59. The cell shows specific capacity values ranging from about 550 to about 450 mAh g⁻¹ (referenced to the Li_2S mass) upon 70 cycles (Fig. 60B), with a Coulombic efficiency approaching 99% after the first few stabilization cycles. The slight capacity decay during cycling can be attributed to minor electrode dissolution during charge-discharge process. The operating temperature (40 °C) has been selected as suitable value for proper operation due to optimized characteristics in terms of electrode-electrolyte interface. Indeed, cycling tests conducted, for comparison, at lower temperature, i.e., at 25 °C, and reported in Figure 61, revealed lower capacity of the cell compared to the higher temperature value. Within the proposed cell configurations, some major problems of Li_2S -based batteries, including polysulphides dissolutions, redox shuttle effects, phase segregation and electrode mechanical instability etc., may be controlled and contained, however not completely

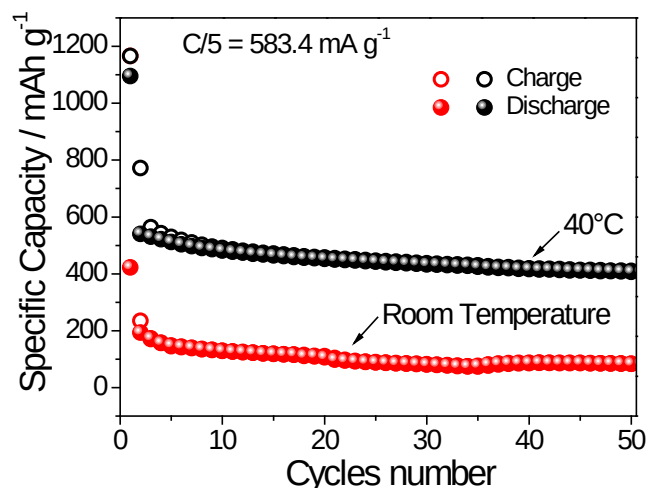


Figure 61 $\text{Li}_2\text{S-C-PEO}_{20}(\text{LiCF}_3\text{SO}_3)$ cathode galvanostatic cycling in lithium half-cell, using LiNO_3 added, 1m LiCF_3SO_3 , DOL:DME (1:1 vol) at 40°C and at room temperature

avoided, using $\text{PEO}_{20}(\text{LiCF}_3\text{SO}_3)$. Further technological optimization of the electrode morphology and surface properties is expected to overcome these issues and to translate into higher cycling performance in terms of efficiency. The specific capacity exhibited by the cathode here presented largely exceeds the ones of conventional LIB cathode materials, such as LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, with the additional advantages of very low cost and reduced environmental impact. The average specific capacity of 470 mAh g⁻¹(Li_2S) delivered by the cathode at about 2.1 V translates into theoretical specific energy content that is significantly higher than that ascribed to the conventional LiCoO_2 electrode. However, the electrode composition here reported, in terms of carbon and binder content, lowers the practical energy to levels comparable to the common battery. This aspect suggests the need for further optimization of the electrode by lowering the carbon and binder contents to enhance the performances of this very promising, low cost system.

Glyme Electrolytes and Sodium

Sodium, because of its ubiquity as the 6th most abundant element in the earth's crust, is readily available at low cost. Therefore, batteries based on this alkali metal appear among the most promising systems in view of a widespread application of grid energy storage from renewable sources, such as solar and wind.^{173–176} Sodium batteries using intercalation materials have been studied alongside lithium batteries during the late 1970s and 1980s.^{177–179} However, the higher energy content of lithium as compared to sodium promoted the rapid development of the lithium-ion systems to the detriment of sodium-ion technologies.^{146,180} The fast development of the lithium-ion battery actually contributed to a rapid rise of the lithium price¹⁸¹, and evidenced possible risk of market dependence in view of the geographical limitation of lithium resources to a few South American countries.¹⁸² These issues renewed the interest in non-lithium energy storage systems and, in particular, on sodium batteries, which are presently attracting a large amount of attention. The energy penalty of sodium with respect to lithium¹⁸³ may be partially mitigated by the use of high energy cathodes, such as sulfur^{22,178,184} which delivers a theoretical capacity of 1700 mAh g⁻¹ and an energy density of 2500 Wh kg⁻¹. This high value

may translate into a practical energy exceeding 300 Wh kg⁻¹, higher than the common lithium-ion battery.^{185–187} However sodium sulfur battery suffers of the same issues previously reported for lithium sulfur system such as the solubility of the polysulfide discharge products in the electrolytes, and slow kinetics. The improving of the electrode morphology by the development of complex sulfur-carbon composites^{188–190} or by designing polysulfide reservoirs in carbon-sulfur composites^{191,192} have been successfully employed in a Na/S cell using a glyme-based electrolyte to improve the system stability.^{52,82,111} Furthermore, solutions of sodium salts in glymes have revealed suitable characteristics allowing their application in sodium and sodium-ion batteries.^{193,194} Therefore, is following reported these aforementioned analytical approaches for the study of two solutions of sodium salt (i.e., NaCF₃SO₃), differing by the glyme used. The solutions, based either on DME or DEGDME, and characterized by NMR and electrochemical techniques, are proposed as suitable media for application in a new sodium sulfur cell. The highest performing cell prototype, using the cathode formed by MWCNTs-sulfur and the solution based on DEGDME, shows a capacity of about 500 mAh g⁻¹, delivered at average working voltage of 1.7V, hence a theoretical energy density of 850 Wh kg⁻¹ and an expected practical energy of interest.

Experimental Section: Electrolyte Preparation

Glyme-based solvents, i.e., 1,2-Dimethoxyethane (CH₃OCH₂CH₂OCH₃) and diethylene glycol dimethyl ether (CH₃OCH₂CH₂)₂O, hence DME and DEG, respectively, were purchased from Sigma Aldrich and dried under molecular sieves (Sigma Aldrich, pores diameter 3 Å) for several days until the water content was lower than 10 ppm. The water content was determined by 889 Karl Fisher Coulometer METROHM. Sodium trifluoromethanesulfonate (sodium triflate, NaCF₃SO₃) and sodium nitrate (NaNO₃), by Aldrich, were dried under vacuum overnight at 80°C. The electrolytes were prepared by dissolving NaCF₃SO₃ either in DME and in DEGDME, in a ratio of 1 mol of salt in 1 kg of solvent. The densities of DME-NaCF₃SO₃ and DEGDME-NaCF₃SO₃ were of 0.984 and 1.068 g/ml. The (1m) molality was selected in order to better compare with previous papers and with literature data, while the glyme/sodium ratios of 1:11 and 1:7.5 for DME and DEGDME, respectively. The same solutions were supplemented with a film forming agent (NaNO₃, 0.4 mol of salt in 1 kg of solvent) for the final test in a sodium cell. The four solutions, i.e., the bare electrolytes (DME-NaCF₃SO₃ and DEGDME-NaCF₃SO₃), and the ones with sodium nitrate (DME-NaCF₃SO₃-NaNO₃ and DEGDME-NaCF₃SO₃-NaNO₃), were prepared and stored in an argon filled glove box with water and oxygen contents lower than 1 ppm.

Sodium Glymes Properties

The thermal characteristics of the electrolyte, in particular evaporation and decomposition features, play a key role for determining its possible application in batteries. Fig. 62 clarifies this aspect by reporting the TGA traces of DME- NaCF_3SO_3 and DEGDME- NaCF_3SO_3 electrolytes performed under nitrogen flow and, in inset, the corresponding differential curves. The figure shows that DME- NaCF_3SO_3 loses weight according to three subsequent steps, centered at 35°C, 102°C and 535°C, due to the fast evaporation of the volatile DME under N_2 flow, partial desolvation of salt-DME complexes, and final degradation of the NaCF_3SO_3 or its solvated crystals, respectively.^{6,195} The DEGDME- NaCF_3SO_3 electrolyte shows weight loss starting at a higher temperature with respect to the DME-based one, and reveals the above mentioned three consecutive steps centered at a 103 °C, 150 °C and 535°C, as most likely due to the lower volatility of DEGDME. Furthermore, the different weight loss ratio at the higher temperatures upon initial solvent evaporation observed for the DME-based electrolyte with respect to the DEGDME-based one suggests salt-solvent complexes and

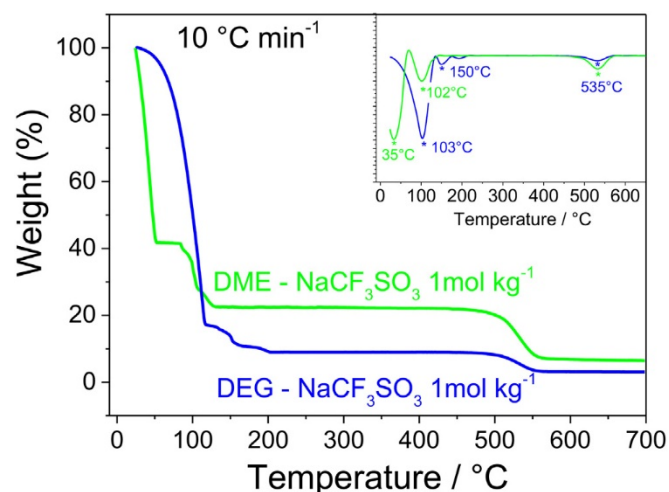


Figure 62 Thermal gravimetric analysis (TGA) of DME- NaCF_3SO_3 (1 mol kg^{-1}) and DEGDME- NaCF_3SO_3 1 mol kg^{-1}) electrolytes, heated under nitrogen flow from 20°C to 700°C. Heating rate 10°C min^{-1} .

solvated salt crystals with a different solvent content, as indeed expected by the different structure of DEG and DME. Concomitant crystallization, evaporation and decomposition of the two electrolytes under nitrogen flow avoids the determination of the stoichiometry by TGA, however the higher residual mass observed for DEGDME based electrolyte with respect to DME may likely reflect a higher content in carbon at the end of the measurement of the less volatile solvent. In summary, the

Experimental Section: Electrolyte Characterization

Thermal gravimetric analysis (TGA) was performed on bare electrolytes by heating the samples under nitrogen flow from 20°C to 700°C at 10°C min^{-1} , using a Mettler Toledo TGA/SDTA85. The **self-diffusion coefficients** of ^1H and ^{19}F nuclei (D_{H} and D_{F} respectively), related to the hydrogen in the glyme chain and the fluorine in the CF_3SO_3^- anion, were measured with a Bruker 400 Avance III NMR spectrometer using a PFG double-stimulated echo sequence to suppress convection effects in the temperature range from 20°C to 60°C. The data were collected every 10°C with gradient pulses of 1-2 ms, a gradient strength g in the range of 1-45 G cm^{-1} , and a diffusion delay Δ of 100-200 ms. The self-diffusion coefficients of ^{23}Na nucleus (D_{Na}) were measured with a Varian 300 WB Direct Drive spectrometer equipped with a DOTY z-gradient probe, using the same double-stimulated echo sequence with gradient pulses of 0.75-1 ms, gradient strength g varied from 2 up to 1000 G cm^{-1} as needed, and a diffusion delay Δ of 12-17 ms. The **electrolyte conductivity** was measured by impedance spectroscopy (δ_{EIS}) in a symmetrical stainless steel/stainless steel, 2032 coin-cell equipped by a Teflon O-ring separator, in a 0.1 Hz – 0.5 MHz frequency range with signal amplitude of 10 mV using a VERSTAT AMETEC instrument. The impedance responses were collected from 40°C to 80°C every 10°C. Ion conduction ratio was calculated from self-diffusion coefficient (δ_{NMR}) by using the Nernst-Einstein equation $\delta_{\text{NMR}} = \frac{F^2[C]}{RT} (D_{\text{Na}} + D_{\text{F}})$ (4), where F is the Faraday constant (96485 Coulomb), $[C]$ represents the solution concentration (mol cm^{-3}), and R is the ideal-gas constant (8.314472 $\text{J K}^{-1} \text{mol}^{-1}$). The **ion association degree** (α) was calculated by combining the conductivity values determined by EIS (δ_{EIS}) and the ion conduction ratio determine by NMR (δ_{NMR}), following the equation $\alpha = \left(1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}}\right)$ (5). The **sodium ion transference number** was calculated by using the equation $t^+ = \frac{D_{\text{Na}}}{D_{\text{Na}} + D_{\text{F}}}$ (6), where D_{Na} is the self-diffusion coefficient of the Na^+ cation and D_{F} is the self-diffusion coefficient of the CF_3SO_3^- anion, as determined by NMR.

thermal analysis of Fig. 62 evidences a lower evaporation degree of DEGDME- NaCF_3SO_3 with respect to DME- NaCF_3SO_3 within the temperature range usually designed for battery application, i.e., at temperatures lower than 100 °C, thus suggesting the former as the preferred electrolyte media. Relevant transport properties of the electrolytes, such as self-diffusion coefficients of the various species, as well as the ion transport number are determined by PFG NMR and reported in Fig. 63. The higher value of the ^1H self-diffusion coefficients with respect to ^{19}F and ^{23}Na evidenced by Fig. 63A suggests for both electrolytes a higher mobility of the solvent molecules with respect to the ions. Furthermore, ^1H , ^{19}F and ^{23}Na self-diffusion coefficients of DME- NaCF_3SO_3 show overall a higher value with respect to the corresponding self-diffusion coefficients of DEGDME- NaCF_3SO_3 electrolyte over the whole temperature range considered. The higher self-diffusion coefficients of the species in the latter electrolyte may be reasonably attributed to the lower viscosity of the DME with respect to DEGDME [37]. Fig. 63B shows the sodium transference number (t^+) of the two electrolytes, calculated by equation (6) taking into account the self-diffusion coefficients of Na^+ and CF_3SO_3^- (represented by D_{Na} and D_{F} taken from Fig. 2a, see experimental section). The figure shows a t^+ value of about 0.5 over the whole temperature range (i.e., about 20-60 °C) for both electrolytes, which is considered a suitable value for application in sodium

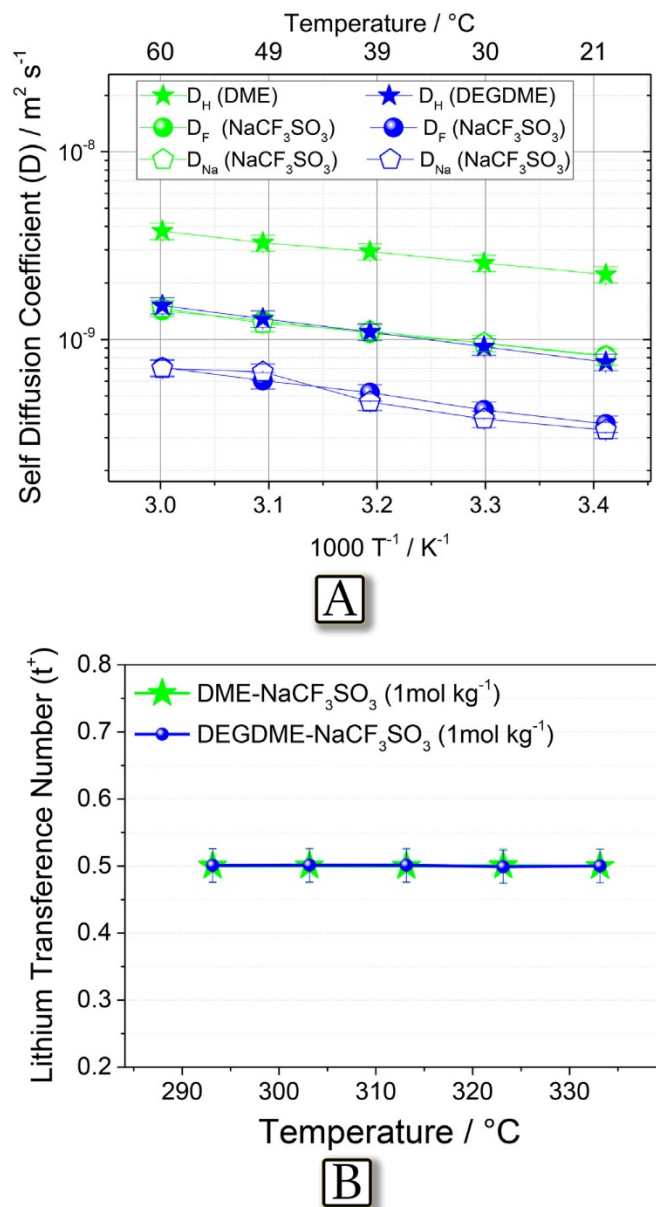


Figure 63 A) Self-diffusion coefficients of ^1H , ^{19}F and ^{23}Na nuclei in DME- NaCF_3SO_3 (1 mol kg^{-1}) and DEGDME- NaCF_3SO_3 (1 mol kg^{-1}) electrolytes determined from 20°C to 60°C by PFG-NMR. B) Sodium transference number (t^+) calculated from self-diffusion coefficients measured by PFG-NMR. Further details are reported in experimental section.

batteries.¹⁹⁶ Therefore, based on the data of Fig. 63 we may consider the two electrolytes possible candidates for battery use.

Experimental Section: Electrolyte Characterization

The cathodic electrochemical stability of the electrolytes was determined by **cyclic voltammetry** (CV) in a three-electrode configuration cell using sodium metal as the reference and counter electrodes, and Super P carbon (Imers) coated on copper as working electrode. The CV was performed using a potential ranging from 2 V to 0 V vs. Na/Na^+ with a scan rate of 0.1 mV sec^{-1} . The anodic electrochemical stability was determined by **linear sweep voltammetry** from 2 V to 5 V vs. Na/Na^+ , using the same cell configuration and scan rate employed for CV, and a Super P carbon (Imers) coated on aluminum as the working electrode. Sodium **stripping/deposition tests** were carried out in a symmetrical sodium/sodium 2032 coin-cell, with a constant current of 0.1 mA cm^{-2} and a step time limit of 1 hour. The chemical stability of the sodium interface in contact with the electrolyte versus time was studied by **impedance spectroscopy** (EIS) in a symmetrical sodium/sodium 2032 coin-cell, in a 0.1 Hz-0.5 MHz frequency range, using a 10 mV signal amplitude.

he combination of NMR and electrochemical measurements reveals very important characteristics of the electrolyte in view of its application in practical cells: ionic conductivity (δ) and anion-cation association degree (α). Fig. 64A shows the conductivity value measured by EIS (δ_{EIS}) and the ion conduction ratio calculated by NMR (δ_{NMR}) according to equation (4). Overall, Fig. 64A evidences practical conductivity (δ_{EIS}) of the order of $10^{-3} \text{ S cm}^{-1}$ for both electrolytes [40], with only minor difference included within the error bar (represented by the symbols). Furthermore, the conductivity values obtained EIS and NMR differ by one order of magnitude, as expected by the different characteristics of the two techniques.¹⁹⁷ Interestingly, DME- NaCF_3SO_3 electrolyte shows higher conductivity as measured by NMR with respect to DEGDME- NaCF_3SO_3 , most likely due to the lower viscosity of the former [40]. We advantageously employ this difference in Fig. 64B to calculate the ion association degree (α) by combining the values of δ_{EIS} and δ_{NMR} obtained from linear fit of the corresponding Arrhenius curves (Fig. 64A) with equation (5) in the experimental section. The ion association degree shows an increasing trend by raising the temperature for both electrolytes, however the DME-based electrolyte exhibits higher ion association with respect to the DEGDME-based one in

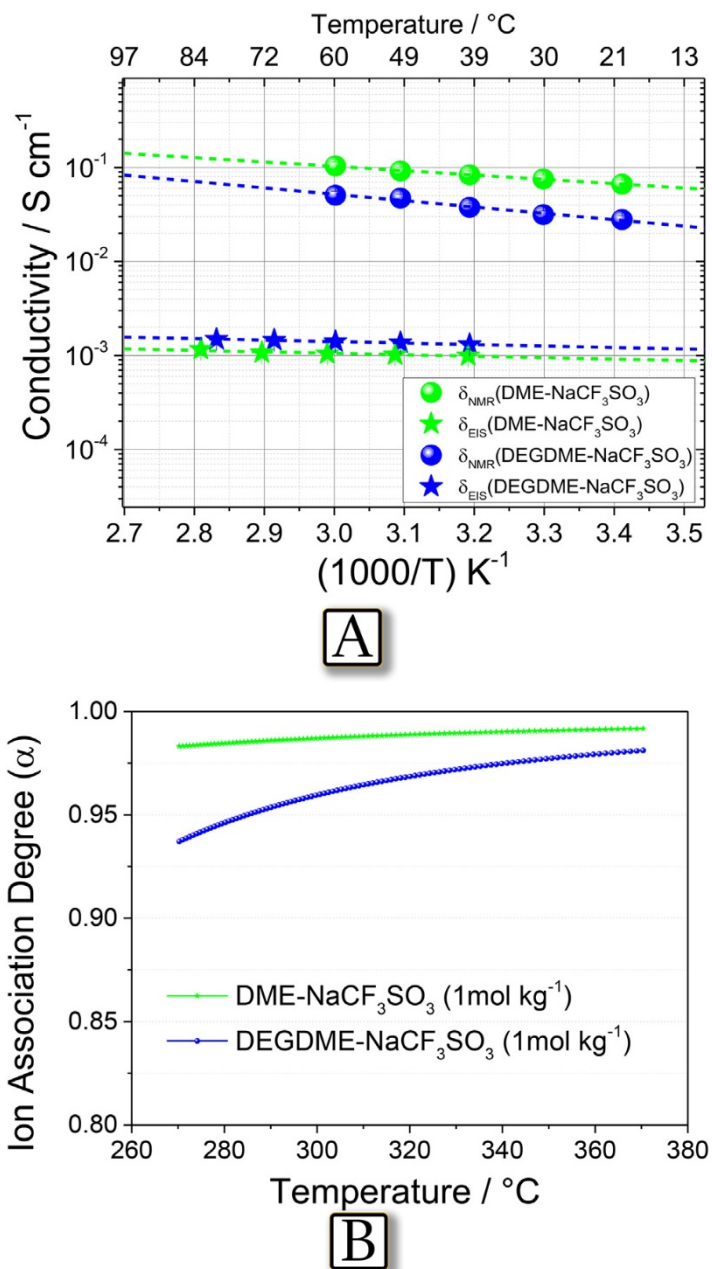


Figure 64 A) Conductivity values DME- NaCF_3SO_3 (1 mol kg^{-1}) and DEGDME- NaCF_3SO_3 (1 mol kg^{-1}) measured by EIS (δ_{EIS}) and calculated from NMR self-diffusion coefficients (δ_{NMR}). B) Ion association degree of the two electrolytes calculated by using Arrhenius linear fits conductivity data obtained by EIS and NMR.

Experimental Section: Cathode Preparation and Characterization

The cathode, already proposed for lithium-sulfur cells in a previous paper [34], was formed by mixing elemental sulfur (S, Sigma Aldrich) and multi-walled carbon nanotubes (MWCNs, Sigma Aldrich), in a 1:1 weight ratio, heating at 135°C in order to melt the sulfur and stirring for 2 hours until complete homogenization. The resulting mixture was cooled at room temperature and treated by high energy ball milling in a stainless-steel jar, with 4 stainless steel balls. The treatment was performed at a frequency of 15 Hz for 2 hours, using 4 steps of 30 minutes of milling and rest steps of 15 minutes. The electrode film was prepared by dispersing the sulfur-carbon powder (S-MWCNs), polyvinylidene difluoride (PVdF Solvey) binder and Super P (Imers) electron conductor (80:10:10 weight ratio) in N-methylpyrrolidone (NMP, Aldrich), stirring until formation of a homogeneous slurry, casting on aluminum foil by Doctor blade and drying at 50°C overnight to remove the solvent. Electrode disks were then punched, dried at 50°C for 24 h under vacuum overnight and introduced in the argon filled glove box to build the cells. The electrochemical reaction of S-MWCNs electrode with Na was studied by cyclic voltammetry tests in a three-electrode cell configuration, equipped with sodium metal reference and counter electrode, using either DME- NaCF_3SO_3 - NaNO_3 or DEGDME- NaCF_3SO_3 - NaNO_3 upgraded electrolyte. The cell potential was ranged from 0.5 V to 2.1 V vs. Na/Na^+ , using a scan rate of 0.1 mV sec^{-1} . Sodium-sulfur 2032 coin cells were assembled using the S-MWCNs cathode, the selected electrolyte, and Na-metal anode. The cells were subjected to galvanostatic cycling within 0.5 V and 2.1 V, using a current rate of C/10 (1 C = 1676 mA g^{-1}).

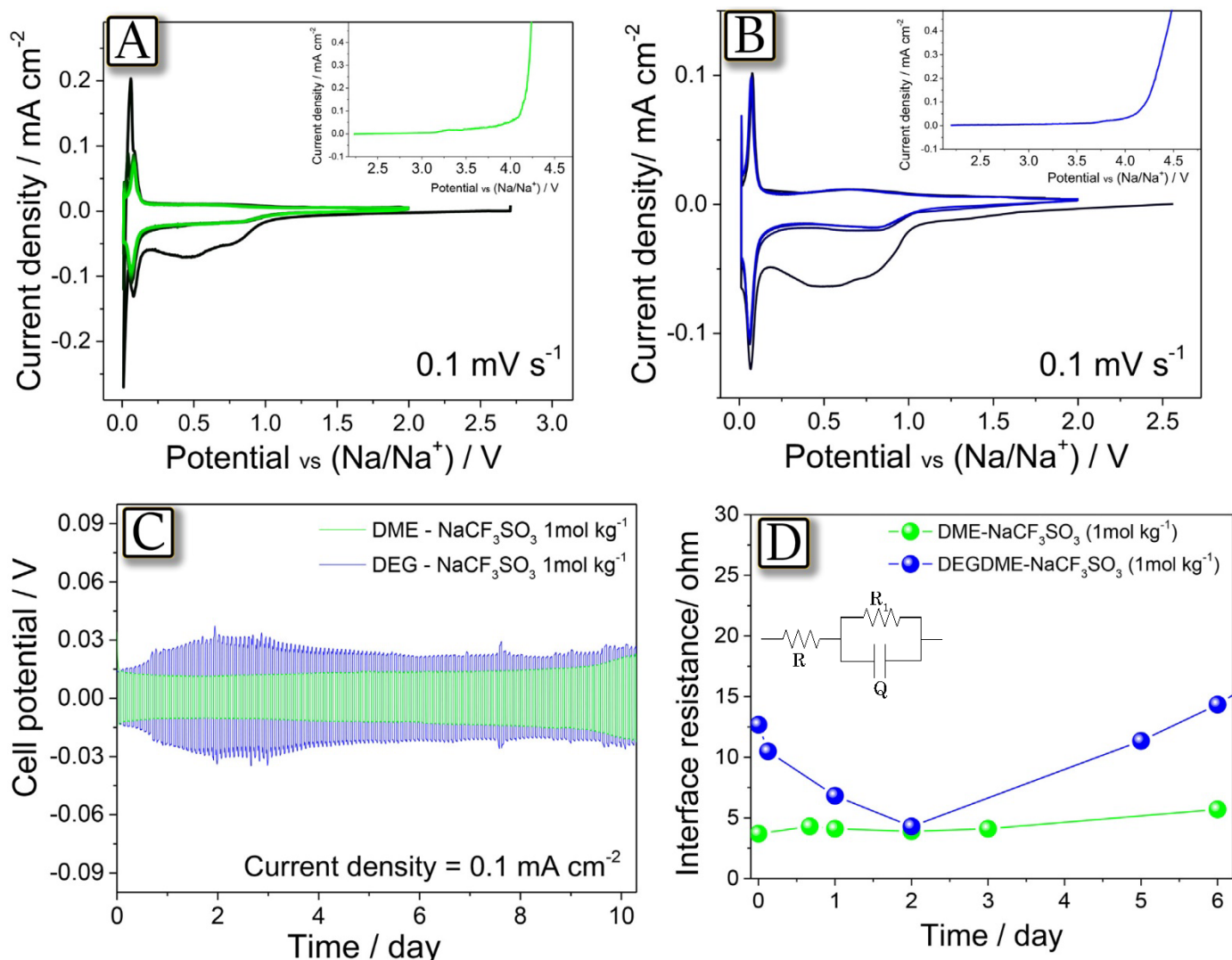


Figure 65 Cyclic voltammetry (CV) and, in inset, linear sweep voltammetry (LSV) of A) sodium/DME-NaCF₃SO₃ (1 mol kg⁻¹)/SP-carbon and B) sodium/DEGDME-NaCF₃SO₃ (1 mol kg⁻¹)/S-MWCN cells, using a three-electrode configuration with sodium metal as reference and counter electrode, and SP-carbon coated on Cu (CV) or Al (LSV) as working electrode. Potential limits 0-2 V vs. Na⁺/Na (CV) and 2-4.5 V vs. Na⁺/Na (LSV). Scan rate 0.1 mV sec⁻¹. C) Voltage profiles of sodium stripping/deposition tests performed in Na/electrolyte/Na symmetrical cells. Electrolytes DME-NaCF₃SO₃ (1 mol kg⁻¹) and DEGDME-NaCF₃SO₃ (1 mol kg⁻¹). Current density 0.1 mA cm⁻², 1 hour of step time limit. D) Sodium interface stability tests determined during time by EIS measurements in Na/electrolyte/Na symmetrical cells. Electrolytes DME-NaCF₃SO₃ (1 mol kg⁻¹) and DEGDME-NaCF₃SO₃ (1 mol kg⁻¹). EIS performed by using 10 mV signal amplitude and 0.1 Hz - 0.5 MHz frequency range.

the investigated temperature range, thus suggesting a lower ion solvating ability¹⁹⁸ of DME with respect to DEGDME, despite the higher ionic conductivity of the DME-NaCF₃SO₃ electrolyte. Increasing ion association with increasing temperature in poly-ethers is well-known and attributed to the decreased solvent dielectric constant at elevated temperature.⁷⁹ Instead, electrolyte of different nature, such as ILs, i.e., molten salt, may show a different trend. In view of possible application in sodium cells, the electrochemical and chemical sta-

bility of the electrolytes are determined by voltammetry, galvanostatic tests and EIS, and reported in figure 65. The cyclic voltammetry (CV) tests of DME-NaCF₃SO₃ (Fig. 65A) and of DEGDME-NaCF₃SO₃ (Fig. 65B) in sodium cells using a Super-P carbon coated on Cu as the working electrode, reveal an irreversible first cycle in which a reaction occurs around 0.5 V vs. Na⁺/Na during the reduction scan, most likely due to solvent decomposition with formation of a solid electrolyte interphase (SEI) film.¹⁹⁹ During subsequent cycles the CV profiles reveal reversible trends, characterized

by peaks centered at the low and intermediate potential values, i.e., at about 0.1 V and 0.7 V vs. Na^+/Na , due to insertion of sodium or solvated ions into the amorphous carbon matrix.²⁰⁰ Linear scan voltammetry (LSV) tests, performed adopting the same cell configuration used for CV except for the working electrode which is coated on Al instead of Cu, are reported in inserts of Fig. 65Aa (DME- NaCF_3SO_3) and Fig. 65B (DEGDME- NaCF_3SO_3). Both insets show an onset current starting at about 3.5 V vs. Na^+/Na and electrolytes stability extending over 4 V vs. Na^+/Na which is indeed considered the top potential limit allowing the electrolytes use in sodium cells. Furthermore, the sodium stripping/deposition tests of Fig. 65C show low polarization with values limited to 15 mV for DME- NaCF_3SO_3 and 30 mV for DEGDME- NaCF_3SO_3 . The polarization changes during the test, as likely attributed to dissolution, following reformation and expected stabilization of the SEI layer at the sodium interface.¹⁹⁹ This trend, as well as the lower polarization of the DME-based electrolyte with respect to the DEGDME-based one, are confirmed by the interface stability test performed by EIS and reported by Fig. 65D (see experimental section for details). Indeed, the figure shows modest interfacial resistances, limited below 15 Ω , for the two electrolytes with a higher value and more relevant changes upon time for the DEGDME-based electrolyte with respect to the DME-based one, thus accounting for the polarization trends already observed in Fig. 65C. Preliminary studies of sodium sulfur cells prove the applicability of the studied electrolyte in batteries. S-MWCNTs electrode is used as the preferred cathode material due to its suitable electrochemical performance already

demonstrated for glyme-based electrolytes in lithium cells in the previous chapters. Prior to cell assembly, the electrolyte solutions have been supplemented with NaNO_3 which is expected to form a protecting film at the Na surface for buffering polysulfide shuttle reaction, as already observed.

Sodium and Glymes in Sulfur Cell

Fig. 66 reports cycling voltammetry and galvanostatic cycling profiles of the Na/DME- NaCF_3SO_3 - NaNO_3 /S-MWCNTs and the DEGDME- NaCF_3SO_3 - NaNO_3 /S-MWCNTs cells. Overall, the CV profiles (Fig. 66A, B) reveal reversible peaks centered at about 1.8 V vs. Na^+/Na , ascribed to the electrochemical process of the sodium with sulfur, as well as peak intensity variation by cycling due to kinetic effects and polysulfide dissolution.²⁰¹ In particular, the cell using DME- NaCF_3SO_3 - NaNO_3 electrolyte (Fig. 66A) shows small peak at about 1.7 V vs. Na^+/Na , and a continuous potential drift until 0.5 V vs. Na^+/Na during the first cathodic scan, and a narrow peak at around 1.9 V vs. Na^+/Na during the anodic scan. The subsequent cycles exhibit an increase of the intensity of the peak at 1.7 V vs. Na^+/Na and the appearance of a broad peak at about 1 V vs. Na^+/Na during reduction, as well as the peak at 1.9 V, thus accounting for the multistep Na/S electrochemical process.⁸² The cell using DEGDME- NaCF_3SO_3 - NaNO_3 (Fig. 66B) evidences a CV profile following the same trend observed for DME-based electrolyte, however with peaks characterized by much improved intensity and shape, thus suggesting faster kinetics for the Na/S electrochemical process in DEGDME. This CV behavior is reflected in better performance of the sodium-sulfur cell using the DEGDME-

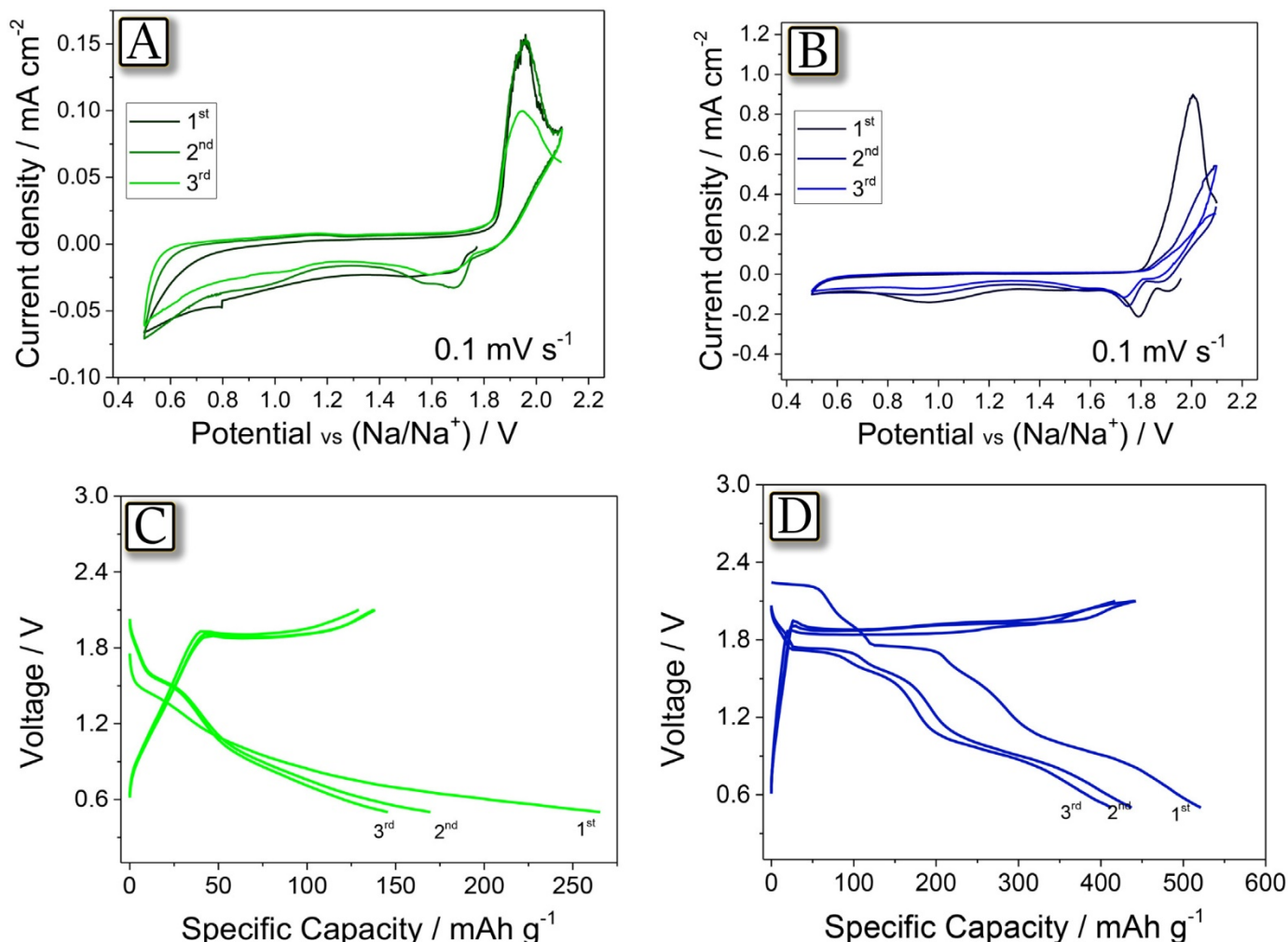


Figure 66 Cyclic voltammetry profiles of A) sodium/DME- NaCF_3SO_3 (1 mol kg^{-1}), NaNO_3 (0.4 mol kg^{-1})/S-MWCN and B) sodium/DEGDME- NaCF_3SO_3 (1 mol kg^{-1}), NaNO_3 (0.4 mol kg^{-1})/S-MWCN cells, using a three-electrode configuration with sodium metal as reference and counter electrode, and S-MWCN as working electrode. Potential limits 0.5–2.1 V vs. Na^+/Na . Scan rate 0.1 mV sec^{-1} . Galvanostatic cycling voltage profiles of C) Sodium/DME- NaCF_3SO_3 (1 mol kg^{-1}), NaNO_3 (0.4 mol kg^{-1})/S-MWCN and D) sodium/DEGDME- NaCF_3SO_3 (1 mol kg^{-1}), NaNO_3 (0.4 mol kg^{-1})/S-MWCN sodium cells (2032 coin-cell configuration). Voltage limits 0.5–2.1 V vs. Na^+/Na . Scan rate 0.1 mV sec^{-1} . Current rate C/10 ($1\text{C}=1676 \text{ mA g}^{-1}$).

NaCF_3SO_3 - NaNO_3 electrolyte (Fig. 66D) with respect to that using DME- NaCF_3SO_3 - NaNO_3 (Fig. 66C). The preliminary galvanostatic cycles show for the Na/DME- NaCF_3SO_3 - NaNO_3 /S-MWCNTs cell (Fig. 66C) a specific capacity of about 250 mAh g^{-1} during the first cycle, which decreases to about 160 mAh g^{-1} during following cycles, and a rather high polarization during the charge/discharge process with a profile reflecting the processes already observed in CV. In spite of this, the Na/DEGDME- NaCF_3SO_3 - NaNO_3 /S-MWCNTs cell (Fig. 55D) reveals a much improved galvanostatic behavior, with multistep process evolving at 2.1 V, 1.8 V and 1.1 V during first discharge, with

specific capacity of about 500 mAh g^{-1} , and a flat charge at 1.9 V. The subsequent cycles have the same trend, a low polarization, and a reversible capacity of about 450 mAh g^{-1} . Despite being very preliminary, and needing further investigation in terms of electrolyte composition, voltage limits and extended cycling, this performance suggests the electrolyte studied here as suitable candidate for sodium batteries.

Glyme electrolyte and Lithium Oxygen battery

Lithium-oxygen battery, generally accepted as lithium-air battery, despite in large part using pure oxygen rather than air, attracted large interest since characterized by a very high energy density, even exceeding the one associated to lithium-sulfur²⁰². This outstanding system has been studied during the initial research stages in a common carbonate-based electrolytes eliciting enthusiastic follow-up²⁰³. So far, the high polarization of the cell, the very short cycle life and the anomalous charge/discharge of the battery have dampened the enthusiasm largely due to the reactivity of the nucleophilic peroxide and superoxide species formed during the Li/O₂ reaction with carbonate solvents including the electrophilic carbonyl bond²⁰⁴. As in the case of the sulfur cell, these issues have been partially mitigated by completely replacing the carbonate with more suitable ether-based electrolytes²⁰⁵, polymers²⁰⁶ and ionic liquids³⁸. The change of the electrolyte, as well as new and more suitable configuration of the cell, in terms of components and engineering²⁰⁷, and new classes of catalysts²⁰⁸ shed a new light on this appealing system. Indeed, these new findings have led to a decreased cell polarization and increased cycle life²⁰⁹. Only recently, new configurations and compositions of the cathode used as the support for

the Li/O₂ process²¹⁰, including carbons of various natures and morphologies²¹¹, nanostructures²¹², doped porous composites²¹³, metal oxide catalysts and separators designed *ad hoc* for avoiding oxygen permeation to the anode²¹⁴, remarkably increased the lithium-oxygen cell performance in terms of delivered capacity, cycle life and low polarization²¹⁵. These breakthrough, in addition to the development of new and very safe cell prototypes in which the lithium metal is replaced by a lithium-ion anode²¹⁶, suggested the lithium oxygen battery as potential systems for next generation energy storage²¹⁷. In this chapter an enhanced system, formed by the combination of a safe electrolyte solution of lithium bistrifluoromethanesulfonimide (CF₃SO₂NLiSO₂CF₃, LiTFSI) in tetra ethylene glycol dimethyl ether solvent (TEGDME), and multi walled carbon nanotubes (MWCNTs) as the reaction support at the oxygen cathode is proposed. The cell shows an outstanding cycle life, extended up to 250 cycles, due to the optimal characteristics of the electrolyte revealed by NMR and electrochemistry, as well as to the reversible formation and dissolution of Li₂O₂ clearly detected by XRD, SEDM and TEM on the MWCNTs surface. Despite further efforts are required for practical employment, the cell studied is proposed as a valid candidate for powering the next generation EVs with extended driving range.

Experimental Section: Electrolyte and Cathode Preparation

The electrolyte was prepared by mixing Tetra ethylene glycol dimethyl ether (CH₃O(CH₂CH₂O)₄CH₃) following named by TEGDME and lithium bistrifluoromethanesulfonimide (CF₃SO₂NLiSO₂CF₃), herein named LiTFSI. Both chemicals purchased from Sigma Aldrich. Molecular sieves of 3Å from Sigma Aldrich were dried under vacuum at 250°C for 48 hours and used to reduce the water content of the TEGDME below 10 ppm. The water content was measured by Karl Fischer titration instrument (831 Karl Fisher Coulometer, Metrohm). Before mixing the TEGDME and the lithium salt in 1 mol kg⁻¹ ratio, the LiTFSI was dried under vacuum at 80°C for 24 hours. Multi walled carbon nanotubes from Sigma Aldrich, following named MWCNTs, were annealed under nitrogen flow at 750°C for 12 hours. The active material (named N₂@MWCNTs) was mixed separately with polyvinylidenedifluoride (PVdF, Solvay) binder in a 80:20 mass ratio and dispersed in N-methylpyrrolidone (NMP, Aldrich). The slurry was cast on a gas diffusion layer (TGP-H-030 carbon paper, Toray) by Doctor blade. The active material ratio on the current collector was of about 0.8 mg cm⁻². The electrode foils were punched in disks, dried overnight at 100°C and finally introduced in argon filled glove box with oxygen and moisture content lower than 1 ppm. Lithium oxygen cells were then assembled by combining lithium metal, the N₂@MWCNTs, and the TEGDME-LiTFSI in a top-meshed 2032 coin-cell inserted into a glass tube filled subsequently by pure oxygen.

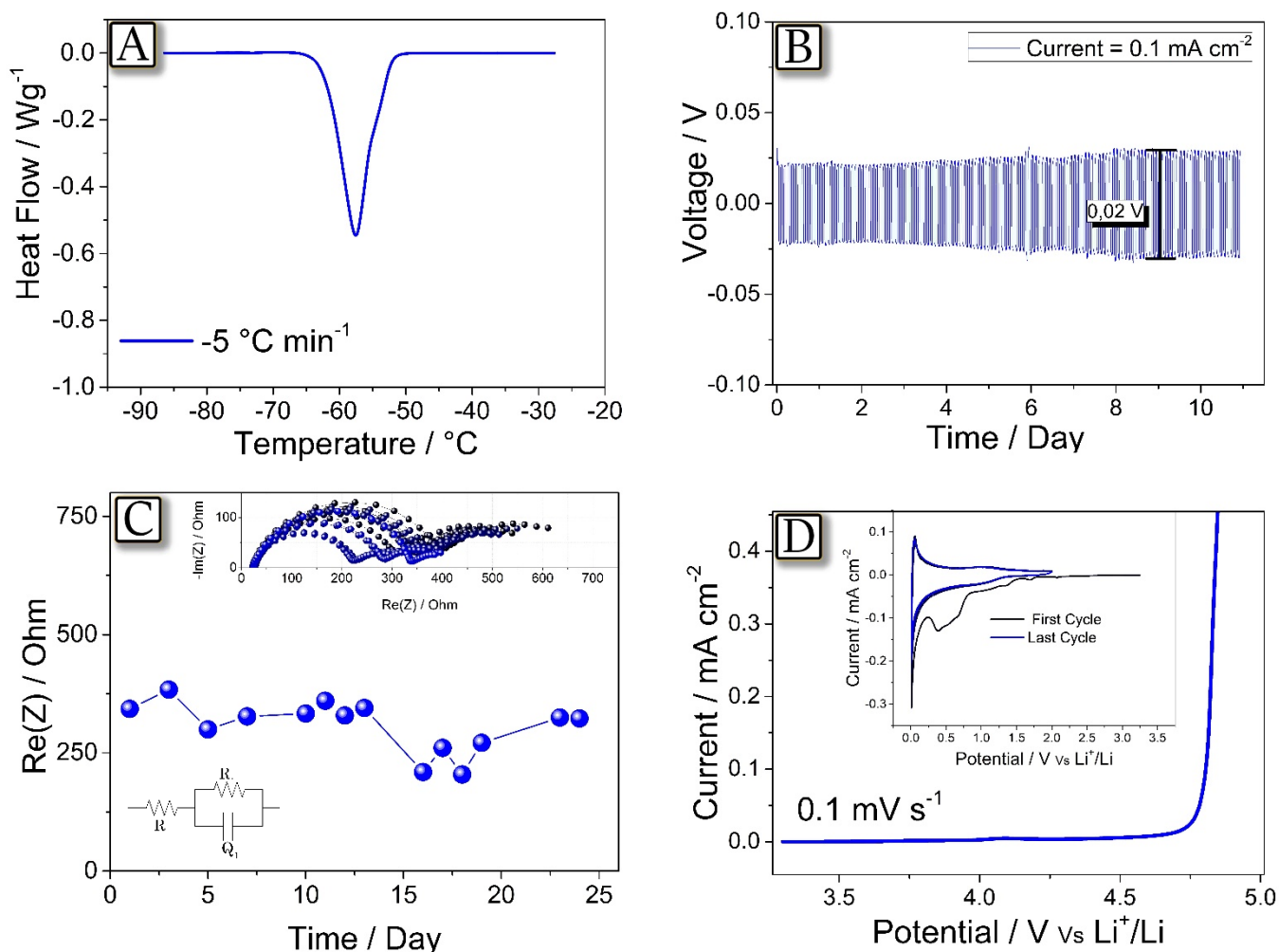


Figure 67 Characteristics of the TEGDME-LiTFSI electrolyte (1 mol kg⁻¹). (A) Differential Scanning Calorimetry (DSC) performed by a cooling rate of 5 °C min⁻¹, ranging the temperature between -30 °C and -90 °C with an argon filled crucible. (B) Lithium stripping/deposition voltage profile of a symmetrical lithium/lithium 2032-coin cell performed with a constant current of 0.1 mA cm⁻² and a step limit of 1 h. (C) Time evolution of the lithium/electrolyte interface resistance, and in inset corresponding Nyquist plots, investigated by impedance spectroscopy in a symmetrical lithium/lithium 2032-coin cell with a signal amplitude of 10 mV in a 0.1 MHz - 0.1 Hz frequency range. (D) Electrochemical stability window of the electrolyte determined by linear sweep voltammetry (LSV) up to 5 V in the anodic region and by cyclic voltammetry (CV) between 0 and 2 V vs. Li⁺/Li in the cathodic region (inset), using a Swagelok T-cell with lithium as counter and reference electrode and Super P as working electrode, scan rate of 0.1 mV s⁻¹.

TEGDME-LiTFSI Properties

This paragraph sheds light on the performance of a TEGDME-LiTFSI electrolyte (1 mol/kg⁻¹) by combining calorimetry, electrochemistry and nuclear magnetic resonance.^{218,219} The DSC traces of Fig. 67A indicates that the electrolyte freezes below -50 °C, hence ensuring the low temperature utilization, while the lithium stripping/deposition profile in symmetrical Li cell in Fig. 67B evidences a very low polarization, limited to about 20 mV during the whole test, thus suggesting a remarkable stability of the electrolyte. Further proof of the electrolyte

stability is evidenced by Fig 67C reporting the lithium/electrolyte interface impedance trend, and, in inset, the corresponding Nyquist plots, as well as by the linear sweep voltammetry of the Li/electrolyte/SP cell in the anodic region (Fig. 67D), and the CV of the cell in the cathodic region between 0 V and 2 V (Fig. 67D inset). Indeed, the electrolyte reveals a stable impedance ranging from 150 to 300 ohm due to solid electrolyte interface (SEI) film changes,⁸⁶ and an applicability extending from 0 V to 4.7 V vs. Li/Li⁺, i.e., a region in which only SEI film formation at about 0.8 V,²²⁰ reversible insertion into amorphous carbon at about 1 V^{221,222} and

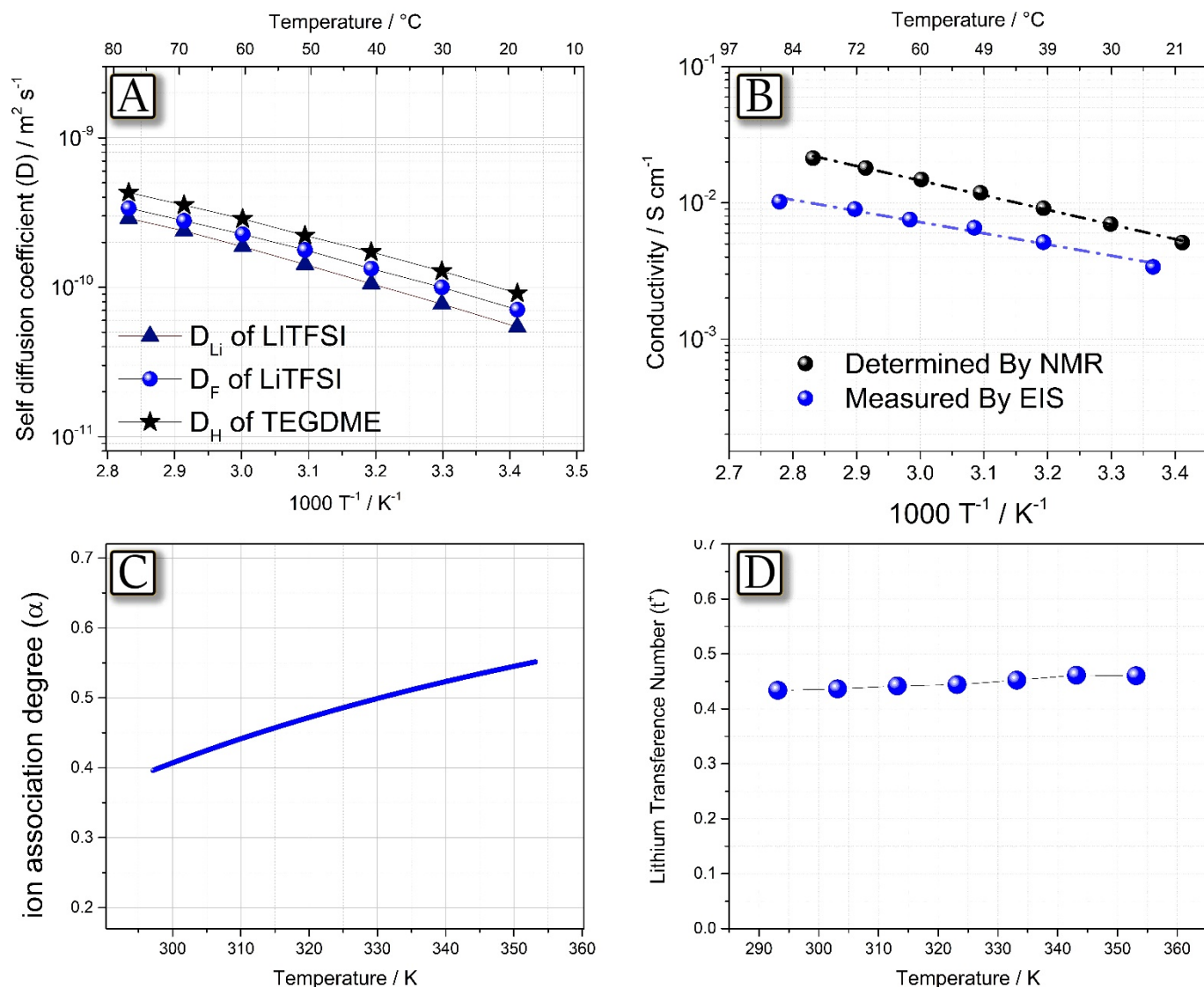


Figure 68 Species mobility in the TEGDME-LiTFSI electrolyte (1 mol kg⁻¹). (A) self-diffusion coefficients of the ¹H, ⁷Li and ¹⁹F nuclei carried out by NMR in the temperature range of 20°C - 80°C. (B) Comparison of the conductivity values calculated from the self-diffusion coefficients and determined by electrochemical impedance spectroscopy (EIS) in a symmetrical SS/Electrolyte/SS 2032 coin-cell equipped with a Teflon O-ring separator in the frequency range of 0.1MHz-0.1Hz with signal amplitude of 10 mV. (C) Ionic association degree of the lithium salt determined by combining NMR and EIS data. (D) Lithium transference number determined using the NMR data in the temperature range 20°C - 80°C.

the lithium deposition/stripping at 0V²²³ can be observed. The transport characteristics of the electrolyte are observed in Figure 68. The PFG-NMR data reported in Fig. 68A show the self-diffusion coefficients of the ¹H, ⁷Li and ¹⁹F nuclei, hence of the TEGDME solvent, lithium cation, and TFSI anion, respectively, in the temperature range between 20°C and 80°C. The data reveal self-diffusion coefficient ranging from 4×10⁻¹¹ m² s⁻¹ at the lower temperature to 3×10⁻¹⁰ m² s⁻¹ at the higher one, and faster mobility of the solvent than the ions. The

combination of the NMR data allows the determination of the *apparent electrolyte conductivity*, which is compared in Fig. 68B with the conductivity determined by impedance spectroscopy, of the ionic association degree (Fig. 68C), as well as of the lithium transference number (Fig. 68D) between 20°C and 80°C.^{68,110,224,225} Raising the temperature reflects into a conductivity and ionic association degree increase, from 3×10⁻³ S cm⁻¹ to 10⁻² S cm⁻¹ (Fig. 68B), and from 0.40 to 0.55 (Fig. 68C), respectively, due to a synergic effect of the in-

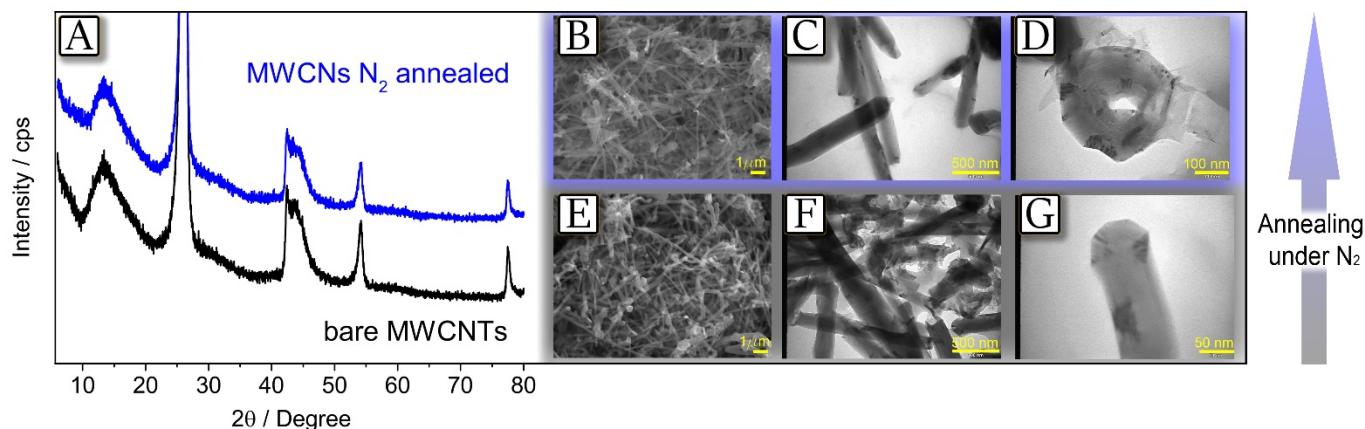


Figure 69 XRD patterns of the bare multi walled carbon nanotubes (MWCNTs) and of the same material after the annealing process under nitrogen atmosphere (N₂@MWCNTs). (B, E) SEM images of the bare and the N₂-annealed MWCNTs. (C, D, F, G) TEM images at various magnifications of the bare and the N₂-annealed MWCNTs.

creased mobility of both ions and solvent which depends on the solution nature and composition.⁵¹ Instead, the *apparent lithium transport number* appears only slightly affected by the temperature increase, with a value of about 0.45 over the whole temperature range, i.e., a high value which may be however influenced by the ion association.⁷⁷ In overall, these results suggest the electrolyte as well suitable ion conducting media for application in efficient lithium cell in a relatively wide temperature range.

TEGDME-LiTFSI in Li/O₂ Cell

Prior to use as the electrode support for Li/O₂ the MWCNTs was treated under nitrogen atmosphere at 750 °C in order to remove possible undesired functional groups which may affect the electrochemical process.^{226,227} The XRD patterns of Fig. 69A reveals the graphitic nature of the MWCNTs, and shows only minor structural changes due to the

Experimental Section: Electrolyte Characterization

The thermal properties were evaluated by **differential scanning calorimetry** (DSC) using the Mattler Toledo DSC821 instrument. The TEGDME-LiTFSI electrolyte was sealed in aluminum crucible under argon atmosphere before the DSC analysis. The measurement was performed by cooling down from -30°C to -90 °C with a rate of -5°C min⁻¹. The lithium **stripping deposition** test was performed with constant current rate of 0.1 mA cm⁻² and step limit of 1 hour using a symmetrical lithium/lithium 2032 coin-cell and a MACCOR 4000 series Battery Test System. The **lithium/electrolyte interface resistance** was measured using the latter cell configuration by electrochemical impedance spectroscopy in the frequency range of 0.1MHz - 0.1Hz with a signal amplitude of 10 mV with a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The impedance spectra were associated to the R(RQ)_nQ equivalent circuit, where R is the resistance and Q a constant phase element (CPE), and analyzed using the nonlinear least square (NLLSQ) fit by Boukamp Software^{235,236}; only the results with a chi-square χ^2 lower than 10⁻⁴ were accepted. The **voltammetry tests** were carried out in Swedglock T-cell with lithium metal as reference and counter electrode and a working electrode formed by depositing super P (Timcal) on Cu or Al support for the cathodic and the anodic scan, respectively. The **cyclic voltammetry (CV)** for the cathodic region was performed in the potential range 0V - 2V vs. Li/Li⁺, while the **linear sweep voltammetry (LSV)** for the anodic region was performed up to 5V vs. Li/Li⁺, both with a scan rate of 0.1 mV sec⁻¹. The measurements were carried out by VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The **self-diffusion coefficient** of the ¹H ⁷Li and ¹⁹F nuclei were measured by a Bruker 400 Avance III NMR spectrometer suppressing the convection effect by PFG double-stimulated echo sequence. The data were collected every 10°C from 20°C to 80°C with a gradient strength *g* of 1-45 G cm⁻¹, gradient pulse of 1-2 ms and a diffusion delay Δ of 100-200 ms. The error on the self-diffusion coefficient is about 3–5%.²²⁵ The **ionic conductivity** of the electrolyte (δ_{NMR}) was calculated from the self-diffusion coefficient by the Nernst-Einstein equation (4)¹¹⁰: $\delta_{\text{NMR}} = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{F}})$ where *F* is the Faraday constant (96485 Coulomb), [*C*] represents the solution concentration (mol cm⁻³), *R* is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹). Furthermore, the ionic conductivity was measured by impedance spectroscopy (δ_{EIS}) in a symmetrical SS/SS 2032-coin cell with a Teflon O-ring separator in the temperature range of 20°C - 80°C, using a signal amplitude of 10 mV in the frequency range of 1MHz and 0.1Hz by employing a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The conductivity values δ_{EIS} and δ_{NMR} were combined in equation 5 to obtain the **ionic association degree** (α)⁸⁴: $\alpha = (1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}})$ The **lithium transport number** (*t*⁺) was calculated by equation (6)⁶⁹: $t^+ = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{F}}}$ where *D*_{Li} is the lithium self-diffusion coefficient and *D*_F is the fluorine self-diffusion coefficient of the TFSI⁻ anion.

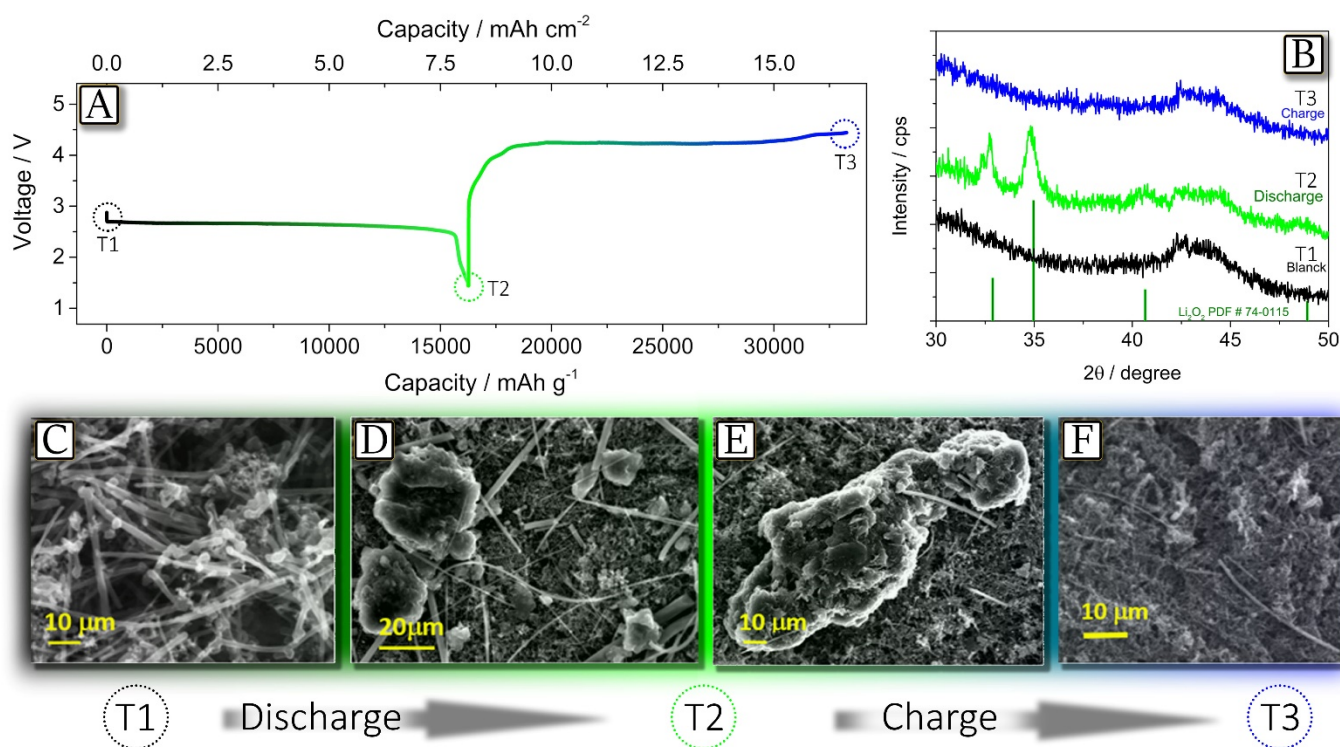


Figure 70 (A) Galvanostatic voltage profile of the lithium oxygen battery using the TEGDME-LiTFSI (1mol kg⁻¹) electrolyte and the N₂@MWCNTs electrode in a 2032 top-meshed coin cell. Current rate of 100 mA g⁻¹. Voltage limit of 1V-4.5V. (B) XRD pattern of the cell at different state of the charge, marked by T1 (OCV), T2 (fully discharged), and T3 (fully charged). SEM images of the N₂@MWCNTs electrode at the OCV (C), at the discharged ((D and E) and at the charged state (F).

thermal treatment suggested by the almost unchanged patterns. More relevant effects of the annealing process are observed for the MWCNTs morphology, as revealed by SEM (Fig. 69B, E) and TEM (C, D, F and G) at various magnification. The images, in particular the TEM, suggest the effective role of the annealing process in cleaning the nanotubes from impurities (Fig. 69F and C), thus increasing the electrode surface and enabling cavities and free spaces (Fig. 69G and D) which may act as the host and the catalyst for the Li/O₂ electrochemical process.²²⁸ This morphology is expected to increase the performances and the cycle life of the lithium oxygen battery using the nitrogen annealed MWCNTs. The TEGDME-LiTFSI electrolyte and the nitrogen annealed MWCNTs electrode (N₂@MWCNTs) are combined and studied in a lithium oxygen cell. The cell is fully discharged and charged, the voltage profile collected (Fig. 70A), and the reaction products studied in terms of

structure by ex-situ XRD (Fig. 70) and morphology by ex-situ SEM (Fig. 70C-F). The voltage profile of Fig. 70A remarkably shows that the N₂@MWCNTs electrode reaches a capacity of about 16 Ah g⁻¹ referred to the carbon weight (i.e., a value of about 9 mA cm⁻² as referred to the electrode geometric area). It is worth mentioning that the cell is cycled using the voltage cutoff of 1V-4.5V which is a cycling mode aimed to detect the full charge discharge products instead of allowing the cell stability, as indeed confirmed by the decay of the performances by ongoing of the test Fig. 71. Lithium oxygen cell stability may be in fact achieved only by limiting the discharge capacity during the cycling as already reported by previous works²²⁹ and fully confirmed hereafter (see following paragraphs). The XRD patterns of the N₂@MWCNTs electrode collected from the lithium oxygen cells at different state of charge reported in Fig. 70B, i.e., at the OCV (marked by T1

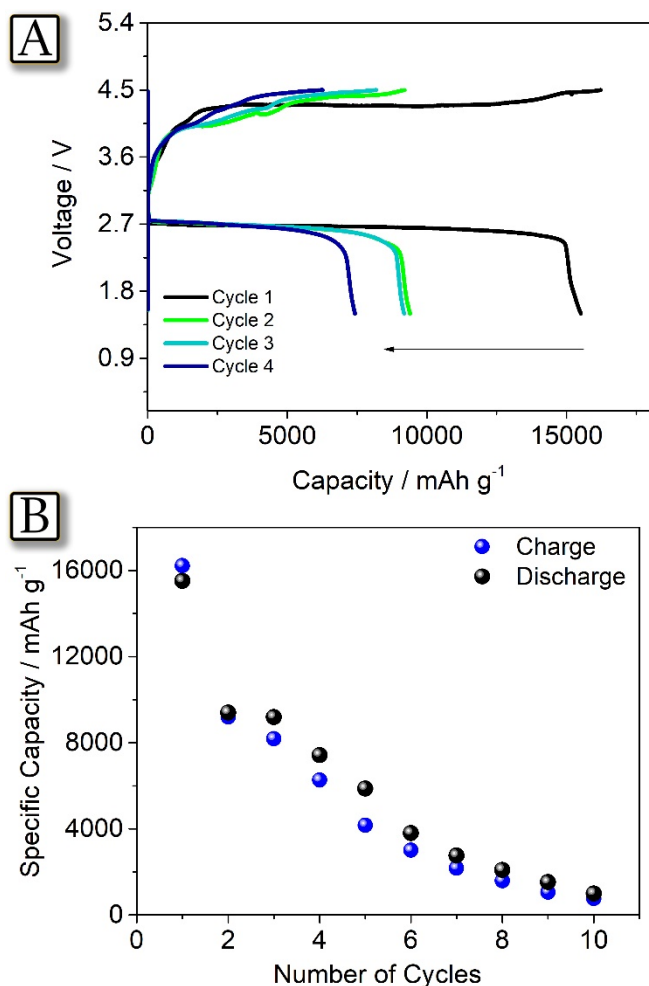


Figure 71 Galvanostatic voltage profile (a) and corresponding cycling trend (b) of the lithium oxygen battery using the TEGDME-LiTFSI (1mol kg⁻¹) electrolyte and the N₂@MWCNTs electrode in a 2032 top-meshed coin cell. Current rate of 100 mA g⁻¹, and voltage limit of 1V-4.5V. The specific capacity is referred the carbon weight.

in Fig. 70A), fully discharged state (marked by T2 in Fig. 70A), and fully charged state (marked by T3 in Fig. 70A), clearly show the formation and complete dissolution of the lithium peroxide during the galvanostatic test, without any residual product, which is in line with the high efficiency approaching 100 % achieved by the galvanostatic test of Fig. 70A. Furthermore, the corresponding SEM images (Fig. 70C-F) reveal the formation of micrometric particles with a size of about 50-100 μm (Fig. 70D, E), and suggest an *electrodeposition mechanism* of Li₂O₂ at the N₂@MWCNTs surface rather than a *solution mechanism* with the formation of the reaction products at the electrode/electrolyte interface, i.e., a pathway generally observed for cells using

ionic liquid electrolytes.^{214,230–234} Remarkably, the SEM of Fig. 70F evidence a complete dissolution of the products upon the full charge process, thus suggesting again the reversibility of the electrochemical process. The lithium oxygen battery is then assembled using the N₂@MWCNTs electrode and the TEGDME LiTFSI electrolyte, and cycled using a capacity limited to 500 mAh g⁻¹ referred to the carbon weight in order to allow the long life of the battery as above mentioned. Remarkable, Fig.72 shows that the cell may achieve 250 cycles of continuous charge and discharge without any sign of polarization increase (Fig. 72A) or capacity

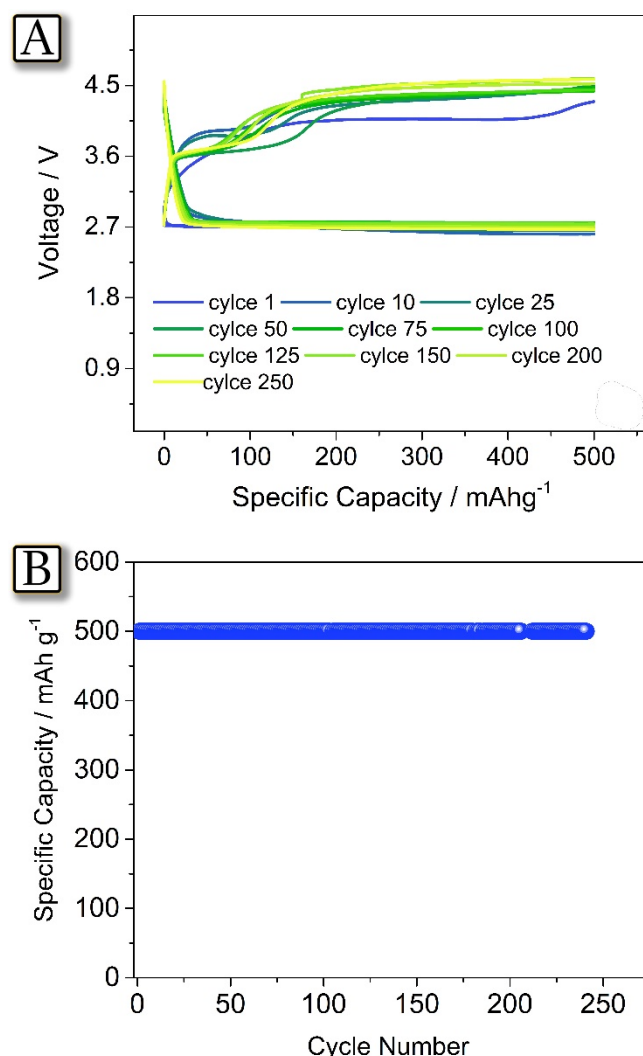


Figure 72(A) Galvanostatic voltage profile, and (B) corresponding cycling trend of the lithium oxygen battery using the TEGDME-LiTFSI (1mol kg⁻¹) electrolyte and the N₂@MWCNTs electrode in a 2032 top-meshed coin cell. Current rate of 100 mA g⁻¹. Capacity limit capacity 500 mAhg⁻¹. Current density and specific capacity are referred to the carbon weight.

fading (Fig. 72 B). The cell operates at about 2.7 V and therefore hold a theoretical energy density of about 1350 Wh kg^{-1} considering the carbon weight, which may be reflected into a relevant value of the practical energy. It is worth mentioning that, even if for few cycles the energy content of the cell may be advantageously increased by raising the capacity limit up to 1000 and 2000 mAh g^{-1} , as indeed evidenced by the voltage profiles reported in Fig.73. These performances reveal the suitability of the cell configuration herein adopted. The lithium oxygen cell using nitrogen annealed MWCNTs electrode and TEGDME-LiTFSI electrolyte revealed remarkable cycle life, extended up to 250 cycles, and excellent characteristics indicated for advanced and high energy storage. This outstanding performance been attributed to fully suitable electrolyte properties, in terms of ion mobility and stability as revealed by NMR and EIS, as well as to an extremely reversible electrochemical process promoted by the optimal morphology of the MWCNTs evidenced by TEM. Hence, formation and reverse dissolution of Li_2O_2 during the reduction and the oxidation, respectively, have been clearly observed by X-ray diffractometry and by electron microscopy. The data indicated the formation of micrometric crystalline peroxide stably supported by the nanotube aggregates at the electrode surface, with no signs of electrode/electrolyte degradation or cell performance decay. Therefore, the results obtained by this study suggest the cell

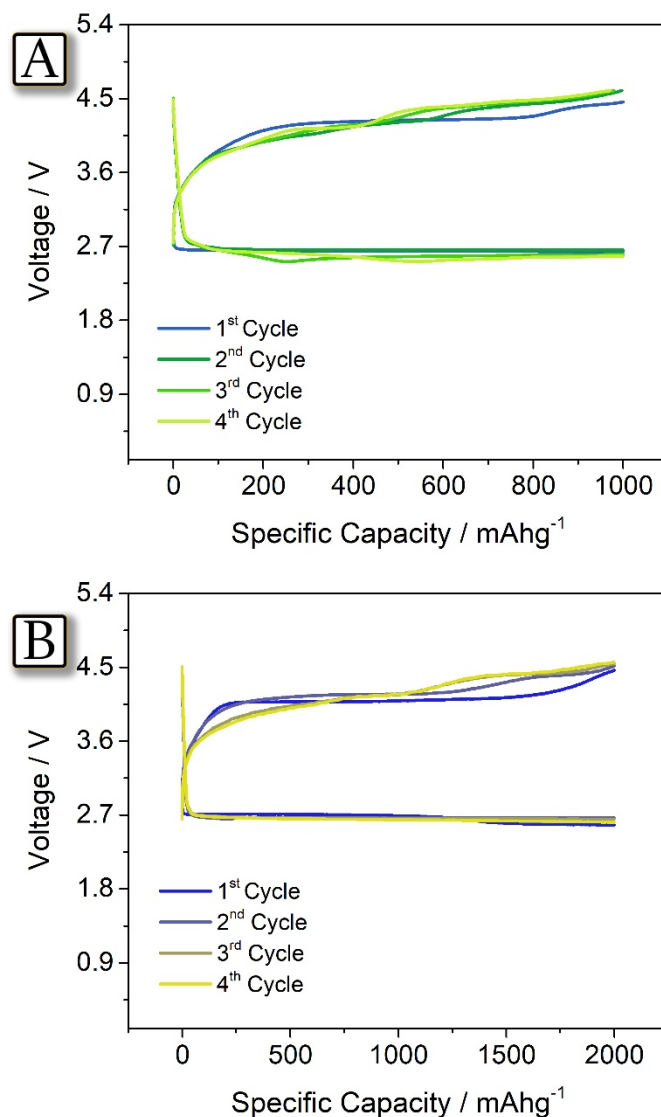


Figure 73 Galvanostatic voltage profile of the lithium oxygen battery using the TEGDME-LiTFSI (1mol kg^{-1}) electrolyte and the $\text{N}_2\text{@MWCNTs}$ electrode in a 2032 top-meshed coin cell. Current rate of 100 mA g^{-1} , and capacity limit of 1000 mAh g^{-1} (A) and 2000 mAh g^{-1} (B). The specific capacity is referred to the carbon weight.

configuration herein adopted as a stable, long life and relatively safe battery for application in modern EVs.

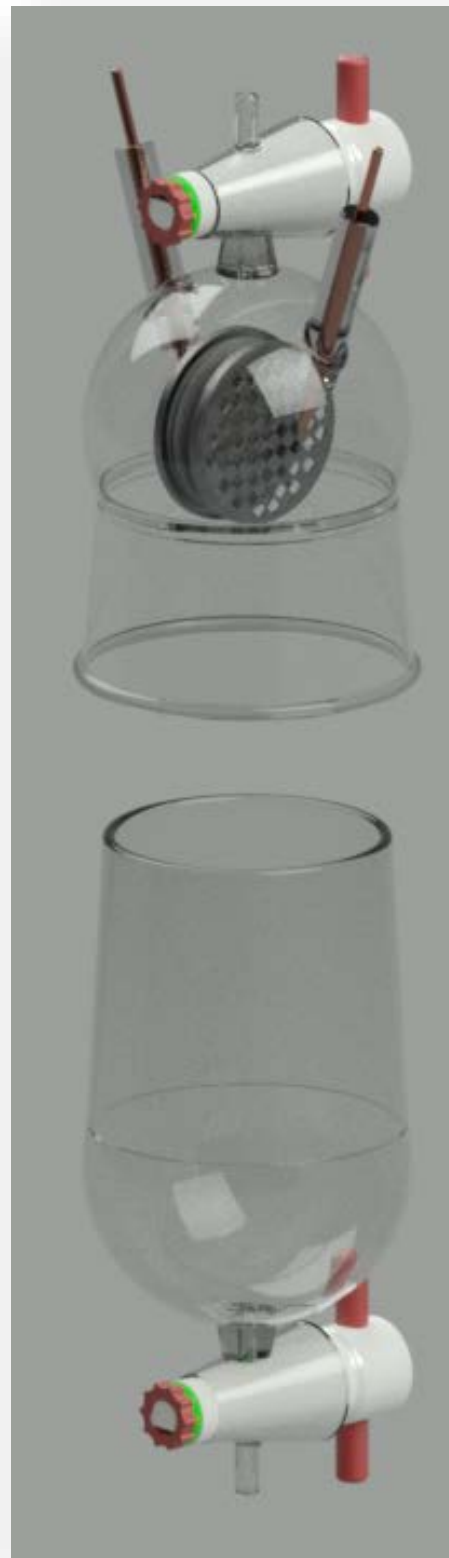
Experimental Section: Cathode Characterization

The powders structure was characterized by X ray diffraction using a Bruker instrument equipped with a $\text{Cu K}\alpha$ source and a graphite monochromator, in the $2\theta/\theta$ scanning mode. The morphology of the samples was evaluated by SEM (Zeiss EVO 40) with a thermionic electron gun equipped by LaB_6 crystal. Lithium oxygen cell was studied by galvanostatic test using voltage cutoff performed with a constant current of 100 mA g^{-1} in a $1\text{V} - 4.5\text{V}$ range. Galvanostatic cycling tests were also carried out with a current rate of 100 mA g^{-1} and limiting the capacity to 500, 1000 and 2000 mAh g^{-1} . The current density and specific capacity was referred to the carbon weight into the electrode, while the surface capacity was determined with respect to the electrode geometric area

Comparison overview

The aim of this chapter is the comparison between the most relevant properties of the electrolytes and active materials presented along this work of thesis. The electrolyte already discussed will be herein compared in terms of self-diffusion coefficients, lithium transference number and ionic conductivity in order to obtain a clear overview of the transport and mobility properties, furthermore the lithium interface stability, lithium stripping deposition and the electrochemical stability windows data will be compared and discussed to clarify the stability of the electrolytes in contact with lithium metal and along galvanostatic cycles. Moreover, a briefly overview of the cathodic active materials such as the olivine cathodes and the lithium-sulfur cells, is proposed in terms of number of cycles, coulombic efficiency and galvanostatic cycles in order to clarify the optimizations and the performances of the cell obtained in this work and maybe shed light on the differences of these new classes of energy storage devices.

Scheme of the cell prototype used for the lithium air battery tests.



Electrolytes

Figure 74 shows the conductivity comparison of the glyme electrolytes. Figure 74 A, B and C are referred to the solution with 1 mol kg⁻¹ of lithium triflate, LiTFSI and sodium triflate respectively. The conductivity comparison of the lithium triflate added solution of figure 74A, clearly evidences an increasing conductivity trend related to the glyme chain length. The electrolytes with long chain reveal higher conductivity, probably due to their higher viscosity. Indeed, the glymes with shorter chain such as TREGDME, DEGDME and DME show about the same conductivity values. Furthermore, this trend is confirmed by Figure 74B where the LiTFSI added solutions, shows higher conductivity for the DEGDME electrolyte with respect to the TEGDME, even though their conductivity values are about one order of magnitude higher than the lithium triflate solutions. Figure 74C shows the conductivity of the sodium triflate added solution with values of about 10⁻³ S cm⁻¹. Figure 75 shows the self-diffusion coefficients and the related lithium transference number of the studied electrolytes. The self-diffusion coefficients values of Figures 75 A, C and E exhibit the increasing trend related to the glymes chain length for all the mixtures. Has to be noticed that the DEGDME solution exhibits the same values of self-diffusion coefficients even with different lithium or sodium salts, of about 10⁻⁹ m s⁻². The lithium transference number of the triflate classes in figure 75 B and F reveal a stable trend along the whole range of temperature of about 0.5, however the glymes with higher viscosity such as the PEG250 and PEG500 reveal a lower lithium transference value of about 0.48, 0.45 respectively.

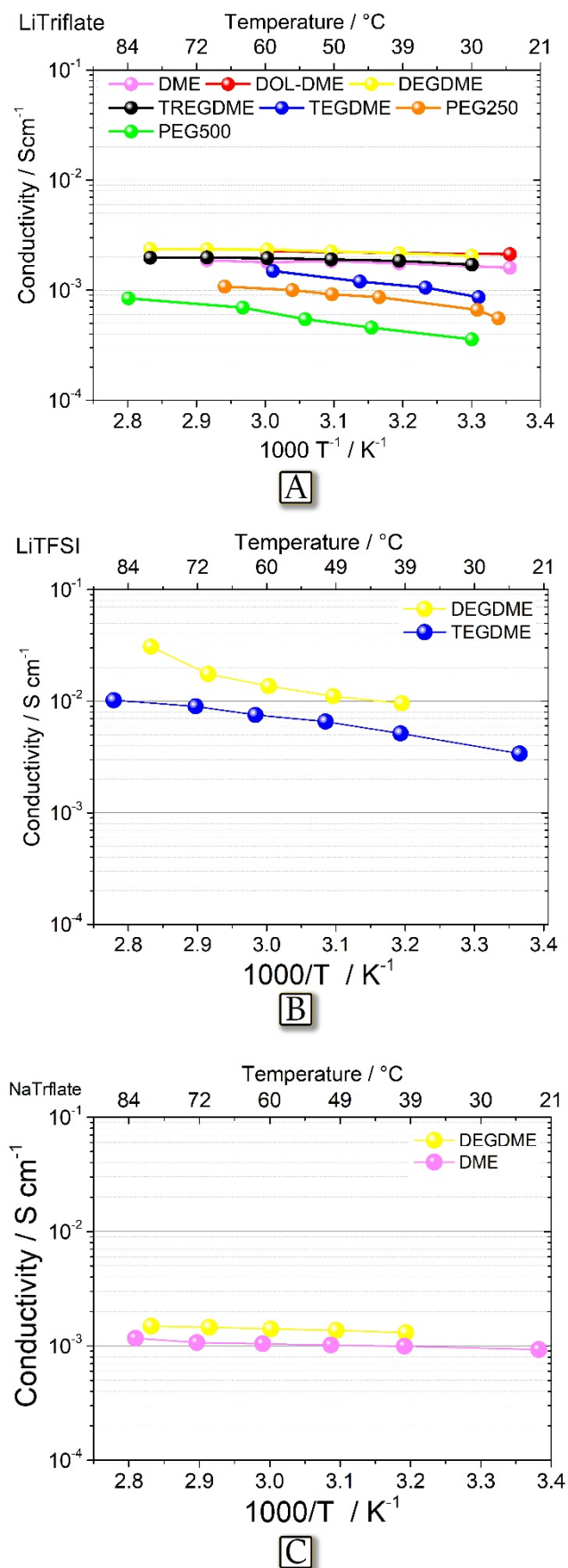


Figure 74 Conductivity values of the ether based electrolyte with (A) 1 mol kg⁻¹ of lithium triflate, (B) 1 mol kg⁻¹ lithium TFSI and (C) 1 mol kg⁻¹ sodium triflate. The measurements have been performed in coin-cell, using electrochemical impedance spectroscopy

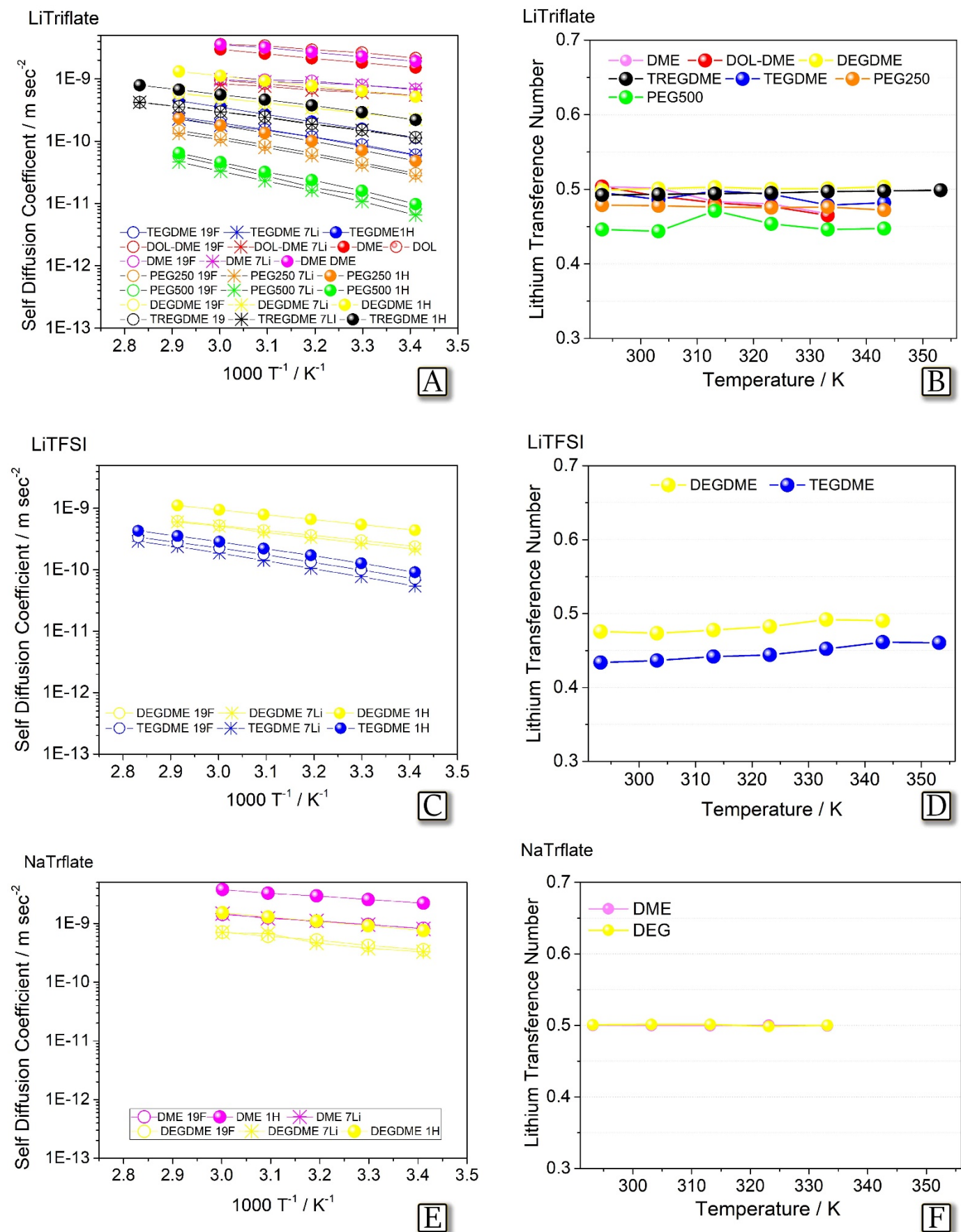


Figure 75 self-diffusion coefficients of the ¹H, ⁷Li and ¹⁹F nuclei carried out by NMR, and lithium transference number calculated from the self-diffusion coefficients of the ether based electrolyte with (A) and (B) 1 mol kg⁻¹ of lithium triflate, (C) and (D) 1 mol kg⁻¹ lithium TFSI and (E) and (F) 1 mol kg⁻¹ sodium triflate.

The LiTFSI added solutions exhibit a slight increasing trend with the temperature increase and values lower than the LiTriflate solutions in the whole range of temperature of about 0.48 and 0.44 for DEGDME and TEGDME electrolyte respectively. The Ion association degree calculated from the ionic conductivity measured by EIS and calculated from the self diffusion coefficients are reported in Figure 76. All the electrolytes reveal an increasing trend with the temperature increase in the whole range of temperature, however the triflate series exhibits higher values with respect the electrolytes with the LiTFSI salt, indeed the DEGDME and TEGDME with LiTriflate report a value ranging from 0.4 and 0.6, instead the LiTriflate based stable at about 0.9. this effect is further confirmed by the sodium based electrolyte with DEGDME and DME stable at about 0.98. Thus suggesting a stronger interaction of the triflate anion with the cations. Figure 77 reports the lithium interface resistance and the lithium stripping/deposition tests of the ether based electrolytes with lithium triflate, LiTFSI and sodium triflate addition in Figure 77A B Figure 77 C D and Figure 77 E F respectively. The lithium triflate series exhibit stable trend over time of the lithium interface resistance for all the solvents except the DME solution which show a fast resistance increase after 10 days probably due to the DME evaporation as previously described. DEGDME and DOL: DME based electrolytes show stable trend with about $100\ \Omega$ of resistance with a slight increase after 25 days. TEGDME, TREGDME, PEG250 and PEG500 based electrolyte of Figure 77A are characterized by high resistance during the first days of test, probably due to the formation of a passivation film, followed by

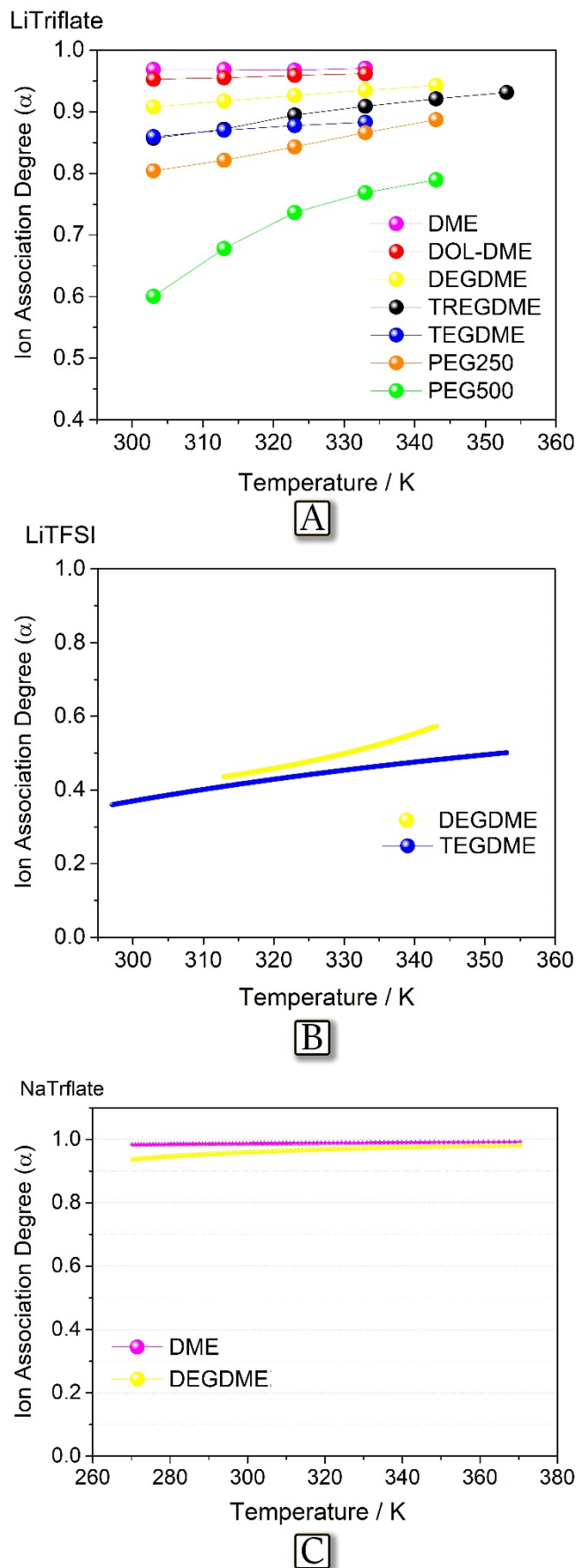


Figure 76 Ion association degree of the ether based electrolytes with (A) $1\ \text{mol kg}^{-1}$ of lithium triflate, (B) $1\ \text{mol kg}^{-1}$ lithium TFSI and (C) $1\ \text{mol kg}^{-1}$ sodium triflate. Calculated by conductivity values from EIS and NMR measurements

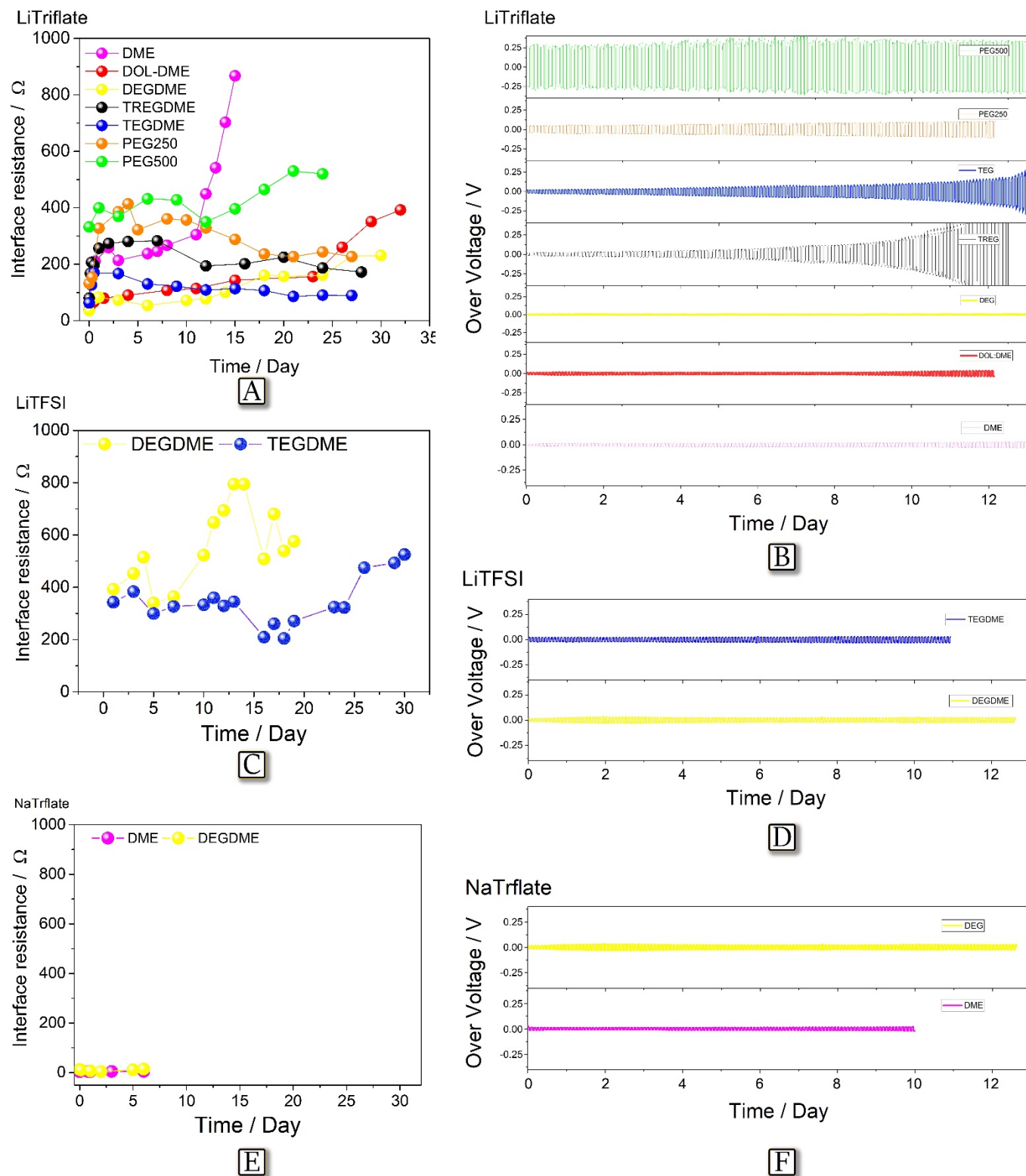


Figure 77 A) Time evolution at room temperature of the lithium-electrolyte interface resistance performed in Swagelok-type, Li/Li symmetrical cell using electrochemical impedance spectroscopy with signal amplitude of 10 mV within 500 MHz-100 mHz frequency range and B) Voltage vs. time profile of lithium deposition/stripping galvanostatic test performed applying a 0.1 mA current to symmetrical Li/electrolyte/Li cell for the ether based electrolyte with 1 mol kg⁻¹ of lithium triflate. C) Time evolution at 23°C of the lithium/electrolyte interface resistance performed in symmetrical Li/Glymes-LiTFSI/Li cell using electrochemical impedance spectroscopy with signal amplitude of 10 mV within 500 MHz-100 mHz frequency range and D) Voltage versus time profile of lithium deposition/stripping galvanostatic test performed by applying a 0.1 mA cm⁻¹ current to symmetrical Li/ Glymes -LiTFSI/Li cell. E) Sodium interface stability tests determined during time by EIS measurements in Na/electrolyte/Na symmetrical cells. Electrolytes DME-NaCF₃SO₃ (1 mol kg⁻¹) and DEGDME-NaCF₃SO₃ (1 mol kg⁻¹). EIS performed by using 10 mV signal amplitude and 0.1 Hz - 0.5 MHz frequency range and F) Voltage profiles of sodium stripping/deposition tests performed in Na/electrolyte/Na symmetrical cells. Electrolytes DME-NaCF₃SO₃ (1 mol kg⁻¹) and DEGDME-NaCF₃SO₃ (1 mol kg⁻¹). Current density 0.1 mA cm⁻², 1 hour of step time limit

the stabilization of the SEI, which is at about 200 Ω for TREG and PEG250, 500 Ω for PEG500 and 100 Ω for TEGDME. Figure 77C shows the lithium interface stability of the LiTFSI added solutions. The TEGDME has a stable trend with a slight increase after 25 days with an average resistance of about 400 Ω . The DEGDME-LiTFSI reveals an increasing trend along the first 15 days until a final stabilization at 500 Ω . Figure 77E reports the sodium interface resistance measurements, as can be noticed the resistance is much lower in comparison with the other solution with lithium salts. Figure 77 B, D and F reports the stripping/deposition test. The TEGDME and TREGDME electrolytes with lithium triflate of figure 77B exhibit a stable trend until 6 days of cycles followed by slight overvoltage increase until cell failure after 13 and 12 days respectively. The other glymes reveal a stable trend along time with an overvoltage of ± 0.01 V, only the PEG250 and PEG500 exhibits an overvoltage of about ± 0.1 V and ± 0.25 V respectively, mainly due to the higher viscosity. Figure 78 reports the linear sweep voltammetry tests performed on the ether based electrolytes. The lithium triflate based electrolytes of Figure 78 A exhibit a stable profile until 4.6 V for TEGDME, PEG250, PEG500 and 4.4 V for DOL:DME, DEGDME and TREGDME, the DME electrolytes is not stable over 2.5V. The LiTFSI based electrolytes shown in Figure 78 B have a stable profile until 4.7 V, has to be noticed the fact that the DEGDME electrolyte is stable until 4.7 V with the LiTFSI addition, until 4.4V with the lithium triflate salt and until 4V with the sodium triflate. However, the sodium triflate has a beneficial effect on the DME electrolyte which is stable until 3.5V instead 2.5V with lithium triflate

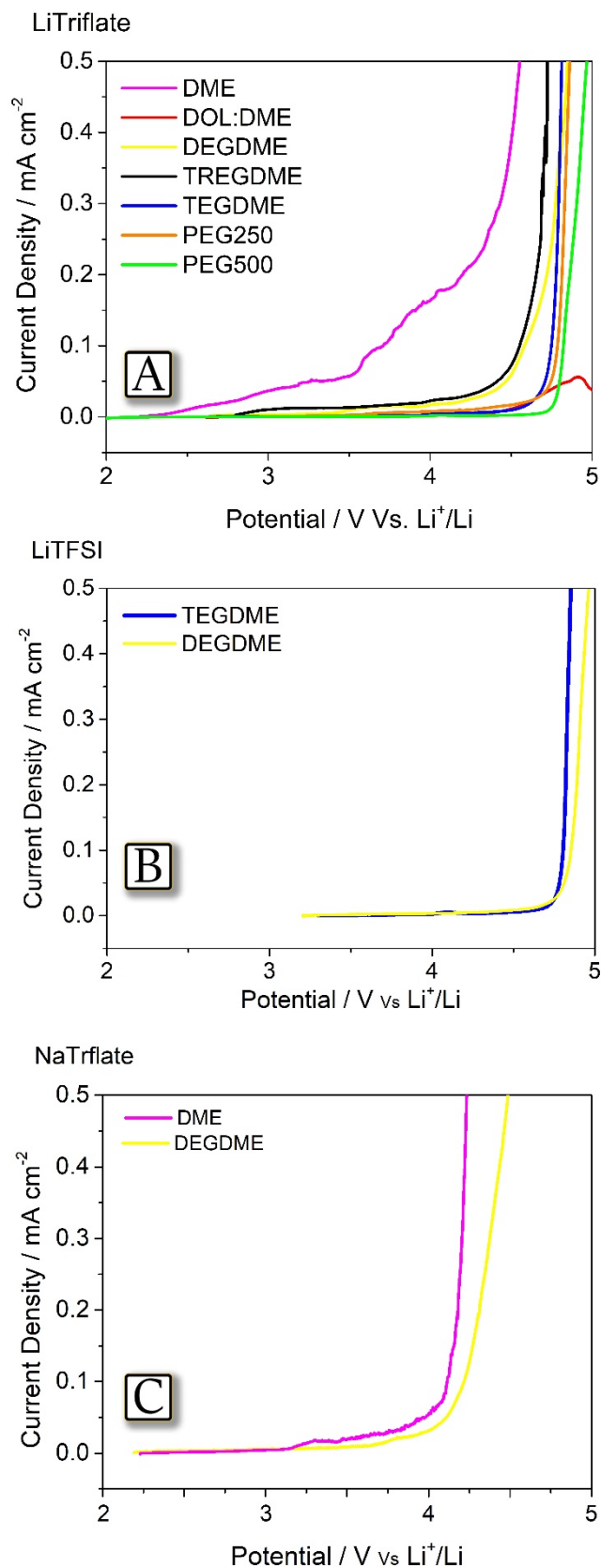


Figure 78 Current vs. potential profile of the linear sweep voltammetry (LSV) performed using the Li/electrolyte/SP cell within the OCV-5.0 V vs. Li/Li⁺ range at 0.1 mV s⁻¹ at room temperature employed for the determination of the electrochemical stability window of the electrolyte with (A) 1 mol kg⁻¹ of lithium triflate, (B) 1 mol kg⁻¹ lithium TFSI and (C) 1 mol kg⁻¹ sodium triflate

Lithium cells

Figure 79 reports the voltage profiles of the olivine cathode materials proposed in the former chapters. The first cycles were performed following the activation procedure in order to ensure the production of a passivation film on the electrodes surface. Figure 79 A, B and C exhibits the characteristic LFP profile with a flat plateau at about 3.5V. The polarization of the cells increases with the increase of the glyme chain length, indeed the PEG500 based cell (Li/ PEG500DME, LiCF_3SO_3 - $\text{LiNO}_3/\text{LiFePO}_4$ of Figure 79A) shows higher polarization toward the TEGDME based (Li /TEGDME, LiCF_3SO_3 - $\text{LiNO}_3/\text{LiFePO}_4$ cell of Figure 79C) and the TREGDME based (Li /TREGDME, LiCF_3SO_3 - $\text{LiNO}_3/\text{LiFePO}_4$ cell of Figure 79B) respectively. However, despite the higher polarization, mainly due to the viscous electrolyte, the cell of figure 79A delivers a specific capacity of about 150 mAh g^{-1} at the current rate of $\text{C}/5$ 34 mA g^{-1} . The TREGDME based cell at the same current rate delivers about 130 mAh g^{-1} and the TEGDME based cell reaches 140 mAh g^{-1} at the current rate of $\text{C}/3$ 56.6 mA g^{-1} . Thus, suggesting the beneficial effect of the chain length on the delivered specific capacity. Figure 79D shows the voltage profile of the $\text{Li}/\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}/\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ at the current rate of $\text{C}/5 = 36 \text{ mA g}^{-1}$ suggesting the glyme electrolyte suitable for high voltage cathode ensuring stable voltage profile delivering 120 mAh g^{-1} . Figure 80 shows the cycling behavior of the cells discussed in Figure 79. Figure 80A (Li/ PEG500DME, LiCF_3SO_3 - $\text{LiNO}_3/\text{LiFePO}_4$) shows the capacity decay from 150 mAh g^{-1} to 125 mAh g^{-1} until the 60th cycle, the coulombic efficiency approaching 100% exhibits a noisy trend along the last cycles.

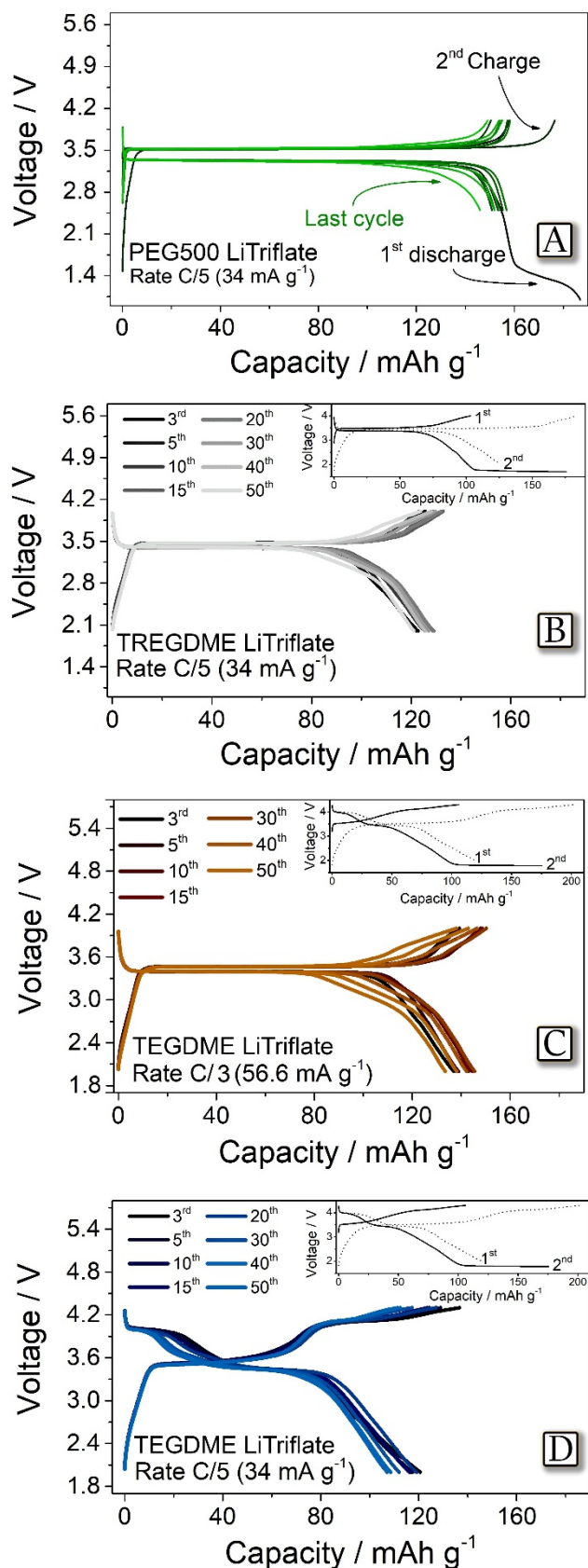


Figure 79 Voltage profile of A) Li/PEG500DME, 1m $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3/\text{LiFePO}_4$ lithium cell cycled at a $\text{C}/5$ rate ($1\text{C} = 170 \text{ mA g}^{-1}$) within 2.5V and 4V voltage range. B) Li/TREG- $\text{LiCF}_3\text{SO}_3\text{-LiNO}_3/\text{LiFePO}_4$ lithium cell cycled at a $\text{C}/5$ rate ($1\text{C} = 170 \text{ mA g}^{-1}$) within 2.5V and 4V voltage range- C) Li /TEGDME, LiCF_3SO_3 - $\text{LiNO}_3/\text{LiFePO}_4$ lithium cell cycled at a $\text{C}/3$ rate ($1\text{C} = 170 \text{ mA g}^{-1}$) within 2.5V and 4V voltage range and D) $\text{Li}/\text{LiCF}_3\text{SO}_3\text{-LiNO}_3\text{-TEGDME}/\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ lithium cell cycled at a $\text{C}/5$ rate ($1\text{C} = 170 \text{ mA g}^{-1}$) within 2.5V and 4.3V voltage range

Figure 80B reports the cycle behavior of the Li /TREGDME, LiCF₃SO₃- LiNO₃/ LiFePO₄ cell at the current rate of C/5, the coulombic efficiency is stable at 99% along cycles, however the cycles trend reveals a slight capacity fading from 130 mAhg⁻¹ to 110 mAhg⁻¹ at 70th cycle. Figure 80C shows the galvanostatic cycling of the Li /TREGDME, LiCF₃SO₃- LiNO₃/ LiFePO₄ cell, the coulombic efficiency is stable at 97% along the cycles, however the specific capacity evidences a constant decrease along the test from 160 mAhg⁻¹ at 10th cycle to 100 mAhg⁻¹ at the 100th cycle. The Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ reported in figure 80D show a stable capacity trend with slight decrease upon cycles from 125 mAh g⁻¹ to 94 mAhg⁻¹ at 100th cycle. The coulombic efficiency is stable at 97% and drops at 94% at 75th cycle. Figure 81 reports the lithium sulfur cell discussed in this work of thesis. Although, the sulfur carbon composite presented are different in terms of carbon morphology, sulfur carbon ratio, preparation pathway, sulfur loading and electrolyte, a briefly comparison overview of all the lithium sulfur cells may shed light on the optimization performed and the performances achieved along this work. Figure 81A report the lithium sulfur cell performed by using MCMB carbon and elemental sulfur treated with high energy ball milling and cycled by using DEGDME LiTriflate LiNO₃ electrolyte in the 1.2V-3.2V voltage range at the current rate of C/20. The voltage profile evolves along the characteristic sulfur processes with a first plateau at about 2.4V and the second one at about 2.1V. The cell exhibits low polarization and high average specific capacity of about 750 mAhg⁻¹ at current rate of C/20. Figure 81B reports the voltage profile of the Li₂S-C-PEO / DOL:DME LiCF₃SO₃ LiNO₃/

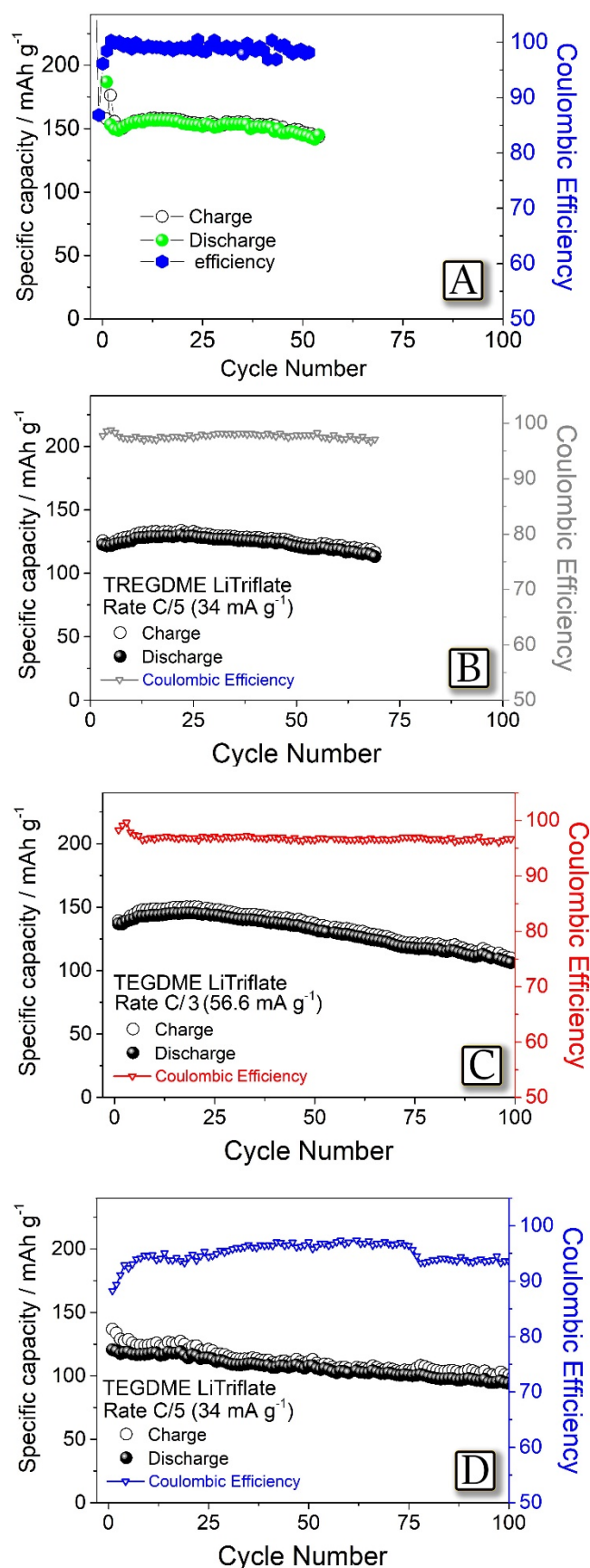


Figure 80 Galvanostatic cycling of A) Li/PEG500DME, 1m LiCF₃SO₃-LiNO₃/LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mA g⁻¹) within 2.5V and 4V voltage range. B) Li/TREGDME, LiCF₃SO₃-LiNO₃/ LiFePO₄ lithium cell cycled at a C/5 rate (1C = 170 mA g⁻¹) within 2.5V and 4V voltage range- C) Li /TEGDME, LiCF₃SO₃- LiNO₃/ LiFePO₄ lithium cell cycled at a C/3 rate (1C = 170 mA g⁻¹) within 2.5V and 4V voltage range and D) Li/LiCF₃SO₃-LiNO₃-TEGDME/LiMn_{0.5}Fe_{0.5}PO₄ lithium cell cycled at a C/5 rate (1C = 170 mA g⁻¹) within 2.5V and 4.3V voltage range

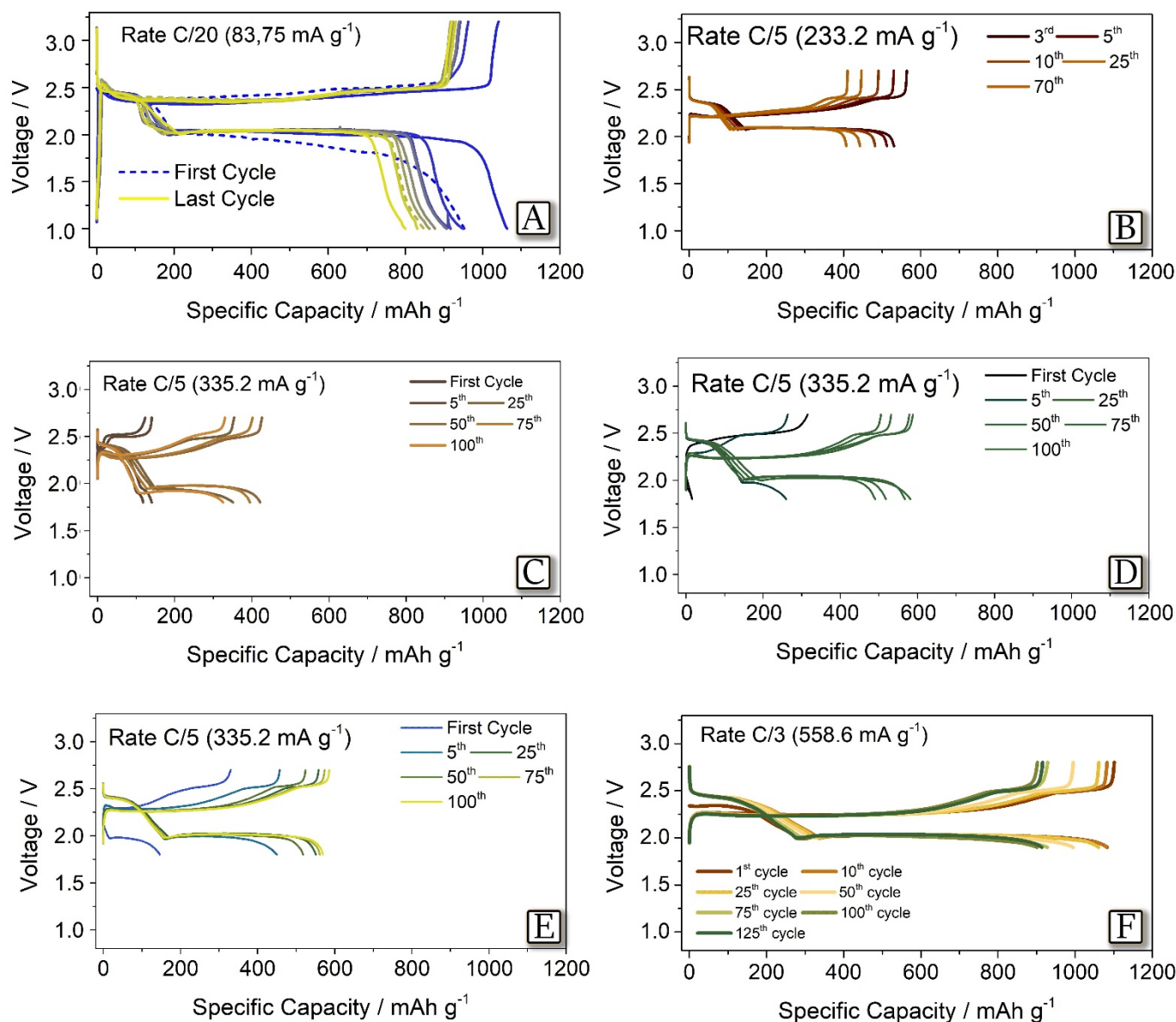


Figure 81 voltage profile of A) Li/DEGDME-LiCF₃SO₃-LiNO₃/S-C coin-cell, current rate C/20 = 83.75 mA g⁻¹, voltage range 1.2–3.2 V. B) of the Li/1m LiCF₃SO₃, 1m LiNO₃, DOL:DME 1:1 v:v/Li₂S-C-PEO cell, voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles), cycling rate C/5 (1C=1166 mA g⁻¹ referred to Li₂S mass), temperature =40°C. C) S-graphite, D) S-MCMB and E) S-CNTs electrodes in lithium cells, easurements performed in 2032 coin-cell using a 1.8 V – 2.7V voltage range at a current rate of C/5 (335 mAh g⁻¹), electrolyte: TEGDME-LiCF₃SO₃ 1mol kg⁻¹. F) a Li/S 2032-coin cell using the DEGDME-LiTFSI-LiNO₃ electrolyte and S-MWCNTs electrode at c-rate of C/3 Sulfur loading 3 mg cm⁻² voltage limits 1.9 V – 2.8 V Temperature 23°C.

lithium metal cell in the voltage range of 1.9V-2.7V at the currant rate of C/5 (1C= 1166 mAhg⁻¹) at 40°C. the cell exhibits low polarization and high columbic efficiency, the specific capacity is about 470 mAhg⁻¹. Figure 81 C, D and E report the sulfur carbon composite cathode materials performed by the same preparation pathway by using different carbon morphology such as graphite, MCMB and MWCNTs respectively. The graphite based cathode exhibits higher polarization with respect the other cathodes, however this effect may be ascribed

to the electrolyte used along the tests. Indeed the cells with MCMB and MWCNT show high polari- zation. The cells in figure 81F shows the galvanos- tatic performances of the optimized sulfur carbon configuration obtained by elemental sulfur and multi walled carbon nanotubes. The cathode mor- phology discussed in the previous chapter reflects the high performance achieved in this system with respect to the other cells. Indeed, the cell is charac- terized by low polarization and the high specific ca- pacity even tough the faster current rate. Figure 82

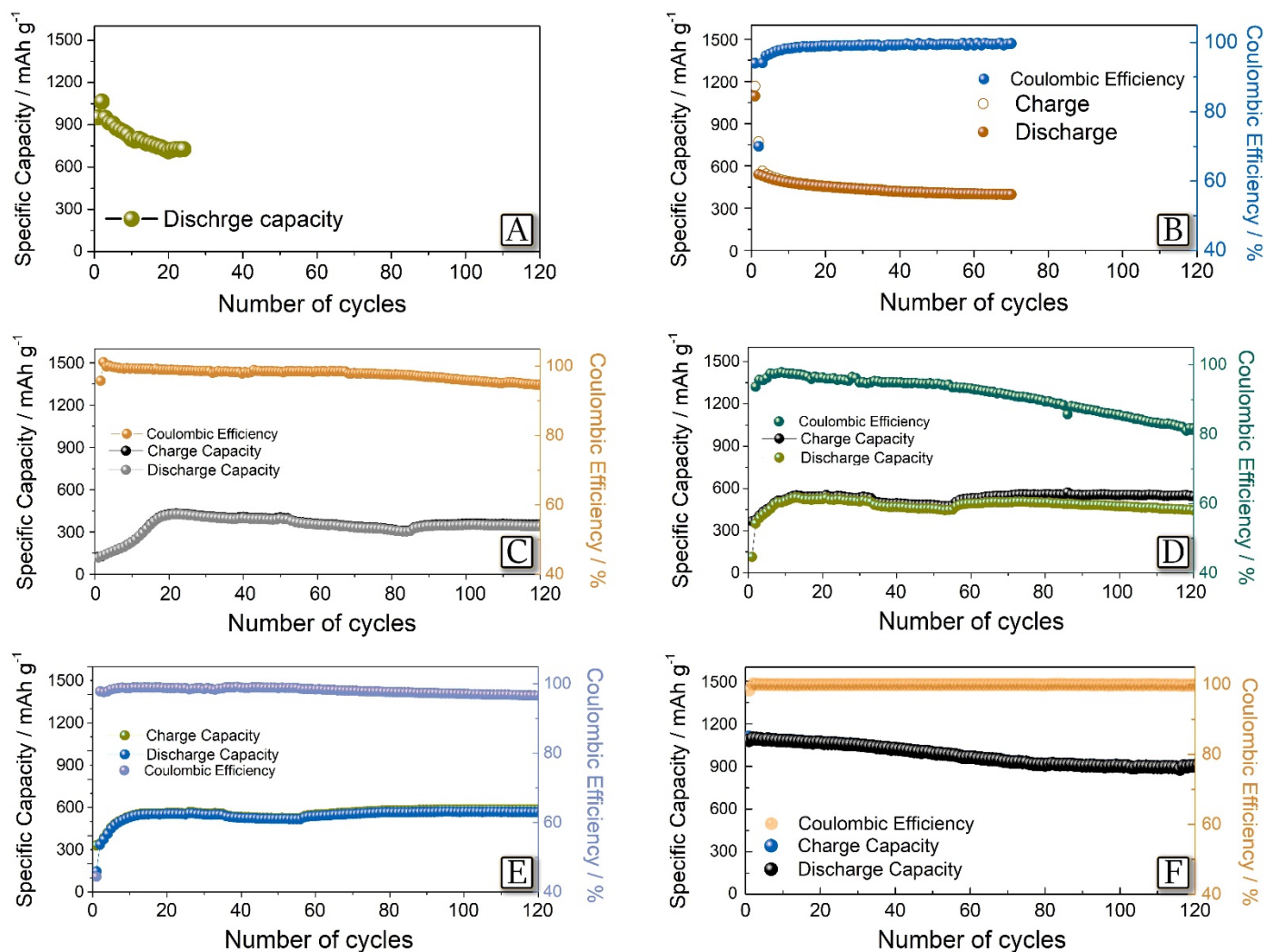


Figure 82 Galvanostatic cycles of A) Li/DEGDME-LiCF₃SO₃-LiNO₃/S-C coin-cell, current rate C/20 = 83.75 mA g⁻¹, voltage range 1.2–3.2 V. B) of the Li/1m LiCF₃SO₃, 1m LiNO₃, DOL:DME 1:1 v:v/Li₂S-C-PEO cell, voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles), cycling rate C/5 (1C=1166 mA g⁻¹ referred to Li₂S mass), temperature =40°C. C) S-graphite, D) S-MCMB and E) S-CNTs electrodes in lithium cells, easurements performed in 2032 coin-cell using a 1.8 V – 2.7V voltage range at a current rate of C/5 (335 mA g⁻¹), electrolyte: TEGDME–LiCF₃SO₃ 1mol kg⁻¹. F) a Li/S 2032-coin cell using the DEGDME-LiTFSI-LiNO₃ electrolyte and S-MWCNTs electrode at c-rate of C/3 Sulfur loading 3 mg cm⁻² voltage limits 1.9 V – 2.8 V Temperature 23°C.

reports the galvanostatic cycles comparison of the lithium sulfur cell. The figure 82A shows the fast capacity decay until cell failure after 20 cycles may be ascribed to the low current rate. Figure 82B shows 60 cycles of the Li₂S-C-PEO based cell, with high columbic efficiency and stable specific capacity profile along cycles. The figures 82C, D and E report the S-graphite, S-MCMB and S-CNTs respectively revealing the same activation trend along the firs 20 cycles, however the specific capacity of the S-graphite based cell decrease upon cycles from 500 mAhg⁻¹ to 300 mAhg⁻¹ and a coulombic efficiency approaching 90% at 120th cycle.

The MCMB-S cell is characterized by a fast columbic efficiency decay until 80% at 120th cycle. The CNT-S evidence a stable trend with specific capacity of about 600 mAhg⁻¹ and a coulombic efficiency of about 95% at 120th cycle. Finally, the S-MWCNTs with DEGDME LiTriflate LiNO₃ of figure 82F shows a stable columbic efficiency of about 100% upon cycles delivering 1100 mAhg⁻¹ of specific capacity at the first cycle and about 900 mAhg⁻¹ at 120th cycle.

Conclusion

Lithium batteries are one of the most important scientific breakthrough of the last decades, their use in revolutionary technologies such as vehicles, medicine, robotic and space, makes this appealing electrochemical system the future of the energy storage devices. Simultaneously, remarkable drawback in terms of safety, and energy density appears following the rise of masses technology spread. In this scenario every person of the modern world is tightly connected with lithium battery. Hence, by the time the life of people is addicted to portable devices an efficient and safe energy system is required. In this thesis I shed light on a new class of electrolyte in order to increase performances and safety of lithium batteries. A deep characterization of the ionic mobility and physical properties were presented, and for the first time was optimized the composition and procedure to use nonflammable electrolytes with commercial cathode materials. Furthermore, the suitability of these electrolyte was evaluated in lithium sulfur cell and the cathode morphology and cell configuration were optimized to ensure high specific capacity and incredible energy density. The outstanding compatibility of the ether based electrolytes were further investigated with lithium sulfur cathode prototype, system based on sodium instead lithium and finally revealing exceptional performances in lithium oxygen battery. Even though further investigations are needed, the promising results herein presented contribute to the brilliant research race forwarding the new generation of energy storage devices

Acknowledgement

Thanks Jusef, you were my professor, but more than that you are my mentor.

You have been a guide during the last years and an inspiration for my future.

Thanks a lot for your patience, your kindness and all the efforts that you provide teaching me how to be a student and may be one day, a scientist as you are.

Thank you professor Greenbaum, accepting me as one of your students, you gifted me one of the best period of my life, and you made me feel one of your group. You and your wonderful team taught me how powerful can be the Physics with the happiness and kindness of Dr. Gobet and the professionalism of Dr. Stallworth. Thanks to you I could experience how amazing your country is.

USA is in my heart.

Thanks to my colleagues that became my friends and doctor at the same time

Peppe Daniele and Kartik.

Thanks to my Family, my Friends in my home town and my Miss

Everything is for you.

List of articles



ACS Appl. Mater. Interfaces DOI: 10.1021/acsami.5b02160
Comparative Study of Ether-Based Electrolytes for Application in
Lithium–Sulfur Battery

Lorenzo Carbone, Mallory Gobet, Jing Peng, Matthew Devany,
Bruno Scrosati, Steve Greenbaum, and Jusef Hassoun

<http://dx.doi.org/10.1021/acsami.5b02160>



Journal of Power Sources DOI: 10.1016/j.jpowsour.2015.08.090
Polyethylene glycol dimethyl ether (PEGDME)-based electrolyte
for lithium metal battery

Lorenzo Carbone, Mallory Gobet, Jing Peng, Matthew Devany,
Bruno Scrosati, Steve Greenbaum, Jusef Hassoun

<http://dx.doi.org/10.1016/j.jpowsour.2015.08.090>



RSC New J. Chem. DOI: 10.1039/c5nj03402g
Insight on the Li₂S electrochemical process in a composite configura-
tion electrode

Lorenzo Carbone, Roberta Verrelli, Mallory Gobet, Jing Peng, Mat-
thew Devany, Bruno Scrosati, Steve Greenbaum and Jusef Hassoun

<http://dx.doi.org/10.1039/c5nj03402g>



Ionics. DOI: 10.1007/s11581-016-1755-5
A low-cost, high-energy polymer lithium-sulfur cell using a compo-
site electrode and polyethylene oxide (PEO) electrolyte

Lorenzo Carbone, Jusef Hassoun

<http://dx.doi.org/10.1007/s11581-016-1755-5>



Electrochimica Acta DOI:10.1016/j.electacta.2016.07.144
Natural Abundance Oxygen-17 NMR Investigation of Lithium Ion
Solvation in Glyme-based Electrolytes

Jing Peng, Lorenzo Carbone, Mallory Gobet, Jusef Hassoun, Mat-
thew Devany, Steven Greenbaum.

<http://dx.doi.org/10.1016/j.electacta.2016.07.144>





Journal of Power Sources DOI: 10.1016/j.jpowsour.2016.09.164
 Rechargeable lithium battery using non-flammable electrolyte
 based on tetraethylene glycol dimethyl ether and olivine cathodes
 Daniele Di Lecce, Lorenzo Carbone, Vincenzo Gancitano, Jusef
 Hassoun

<https://doi.org/10.1016/j.jpowsour.2016.09.164>



CHEMELECTROCHEM DOI: 10.1002/celc.201600586
 Carbon Composites for a High-Energy Lithium-Sulfur Battery with
 a Glyme-Based Electrolyte
 Carbone L. , Jing P. , Marco A. , Mallory G. , Matthew D. , Scrosati
 B. , Steve G. Greenbaum, Jusef H.

<https://doi.org/10.1002/celc.201600586>



Electrochimica Acta DOI: 10.1016/j.electacta.2017.02.007
 Characteristics of glyme electrolytes for sodium battery: nuclear mag
 netic resonance and electrochemical study

Carbone Lorenzo, Steve Munoz, Mallory Gobet, Matthew Devany,
 Steve G. Greenbaum, Jusef Hassoun

<https://doi.org/10.1016/j.electacta.2017.02.007>



Sustainable Energy & Fuels DOI: 10.1039/C6SE00124F
 Lithium sulfur and lithium oxygen batteries: new frontiers of sus-
 tainable energy storage

Carbone Lorenzo, Steve G. Greenbaum, Jusef Hassoun

<http://dx.doi.org/10.1039/C6SE00124F>



ACS Appl. Mater. Interfaces. (Submitted under revision)
 A Simple Approach for Making Viable Safe and High-Performances
 Lithium-Sulfur Battery

Lorenzo Carbone Thomas Coneglian, Mallory Gobet, Stephen
 Munoz, Matthew Devany, Steve Greenbaum, and Jusef Hassounb



Nano Letters (Submitted under revision)
 An Enhanced Lithium Oxygen Battery using Glyme Electrolyte
 and Carbon Nanotubes
 Lorenzo Carbone, Paolo Tomislav Moro, Mallory Gobet, Stephen
 Munoz Matthew Devany Steve Greenbaum , Jusef Hassoun.



Reference

1. Noorden, R. Van. The rechargeable revolution: A better battery. *Nature* **507**, 26–28 (2014).
2. Yoo, H. D., Markevich, E., Salitra, G., Sharon, D. & Aurbach, D. On the challenge of developing advanced technologies for electrochemical energy storage and conversion. *Mater. Today* **17**, 110–121 (2014).
3. Erickson, E. M., Ghanty, C. & Aurbach, D. New horizons for conventional lithium ion battery technology. *J. Phys. Chem. Lett.* **5**, 3313–3324 (2014).
4. Carbone, L., Gobet, M., Peng, J., Devany, M., Scrosati, B., Greenbaum, S. & Hassoun, J. Comparative Study of Ether-Based Electrolytes for Application in Lithium–Sulfur Battery. *ACS Appl. Mater. Interfaces* **7**, 13859–13865 (2015).
5. Devaux, D., Bouchet, R., Glé, D. & Denoyel, R. Mechanism of ion transport in PEO/LiTFSI complexes: Effect of temperature, molecular weight and end groups. *Solid State Ionics* **227**, 119–127 (2012).
6. Henderson, W. a. Glyme-lithium salt phase behavior. *J. Phys. Chem. B* **110**, 13177–13183 (2006).
7. Agostini, M. & Hassoun, J. A lithium-ion sulfur battery using a polymer, polysulfide-added membrane. *Sci. Rep.* **5**, 7591 (2015).
8. Kim, H., Lee, J. T., Magasinski, A., Zhao, K., Liu, Y. & Yushin, G. In Situ TEM Observation of Electrochemical Lithiation of Sulfur Confined within Inner Cylindrical Pores of Carbon Nanotubes. *Adv. Energy Mater.* **5**, 1501306 (2015).
9. Carbone, L. & Hassoun, J. A low-cost, high-energy polymer lithium-sulfur cell using a composite electrode and polyethylene oxide (PEO) electrolyte. *Ionics (Kiel)*. **22**, 2341–2346 (2016).
10. Busche, M. R., Adelhelm, P., Sommer, H., Schneider, H., Leitner, K. & Janek, J. Systematical electrochemical study on the parasitic shuttle-effect in lithium-sulfur-cells at different temperatures and different rates. *J. Power Sources* **259**, 289–299 (2014).
11. Yamada, T., Ito, S., Omoda, R., Watanabe, T., Aihara, Y., Agostini, M., Ulissi, U., Hassoun, J. & Scrosati, B. All Solid-State Lithium-Sulfur Battery Using a Glass-Type P2S5-Li2S Electrolyte: Benefits on Anode Kinetics. *J. Electrochem. Soc.* **162**, A646–A651 (2015).
12. Zhang, J., Dong, Z., Wang, X., Zhao, X., Tu, J., Su, Q. & Du, G. Sulfur nanocrystals anchored graphene composite with highly improved electrochemical performance for lithium-sulfur batteries. *J. Power Sources* **270**, 1–8 (2014).
13. Zhang, H., Liu, C., Zheng, L., Xu, F., Feng, W., Li, H., Huang, X., Armand, M., Nie, J. & Zhou, Z. Lithium bis(fluorosulfonyl)imide/poly(ethylene oxide) polymer electrolyte. *Electrochim. Acta* **133**, 529–538 (2014).
14. Chen, S., Dai, F., Gordin, M. L. & Wang, D. Exceptional electrochemical performance of rechargeable Li-S batteries with a polysulfide-containing electrolyte. *RSC Adv.* **3**, 3540–3543 (2013).
15. Liu, J., Yuan, L., Yuan, K., Li, Z., Hao, Z., Xiang, J. & Huang, Y. SnO₂ as a high-efficiency polysulfide

- trap in lithium–sulfur batteries. *Nanoscale* **8**, 13638–13645 (2016).
16. Hagen, M., Hanselmann, D., Ahlbrecht, K., Maça, R., Gerber, D. & Tübke, J. Lithium-Sulfur Cells: The Gap between the State-of-the-Art and the Requirements for High Energy Battery Cells. *Adv. Energy Mater.* **5**, 1401986 (2015).
 17. Barchasz, C., Molton, F. & Duboc, C. Lithium/Sulfur Cell Discharge Mechanism: An Original Approach for Intermediate Species Identification. *Anal. Chem.* **84**, 3973–3980 (2012).
 18. Diao, Y., Xie, K., Xiong, S. & Hong, X. Analysis of Polysulfide Dissolved in Electrolyte in Discharge-Charge Process of Li-S Battery. *J. Electrochem. Soc.* **159**, A421 (2012).
 19. Li, Z., Huang, Y., Yuan, L., Hao, Z. & Huang, Y. Status and prospects in sulfur-carbon composites as cathode materials for rechargeable lithium-sulfur batteries. *Carbon N. Y.* **92**, 41–63 (2015).
 20. Xiao, J., Hu, J. Z., Chen, H., Vijayakumar, M., Zheng, J., Pan, H., Walter, E. D., Hu, M., Deng, X., Feng, J., Liaw, B. Y., Gu, M., Deng, Z. D., Lu, D., Xu, S., Wang, C. & Liu, J. Following the Transient Reactions in Lithium–Sulfur Batteries Using an In Situ Nuclear Magnetic Resonance Technique. *Nano Lett.* **15**, 3309–3316 (2015).
 21. Gorlin, Y., Patel, M. U. M., Freiberg, A., He, Q., Piana, M., Tromp, M. & Gasteiger, H. A. Understanding the Charging Mechanism of Lithium-Sulfur Batteries Using Spatially Resolved Operando X-Ray Absorption Spectroscopy. *J. Electrochem. Soc.* **163**, A930–A939 (2016).
 22. Aurbach, D., Pollak, E., Elazari, R., Salitra, G., Kelley, C. S. & Affinito, J. On the Surface Chemical Aspects of Very High Energy Density, Rechargeable Li–Sulfur Batteries. *J. Electrochem. Soc.* **156**, A694 (2009).
 23. Waluś, S., Barchasz, C., Bouchet, R., Leprêtre, J. C., Colin, J. F., Martin, J. F., Elkaïm, E., Baehtz, C. & Alloin, F. Lithium/Sulfur Batteries Upon Cycling: Structural Modifications and Species Quantification by in Situ and Operando X-Ray Diffraction Spectroscopy. *Adv. Energy Mater.* **5**, 1500165 (2015).
 24. Waluś, S., Barchasz, C., Colin, J.-F., Martin, J.-F., Elkaïm, E., Leprêtre, J.-C. & Alloin, F. New insight into the working mechanism of lithium-sulfur batteries: in situ and operando X-ray diffraction characterization. *Chem. Commun. (Camb)*. **49**, 7899–901 (2013).
 25. Wang, Q., Zheng, J., Walter, E., Pan, H., Lv, D., Zuo, P., Chen, H., Deng, Z. D., Liaw, B. Y., Yu, X., Yang, X., Zhang, J.-G., Liu, J. & Xiao, J. Direct Observation of Sulfur Radicals as Reaction Media in Lithium Sulfur Batteries. *J. Electrochem. Soc.* **162**, A474–A478 (2015).
 26. Ji, L., Rao, M., Zheng, H., Zhang, L., Li, O. Y. & Duan, W. Graphene Oxide as a Sulfur Immobilizer in High Performance Lithium/Sulfur cells. *J. Am. Chem. Soc.* **133**, 18522–18525 (2011).
 27. Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* **414**, 359–367 (2001).
 28. Wang, Q., Ping, P., Zhao, X., Chu, G., Sun, J. & Chen, C. Thermal runaway caused fire and explosion of lithium ion battery. *J. Power Sources* **208**, 210–224 (2012).
 29. Dahbi, M., Ghamouss, F., Tran-Van, F., Lemordant, D. & Anouti, M. Comparative study of EC/DMC

- LiTFSI and LiPF₆ electrolytes for electrochemical storage. *J. Power Sources* **196**, 9743–9750 (2011).
30. Agostini, M., Scrosati, B. & Hassoun, J. An Advanced Lithium-Ion Sulfur Battery for High Energy Storage. *Adv. Energy Mater.* **5**, 1500481 (2015).
 31. Kim, J., Lee, D. J., Jung, H. G., Sun, Y. K., Hassoun, J. & Scrosati, B. An advanced lithium-sulfur battery. *Adv. Funct. Mater.* **23**, 1076–1080 (2013).
 32. Suo, L., Hu, Y.-S., Li, H., Armand, M. & Chen, L. A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nat. Commun.* **4**, 1481 (2013).
 33. Xu, W., Wang, J., Ding, F., Chen, X., Nasybulin, E., Zhang, Y. & Zhang, J.-G. Lithium metal anodes for rechargeable batteries. *Energy Environ. Sci.* **7**, 513 (2014).
 34. Zheng, G., Lee, S. W., Liang, Z., Lee, H.-W., Yan, K., Yao, H., Wang, H., Li, W., Chu, S. & Cui, Y. Interconnected hollow carbon nanospheres for stable lithium metal anodes. *Nat. Nanotechnol.* **9**, 618–623 (2014).
 35. Rajendran, S., Mahalingam, T. & Kannan, R. Experimental investigations on PAN – PEO hybrid polymer electrolytes. **130**, 143–148 (2000).
 36. Croce, F., Appetecchi, G. B., Persi, L. & Scrosati, B. Nanocomposite polymer electrolytes for lithium batteries. *Nature* **394**, 456–458 (1998).
 37. Croce, F., Curini, R., Martinelli, a., Persi, L., Ronci, F., Scrosati, B. & Caminiti, R. Physical and Chemical Properties of Nanocomposite Polymer Electrolytes. *J. Phys. Chem. B* **103**, 10632–10638 (1999).
 38. Elia, G. A., Bernhard, R. & Hassoun, J. A lithium-ion oxygen battery using a polyethylene glyme electrolyte mixed with an ionic liquid. *RSC Adv.* **5**, 21360–21365 (2015).
 39. Marmorstein, D., Yu, T. H., Striebel, K. a., McLarnon, F. R., Hou, J. & Cairns, E. J. Electrochemical performance of lithium/sulfur cells with three different polymer electrolytes. *J. Power Sources* **89**, 219–226 (2000).
 40. Bernhard, R., Latini, A., Panero, S., Scrosati, B. & Hassoun, J. Poly(ethyleneglycol)dimethylether–lithium bis(trifluoromethanesulfonyl)imide, PEG500DME–LiTFSI, as high viscosity electrolyte for lithium ion batteries. *J. Power Sources* **226**, 329–333 (2013).
 41. Hassoun, J., Kim, J., Lee, D. J., Jung, H. G., Lee, S. M., Sun, Y. K. & Scrosati, B. A contribution to the progress of high energy batteries: A metal-free, lithium-ion, silicon-sulfur battery. *J. Power Sources* **202**, 308–313 (2012).
 42. Aurbach, D., Gamolsky, K., Markovsky, B., Gofer, Y., Schmidt, M. & Heider, U. On the use of vinylene carbonate (VC) as an additive to electrolyte solutions for Li-ion batteries. *Electrochim. Acta* **47**, 1423–1439 (2002).
 43. Rosenman, A., Elazari, R., Salitra, G., Markevich, E., Aurbach, D. & Garsuch, A. The Effect of Interactions and Reduction Products of LiNO₃, the Anti-Shuttle Agent, in Li-S Battery Systems. *J. Electrochem. Soc.* **162**, A470–A473 (2015).
 44. Xiong, S., Xie, K., Diao, Y. & Hong, X. Characterization of the solid electrolyte interphase on lithium

- anode for preventing the shuttle mechanism in lithium-sulfur batteries. *J. Power Sources* **246**, 840–845 (2014).
45. Profatilova, I. A., Stock, C., Schmitz, A., Passerini, S. & Winter, M. Enhanced thermal stability of a lithiated nano-silicon electrode by fluoroethylene carbonate and vinylene carbonate. *J. Power Sources* **222**, 140–149 (2013).
 46. Elazari, R., Salitra, G., Gershtinsky, G., Garsuch, A., Panchenko, a. & Aurbach, D. Li Ion Cells Comprising Lithiated Columnar Silicon Film Anodes, TiS_2 Cathodes and Fluoroethylene Carbonate (FEC) as a Critically Important Component. *J. Electrochem. Soc.* **159**, A1440–A1445 (2012).
 47. Barchasz, C., Lepretre, J.-C., Patoux, S. & Alloin, F. Revisiting TEGDME/DIOX Binary Electrolytes for Lithium/Sulfur Batteries: Importance of Solvation Ability and Additives. *J. Electrochem. Soc.* **160**, A430–A436 (2013).
 48. Xiong, S., Xie, K., Diao, Y. & Hong, X. Properties of surface film on lithium anode with LiNO_3 as lithium salt in electrolyte solution for lithium-sulfur batteries. *Electrochim. Acta* **83**, 78–86 (2012).
 49. Li, W., Yao, H., Yan, K., Zheng, G., Liang, Z., Chiang, Y.-M. & Cui, Y. The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth. *Nat. Commun.* **6**, 7436 (2015).
 50. Zhang, S. S. Role of LiNO_3 in rechargeable lithium/sulfur battery. *Electrochim. Acta* **70**, 344–348 (2012).
 51. Peng, J., Carbone, L., Gobet, M., Hassoun, J., Devany, M. & Greenbaum, S. Natural Abundance Oxygen-17 NMR Investigation of Lithium Ion Solvation in Glyme-based Electrolytes. *Electrochim. Acta* **213**, 606–612 (2016).
 52. Carbone, L., Gobet, M., Peng, J., Devany, M., Scrosati, B., Greenbaum, S. & Hassoun, J. Polyethylene glycol dimethyl ether (PEGDME)-based electrolyte for lithium metal battery. *J. Power Sources* **299**, 460–464 (2015).
 53. Carbone, L., Di Lecce, D., Gobet, M., Munoz, S., Devany, M., Greenbaum, S. & Hassoun, J. Relevant Features of a Triethylene Glycol Dimethyl Ether-Based Electrolyte for Application in Lithium Battery. *ACS Appl. Mater. Interfaces* **9**, 17085–17095 (2017).
 54. Di Lecce, D., Carbone, L., Gancitano, V. & Hassoun, J. Rechargeable lithium battery using non-flammable electrolyte based on tetraethylene glycol dimethyl ether and olivine cathodes. *J. Power Sources* **334**, 146–153 (2016).
 55. Carbone, L., Peng, J., Agostini, M., Gobet, M., Devany, M., Scrosati, B., Greenbaum, S. & Hassoun, J. Carbon Composites for a High-Energy Lithium–Sulfur Battery with a Glyme-Based Electrolyte. *ChemElectroChem* **4**, 209–215 (2017).
 56. Carbone, L., Munoz, S., Gobet, M., Devany, M., Greenbaum, S. & Hassoun, J. Characteristics of glyme electrolytes for sodium battery: nuclear magnetic resonance and electrochemical study. *Electrochim. Acta* **231**, 223–229 (2017).
 57. Bérardin, M.-T., Vauthier, E. & Fliszár, S. Charge distributions and chemical effects. XXVI. Relationships between nuclear magnetic resonance shifts and atomic charges for ^{17}O nuclei in ethers

- and carbonyl compounds. *Can. J. Chem.* **60**, 106–110 (1982).
58. Smith, V. H. Theoretical Determination and Analysis of Electronic Charge Distributions. *Phys. Scr.* **15**, 147–162 (1977).
 59. St-Jacques, M., Vaziri, C., Frenette, D. A., Goursot, A. & Fliszár, S. Conformations of Methylated Cycloheptanones. *J. Am. Chem. Soc.* **98**, 5759–5765 (1976).
 60. Fliszár, S. Charge distributions and Chemical effects. XII. A unifying concept. *Can. J. Chem.* **54**, 2839–2846 (1976).
 61. Delseth, C. & Kintzinger, J.-P. Résonance magnétique nucléaire de ^{13}C et ^{17}O d'éthers aliphatiques. Effets γ entre les atomes d'oxygène et de carbone. *Helv. Chim. Acta* **61**, 1327–1334 (1978).
 62. Tobishima, S., Morimoto, H., Aoki, M., Saito, Y., Inose, T., Fukumoto, T. & Kuryu, T. Glyme-based nonaqueous electrolytes for rechargeable lithium cells. *Electrochim. Acta* **49**, 979–987 (2004).
 63. Bogle, X., Vazquez, R., Greenbaum, S., Cresce, A. V. W. & Xu, K. Understanding Li + –Solvent Interaction in Nonaqueous Carbonate Electrolytes with ^{17}O NMR. *J. Phys. Chem. Lett.* **4**, 1664–1668 (2013).
 64. Huang, W., Frech, R. & Wheeler, R. A. Molecular structures and normal vibrations of trifluoromethane sulfonate (CF_3SO_3^-) and its lithium ion pairs and aggregates. *J. Phys. Chem.* **98**, 100–110 (1994).
 65. Dependence of ionic association on polymer chain length in poly(ethylene oxide)-lithium triflate complexes. *Polymer (Guildf)*. **35**, 235–242 (1994).
 66. Chrétien, F., Jones, J., Damas, C., Lemordant, D., Willmann, P. & Anouti, M. Impact of Solid Electrolyte Interphase lithium salts on cycling ability of Li-ion battery: Beneficial effect of glymes additives. *J. Power Sources* **248**, 969–977 (2014).
 67. Bernhard, R., Latini, A., Panero, S., Scrosati, B. & Hassoun, J. Poly(ethyleneglycol)dimethylether–lithium bis(trifluoromethanesulfonyl)imide, PEG500DME–LiTFSI, as high viscosity electrolyte for lithium ion batteries. *J. Power Sources* **226**, 329–333 (2013).
 68. Frömling, T., Kunze, M., Schönhoff, M., Sundermeyer, J. & Roling, B. Enhanced lithium transference numbers in ionic liquid electrolytes. *J. Phys. Chem. B* **112**, 12985–12990 (2008).
 69. Zugmann, S., Fleischmann, M., Amereller, M., Gschwind, R. M., Wiemhöfer, H. D. & Gores, H. J. Measurement of transference numbers for lithium ion electrolytes via four different methods, a comparative study. *Electrochim. Acta* **56**, 3926–3933 (2011).
 70. Saito, Y., Yamamoto, H., Nakamura, O., Kageyama, H., Ishikawa, H., Miyoshi, T. & Matsuoka, M. Determination of ionic self-diffusion coefficients of lithium electrolytes using the pulsed field gradient NMR. *J. Power Sources* **81–82**, 772–776 (1999).
 71. Lee, D. J., Agostini, M., Park, J. W., Sun, Y. K., Hassoun, J. & Scrosati, B. Progress in lithium-sulfur batteries: The effective role of a polysulfide-added electrolyte as buffer to prevent cathode dissolution. *ChemSusChem* **6**, 2245–2248 (2013).
 72. Mikhaylik, Y. V. & Akridge, J. R. Polysulfide Shuttle Study in the Li/S Battery System. *J. Electrochem. Soc.* **151**, A1969 (2004).

73. Bruce, P. G., Freunberger, S. a., Hardwick, L. J. & Tarascon, J.-M. Li–O₂ and Li–S batteries with high energy storage. *Nat. Mater.* **11**, 172–172 (2011).
74. Agostini, M., Lee, D. J., Scrosati, B., Sun, Y. K. & Hassoun, J. Characteristics of Li₂S₈-tetraglyme catholyte in a semi-liquid lithium-sulfur battery. *J. Power Sources* **265**, 14–19 (2014).
75. Li, W., Yao, H., Yan, K., Zheng, G., Liang, Z., Chiang, Y.-M. & Cui, Y. The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth. *Nature communications* **6**, 7436 (2015).
76. Zhang, S. S. Effect of Discharge Cutoff Voltage on Reversibility of Lithium/Sulfur Batteries with LiNO₃-Contained Electrolyte. *J. Electrochem. Soc.* **159**, A920–A923 (2012).
77. Farnicola, a., Weise, F. C., Greenbaum, S. G., Kagimoto, J., Scrosati, B. & Soletto, a. Lithium-Ion-Conducting Electrolytes: From an Ionic Liquid to the Polymer Membrane. *J. Electrochem. Soc.* **156**, A514 (2009).
78. Abbrent, S. & Greenbaum, S. Recent progress in NMR spectroscopy of polymer electrolytes for lithium batteries. *Curr. Opin. Colloid Interface Sci.* **18**, 228–244 (2013).
79. Greenbaum, S. G., Pak, Y. S., Wintersgill, M. C., Fontanella, J. J., Schultz, J. W. & Andeen, C. G. NMR, DSC, DMA, and High Pressure Electrical Conductivity Studies in PPO Complexed with Sodium Perchlorate. *Status Solidi A Surf. Sci. This J. J. E. Jones, This J. Solid-State Electron. M. P. Seah, Vac. Crit. Rev. Solid State Sci. This J.* **135**, 530–705 (1984).
80. Lee, D. J., Hassoun, J., Panero, S., Sun, Y. K. & Scrosati, B. A tetraethylene glycol dimethylether-lithium bis(oxalate)borate (TEGDME-LiBOB) electrolyte for advanced lithium ion batteries. *Electrochem. commun.* **14**, 43–46 (2012).
81. Di Lecce, D. & Hassoun, J. Lithium Transport Properties in LiMn_{1-α}Fe_αPO₄ Olivine Cathodes. *The Journal of Physical Chemistry C* 150901100952007 (2015). doi:10.1021/acs.jpcc.5b06727
82. Lee, D.-J., Park, J.-W., Hasa, I., Sun, Y.-K., Scrosati, B. & Hassoun, J. Alternative materials for sodium ion–sulphur batteries. *J. Mater. Chem. A* **1**, 5256 (2013).
83. Di Lecce, D., Fasciani, C., Scrosati, B. & Hassoun, J. A Gel-Polymer Sn-C/LiMn_{0.5}Fe_{0.5}PO₄ Battery Using a Fluorine-Free Salt. *ACS Appl. Mater. Interfaces* **7**, 21198–207 (2015).
84. Bogle, X., Vazquez, R., Greenbaum, S., Cresce, A. von W. & Xu, K. Understanding Li⁺–Solvent Interaction in Nonaqueous Carbonate Electrolytes with ¹⁷O NMR. *J. Phys. Chem. Lett.* **4**, 1664–1668 (2013).
85. Padhi, A. K., Nanjundaswamy, K. S. & Goodenough, J. B. Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **144**, 1188–1194 (1997).
86. Goodenough, J. B. & Kim, Y. Challenges for rechargeable Li batteries. *Chem. Mater.* **22**, 587–603 (2010).
87. Vetter, J., Novák, P., Wagner, M. R., Veit, C., Müller, K. C., Besenhard, J. O., Winter, M., Wohlfahrt-Mehrens, M., Vogler, C. & Hammouche, A. Ageing mechanisms in lithium-ion batteries. *J. Power Sources* **147**, 269–281 (2005).

88. Martha, S. K., Markovsky, B., Grinblat, J., Gofer, Y., Haik, O., Zinigrad, E., Aurbach, D., Drezen, T., Wang, D., Deghenghi, G. & Exnar, I. LiMnPO₄ as an Advanced Cathode Material for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **156**, A541 (2009).
89. Aurbach, D. Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries. *J. Power Sources* **89**, 206–218 (2000).
90. Franceschetti, D. R. Interpretation of Finite-Length-Warburg-Type Impedances in Supported and Unsupported Electrochemical Cells with Kinetically Reversible Electrodes. *J. Electrochem. Soc.* **138**, 1368 (1991).
91. Croce, F., Deptula, A., Lada, W., Marassi, R., Olczak, T. & Ronci, F. Electrochemical characterization of a lithiated mixed nickel-cobalt oxide (LiNi_{0.5}Co_{0.5}O₂) prepared by sol-gel process. *Ionics (Kiel)*. **3**, 390–395 (1997).
92. Aravindan, V., Gnanaraj, J., Lee, Y.-S. & Madhavi, S. LiMnPO₄ – A next generation cathode material for lithium-ion batteries. *J. Mater. Chem. A* **1**, 3518–3539 (2013).
93. Yamada, A., Chung, S. C. & Hinokuma, K. Optimized LiFePO₄ for Lithium Battery Cathodes. *J. Electrochem. Soc.* **148**, A224 (2001).
94. Di Lecce, D., Fasciani, C., Scrosati, B. & Hassoun, J. A Gel–Polymer Sn–C/LiMn_{0.5}Fe_{0.5}PO₄ Battery Using a Fluorine-Free Salt. *ACS Appl. Mater. Interfaces* **7**, 21198–21207 (2015).
95. Chen, J., Vacchio, M. J., Wang, S., Chernova, N., Zavalij, P. Y. & Whittingham, M. S. The hydrothermal synthesis and characterization of olivines and related compounds for electrochemical applications. *Solid State Ionics* **178**, 1676–1693 (2008).
96. Murugan, a. V., Muraliganth, T. & Manthiram, a. Comparison of microwave assisted solvothermal and hydrothermal syntheses of LiFePO₄/C nanocomposite cathodes for lithium ion batteries. *J. Phys. Chem. C* **112**, 14665–14671 (2008).
97. Sun, Y. K., Oh, S. M., Park, H. K. & Scrosati, B. Micrometer-sized, nanoporous, high-volumetric-capacity LiMn_{0.85}Fe_{0.15}PO₄ cathode material for rechargeable lithium-ion batteries. *Adv. Mater.* **23**, 5050–5054 (2011).
98. Oh, S.-M., Myung, S.-T., Park, J. B., Scrosati, B., Amine, K. & Sun, Y.-K. Double-structured LiMn_(0.85)Fe_(0.15)PO₄ coordinated with LiFePO₄ for rechargeable lithium batteries. *Angew. Chemie Int. Ed.* **51**, 1853–6 (2012).
99. Saravanan, K., Ramar, V., Balaya, P. & Vittal, J. J. Li(MnxFe_{1-x})PO₄/C (x = 0.5, 0.75 and 1) nanoplates for lithium storage application. *J. Mater. Chem.* **21**, 14925 (2011).
100. Lu, Z., Chen, H., Robert, R., Zhu, B. Y. X., Deng, J., Wu, L., Chung, C. Y. & Grey, C. P. Citric Acid- and Ammonium-Mediated Morphological Transformations of Olivine LiFePO₄ Particles. *Chem. Mater.* **23**, 2848–2859 (2011).
101. Di Lecce, D., Brescia, R., Scarpellini, A., Prato, M. & Hassoun, J. A High Voltage Olivine Cathode for Application in Lithium-Ion Batteries. *ChemSusChem* **9**, 223–230 (2016).
102. Yang, S., Hu, M., Xi, L., Ma, R., Dong, Y. & Chung, C. Y. Solvothermal Synthesis of Monodisperse

- LiFePO₄ Micro Hollow Spheres as High Performance Cathode Material for Lithium Ion Batteries. *ACS Appl. Mater. Interfaces* **5**, 8961–8967 (2013).
103. Zheng, J. M., Wu, X. B. & Yang, Y. A comparison of preparation method on the electrochemical performance of cathode material Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ for lithium ion battery. *Electrochim. Acta* **56**, 3071–3078 (2011).
 104. Zaghib, K., Guerfi, A., Hovington, P., Vijh, A., Trudeau, M., Mauger, A., Goodenough, J. B. & Julien, C. M. Review and analysis of nanostructured olivine-based lithium rechargeable batteries: Status and trends. *J. Power Sources* **232**, 357–369 (2013).
 105. Di Lecce, D. & Hassoun, J. Lithium Transport Properties in LiMn_{1- α} Fe α PO₄ Olivine Cathodes. *J. Phys. Chem. C* **119**, 20855–20863 (2015).
 106. Arbizzani, C., Gabrielli, G. & Mastragostino, M. Thermal stability and flammability of electrolytes for lithium-ion batteries. *J. Power Sources* **196**, 4801–4805 (2011).
 107. Hassoun, J., Reale, P., Panero, S., Scrosati, B., Wachtler, M., Fleischhammer, M., Kasper, M. & Wohlfahrt-Mehrens, M. Determination of the safety level of an advanced lithium ion battery having a nanostructured Sn-C anode, a high voltage LiNi_{0.5}Mn_{1.5}O₄ cathode, and a polyvinylidene fluoride-based gel electrolyte. *Electrochim. Acta* **55**, 4194–4200 (2010).
 108. Lee, K. T. & Cho, J. Roles of nanosize in lithium reactive nanomaterials for lithium ion batteries. *Nano Today* **6**, 28–41 (2011).
 109. Xu, K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem. Rev.* **104**, 4303–4417 (2004).
 110. Suarez, S., Jayakody, J., Abbrent, S., Greenbaum, S. G., Shin, J. H. & Passerini, S. A multinuclear NMR study of ion transport in P(EO)_nLiBETI complexes. *Solid State Ionics* **176**, 1113–1121 (2005).
 111. Carbone, L., Verrelli, R., Gobet, M., Peng, J., Devany, M., Scrosati, B., Greenbaum, S. & Hassoun, J. Insight on the Li₂S electrochemical process in a composite configuration electrode. *New J. Chem.* **40**, 2935–2943 (2016).
 112. Ding, M. S., Xu, K., Zhang, S. S., Amine, K., Henriksen, G. L. & Jow, T. R. Change of Conductivity with Salt Content, Solvent Composition, and Temperature for Electrolytes of LiPF₆ in Ethylene Carbonate-Ethyl Methyl Carbonate. *J. Electrochem. Soc.* **148**, A1196 (2001).
 113. Valoën, L. O. & Reimers, J. N. Transport Properties of LiPF₆-Based Li-Ion Battery Electrolytes. *J. Electrochem. Soc.* **152**, A882 (2005).
 114. Wang, J. & Sun, X. Understanding and recent development of carbon coating on LiFePO₄ cathode materials for lithium-ion batteries. *Energy Environ. Sci.* **5**, 5163 (2012).
 115. Zhu, J., Fiore, J., Li, D., Kinsinger, N. M., Wang, Q., DiMasi, E., Guo, J. & Kisailus, D. Solvothermal Synthesis, Development, and Performance of LiFePO₄ Nanostructures. *Cryst. Growth Des.* **13**, 4659–4666 (2013).
 116. Yang, S., Zhou, X., Zhang, J. & Liu, Z. Morphology-controlled solvothermal synthesis of LiFePO₄ as a cathode material for lithium-ion batteries. *J. Mater. Chem.* **20**, 8086 (2010).

117. Rui, X., Zhao, X., Lu, Z., Tan, H., Sim, D., Hng, H. H., Yazami, R., Lim, T. M. & Yan, Q. Olivine-type nanosheets for lithium ion battery cathodes. *ACS Nano* **7**, 5637–5646 (2013).
118. Wang, Y., Zhu, B., Wang, Y. & Wang, F. Solvothermal synthesis of LiFePO₄ nanorods as high-performance cathode materials for lithium ion batteries. *Ceram. Int.* **42**, 10297–10303 (2016).
119. Barchasz, C., Leprêtre, J. C., Alloin, F. & Patoux, S. New insights into the limiting parameters of the Li/S rechargeable cell. *J. Power Sources* **199**, 322–330 (2012).
120. Zu, C., Li, L., Qie, L. & Manthiram, A. Expandable-graphite-derived graphene for next-generation battery chemistries. *J. Power Sources* **284**, 60–67 (2015).
121. Zhang, S., Li, N., Lu, H., Zheng, J., Zang, R. & Cao, J. Improving lithium-sulfur battery performance via a carbon-coating layer derived from the hydrothermal carbonization of glucose. *RSC Adv.* **5**, 50983–50988 (2015).
122. Jia-Jia, C., Xin, J., Qiu-Jie, S., Chong, W., Qian, Z., Ming-Sen, Z. & Quan-Feng, D. The preparation of nano-sulfur/MWCNTs and its electrochemical performance. *Electrochim. Acta* **55**, 8062–8066 (2010).
123. Wang, B., Wen, Y., Ye, D., Yu, H., Sun, B., Wang, G., Hulicova-Jurcakova, D. & Wang, L. Dual protection of sulfur by carbon nanospheres and graphene sheets for lithium-sulfur batteries. *Chem. - A Eur. J.* **20**, 5224–5230 (2014).
124. Zhao, Z., Qin, D., Wang, S., Chen, G. & Li, Z. Fabrication of High Conductive S/C Cathode by Sulfur Infiltration into Hierarchical Porous Carbon/Carbon Fiber Weave-Structured Materials via Vapor-Melting Method. *Electrochim. Acta* **127**, 123–131 (2014).
125. Li, S., Xie, M., Liu, J., Wang, H. & Yan, H. Layer Structured Sulfur/Expanded Graphite Composite as Cathode for Lithium Battery. *Electrochem. Solid-State Lett.* **14**, A105 (2011).
126. Yin, L., Wang, J., Yang, J. & Nuli, Y. A novel pyrolyzed polyacrylonitrile-sulfur@MWCNT composite cathode material for high-rate rechargeable lithium/sulfur batteries. *J. Mater. Chem.* **21**, 6807 (2011).
127. Liang, J., Sun, Z. H., Li, F. & Cheng, H. M. Carbon materials for Li-S batteries: Functional evolution and performance improvement. *Energy Storage Mater.* **2**, 76–106 (2016).
128. Wang, J. G., Xie, K. & Wei, B. Advanced engineering of nanostructured carbons for lithium-sulfur batteries. *Nano Energy* **15**, 413–444 (2015).
129. Zhou, G., Yin, L. C., Wang, D. W., Li, L., Pei, S., Gentle, I. R., Li, F. & Cheng, H. M. Fibrous hybrid of graphene and sulfur nanocrystals for high-performance lithium-sulfur batteries. *ACS Nano* **7**, 5367–5375 (2013).
130. Sohn, H., Gordin, M. L., Xu, T., Chen, S., Lv, D., Song, J., Manivannan, A. & Wang, D. Porous spherical carbon/sulfur nanocomposites by aerosol-assisted synthesis: The effect of pore structure and morphology on their electrochemical performance as lithium/sulfur battery cathodes. *ACS Appl. Mater. Interfaces* **6**, 7596–7606 (2014).
131. Sang-Eun, C., Ki-Seok, K., Ji-Hoon, C., Sun-Wook, K., Eog-Yong, C. & Hee-Tak, K. 082 Rechargeable Lithium Sulfur Battery. *J. Electrochem. Soc.* **150**, A796 (2003).

132. Manthiram, A., Fu, Y., Chung, S., Zu, C. & Su, Y. Rechargeable Lithium – Sulfur Batteries. *Chemical Reviews* **114**, 11751–87 (2014).
133. Li, C., Ward, A. L., Doris, S. E., Pascal, T. A., Prendergast, D. & Helms, B. A. Polysulfide-Blocking Microporous Polymer Membrane Tailored for Hybrid Li-Sulfur Flow Batteries. *Nano Lett.* **15**, 5724–5729 (2015).
134. Zhang, S. S. Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions. *J. Power Sources* **231**, 153–162 (2013).
135. Demir-Cakan, R., Morcrette, M., Gangulibabu, Guéguen, A., Dedryvère, R. & Tarascon, J. Li-S batteries: simple approaches for superior performance. *Energy Environ. Sci.* **6**, 176 (2013).
136. Lee, J. T., Zhao, Y., Kim, H., Cho, W. Il & Yushin, G. Sulfur infiltrated activated carbon cathodes for lithium sulfur cells: The combined effects of pore size distribution and electrolyte molarity. *J. Power Sources* **248**, 752–761 (2014).
137. Ding, N., Chien, S. W., Hor, T. S. A., Liu, Z. & Zong, Y. Key parameters in design of lithium sulfur batteries. *J. Power Sources* **269**, 111–116 (2014).
138. Xiao, L., Cao, Y., Xiao, J., Schwenzer, B., Engelhard, M. H., Saraf, L. V., Nie, Z., Exarhos, G. J. & Liu, J. A soft approach to encapsulate sulfur: Polyaniline nanotubes for lithium-sulfur batteries with long cycle life. *Adv. Mater.* **24**, 1176–1181 (2012).
139. Su, Y. S. & Manthiram, A. Lithium-sulphur batteries with a microporous carbon paper as a bifunctional interlayer. *Nat Commun* **3**, 1166 (2012).
140. Hwang, J. Y., Kim, H. M., Lee, S. K., Lee, J. H., Abouimrane, A., Khaleel, M. A., Belharouak, I., Manthiram, A. & Sun, Y. K. High-Energy, High-Rate, Lithium-Sulfur Batteries: Synergetic Effect of Hollow TiO₂-Webbed Carbon Nanotubes and a Dual Functional Carbon-Paper Interlayer. *Adv. Energy Mater.* **6**, 1–7 (2016).
141. Kim, M. S., Ma, L., Choudhury, S., Moganty, S. S., Wei, S. & Archer, L. A. Fabricating multifunctional nanoparticle membranes by a fast layer-by-layer Langmuir–Blodgett process: application in lithium–sulfur batteries. *J. Mater. Chem. A* **4**, 14709–14719 (2016).
142. Carbone, L., Peng, J., Agostini, M., Gobet, M., Devany, M., Scrosati, B., Greenbaum, S. & Hassoun, J. Carbon Composites for a High-Energy Lithium-Sulfur Battery with a Glyme-Based Electrolyte. *ChemElectroChem* **4**, 209–215 (2017).
143. Tao, X., Wang, J., Liu, C., Wang, H., Yao, H., Zheng, G., Seh, Z. W., Cai, Q., Li, W., Zhou, G., Zu, C. & Cui, Y. Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium–sulfur battery design. *Nat. Commun.* **7**, 11203 (2016).
144. Park, J., Hassoun, J., Jung, H., Kim, H., Yoon, C. S., Oh, I., Scrosati, B. & Sun, Y. Influence of Temperature on Lithium – Oxygen Battery Behavior. *Nano Lett.* **13**, 2971–2975 (2013).
145. Gireaud, L., Grugeon, S., Laruelle, S., Yrieix, B. & Tarascon, J. M. Lithium metal stripping/plating mechanisms studies: A metallurgical approach. *Electrochem. commun.* **8**, 1639–1649 (2006).
146. Scrosati, B. & Garche, J. Lithium batteries: Status, prospects and future. *J. Power Sources* **195**, 2419–

2430 (2010).

147. Waluś, S., Barchasz, C., Bouchet, R., Leprêtre, J.-C., Colin, J.-F., Martin, J.-F., Elkaïm, E., Baehitz, C. & Alloin, F. Lithium/Sulfur Batteries Upon Cycling: Structural Modifications and Species Quantification by In Situ and Operando X-Ray Diffraction Spectroscopy. *Adv. Energy Mater.* **5**, 1500165 (2015).
148. Rui, X. H., Ding, N., Liu, J., Li, C. & Chen, C. H. Analysis of the chemical diffusion coefficient of lithium ions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material. *Electrochim. Acta* **55**, 2384–2390 (2010).
149. Xie, J., Imanishi, N., Zhang, T., Hirano, A., Takeda, Y. & Yamamoto, O. Li-ion diffusion kinetics in LiFePO_4 thin film prepared by radio frequency magnetron sputtering. *Electrochim. Acta* **54**, 4631–4637 (2009).
150. Saraceno, R. A., Riding, G. H., Allcock, H. R. & Ewing, A. G. Electronic properties and redox conduction of ferrocene-substituted high polymeric phosphazenes. *J. Am. Chem. Soc.* **110**, 7254–7255 (1988).
151. Tang, K., Yu, X., Sun, J., Li, H. & Huang, X. Kinetic analysis on LiFePO_4 thin films by CV, GITT, and EIS. *Electrochim. Acta* **56**, 4869–4875 (2011).
152. Di Lecce, D., Brescia, R., Scarpellini, A., Prato, M. & Hassoun, J. A High Voltage Olivine Cathode for Application in Lithium-Ion Batteries. *ChemSusChem* **9**, 223–230 (2016).
153. Qie, L., Zu, C. & Manthiram, A. A High Energy Lithium-Sulfur Battery with Ultrahigh-Loading Lithium Polysulfide Cathode and its Failure Mechanism. *Adv. Energy Mater.* **6**, 1502459 (2016).
154. Chung, S.-H., Chang, C.-H. & Manthiram, A. A core-shell electrode for dynamically and statically stable Li-S battery chemistry. *Energy Environ. Sci.* **9**, 3188–3200 (2016).
155. Larcher, D. & Tarascon, J. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* **7**, 19–29 (2014).
156. Hassoun, J. & Scrosati, B. Moving to a solid-state configuration: A valid approach to making lithium-sulfur batteries viable for practical applications. *Adv. Mater.* **22**, 5198–5201 (2010).
157. Appetecchi, G. ., Croce, F., Persi, L., Ronci, F. & Scrosati, B. Transport and interfacial properties of composite polymer electrolytes. *Electrochim. Acta* **45**, 1481–1490 (2000).
158. Li, Q., Sun, H. Y., Takeda, Y., Imanishi, N., Yang, J. & Yamamoto, O. Interface properties between a lithium metal electrode and a poly(ethylene oxide) based composite polymer electrolyte. *Spec. Issue Interfacial Phenom. Batter.* **94**, 201–205 (2001).
159. Demir Cakan, R., Morcrette, M., Gangulibabu, B., Guéguen, A., Dedryvere, R. & Tarascon, J. Li-S batteries: simple approaches for superior performances. *Energy Environ. Sci.* 176–182 (2012). doi:10.1039/c2ee23411d
160. Agostini, M., Hassoun, J., Liu, J., Jeong, M., Nara, H., Momma, T., Osaka, T., Sun, Y. K. & Scrosati, B. A lithium-ion sulfur battery based on a carbon-coated lithium-sulfide cathode and an electrodeposited silicon-based anode. *ACS Appl. Mater. Interfaces* **6**, 10924–10928 (2014).
161. Cheon, S.-E., Cho, J.-H., Ko, K.-S., Kwon, C.-W., Chang, D.-R., Kim, H.-T. & Kim, S.-W. Structural

- Factors of Sulfur Cathodes with Poly(ethylene oxide) Binder for Performance of Rechargeable Lithium Sulfur Batteries. *J. Electrochem. Soc.* **149**, A1437–A4141 (2002).
162. Seh, Z. W., Wang, H., Hsu, P.-C., Zhang, Q., Li, W., Zheng, G., Yao, H. & Cui, Y. Facile synthesis of Li₂S–polypyrrole composite structures for high-performance Li₂S cathodes. *Energy Environ. Sci.* **7**, 672–676 (2014).
 163. Wang, C., Wang, X., Yang, Y., Kushima, A., Chen, J., Huang, Y. & Li, J. Slurryless Li₂S/Reduced Graphene Oxide Cathode Paper for High-Performance Lithium Sulfur Battery. *Nano Lett.* **15**, 1796–1802 (2015).
 164. Cai, K., Song, M. K., Cairns, E. J. & Zhang, Y. Nanostructured Li₂S–C composites as cathode material for high-energy lithium/sulfur batteries. *Nano Lett.* **12**, 6474–6479 (2012).
 165. Nagao, M., Hayashi, A. & Tatsumisago, M. High-capacity Li₂S–nanocarbon composite electrode for all-solid-state rechargeable lithium batteries. *J. Mater. Chem.* **22**, 1001510020 (2012).
 166. Hayashi, A., Ohtsubo, R., Ohtomo, T., Mizuno, F. & Tatsumisago, M. All-solid-state rechargeable lithium batteries with Li₂S as a positive electrode material. *J. Power Sources* **183**, 422–426 (2008).
 167. Agostini, M., Xiong, S., Matic, A. & Hassoun, J. Polysulfide-containing Glyme-based Electrolytes for Lithium Sulfur Battery. *Chem. Mater.* **27**, 4604–4611 (2015).
 168. Manthiram, A., Chung, S.-H. & Zu, C. Lithium–Sulfur Batteries: Progress and Prospects. *Adv. Mater.* **27**, 1980–2006 (2015).
 169. Bresser, D., Passerini, S. & Scrosati, B. Recent progress and remaining challenges in sulfur-based lithium secondary batteries--a review. *Chem. Commun. (Camb)*. **49**, 10545–62 (2013).
 170. Shim, J., Striebel, K. A. & Cairns, E. J. The Lithium/Sulfur Rechargeable Cell. *J. Electrochem. Soc.* **149**, A1321 (2002).
 171. Yang, Y., Zheng, G., Misra, S., Nelson, J., Toney, M. F. & Cui, Y. High-capacity micrometer-sized Li₂S particles as cathode materials for advanced rechargeable lithium-ion batteries. *J. Am. Chem. Soc.* **134**, 15387–94 (2012).
 172. Koh, J. Y., Park, M.-S., Kim, E. H., Jeong, B. O., Kim, S., Kim, K. J., Kim, J.-G., Kim, Y.-J. & Jung, Y. Understanding of Electrochemical Oxidation Route of Electrically Isolated Li₂S Particles. *J. Electrochem. Soc.* **161**, A2133–A2137 (2014).
 173. Ellis, B. L. & Nazar, L. F. Sodium and sodium-ion energy storage batteries. *Curr. Opin. Solid State Mater. Sci.* **16**, 168–177 (2012).
 174. Chevrier, V. L. & Ceder, G. Challenges for Na-ion Negative Electrodes. *J. Electrochem. Soc.* **158**, A1011 (2011).
 175. Cao, Y., Xiao, L., Wang, W., Choi, D., Nie, Z., Yu, J., Saraf, L. V., Yang, Z. & Liu, J. Reversible sodium ion insertion in single crystalline manganese oxide nanowires with long cycle life. *Adv. Mater.* **23**, 3155–3160 (2011).
 176. Kim, D., Kang, S. H., Slater, M., Rood, S., Vaughey, J. T., Karan, N., Balasubramanian, M. & Johnson, C. S. Enabling sodium batteries using lithium-substituted sodium layered transition metal oxide

- cathodes. *Adv. Energy Mater.* **1**, 333–336 (2011).
177. Nagelberg, A. S. & Worrell, W. L. A thermodynamic study of sodium-intercalated TaS₂ and TiS₂. *J. Solid State Chem.* **29**, 345–354 (1979).
178. Yamin, H. & Peled, E. Electrochemistry of a nonaqueous lithium/sulfur cell. *J. Power Sources* **9**, 281–287 (1983).
179. Ge, P. & Foulletier, M. Electrochemical intercalation of sodium in graphite. *Solid State Ionics* **28–30**, 1172–1175 (1988).
180. Scrosati, B., Hassoun, J. & Sun, Y.-K. Lithium-ion batteries. A look into the future. *Energy Environ. Sci.* **4**, 3287 (2011).
181. U.S. Geological Survey. Mineral Commodities Summaries. *Miner. Commod. Summ.* 202 (2016). doi:10.3133/70140094.
182. Scrosati, B. Technology: Charging towards the superbattery. *Nature* **473**, 448–449 (2011).
183. Slater, M. D., Kim, D., Lee, E. & Johnson, C. S. Sodium-ion batteries. *Adv. Funct. Mater.* **23**, 947–958 (2013).
184. Hassoun, J. & Scrosati, B. A high-performance polymer tin sulfur lithium ion battery. *Angew. Chem. Int. Ed. Engl.* **49**, 2371–2374 (2010).
185. Xiao, L., Cao, Y., Xiao, J., Wang, W., Kovarik, L., Nie, Z. & Liu, J. High capacity reversible alloying reactions in SnSb/C nanocomposites for Na-ion battery applications. *Chem. Commun.* **48**, 3321–3323 (2012).
186. Ellis, L. D., Hatchard, T. D. & Obrovac, M. N. Reversible Insertion of Sodium in Tin. *J. Electrochem. Soc.* **159**, A1801–A1805 (2012).
187. Komaba, S., Matsuura, Y., Ishikawa, T., Yabuuchi, N., Murata, W. & Kuze, S. Redox reaction of Sn-polyacrylate electrodes in aprotic Na cell. *Electrochem. commun.* **21**, 65–68 (2012).
188. Hassoun, J., Agostini, M., Latini, A., Panero, S., Sun, Y.-K. & Scrosati, B. Nickel-Layer Protected, Carbon-Coated Sulfur Electrode for Lithium Battery. *J. Electrochem. Soc.* **159**, A390 (2012).
189. Ji, X., Lee, K. T. & Nazar, L. F. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat. Mater.* **8**, 500–506 (2009).
190. Lee, K. T., Ji, X., Rault, M. & Nazar, L. F. Simple synthesis of graphitic ordered mesoporous carbon materials by a solid-state method using metal phthalocyanines. *Angew. Chemie - Int. Ed.* **48**, 5661–5665 (2009).
191. Jayaprakash, N., Shen, J., Moganty, S. S., Corona, a. & Archer, L. A. Porous hollow carbon@sulfur composites for high-power lithium-sulfur batteries. *Angew. Chemie - Int. Ed.* **50**, 5904–5908 (2011).
192. Ji, X., Evers, S., Black, R. & Nazar, L. F. Stabilizing lithium-sulphur cathodes using polysulphide reservoirs. *Nat. Commun.* **2**, 325 (2011).
193. Jache, B. & Adelhelm, P. Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of co-intercalation phenomena. *Angew. Chemie - Int. Ed.* **53**, 10169–10173 (2014).

194. Hasa, I., Dou, X., Buchholz, D., Shao-Horn, Y., Hassoun, J., Passerini, S. & Scrosati, B. A sodium-ion battery exploiting layered oxide cathode, graphite anode and glyme-based electrolyte. *J. Power Sources* **310**, 26–31 (2016).
195. Tu, X., Chu, Y. & Ma, C. New ternary molten salt electrolyte based on alkali metal triflates. *Ionics (Kiel)*. **16**, 81–84 (2010).
196. Forsyth, M., Girard, G., Basile, A., Macfarlane, D. R., Chen, F. & Howlett, P. C. Title: Inorganic-Organic Ionic Liquid Electrolytes Enabling High Energy-Density Metal Electrodes for Energy Storage Inorganic-Organic Ionic Liquid Electrolytes Enabling High Energy-Density Metal Electrodes for Energy Storage. *Electrochim. Acta* **220**, 609–617 (2016).
197. Wu, T. Y., Wang, H. C., Su, S. G., Gung, S. T., Lin, M. W. & Lin, C. B. Characterization of ionic conductivity, viscosity, density, and self-diffusion coefficient for binary mixtures of polyethyleneglycol (or polyethyleneimine) organic solvent with room temperature ionic liquid BMIBF₄ (or BMIPF₆). *J. Taiwan Inst. Chem. Eng.* **41**, 315–325 (2010).
198. Kaulgud, T., Dhumal, N. & Gejji, S. Electronic Structure and Normal Vibrations of CH₃ (OCH₂CH₂)_n OCH₃-M⁺-CF₃SO₃-(n= 2-4, M= Li, Na, and K). *J. Phys. ...* **110**, 9231–9239 (2006).
199. Bridel, J. S., Grugeon, S., Laruelle, S., Hassoun, J., Reale, P., Scrosati, B. & Tarascon, J. M. Decomposition of ethylene carbonate on electrodeposited metal thin film anode. *J. Power Sources* **195**, 2036–2043 (2010).
200. Stevens, D. a. & Dahn, J. R. An in situ small-angle X-ray scattering study of sodium insertion into a nanoporous carbon anode material within an operating electrochemical cell. *J. Electrochem. Soc.* **147**, 4428–4431 (2000).
201. Jayaprakash, N., Shen, J., Moganty, S. S., Corona, a. & Archer, L. A. Porous Hollow Carbon@Sulfur Composites for High-Power Lithium-Sulfur Batteries. *Angew. Chemie Int. Ed.* **50**, 5904–5908 (2011).
202. Scrosati, B., Hassoun, J. & Sun, Y.-K. Lithium-ion batteries. A look into the future. *Energy Environ. Sci.* **4**, 3287–3295 (2011).
203. Ogasawara, T., Débart, A., Holzapfel, M., Novák, P. & Bruce, P. G. Rechargeable Li₂O₂ electrode for lithium batteries. *J. Am. Chem. Soc.* **128**, 1390–1393 (2006).
204. Freunberger, S. A., Chen, Y., Peng, Z., Griffin, J. M., Hardwick, L. J., Bardé, F., Novák, P. & Bruce, P. G. Reactions in the rechargeable lithium-O₂ battery with alkyl carbonate electrolytes. *J. Am. Chem. Soc.* **133**, 8040–8047 (2011).
205. Adams, B. D., Black, R., Williams, Z., Fernandes, R., Cuisinier, M., Berg, E. J., Novak, P., Murphy, G. K. & Nazar, L. F. Towards a stable organic electrolyte for the lithium oxygen battery. *Adv. Energy Mater.* **5**, 1–11 (2015).
206. Abraham, K. M. & Jiang, Z. A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery. *J. Electrochem. Soc.* **143**, 1 (1996).
207. Zhu, X., Zhao, T. S., Wei, Z., Tan, P. & An, L. A high-rate and long cycle life solid-state lithium-air battery. *Energy Environ. Sci.* 1–10 (2015). doi:10.1039/C5EE02867A

208. Débart, A., Bao, J., Armstrong, G. & Bruce, P. G. An O₂ cathode for rechargeable lithium batteries: The effect of a catalyst. *J. Power Sources* **174**, 1177–1182 (2007).
209. Mitchell, R. R., Gallant, B. M., Thompson, C. V. & Shao-Horn, Y. All-carbon-nanofiber electrodes for high-energy rechargeable Li–O₂ batteries. *Energy Environ. Sci.* **4**, 2952 (2011).
210. Ryu, W. H., Gittleson, F. S., Schwab, M., Goh, T. & Taylor, A. D. A mesoporous catalytic membrane architecture for lithium-oxygen battery systems. *Nano Letters* **15**, 434–441 (2015).
211. Li, F., Tang, D. M., Chen, Y., Golberg, D., Kitaura, H., Zhang, T., Yamada, A. & Zhou, H. Ru/ITO: A carbon-free cathode for nonaqueous Li-O₂ battery. *Nano Letters* **13**, 4702–4707 (2013).
212. Xu, Y., Chen, Y., Xu, G., Zhang, X., Chen, Z., Li, J., Huang, L., Amine, K. & Sun, S. Nano Energy RuO₂ nanoparticles supported on MnO₂ nanorods as high efficient bifunctional electrocatalyst of lithium-oxygen battery. **28**, 63–70 (2016).
213. Wu, F., Xing, Y., Zeng, X., Yuan, Y., Zhang, X., Shahbazian-Yassar, R., Wen, J., Miller, D. J., Li, L., Chen, R., Lu, J. & Amine, K. Platinum-Coated Hollow Graphene Nanocages as Cathode Used in Lithium-Oxygen Batteries. *Adv. Funct. Mater.* 7626–7633 (2016). doi:10.1002/adfm.201602246
214. Elia, G. A., Bresser, D., Reiter, J., Oberhumer, P., Sun, Y.-K., Scrosati, B., Passerini, S. & Hassoun, J. Interphase Evolution of a Lithium-Ion/Oxygen Battery. *ACS Appl. Mater. Interfaces* **7**, 22638–22643 (2015).
215. Song, K., Agyeman, D. A., Jung, J., Jo, M. R., Yang, J. & Kang, Y. M. A Review of the Design Strategies for Tailored Cathode Catalyst Materials in Rechargeable Li-O₂ Batteries. *Isr. J. Chem.* **715**, 458–471 (2015).
216. Sennu, P., Christy, M., Aravindan, V., Lee, Y. G., Nahm, K. S. & Lee, Y. S. Two-Dimensional Mesoporous Cobalt Sulfide Nanosheets as a Superior Anode for a Li-Ion Battery and a Bifunctional Electrocatalyst for the Li-O₂ System. *Chem. Mater.* **27**, 5726–5735 (2015).
217. Cui, Z., Li, L., Manthiram, A. & Goodenough, J. B. Enhanced Cycling Stability of Hybrid Li–Air Batteries Enabled by Ordered Pd₃Fe Intermetallic Electrocatalyst. *J. Am. Chem. Soc.* **137**, 7278–7281 (2015).
218. Zheng, X. & Zhang, L. Photonic nanostructures for solar energy conversion. *Energy Environ. Sci.* **9**, 2511–2532 (2016).
219. Lau, S. & Archer, L. A. Nucleation and Growth of Lithium Peroxide in the Li–O₂ Battery. *Nano Lett.* **15**, 5995–6002 (2015).
220. Ismail, I., Noda, A., Nishimoto, A. & Watanabe, M. XPS study of lithium surface after contact with lithium-salt doped polymer electrolytes. *Electrochim. Acta* **46**, 1595–1603 (2001).
221. Aurbach, D., Levi, M. D., Levi, E. & Schechter, A. Failure and Stabilization Mechanisms of Graphite Electrodes. *J. Phys. Chem. B* **101**, 2195–2206 (1997).
222. Andersson, A. ., Henningson, A., Siegbahn, H., Jansson, U. & Edström, K. Electrochemically lithiated graphite characterised by photoelectron spectroscopy. *J. Power Sources* **119–121**, 522–527 (2003).
223. Cohen, Y. S., Cohen, Y. & Aurbach, D. Micromorphological Studies of Lithium Electrodes in Alkyl

- Carbonate Solutions Using in Situ Atomic Force Microscopy. *J. Phys. Chem. B* **104**, 12282–12291 (2000).
224. Alexej, Jerschow, M. N. Suppression of Convection Artifacts in Stimulated-Echo Diffusion Experiments. Double-Stimulated-Echo Experiments. *J. Magn. Reson.* **375**, 372–375 (1997).
 225. Stejskal, E. O. & Tanner, J. E. Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem. Phys.* **42**, 288–292 (1965).
 226. Meini, S., Piana, M., Beyer, H., Schwammlein, J. & Gasteiger, H. A. Effect of Carbon Surface Area on First Discharge Capacity of Li-O₂ Cathodes and Cycle-Life Behavior in Ether-Based Electrolytes. *J. Electrochem. Soc.* **159**, A2135–A2142 (2012).
 227. Zhai, D., Lau, K. C., Wang, H. H., Wen, J., Miller, D. J., Lu, J., Kang, F., Li, B., Yang, W., Gao, J., Indacochea, E., Curtiss, L. A. & Amine, K. Interfacial effects on lithium superoxide disproportionation in Li-O₂ batteries. *Nano Lett.* **15**, 1041–1046 (2015).
 228. Ottakam Thotiyl, M. M., Freunberger, S. A., Peng, Z. & Bruce, P. G. The Carbon Electrode in Nonaqueous Li–O₂ Cells. *J. Am. Chem. Soc.* **135**, 494–500 (2013).
 229. Jung, H.-G., Hassoun, J., Park, J.-B., Sun, Y.-K. & Scrosati, B. An improved high-performance lithium–air battery. *Nat. Chem.* **4**, 579–585 (2012).
 230. Elia, G. A., Hassoun, J., Kwak, W.-J. J. W.-J., Sun, Y.-K. Y.-K. K., Scrosati, B., Mueller, F., Bresser, D., Passerini, S., Oberhumer, P., Tsiouvaras, N. & Reiter, J. An Advanced Lithium–Air Battery Exploiting an Ionic Liquid-Based Electrolyte. *Nano Lett.* **14**, 6572–6577 (2014).
 231. Lu, J., Jung Lee, Y., Luo, X., Chun Lau, K., Asadi, M., Wang, H.-H., Brombosz, S., Wen, J., Zhai, D., Chen, Z., Miller, D. J., Sub Jeong, Y., Park, J.-B., Zak Fang, Z., Kumar, B., Salehi-Khojin, A., Sun, Y.-K., Curtiss, L. A. & Amine, K. A lithium–oxygen battery based on lithium superoxide. *Nature* **529**, 1–7 (2016).
 232. Gallant, B. M., Kwabi, D. G., Mitchell, R. R., Zhou, J., Thompson, C. V & Shao-Horn, Y. Influence of Li₂O₂ morphology on oxygen reduction and evolution kinetics in Li–O₂ batteries. *Energy Environ. Sci.* **6**, 2518 (2013).
 233. Lee, H., Kim, Y.-J., Lee, D. J., Song, J., Lee, Y. M., Kim, H.-T. & Park, J.-K. Directly grown Co₃O₄ nanowire arrays on Ni-foam: structural effects of carbon-free and binder-free cathodes for lithium–oxygen batteries. *J. Mater. Chem. A* **2**, 11891 (2014).
 234. Adams, B. D., Radtke, C., Black, R., Trudeau, M. L., Zaghib, K. & Nazar, L. F. Current density dependence of peroxide formation in the Li–O₂ battery and its effect on charge. *Energy Environ. Sci.* **6**, 1772 (2013).
 235. Boukamp, B. A. A package for impedance/admittance data analysis. *Solid State Ionics* **18–19**, 136–140 (1986).
 236. BOUKAMP, B. A Nonlinear Least Squares Fit procedure for analysis of immittance data of electrochemical systems. *Solid State Ionics* **20**, 31–44 (1986).
 237. Transactions, E. C. S., Society, T. E., Hanzu, I., Djenizian, T. & Knauth, P. Electrical and Proton

Conduction Properties of Amorphous TiO₂ Nanotubes Fabricated by Electrochemical Anodization. *ECS Trans.* **35**, 21–31 (2011).

238. Boukamp, B. A. No Title. **19**, 136–140 (1986).

Experimental section

Chapter: ^{17}O NMR study

Experimental section: *Sample preparation*

All reagents were purchased from Sigma Aldrich. Electrolyte solutions were prepared by dissolving 1 mol of LiTf or LiTFSI in 1 kg of either in DME, DEGDME, TREGDME, TEGDME, PEG250, or PEG500. The neat solvents without salts as standards were also set aside for comparison. All solvents were dried under molecular sieves (5A) for several days until the water content was under 10 ppm, as verified by 831 Karl Fisher Coulometer METROHM. All the salts were dried under vacuum for 24 hours at 100°C before solution preparation.

Experimental section: *NMR Characterization*

For ^{17}O NMR characterization, the chemical shift reference dimethyl carbonate (DMC) was placed in a 4 mm borosilicate tube which was inserted into a 5 mm NMR borosilicate tube containing the electrolyte solution or neat solvent. This coaxial arrangement yields convenient a reference spectrum while preventing contact between the reference and the sample. All sample handling procedures were performed in an Ar-filled glovebox, and inserts and outer tubes were all sealed under Ar. The ^{17}O NMR experiments were acquired on a 400 SB Bruker Avance III spectrometer with a broadband probe working at ^{17}O frequency of 54.25 MHz. All experiments were performed at 60°C in order to improve spectra resolution and each spectrum was collected between 32k to 128k scans for good Signal/Noise ratio. The average number of $(\text{OCH}_2\text{CH}_2)$ - units (n) in PEG250 (M.W. 250 g/mol) and PEG500 (M.W. 500 g/mol) molecule, with formula $\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_n\text{OCH}_3$, has been estimated as $n \approx 4.6$ and 10.3, respectively, by using Eq. 1:

$$(2 + 2n) * 12.011 \frac{\text{g}}{\text{mol}} + (6 + 4n) * 1.008 \frac{\text{g}}{\text{mol}} + (n + 1) * 15.999 \frac{\text{g}}{\text{mol}} = M_{ave} \quad (1)$$

Where M_{ave} is the average of molecular weight of PEG250 or PEG500. $(N_{(O)})$ to $\text{Li}^+ (N_{(\text{Li}^+)})$ molecular ratio in chain of solvent for both LiTf and LiTFSI electrolyte series has been calculated by using Eq.2:

$$\frac{N_{(O)}}{N_{(\text{Li}^+)}} = \frac{\frac{1000\text{g}}{M_{ave}} * N_{(O)}}{n_{\text{Li}^+}} \quad (2)$$

the salt concentration is 1 mol kg^{-1} ; n_{Li^+} is 1 mol; m_{elec} is 1 kg, and $N_{(O)}$ is $n+1$. $N_{(\text{Oxygen in R-O-R'})}$ always equal to $N_{(O)}^{-2}$.

Chapter: Glymes in Li/S cell

Experimental section: Cathode preparation

The cathode material was based on elemental sulfur and mesophase micro bead (MCMB) carbon, in a weight ratio of 1:1. Before mixing with MCMB, the sulfur was melted at 135°C. The mixture was stirred for 3 hours at 135°C and then cooled down to room temperature. A stainless-steel jar was used to hold and mechanically treat the sample by high-energy ball milling system (Retsch Mill MM400) with a frequency of 15 Hz for a total time of 2 hours, using a milling time of 30 minutes, rest period of 15 minutes and repeating the above procedure four times. The electrodes were prepared by mixing the carbon-sulfur composite, super P carbon (Timcal) and polyvinylidenedifluoride (PVDF) binder in 80:10:10 mass ratio in N-methylpyrrolidone (NMP) solution. The slurry was casted on aluminum foil by Doctor Blade, punched as disks and then vacuum-dried at 50°C for 24 h before assembling the cells in argon filled glove box.

Experimental section: Electrolyte preparation

Before mixing, the solvents were dried for several days under molecular sieves until the water content was below 10 ppm as determined by 831 Karl Fisher Coulometer – METROHM. The electrolyte solutions were prepared by dissolving lithium trifluoromethanesulfonate (LiCF₃SO₃, i.e. lithium triflate) in 1 mol kg⁻¹ ratio in an argon filled glove-box. Lithium nitrate was then added to the solution in a 0.4 molar ratio

Experimental section: Electrolyte Characterization

The thermal characterization was performed by **thermo-gravimetric analysis TGA** (Mettler Toledo TGA/SDTA851) and by **differential scanning calorimetry DSC** (Mettler Toledo DSC821). TGA was performed by raising the temperature from 25°C to 700 °C, with a heat rate of 10°C/min. DSC was performed by cooling from 25°C to -80°C at -5°C/min. **Conductivity tests** were performed by using 2032 coin cells including stainless steel symmetrical electrodes and Teflon O-ring separator with a constant and known size in order to ensure a fixed cell constant. **Electrochemical impedance spectroscopy (EIS)** was performed by using a Biological VMP3 with 10mV-signal amplitude, within 500 MHz-100 Hz frequency range. The interface resistance has been calculated by Non-linear least-squares (NLLSQ) fit of the impedance spectra, carried out by using a Boukamp software product. An R(RQ)nQ equivalent circuit was used for the Nyquist plot analysis, where R represents a resistance and Q a constant-phase element (CPE). The Chi-square (χ^2), a parameter used to evaluate the fitting quality, was below 10⁻⁴.^{235,236} The electrochemical stability window was studied by **linear sweep voltammetry (LSV)** at a scan rate of 0.1 mV s⁻¹, in a three electrodes lithium cell using a Biological VMP3. The configuration cell has lithium metal as counter and reference electrode and super P on aluminum as working electrode in the OCV- 5.0V Vs Li/Li⁺ range at room temperature. **Lithium stripping/deposition** galvanostatic test was performed by applying a 0.1 mA cm⁻² current to Li/Li symmetrical cell, using a MACCOR Series 4000 Battery Test System (Maccor Inc.). Temperature dependence of the self-diffusion coefficient for ¹H, ¹⁹F, and ⁷Li nuclei was measured on a Bruker 400 Avance III NMR spectrometer using a double stimulated echo pulse sequence to suppress convection effects. ²²⁴Gradient pulses, of sine shape with duration $\delta = 2$ -5 ms and strength $g = 0$ -45 G/cm, were applied with a diffusion delay of $\Delta = 80$ -800 ms within a temperature ranging 20°C and 70°C, in steps of 10°C. The self-diffusion activation energies were estimated by the Arrhenius plot linear slope of the corresponding self-diffusion coefficients measured at various temperatures. The room temperature lithium transference number (t^+), corresponding to the fraction of current carried out by the lithium ions, was determined as the ratio of the self-diffusion coefficient of Li⁺ with respect to overall charge carriers, i.e. Li⁺ (⁷Li nuclei) and CF₃SO₃⁻ (¹⁹F nuclei) measured at 25°C. This method does not take into account the effects of ion association and is therefore used only as guide to comparative behavior in electrolytes

Experimental section: Cathode Characterization

Cycling tests were performed using a Maccor instrument at a C/20 current rate ($1C = 1675 \text{ mA g}^{-1}$ based on the sulfur weight), within 1 V – 3.2 V limit.

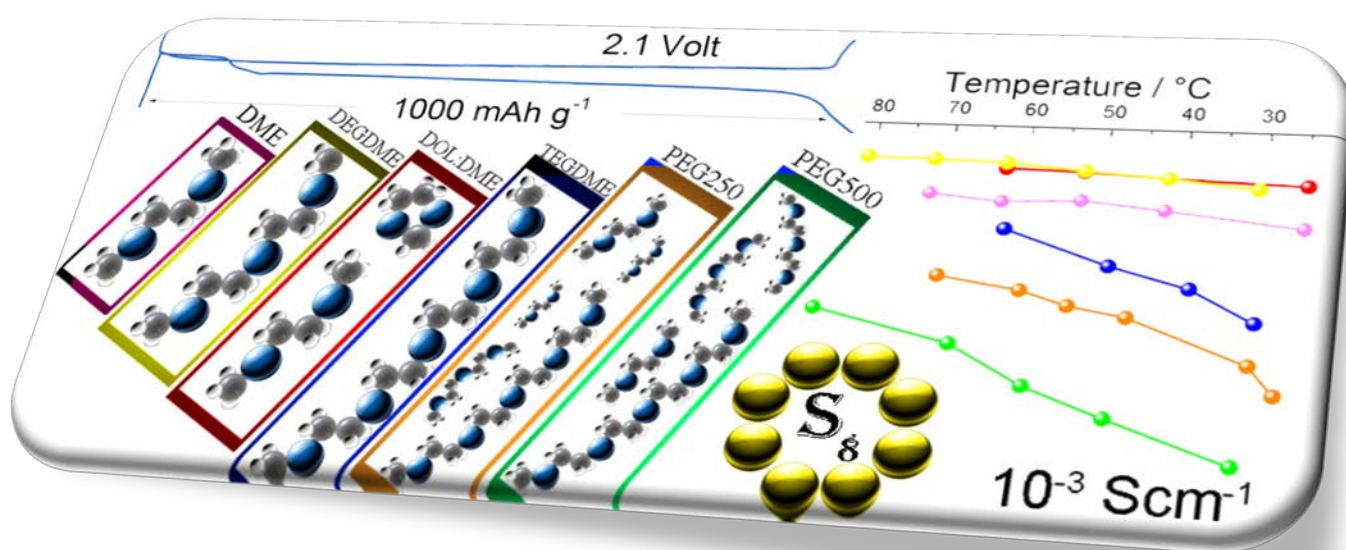


Table of content of the chapter Glymes
in Li/S cell

Chapter: LiNO₃ Effect

Experimental section: Electrolyte and Cathode Preparation

Poly ethylene glycol dimethyl ether (Sigma Aldrich, average MW 500, indicated by the acronym PEG500DME) was dried under molecular sieves (5Å) for several days until the water content was under 10 ppm as determined by Karl Fisher instrument (Metrohm). Lithium-trifluoromethanesulfonate (LiCF₃SO₃ Sigma Aldrich) and lithium-nitrate (LiNO₃, Sigma Aldrich) were dried at 100°C under vacuum for 24 hours. The electrolyte solution was prepared by dissolving 1 mol of LiCF₃SO₃ in 1 kg of PEG500DME. A second solution of the same composition of the previous was added by 0.4 mol of LiNO₃. The cathode was prepared by dispersing an homogeneous slurry of LiFePO₄,⁸⁰ super P carbon conductor (Timcal) and polyvinylidenedifluoride (PVDF, Solvay) binder in 80:10:10 mass ratio in N-methylpyrrolidone (NMP, Aldrich). The cathode film was cast onto aluminum foil by doctor Blade, dried at 70°C, disk-punched and finally dried under vacuum at 100°C for 3 hours.

Experimental section: Electrolyte Characterization

Self-diffusion coefficient was measured by using a Bruker 400 Avance III NMR spectrometer operating by double-stimulated echo pulse sequence in order to suppress convection effects. The measurements were performed by within temperature ranging from 20°C to 70°C, collecting the signal each 10 °C, by gradient pulses of sine-shape with duration $\delta = 2-5$ ms, strength $g = 0-45$ G/cm and diffusion delay of $\Delta = 80-800$ ms. The electrolyte conductivity (δ) was calculated by using the diffusion coefficient of the anion and the cation along with the Nernst-Einstein equation (4)

$$\delta = \frac{F^2[C]}{RT} (D_{Li} + D_{CF_3SO_3})$$

where F is the Faraday constant (96485 Coulomb), [C] is the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the selected temperature value, D_{Li} and $D_{CF_3SO_3}$ are the self-diffusion coefficient Li⁺ cation and CF₃SO₃⁻ anion, respectively, measured of by NMR technique. The ionic conductivity was also directly determined within temperature ranging from 20°C to 90°C by electrochemical impedance spectroscopy (EIS) in symmetric stainless steel/electrolyte/stainless steel 2032 coin cell. The cell was equipped by Teflon separator in order to fix the cell thickness, and the impedance spectroscopy was performed in a 100 mHz - 100 kHz frequency range with a signal amplitude of 10 mV using Biological VMP3 instrument. The ion association degree (α) was determined by using equation (5)

$$\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}} \right)$$

where δ_{EIS} and δ_{NMR} are the conductivity values measured by EIS and calculated by equation (4), respectively. The cation transference number (t^+), corresponding to the fraction of current carried out by the lithium ions, was calculated by using equation

$$(6) : t^+ = \frac{D_{Li}^+}{D_{Li}^+ + D_{CF_3SO_3^-}}$$

Experimental section: Cathode Characterization

Cyclic voltammetry was carried out by using a three-electrodes cell equipped by lithium metal counter and reference electrode and a Super P coated on copper working electrode. The measurement was performed by a 10 mV s⁻¹ scan rate, within 0.01V and 3V potential window using a Biological VMP3 instrument. Swagelok, T-type lithium cells using lithium iron phosphate (LiFePO₄) cathode and PEG500DMEDME-based electrolyte soaked in a Whatman® glass fiber separator, were galvanostatically characterized at C/5 rate (1C = 170 mA g⁻¹) using MACCOR Series 4000 Battery Test System (Maccor Inc.).

Chapter: LiNO_3 Added Electrolyte a Deep Investigation

Experimental section: Cathode Preparation

The LiFePO_4 (LFP) powder was synthesized by solvothermal treatment and following high-temperature annealing in inert atmosphere, as reported in our paper.⁸¹ The cathode film was prepared mixing the active material, poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP copolymer, Kynar Flex 2801) as binder, and Super P Carbon (Timcal) as conductive additive in the ratio 80:10:10% w/w in Tetrahydrofuran (THF, Sigma-Aldrich). The slurry thus obtained was casted on either aluminum foil or carbon cloth current collector by doctor blade. The carbon cloth support was used for cycling test at constant current rate, while the aluminum support was used for cyclic voltammetry and rate capability tests. The carbon cloth electrode supports may enhance the electrochemical performances of olivine cathode materials synthesized in our laboratory, particularly in terms cycling stability. This phenomenon is likely related to the improved electric contact between active material particles and current collector as well as to the higher electrode contact area of carbon cloth with respect to Al foil. Therefore, we used the carbon cloth for cycling test at a constant rate. Beside cycle life, cyclic voltammetry and rate capability tests were performed in order to detect the electrochemical processes due to LiFePO_4 and LiNO_3 , hence we considered the aluminum support as the most suitable current collector for evaluation. The electrode films were dried overnight under vacuum at 110 °C, cut in the form of 10 mm diameter disks, and brought in an argon-filled glovebox before cell assembling. The electrodes had mass loading of about 4 mg cm^{-2} .

Experimental section: Electrolyte Preparation

Triethylene glycol dimethyl ether (TREGDME, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$, Sigma-Aldrich) was dried under molecular sieves (5Å) until the water content was below 10 ppm, as determined by using the Karl Fischer titration instrument (831 Karl Fisher Coulometer, Metrohm). Lithium trifluoromethanesulfonate (lithium triflate, LiCF_3SO_3 , Sigma-Aldrich) and lithium nitrate (LiNO_3 , Sigma-Aldrich) were dried overnight under vacuum at 80 °C before use. The electrolyte was prepared by dissolving LiCF_3SO_3 in TREGDME in 1 mol kg^{-1} concentration with respect to the solvent (solution indicated by the acronym TREG- LiCF_3SO_3). A second electrolyte solution was prepared by dissolving LiCF_3SO_3 and LiNO_3 in TREGDME; both salts were used in 1 mol kg^{-1} concentration with respect to the solvent (solution indicated by the acronym TREG- LiCF_3SO_3 - LiNO_3). The electrolyte preparation was carried out in an argon-filled glovebox with moisture and oxygen content lower than 1 ppm.

Experimental section: Cathode Characterization

Galvanostatic cycling tests were performed through a Maccor 4000 series Battery Test System on Li/TREG- LiCF_3SO_3 - LiNO_3 /LFP Swagelok-type two-electrode cells with a Whatman® separator. The cells were electrochemically activated by 4 galvanostatic cycles at C/5 rate ($1\text{C} = 170 \text{ mAhg}^{-1}$); the first discharge was performed by decreasing the voltage below 2 V and limiting the time to 5.15 h, in order to form a stable solid electrolyte interphase (SEI) layer at the electrode surface. The subsequent cycles were performed within the 2 – 4 V voltage range at C/5 rate for test at single current, and at C/10, C/5, C/3, C/2, 1C, and 2C for rate capability test ($1\text{C} = 170 \text{ mAhg}^{-1}$). SEM Zeiss EVO 40 with a thermionic electron gun equipped by LaB_6 crystal was employed to study the morphology of the electrodes at various cycling stages.

Experimental section: Electrolyte Characterization

The thermal properties of TREG-LiCF₃SO₃ were evaluated by **differential scanning calorimetry (DSC)**. The samples were put in a sealed Al crucible in an argon-filled glovebox for DSC; the measurement was performed from 20 °C to −90 °C with a cooling rate of 5 °C min^{−1}. **Thermogravimetric analyses (TGA)** of TREGDME, TREG-LiCF₃SO₃, and TREG-LiCF₃SO₃-LiNO₃ were carried out by using a TG209 F1 Libra, Netzsch, instrument. The samples were heated at a rate of 10 °C min^{−1} from room temperature to 600 °C under a nitrogen purge (40 mL min^{−1}). The samples were hermetically sealed inside a dry room (dew point < −70 °C) in aluminum pans, which were punched under nitrogen atmosphere just before the measurement. **The viscosity** of TREGDME, TREG-LiCF₃SO₃, and TREG-LiCF₃SO₃-LiNO₃ was evaluated at various temperatures in a dry room (dew point < −70 °C) through an Anton-Paar Physica MCR102 rheometer, by applying constant shear rates and using a Peltier system for cooling/heating. The measurements were performed every 10 °C upon sample heating after 15 min of equilibration at constant temperature. **The self-diffusion coefficients** of TREG-LiCF₃SO₃ for the ¹H, ¹⁹F and ⁷Li nuclei were investigated with a Bruker 400 Advance III NMR spectrometer. Screw-cap gas-tight NMR tubes were used. The measurements were carried out using a double stimulated echo sequence with pulsed field gradients (PFG) in order to suppress convection; data were collected every 10 °C from 20 °C to 80 °C for each nucleus. Gradient pulse duration (δ) of 1.4 – 4 ms, diffusion delay (Δ) of 200 – 400 ms, and a gradient pulse strength increased linearly in 32 steps from 1 to 45 G cm^{−1} were used. A longitudinal eddy-current delay (LED) of 5 ms was used to avoid eddy current effects. error on the self-diffusion coefficient is about 3-5%.⁶¹ **Ionic conductivity** was measured by impedance spectroscopy (EIS) using 10 mV signal amplitude in the 100 kHz – 100 mHz frequency range through a VSP (Biologic) instrument. The measurements were performed every 10 °C from 30 °C to 80 °C on symmetrical stainless steel/electrolyte/stainless steel 2032-coin cell, using a Teflon ring (thickness = 500 μm) as the separator in order to fix the cell constant. The conductivity values obtained by EIS were compared with those calculated using the self-diffusion coefficient (δ_{NMR}) through the Nernst-Einstein eq.

$$(4): \delta = \frac{F^2[C]}{RT} (D_{Li} + D_{CF_3SO_3})$$

where δ_{NMR} is the conductivity determined by the NMR, F is the Faraday constant (96485 C), [C] is the concentration of the salt in the electrolyte (mol cm^{−3}), R is the ideal-gas constant (8.314472 J K^{−1} mol^{−1}), T is the temperature (K), D_{Li} and D_{CF₃SO₃} are the corresponding self-diffusion coefficient. The **ion association degree** was derived from equation

$$(5): \alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right)$$

where α is the ion association degree, δ_{NMR} and δ_{EIS} are the conductivity by PFG NMR and EIS, respectively. The **lithium transference number** was obtained by the following equation

$$(6): t^+ = \frac{D_{Li}}{D_{Li} + D_{CF_3SO_3}}$$

where t⁺ is the transference number of the cation, D_{Li} is the self-diffusion coefficient of lithium, and D_{CF₃SO₃} is the self-diffusion coefficient of the CF₃SO₃[−] anion. **Lithium stripping-deposition** tests were carried out on TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ solutions using Swagelok-type symmetrical cell with a Whatman® separator, by applying constant current of 0.1 mA cm^{−1} with step duration of 1 h through a Maccor 4000 series Battery Test System.

The **anodic stability** of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ was investigated by linear sweep voltammetry at 0.1 mV s^{−1} on Swagelok-type 3-electrodes cells with lithium metal for the counter and reference electrodes, and carbon-coated on aluminum foil as working electrode. Carbon-coated Al electrode allows determination of the actual electrochemical anodic stability window, which may be underestimated with Ni or Pt working electrodes

The same cell configuration, was used for **cyclic voltammetry** measurements; the working electrode reasonably reproduces the electrolyte behavior on composite cathodes, usually formed by active material, conductive carbon and polymer binder. The tests were performed on TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ to evaluate electrolyte behavior and the effect of LiNO₃ addition, at a scan rate of 0.1 mV s⁻¹ within the 1 – 4.3 V vs. Li⁺/Li potential range for the first cycle, and within the 2 – 4.3 V vs. Li⁺/Li potential range for the subsequent cycles. Further voltammetry experiments were carried out employing LFP (on aluminum support) as the working electrode, with a scan rate of 0.1 mV s⁻¹ within the 1 – 4.3 V vs. Li⁺/Li potential range for the first cycle, and within the 2 – 4.3 V vs. Li⁺/Li potential range for the subsequent cycles. The voltammetry measurements were performed though a VersaSTAT MC Princeton Applied Research – AMETEK potentiostat. The **lithium/electrolyte interfacial stability** of TREG-LiCF₃SO₃ and TREG-LiCF₃SO₃-LiNO₃ were evaluated by performing EIS tests on symmetrical lithium/electrolyte/lithium Swagelok-type cells with a Whatman® separator, using 10 mV signal amplitude in the 500 kHz–200 mHz frequency range through a VersaSTAT MC Princeton Applied Research–AMETEK potentiostat. The impedance spectra were analyzed by nonlinear least-square (NLLS) fit using the Boukamp software;^{62,63} the fit reliability was confirmed by chi-square (χ^2) values lower than 10⁻⁴. The equivalent circuit adopted for the Nyquist plot was $R_a(R_iQ_i)_nQ_b$, where R represents a resistance and Q a constant phase element (CPE).

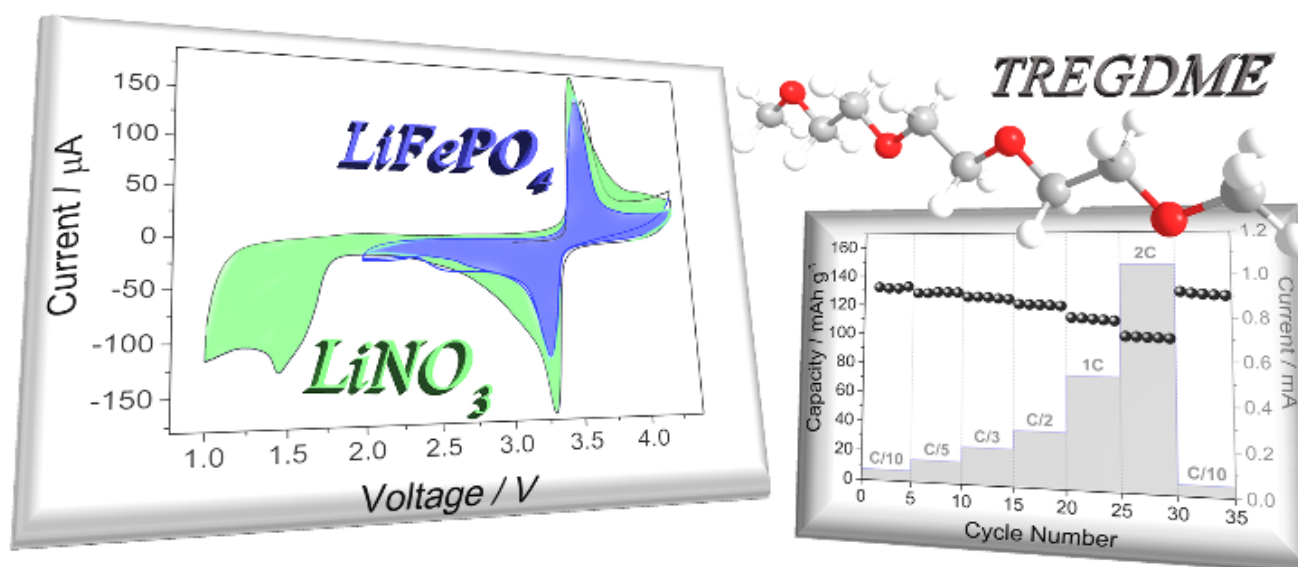


Table of content of the chapter LiNO₃
Added Electrolyte a Deep Investigation

Chapter: LiNO₃-Glymes electrolytes toward better performances

Experimental section: Cathode Preparation

C-coated LiFePO₄ and LiMn_{0.5}Fe_{0.5}PO₄ powders (C content of about 5 wt. %) with olivine structure were synthesized by using a solvothermal pathway followed by high-temperature annealing in Ar atmosphere as previously reported^{94,105}. Sample morphology was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were acquired by using a Zeiss EVO 40 microscope, equipped with a LaB₆ thermo-ionic electron gun. The atomic composition of the samples was studied by SEM-energy dispersive X-ray spectroscopy (EDS), by using a X-ACT, Cambridge Instruments analyzer. TEM images were taken by a Zeiss EM 910 microscope, equipped with a tungsten thermo-ionic electron gun operating at 100 kV. The samples were suspended in water, sonicated, and deposited onto a Formvar[®] support film applied to Cu grid for TEM. The cathode slurries were prepared by mixing active material (LiFePO₄, LiMn_{0.5}Fe_{0.5}PO₄), poly (vinylidene fluoride-hexafluoropropylene) (PVdF-HFP copolymer, Kynar Flex 2801) binder, and Super P Carbon (Timcal) conductive additive in the ratio 80:10:10% w/w. Tetrahydrofuran (THF, Sigma-Aldrich) was used as solvent for the electrode slurries. The slurries were de-positated on carbon-cloth current collector by doctor blade, casted, dried overnight under vacuum at 110 °C, and cut in the form of 10 mm diameter disks. The electrode mass loading was about 4 mg cm⁻². Additional LiFePO₄ electrodes were prepared using Al foil, in order to evaluate the effect of the current collector. T-type cells were assembled in Ar-filled glovebox by stacking cathode, glass fiber separator (Whatman) soaked in the electrolyte solution (LiCF₃SO₃-LiNO₃-TEGDME), and lithium metal an-ode. Benchmark electrolyte solution, i.e., 1 M LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC) 1:1 w/w, was used for flammability tests and Li/LiFePO₄ reference cells. The cell case had three stainless steel cylinders as current collectors and polypropylene holder; the cell was sealed by polypropylene screws. The flammability tests were carried out on the electrolytes just taken out from

Experimental section: Electrolyte Preparation

The electrolyte solution was prepared in Ar-filled glovebox by dissolving lithium trifluoromethanesulfonate (lithium triflate, LiCF₃SO₃, Sigma-Aldrich) and lithium nitrate (LiNO₃, Sigma-Aldrich) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich) solvent; both salts were used in 1 mol kg⁻¹ concentration with respect to the solvent. Prior to electrolyte preparation, the salts were dried under vacuum at 100 °C for 24 h and TEGDME was dried under molecular sieves. The final water content in TEGDME was below 10 ppm by Karl Fisher titration (831 Karl Fisher Coulometr, Metrohm).

Experimental section: Cathode Characterization

Rate capability tests on two-electrodes lithium cells were performed by galvanostatic cycling at C/10, C/5, C/3, C/2, 1C, and 2C rates (1C = 170 mA g⁻¹), within the 2 – 4 V and 2 – 4.3 V voltage ranges for LiFePO₄ and LiMn_{0.5}Fe_{0.5}PO₄, respectively. **Galvanostatic cycling** tests using a single current rate were performed at C/5, C/3, and 2C rates. All the cells using glyme-based electrolyte were activated by 4 galvanostatic cycles at C/5 rate; the first discharge was performed by decreasing the voltage below 2 V and limiting the time to 5.15 h, according to a previously reported procedure suitable for the formation of a stable SEI layer at the electrode surface, see Fig. 29. All the cycling tests were carried out at room temperature through a Maccor 4000 series Battery Test System.

Experimental section: Electrolyte Characterization

The TEGDME–LiCF₃SO₃ 1 mol kg⁻¹ electrolyte was characterized by a Bruker 400 Avance III NMR spectrometer in order to determine **self-diffusion coefficients** of ¹H, ⁷Li and ¹⁹F nuclei using PFG double-stimulated echo sequence to suppress convection effects.²²⁴ The gradient pulse widths were 4-5 ms, gradient strength g was varied from 0-45 G/cm and diffusion delay Δ of 500-800 ms was employed. Measurements were made each 10°C from 20°C to 70°C. The Nernst-Einstein equation (4) was used to calculate the **electrolyte conductivity** (δ_{NMR}) from Li⁺ cation and CF₃SO₃⁻ anion self-diffusion coefficients:

$$\delta_{NMR} = \frac{F^2 [C]}{RT} (D_{Li^+} + D_{CF_3SO_3^-}) \quad (4)$$

Where F is the Faraday constant (96485 C), $[C]$ is the salt concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature (K) and D_{Li^+} and $D_{CF_3SO_3^-}$ are the self-diffusion coefficient of lithium cation and triflate anion respectively. The electrolyte conductivity was also measured by electrochemical **impedance spectroscopy (EIS)** in symmetric stainless steel/electrolyte/stainless steel 2032-coin cell, with an O-ring Teflon separator to keep the volume of the cell constant. VSP (Biologic) instrument was used to perform the measurements in a 100 mHz – 100 kHz frequency range with signal amplitude of 10 mV, acquiring data from 30°C to 60°C each 10°C. The equation (5) was used to calculate the **ion association degree** (α):

$$\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right) \quad (5)$$

Where δ_{EIS} is the conductivity value obtained from EIS measures and δ_{NMR} is the conductivity from equation (4). The **lithium transference number** (t^+) can also be calculated from the self-diffusion coefficients according to equation (6):

$$t^+ = \frac{D_{Li^+}}{D_{Li^+} + D_{CF_3SO_3^-}} \quad (6)$$

where D_{Li^+} and $D_{CF_3SO_3^-}$ are the self diffusion coefficient of the lithium cation and the triflate anion

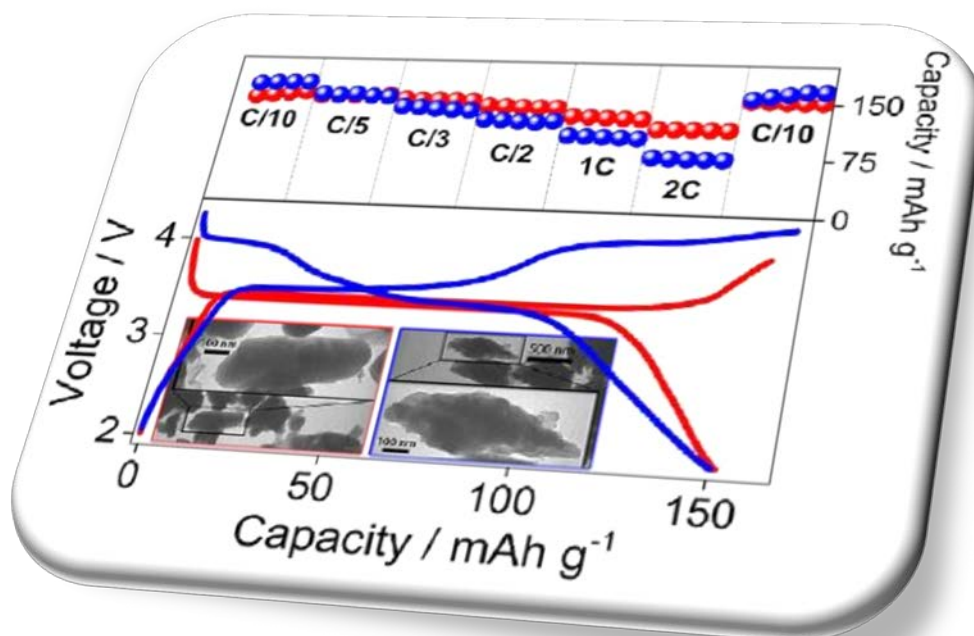


Table of content of the chapter LiNO₃-Glymes electrolytes
toward better performances

Chapter: Carbon composites for Sulfur

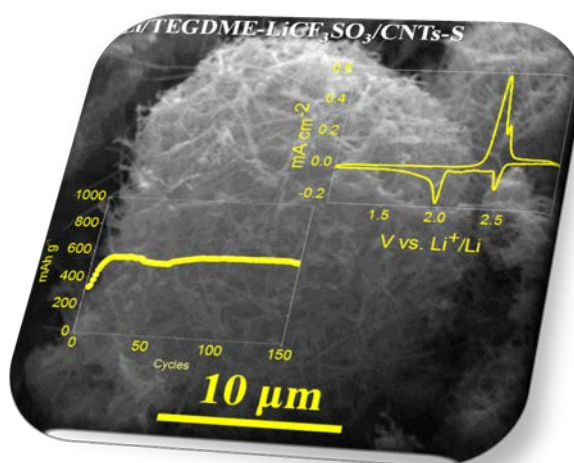
Experimental section: Cathode and electrolyte Preparation

The **active materials** were prepared by mixing elemental sulfur and either mesophase micro bead carbon (MCMB), graphite or multi walled carbon nanotubes (CNTs), by Sigma Aldrich. Elemental sulfur was melted at 135°C, added to the selected carbon powder in a 2:3 weight ratio, and subsequently stirred for 3 hours until homogenous mixture was obtained. The mixture was subsequently cooled down to room temperature, refined by mortar and high energy ball milling four times for 15 min with a frequency of 15 Hz and 30 min of rest between steps, using a Retsch Mill MM400. For electrode preparation the active material powders, i.e., S–Graphite, S–MCMB and S–CNTs, were mixed together with polyvinylidenedifluoride (PVdF, Solvay Solef) binder in an 85:15 weight ratio, and dispersed in N-methylpyrrolidone (NMP) solution. The resulting slurries were stirred for 1 hour, casted on aluminum foil by Doctor Blade technique with a wet thickness of 300 μm and dried for 3 hours at 60°C under air. Before cell assembly in the glove box, the electrodes were disk punched and vacuum dried overnight at 60°C. The cells were filled by 30 μl of electrolyte and by an overall amount of sulfur of about 2 mg, thus leading to an electrolyte-to-sulfur ratio of 15 ml/g. The loading of sulfur into electrode surface was of 1.3 mg cm^{-2} : taking into account the delivered specific capacity of about 600 mAh g^{-1} , the surface capacity may be calculated to be of 0.8 mAh cm^{-2} . This capacity is of the same order of magnitude with respect to the one delivered by common batteries, such as those using LiFePO_4 and LiCoO_2 , which is of about 1 mA cm^{-2} (taking into account a mass loading of about 5-6 mg cm^{-2} and delivered capacity of about 150 mAh g^{-1}). The **electrolyte** was prepared by dissolving 1 mole of lithium trifluoromethanesulfonate salt (LiCF_3SO_3 , Sigma Aldrich) in 1 kg of tetra ethylene glycol dimethyl ether (TEGDME, Sigma Aldrich). Before mixing in argon filled glove box, TEGDME was dried by molecular sieves until the water content was lower than 10 ppm (determined by Karl Fischer titration instrument Metrohm) and the LiCF_3SO_3 was dried under vacuum at 80°C for 24 hours.

Experimental section: Cathode Characterization

The active materials structure was characterized by X-ray diffraction by a XRD Bruker instruments using Cu $\text{K}\alpha$ source and a graphite monochromator, in the $2\theta/\theta$ scanning mode. Scanning electron microscope (SEM) Zeiss EVO 40, using thermionic electron gun equipped with LaB_6 crystal, was employed to study the samples morphology. Cycle voltammetry in three electrode T-cell configuration, using lithium metal as counter and reference electrode, was carried out in a 1 V – 3 V potential range, with a current scan of 0.05 mV s^{-1} by a VersaSTAT MC, Princeton Applied Research. Galvanostatic cycling of Sulfur-Carbon electrodes was performed using a MACCOR Series 4000 Battery Test System in a 2032-coin cell, with lithium metal anode and a Whatman® glass fiber separator soaked with TEGDME– LiCF_3SO_3 electrolyte, at C/5 current rate ($1\text{C} = 1675 \text{ mAh g}^{-1}$) in the voltage range of 1.8V - 2.7V.

Table of content of the chapter:
Carbon composites for Sulfur



Chapter: Optimizing the Li/S cell

Experimental Section: Cathode Preparation

The S-carbon powder was prepared by melting elemental sulfur (Sigma-Aldrich) at 135°C and mixing with multi-walled carbon nanotubes MWCNTs (from Sigma-Aldrich) by a 60:40 S to C weight ratio. The sample was stirred 3 hours under heating at 135°C in order to obtain a homogeneous mixture, cooled down to room temperature and refined by mortar. The electrode slurry was prepared by mixing the S-MWCNTs-S powder, Super P Carbon conductive additive (Timcal) and polyvinylidene difluoride binder (PVdF; Solvay Solef) binder in 80:10:10 weight ratio, using N-methylpyrrolidone (NMP) as solvent. The slurry was cast onto carbon cloth support (GDL ELAT) by the Doctor Blade method with a wet thickness varying from 300 μm to 600 μm , in order to obtain various sulfur loadings. The electrode foils were punched into 10 mm and 16 mm disks, dried for 48 hours at 60°C under vacuum before assembling the cell in the argon filled glovebox with oxygen and water content lower than 1 ppm. The sulfur loading of the final electrodes was 2, 2.5, 3 and 4 mg cm^{-2}

Experimental Section: Electrolyte Preparation

Diethylene glycol dimethyl ether ($\text{CH}_3\text{OCH}_2\text{CH}_2$)₂O (Sigma-Aldrich), denoted hereafter by DEGDME, was dried before use with molecular sieves (5 Å) until the water content was below 10 ppm as measured by 831 Karl Fischer Coulometer (Metrohm). Lithium bis-trifluoromethanesulfonimide ($\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)_2$, LiTFSI) and lithium nitrate (LiNO_3), from Sigma-Aldrich, were separately dried under vacuum overnight at 80 °C. All the samples were subsequently handled in argon filled glove box, with oxygen and moisture content lower than 1 ppm. LiTFSI was dissolved in DEGDME by a salt to solvent ratio of 1 mol kg^{-1} to obtain the electrolyte (indicated by DEGDME-LiTFSI). The electrolyte for battery application (DEGDME-LiTFSI- LiNO_3) was prepared by dissolving LiNO_3 (film forming sacrificial additive with salt to solvent ratio of 1 mol kg^{-1}) and LiTFSI (ions conductor with salt to solvent ratio 1 mol kg^{-1}) in DEGDME.

Experimental Section: Electrolyte Characterization

Lithium/stripping deposition test was carried out in a symmetrical lithium/lithium 2032-coin cell using a current of 0.1 mA cm^{-2} with a step time of 1 hour at 23 °C, the test was performed by a MACCOR 4000 series Battery Test System. The electrochemical **anodic stability widow** was evaluated by linear sweep voltammetry (LSV) using a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat, with scan rate of 0.1 mV s^{-1} within OCV and 5V vs Li/Li^+ with a three electrode Swagelok T-cell equipped with lithium metal reference and counter electrodes, and a Super P carbon coated on carbon cloth working electrode. The same cell configuration and instrument were used to study the cathodic electrochemical stability of the electrolytes by **cyclic voltammetry (CV)**. The CV was performed with a scan rate of 0.1 mV s^{-1} in a 0 - 2 V vs Li/Li^+ potential range. The **lithium/electrolyte interface** chemical stability was evaluated by electrochemical impedance spectroscopy in a symmetrical lithium/lithium 2032-coin cell, acquiring with a VersaSTAT MC Princeton Applied Research-AMETEK the impedance spectra every day, using 10 mV signal amplitude in a 0.1 Hz - 0.5 MHz frequency range. The impedance spectra were analyzed by non-linear least squares fit (NLLSQ) using a Boukamp software.^{235,236} Only fitting results with a chi-square (χ^2) lower than 10^{-4} were accepted. **Flammability tests** was performed on the DEGDME-LiTFSI- LiNO_3 electrolyte by direct ignition of the solution in standard room environment, and reported in Fig.45. The **self-diffusion coefficient** of the ^1H , ^{19}F , and ^7Li nuclei in the DEGDME-LiTFSI electrolyte were measured by a Bruker 400 Advance III NMR spectrometer within screw-cap gastight NMR tubes in order to overcome possible evaporation along the temperature scan from 20°C to 70°C. The data were collected every 10 °C for each nucleus using a double-stimulated echo sequence with pulse field gradients (PFG) to suppress convection

The gradient pulse strength was increased linearly in 32 steps from 1 to 45 G cm⁻¹, the gradient pulse duration (δ) was of 1.4 – 4 ms with a diffusion delay (Δ) of 200 – 400 ms. Eddy current effects were avoided by using a longitudinal eddy-current delay (LED) of 5 ms. The error on the self-diffusion coefficient is about 3-5%.²²⁵ **Ion conductivity** was calculated from the self-diffusion coefficients by the

$$\text{Nernst-Einstein equation eq. 4: } \delta_{\text{NMR}} = \frac{F^2[C]}{RT} (D_{\text{Li}} + D_{\text{CF}_3\text{SO}_3})$$

where δ_{NMR} is the conductivity determined by the NMR, F is the Faraday constant (96485 C), $[C]$ is the concentration of the salt in the electrolyte (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature (K), D_{Li} and D_{LiTFSI} are the corresponding self-diffusion coefficients. Ion conductivity was also measured by electrochemical **impedance spectroscopy (EIS)** using a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. A symmetrical stainless steel/ stainless steel 2032 coin-cell with a Teflon ring separator was used to ensure a fixed cell constant during the measurements. The data were collected every 10°C by heating and cooling the cell within 40°C - 80°C temperature range using a signal amplitude of 10 mV and in a 0.1 Hz-0.5 MHz frequency range. The conductivity values determined by NMR (δ_{NMR}) and measured by EIS (δ_{EIS}) were used to obtain the **ion association degree** (α) of the LiTFSI salt by eq. 5: $\alpha = (1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}})$

The **lithium transport** (t^+) number was calculated from the self-diffusion coefficient by

$$\text{eq. 6: } t^+ = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{LiTFSI}}}$$

where D_{Li} is the self-diffusion coefficient of lithium, and D_{LiTFSI} is the self-diffusion coefficient of the TFSI anion [N(SO₂CF₃)₂⁻].

Experimental Section: Cathode Characterization

Bruker instrument **x-ray** diffractometer equipped with a Cu K α source and a graphite monochromator in the 2 θ / θ scanning mode was used to evaluate the structure of the sulfur-carbon electrode. The morphology of the sample was studied by a **scanning electron microscopy** (SEM, Zeiss EVO 40) with a thermionic electron gun equipped with LaB₆ crystal and by energy dispersive x-ray spectrometry (SEM-EDX) by a X-ACT Cambridge Instruments analyzer. **Cyclic voltammetry** of S-MWCNTs working electrode with a sulfur loading of 3 mg cm⁻² was performed in a three-electrode cell with lithium metal as reference and counter electrode using the DEGDME-LiTFSI-LiNO₃ as the electrolyte. The test was performed with a scan rate of 0.1 mV s⁻¹ in a 1.8 V - 2.8 V potential range. A second cyclic voltammetry test in the above reported potential range was carried using the same cell configuration at various scan rates (i.e., 0.1, 0.2, 0.3, 0.4 and 0.5 mV s⁻¹) in order to evaluate the Li⁺ diffusion coefficients (D) within the cathode material

by the **Randles-Sevcik equation** (Eq. 7):^{152,237} $I_p = 0.4463 z F A C \sqrt{\frac{z F v D}{RT}}$

where I_p is the peak current value (A), z is the number of exchanged electrons for the taken peak, F is the Faraday constant (96485 C mol⁻¹), A is the electrode geometric area (cm²), C is the Li⁺ concentration in the active material (mol cm⁻³), v is the scan rate (V s⁻¹), R is the gas constant (J K⁻¹ mol⁻¹), and T is the used temperature (K). The **CV tests** were performed at 23°C by a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. **Galvanostatic cycling** tests of the electrodes with various sulfur loadings (2 mg, 2.5, 3 and 4 mg cm⁻²) were carried out at the current rate of $C/3$, while the electrode with a sulfur mass loading of 4 mg cm⁻² required a current of $C/8$ for significant cycling ($1C = 1675 \text{ mAhg}^{-1}$), in a 1.9V – 2.8V voltage range. A **cycling test** at various c-rates (i.e., $C/10$, $C/8$, $C/5$, $C/3$, $C/2$ and $1C$) was performed using an electrode with 3 mg cm⁻² sulfur loading in a 1.9 V – 2.8 V voltage range. Cycling tests prolonged over 100 cycles were performed at $C/3$ in a 1.9 V – 2.8 V voltage range and at $1C$ in a 1.8 V – 2.8 V voltage range, using an electrode with 3 mg cm⁻² sulfur loading. All the galvanostatic tests were performed by a MACCOR 4000 series Battery Test System using a 3032-coin cells (electrode geometric surface 1.54 cm²) filled by 50 μ l of the DEGDME-LiTFSI-LiNO₃ electrolyte at 23°C. Cells were cycled following 3 hours of rest at the OCV.

Chapter: Lithium-Sulfur Cell with Polyethylene Oxide (PEO) Solid Electrolyte

Experimental part: Cathode Preparation

Elemental sulphur and mesophase micro bead (MCMB) carbon were mixed into 1:1 weight ratio at 130°C under stirring for 3 hours. The mixture was cooled down at room temperature and ground into fine particles by mortar. The powder was then planetary ball-milled for 54 minutes in overall, using milling steps of 5 min and 2 minutes of rest at a speed rate of 300 Rpm. The obtained sulfur-carbon active material was dispersed together with super P carbon (Timcal) and polyvinylidenedifluoride (PVdF) binder in a 80:10:10 weight ratio in N-methylpyrrolidone (NMP) and stirred for 3 hours. The resulting slurry was cast by Doctor-Blade onto aluminum foil and punched as 14-mm disks. The electrodes were dried under vacuum at 50 °C for 24 hours and transferred to Argon filled glove-box for cell assembling.

Experimental part: Electrolyte Preparation

Poly ethylene oxide (PEO) with molecular weight of 600KDa (0.6M) and lithium trifluoromethanesulfonate (lithium triflate, LiCF_3SO_3) from Sigma-Aldrich, were used to prepare electrolyte membrane by solvent casting method. Acetonitrile from Sigma-Aldrich was used as solvent and dried several days under molecular sieves until the water content was under 10 ppm as determined by 831-Karl Fisher Coulometer (METROHM) while lithium triflate was dried at 80°C under vacuum for 2 days. PEO powder, salt and acetonitrile were then mixed to and stirred until homogeneous slurry is obtained. The salt concentration, considered as the molar ratio between the ethylene oxide (EO) oxygen of and the lithium in the salt (LiCF_3SO_3), was O:Li = 20:1. The mixture was cast onto a flat glass plate by Doctor-Blade and dried under vacuum at 80°C for 3 hours. The membranes thus obtained had a thickness of 100 μm and was cut into disks of 18 mm of diameter. All the procedures involved in solid polymer electrolyte preparation were carried out in the Argon filled glove box with oxygen water content lower than 10 ppm. A 1M tetra ethyleneglycol dimethylether-lithium trifluoromethan sulfonate (TEGDME- LiCF_3SO_3) containing 5% w:w of dissolved Li_2S_8 was used as the reference liquid electrolyte for preliminary tests of the cathode material

Experimental part: Electrolyte Characterization

Conductivity tests were performed with 2032 coin cells in a symmetrical stainless steel current collector configuration using a Teflon O-ring separator to keep fixed the cell constant. The electrochemical impedance spectroscopy (EIS) tests were performed by VSP (Biologic), setting the signal amplitude at 10mV and using 0.1 Hz – 1 MHz as frequency range. The temperature range considered for the analyses was from 60° to 120°C collecting data each 20°C. The same instrument and frequency range reported for conductivity study were used for the lithium interface stability study. The latter was carried out in a symmetrical Li/PEO electrolyte/Li 2032-coin cell hold at an operating temperature of 80°C. Nonlinear least-squares (NLLSQ) fit of the impedance Nyquist plots was used to determinate the interface resistance by employing a Boukamp software and $\text{R(RQ)}_n\text{Q}$ equivalent circuit (R = resistance, Q= constant phase element). In order to ensure high quality, only fitting characterized by a chi-square (χ^2) parameter lower than 10^{-4} has been considered²³⁶²³⁸. Differential scanning calorimetry DSC (Mettler Toledo DSC821) was performed by heating up electrolyte sample, sealed in crucibles under argon atmosphere in the Glove-Box, from 20°C to 200°C at 5°C min⁻¹ rate. Thermogravimetric analysis TGA (Mettler Toledo TGA/SDTA851) was performed by heating the sample from room temperature to 600°C at 10°C min⁻¹ rate under nitrogen flow.

Experimental part: Cathode Characterization

Galvanostatic test applying a 0.1 mA cm^{-2} current to Li/Li symmetrical cell was carried out to determine the lithium stripping-deposition ability by using a MACCOR Series 4000 Battery Test System (Maccor Inc.). The first screening of S-C composite cathode in lithium cell was performed using a liquid electrolyte (See electrolyte preparation section) within 1V – 3.2V voltage range at room temperature, with a current rate ranging from C/10 (167.6 mA g^{-1}), to C/5 (335.2 mA g^{-1}), and to C/3 (558.6 mA g^{-1}). The galvanostatic cycling of S-C composite cathode in polymer configuration lithium cell was carried out at 80°C with 1.2V-3V voltage range at a current rate of C/20 (83.85 mA g^{-1}), using a MACCOR Series 4000 Battery Test System (Maccor Inc.). All the galvanostatic tests of the Li-S cells were performed by using a MACCOR Series 4000 Battery Test System (Maccor Inc.).



Scheme of the T-cell used for the electrochemical tests. The current collectors (grey parts on the left side of the panel) are in stainless steel, the remain parts are in Polypropylene (PP). The cells were assembled in argon filled glove box. After that all parts were tightly screw, Parafilm™ tape is used to sealed the cell and avoid the possible interaction of the active materials with the external environment. This kind of cell can be reused after a chemical wash

Chapter: The Li₂S-C-PEO Electrode

Experimental part: Cathode and Electrolyte Preparation

Dry Polyethylene Oxide (PEO, Mw 600000 Da, Sigma Aldrich), LiCF₃SO₃ (>99.9% Sigma Aldrich), in a EO:LiCF₃SO₃ molecular ratio of 20:1 (PEO₂₀LiCF₃SO₃), Li₂S (>99.9% Sigma Aldrich) and Super P carbon (Timcal) powders were mixed under Ar atmosphere in a PEO₂₀LiCF₃SO₃:Li₂S:Super P weight ratio of 30:35:35. The mixture was subjected to soft, glass-ball milling under Argon atmosphere for 24 hours. The cathode, hereafter referred to as Li₂S-C-PEO was prepared by doctor-blade casting on Al foil a slurry obtained by dispersing the soft milled (PEO)₂₀LiCF₃SO₃ - Li₂S - Super P carbon mixture in 1,3 dioxolane (DOL, Sigma Aldrich) in Ar filled glove box. The electrode mass loading was 1.5 mg cm⁻². The electrolyte solutions were prepared by dispersing LiCF₃SO₃ (>99.9% Sigma Aldrich) powder in a 1:1 wt mixture of 1,3 dioxolane (DOL, Sigma Aldrich), 1,2 dimethoxyethane (DME, Sigma Aldrich), with 1 mol/kg (1m) triflate concentration. LiNO₃ additive (1m) was subsequently added to the solution. 1,2 dimethoxyethane (DME Sigma Aldrich) and 1,3-dioxolane (DOL, Sigma Aldrich) herein reported as DOL-DME were dried under molecular sieves separately until the water content was lower than 10 ppm of water. Karl Fischer titration instrument (Metrohm) to control the water content was used. Before electrolyte preparation, both LiCF₃SO₃ and LiNO₃ salts were dried under vacuum at 100°C.

Experimental part: Cathode Characterization

The **electrochemical tests** were performed on coin cells assembled in Ar filled dry box using Celgard separators. The cell were assembled using the Li₂S-C-PEO cathode and a 1 m LiCF₃SO₃, DOL:DME 1:1 v/v electrolyte, to which 1 m LiNO₃ was added as a film-forming agent, in order to avoid shuttle reaction (evidenced by a cycling test performed by using a LiNO₃-free electrolyte). About 30 µl of electrolyte solution were used for the cell assembly. A Maccor Series 4000 Battery Test System was used for the **galvanostatic cycling** tests, within the voltage limits 1.4 –3.7 V and 1.9-2.7 V during the first and subsequent cycles, respectively, at a C/5 C-rate (1C = 1166 mA g⁻¹). **Electrochemical Impedance Spectroscopy (EIS)** tests were performed by applying 10mV AC amplitude signal to the cells within the 1MHz – 0.1 Hz frequency range. The equivalent circuit used for the analysis of the impedance data is R_e(RQ)_{PF}(R_{CT}Q_{DL})Q, where R_e is the electrolyte resistance, the (RQ)_{PF} elements are associated to the passivation of the electrode surface, R_{CT} and Q_{DL} describe the charge transfer and double layer capacitance associated to the cathode lithiation/delithiation, respectively, and Q is related to Li⁺ diffusion within the electrode. A VSP (Biologic) was used for the EIS measurements upon cycling. The EIS responses were analysed by using the Boukamp program. All the electrochemical tests were run at 40°C. **Ex-situ XRD** measurements were performed on the electrode at different stages of charge/discharge by using a Rigaku D-Max Ultima + diffractometer, with Cu Kα source and a graphite monochromator, in 2θ/θ scanning mode. The electrodes were collected from the cell in Ar-filled glove box, washed with DME, and sealed in plastic-bags into the XRD-sample holder in order to avoid the change of the electrode structure by contact with air. The electrode morphology was investigated by means of **Scanning Electron Microscopy**, using a Phenom-FEI instrument. The electrode was then transferred into the instrument under argon, and subjected to fast vacuum upon introduction into SEM-sample holder, in order to avoid excessive contact with atmosphere.

Experimental part: *Electrolyte Characterization*

A Bruker 400 Avance III NMR spectrometer was used to measure self-diffusion coefficients with a pulse field gradient double-stimulated echo sequence. The data were acquired each 10°C from 20 to 60 C°, using a diffusion delay of 80-250 ms between the gradient pulses of strength of 0-45 G/cm and duration of 1-2.5 ms. The Nernst-Einstein equation (4) was used to calculate conductivity values from the self-diffusion coefficient following indicated by. $\delta_{NMR} = \frac{F^2[C]}{RT} (D_{Li} + D_{CF_3SO_3})$

where F is the Faraday constant (96485 Coulomb), [C] represents the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature value, D_{Li} and D_{CF₃SO₃} are the self-diffusion coefficients of the Li⁺ cation and CF₃SO₃⁻ anion, respectively. The electrochemical impedance spectroscopy to obtain conductivity values of the electrolyte was carried out in a 2032 coin cell, stainless steel current collectors and a Teflon ring as a separator were used to keep the cell constant fixed. The measurements were carried out with a signal amplitude of 10 mV in a frequency range from 100 mHz to 100 KHz using a biological VSP instrument. The ion association was calculated following the equation (5): $\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right)$

where δ_{EIS} and δ_{NMR} are the conductivity measured by EIS and calculated by equation (1), respectively.

Chapter: Glyme Electrolytes and Sodium

Experimental Section: *Electrolyte Preparation*

Glyme-based solvents, i.e., 1,2-Dimethoxyethane ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$) and diethylene glycol dimethyl ether ($(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$), hence DME and DEG, respectively, were purchased from Sigma Aldrich and dried under molecular sieves (Sigma Aldrich, pores diameter 3 Å) for several days until the water content was lower than 10 ppm. The water content was determined by 889 Karl Fisher Coulometer METROHM. Sodium trifluoromethanesulfonate (sodium triflate, NaCF_3SO_3) and sodium nitrate (NaNO_3), by Aldrich, were dried under vacuum overnight at 80°C. The electrolytes were prepared by dissolving NaCF_3SO_3 either in DME and in DEGDME, in a ratio of 1 mol of salt in 1 kg of solvent. The densities of DME- NaCF_3SO_3 and DEGDME- NaCF_3SO_3 were of 0.984 and 1.068 g/ml. The (1m) molality was selected in order to better compare with previous papers and with literature data, while the glyme/sodium ratios of 1:11 and 1:7.5 for DME and DEGDME, respectively. The same solutions were supplemented with a film forming agent (NaNO_3 , 0.4 mol of salt in 1 kg of solvent) for the final test in a sodium cell. The four solutions, i.e., the bare electrolytes (DME- NaCF_3SO_3 and DEGDME- NaCF_3SO_3), and the ones with sodium nitrate (DME- NaCF_3SO_3 - NaNO_3 and DEGDME- NaCF_3SO_3 - NaNO_3), were prepared and stored in an argon filled glove box with water and oxygen contents lower than 1 ppm.

Experimental Section: *Electrolyte Characterization*

Thermal gravimetric analysis (TGA) was performed on bare electrolytes by heating the samples under nitrogen flow from 20°C to 700°C at 10°C min⁻¹, using a Mettler Toledo TGA/SDTA85. The **self-diffusion coefficients** of ¹H and ¹⁹F nuclei (D_H and D_F respectively), related to the hydrogen in the glyme chain and the fluorine in the CF_3SO_3^- anion, were measured with a Bruker 400 Avance III NMR spectrometer using a PFG double-stimulated echo sequence to suppress convection effects in the temperature range from 20°C to 60°C. The data were collected every 10°C with gradient pulses of 1-2 ms, a gradient strength g in the range of 1-45 G cm⁻¹, and a diffusion delay Δ of 100-200 ms. The self-diffusion coefficients of ²³Na nucleus (D_{Na}) were measured with a Varian 300 WB Direct Drive spectrometer equipped with a DOTY z-gradient probe, using the same double-stimulated echo sequence with gradient pulses of 0.75-1 ms, gradient strength g varied from 2 up to 1000 G cm⁻¹ as needed, and a diffusion delay Δ of 12-17 ms. The **electrolyte conductivity** was measured by impedance spectroscopy (δ_{EIS}) in a symmetrical stainless steel/stainless steel, 2032 coin-cell equipped by a Teflon O-ring separator, in a 0.1 Hz – 0.5 MHz frequency range with signal amplitude of 10 mV using a VERSTAT AMETEC instrument. The impedance responses were collected from 40°C to 80°C every 10°C. Ion conduction ratio was calculated from self-diffusion coefficient (δ_{NMR}) by using the Nernst-Einstein equation $\delta_{NMR} = \frac{F^2[C]}{RT} (D_{Na} + D_F)$ (4), where F is the Faraday constant (96485 Coulomb), $[C]$ represents the solution concentration (mol cm⁻³), and R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹). The **ion association degree** (α) was calculated by combining the conductivity values determined by EIS (δ_{EIS}) and the ion conduction ratio determine by NMR (δ_{NMR}), following the equation $\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right)$ (5). The **sodium ion transference number** was calculated by using the equation $t^+ = \frac{D_{Na}}{D_{Na} + D_F}$ (6), where D_{Na} is the self-diffusion coefficient of the Na⁺ cation and D_F is the self-diffusion coefficient of the CF_3SO_3^- anion, as determined by NMR. The cathodic electrochemical stability of the electrolytes was determined by **cyclic voltammetry** (CV) in a three-electrode configuration cell using sodium metal as the reference and counter electrodes, and Super P carbon (Imers) coated on copper as working electrode. The CV was performed using a potential ranging from 2 V to 0 V vs. Na/Na⁺ with a scan rate of 0.1 mV sec⁻¹.

The anodic electrochemical stability was determined by **linear sweep voltammetry** from 2 V to 5 V vs. Na/Na⁺, using the same cell configuration and scan rate employed for CV, and a Super P carbon (Imers) coated on aluminum as the working electrode. Sodium **stripping/deposition tests** were carried out in a symmetrical sodium/sodium 2032 coin-cell, with a constant current of 0.1 mA cm⁻² and a step time limit of 1 hour. The chemical stability of the sodium interface in contact with the electrolyte versus time was studied by **impedance spectroscopy** (EIS) in a symmetrical sodium/sodium 2032 coin-cell, in a 0.1 Hz-0.5 MHz frequency range, using a 10 mV signal amplitude.

Experimental Section: *Cathode Preparation and Characterization*

The cathode, already proposed for lithium-sulfur cells in a previous paper [34], was formed by mixing elemental sulfur (S, Sigma Aldrich) and multi-walled carbon nanotubes (MWCNs, Sigma Aldrich), in a 1:1 weight ratio, heating at 135°C in order to melt the sulfur and stirring for 2 hours until complete homogenization. The resulting mixture was cooled at room temperature and treated by high energy ball milling in a stainless-steel jar, with 4 stainless steel balls. The treatment was performed at a frequency of 15 Hz for 2 hours, using 4 steps of 30 minutes of milling and rest steps of 15 minutes. The electrode film was prepared by dispersing the sulfur-carbon powder (S-MWCNs), polyvinylidenedifluoride (PVdF Solvey) binder and Super P (Imers) electron conductor (80:10:10 weight ratio) in N-methylpyrrolidone (NMP, Aldrich), stirring until formation of a homogeneous slurry, casting on aluminum foil by Doctor blade and drying at 50°C overnight to remove the solvent. Electrode disks were then punched, dried at 50°C for 24 h under vacuum overnight and introduced in the argon filled glove box to build the cells. The electrochemical reaction of S-MWCNs electrode with Na was studied by cyclic voltammetry tests in a three-electrode cell configuration, equipped with sodium metal reference and counter electrode, using either DME-NaCF₃SO₃-NaNO₃ or DEGDME-NaCF₃SO₃-NaNO₃ upgraded electrolyte. The cell potential was ranged from 0.5 V to 2.1 V vs. Na/Na⁺, using a scan rate of 0.1 mV sec⁻¹. Sodium-sulfur 2032 coin cells were assembled using the S-MWCNs cathode, the selected electrolyte, and Na-metal anode. The cells were subjected to galvanostatic cycling within 0.5 V and 2.1 V, using a current rate of C/10 (1 C = 1676 mA g⁻¹).

Chapter: Glyme Electrolytes and Lithium Oxygen Battery

Experimental Section: *Electrolyte and Cathode Preparation*

The electrolyte was prepared by mixing Tetra ethylene glycol dimethyl ether ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$) following named by TEGDME and lithium bistrifluoromethanesulfonimide ($\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)$), herein named LiTFSI. Both chemicals purchased from Sigma Aldrich. Molecular sieves of $3\text{\AA}$ from Sigma Aldrich were dried under vacuum at 250°C for 48 hours and used to reduce the water content of the TEGDME below 10 ppm. The water content was measured by Karl Fischer titration instrument (831 Karl Fisher Coulometer, Metrohm). Before mixing the TEGDME and the lithium salt in 1 mol kg^{-1} ratio, the LiTFSI was dried under vacuum at 80°C for 24 hours. Multi walled carbon nanotubes from Sigma Aldrich, following named MWCNTs, were annealed under nitrogen flow at 750°C for 12 hours. The active material (named $\text{N}_2@\text{MWCNTs}$) was mixed separately with polyvinylidenedifluoride (PVdF, Solvay) binder in a 80:20 mass ratio and dispersed in N-methylpyrrolidone (NMP, Aldrich). The slurry was cast on a gas diffusion layer (TGP-H-030 carbon paper, Toray) by Doctor blade. The active material ratio on the current collector was of about 0.8 mg cm^{-2} . The electrode foils were punched in disks, dried overnight at 100°C and finally introduced in argon filled glove box with oxygen and moisture content lower than 1 ppm. Lithium oxygen cells were then assembled by combining lithium metal, the $\text{N}_2@\text{MWCNTs}$, and the TEGDME-LiTFSI in a top-meshed 2032 coin-cell inserted into a glass tube filled subsequently by pure oxygen.

Experimental Section: *Cathode Characterization*

The powders structure was characterized by X ray diffraction using a Bruker instrument equipped with a Cu $K\alpha$ source and a graphite monochromator, in the $2\theta/\theta$ scanning mode. The morphology of the samples was evaluated by SEM (Zeiss EVO 40) with a thermionic electron gun equipped by LaB_6 crystal. Lithium oxygen cell was studied by galvanostatic test using voltage cutoff performed with a constant current of 100 mA g^{-1} in a 1V - 4.5V range. Galvanostatic cycling tests were also carried out with a current rate of 100 mA g^{-1} and limiting the capacity to 500, 1000 and 2000 mAh g^{-1} . The current density and specific capacity was referred to the carbon weight into the electrode, while the surface capacity was determined with respect to the electrode geometric area

Experimental Section: *Electrolyte Characterization*

The thermal properties were evaluated by **differential scanning calorimetry** (DSC) using the Mattler Toledo DSC821 instrument. The TEGDME-LiTFSI electrolyte was sealed in aluminum crucible under argon atmosphere before the DSC analysis. The measurement was performed by cooling down from -30°C to -90°C with a rate of $-5^\circ\text{C min}^{-1}$. The lithium **stripping deposition** test was performed with constant current rate of 0.1 mA cm^{-2} and step limit of 1 hour using a symmetrical lithium/lithium 2032 coin-cell and a MACCOR 4000 series Battery Test System. The **lithium/electrolyte interface resistance** was measured using the latter cell configuration by electrochemical impedance spectroscopy in the frequency range of 0.1MHz - 0.1Hz with a signal amplitude of 10 mV with a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The impedance spectra were associated to the $R(\text{RQ})_n\text{Q}$ equivalent circuit, where R is the resistance and Q a constant phase element (CPE), and analyzed using the nonlinear least square (NLLSQ) fit by Boukamp Software^{235,236}; only the results with a chi-square χ^2 lower than 10^{-4} were accepted. The **voltammetry tests** were carried out in Swedglock T-cell with lithium metal as reference and counter electrode and a working electrode formed by depositing super P (Timcal) on Cu or Al support for the cathodic and the anodic scan, respectively.

The **cyclic voltammetry (CV)** for the cathodic region was performed in the potential range 0V - 2V vs. Li/Li⁺, while the **linear sweep voltammetry (LSV)** for the anodic region was performed up to 5V vs. Li/Li⁺, both with a scan rate of 0.1 mV sec⁻¹. The measurements were carried out by VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The **self-diffusion coefficient** of the ¹H ⁷Li and ¹⁹F nuclei were measured by a Bruker 400 Avance III NMR spectrometer suppressing the convection effect by PFG double-stimulated echo sequence. The data were collected every 10°C from 20°C to 80°C with a gradient strength *g* of 1-45 G cm⁻¹, gradient pulse of 1-2 ms and a diffusion delay Δ of 100-200 ms. The error on the self-diffusion coefficient is about 3–5%.²²⁵ The **ionic conductivity** of the electrolyte (δ_{NMR}) was calculated from the self-diffusion coefficient by the Nernst-Einstein equation (4)¹¹⁰

$$\delta_{NMR} = \frac{F^2[C]}{RT} (D_{Li} + D_F)$$

where F is the Faraday constant (96485 Coulomb), [C] represents the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹). Furthermore, the ionic conductivity was measured by impedance spectroscopy (δ_{EIS}) in a symmetrical SS/SS 2032-coin cell with a Teflon O-ring separator in the temperature range of 20°C - 80°C, using a signal amplitude of 10 mV in the frequency range of 1MHz and 0.1Hz by employing a VersaSTAT MC Princeton Applied Research-AMETEK potentiostat. The conductivity values δ_{EIS} and δ_{NMR} were combined in equation 5 to obtain the **ionic association** degree (α)⁸⁴

$$\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}} \right)$$

The **lithium transport number** (t⁺) was calculated by equation (6)⁶⁹:

$$t^+ = \frac{D_{Li}}{D_{Li} + D_F}$$

where D_{Li} is the lithium self-diffusion coefficient and D_F is the fluorine self-diffusion coefficient of the TFSI⁻ anion.

Scheme of cell prototype for lithium oxygen galvanostatic cycling tests

