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Bis(2,2,2-trifluoroethyl) Ether As an Electrolyte Co-solvent for Mitigating Self-Discharge in Lithium−Sulfur Batteries

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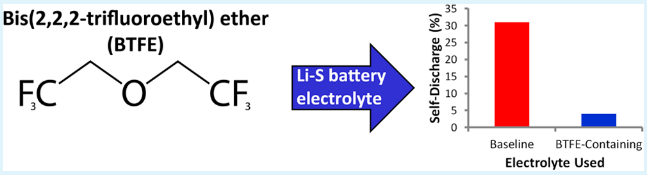
Supporting Information

ABSTRACT: Lithium−sulfur batteries suffer from severe self-discharge because of polysulfide dissolution and side reaction. In this work, a novel electrolyte containing bis(2,2,2-trifluoroethyl) ether (BTFE) was used to mitigate self-discharge of Li−S cells having both low- and high-sulfur-loading sulfur cathodes. This electrolyte meaningfully decreased self-discharge at elevated temperature, though differences in behavior of cells with high- and low-sulfur-loading were also noted. Further investigation showed that this effect likely stems from the formation of a more robust protective film on the anode surface.



KEYWORDS: *lithium−sulfur batteries, self-discharge, fluorinated ether, electrolyte, polysulfide shuttle, solid-electrolyte interphase*

Lithium-sulfur (Li−S) batteries are one of the most promising rechargeable batteries currently being developed thanks to the very high theoretical capacity of sulfur (S) cathodes (1672 mAh/g S). However, they have been plagued by a number of serious problems, including modest practical capacity, poor stability, low efficiency, and high self-discharge. These problems stem in large part from the dissolution, diffusion, and side-reaction of soluble lithium polysulfides in the electrolyte, behaviors which lead to loss of active material by irreversible formation of insoluble Li_2S and Li_2S_2 and partial lithiation of sulfur by the polysulfide shuttle effect.[1−4] Though several methods of mitigating these issues have been proposed, most prominently polysulfide trapping by using porous cathode frameworks[4−7] and modification of the electrolyte to prevent polysulfides from reacting with the anode and shuttling,[8−10] these have largely focused on capacity, stability, and efficiency.

In contrast, comparatively few studies have focused on direct mitigation of self-discharge in Li−S batteries. Mikhaylik and Akridge mathematically related the self-discharge to the polysulfide shuttle effect,[1] whereas Ryu et al. studied Li−S battery self-discharge with several different current collectors and electrolytes.[11−13] Very recently, Zhang et al. reported a fluorinated ether co-solvent (1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether, TTE) which can, in combination with the $LiNO_3$ electrolyte additive, arrest self-discharge over very short storage times.[14] However, a method of significantly mitigating self-discharge over long storage times at elevated temperature has not been demonstrated in the literature. To contribute to this critical effort, taking a cue from the use of fluoroethylene carbonate as an SEI-improving additive for LIBs[15−17] and from a previous study on a partially fluorinated ether (1,1,2,2-tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)-propane, D2) co-solvent for improving the efficiency of Li−S batteries,[18] we investigated bis(2,2,2-trifluoroethyl) ether (BTFE, Figure 1) as a co-solvent for preventing self-discharge in Li−S batteries. It was found that use of BTFE in combination with $LiNO_3$ could meaningfully decrease self-discharge after 2 weeks of elevated-temperature storage, likely due to formation of a more robust protective layer on the anode. Cells with both high- (~5 mg S/cm^2) and low-sulfur-loading (< 1 mg S/cm^2) cathodes were tested; low-loading cells were found to show significantly more self-discharge from active material loss than high-loading cells. This work identifies a direction for future work on decreasing the self-discharge of lithium−sulfur cells by further improving the choice of fluorinated ether co-solvent, co-salt additive, and cell fabrication.

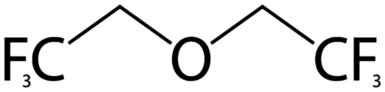


Figure 1. Chemical structure of bis(2,2,2-trifluoroethyl) ether.

For this study, low-sulfur-loading cathodes were prepared by simply ball-milling Super P carbon and sulfur, followed by making a slurry of this ball-milled material with a solution of poly(vinylidene fluoride) (PVDF) in n-methylpyrrolidone (NMP) (5:4:1 sulfur:Super P:PVDF by weight) and casting it

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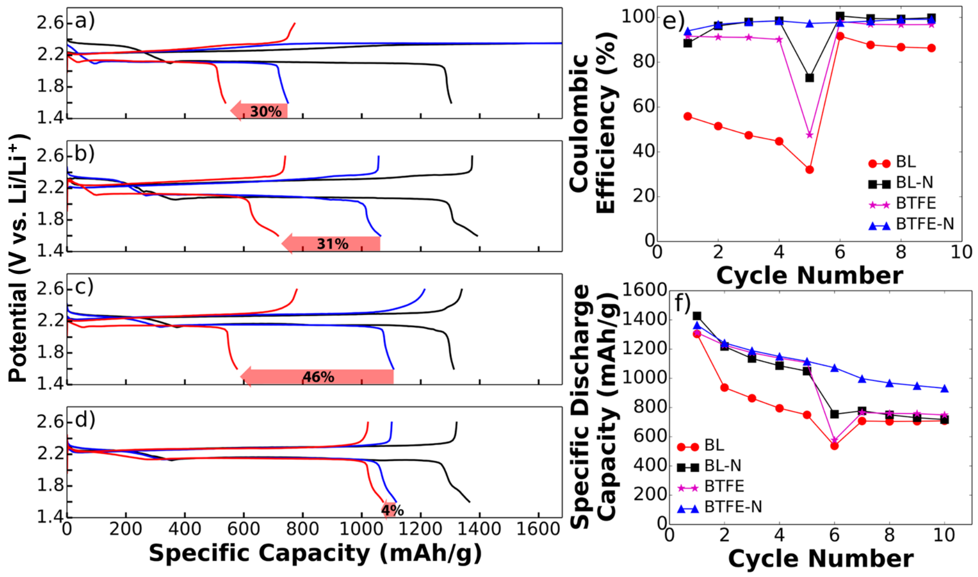

Figure 2. (a−d) Charge/discharge curves and average self-discharge of cells with low-sulfur-loading cathodes and (a) BL, (b) BL-N, (c) BTFE, and (d) BTFE-N electrolytes, with black, blue, and red curves indicating the 1st, 5th, and 6th cycles, respectively, and arrows indicating average self-discharge for cells with that electrolyte; (e) coulombic efficiency; and (f) cycling performance.

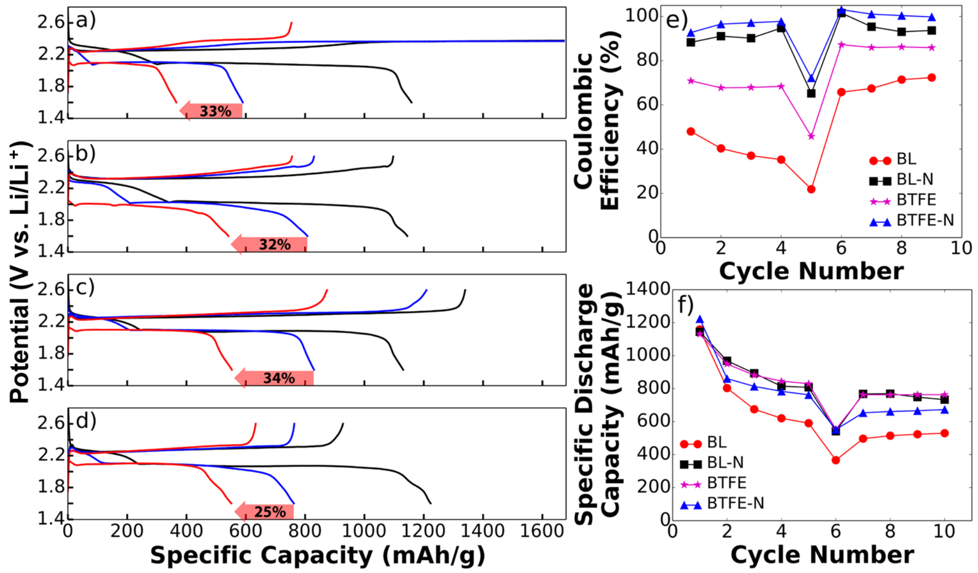

Figure 3. (a−d) Charge/discharge curves and average self-discharge of cells with high-sulfur-loading cathodes and (a) BL, (b) BL-N, (c) BTFE, and (d) BTFE-N electrolytes, with black, blue, and red curves indicating the 1st, 5th, and 6th cycles, respectively, and arrows indicating average self-discharge for cells with that electrolyte; (e) coulombic efficiency; and (f) cycling performance.

onto aluminum foil. High-sulfur-loading cathodes were prepared by making a slurry of micro-sized spherical mesoporous carbon/sulfur composite with 70 wt % sulfur loading, which was synthesized as described in our previous work,[5] with Super P carbon and PVDF (8:1:1 by weight) in NMP, followed by casting onto carbon-coated aluminum foil. Four different electrolytes were used for electrochemical testing: 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v), 0.5 M LiTFSI and 0.2 M $LiNO_3$ in DOL/DME (1:1 v/v), 0.5 M LiTFSI in DOL/DME/BTFE (1:1:2 v/v/v), and 0.5 M LiTFSI and 0.2 M LiNO3 in DOL/DME/BTFE (1:1:2 v/v). These were dubbed BL, BL-N, BTFE, and BTFE-N, respectively. CR2016 coin cells made with the low- and high-sulfur-loading cathodes, Celgard 2400 polypropylene membrane separators, lithium metal anodes, and the above four electrolytes were electrochemically tested by galvanostatic cycling at 45°C. More information on the experimental methods is presented in the Supporting Information.

Charge−discharge curves, average self-discharge, cycling, and efficiency of Li−S cells with low-loading sulfur cathodes using different electrolytes were studied and are presented in Figure 2. Cells were cycled for five cycles, rested for 2 weeks, and then cycled for a further five cycles, all at 45°C. Before resting, cells with BL-N, BTFE, and BTFE-N electrolytes had similar capacity. Cells with BL electrolyte had poor capacity, cycling stability, and efficiency, and were not able to reach 2.6 V during charging, as polysulfide diffusion and shuttling are largely unrestrained in these cells.[9] After their two-week rest, the

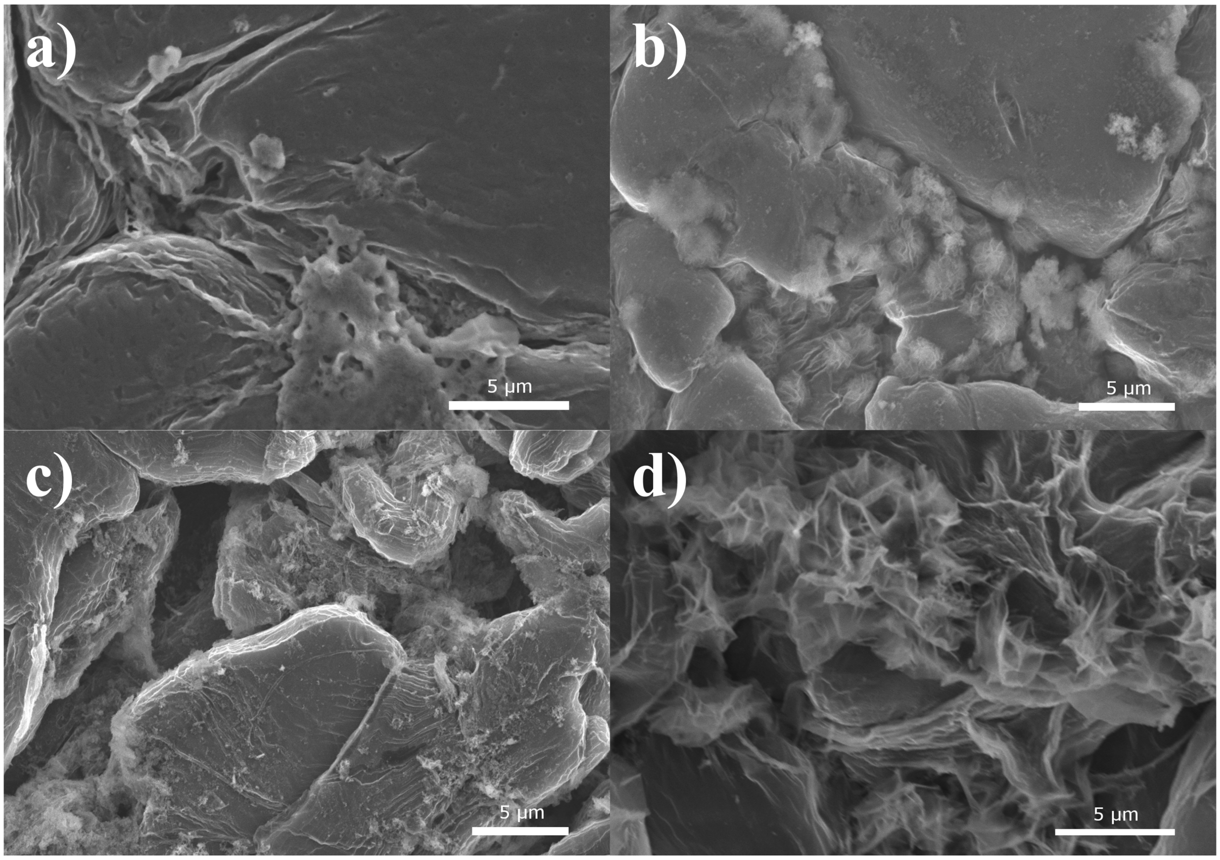

Figure 4. SEM images of lithium anodes from cells cycled five times at 45°C in cells with high-sulfur-loading cathodes and (a) BL, (b) BL-N, (c) BTFE, and (d) BTFE-N electrolytes.

average self-discharge of cells with BL, BL-N, and BTFE electrolytes was around or above 30%, compared to only around 4% for cells with BTFE-N electrolyte. On the second discharge after rest, cells with BL-N electrolyte recovered little of the capacity lost during self-discharge, whereas cells with BL and BTFE electrolytes showed significant and moderate recovery, respectively—average irreversible capacity loss was approximately 0, 22, and 28% for cells with BL, BL-N, and BTFE electrolyte, respectively. All three cell types stabilized to a similar capacity after self-discharge. This indicates that a large portion of self-discharge in low-sulfur-loading cells with BL-N and BTFE electrolytes stems from irreversible loss of active material, rather than from reversible polysulfide shuttling. Cells with BL electrolyte, having already suffered significant active material loss during their initial cycling and reached a roughly stable capacity, did not appear to suffer from much more material loss.

In an effort to clarify the nature of self-discharge by active material loss and determine whether self-discharge was influenced by sulfur content in the cell, and to extend this work to cells having cathodes with more practical sulfur loadings, cells with high-sulfur-loading cathodes (~5 mg/cm^2) were also tested. Charge−discharge curves, cycling, efficiency, and self-discharge of high-sulfur-loading cells are presented in Figure 3. These cells were cycled in the same manner as those with low-loading cathodes. Self-discharge in these cells was also lowest with BTFE-N electrolyte, averaging 25% self-discharge, compared to 30+% with the other electrolytes. High-loading cells all show fairly significant capacity recovery after rest, with irreversible loss of 11, 4, and 6% for cells with BL, BL-N, and BTFE electrolyte, respectively. This much better capacity recovery with the BL-N and BTFE electrolytes indicates that, unlike in low-sulfur-loading cells, self-discharge in these cells is likely due to polysulfide shuttling rather than active material loss. Cells with BTFE-N electrolyte also had an irreversible capacity loss of 11%. Although the benefit of the BTFE-N electrolyte appears significantly lower in these high-sulfur-loading cells, it is important to note that while all the low-sulfur-loading cells used the same amount of electrolyte, cells with high-loading electrodes and BTFE-N electrolyte were fabricated with more electrolyte (90 μL) than their counterparts with other electrolytes (75 μL). This is because cells with 75 μL of BTFE-N electrolyte were found, despite their lower self-discharge and better capacity recovery after self-discharge, to show steadily increasing polarization after rest. Although the reason for this increased polarization was not further investigated, it may stem from factors such as consumption of electrolyte to form the protective anode film (discussed below), which may be more severe with high-net-capacity, high-sulfur-loading cathodes and the consequent increased lithium dissolution, or formation of a thicker film, why may happen for the same reasons. The increased self-discharge with increased electrolyte amount is unsurprising, since it is known that increased amount of electrolyte relative to the sulfur content of the cathode can exacerbate the polysulfide shuttle;[19] this topic is further commented on in the Supporting Information. This implies that fine-tuning of the electrolyte amount could lead to further decrease in self-discharge with high-loading sulfur cathodes while still avoiding severe polarization. Interestingly, the net capacity loss for cells with BL-N and BTFE electrolyte is quite similar for cells with low- and high-sulfur-loading cathodes: approximately 0.14 mAh and 0.23 mAh with low sulfur loading and 0.23 and 0.34 mAh with high sulfur loading for these two electrolytes, respectively. In addition, considering the lower irreversible loss in high-sulfur-loading cells with these electrolytes, it can be expected that the polysulfide concentration during rest is similar or higher than in low-sulfur-loading cells. It thus appears that irreversible loss is not dictated simply by the net amount or concentration of soluble polysulfides in the cell, but by other factors, such as perhaps gradual passivation of the lithium surface. This also shows that it may be feasible to combine the self-discharge suppression of an electrolyte containing BTFE or another fluorinated ether with the improved capacity and stability granted by polysulfide-containing electrolytes, such as have previously been reported,[20,21] without sacrificing self-discharge performance.

To investigate the reason behind this decreased self-discharge, Li anodes from cells cycled five times with high-loading cathodes were imaged via SEM; representative images are presented in Figure 4. Lithium electrodes from cells with BL and BTFE electrolyte had a relatively small amount of irregular deposits, while lithium from cells with BL-N electrolyte had more and larger deposits; none of the three had visible surface-covering film. In contrast, lithium from cells with BTFE-N electrolyte did have a pronounced surface film, which can be observed across the electrode, albeit with varying thickness. Although formation of a thicker film on the anode might be expected to lead to increased cell impedance and thus greater polarization of the cell during charge and discharge, such an effect is not noted from the charge/discharge curves presented in Figures 2 and 3; polarization with BTFE-N electrolyte actually appears somewhat lower than with BL-N electrolyte. This implies that the film does not significantly hinder ion transport in the conditions used.

To further probe these differences, we conducted FTIR on lithium anodes after five cycles, and the resultant spectra are presented in Figure 5. Spectra of lithium electrodes cycled in all electrolytes exhibit a number of peaks which have been previously identified as belonging to SEI components formed by reaction and decomposition of electrolyte solvents, salts, and polysulfide species, as described below.[9,22] The peak around 1620 $\mathrm{cm^{-1}}$ is indicative of C═O stretching in lithium formate, while the higher-wavenumber shoulder (around 1650 $\mathrm{cm^{-1}}$) may be due to $\mathrm{ROCO_2Li}$ species. The broad peak around 1500 $\mathrm{cm^{-1}}$ is attributed to $\mathrm{Li_2CO_3}$. Peaks around 2800−3000 $\mathrm{cm^{-1}}$ and 1500−1200 $\mathrm{cm^{-1}}$, attributed to C−H stretching and bending vibrations, respectively, are in line with various ROLi and $\mathrm{ROCO_2Li}$ species reported in the literature. The sharper peak around 3200 $\mathrm{cm^{-1}}$ is attributed to LiOH, whereas the broad peak at around 550−650 $\mathrm{cm^{-1}}$ is likely due to Li−O stretching, such as from $\mathrm{Li_2O}$. The slight dip around 3400 $\mathrm{cm^{-1}}$ is attributed to trace moisture in the KBr reference sample. Previous publications have also assigned peaks in the 1400−1000 $\mathrm{cm^{-1}}$ region to various vibrations, including those of S−O, S═O, N−O, N−S, C−C, and C−O bonds; because of the broad peaks seen in this region in Figure 3a−c, and the overlapping wavenumber ranges in which many of these vibrations may be found, we hesitate to make individual peak assignments in this region for electrodes cycled in BL, BL-N, and BTFE electrolytes. Spectra of electrodes cycled in BTFE-N electrolyte, however, also show distinctive new peaks around 1325−1250, 1225−1050, 960, and 830 $\mathrm{cm^{-1}}$. These peaks are tentatively assigned to asymmetric and symmetric C−O−C stretching and/or C−F stretching and bending.[9,23−25] It is interesting that these peaks are not evident in spectra of electrodes cycled in BTFE electrolyte; BTFE must be paired with $\mathrm{LiNO_3}$ for generation of the species to which these peaks correspond. The clear differences in this region, along with smaller but also evident differences in other parts of the spectrum, indicate a difference in the composition of the surface film on the lithium anode with BTFE-N electrolyte compared with other electrolytes. Taken together with the significantly enhanced growth of surface film seen by SEM, this is believed to signal formation of a more robust SEI layer on the lithium anode by reaction of the BTFE with $\mathrm{LiNO_3}$. Such a robust SEI could help prevent contact between soluble lithium polysulfides and the anode, thereby mitigating the polysulfide shuttle effect and decreasing self-discharge. On the basis of only the above data, the precise composition of the film cannot be determined; doing so would require significant additional chemical characterization. We expect that the improved anode SEI may work in conjunction with cathode-side protection, such as preventing the formation of large $\mathrm{Li_2S}$ agglomerates, as other researchers have shown to be the case with the fluorinated ether TTE.[14] In contrast, despite being known to form a better SEI on the anode and consequently suppress the polysulfide shuttle during battery charge/discharge, $\mathrm{LiNO_3}$ alone has no meaningful effect on self-discharge over a two-week timeframe. It thus appears that, despite its ability to improve battery efficiency, improvements made to the SEI by $\mathrm{LiNO_3}$ are insufficient to prevent contact and side reaction of polysulfides with the anode over a prolonged time frame, with the resultant shuttle and self-discharge.

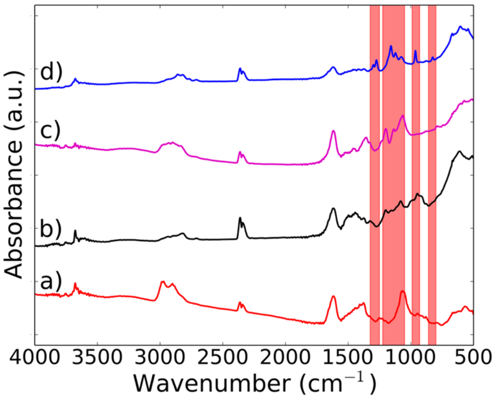

Figure 5. FTIR spectra of lithium anodes from cells cycled five times at 45 °C in cells with high-sulfur-loading cathodes and (a) BL, (b) BL-N, (c) BTFE, and (d) BTFE-N electrolytes. Regions of particular interest are highlighted.

■ CONCLUSION

In this work, electrolytes containing the fluorinated ether BTFE and $\mathrm{LiNO_3}$ were used to decrease self-discharge of Li−S batteries with both low-loading ($< 1\ \mathrm{mg/cm^2}$) and high-loading ($\sim 5\ \mathrm{mg/cm^2}$) sulfur cathodes over 2 weeks of storage at 45°C, and differences in self-discharge behavior in cells with low-sulfur-loading and high-sulfur-loading cathodes were studied. Self-discharge was decreased from 30+% in 2 weeks to ∼4% and ∼25% in low- and high-sulfur-loading cells, respectively. Self-discharge in low-loading cathodes was found to be mainly due to irreversible active material loss, while cells with high-loading cathodes suffered primarily from shuttle-based self-discharge. Combined with these results, FTIR and SEM analyses indicate that BTFE and $LiNO_3$ together can likely form a more protective SEI layer on the anodes of tested cells, thereby slowing the polysulfide shuttle and decreasing self-discharge. This effect may be in conjunction with improved protection of the cathode. In contrast, $LiNO_3$ alone, despite being known as a shuttle-suppressing additive, had minimal effect on self-discharge. In addition, the precise amount of electrolyte used appears to be critical to hitting a balance of good performance and low self-discharge. It is likely that future work can expand on this method by tuning factors such as type and concentration of fluorinated ether, co-salt additive, and electrolyte amount, and thus further decrease self-discharge in Li−S batteries.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, as well as some further comments on the effect of electrolyte/sulfur ratio in this system, as included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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