Radical or Not Radical: Revisiting Lithium–Sulfur Electrochemistry in Nonaqueous Electrolytes

Marine Cuisinier, Connor Hart, Mahalingam Balasubramanian, Arnd Garsuch, and Linda F. Nazar*

Sulfur electrochemistry is fundamentally different from the intercalation process that governs Li-ion cells; lithium incorporation via phase transformations promises a dramatic increase in energy density,[1] yet it comes with several challenges. Lithium–Sulfur (Li–S) cells experience a large volumetric expansion upon formation of lithium sulfide (Li$_2$S); and the dissolution of lithium polysulfide intermediate species (Li$_2$S$_n$, 2 ≤ n ≤ 8) in commonly used liquid electrolytes triggers a polysulfide shuttle process that results in low Coulombic efficiency.[2] Consequently, Li–S batteries have suffered from low sulfur utilization and poor long-term cycling in the past. More encouragingly, however, several recent academic studies have reported 1500+ cycles,[3] and commercialization should soon be realized. Rather than a clear “quantum leap”, these achievements were made possible by holistic approaches and incremental improvements of both the active (positive and negative electrodes, electrolyte) and inactive (binder, separator) constituents of the Li–S cell.[3]

The gap between synthesis efforts, electrochemistry, and fundamental understanding of the Li–S chemistry has not yet been closed. Nonetheless, it is believed that the complex interplay between electrochemical and chemical processes is an impediment to reaching full theoretical capacity (1675 mAh g$^{-1}$).[4,5] Carbonate-based electrolytes undergo irreversible nucleophilic attack from polysulfide intermediates,[6,7] although the nature of the nucleophile (dianion S$^{-2}$ or radical S$_{n/2}$) has not been clearly determined. As of today, both linear and cyclic ether-based electrolytes appear stable toward sulfur species. There is a natural parallel with Li–O$_2$ cells, where the reactivity of the aggressively nucleophilic peroxide radical results in hydrogen abstraction from glycmes.[8] It is well known that sulfur-free radicals can be stabilized in electron pair donor (EPD) solvents such as dimethysulfoxide (DMSO), dimethylacetamide (DMA), and dimethylformamide (DMF).[9,10] While a recent report by Vijayakumar et al.[11] states that S$_3^-$ is the only free radical present in DMSO solutions of lithium polysulfides (neither S$_4^-$ or S$_2^-$ were detected). This was also the only radical species observed by Barchasz et al.[12] upon discharge of a sulfur electrode in tetraethylene glycol dimethyl ether (TEGDME). None of these studies, however, gives a quantitative estimate of the free radical content in the electrolyte, as compared with the various S$_n^{2-}$ dianions. Is the S$_3^-$ radical prominent upon cycling in Li–S cells using dimethoxyethane (DME) and 1,3-dioxolane (DOL) solvents? In this event, could its reactivity be held responsible—through electrolyte decomposition—for capacity fading over extended cycling? If not, could the practical capacity of a Li–S cell be augmented by favoring free radicals by tuning the dielectric characteristics of the electrolyte?

Herein, we assess the effect of sulfur radical species formed upon cycling of Li–S cells; in particular S$_3^-$. Based on our unequivocal observation of sulfur radicals in a Li–S cell by X-ray absorption near edge structure (XANES)—for the first time under operating conditions—using an EPD solvent (DMA), we show that radicals are not stabilized in glycme-based electrolytes. However, we do show that S$_3^-$ reacts with DOL at elevated temperatures, while DME remains intact. In contrast, the much greater dissociation of the anion precursor, S$_6^{2-}$, to the trisulfur radical in donor solvents such as DMA and DMSO—where tri-sulfur is in high concentration but nonreactive—surprisingly and importantly allows the full utilization of both sulfur and Li$_2$S. The effective solvation of the latter results in the complete absence of an overpotential on charge. Chemical incompatibility between the lithium metal negative electrode and EPD-solvents can be overcome with anode protection, demonstrating their applicability as electrolytes for the Li–S or Li$_2$S batteries in hybrid cells.

The nature of sulfur species in nonaqueous solutions of alkali polysulfides has been well established since the 1970s, using UV–Visible or electron spin resonance spectroscopies in various solvents.[9,10,12] It is not the scope of this work to repeat such experiments, and we accept that solvents with low donor number (DN), such as tetrahydrofuran (THF) contain exclusively dianions, and in particular S$_4^{2-}$ and S$_6^{2-}$ that give rise to a yellow coloration (Figure 1a,e). In contrast, solvents with high DN give intensely colored blue solutions owing to the S$_3^-$ radical (DMA, Figure 1d), as observed in ultramarine pigments (Figure 1f).[9,13] Comparing DME (Figure 1b) and TEGDME (Figure 1c) that both exhibit a glyme structure, the small differences in dielectric constant and DN are not sufficient to explain the evolution of coloration (hence distribution of lithium polysulfides and their solvate structure), whereas the increased number of solvating oxygen atoms in the solvent molecule has a larger impact.[14] In fact, the deep green coloration of TEGDME solutions (Figure 1c), has been assigned spectroscopically to the coexistence of free radicals and dianions in equilibrium.[12]
The study of solutions of known stoichiometry at rest, is, however, of little help to assess sulfur speciation upon operation of a Li–S cell. Indeed, disproportionation and dissociation equilibria between polysulfide dianions and radicals are constantly competing with their respective electrochemical reduction (oxidation) during discharge (charge). More realistically, for any state of (dis)charge, the distribution of sulfur species depends on the nature of the electrolyte (solvent, lithium salt),\textsuperscript{[15]} the sulfur to electrolyte ratio ([S]\textsubscript{tot}),\textsuperscript{[16]} the current density (expressed as a C rate, which refers to discharge/charge in 1 h), and also the sulfur electrode composition and architecture.\textsuperscript{[17]}

In order to determine the importance of the S\textsubscript{3}\textsuperscript{−}-free radical in the Li–S system, we carried out operando X-ray absorption spectroscopy (XAS) measurements at the sulfur K-edge on a Li–S cell using a DMA-based electrolyte (Figure 2 and Figure 3). The spectral signature of polysulfide dianions S\textsubscript{n}\textsuperscript{2−} were obtained previously, both individually in the solid state and at equilibria in DOL:DME solution under similar operando conditions.\textsuperscript{[4]} It was shown that the physical state (crystalline, amorphous, solute) does not affect the spectral signature in the near edge XAS region (XANES), so that data analysis can be carried throughout cycling using a single set of reference spectra.\textsuperscript{[4]} Our assignment of the low energy feature (2470.5 eV, Figure 2a) to dianions S\textsubscript{n}\textsuperscript{2−} was later confirmed both experimentally,\textsuperscript{[18,19]} and by first principle calculations,\textsuperscript{[19,20]} although it was speculated by others that this feature arises instead from S\textsubscript{n}/2\textsuperscript{−} free radicals.\textsuperscript{[5]} First-principle calculations show that the low energy feature is ascribed to the terminal sulfur atoms of the S\textsubscript{n}\textsuperscript{2−} chains,\textsuperscript{[19]} with a relative intensity that scales inversely with the length of the chain (i.e., number of terminal atoms). Our experimental XANES fingerprint of S\textsubscript{3}\textsuperscript{−} from ultramarine pigment shown in Figure 2a, in agreement with previously

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Figure 1. Change in the distribution of colored sulfur species from Li\textsubscript{2}S\textsubscript{6} (1 mg mL\textsuperscript{−1}) with the solvent a–d), compared with Li\textsubscript{2}S\textsubscript{6} e) and ultramarine Na\textsubscript{4.1}Ca\textsubscript{0.1}K\textsubscript{0.1}Al\textsubscript{3.5}Si\textsubscript{8.5}O\textsubscript{24}S\textsubscript{3}* (SO\textsubscript{4})\textsubscript{0.2} f) powders. Gutmann's donor number (DN) and dielectric constant (ε) are given in each case.\textsuperscript{[11]}

Figure 2. Sulfur K-edge XANES studies: a) experimental spectra collected during discharge (around 340 mAh g\textsuperscript{−1}) in Li–S cells using DMA or DOL:DME electrolytes compared with S\textsubscript{3}\textsuperscript{−} and S\textsubscript{6}\textsuperscript{2−} reference materials; b) linear combination fit illustrating—among others—the contribution of S\textsubscript{3}\textsuperscript{−} and S\textsubscript{4}\textsuperscript{2−} to the electrode partially discharged in DMA; c) evolution of X-ray absorbance upon discharge in DOL:DME as compared with d) in DMA.
The electroreduction of sulfur in EPD solvents (DMF, DMSO, etc.) has been studied by several groups over the past 40 years and is summarized below.\cite{9,10}

Step 1: \( \approx 2.7 \text{ V} \). The dissociation of \( S_8^{2–} \) is always weak (in fact, \( S_4^{–} \) has never been detected in DMA); however, its disproportionation is moderate. The main difference with typical Li–S glyme electrolytes is that the product of \( S_8^{2–} \)-disproportionation (Equation (2)) in EPD solvents is mostly the free radical \( S_4^{–} \) since the dissociation of \( S_6^{2–} \) is now quite substantial (Equation (3)).\cite{10}

\[
\begin{align*}
S_8^{2–} + 2e^- & \rightarrow S_4^{2–} \\
S_4^{–} & \leftrightarrow S_4^{2–} + 1/4 S_8 \\
2S_4^{–} & \leftrightarrow S_6^{2–}
\end{align*}
\]

Step 2: \( \leq 2.2 \text{ V} \). In our XANES experiment, the maximum \( S_4^{–} \) concentration coincides with the voltage drop from 2.7 to 2.2 V (Figure 3a,b). The free radicals are further reduced (Equation (4) and Equation (5)), and since the disproportionation reaction (Equation (2)) is slow, \( S_8^{2–} \) is simultaneously reduced (Equation (6)).\cite{10} The combination of (Equation (5)) and (Equation (6)) explain the massive fraction of \( S_4^{2–} \) in the second step of discharge (Figure 3b).

\[
\begin{align*}
S_4^{–} + e^- & \rightarrow S_4^{2–} \\
2S_4^{2–} + 2S_4^{–} & \rightarrow 3S_6^{2–} \\
S_6^{2–} + 2e^- & \rightarrow 2S_4^{2–}
\end{align*}
\]

It is also reported that medium-length polysulfide dianions \( S_8^{2–} \) and \( S_6^{2–} \) can be chemically reoxidized to the trisulfur radical by sulfur or \( S_8^{2–} \) (Equation (7) is one example),\cite{10} so that the disappearance of \( S_4^{–} \) in the course of discharge (Figure 3b) must indicate the full consumption of elemental sulfur and long-chain polysulfides (also implying that the electrolyte can access all the sulfur active mass in these electrodes). In agreement, the contribution of \( \alpha S_8 \) to the sulfur K-edge reaches 2% at the end of discharge, for a capacity of 1250 mAh g\(^{-1}\) (Figure 3b). After the exhaustion of primary discharge products (\( S_8^{2–} \) and \( S_4^{–} \)), the electrochemical reduction proceeds further to \( Li_2S \) (Equation (8)), so that the positive electrode in its discharged state—as monitored by operando XANES (Figure 3b)—is composed of only short chain \( Li_2S_6 \) and \( Li_2S \).

\[
\begin{align*}
S_6^{2–} + 1/4 S_8 & \rightarrow 2S_4^{–} \\
S_4^{2–} + 6e^- & \rightarrow 4S^{2–} \\
S^{2–} + 1/4 S_8 & \rightarrow S_4^{–}
\end{align*}
\]

The use of LiNO\(_3\) as the electrolyte salt to prevent the chemical reaction of DMA with metallic lithium prevents one from scanning low in voltage,\cite{21} so that the capacity limiting factor...
is not clear at this stage. Nonetheless, no elemental sulfur remains in the discharged positive electrode, so that the mechanism discussed previously for DOL:DME—best summarized as electrode passivation by Li$_2$S from polysulfide reduction before elemental sulfur can be fully reacted—does not apply here.[6] Instead, we suspect that in EPD-solvents, even more so than in glymes, any sulfur species formed via electrochemical reduction (such as $S_2^{2−}$ or $S^{2−}$) must equilibrate with leftover oxidized species (α-S$_8$ or S$_8^{2−}$) to form more stable intermediates ($S_{1.4}^{2−}$ or $S_{1.4}^{2−}$; Equation (9) is an example). This not only drives the full consumption of α-S$_8$, but also prevents the early precipitation of Li$_2$S in the presence of long-chain polysulfides.

Nonetheless, the overall performance of DMA-based Li–S cells is unsatisfactory: Coulombic efficiency is low, and the cyclability is poor (see Figure S1, Supporting Information). To understand this further and in order to determine whether electrolyte reactivity at the anode is the source of the problem, we isolated the lithium metal from the positive sulfur electrode. Our custom-made 2-compartment Swagelok-type cell incorporates an Ohara glass membrane, proven to be a single-ion conductor.[22] A comparison between TEGDME- and DMA-based electrolytes (1 M LiClO$_4$) in the positive electrode (i.e., sulfur) compartment is shown in Figure 4a. In both cases, the lithium compartment was filled with the TEGDME-based control electrolyte, and after dismantling of the cell, no coloration was observed on that side of the Ohara glass separator.

The reference experiment in TEGDME (Figure 4a, black line) confirms the sulfur redox mechanisms previously reported for glyme electrolytes.[4] The voltage profile and specific capacity (first discharge at 1300 mAh g$^{-1}$) correlate nicely with results obtained in coin cells, as expected from an electrolyte solution that is chemically stable versus metallic lithium. Since lithium passivation can be ruled out, the loss of capacity observed between the first discharge and the first charge is accounted for by polysulfides trapped in the separator owing to the viscosity of TEGDME. This is visually supported by the strong green/red coloration of the separator in the positive electrode compartment. When DMA in the positive electrode compartment is prevented from reacting with metallic lithium, the sulfur redox is very well defined in potential (Figure 4a, blue line). In excellent agreement with the quantitative XANES analysis (Figure 3b), the second electrochemical reduction step discussed above can now clearly be separated in two:

- Reduction to $S_{3.4}^{2−}$ (Equation (4)–(6)) at 2.1 V
- Reduction to Li$_2$S (Equation (8)) at 1.9 V

As discussed above, EPD solvents exacerbate the electrochemical equilibration among sulfur species so that ideally, Li$_2$S could be chemically reoxidized into soluble $S_{n}^{2−}$. This would prevent passivation of the positive electrode until the electrochemical reduction is complete; i.e., when no α-S$_8$ or $S_8^{2−}$ is left over. We demonstrate this experimentally, by achieving 1575 mAh g$^{-1}$ capacity for the first discharge in DMA. Hence, electrodes cut from the same film and cycled under the same conditions can deliver 24% more capacity in an EPD-solvent than in TEGDME. Moreover, a reversibility of 95% is observed between the first charge and the first discharge, illustrating that not only Li$_2$S is indeed fully reoxidized, but also that polysulfide trapping in the electrolyte is very limited in DMA compared with TEGDME (5% and 18%, respectively).

As shown in Figures 2d and Figure 3b, $S_{3}^{2−}$ is detected by XANES throughout charge (up to 25% of total sulfur) but it is absent in the recharged state. Its role as an internal redox mediator is thus confirmed, and the trisulfur radical is finally oxidized at 2.8 V, only after all more reduced species have reacted. Along with the stabilization of $S_{1}^{−}$ in the electrolyte, the phase transfer from solid Li$_2$S to soluble sulfide and polysulfides in EPD solvents opens up various lines of research.[23] In particular, the electrochemical oxidation of Li$_2$S-loaded electrodes is known to be difficult, owing to the insulating character of Li$_2$S.[24] and its negligible solubility in most common electrolytes.[1,2] As shown in Figures 3a and 4a, the oxidation of Li$_2$S occurs with virtually no initial overpotential in DMA. This is suggestive of a solution-based charge reaction, in contrast with the potential barrier typically observed in glymes.[23] In comparison, the Li$_2$S utilization rate and therefore the practical capacity of Li$_2$S batteries could be greatly improved via solvation in EPD solvents.

To confirm this point, we assembled hybrid cells using Li$_2$S as the positive electrode material. The comparison between TEGDME- and DMA-based electrolytes is presented in Figure 4b. The C/10 rate is based on elemental sulfur loading (1.0 mg cm$^{-2}$). As typically reported, an energy barrier must be overcome in order to initiate Li$_2$S oxidation in TEGDME (here about 2.55 V). Although the charging voltage remains

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**Figure 4.** First (solid lines) and second (dashed lines) galvanostatic cycles of a) sulfur and b) Li$_2$S in TEGDME (black) and DMA (blue) electrolytes at C/10 in the hybrid cell. The vertical dotted lines highlight the irreversible capacity loss observed during the first cycle. The difference in polarization between the S/DMA and Li$_2$S/DMA cells on the first cycle is attributed to their different cathode fabrication methods (see Supporting Information); the profiles start to converge owing to improved wetting of the active material on cycling as noted by the decreased polarization exhibited for S/DMA on the second cycle.
below 3.0 V owing to optimum material particle dimensions, the reversibility is only 78% on the first cycle (Figure 4b, black line), so that the practical capacity is limited to 1100 mAh g S\(^{-1}\). In contrast, no overpotential is observed in DMA (Figure 4b, blue line), while a reversibility of 99% and a capacity retention of 98% are achieved on the first cycle and on the second cycle, respectively. Two main factors contribute to the unique behavior of Li\(_2\)S in EPD solvents: first, the partial solvation of Li\(_2\)S in DMA alleviates the problem of electrochemically disconnected Li\(_2\)S (because it can be accessed anywhere in the electrolyte, see Equation (9)). As illustrated in Figure 5, phase-transfer also alleviates the need for triple-phase boundaries to initiate and carry out electrochemical oxidation of Li\(_2\)S. Second, the stabilization of the radical S\(_3\)\(^{-}\) provides additional chemical pathways to assist the electrochemical processes (via Equations (2),(5),(7)).

The question of reactivity of sulfur intermediates toward electrolyte solvents is well-founded, given the reported decomposition of carbonates, and the analogy with Li–O\(_2\) cell chemistry. Although many electrolytes were initially thought to be stable to the superoxide radical O\(_2\)\(^{-}\)\(^{-}\), degradation of DME\[^{[8,26]}\] TEGDME\[^{[27]}\] and later EPD-solvents were all demonstrated experimentally using NMR or FTIR spectroscopies, and the mechanisms were elucidated\[^{[8,28]}\]. The stabilization of S\(_3\)\(^{-}\) in DMA, as evidenced by XANES (Figure 2), offers us the opportunity to assess its reactivity not only toward glymes, but also to EPD solvents. To probe this, Li\(_2\)S\(_6\) was synthesized in DOL:DME-based electrolyte (Figure 2b) and stored over 4 Å molecular sieves prior use.

We previously investigated nonsolvents for polysulfides\[^{[15]}\] and showed that impeding chemical equilibria could allow the full reduction of sulfur into Li\(_2\)S in a Li–S cell. It is interesting to observe that the opposite approach of exacerbating these chemical equilibria between polysulfide intermediates can also lead to the same result. Whereas nonsolvents compromise the cell energy density due to a significant increase in polarization,\[^{[15]}\] EPD solvents exacerbate solvation, and chemical equilibration between redox-active sulfur species. This assisted phase-transfer, from Li\(_2\)S to soluble polysulfides, translates into a decreased cell polarization and an improved rate capability.

For all the reasons detailed above, the use of low volatility EPD solvents would be beneficial in a catholyte-type or redox-flow type battery, where Li\(_2\)S deposition is controlled by surface interactions; but detrimental when trying to limit diffusion by physically entrapping sulfur species in a mesoporous carbon matrix. Instead, we believe that the combination of highly adsorptive electrode material with a highly dissociative solvent could be extremely advantageous. Obviously, chemical interaction and adsorption of polysulfides onto polar host materials would need to be re-evaluated in EPD solvents,\[^{[15]}\] yet we foresee that this kind of concerted chemical approach will enable us to overcome the current 1200 mA h g S\(^{-1}\) capacity threshold in Li–S batteries today.

**Experimental Section**

**Materials:** Solid Li\(_2\)S\(_6\) was synthesized by reacting elemental sulfur and lithium superhydride (1 × LiEt\(_3\)BH in anhydrous THF, Sigma-Aldrich) at room temperature for 1 h inside an Ar-filled glovebox. The THF and by-products were removed in vacuo as reported previously.\[^{[4]}\] Ultramarine pigment of composition Na\(_{4.1}\)Ca\(_{0.1}\)K\(_{0.1}\)Al\(_{3.5}\)Si\(_{8.5}\)O\(_{24}\)S\(_{3}\) * (SO\(_4\))\(_{0.2}\) was purchased from Kama pigments and used as-received. Lithium perchlorate (LiClO\(_4\)) and lithium nitrate (LiNO\(_3\)) were dried at 120 °C under vacuum for 48 h, while DMA and TEGDME solvents were distilled and stored over 4 Å molecular sieves prior use.

**Sulfur Electrode Preparation:** A 70 wt% sulfur containing composite was prepared by via a melt diffusion method in Vulcan carbon at 155 °C. The composite was dispersed with Super P into a 2-propanol and water mixture (1:2 volume) by ultrasonication. Next, PTFE was added (60 wt% dispersion in H\(_2\)O, Sigma-Aldrich) such that the sulfur:carbon:PTFE mass ratio was 54:34:12, and mixed well. The film was cast onto AvCarb P50 carbon paper (Fuel Cell Store) to reach a final sulfur loading of 1.5 mg cm\(^{-2}\) and dried at 60 °C overnight.

**Li\(_2\)S Electrode Preparation:** Li\(_2\)S was synthesized by reacting elemental sulfur and lithium superhydride and drying the mixture at 300 °C under vacuum for 3 h. A 60 wt% Li\(_2\)S-containing composite was prepared by ball-milling with Ketjenblack and titanium nitride nanoparticles. The composite was dispersed with Super P and PTFE binder (1 µm powder, Sigma-Aldrich) in anhydrous THF such that the Li\(_2\)S:carbon:Tin:PTFE mass ratio was 50:25:15:10, and mixed well. The slurry was drop-cast onto AvCarb P50 carbon paper (Fuel Cell Store) to reach a final sulfur loading of 1.5 mg cm\(^{-2}\) and dried at room temperature overnight. All of the above procedures were carried-out in an Ar-filled glovebox.

**XANES Measurements:** Spectra from sulfur K-edge X-ray absorption near edge spectroscopy (XANES) were acquired at sector 13-ID-E of the X-ray absorption spectroscopy beamline 13-ID-E at the Advanced Photon Source, Argonne National Laboratory.

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**Figure 5.** Schematic representation of Li\(_2\)S electro-oxidation: a) in the absence of any solubility—which is the case in glymes—triple-phase boundaries (conductive substrate/Li\(_2\)S/electrolyte) are required; b) in the case of EPD-solvent-assisted phase transfer, all electroactive species are in solution, hence only necessitating a good wetting of the conductive substrate by the electrolyte.
Advanced Photon Source at Argonne National Laboratory by using an energy-dispersive, four-element Vortex detector in fluorescence detection mode. The cell used to perform operando XANES was adapted from the 2325 coin cell as described in ref. [4] in order to significantly reduce self-absorption, the working electrode was made of VC/S-15 wt%, 96% P carbon and PTFE (10 wt% sulfur overall), and residual self-absorption was corrected prior to detailed, quantitative analysis of the spectra (ref. [4]. Lithium metal was used as the counter-electrode, and the electrolyte consisted of 50 µL of a 2 m LiNO₃ solution in DMSO. Galvanostatic cycling was carried out on a Macor instrument at D/10 (167.5 mAg⁻¹) for the first discharge and C/5 (335 mA g⁻¹) for the following charge. See Supporting Information section for additional experimental details.

**Electrochemistry in the Two-Compartment Cell:** Sulfur electrochemistry was investigated with a protected metallic lithium anode using a custom-made 2-compartment Swagelok-type cell incorporating an Ohara glass membrane (LIC-GC, 1in. square, 150 µm thick). Each compartment was investigated with a protected metallic lithium anode using a custom-made 2-compartment Swagelok-type cell incorporating an Ohara glass membrane (LIC-GC, 1in. square, 150 µm thick). Each compartment held two layers of glass fiber separator wetted by 100 µL of electrolyte. The negative electrode compartment contained 1M LiClO₄, 2% LiNO₃ in TEGDME to interface with metallic lithium. The positive electrode compartment contained 1 M LiClO₄ in either DMA or TEGDME. Cells were cycled in a 3-Ar-filled glovebox to minimize risks of moisture/oxygen contamination, at 167.5 mAg⁻¹ using a MacPile II instrument (Bio-LUGC).

**Supporting Information**

Supporting Information (long-term cycling of a Li−S cell in DMA without lithium protection and ¹H NMR investigation of solvents stability via a vis the S³⁻ radical) is available from the Wiley Online Library or from the author.

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