



## Short communication

Improved cycling performances of lithium sulfur batteries with  $\text{LiNO}_3$ -modified electrolyte

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## ABSTRACT

$\text{LiNO}_3$  is selected as the additive to modify the electrolyte for lithium sulfur battery. The cycling efficiency (EFF) shows that  $\text{LiNO}_3$  additive is favorable for the lithium deposition and dissolution on the Cu foil. SEM and XPS are applied to analyze the surface changes of the lithium cycled in the electrolytes. The  $\text{LiNO}_3$  additive is conducive for the construction of protective film on the surface of the lithium anode. Lithium sulfur batteries are also cycled with the 0.4 M  $\text{LiNO}_3$  modified electrolyte. The lithium sulfur battery tested shows improved cycling performance with the coulombic efficiency above 95% and highly stable reversible discharge capacity of ca. 527  $\text{mAh g}^{-1}$  after 50 cycles.

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## 1. Introduction

The rapid demanding of power sources for portable devices and electric vehicles calls for the advanced batteries with high specific energy. Lithium–sulfur redox couple is one of the most promising candidates for the high theoretical capacity of sulfur and lithium, which corresponds to 1675 [1] and 3680  $\text{mAh g}^{-1}$  [2], respectively. In addition, the lithium–sulfur battery can be cost-effective due to the low cost and abundance of sulfur [3,4]. In spite of these advantages of lithium–sulfur batteries, there are still many problems to be overcome for practical applications. Because of the insulating nature of sulfur and the corrosion of the lithium anode by the soluble polysulfides generated during the charge–discharge process, the utilization of the sulfur is very low and the battery experienced a serious capacity fading during long cycling [5–7]. Many researchers have been endeavored to dissolve the conductivity of the sulfur electrode by incorporating the conducting agent of MWCNT [8], conductive polymer [9–11] and mesoporous carbon [12,13]. B. Zhang induced the high specific surface area material (acetylene black) as the conducting agent to slow down the dissolution of the polysulfides [14]. However, the application of Li electrode is still difficult due to its low cycling efficiency, deleterious dendritic morphology of deposited Li and safety concerns [15]. These problems are resulted from the reaction of freshly deposited Li with the electrolyte components such as solvents and contami-

nants [16,17]. For these reasons, many efforts have been made to improve the performance of Li electrodes by surface modifications. Li-ion conductor  $\text{Li}_3\text{N}$  [18] and LiPON [19] have been coated on the surface of the lithium foil. Lee [20] introduced a protective film on the surface of the Li by UV cured polymerization for the lithium sulfur battery. This film was acted as a guarantee to protect the lithium from the corrosion by the soluble polysulfides. However, the fabrication procedure is complicated and costly. It was reported that components with N–O bond, especially  $\text{LiNO}_3$  in the electrolyte is favorable to form an in situ protective surface film on the lithium foil [21,22]. This convenient method had brought in high charge efficiency of the lithium sulfur battery.

In this study,  $\text{LiNO}_3$  was added in the electrolyte as the additive. In order to evaluate the long time cycling performance of the lithium sulfur battery in the  $\text{LiNO}_3$  modified electrolyte, the sulfur cathode adopted with a high specific surface area conducting agent of acetylene black was used. The effects of the  $\text{LiNO}_3$  additive on the coulombic efficiency of the lithium deposition were discussed on the basis of AC impedance and lithium dissolution and deposition experiment. The composition of the protective film on the lithium was analyzed by X-ray photoelectron spectroscopy (XPS). An improved cycling performance of the lithium sulfur battery was obtained in the modified electrolyte.

## 2. Experimental

The sulfur composite was prepared by co-heating the sulfur and acetylene black at 155 °C for 4 h. The sulfur composite with 52 wt.% S was mixed with acetylene black and PVDF (polyvinylidene fluoride), using NMP (N-methyl-2-pyrrolidone) as the dispersant. The

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weight ratio of sulfur composite, acetylene and PVDF in the mixture is 70:10:20. The slurries were cast onto aluminum foil substrates. After the organic solvent was evaporated, the electrode film was cut to sheets with 14 mm in diameter and then dried at 50 °C under vacuum for 12 h.

The basic electrolyte is 0.5 M LiCF<sub>3</sub>SO<sub>3</sub> dissolved in DOL (1,3-dioxolane)/TEGDME (tetraethylene glycol dimethyl ether) (5/5, vol/vol). The modified electrolytes are prepared by adding *x* M LiNO<sub>3</sub> into the basic electrolyte, where *x* = 0.1, 0.2, 0.3, 0.4 and 0.5 M. The lithium deposition and dissolution measurements were performed with sealed CR2025 coin cells in which copper foils with the same size of the Li foils were used as working electrode, Celgard 2400 as the separators and Li foils as the counter and reference electrodes. Before the tests, the copper foil was polished, washed with distilled water and acetone, and finally dried for 6 h under vacuum at room temperature. Lithium sulfur cells were assembled by the same way except with sulfur electrode as the working electrode.

AC impedance of the cell was measured by a Frequency Response Analyzer (FRA) technique on a Autolab Electrochemical Workstation over the frequency rang from 1 MHz to 10 mHz with the amplitude of 10 mV. The galvanostatic charge and discharge tests were conducted on a LAND CT2001A battery test system in a voltage range of 1.0–3.0 V (vs. Li/Li<sup>+</sup>) at a current density of 0.1 mA cm<sup>-2</sup>. The cut-off potential was controlled at 1 V (vs. Li/Li<sup>+</sup>) for the Li dissolution.

After the electrochemical tests, the cells were disassembled in an argon-filled glove-box. The Li electrodes or sulfur electrodes were washed with polycarbonate (PC) and further dried in an argon-filled glove-box for 12 h. Then they were enclosed in a sealed vessel which was filled with Ar gas for further testing. Morphology changes of the lithium were observed on a scanning electron microscope (SEM, HITACHI S-3400). XPS (Thermo scientific ESCALAB 250) was used to examine the elements at the surface of the lithium with different electrolytes. X-ray diffraction (XRD, Rigaku RINT-2000) with Cu K $\alpha$  radiation was applied to identify the composition of the lithium anode after cycling. The lithium sample was enclosed inside a polyimide bag to prevent undesirable reactions with air during XRD testing. In EDS (XEDS) investigation, at least three measurements were conducted for each sample to calculate the average composition.

### 3. Results and discussion

#### 3.1. Lithium deposition and dissolution on Cu foil

The cycling efficiency (EFF) of lithium deposition and dissolution in different concentration of LiNO<sub>3</sub> modified electrolytes are presented in Fig. 1. EFF is calculated with the following:

$$\text{EFF} = \left[ \frac{Q_{\text{dissolution}}}{Q_{\text{deposition}}} \right] \times 100\%$$

where  $Q_{\text{deposition}}$  is the charge quantity of the deposited Li,  $Q_{\text{dissolution}}$  is the dissolution quantity of the deposited Li. As seen, almost all the first cycling efficiencies are very low, probably due to the surface oxides on the Cu substrate, which may produce a Li<sub>2</sub>O layer before Li deposition [23]. An obvious function of the LiNO<sub>3</sub> addition on the EFF is observed, the EFF increased with the increased concentration of the LiNO<sub>3</sub> in the electrolyte, and it reaches the highest value of above 90% for the electrolyte contains 0.4 M LiNO<sub>3</sub>.

Fig. 2 shows the morphologies of the lithium foils before and after cycled for 20th cycles in the basic electrolyte and the 0.4 M LiNO<sub>3</sub>-modified electrolyte. It is observed that the lithium cycled in LiNO<sub>3</sub>-modified electrolyte is quite smooth and dense, a passive film was coated on the surface of the lithium foil. On the contrary,

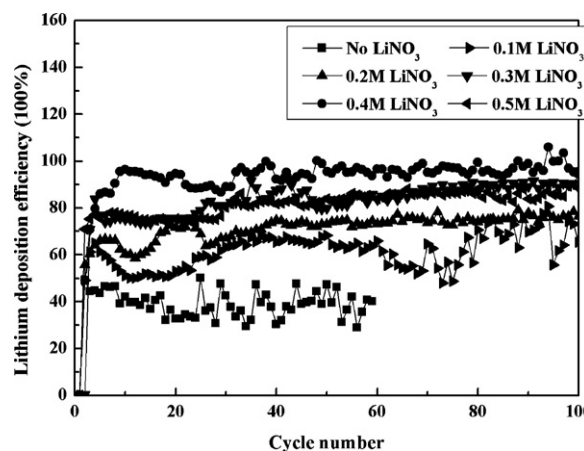


Fig. 1. Cycling efficiency (EFF) of the lithium deposition and dissolution on the Cu foil in different electrolytes.

lithium cycled with the basic electrolyte was loose with most of Li deposits in rod shape.

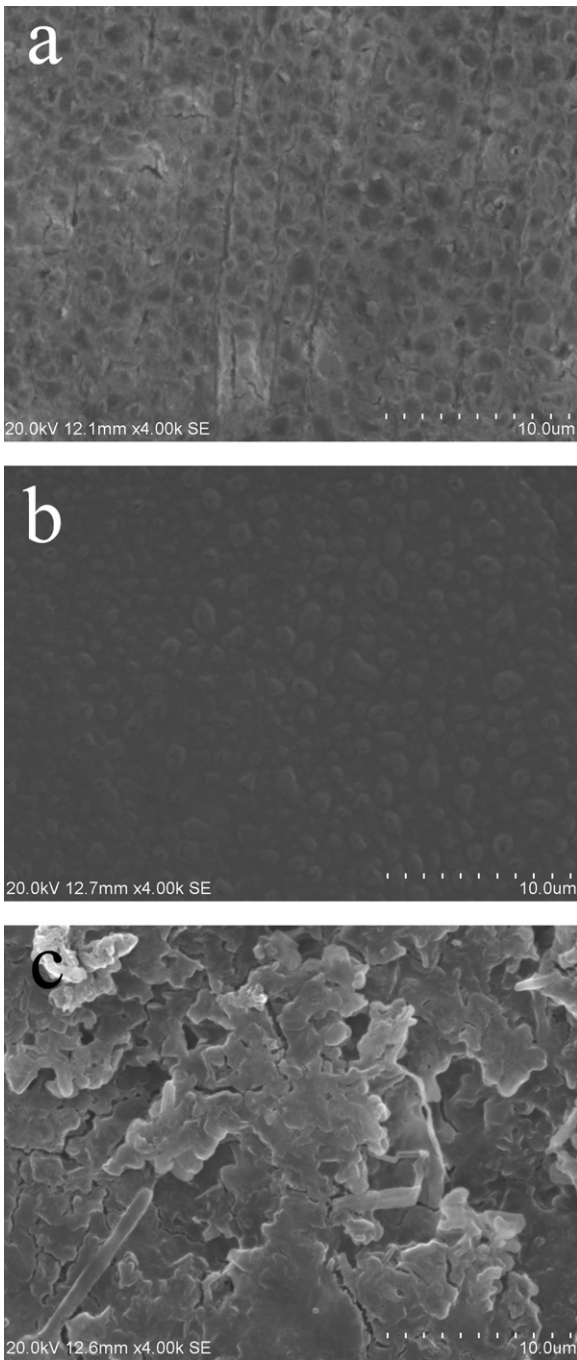
XPS was applied to identify the elements on the surface of the lithium after cycling for 20 cycles, as shown in Fig. 3. There are traces of O and C elements on the surface of the lithium cycled in the basic electrolyte, indicating the formation of LiOH and LiCO<sub>3</sub>, by the reaction of lithium and the electrolyte. Compared with the basic electrolyte, N element was detected on the lithium surface cycled in the 0.4 M LiNO<sub>3</sub> modified electrolyte. Aurbach's ever reported the formation of an inorganic film with element Li, C, N, O, etc. on the surface of lithium in the electrolyte containing LiNO<sub>3</sub> additive [22].

EIS measurements were carried out to compare the impedance differences of the lithium anode in these two electrolytes. Normally, the high frequency semicircle relates to Li-ion migration through the SEI films, and the low frequency semicircle relates to charge transfer (probably across the passive film) [24]. As shown in Fig. 4, the impedance plots of the lithium anode in the two electrolytes have very little differences before cycling. A sloping line in the high frequency range suggests a very low charge transfer resistance  $R_{ct}$ . It is indicated that the function of LiNO<sub>3</sub> additive is not active before cycling. After cycling, the SEI surface was built in both the electrolytes. The  $R_{ct}$  of the lithium in the basic electrolyte is higher than that in the LiNO<sub>3</sub> modified electrolyte. Besides, there is another half-circle in the EIS spectrum at the low frequency region for the LiNO<sub>3</sub> modified electrolyte. This may originate from the passive film covered on the surface of the lithium. According to Lee's report [19], the passive film acted as a barrier to protect the lithium from further corrosion in the electrolyte. As a result, the SEI film is depressed in the modified electrolyte, and the  $R_{ct}$  decreased.

#### 3.2. Lithium sulfur cells with the LiNO<sub>3</sub> modified electrolyte

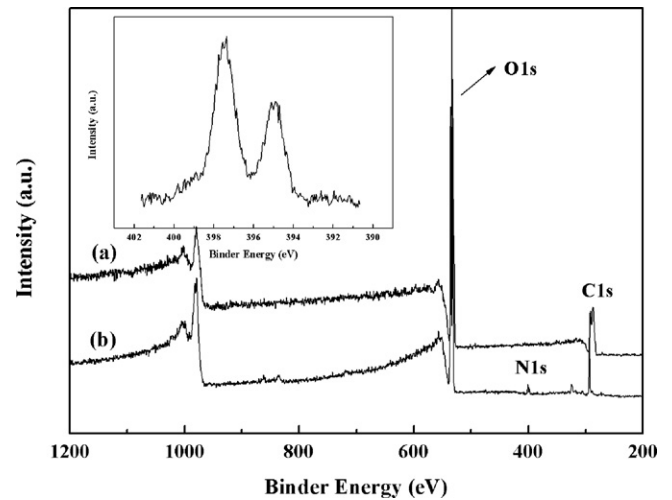
Sulfur electrodes were tested in the electrolyte with 0.4 M LiNO<sub>3</sub>, and also in the basic electrolyte for comparison.

To identify whether the LiNO<sub>3</sub> additive has the effect on suppressing the dissolution of polysulfides into the electrolytes, the relative concentrations of sulfur in the cathode after cycling were measured by EDS, the results were shown in Fig. 5. As seen, the sulfur content in the cathode decreased dramatically before the 20th cycles, then it maintains at about 17 wt.%. The difference between the LiNO<sub>3</sub> modified electrolyte and the basic electrolyte is ignorable. As a result, the LiNO<sub>3</sub> additive has no effect on suppressing the dissolution of polysulfides into the electrolyte.



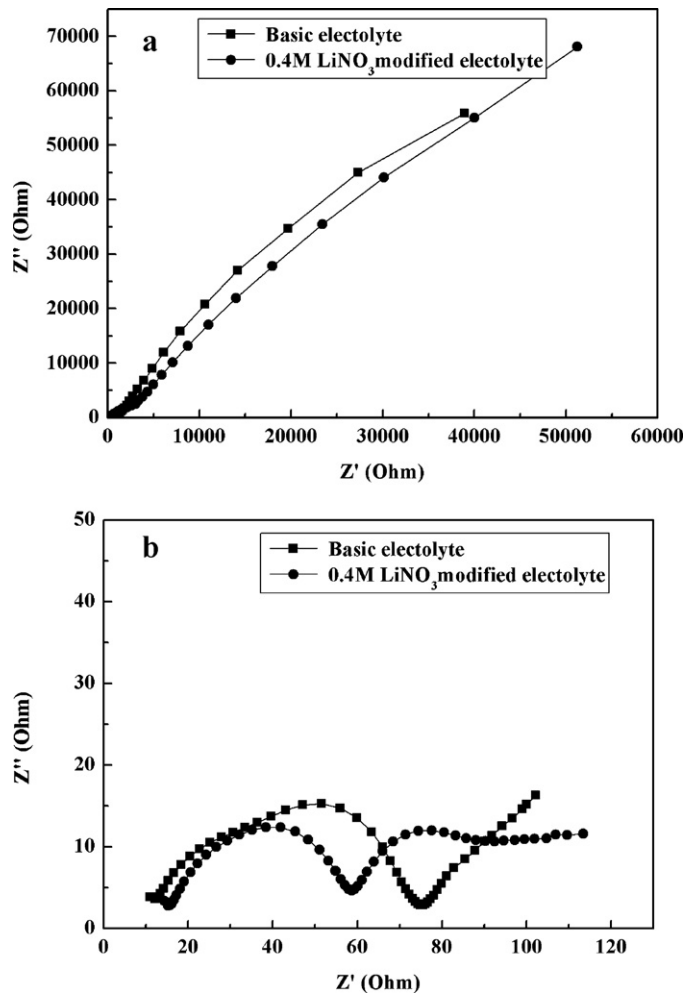
**Fig. 2.** SEM morphology of the fresh lithium (a), lithium after cycled in the 0.4 M LiNO<sub>3</sub> modified electrolyte (b), and in the basic electrolyte for 20 cycles (c).

After the lithium sulfur cells were cycled in these two different electrolytes for 20 cycles, XRD patterns of the lithium anodes were measured. As indicated in Fig. 6(a), the polyimide film displayed no any sharp diffraction peaks besides a broad band at the lower diffraction angle. Fig. 6(b) shows the XRD pattern of the fresh Li foil, indicating three crystal peaks indexed to the Li metal. Li<sub>2</sub>S phase was observed from the lithium anode cycled in the basic electrolyte, as shown in Fig. 6(d). As known, the electrolyte contained soluble polysulfides after cycling [7]. The lithium is so reactive that it corroded by the polysulfides immediately to form Li<sub>2</sub>S on its surface. However, as shown in Fig. 6(c), no any Li<sub>2</sub>S corrosion products were found on the Li anode after 20 cycles, owing to the protective



**Fig. 3.** XPS spectrum of the lithium surface after cycled in the 0.4 M LiNO<sub>3</sub> modified electrolyte and the basic electrolyte for 20 cycles, the insertion is the spectrum of N 1s.

film formed on the lithium anode in the LiNO<sub>3</sub> modified electrolyte, which means that the polysulfides in the electrolyte were prevented to contact with the lithium directly by the protective film successfully.



**Fig. 4.** EIS spectra of the Li|electrolyte|Cu cell with the 0.4 M LiNO<sub>3</sub> modified electrolyte and the basic electrolyte before cycling (a), and after 20 cycles (b).

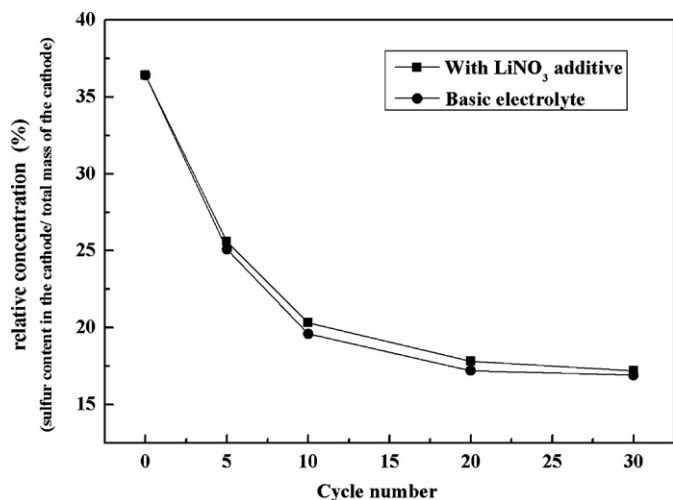


Fig. 5. Relative contents (by EDS) of the sulfur in the cathode.

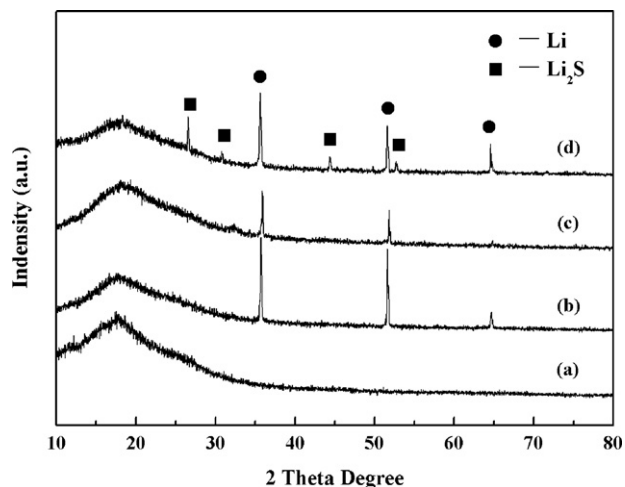


Fig. 6. XRD patterns of (a) polyimide film; (b) fresh Li; (c) Li anode cycled with the  $\text{LiNO}_3$  modified electrolyte; (d) Li anode cycled with the basic electrolyte.

Fig. 7 shows the CV curves of the sulfur electrodes in the two electrolytes. Two cathodic peaks of sulfur cathode in both the electrolyte are observed at about 2.4 V and 2.0 V, respectively. They are corresponding to the two steps of the reaction of sulfur and lithium.

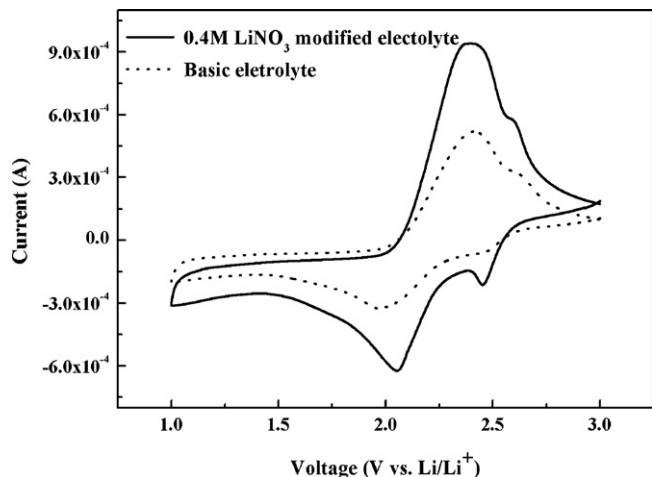


Fig. 7. CV curves of the lithium sulfur batteries with the 0.4M  $\text{LiNO}_3$  modified electrolyte and the basic electrolyte.

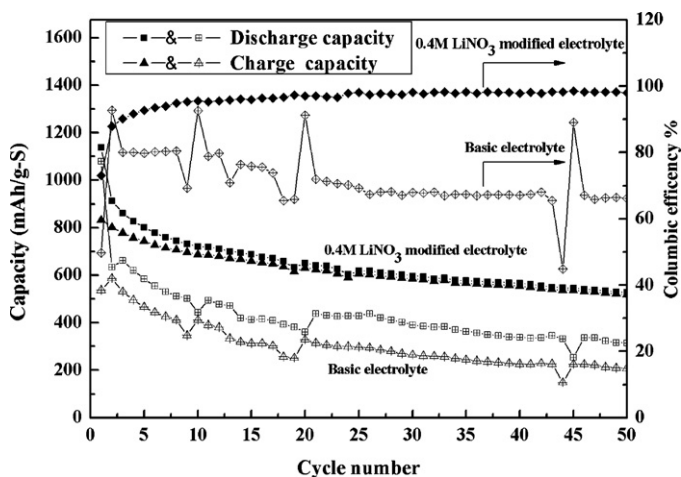


Fig. 8. Cycling performances of the lithium sulfur batteries cycled with the 0.4M  $\text{LiNO}_3$  modified electrolyte and the basic electrolyte,  $0.1 \text{ mA cm}^{-2}$ .

The 2.4 V plateau is caused by the change from element sulfur to higher-order lithium polysulfides ( $\text{Li}_2\text{S}_n$ ,  $n \geq 4$ ), which are soluble in the liquid electrolyte. The 2.0 V plateau is related to the reduction of higher-order polysulfides to lower-order polysulfides ( $n < 4$ ) [1]. No obvious difference between the CV curves except for the current density of the redox reaction is found, implying that the  $\text{LiNO}_3$  additive has no effect on the redox mechanism of lithium sulfur battery. On the other hand, the increased peak current could be attributed to the smoother passive film of the lithium anode.

The cycling performances of the sulfur electrodes were tested in both the electrolytes. Fig. 8 shows the capacities and coulombic efficiencies of the sulfur cathodes. The initial discharge capacities of sulfur cathodes in the 0.4M  $\text{LiNO}_3$  modified electrolyte and the basic electrolyte are about ca.  $1138.2 \text{ mAh g}^{-1}$  and ca.  $1079.6 \text{ mAh g}^{-1}$ , respectively. However, the initial charge capacities of these two electrolytes show the large difference, i.e., ca.  $832 \text{ mAh g}^{-1}$  for the modified electrolyte vs. ca.  $537 \text{ mAh g}^{-1}$  for basic electrolyte, respectively. After 50 cycles,  $527 \text{ mAh g}^{-1}$  reversible discharge capacity was maintained for the modified electrolyte. It is important to notice that the coulombic efficiency of the lithium sulfur cell with the modified electrolyte is kept above 95% after 10th cycle and exhibits very stable cycling performance than that of the basic electrolyte. The advantage of the modified electrolyte may originate from the protective film on the lithium anode. This film is favorable for the transportation of lithium ion, and acts as an obstacle to protect the lithium from the corrosion of the polysulfides.

#### 4. Conclusions

The modified electrolyte is prepared by adding the proper amount of  $\text{LiNO}_3$  into 0.5 M  $\text{LiCF}_3\text{SO}_3$ -DOL/TEGDME. Owing to the protective film generated on the lithium anode in the modified electrolyte, the increased lithium cycling efficiency was obtained in the lithium deposition and dissolution experiment. Polysulfides in the electrolyte were prevented to contact with the lithium directly by the protective film successfully. Lithium sulfur battery with the modified electrolyte shows improved cycling stability with the coulombic efficiency above 95% and highly stable reversible discharge capacity of ca.  $527 \text{ mAh g}^{-1}$  after 50 cycles, respectively.

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