Figures and Captions

Figure 1. (a) Galvanostatic voltage profiles of Li-S cell with 1.0M LiPF₆-1NM3 electrolyte at 1st and 10th charge and discharge. (b) Capacity retention and coulombic efficiency of Li-S cell with 1.0M LiPF₆-1NM3 electrolyte at 0.1C rate.

Figure 2. (a) Galvanostatic potential profiles of Li-S cells with 1.0 M LiPF₆-1NM3 + 2% LiDFOB at the 1st and 20th charge and discharge cycle. Capacity retention and coulombic efficiency of Li-S cells with (b) 1.0 M LiPF₆-1NM3+2% LiDFOB, (c) 1.0 M LiPF₆-1NM3+5% LiDFOB, and (d) 1.0 M LiPF₆-1NM3+10% LiDFOB at a 0.1C rate.

Figure 3. Differential capacity (dQ/dV) profiles of Li-S cell with 1.0 M LiPF₆-1NM3+2% LiDFOB at (a) the 1st, (b) 10th, (c) 30th, and (d) 50th discharge.

Figure 4. Galvanostatic potential profiles of Li-S cell for the 1st through 20th charge and discharge cycles at 0.1C rate with (a) 1.0M LiTFSI-1NM3 and (b) 1.0M LiTFSI-1NM3 + 2% LiDFOB electrolyte.

Figure 5. (a) Coulombic efficiency and (b) discharge capacity retention of Li-S cells with 1.0M LiPF₆-1NM3 and 1.0 M LiPF₆-1NM3 + 2% LiNO₃ electrolyte.

Figure 6. SEM image of sulfur cathode surface at the 1st discharged state with (a) 1.0 M LiPF₆-1NM3, (b) 1.0 M LiPF₆-1NM3+2% LiDFOB and the 10th discharge state with (c) 1.0 M LiPF₆-1NM3, (d) 1.0 M LiPF₆-1NM3+2% LiDFOB.

Figure 7. (a) Nyquist plots of the impedance response for Li-S cells after first discharge with 0.8M LiPF₆-1NM3 and 0.8M LiPF₆-1NM3+2% LiDFOB, and (b) cell resistance (R_e), interphasial resistance (R_{int}), and the charge transfer resistance (R_{ct}) fitted from the experimental data for the Li-S cell with and without LiDFOB additive.

Figure 1.

Figure 2.

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Figure 6.

Figure 7.

Additive Effect on the Electrochemical Performance of Lithium-Sulfur Battery

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Keywords: Electrolyte; LiDFOB additive; Silicon-based electrolyte; Coulombic efficiency; Lithium-sulfur batteries

Abstract:

Lithium difluoro(oxalato) borate (LiDFOB) was investigated as an electrolyte additive for the Li-S battery. This additive was identified to be an efficient electrolyte additive to suppress the polysulfide shuttling effect existing in the conventional Li-S chemistry. To detect the positive impact of the new additive, oligo(ethylene glycol) functionalized silane was employed as the electrolyte solvent due to its high solvation capability with the lithium polysulfides. The electrochemical results and the SEM data of Li-S battery using the new electrolyte confirmed the role of the LiDFOB as a critical component to eliminate the shuttling of the dissolved polysulfides thus enabling a high coulombic efficiency.

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1. Introduction

Even though the Li-ion battery has proven to be one of the best candidates for energy storage, new systems are required so that the next generation of batteries delivers higher energy density at lower cost. The lithium-sulfur (Li-S) battery has the potential to meet the performance requirements for high-energy-density batteries in various electronics and transportation applications, such as electric vehicles [1-3]. In Li-S battery, sulfur is electrochemically reduced to Li_2S , resulting in an extremely high capacity (1675 mAh per gram of sulfur) and making it one of the best cathode materials for energy storage devices. In addition, sulfur is a naturally abundant element and one of the cheapest energy storage materials for commercial production. However, the practical application of the Li-S battery has been hampered by serious challenges, such as poor cycle life and low practical capacity and energy [4,5].

During the discharge of a Li-S battery, sulfur is reduced by accepting electrons from the lithium anode, generating a series of reduction products in the form of lithium polysulfides. The first stage is associated with the formation of high-order lithium polysulfides with the general formula of Li_2S_x ($4 < x < 8$), which tend to dissolve in the electrolyte. In the later stages of discharge, the high-order polysulfides are further reduced to lower-order polysulfides, Li_2S_x ($2 < x < 4$). Formation of Li_2S_2 and Li_2S , which are not soluble in the electrolyte, is dominant in the last discharge stage. The loss of sulfur as a result of dissolution of the polysulfides through this reduction process is the main factor contributing to the capacity fading of the cell during extended cycling [6]. During charge, Li_2S is oxidized and converted to various lithium polysulfides with the

high-order ones suffering from the same issue of dissolution into the electrolyte. Moreover, the dissolved high-order Li_2S_x diffuses to the Li anode surface during the charge and is reduced to low-order ones and/or Li_2S , after which it diffuses back to the sulfur cathode surface and is oxidized. This continuous *diffusion-reduction-diffusion-oxidation* shuttling process leads to an extremely low coulombic efficiency [7,8] and the loss of the active material due to the deposition of the Li_2S on the lithium metal.

The high solubility, basicity and reactivity of the discharge product of lithium polysulfides dictate that the carbonate-based electrolytes used for conventional Li-ion batteries will not be compatible with the Li-S chemistry [9]. To be effective, the Li-S battery electrolyte must meet certain requirements such as chemical inertness with Li_2S_x , capability of formation of a solid-electrolyte interphase (SEI), and good electrochemical stability. The ether-type solvents, such as dimethoxy ethane (DME), have good solubility of lithium salts and good stability with Li_2S_x in the electrolyte solution and afford fast polysulfide reaction kinetics. Alternatively, cyclic solvents such as 1,3-dioxolane (DOL) can be electrochemically polymerized by a ring-opening reaction on the lithium surface, providing a certain degree of anode protection and lower polysulfide solubility compared with DME [10-12].

At present, there is no single organic solvent that satisfies the above requirements for the Li-S battery electrolyte. A practical solution is to develop an electrolyte with an optimized formula based on a mixture of solvents and additives. A combination of lithium salt and ether-type solvents, such as 1.0 M lithium bis(trifluoromethylsulfonyl)

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4 imide (LiTFSI) dissolved in DOL/DME with a volume ratio of 1:1, leads to improved
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6 electrochemical performance as compared to each solvent alone and is currently the state-
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8 of-the-art electrolyte for the Li-S battery.
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14 To further extend the cycle life and sulfur utilization of the Li-S battery, various
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16 approaches have been investigated [13]. To date, many researchers have focused their
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18 efforts on developing new sulfur materials with unique structures [14-18], yet the
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20 electrolyte plays a pivotal role in the Li-S cell performance. Although LiNO₃ is widely
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22 adopted as an electrolyte additive for Li-S batteries [12,19], recent reports of new
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24 electrolytes [20-22] and new additives [23-26] suggest that they can make a major
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26 contribution to improving the performance. Since the redox shuttle effect of polysulfide
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28 originates from its high solubility and fast diffusion in the organic electrolyte, polymer-
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30 based electrolytes with high molecular weight could be a potential candidate in
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32 restraining the dissolution of the polysulfide and its fast diffusion to the anode. It is
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34 assumed that the polymer shell acts as a physical barrier and prevents the contact of the
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36 polysulfides produced at the cathode with the liquid electrolyte [3]. The widely studied
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38 polymer electrolytes for the Li-S battery are based on high molecular weight of
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40 poly(ethylene oxide) (PEO). However, high molecular weight PEO has a relatively high
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42 glass transition temperature (T_g) and tends to crystallize at temperatures below 60°C, both
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44 of which significantly reduce the conductivity of the electrolyte [27]. This issue can be
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46 mitigated by attaching the PEO groups onto a flexible siloxane (Si-O-Si) backbone (T_g =
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48 -123°C) due to their extremely low energy barrier for Si-O bond rotation [28]. In this
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50 paper, we report the electrochemical performance of lithium-sulfur batteries that use
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tri(ethylene glycol)-substituted silane, $(\text{CH}_3)_3\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$ (1NM3), as solvent and the effect of lithium salts and additives on this new electrolyte.

2. Experimental

2.1. Materials and cell testing

The sulfur cathodes were fabricated by mixing sulfur, Super P-Li carbon black, and PVDF binder with NMP solvent to form a slurry, which was casted onto an aluminum current collector and dried at 70°C under vacuum. Tri(ethylene glycol)-substituted trimethylsilane (1NM3) and lithium difluoro(oxalato) borate (LiDFOB) were prepared in our laboratory following the literature procedures reported by Dong et al. [28] and Zhang et al. [29]. LiPF_6 , LiTFSI, and LiNO_3 were purchased from Sigma-Aldrich. Cell cycling tests and cyclic voltammetry were conducted with 2032 coin cells. The following electrolytes were tested: 1.0 M LiPF_6 in 1NM3 with and without LiDFOB additive in various concentrations (2 wt%, 5 wt%, and 10 wt%); 1.0 M LiPF_6 in 1NM3 with and without 2 wt% LiNO_3 additive, and 1.0 M LiTFSI in 1NM3 with and without 2 wt% LiDFOB additive. All cells were assembled in a glove-box filled with argon and cycled at the C/10 rate with a Maccor series 4000 cycler over a voltage range of 1.6-2.6 V at room temperature.

2.2. Electrode characterization

A cycled sulfur electrode in the discharged state was harvested inside the glove-box and was thoroughly rinsed with anhydrous DME. Its morphology was examined by a high-resolution Hitachi S-4700 scanning electron microscope (SEM) with a field emission

electron source. Electrochemical impedance spectroscopy (EIS) was carried out with a Solartron analytical 1400 cell test impedance system by applying a 10 mV voltage over a frequency range from 0.01 Hz to 1.0 MHz.

3. Results and Discussion

3.1. Electrolyte 1.0 M LiPF₆ in 1NM3

1NM3 is a colorless liquid at ambient temperature. Since 1NM3 has a strong Li⁺ chelating group in the oligo(ethylene glycol) chain, it dissolves most of the lithium salts used in a lithium-ion battery electrolyte, including LiPF₆, LiTFSI, LiBF₄, and LiBOB. The electrolyte solution of 1.0 M LiPF₆ in 1NM3 affords an ambient conductivity of 1.2 x 10⁻³ S/cm, which is comparable with the traditional DOL/DME based electrolyte. The electrochemical performance of a Li-S cell using 1.0 M LiPF₆-1NM3 electrolyte is presented in Fig. 1. As can be deduced from the voltage profiles of the 1st and 10th cycle in Fig. 1a, the first plateau at 2.4-2.3 V is the sulfur reduction reaction to high-order lithium polysulfides (Li₂S_x, where x=4-8), and further reduction of these polysulfides to lower order species (Li₂S₂ and/or Li₂S) occurs at the lower voltage plateau observed at 2.0-1.9 V. The formation of these lower-order polysulfides contributes to the major capacity of the Li-S cell. The initial discharge capacity was 1200 mAh/g, 70% of sulfur utilization based on the theoretical capacity of sulfur of 1675 mAh/g. It is very surprising that no shuttling effect of lithium polysulfide was apparent during the 1st charge, as indicated in Fig.1a, probably due to the low solubility of the Li₂S_x and the low kinetics of the Li₂S_x diffusion in this electrolyte with LiPF₆ salt. Although no redox shuttling was observed in the subsequent cycles, the cell performance faded rapidly with cycling. The

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4 discharge capacity rapidly declined to 400 mAh/g at the 50th cycle, probably due to the
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6 side reaction of LiPF₆ with Li₂S_x as evidenced by the fluctuations on the voltage profile
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8 during charge and the decreasing coulombic efficiency with cycling as shown in Fig.1b.
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11 12 13 14 3.2. Electrolyte additives

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16 Just as is the case for Li-ion battery electrolytes, functional additives play an important
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18 role in the Li-S battery. In Li-S batteries, an additive is introduced to the liquid
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20 electrolyte mainly to passivate the surface of the Li anode and protect Li from chemical
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22 and electrochemical reaction with the lithium polysulfides. The additive LiNO₃ has been
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24 widely studied and proved to assist the formation of the passivation layer on the lithium
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26 anode surface through the *in-situ* reduction of LiNO₃, thus preventing the continuous
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28 reaction between Li and the lithium polysulfides [12,30].
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36 Zhang et al. [29] first reported LiDFOB as an effective electrolyte salt for lithium-ion
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38 batteries. Later, Hu et al. [31] found that LiDFOB participates in the formation of an SEI
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40 layer on graphite anodes and greatly improves the cycling performance and the thermal
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42 stability of the Li-ion battery. Very recently, Wu et al. reported that LiDFOB [32]
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44 functioned as an efficient additive to improve the capacity retention of the Li-S battery
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46 when added to the DOL/DME electrolyte due to the formation of the LiF-rich passivation
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48 layer on the lithium anode surface. In fact, we have been evaluating LiDFOB as a
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50 potential additive for Li-S battery independently at the same time Wu did his study.
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52 However, our initiative idea is quite different from Wu's as we conceived of using
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54 LiDFOB as an electrolyte additive due to its positive effect on both the anode and the
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sulfur cathode. LiDFOB can form a protective layer on the surface of lithium anode chemically and electrochemically. This layer serves as a physical barrier to shut down the parasitic reactions of the polysulfides with lithium. However, the major effect of LiDFOB on the sulfur cathode has not been considered in the previous publications. Due to the fact that fluorinated ether solvent is capable of forming a solid-electrolyte-interface (SEI) on the sulfur cathode,[21] the same effect of this additive was also observed for LiDFOB. The two fluorine-boron bonds in the structure of LiDFOB might provide the same functionality as the fluorinated ether does on the sulfur cathode side.

The experimental data validated our initial idea. When 2 wt% LiDFOB was added to the 1.0M LiPF₆-1NM3 electrolyte, the Li-S cell performance improved significantly. The charge-discharge voltage profile of this Li-S cell is shown in Figure 2. Apparently, the performance of the additive cell (Fig. 2a) is improved compared with that of the cell without additive (Fig.1a) in terms of the specific capacity and the stability of the charging. The additive cell showed a coulombic efficiency of 76% for the initial cycle with minor shuttling, and it increased rapidly in couple of cycles and stabilized at 97% (Fig.2b) without shuttling. It is clear that the SEI formation of low concentration LiDFOB is a gradual process. By increasing the concentration of LiDFOB additive from 2 wt% to 5 wt%, the initial coulombic efficiency increased from 76% to 100% (Fig. 2c). LiDFOB participates in the reduction reaction during the discharge, as evidenced by the presence of the short plateau on the discharge voltage profiles. This plateau is buried by the polysulfide reduction peak in the first cycle and showed up clearly in the voltage profiles (red arrow in Fig.2a) from the subsequent cycles indicating a gradual reduction

of the LiDFOB additive, which forms a protective layer over the cathode surface and thus improves the coulombic efficiency. However, when the concentration of LiDFOB additive is increased from 2 wt% to 5 wt% and 10 wt%, as illustrated in Fig. 2c and Fig. 2d, respectively, the capacity dropped dramatically. The fast fading in capacity was attributed to the formation of a thick and resistive decomposition layer on the electrode surface resulting in high interphasial impedance.

Although the coulombic efficiency of the additive cells is greatly improved, the capacity generally fades with cycling which showed the similar result as the LiNO_3 additive. However, it is noteworthy that in our study, 1NM3 is used as a solo-solvent with higher chelating ability with Li cation than the conventional solvent DOL and DME leading to high dissolution of lithium polysulfides. Furthermore, LiPF_6 is not a compatible lithium salt for Li-S battery due to its chemical reactivity with polysulfide anions. Without LiDFOB additive, 1NM3/ LiPF_6 electrolyte showed severe redox shuttling and enormous capacity fade. Considering these facts, the capacity retention of 1NM3/ LiPF_6 /LiDFOB cell is not at its best; however, the impact of the LiDFOB additive is significant.

To confirm the electrochemical reduction reaction of LiDFOB on the surface of the cathode, dQ/dV profiles for the 1st, 10th, 30th and 50th cycle are presented in Figs. 3a-3d. In addition to the two peaks which are observed for Li-S batteries due to the reduction of the polysulfides at 2.4 V and 2.1 V, there is a 3rd peak observed at 1.95 V when LiDFOB was added as an additive. The intensity of this peak gradually decreased and eventually disappeared after 50 cycles. This discovery is in good agreement with our previous

findings for the fluorinated electrolyte [21]. The formation of this artificial SEI associated with the reductive decomposition of the LiDFOB on the surface of the sulfur/carbon particles acts as barrier to prevent the side reaction with the polysulfide and mitigate the dissolution of the polysulfide into the electrolyte. Our test results indicate that LiDFOB not only provides protection on Li metal anode [32], but also on the sulfur cathode.

LiTFSI is considered as the most suitable lithium salt for the Li-S battery due to its greater thermal and hydrolytic stability compared with LiPF_6 . The electrochemical performance of 1NM3 electrolyte with LiTFSI salt is quite different from the LiPF_6 salt. Fig.4 showed the voltage profiles for Li-S cells containing 1.0 M LiTFSI-1NM3 with and without 2 wt% LiDFOB additive. The initial discharge capacity was 1300 mAh/g for both cells; however, the cell without the LiDFOB additive suffered from a severe redox shuttle reaction during the 1st charge, as evidenced by the flat and long plateau on the charge profile (Fig. 4a), resulting in a low coulombic efficiency (45.5%). Even lower efficiency was observed for subsequent cycles. However, with 2 wt% LiDFOB electrolyte additive, the coulombic efficiency significantly increased in the first cycle and stabilized in the following cycles, as clearly evidenced by the data shown in Fig. 4b.

While LiDFOB additive proved to be effective, we also explored the effect of LiNO_3 additive when combined with 1NM3 electrolyte. Fig. 5 shows the cell data for 2 wt% LiNO_3 added to the 1.0M LiPF_6 -1NM3 electrolyte. As shown in Fig. 5a, the coulombic efficiency was about 100% for all cycles with the LiNO_3 additive cell; however, the

capacity decline of this cell is almost identical to the cell without LiNO₃ additive, as illustrated in Fig. 5b.

3.3. Electrode morphology

To understand the LiDFOB additive effect in the Li-S battery, we examined the morphology of the discharged sulfur cathode by SEM. Fig. 6a is an SEM image of the sulfur electrode after the first discharge in 1.0 M LiPF₆-1NM3 electrolyte. The surface of this electrode was covered by large quantities of crystal-like discharged products of insoluble lithium polysulfide (Li₂S₂ and Li₂S) species [21, 33]. The formation of these low-order polysulfides has a major effect in causing the capacity loss during long-term cycling. In contrast, the sulfur electrode showed a different morphology when cycled in 1.0 M LiPF₆-1NM3 electrolyte with 2 wt% LiDFOB additive, as illustrated in Fig.6b. The particle size in the discharge products on the electrode surface was much smaller and uniformly distributed on the surface of the electrode. This morphology of the cathode maintained even at the 10th cycle, as shown in Fig.6d. This observation is consistent with the electrochemical cell data presented in Figs. 1, 2a, and 2b.

3.4. EIS characterization

The effect of the LiDFOB additive was investigated by electrochemical impedance spectroscopy (EIS). Fig. 7a showed the EIS spectra for cells at the 1st discharge stage using 1.0 M LiPF₆-1NM3 and 1.0 M LiPF₆-1NM3+2 wt% LiDFOB electrolyte. The frequency-dependent impedance signifies the response of several parallel processes occurring in the cell. The Nyquist plots consist of two semicircles and a straight sloping

line in the low frequency region. The semicircle in the high frequency region corresponds to the ionic conduction at the interphase of the sulfur/electrolyte (R_{int}), and the semicircle in the medium frequency region corresponds to the charge-transfer process (R_{ct}) occurring on the conductive agent of the sulfur electrode [34]. As summarized in Fig. 7b, the charge transfer resistance for the cell containing 1.0 M LiPF_6 -1NM3+2 wt% LiDFOB ($R_{\text{ct}} = 254.7 \text{ ohm}$) was significantly higher than that of the cell without LiDFOB ($R_{\text{ct}} = 52.1 \text{ ohm}$) at the fully discharged state. The much higher R_{ct} for the additive cell is caused by the more discharged products (deep discharge) and the insulating property of the discharge products [35]. The interphasial resistance (R_{int}) was higher for the additive cell than that of the no additive cell, which was attributed to resistive SEI layer formed on the cathode surface during the discharge process, verifying that the LiDFOB participated in the reductive decomposition reaction as observed by the short plateau in the discharge voltage profile and the dQ/dV profiles. Interestingly, the cell with 2 wt% LiDFOB showed lower cell resistance ($R_e = 12.4 \text{ ohm}$), indicating that the SEI mitigated the dissolution of the lithium polysulfides, leading to lower viscosity and higher conductivity of the electrolyte.

4. Conclusions

We evaluated the new electrolyte solvent 1NM3 and the effects of the lithium salts and additives for Li-S cell. In this work, coin cell data and EIS data showed the LiDFOB to be an efficient additive in passivating the sulfur cathode surface and enabling reversible sulfur reduction and oxidation in the Li-S chemistry. By contrast, 1NM3 solvent with LiNO_3 additive in the electrolyte showed little improvement over the 1NM3 with no

additive. The SEM analysis of a discharged sulfur cathode from a cell tested with the 1NM3 electrolyte confirmed that the LiDFOB additive is critical in improving the performance of the Li-S cell.

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