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Research Article

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Partially fluorinated ether as an electrolyte additive to modify electrode surface and suppress dissolution of polysulfides in Li-S batteries

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Abstract: 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), a kind of fluorinated ether, was used as an electrolyte additive for Li-S batteries. A compact, smooth, and homogenous surface layer was formed on lithium anode at the optimized amount of added TTE. In addition, TTE additive played a crucial role in modifying the composition of the passivation layer on the sulfur/carbon cathode. Consequently, the dissolution and shuttling of polysulfides were effectively prevented. The reversible capacity, initial coulombic efficiency, electrode reaction kinetic, and cycling stability of Li-S batteries were greatly improved.

Keywords: additive; electrolyte; lithium-sulfur batteries

1 Introduction

With the advantages of high theoretical specific capacity, inexpensive, highly abundant, and nontoxic nature of the element sulfur, lithium-sulfur (Li-S) batteries have been considered as the most promising secondary batteries systems with extremely high energy density [1–8]. Nonetheless, the practical application of Li-S batteries is seriously hindered by the fast capacity fading upon long-term cycling, which mainly results from the dissolution of polysulfide species (intermediate discharge products of sulfur) and the resultant shuttling between the sulfur cathode and the lithium anode. The shuttling effect gives rise to the deposition of insoluble sulfides on the surface of both cathode and anode, reducing the utilization efficiency of sulfur and leading to electrode passivation/degradation [9–12]. To overcome these problems, various strategies have been presented over the past few years. One of the most effective approaches is to construct advanced sulfur-based cathode materials, such as composites of sulfur with various carbons [13], electronically conductive polymers, metal oxides, and metal organic frameworks [14–20]. However, the manufacturing procedures for these composites are usually complex, reducing the feasibility for commercial application [21, 22]. Another strategy is the modification of lithium anode surface through the use of protecting/coating layers, which can prevent the direct contact and interaction of polysulfides with lithium metal, thereby weakening the shuttle effect. However, an appropriate method regarding the surface treatment of lithium metal under inert atmosphere is difficult to find. Recently, the design of electrolyte components is proposed to be a new and much easier strategy to restrict the shuttle effect as this approach does not add any procedures to the assembly of Li-S batteries. Like the former two strategies, the long-term cycling performance of Li-S batteries also can be greatly improved through the utilization of functional solvents, lithium salts, or additives [23–25]. High concentration [26] or ionic liquid-based electrolytes [27, 28], where the solvent molecules are all strongly coordinated with Li^+ ions, were proven to be quite effective for suppression of polysulfide dissolution and shuttling, enabling good cyclability of Li-S batteries. By analogy to the successful application of fluoroethylene carbonate solvent to the silicon anodes of Li-ion batteries, fluorinated ethers are also attracting much attention for the purpose of application in Li-S batteries. It is reported that the electrolyte with the co-solvents bis(2,2,2-trifluoroethyl) ether (BTFE) and 1,3-dioxolane (DOL) at a volumetric ratio of 1/1 can significantly reduce polysulfide solubility, mitigate self-

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discharge, and improve capacity retention of Li-S batteries [29, 30]. Ethyl 1,1,2,2-tetrafluoroethyl ether (ETFE) [31] and 1,3-(1,1,2,2-tetrafluoroethoxy)propane (FDE) [32] were also separately used as the electrolyte co-solvents, which play a key role in forming a protective film on the Li anode during cycling, thereby improving the electrochemical performance. In particular, 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) as the co-solvent in Li-S batteries shows impressive behavior in preventing polysulfides from dissolving in electrolyte solution and facilitating the formation of a stable solid electrolyte interphase (SEI) on sulfur cathode via the reduction reaction of TTE [33–36]. Despite the early success of these fluorinated ethers as co-solvents in Li-S batteries, the effect of fluorinated ethers as electrolyte additives has not been studied to the best of our knowledge.

As we know, the use of electrolyte additives has insignificant influence on the cost of Li-S batteries due to its extremely low dosage, while an excellent electrolyte additive can facilitate the formation of a protective passivation layer on the sulfur-based cathode or lithium anode, reducing the shuttling of polysulfides and greatly improve the cycling performance of Li-S batteries. Several inorganic and organic salts, such as cesium nitrate, copper acetate, lithium iodide, lithium nitrate, and lithium oxalyldifluoroborate have been studied as electrolyte additives to improve the performance of Li-S batteries [37–41]. In this work, we for the first time investigate the effect of fluorinated ether TTE as an electrolyte additive in Li-S batteries. It is found that at the optimized addition amount of 2%, TTE favors the formation of an effective protective layer on sulfur-based cathode, prevents the dissolution of polysulfides, and enables a smooth and compact surface of lithium anode. As a result, excellent cycling performance with capacity maintaining above 650 mAh g^{-1} after 300 cycles at 0.2 C is obtained for the Li-S batteries.

2 Experimental

Preparation of electrolytes

The conventional electrolyte contains 1.0 mol L^{-1} of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1 mol L^{-1} of anhydrous lithium nitrate dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) at a volume ratio of 1:1. The conventional electrolyte was purchased from Suzhou Qian Min chemical reagents Co. Ltd. Different amounts of 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) (volumetric percentages: 1%, 2%, and 4%) were added separately to the conventional electrolyte in an argon-filled glove-box to prepare the electrolytes with TTE additives. The TTE additive was provided by J&K China chemical Ltd.

Assembly of Li-S batteries

Pure untreated sulfur powder was first mixed with carbon black and poly(vinylidene fluoride) (PVDF) binder at a weight ratio of 7/2/1 by grinding in a mortar. The obtained mixture was then uniformly dispersed in N-methylpyrrolidone using high speed shearing machine to form an electrode slurry, which was spread onto aluminum foil and then dried in a vacuum oven at 60°C for 24 h to prepare the cathode disks. Lithium disks and porous polypropylene film (Celgard 2500) were used as the anode and separator, respectively. During the assembly of CR2032-type coin cells, one extra layer of electrospun carbon nanofiber paper was sandwiched between the sulfur cathodes and separators to observe the dissolution of polysulfides from the sulfur cathodes. The electrospun carbon nanofibers paper was prepared according to our previously reported method [42]. The average weight of electrospun carbon nanofibers interlayer used in every coin cell was about 2.5 mg, and the diameter of the interlayer discs was 13 mm. The mass loading of active sulfur material on each cathode discs was about 0.5 mg cm^{-2}.

Electrochemical testing

The long-term charge-discharge cycling test was carried out at a constant current rate of 0.2 C on a LAND-CT2001A battery cycler. Cyclic voltammograms (CV) were obtained using a potentiostat (PGSTAT302N, Autolab Instruments, Switzerland) at a scan rate of 0.5 mV s^{-1} in the potential range of 1.7-2.6 V vs. Li/Li^+. Electrochemical impedance spectroscopy (EIS) was conducted on an electrochemical workstation (IM6, Zahner, Germany) with an sinusoidal amplitude of 5 mV over the frequency from 10^5 to 10^{-2} Hz. The electrodes were discharged/charged for five full cycles and then discharged to a potential of 1.95 V to obtain their Nyquist plots.

Electrode characterization

The lithium anodes and carbon nanofiber paper interlayers were carefully taken out from Li-S cells after 50 charge-discharge cycles, washed with DME in a glove-box, and

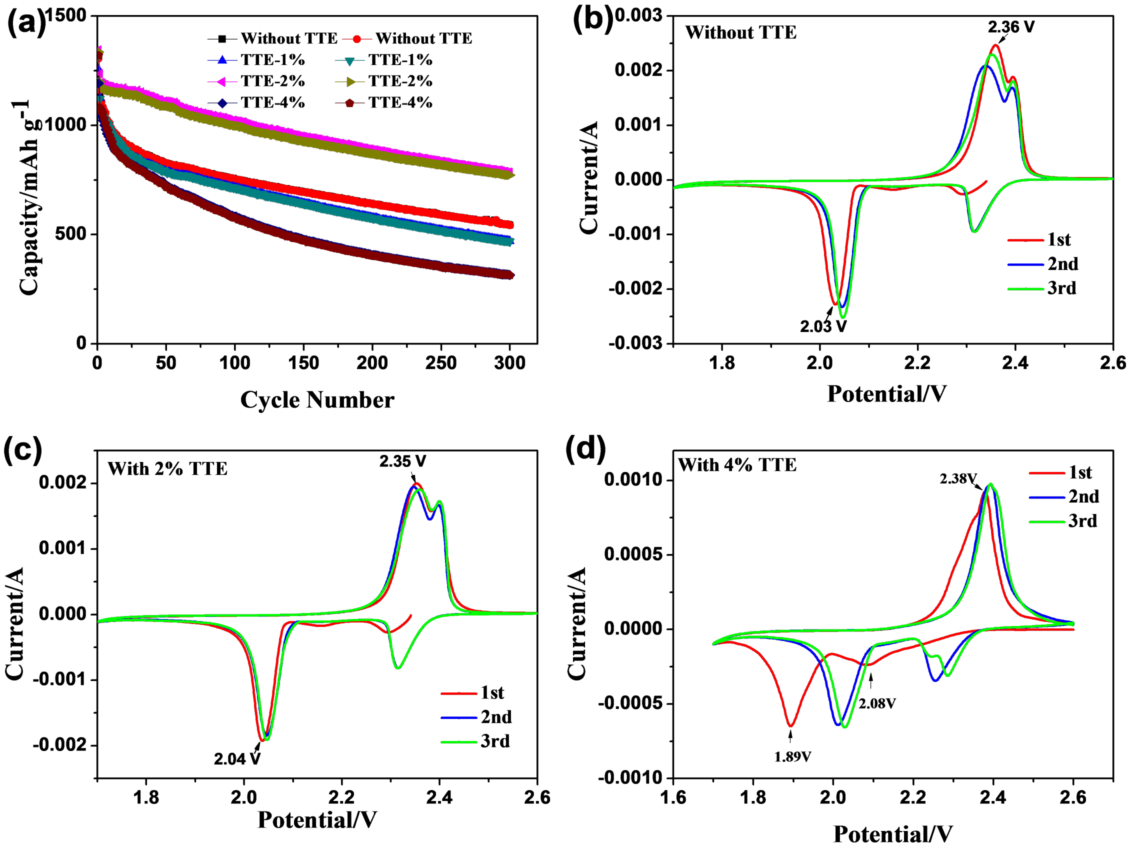

Figure 1: (a) The long-term cycling performance and (b-d) CV curves of Li-S cells with different electrolytes.

then dried overnight under vacuum at room temperature to remove residual solvents. Before being transferred from the glove-box to any other testing equipment, the lithium anodes and carbon nanofibers paper interlayers were put into sealed tubes that were further stored in a vacuum desiccator. The surface morphologies and elemental composition of the electrodes were investigated by scanning electron microscopy (SEM, Hitachi S-4700) and X-ray photoelectron spectroscopy (XPS, Escalab 250xi), respectively.

3 Results and discussion

Figure 1a shows the long-term cycling performance of Li-S cells assembled with different electrolytes. With addition of 1% TTE, the capacity decreases rather quickly during the initial 50 cycles, and the fading rate of capacity is similar to the electrolyte without TTE additive. With addition of 2% TTE the capacity loss during the initial 50 cycles is considerably smaller as compared to the electrolyte without TTE, leading to a reversible capacity of 772 mAh g^{-1}after 300 cycles. Thus the cycle stability has been significantly improved through addition of 2% TTE. Nevertheless, when the content of TTE is increased to 4%, the capacity attenuation is very fast, and about 314 mAh g^{-1} of capacity is retained after 300 cycles. Therefore, it is assumed that addition of appropriate amounts of TTE, here 2%, beneficial for the performance improvement of Li-S cells, the reasons for which will be analyzed from the following various characterization.

To compare the electrochemical reaction of Li-S cells with different electrolytes, cyclic voltammetry was used and the initial three CV curves at a scan rate of 0.5 mV s^{-1} are shown in Figure 1b-1d. For the electrolyte without TTE additive, two major cathodic peaks appeared at 2.30 and 2.03 V during the first negative scan corresponding to the reduction of sulfur to lower-order polysulfides and the further reduction of polysulfides to Li_2S_2/Li_2S, respectively. The positive scan shows the opposite reaction from Li_2S_2/Li_2S to sulfur. With addition of 2% TTE, there are no obvious changes in terms of shape and potential of the redox peaks except a very slight decrease of the peak separa-

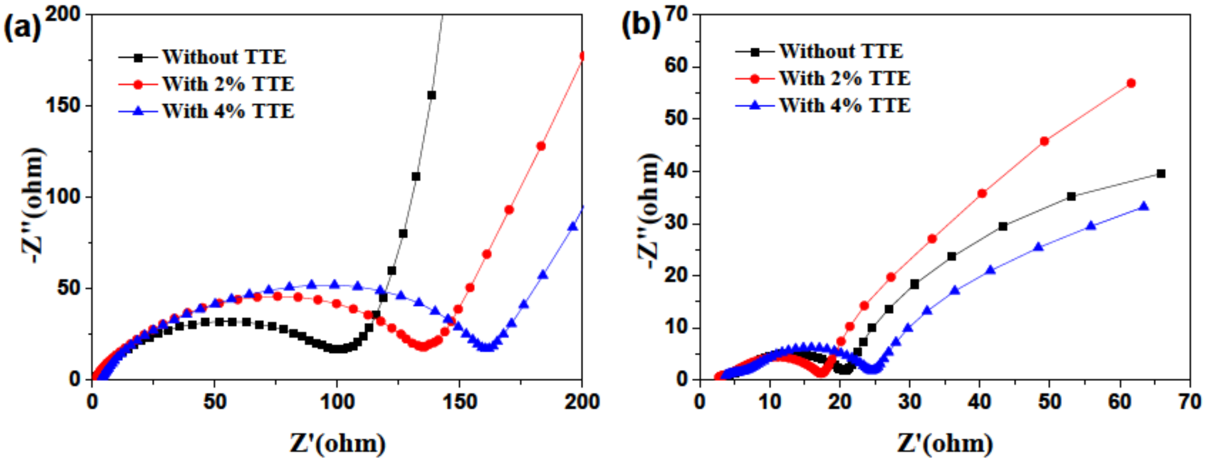

Figure 2: The Nyquist plots of Li-S cells with different electrolytes (a) at the open circuit voltage and (b) after five cycles.

tion between the redox peaks at 2.04 V/2.35 V (as compared to 2.03 V/2.36 V). This phenomenon suggests a slightly accelerated kinetic for the electrochemical reaction of polysulfides to Li_2S_2/Li_2S. In addition, the intensity of the anodic peaks during the initial three cycles stays almost constant for the electrolyte with addition of 2% TTE, whereas the corresponding anodic peaks exhibit obvious changes with the electrolyte without TTE. These results suggest reduced polarization and improved reversibility for the electrode reactions of Li-S cells through addition of 2% TTE. When the content of TTE is increased to 4%, the two major cathodic peaks down-shifts drastically to 2.08 and 1.89 V during the first scan, indicating that the transformation reactions from sulfur to Li_2S_2/Li_2S become sluggish, which can be correlated to the high resistance of Li-S cells through addition of 4% TTE (see Figure 2).

The electrochemical impedance spectra of Li-S cells with different electrolytes at the open-circuit potential and after five cycles are shown in Figure 2a and 2b, respectively. At the open-circuit potential, there is one semicircle at high-to-medium frequencies [43], whose diameter reflects the charge-transfer resistance (R_c) at the electrode/electrolyte interface. The straight line in the low-frequency region corresponds to a semi-infinite Warburg diffusion process [28]. As can be seen in Figure 2a, the charge-transfer resistance of the Li-S cells gradually increases with the increase of TTE content. This phenomenon can be ascribed to the poor solvation of TTE for other salts, which to some extent hinders the transport of ions through the electrode/electrolyte interface. After 5 discharge/charge cycles, the resistance of all Li-S cells exhibits drastic decrease as compared to that before cycling. The reasons can be attributed to the following two aspects. On the one hand, the dissolution of polysulfides upon discharge/charge cycling could facilitate the ‘quasi-liquid’ reaction of sulfur-based cathode [42], enabling an electrochemical activation process. On the other hand, the gradually formed solid-electrolyte interphase on the surface of both sulfur cathode and lithium anode as shown in the following morphological characterization may also contribute to an improved charge transfer reaction. In addition, it is observed from Figure 2b that the charge transfer resistance of Li-S cells with electrolyte containing 2% TTE is the smallest, suggesting the formation of an optimal interface environment for the electrode reaction. Higher content of TTE (4%) generates a higher resistance than the reference electrolyte without TTE, which also should be related to the interface properties as observed from the following study. The electrochemical resistance results of Li-S cells with different electrolytes perfectly explain their different long-term cycling performance in Figure 1a.

The initial three discharge/charge curves of the Li-S cells in the presence or absence of 2% TTE are compared in Figure 3. The two discharge plateaus at 2.34 and 2.10 V and the two charge plateaus at 2.38 and 2.22 V correspond well to the two couples of redox peaks in CV curves, which arise from the multistep conversion reaction of sulfur/Li_2S. Relative to the mass of active sulfur material, the discharge capacities of the first three cycles for the Li-S cell with 2% TTE-containing electrolyte are 1337, 1199, and 1173 mAh g^{-1}, respectively, which are over 100 mAh g^{-1} higher than those without TTE additive (1238, 1108, and 1089 mAh g^{-1}, respectively). The initial coulombic efficiency, defined as the ratio of charge capacity to discharge capacity, of the Li-S cells without and with 2% TTE additive is 98.9 and 100.2%, respectively. The discharge/charge results suggest the enhanced utilization of sulfur active materials and

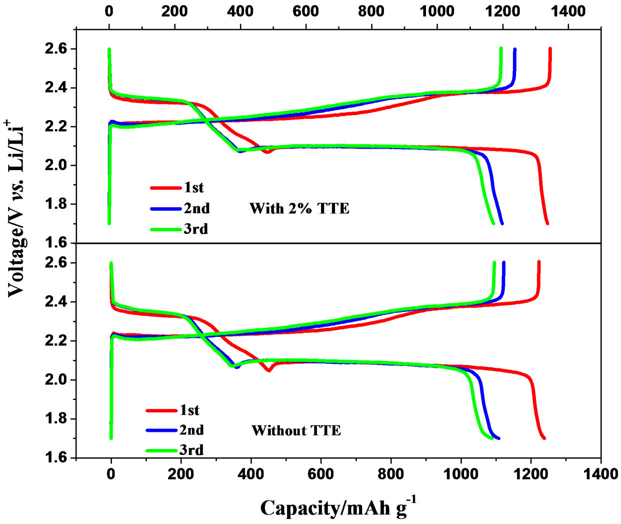

Figure 3: The initial three discharge/charge curves of Li-S cells in the presence or absence of 2% TTE.

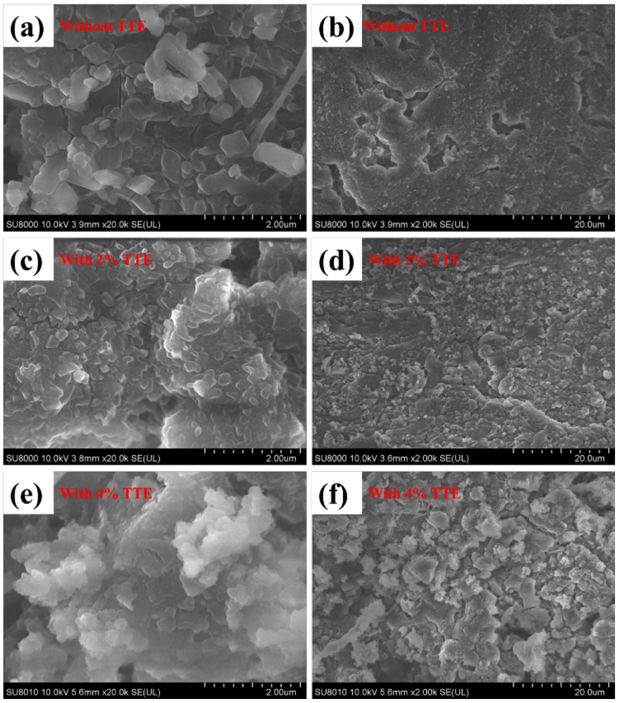

Figure 4: SEM images of the lithium anode surface after 50 electrochemical cycles in the electrolytes (a, b) without, (c, d) with 2%, and (e, f) 4% addition of TTE.

improved reversibility of sulfur/Li$_2$S conversion reaction through addition of 2% TTE into the electrolyte.

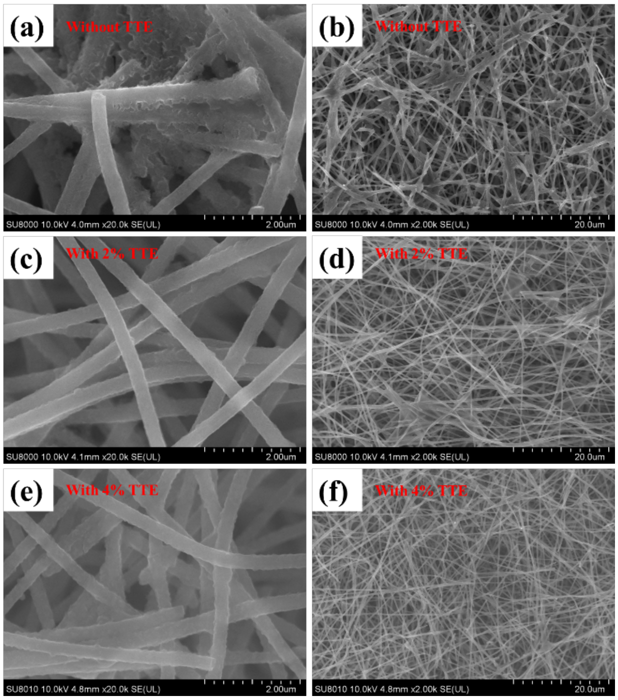

Figure 5: SEM images of the carbon nanofiber interlayers after 50 electrochemical cycles in the electrolytes (a, b) without, (c, d) with 2%, and (e, f) 4% addition of TTE.

To shed light on the reasons for the improved performance of Li-S cells through use of TTE additive, the cells were disassembled after 50 cycles and the morphological changes of electrode surface were investigated. SEM images of the lithium anode surface after electrochemical cycling in the electrolytes without and with addition of TTE are shown in Figure 4. After cycling in the conventional electrolyte without TTE, the surface of lithium anode is covered by a layer of deposits that is mainly composed of particles larger than 500 nm. This layer of deposits is believed to mainly originate from the reaction between dissolved polysulfides and lithium anode accompanied by the formation of insoluble Li$_2$ [36]. Moreover, many holes/cracks appear in this layer of deposits, indicating that the surface of lithium anode is uneven, which makes it difficult to achieve a stable and uniform lithium plating/deplating. In the case of lithium anode cycled in 2% TTE-containing electrolyte, the particle size of the deposits on lithium surface is less than 200 nm. Moreover, the surface layer is compact, smooth, and homogenous, indicating that addition of 2% TTE to some extent inhibits the violent reaction between polysulfides and lithium anode. Such a compact and uniform electrode/electrolyte interfacial layer can effectively prevent further reaction between polysulfides and lithium anode so as to mitigate the shuttling effect of polysulfides. Consequently, the reversible capacity, initial coulombic efficiency, and cycling stability of the Li-S cells are greatly improved during the charge/discharge test. The slightly reduced electrode polarization as observed from CV curves and the small charge-transfer resistance obtained from electrochemical

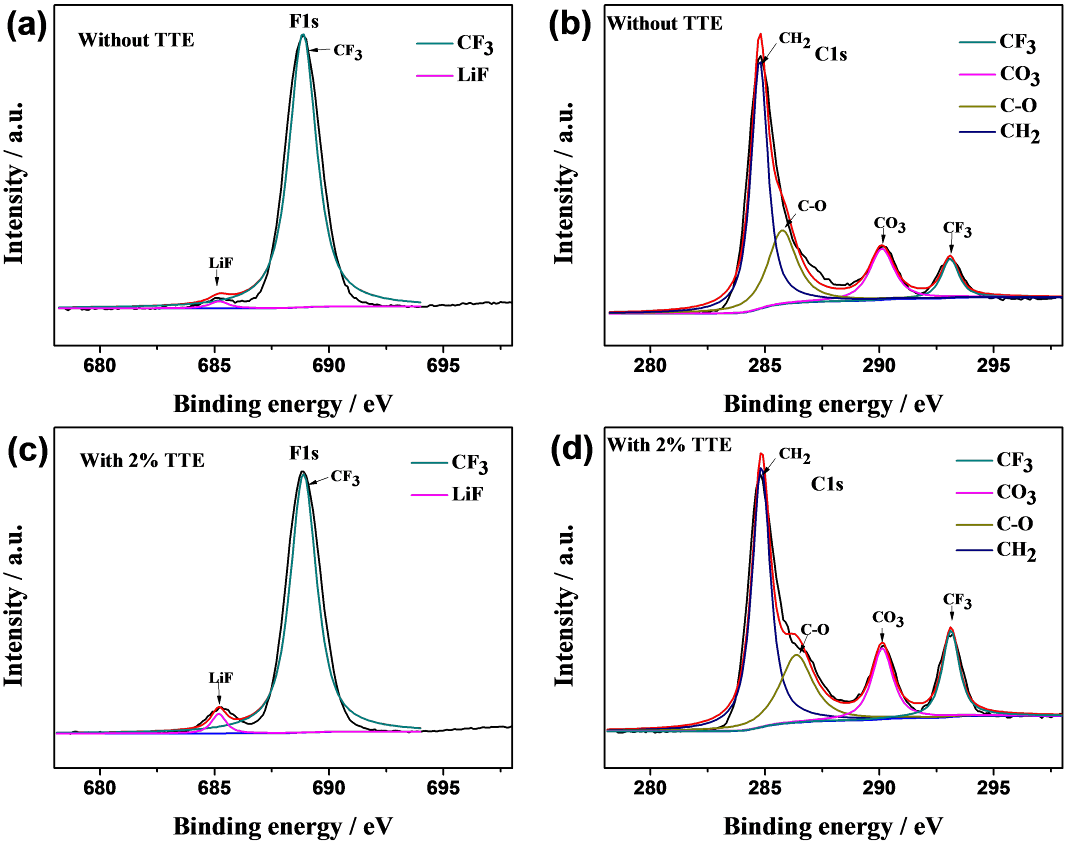

Figure 6: The deconvoluted XPS spectra of the carbon nanofibers interlayers in the core-level regions of F_{1s} and C_{1s} after 50 electrochemical cycles in the electrolytes (a, b) without and (c, d) with 2% addition of TTE.

impedance measurement also are related to the formation of such a compact and even interface layer on lithium. With the increase of TTE content to 4%, the lithium anode shows a rough surface composed of loosely stacked deposits. The different morphologies of lithium surface after cycling in different electrolytes further suggest that addition of TTE can influence the surface properties of lithium anode. On the basis of the quite poor electrochemical performance of Li-S cells with 4% TTE-containing electrolyte, it is assumed that the loosely stacked deposits are not effective in preventing further reaction between polysulfides and lithium anode, and lead to an increased resistance for the charge-transfer reaction occurring on the electrode surface.

The effect of TTE addition on preventing dissolution of polysulfides from sulfur cathode is further proven through SEM observations on the surface of carbon nanofiber paper interlayers (the side that is in direct contact with sulfur cathode) that were taken out from Li-S cells after 50 cycles. As shown in Figure 5, after cycling in the electrolyte without TTE, the surface of carbon nanofibers paper is obviously covered by some agglomerated amorphous substances. The deposited substances are believed to originate from the dissolved long-chain polysulfides, which diffuse from the sulfur cathode to the surface of carbon nanofiber interlayer, and was intercepted and further reduced to lower-order sulfides during discharge. In contrast, the surface of the carbon nanofiber interlayer after cycling in the electrolyte with 2% TTE additive is much cleaner with no obvious agglomerates appeared, validating that the dissolution of polysulfides from sulfur cathode as well as its electrochemical reaction on carbon nanofibers interlayer has been inhibited through addition of 2% TTE. After cycling in 4% TTE-containing electrolyte, the surface morphology of carbon nanofibers interlayer exhibits no obvious difference as compared to that cycled in 2% TTE-containing electrolyte, indicating that the dissolution of polysulfides from sulfur cathode is still effectively prevented through addition of higher content of TTE. Therefore, the rapid capacity fading of Li-S cells with 4% TTE-containing electrolyte should mainly result from the quite loose structure of the interface layer on lithium anode (see Figure 4e and 4f), which cannot provide enough protection for lithium anode and leads to high resistance for the charge-transfer reaction.

The chemical state of the elements on the surface of the cycled carbon nanofiber interlayer was investigated using XPS to further study the effect of TTE additive on the interface properties. The deconvoluted XP spectra in the core-level regions of F_{1s} and C_{1s} are shown in Figure 6. After cycling in the conventional electrolyte without TTE, the two components of F_{1s} spectra can be assigned to $-CF_3$ (689.0 eV) and LiF (685.0 eV), while the four components of C_{1s} spectra at 284.9 eV, 286.8 eV, 288.5 eV, and 293.1 eV indicate the presence of $-CH_2$, -C-O, $-CO_3$, and $-CF_3$, respectively. The appearance of $-CF_3$ originates from the residual salt LiTFSI at the surface of carbon nanofiber paper [44-45]. After cycling in the 2% TTE-containing electrolyte, the peaks corresponding to the presence of LiF, $-CO_3$, and $-CF_3$ are much stronger as compared to those obtained in the absence of TTE. The increased intensity of these peaks can be associated with the reductive decomposition of TTE on the surface of sulfur/carbon cathode [34]. As Li_2CO_3 and LiF have been known to be the important components of SEI film, it is proposed that TTE additive plays a crucial role in constructing a superior passivation film on the sulfur/carbon cathode. Therefore, the decreased dissolution of polysulfides through use of TTE additive as observed from Figure 5 can be attributed to the optimized composition of passivation layer, which contributes to the improved electrochemical performance of Li-S cells.

4 Conclusion

The effect of fluorinated ether TTE as the electrolyte additive of Li-S cells was investigated. At the optimized addition amount of 2%, a compact, smooth, and homogenous surface layer is formed on lithium anode, which can effectively prevent the further reaction between polysulfides and lithium anode. In addition, TTE additive plays a crucial role in constructing a superior passivation film on sulfur/carbon cathode, which can inhibit the dissolution of polysulfides from sulfur cathode. Consequently, the reversible capacity, initial coulombic efficiency, electrode reaction kinetic, and cycling stability of Li-S cells are greatly improved during charge/discharge test. The good performance of TTE additive makes it promising for practical application in Li-S batteries.

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