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Fluorinated Electrolytes for Li-S Battery: Suppressing the Self-Discharge with an Electrolyte Containing Fluoroether Solvent

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The fluorinated electrolyte containing a fluoroether 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) was investigated as a new electrolyte for lithium-sulfur (Li-S) batteries. The low solubility of lithium polysulfides (LiPS) in the fluorinated electrolyte reduced the parasitic reactions with Li anode and mitigated the self-discharge by limiting their diffusion from the cathode to the anode. The use of fluorinated ether as a co-solvent and $LiNO_3$ as an additive in the electrolyte shows synergetic effect in suppressing the self-discharge of Li-S battery due to the formation of the solid electrolyte interphase (SEI) on both sulfur cathode and the lithium anode. The Li-S cell with the fluorinated electrolyte showed prolonged shelf life at fully charged state.

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Lithium-sulfur (Li-S) batteries are considered to be promising candidates which can satisfy the demand for high energy density batteries in electronic and transportation devices due to their high theoretical capacity, intrinsic overcharge protection, low cost and nontoxicity.[1,2] Sulfur, one of the most abundant elements in the earth's crust, has a theoretical capacity value of 1675 mAh/g and is the cheapest solid state cathode material for energy storage devices.

Despite the considerable advantages, there are several major issues that impede the practical applications of the Li-S battery.[3] Sulfur undergoes a series of structural and morphological changes during charge and discharge, which results in the formation of soluble Li_2S_x $(4 < x < 8)$ and insoluble Li_2S_2 and Li_2S. The formation of soluble lithium polysulfides (LiPS) and their chemical reaction with the electrolyte and lithium anode leads to low coulombic efficiency and rapid capacity fading.[4–7] In addition, Li-S battery suffers from severe self-discharge, which is the biggest hurdle for the commercialization of this battery.[8] A secondary battery will lose charge capacity when stored for a period of time at a certain temperature. This behavior is known as self-discharge and depends on the battery chemistry, electrode composition, choice of current collector, electrolyte formulation, and the storage temperature. For Li-S batteries, the self-discharge is a well-known issue due to the severe corrosion of lithium metal anode in the presence of the LiPS in the electrolyte.[5,6,8]

Many attempts have been made to overcome the poor cycle life and low sulfur utilization of Li-S batteries.[7–14] However, there are only a few publications focused on solving the self-discharge issue of the Li-S battery. Kazazi et al. have reported that the corrosion of the aluminum current collector and the shuttle mechanism play a significant role in the self-discharge of Li-S cells; therefore, $LiNO_3$ is a suitable electrolyte additive candidate to prevent self-discharge due to its effect on shuttle prevention.[8] Mikhaylik and Akridge reported that self-discharge mainly attributed from the high plateau polysulfides. Electrolytes with higher salt concentration also showed lower rates of Li corrosion with LiPS and a lower shuttle constant.[15] Ryu et al. reported that self-discharge of Li-S battery is dependent on the current collectors. The stainless steel current collector showed the highest self-discharge rate of 59% per month caused by the corrosion of the stainless steel current collectors by LiPS. In comparison, average self-discharge rate for aluminum current collector is 3% per month.[16–18] Recently, our group reported for the first time that the fluorinated electrolyte could significantly prevent the redox shuttling effect, thus greatly improve the coulombic efficiency and capacity retention of Li-S battery.[13,19] Fluoroether-containing electrolytes have been reported by other groups to enhance the performance of the Li-ion battery due to their unique physical and chemical properties;[20–23] however, it is our idea to use it as an electrolyte co-solvent/additive for the Li-S battery. In this paper, we report the self-discharge characteristics of Li-S battery with the fluorinated electrolyte containing 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE). As severe self-discharge has become the major issue for high-loading sulfur cathodes (>5 mg S/cm^2), our test results suggest that utilizing fluorinated electrolyte to effectively suppress this fatal effect shall pave the way for practical applications with high energy density Li-S battery.

Experimental

Sulfur material and electrode preparation.— The sulfur-carbon nanocomposite was prepared by impregnating sulfur into a micro-sized spherical nanoporous carbon.[24,25] The cathodes for Li/S batteries were prepared by mixing 80 wt% of carbon/sulfur composite (70 wt% sulfur), 10 wt% carbon black (Super-P), and 10 wt% polyvinylidenedifluoride (PVdF) dissolved in 1-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. The slurry was then coated onto a carbon-coated aluminum foil. The coated electrodes were dried at 60°C under vacuum for 12 h and punched into discs of 1.27 cm^2. The electrodes had 56% sulfur active material with loadings of 5 mg S/cm^2.

Electrolyte preparation.— 1,2-Dimethoxyethane (DME), 1,3-dioxolane (DOL), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and $LiNO_3$ were purchased from Sigma-Aldrich. 1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) is purchased from Synquest. The solvents were dried over activated 4 Å molecular sieves for 24 hours and further purified by fractional distillation prior to use. Electrolytes were prepared in an Ar-filled glove-box with controlled moisture and oxygen level <5 ppm. The electrolytes examined in this self-discharge study were (1) 1.0 M LiTFSI DOL/DME (v/v, 1/1); (2) 1.0 M LiTFSI DOL/DME (v/v, 1/1)+0.2 M $LiNO_3$; (3) 1.0 M LiTFSI DOL/TTE (v/v, 1/1); (4) 1.0 M LiTFSI DOL/TTE (v/v, 1/1)+0.2 M $LiNO_3$ and (5) 1.0 M LiTFSI DOL/DME (v/v, 1/1)+1.0 M $LiNO_3$. For electrolyte (5), LiTFSI salt dissolves easily in DOL/DME (v/v, 1/1) to 1.0 M. This solution can further dissolve $LiNO_3$ to the maximum 1.0 M. The electrolyte (5) is oversaturated and the solution is not completely transparent. The electrolyte amount of 40 μL was used for each cell.

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Electrochemical measurements.— 2032 coin cells were assembled using lithium as the negative electrode and the above described sulfur electrode as the positive electrode. Cells were assembled in an Ar-filled glove box and cycled at C/10 (1 C = 1675 mA/$g_{(sulfur)}$) rate on a Maccor series 4000 cycler with a 1.6−2.6 V voltage range. The cells were cycled at a C/10 rate for five cycles at room temperature. After the fifth charge, the cells were rested for 10 hours at room temperature or 55°C. The discharge capacity of the 6th cycle was compared with that of the 5th cycle to obtain the self-discharge data.

Morphology characterization.— Coin cells with different cycling history were disassembled inside the glove-box and the electrodes were thoroughly rinsed with DOL solvent. After dried in the glove-box, the samples were loaded onto an air-tight SEM sample holder. The morphology of the electrodes was examined by a high resolution JEOL JSM6610 scanning electron microscopy (SEM) operated at 5–10 kV for imaging and 10–20 keV for EDS data.

Results and Discussion

Self-discharge of high-loading sulfur electrode.— Self-discharge of Li-S cells employing high-loading sulfur electrodes (5 mg S/cm^2) was investigated by resting the cells for 10 hours at the fully charged state after the 5th cycle. The discharge capacity of the 6th cycle was then compared with that of the 5th cycle to obtain the corresponding capacity decrease ratio. As shown in Figure 1a, the baseline cell with DOL/DME-1.0 M LiTFSI electrolyte showed severe redox shuttling even at room temperature, as indicated by the long and flat plateau on the charging voltage profile. As expected, the self-discharge of this cell is severe. After the 10 hour rest, the 6th discharge capacity dropped to 640 mAh/g, a 17% decrease from the 5th cycle discharge capacity. In contrast, the self-discharge is only 4% for the cell with fluorinated electrolyte, DOL/TTE-1.0 M LiTFSI, as shown in Figure 1b. Furthermore, the cell with fluorinated electrolyte showed a high coulombic efficiency of 98% for all the charge-discharge cycles, indicating the redox shuttle effect of LiPS has been largely suppressed. In a previous account, we have demonstrated that TTE solvent benefits the performance of the Li-S cell by reducing the diffusion of LiPS in the electrolyte due to their lower solubility and the formation of a SEI on the surface of the cathode by the reduction of TTE.[13] To the best of our knowledge, this is the first example of using novel electrolyte to improve the shelf life of Li-S battery at fully charged state.

A fundamental analysis reveals that the charge-discharge efficiency, redox shuttling phenomenon, and self-discharge are all facets of the same issue, which in principle could be solved by a single solution. In practice, $LiNO_3$ has become a mandatory additive in conventional DOL/DME-based electrolyte in order for Li-S cells to operate normally.[26,27] The main function of $LiNO_3$ is to reduce shuttling of the soluble LiPS during charge-discharge cycles. Surface analysis shows that, in the presence of $LiNO_3$, a protective film composed of Li_xNO_y and Li_mSO_n is generated on the surface of the lithium anode. However, $LiNO_3$ alone is still not able to completely eliminate the active material loss caused by shuttling, and repeated cycling destroys the protective film.[28] Figure 2a shows the self-discharge result of a Li-S cell with DOL/DME-1.0 M LiTFSI in the presence of 0.2 M $LiNO_3$. A 3.8% loss in discharge capacity was observed after 10 hour rest at room temperature, indicating much less self-discharge had occurred during the storage of the battery compared to the cell without $LiNO_3$ additive. However, when the 10 hour rest was performed at 55°C, the capacity loss resulting from self-discharge increased to 8.6% (Figure 2b), which is likely due to increased diffusion rate of LiPS and instability of the protective layer on the Li surface at elevated temperatures. In comparison, $LiNO_3$ was found to further suppress self-discharge in combination with the fluorinated electrolyte. As shown in Figure 2c, with the addition of 0.2 M $LiNO_3$ in the DOL/TTE-1.0 M LiTFSI electrolyte, only minor capacity loss (0.7 %) was observed for the cell rested at room temperature. More surprisingly, negligible self-discharge was also evident when the cell was stored at fully charged state at 55°C for 10 h, as shown in Figure 2d.

As mentioned above, there are two main strategies for preventing self-discharge of Li-S cells: (1) by increasing the corrosion resistance of the metallic current collector in the electrolyte[17] and (2) by inhibiting the shuttle mechanism.[8] To understand the effect of $LiNO_3$ as a self-discharge suppressor, high concentrations of $LiNO_3$ was introduced in the electrolyte solvent. The self-discharge behavior of a Li-S cell with DOL/DME-1.0 M LiTFSI electrolyte containing 1.0 M $LiNO_3$ was studied. The result in Figure 3 shows that the discharge capacity decreased about 2.7% at room temperature and 5% at 55°C between the 6th and 5th cycle. Even though lower capacity loss was achieved with large excess of $LiNO_3$ additive in the conventional electrolyte, self-discharge was not completely inhibited. In addition, using a high concentration of $LiNO_3$ additive was found to have a negative effect on the cell performance.[28] The irreversible reduction of $LiNO_3$ reduces the reversibility of Li_2S formation and thus results in permanent capacity loss. These results indicate that the best electrolyte for self-discharge suppression is the combination of TTE solvent with $LiNO_3$ as an additive in the electrolyte. The synergetic functions are the result of (1) lower solubility of LiPS in the fluorinated electrolyte, (2) formation of an SEI layer on the surface of the sulfur/carbon cathode by the fluoroether solvent,[13] and (3) formation of the protective layer on the lithium anode by $LiNO_3$ and TTE reduction reaction.[13,19,26,27]

Long-term self-discharge behavior of the cells with different electrolyte compositions was then evaluated by monitoring the voltage decay during resting. As shown in Figure 4a, the cell containing DOL/DME-1.0 M LiTFSI electrolyte without $LiNO_3$ additive showed severe shuttling during the 1st and 2nd charge. In addition, after the 5th charge, the cell voltage dropped from 2.39 V to 2.11 V within 7 h and stabilized at this voltage for the rest of testing period. The voltage drop was likely caused by the continuous depletion of the soluble,

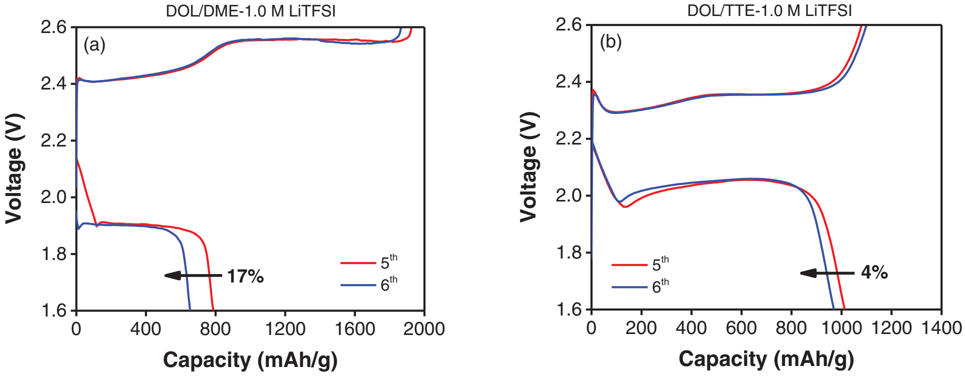

Figure 1. The 5th and 6th cycle voltage profile for Li-S cells with high-loading sulfur cathodes rested at room temperature between the 5th charge and 6th discharge: (a) DOL/DME-1.0 M LiTFSI electrolyte and (b) DOL/TTE-1.0 M LiTFSI electrolyte.

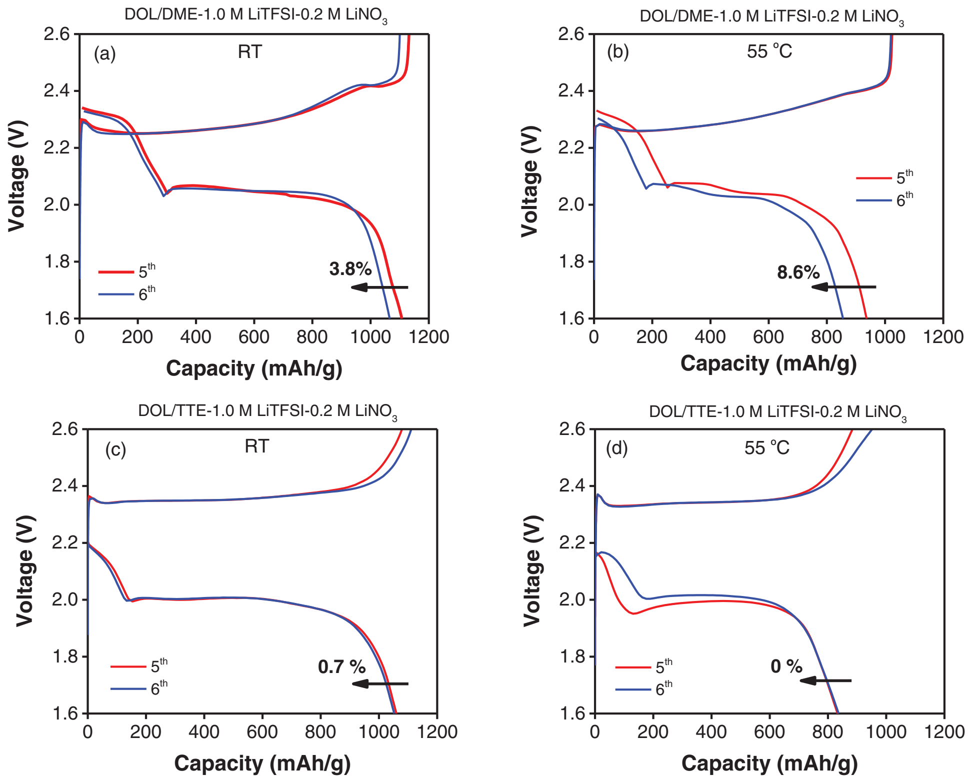

Figure 2. The 5th and 6th cycle voltage profile for Li-S cells with high-loading sulfur cathodes rested between the 5th charge and 6th discharge, with (a, b) DOL/DME-1.0 M LiTFSI+0.2 M $LiNO_3$ electrolyte and (c, d) DOL/TTE-1.0 M LiTFSI+0.2 M $LiNO_3$ electrolyte rested at (a, c) room temperature and (b, d) 55°C.

higher-order LiPS in the cathode. The LiPS could diffuse out of the cathode and migrate to the anode until concentration equilibrium of the polysulfide species in the electrolyte was to be reached. During this process, the polysulfides could undergo reduction reactions with Li metal and deposit on the anode surface, further driving migration of LiPS and resulting in lower capacity in the subsequent discharge step.[29] In comparison, the cell containing the fluorinated electrolyte exhibited much slower voltage drop during resting. The cell voltage maintained at a short plateau above 2.25 V for a period of 14 hours before slowly decreasing to a stable plateau of 2.13 V in another 34 hours. This result suggests that the diffusion of LiPS from the cathode and their reaction with the anode was retarded significantly, although prolonged resting still resulted in consumption of the soluble LiPS by Li anode. In the presence of $LiNO_3$ additive, the self-discharge was found to be suppressed for cells with both the baseline and fluorinated electrolyte. Figure 4b shows that the cell containing DOL/DME-1.0 M LiTFSI -0.2 M $LiNO_3$ promptly underwent self-discharge from 2.42 V to 2.14 V. A short voltage plateau above 2.35 V was observed for this cell; however, the cell was only able to hold this voltage for 25 hours. The cell containing DOL/TTE-1.0 M LiTFSI with 0.2 M $LiNO_3$ showed much better performance in suppressing self-discharge. The cell voltage remained at a high 2.27 V plateau for over 1 week (170 hours) and gradually dropped to 2.16 V after another 70 h. These results indicate that the presence of $LiNO_3$ and thus the protective layer on Li surface effectively inhibited the reaction of polysulfides with Li, and LiPS diffusion was only suppressed when the fluorinated ether was present. For the fluorinated electrolyte, the rapid voltage drop after 170 hours of rest may be a result of depletion of the protective layer on Li surface. In this regard, a more detailed study is required to investigate the stability of the protective layer formed by decomposition of $LiNO_3$ and fluorinated ether TTE.

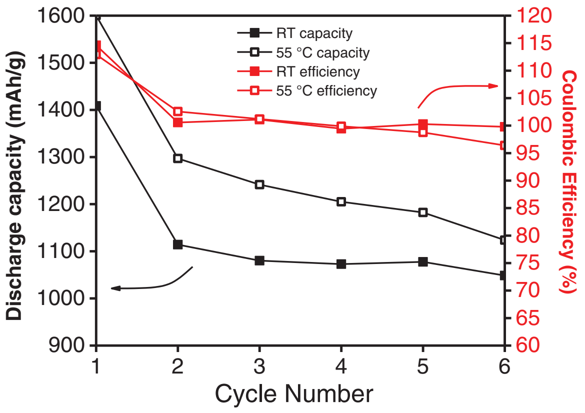

Figure 3. Discharge capacity and coulombic efficiency of Li-S cells with high-loading sulfur cathodes and DOL/DME-1.0 M LiTFSI+1.0 M $LiNO_3$ electrolyte at room temperature and 55°C.

Electrode characterization.— To further study the effect of fluorinated electrolyte on the cell performance, the structural changes in the lithium anodes cycled in both electrolytes were investigated by means of SEM. As observed in Figure 5a, the surface of lithium anode after the 1st cycle using conventional DOL/DME-1.0 M LiTFSI electrolyte has structures that appear to be voids on the surface of the lithium. There is also another layer of material on top of the anode which is beam sensitive. This layer of material, which is formed by the deposition of insoluble LiPS, disappears with prolonged exposure to the electron beam. EDS spectrum in Figure 5c clearly indicates that sulfur has the highest concentration inside these pits on the surface of the anode. In comparison, a more dense layer of passivation was observed on the cycled Li anode with fluorinated electrolyte (Figure 5d, 5e) and EDS spectrum of this layer showed less sulfur deposition (Figure 5f), which is in agreement with the observations reported in our previous

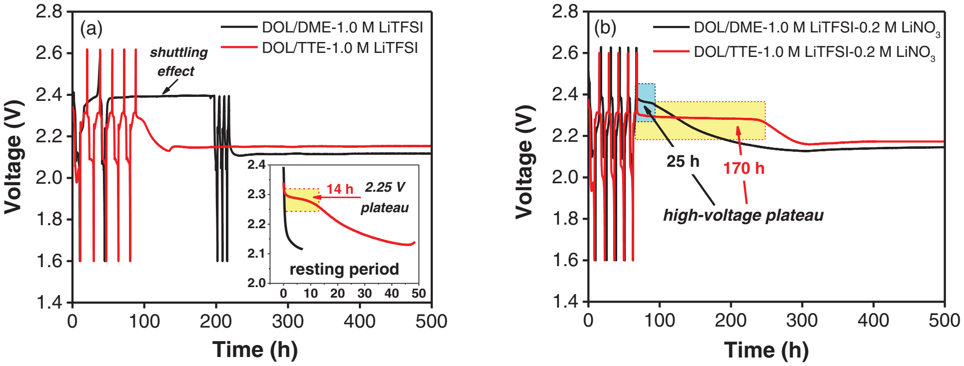

Figure 4. Voltage profile for Li-S cells rested for extended period of times with DOL/DME-1.0 M LiTFSI and DOL/TTE-1.0 M LiTFSI (a) without $LiNO_3$ and (b) with 0.2 M $LiNO_3$. Inset in (a) shows the voltage profile for up to 50 hours after the 5th charge.

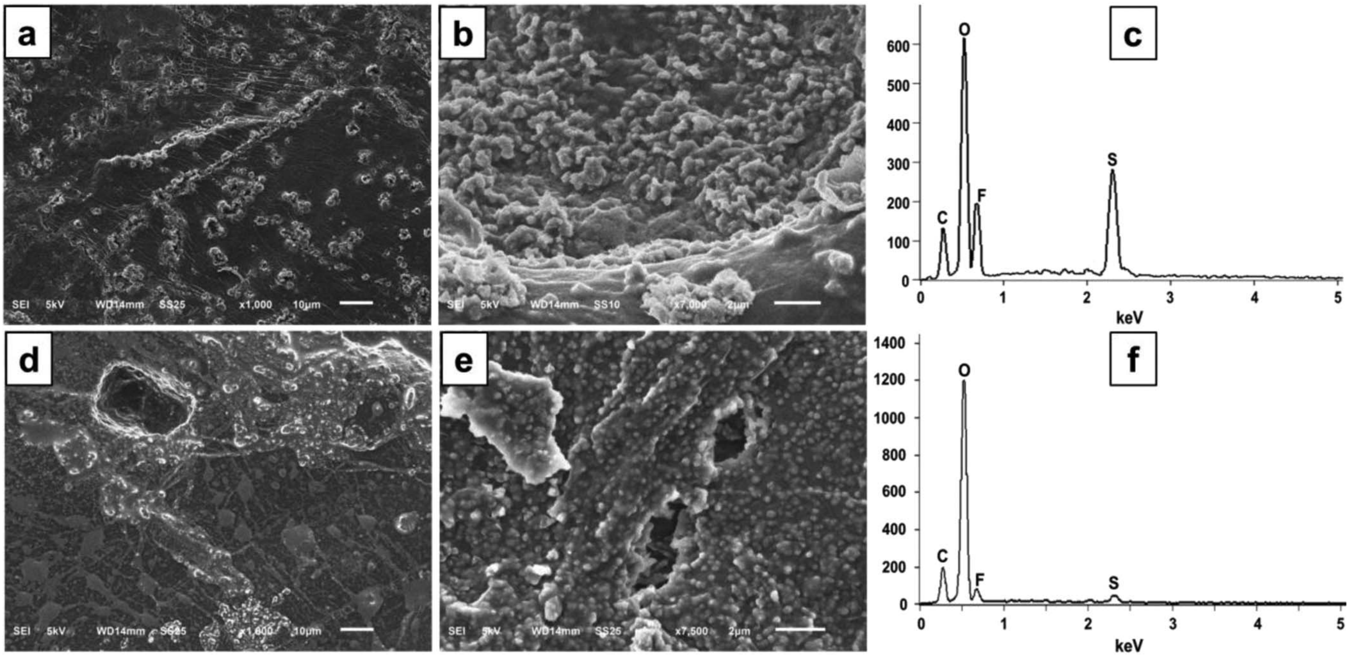

Figure 5. SEM images and EDS data of lithium anodes cycled after 1st discharge: (a), (b) and (c) with DOL/DME-1.0 M LiTFSI; (d), (e), and (f) with DOL/TTE-1.0 M LiTFSI.

study.[13] The lower diffusion of LiPS and mitigated parasitic reaction of these species with the lithium anode results in higher coulombic efficiency and less self-discharge of the Li-S cell.

Conclusions

In this study, the self-discharge behavior of lithium-sulfur cells was investigated with high- loading sulfur electrodes. It is shown that using partially fluorinated electrolyte, DOL-TTE-1.0 M LiTFSI with the addition of $LiNO_3$, has an outstanding effect in reducing self-discharge – almost no self-discharge is observed after 10 hours of rest at room temperature and 55°C. In contrast, using even a very high concentration of $LiNO_3$ with conventional electrolyte had a relatively low effect on self-discharge. It was found that the combination of TTE and $LiNO_3$ can protect both the sulfur cathode due to the formation of a stable SEI layer by TTE[13] and the lithium anode due to the SEI formed by $LiNO_3$ and TTE reduction. SEM and EDS results confirm the decreased deposition of sulfur species on the surface of the lithium anode while using the TTE-containing electrolyte, which results in improved self-discharge of the Li-S cell.

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