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Full Paper

An Advanced Lithium-Ion Sulfur Battery for High Energy Storage

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ABSTRACT: Herein a lithium-ion battery is reported using a sulfur-carbon composite cathode, a graphite anode, and a dimethoxyethane-dioxolane-LiTFSI electrolyte advantageously added by lithium nitrate (LiNO_3) and a selected polysulfide (Li_2S_8). The suppressed sulfur dissolution, due to the Li_2S_8 buffer action, as well as reduced shuttle reactions by the film-forming properties of the LiNO_3 positively affect the lithium-ion cell behavior in terms of delivered capacity, Coulombic efficiency, and cycle life. The lithium-sulfur cell shows a stable capacity of 750 mAh g^{-1} for over 200 cycles with an enhanced cycling efficiency. Furthermore, the full lithium-ion sulfur battery using a graphite-based anode shows a working voltage of about 2 V and delivers a stable capacity of 500 mAh g^{-1} . The full cell has enhanced safety content, due to the replacement of the lithium metal anode by suitable intercalation electrode, and shows a theoretical energy density as high as 1000 Wh kg^{-1} at high current rate of 1 C. The remarkable safety level, low materials cost, and high practical energy density, expected to exceed 300 Wh kg^{-1} , suggest the battery here reported as suitable energy storage system for future applications.

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1. Introduction

Recently, increasing consumption of fossil fuels with atmosphere pollution and consequent climate changes focused renewed attention on alternative energy production systems. Indeed, the discontinuity of these systems and, more recently, the emerging market of the electric vehicles triggered the development of advanced energy storage systems. In this respect, lithium batteries (LIBs) appeared the most promising among the various candidates due to their high theoretical energy and long calendar life.^[1] However, the severe targets of the electric vehicle market, as well the need for decreasing cost of side storage in renewable energy plants, so far required new systems characterized by higher energy density and lower economic impact. Lithium-sulfur battery has high theoretical energy density, i.e., of about 2600 Wh kg^{-1} , and, contemporary, very low cost and earth abundance of the cathode material, hence it is considered the most promising system to meet the emerging market requirements.^[2-7] However, the use of sulfur in lithium batteries is still hindered by several issues, preventing a practical application, such as the insulator nature of the cathode,

the volume changes during operation and the high solubility of reaction intermediates (e.g., polysulfides) in conventional organic solvents.^[8] Lithium sulfur electrochemical process is a multistep reaction involving the initial formation of the highly soluble Li_2S_8 and final precipitation of Li_2S , with an overall capacity of 1675 versus sulfur mass.^[9] The dissolved polysulfide may migrate through the electrolyte from the sulfur cathode to the lithium metal anode, thus leading to a shuttle reaction, an increasing polarization, and a final capacity fading.^[10,11] Several researches, involving both the electrodes and the electrolyte, have been devoted to the lithium-sulfur battery in order to mitigate the shuttle reaction and the cathode dissolution. Cathode optimization, mainly focused on sulfur impregnation in modified carbons or functionalized graphene, has been reported as efficient strategy to enhance the electronic conductivity and the cycling stability.^[12-15] Ether-based electrolytes, such as tetraethylene glycol dimethyl ether (TEGDME)^[8,10,16] and 1,3 dioxolane (DOL) dimethoxyethane (DME), have been selected as suitable media in alternative to conventional carbonate solutions.^[17-19] Recent studies demonstrated the positive effect of electrolyte-additives, such as LiNO_3 , in inhibiting the polysulfide shuttle reaction, due to the formation of a stable layer at the lithium anode surface, thus leading to a remarkable enhancement of the lithium-sulfur cell performance.^[18-21] Further studies evidenced that the dissolution of a selected polysulfide, of different nature and concentration, into the electrolyte may efficiently stabilize the sulfur cathode by mass and electrochemical effect.^[22-25] A relevant issue affecting the lithium

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sulfur cell in its conventional configuration is represented by the use of a lithium metal anode that is characterized by safety issues, associated to possible dendrite formation, short circuit, and cell thermal runaway. Previous papers demonstrated the possible replacement of lithium metal by Li-alloying materials in an efficient lithium-ion sulfur cell.^[3, 16, 26–28] In this work we report a metal-free, full lithium-ion sulfur battery using graphite-based, intercalation anode, and sulfur–carbon cathode, benefitting by the contemporary positive effect of two additives, i.e., Li_2S_8 and LiNO_3 dissolved within a DOL-DME electrolyte. The cell operates at about 2 V and delivers a capacity as high as 500 mAh g^{-1} with extended stability, limited polarization, and high charge–discharge efficiency, i.e., a relevant performance suitable for the development of a safe, high energy storage system.

2. Results and Discussion

Figure 1 reports the comparison of the electrochemical characteristics of the bare DOL-DME-LiTFSI electrolyte, and the solutions added by LiNO_3 and by Li_2S_8 in terms of cyclic voltammetry (a), lithium stripping–deposition polarization (b), stability against lithium metal (c), and Li-transference number (d). The cyclic voltammetry performed using the pristine solution (Figure 1a, black line) shows a flat profile and absence of relevant peaks. The presence of LiNO_3 within the solutions (Figure 1a, red and blue lines) reveals a reduction peak at around 1.5 V, associated to the irreversible reaction of the LiNO_3 .^[29] The reversible electrochemical reduction of the polysulfide appears for final solution, added by both LiNO_3 and Li_2S_8 (Figure 1a, blue line), at around 2.4 and 2.0 V versus Li^+/Li in discharge, while the following oxidation is merged at about 2.6 V in charge.^[10] The Li-stripping-deposition tests reported in Figure 1b evidence a polarization limited to few mV and a stable trend for several cycles, thus suggesting the compatibility of the lithium with the selected electrolytes. The suitability of the electrolytes in lithium cell is further confirmed by Figure 1c, reporting the time evolution of the interphase resistance. The figure reveals a slight resistance growth during the initial 10 h of test, associated to the solid electrolyte interphase (SEI) film formation upon chemical reaction of lithium with the electrolyte, and a following stabilization due to the consolidation of the SEI.^[10, 24] The same figure evidences that the solution added by LiNO_3 and Li_2S_8 , selected as the preferred electrolyte media for sulfur cell application, is characterized by the lowest cell resistance, due to the beneficial effect of the two additives. The lithium transference number (t_{Li^+}) of the electrolytes has been calculated according to the Bruce–Vincent equation.^[30] Figure 1d reports the comparison of the current–time curves of the symmetrical lithium cell assembled using the three electrolytes and polarized at 10 mV (the corresponding impedance responses used for t_{Li^+} determination are reported in the Supporting Information, Figure S1). The t_{Li^+} , calculated to be of 0.47 for the pristine electrolyte in agreement with literature data,^[31] decreases to 0.35 by addition of LiNO_3 salt due to the increased ionic force of the solution, and rises back up to 0.45 by Li_2S_8 addition, thus suggesting that the addition of LiNO_3

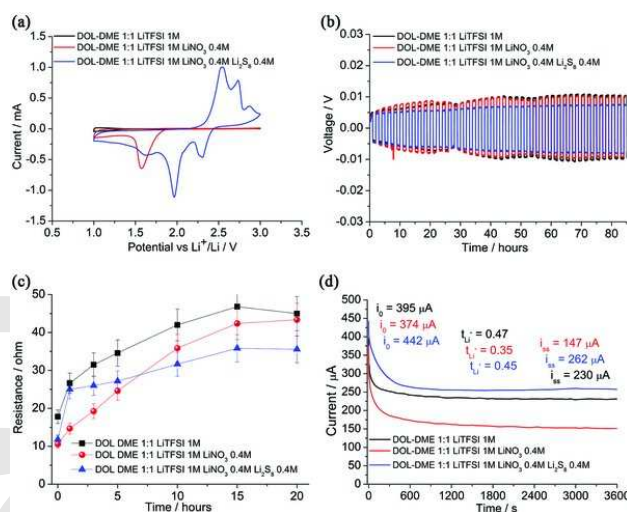


Figure 1. Electrochemical characterization of the DOL-DME (1:1, v/v), 1 M LiTFSI (black), 0.4 M LiNO_3 -added (red), and 0.4 M LiNO_3 –0.05 M Li_2S_8 -added (blue) electrolytes. a) Cyclic voltammetry performed using a scan rate of 0.1 mV s^{-1} versus Li^+/Li ; b) lithium deposition stripping overvoltage in lithium symmetrical cell using a current of 0.1 mA cm^{-2} ; c) time evolution of the lithium symmetrical cell resistance; and d) current–time evolution of the lithium symmetric cells following a DC polarization of 10 mV and, in inset, corresponding t^+ number calculated. Room temperature ($25 \text{ }^\circ\text{C}$).

finally affects the lithium transference number and the contribution of the Li_2S_8 to the lithium ion mobility.

The sulfur–carbon electrode employed in this work has micrometric morphology and S-loading of about 50%, evidenced by SEM and TGA analysis reported in the Supporting Information, Figure S2a,b, respectively.^[32] This electrode configuration is characterized by remarkable solubility during operation in lithium cell using the bare electrolytes, while the electrode shows a significant improvement, both in terms of cycling stability and Coulombic efficiency, in lithium cell using the polysulfide (Li_2S_8) added electrolyte, as evidenced by the cycling behavior reported in **Figure 2**. The Li/S cell cycled at a current as high as 1.675 A g^{-1} (1 C) shows a capacity of 900 mAh g^{-1} and an efficiency of 95% during the 1st cycle. During the following cycles the capacity decreases to a value of about 750 mAh g^{-1} stable for over 200 cycles, with an average working voltage of 2.2 V and an efficiency approaching 99% (Figure 2a,b). The lithium cell using the bare electrolyte shows remarkable dissolution of the sulfur electrode (Figure 2c) and a low Coulombic efficiency (Figure 2d) due to the shuttle reaction of the dissolved cathode. The efficiency rises by LiNO_3 addition, due to the formation of a favorable SEI film, however the cell appears still affected by capacity fading. Furthermore, the contemporary effect of the two additives, i.e., LiNO_3 and Li_2S_8 , well stabilizes the cell capacity and enhancing the Coulombic efficiency to value close to 100%. Indeed, the specific capacity delivered by the Li/S cell using the modified electrolyte is about 750 mAh g^{-1} as referred to the sulfur mass in the elec-

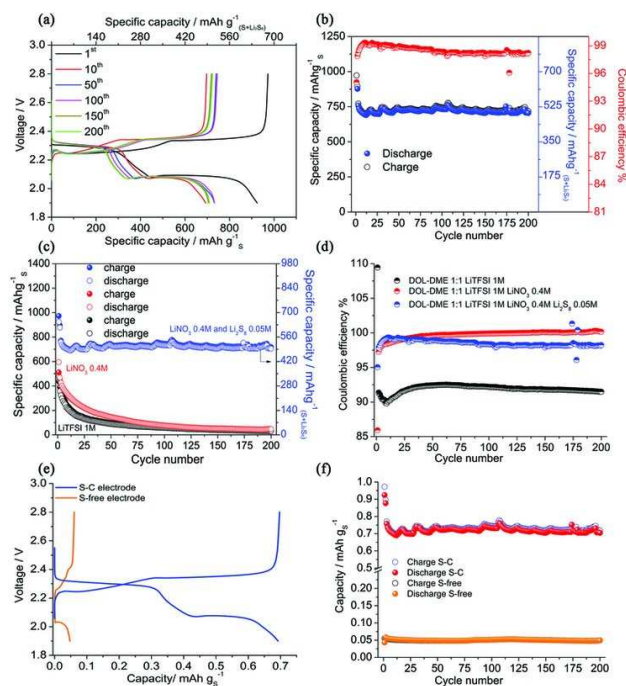


Figure 2. a) Voltage profiles and b) cycling behavior (with corresponding Coulombic efficiency reported by red circles in right side) of a Li/ DOL-DME (1:1, v/v), 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈/S-C cell. Comparison of the c) cycling behavior and d) Coulombic efficiency of the Li/S-C cells using the three electrolytes: bare DOL DME 1:1 LiTFSI 1 M, 0.4 M LiNO₃-added, and 0.4 M LiNO₃-0.05 M Li₂S₈-added electrolyte; specific capacity versus total sulfur amount on the right axis. e) Cycling behavior and f) corresponding voltage profile of a lithium cell using a sulfur-free carbon electrode (MCMC, Super P, and PVdF 6020 in the 8:1:1 weight) in comparison to a cell using the S-C electrode. Voltage range 1.9–2.8 V, current of 1.675 A g⁻¹ (corresponding to 1 C of sulfur electrode). Room temperature (25 °C).

trode that is reduced to 525 mAh g⁻¹ considering the overall S mass, including dissolved polysulfide (right-side Y axis). In this work, the Li-S cell capacity has been referred to the sulfur mass within the cathode neglecting the direct participation of Li₂S₈ dissolved within the electrolyte to the electrochemical process. Indeed, this process has been directly investigated by the cycling test employing a sulfur-free carbon electrode and Li₂S₈-added electrolyte. The response of this cell in terms of cycling behavior (Figure 2e) and voltage profile (Figure 2f), in comparison to the corresponding test in lithium cell using the sulfur carbon electrode, demonstrates a minor contribution of the polysulfide to the overall Li/S cell capacity, i.e., of about 7%. Indeed, the dissolved Li₂S₈ mainly acts as mass buffer leading to cell stabilization, while LiNO₃ salt increases the cell efficiency.

A graphite-based anode has been characterized in lithium cell using the DOL DME 1:1 LiTFSI 1 M, LiNO₃ 0.4 M, Li₂S₈ 0.05 M electrolyte solution in order to verify its suitability for appli-

cation in full, lithium-ion sulfur cell. Prior to test, the graphite electrode has been fully prelithiated by direct contacting with a lithium foil metal wetted by LP30 electrolyte, as reported in previous paper.^[27] The interphase of the lithiated graphite electrode has been studied in lithium cell by using electrochemical impedance spectroscopy (EIS). Figure 3a reports the voltage profile of the 1st and 2nd cycles of the Li/ DOL-DME (1:1, v/v), 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈/graphite cell cycled using a current of 200 mA g⁻¹ within voltage ranging from 0.01 to 2.0 V. The figure evidences a delivered capacity of about 100 mAh g⁻¹ during the first discharge, increasing to about 310 mAh g⁻¹ during the following charge. This trend is due to the activation process (see the Experimental Section) that leads to a partial lithium insertion into the electrode structure, reduction of the pristine cell working voltage as well as to the formation of a stable SEI film thus avoiding further reaction of the electrode with the electrolyte components, e.g., Li₂S₈ and LiNO₃. Hence, the formation of a passivation layer kinetically protects the graphite electrode surface. Indeed, the inset of Figure 3a, reporting the impedance Nyquist plot of the cell at the pristine state, demonstrates a low cell resistance, i.e., limited to about 45 Ω. Furthermore, the Nyquist plots of the cell upon the first discharge (empty black circles) and the following charge (plain blue circles) reported in Figure 3b and the evolution of the cell resistance during cycling (in inset) further confirm the stability of the SEI film formed by prelithiation of graphite electrode prior to cycle. The slight changes observed in Figure 3b may be most likely attributed to minor changes in SEI film composition by cycling in DOL-DME-LiTFSI-LiNO₃-Li₂S₈ electrolyte. Figure 3c, reporting the voltage profile of the lithiated graphite electrode, reveals an average working voltage of about 0.2 V versus Li⁺/Li, while the cycling behavior of Figure 3d evidences a decay during the initial ten cycles, followed by a stabilization of the capacity at about 240 mAh g⁻¹, i.e., about 65% of the expected theoretical value (370 mAh g⁻¹). The capacity decay, and the low initial cell efficiency, during the initial cycles may be attributed to SEI film formation and structural organization of the electrode surface in presence of the additional salts, i.e., LiNO₃ and Li₂S₈, required for an optimal operation of the sulfur cathode side.^[10,24,27,29] However, the stable trend of the cycling test during the following cycles is considered convincing proof, suggesting the suitability of the lithiated-graphite electrode in full Li-ion sulfur cell.

Figure 4 reports the electrochemical response of the Li-ion sulfur cell formed by coupling the sulfur-carbon cathode, the prelithiated graphite anode and the selected electrolyte solution, e.g., added by LiNO₃ and Li₂S₈, using a current-rate as high as of 1675 mA g⁻¹ (1 C). During the first cycle, the discharge of about 1000 mAh g⁻¹ is not completely reversed upon the following charge process, due to partial electrolyte decomposition at the graphite surface, thus leading to a Coulombic efficiency higher than 100% (i.e., calculated as percentage of the discharge capacity in respect to charge capacity). Furthermore, the cell shows capacity decay during the first 10th cycles, as most likely ascribed to the anode stabilization already observed in the cycling test of the anode reported in Figure 3. During the following cycles a stable capacity of about 500 mAh g⁻¹, working voltage of about 2 V, high Coulombic efficiency, and limited polarization are shown. The steady state voltage profile

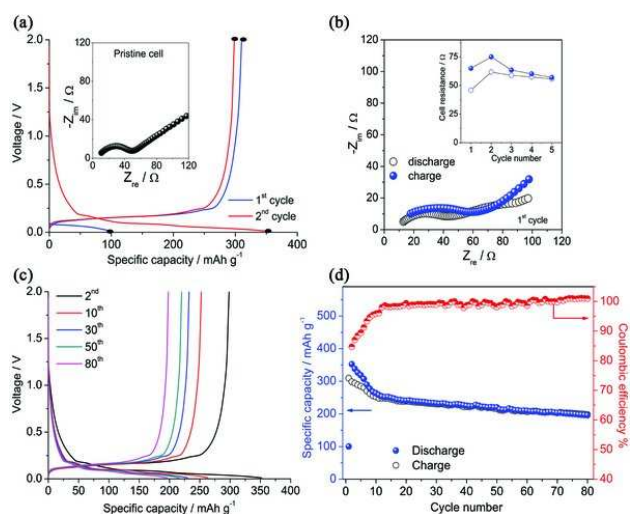
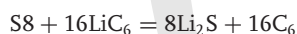


Figure 3. a) Voltage profile of the 1st and 2nd cycles of the Li/ DOL-DME (1:1, v/v), 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈/graphite lithium-cell cycled using a current of 200 mA s⁻¹ within voltage ranging from 0.01 to 2.0 V voltage range and, in inset, impedance Nyquist plot of the cell at the pristine state. b) Nyquist plots of the cell upon the first discharge (empty black circles) and the following charge (plain blue circles) and, in inset, evolution of the cell resistance during cycling. c) Voltage profiles and d) cycling behavior (with corresponding Coulombic efficiency reported by red circles in right side) of the cell upon prolonged cycling. Room temperature (25 °C).

of Figure 4a reflects the reversible electrochemical process of sulfur with lithiated graphite



This notable performance suggests a stable energy density, theoretically of about 1000 W h kg⁻¹ that is a value much higher than that offered by the commercial Li-ion battery.^[1] The cell has additional bonus: the extremely reduced cost of the component materials, i.e., sulfur and graphite, and the high safety content.

3. Conclusions

The lithium-ion sulfur cell here reported shows enhanced performances due to the beneficial addition of LiNO₃ and Li₂S₈ to the DOL-DME-LiTFSI solution used as the electrolyte media. The two additives properly suppress the polysulfide shuttle reaction and buffer the sulfur dissolution within the electrolyte, thus leading to optimized electrochemical process. Furthermore, the replacement of the lithium metal by a carbon anode based on intercalation process well increases the cell safety. The excellent performances of the full cell, in terms of delivered capacity, current rate, energy density, and cycling life, confirm the suitability of the system here proposed for high energy applications.

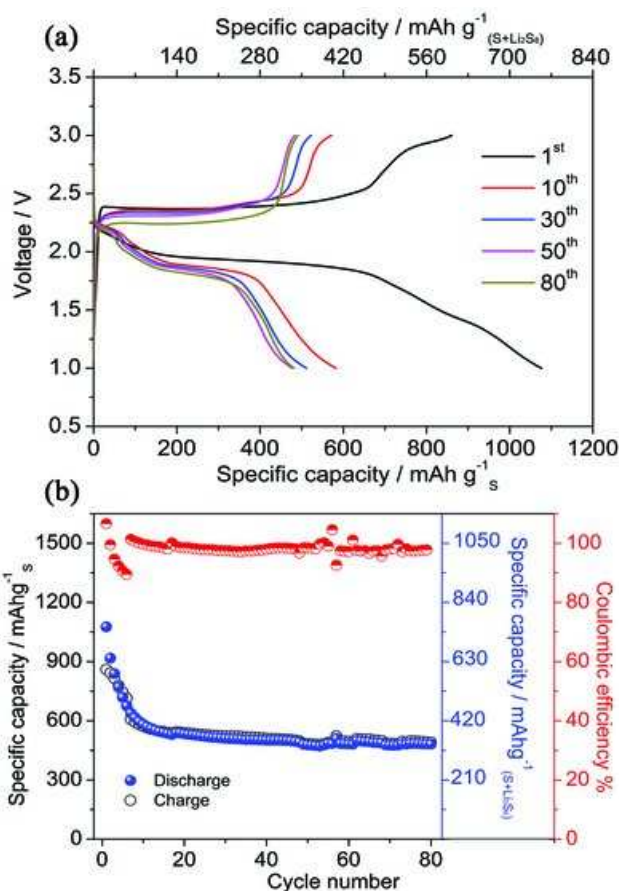


Figure 4. a) Voltage profile at the 1st, 10th, 30th, 50th, 80th cycle and b) cycling behavior (with corresponding Coulombic efficiency reported by red circles in right side) of the LiC₆/ DOL-DME (1:1, v/v), 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈/S-C lithium-ion sulfur cell performed at a current of 1.675 A g⁻¹ (1 C) within 1.0–3.0 V voltage range. Room temperature (25 °C).

4. Experimental Section

Electrodes Preparation: The cathode material was prepared by melting sulfur (Aldrich 99.9%) at 135 °C and then mixing it with MCMB (mesophase carbon micro beads, Osaka gas) with a 1:1 weight ratio as reported in a previous paper.^[32] Following, the mixture was refined for 2 h by using the high energy mechanical milling (HEMM). The sulfur-carbon electrode morphology was investigated by scanning electron microscopy using a Phenom-FEI instrument. The S-C thin film electrode was prepared by mixing the active material powder with Super P carbon (conducting agent, Timcal) and polyvinylidene fluoride (PVdF 6020, binder, Solvay) in a weight ratio of 8:1:1 using *N*-methyl pyrrolidone (NMP). The resulting slurry was then cast on an Al foil of approximately 40 μm thickness to achieve a sulfur loading of about 1.3 mg cm⁻². The electrodes were dried at 50 °C under vacuum to remove residual solvent, prior to be used in lithium cells. The anode was prepared by mixing MCMB powder with Super P carbon (conducting agent,

Timcal) and PVdF 6020, binder, Solvay in the ratio of 8:1:1 and dissolving the mixture in NMP, Aldrich. The resulting slurry was plated on a Cu foil, with a final graphite loading of 5 mg cm⁻². The electrodes were dried at 100 °C under vacuum, prior to be used in lithium cells.

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Electrolytes Preparation: The bare, additive-free electrolyte was prepared in argon-filled glove box by dissolving 1 mole of LiTFSI (Aldrich) in 1 L of DME (Dimethoxyethane, Aldrich)/DOL (Dioxolane, Aldrich) with a 1:1 volume ratio. A second test-solution was prepared by adding to the bare solution 0.4 M of LiNO₃. The final, polysulfide-containing electrolyte was prepared by following two steps: (i) mixing lithium metal and elemental sulfur in a molar ratio of 2:8 in DME/DOL solution to reach a Li₂S₈ concentration of 0.05 mol L⁻¹, and heating at 80 °C for 12 h, until a red-color solution is obtained, (ii) dissolving LiTFSI and LiNO₃ to the DME-DOL-Li₂S₈ solution above described to reach the following electrolyte configuration: 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈ in DME/DOL (1:1 = v/v).

Electrochemical Measurements: The lithium–electrolyte interface resistance was determined using a lithium–lithium symmetric 2032 coin type cell by electrochemical impedance spectroscopy applying a 10 mV AC amplitude signal within 500 kHz–10 mHz frequency range. The determination of lithium transference numbers were obtained by using the Bruce–Vincent^[30] method that combines AC and DC polarization to a Li/Li symmetrical cell using the selected electrolyte. The formula used for the lithium transference number determination was $t_{Li^+} = I_{ss}(\Delta V - R_0 I_0) / I_0(\Delta V - R_{ss} I_{ss})$, where I_0 is the initial current, I_{ss} the steady state current, ΔV the applied voltage, and R_0 and R_{ss} are resistances before and after dc polarization, respectively. The applied DC signal was of 10 mV while the EIS was performed before and after polarization within 500 kHz–10 mHz frequency range, using 10 mV amplitude AC pulses. The cyclic voltammetry (CV) tests were performed using a three electrode polypropylene T-cell, with lithium foil as reference and counter electrode and carbon Super P (Super P, PVdF 6020 8:2 on Al foil) as working electrode. The CV tests were run with a scan rate of 0.1 mV s⁻¹, within 1–3V voltage range. The resistance of the films formed by the electrolytes was evaluated by using EIS technique on a Li/DOL-DME (1:1, v/v), 1 M LiTFSI, 0.4 M LiNO₃, 0.05 M Li₂S₈/Li cell. The measurement was performed within 500 kHz and 10 mHz frequency, by applying a 10 mV amplitude AC pulse from pristine condition and upon 20 h of aging after cell assembling. The interphase resistance value was evaluated by nonlinear least squares (NLLS) fit of the high-frequency semicircles related to the film formation process. All the above tests were performed using VMP3 Biologic instrument. The galvanostatic tests were carried out in a 2032 coin-type cell by using a Maccor Series 4000 Battery Test System (Maccor, Inc.). Electrochemical charge–discharge study in lithium cell was performed within 1.9–2.8 V at a current of 1.675 A g⁻¹ (1 C) for the S–C electrode and within 0.01–2.0 V at a current of 200 mA g⁻¹ for the graphite electrode. The lithium ion full cell was assembled by coupling the S–C cathode and the graphite anode. Prior to the cell testing the graphite anode was prelithiated by contacting with a lithium foil wet by EC:DMC, LiPF₆, and following rinsing by dimethyl carbonate (DMC, Aldrich, 99%) as reported in previ-

ous paper.^[27] The graphite/lithium interphase was investigated by coupling EIS and GC techniques. The EIS was performed in 500 kHz–10 mHz frequency range, using 10 mV amplitude AC pulses, in the pristine state of the cell and after discharge and charge process, from 1st to 5th cycles. Before the test in lithium cell the graphite electrode was pretreated by Li-metal as above reported. GC was performed in lithium cell within 0.01 and 2.0 V at a current of 200 mA g⁻¹. The full cell was balanced by selecting 1:4 cathode to anode mass ratio. The lithium ion cell was cycled at 1 C current rate (1.675 Ag⁻¹), referring to the sulfur–cathode active mass, within 1–3V voltage range. The cell capacity was referred to the sulfur active mass, about 1 mg. An Advantec glass fiber was used as separator and soaked by 40 μL of the selected electrolyte solution, with a Li₂S₈ content of about 0.5 mg (0.45 mg of sulfur) not considered for the specific capacity calculation (see results and discussion of Figure 2 for clarification).

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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