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ORIGINAL PAPER

The electrochemical performance of lithium–sulfur batteries with $LiClO_4$ DOL/DME electrolyte

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Abstract The electrochemical performance of lithium–sulfur batteries with $LiClO_4$ DOL/DME as electrolyte was investigated. Impedance and SEM analysis indicated that too high content of DME(Dimethoxy ethane) in electrolyte could raise the interfacial resistance of battery due to the impermeable layer formed on the surface of the sulfur cathode, which led to bad cycle performance, while the increase of DOL(1,3-dioxolane) could change those phenomena. The optimal composition of electrolyte was DME:DOL = 2:1 (v/v). With this electrolyte, the lithium–sulfur battery obtained a high initial discharge capacity of 1,200 mA h g^{-1} and still remained 800 mA h g^{-1} after 20 cycles.

Keywords Lithium–sulfur batteries · Electrolyte · Dimethoxy ethane · 1,3-dioxolane

1 Introduction

Lithium–sulfur batteries, which are composed of composite positive electrode (cathode), a polymer or liquid electrolyte, and a lithium negative electrode (anode), are expected to exhibit a high theoretical energy density of 2,600 W h g^{-1} based on the lithium/(elemental) sulfur redox couple. Moreover, utilization of sulfur as a cathode material is advantageous because of its abundance, low cost, and environmental friendliness. Therefore, the lithium/sulfur battery shows great potential for the next generation of lithium batteries [1–3].

Among the components in lithium–sulfur batteries, electrolyte plays an important role in improving not only the initial capacity but also the cycle stability. The requirements for the electrolyte of lithium–sulfur battery are high ionic conductivity, moderate polysulfide solubility, low viscosity, electrochemical stability, chemical stability against lithium, and safety [4]. It is reported that ether type solvents have good solubility of elemental sulfur and good stability of polysulfide in electrolyte solution. It is also known that cyclic solvents are superior for stabilizing the surface of Li metal by forming a protective layer through the ring-opening reaction [5, 6]. In this case, it is a good idea to use a mixture solvent containing ether type solvent and cyclic solvent for improving the electrochemical performance of lithium–sulfur battery.

In the past time, many cyclic or linear type ether electrolyte have been studied. However, the effects of solvent composition on the discharge properties are not fully investigated. In our previous work [7, 8], the natural macromolecule gelatin was used as a binder with multi-functional effects in lithium–sulfur battery. However, the matched electrolyte needs advanced research. DME, a polar solvent with high solubility to polysulfide, could provide a good surrounding for the redox reaction during charge-discharge process of lithium–sulfur battery [9, 10]. But too high content of DME would cause high viscosity of electrolyte due to polysulfide dissolving into the electrolyte, further prevent the Li ions from penetrating into inside of the cathode. Hence, the redox reaction were greatly

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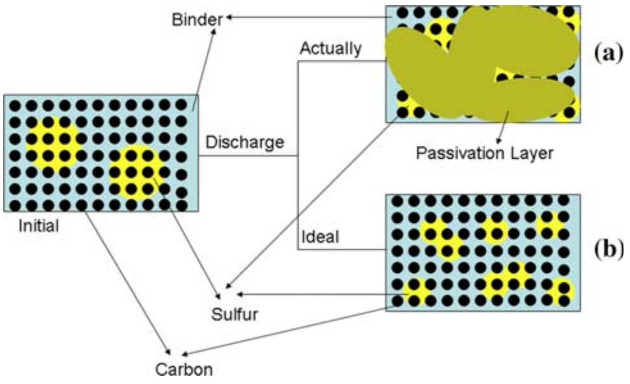

Fig. 1 The surface image changes model of sulfur cathode after discharge

localized on the surface of the cathode and compact passivation layer were formed (Fig. 1a), which decreased the cycle performance of batteries. Addition of DOL could change this instance to a certain extent. The ideal electrolyte chosen for lithium–sulfur battery should have the suitable solubility of polysulfide, which could provide good environment for redox reaction and abundant channel for Li ions penetration into inside of the cathode (Fig. 1b). In our research, the lithium–sulfur battery with DME/DOL = 1:1 (v/v) exhibited good cycle performance, however the optimal composition of electrolyte for gelatin–sulfur cathode was still unclear. In this article, we altered the content of DOL in DME and investigated its effects on lithium–sulfur battery by using electrochemical impedance spectroscopy and SEM analysis.

2 Experimental

2.1 Preparation and analysis of the cathode

Elemental sulfur (99.5%, analytically grade, Beijing, China) and acetylene black (AB, Jinpu. Corp., China) were dried at 60 and 120 °C for 5 h under vacuum before use, respectively. Gelatin (180Bloomg, type B, derived from bovine bones) was used as a binder for sulfur cathode. The proportion of elemental sulfur, acetylene black, and binder were 63:30:7 (weight ratio). The gelatin binder used water as the solvent. The cathode slurry was prepared by ball milling and then coated onto an Al foil by using a doctor blade.

This cathode was dried under vacuum at 60 °C for 10 h, then cut into a square with an area of 1 cm^2 (1 cm × 1 cm) to assemble the CR2025 coin-type battery in a Ar-filled glove box for electrochemical tests, with lithium foils as anode and 1 M $\mathrm{LiClO_4}$ DME/DOL (received from Beijing Chemical Reagent Research Institute) as electrolyte.

2.2 Measurements

The discharge and charge performance of the battery were measured galvanostatically at the current density of 0.4/1 mA cm^{-2} between 1.5 and 2.8 V by the cell test instrument (LAND Electronic Co. CT2001A) at room temperature. Electrochemical impedance spectroscopy (EIS) was measured at OCV (open-circuit voltage) by using electrochemical work station (Solartron 1280Z). The morphology changes of sulfur cathodes were examined using Scanning Electron Microscopy (SEM, HITACHI S-4700).

3 Results and discussion

Figure 2 showed the result for cycle performance of lithium–sulfur battery with different solvent composition. The battery with the electrolyte of DME:DOL = 2:1 (v/v) exhibited the highest initial discharge capacity of 1,200 mA h g^{-1} and the best cycle performance compared with other electrolyte composition samples in this research. Moreover, the fading rate of the battery with the electrolyte of DME:DOL = 2:1 was the lowest. The discharge capacity of the cathode still remained at 750 mA h g^{-1} after 20 cycles, almost 67% of the initial capacity. After the 20th cycle, the discharge capacities of the test batteries with different electrolyte composition followed this order: DME:DOL = 2:1 (750 mA h g^{-1}) >DME:DOL = 1:1 (532 mA h g^{-1}) >DME:DOL = 1:2 (505 mA h g^{-1}) >DME:DOL = 4:1 (326 mA h g^{-1}) >DME:DOL = 1:4 (273 mA h g^{-1}). This result showed that too high content of DME or DOL was not suitable for good cycle performance.

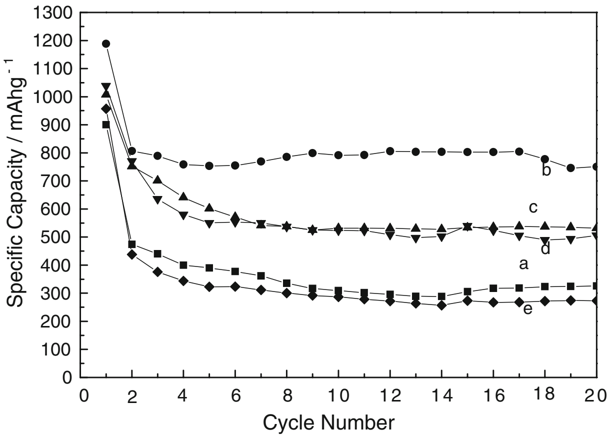

Fig. 2 Cycle performance of lithium–sulfur battery with different electrolyte composition [DME:DOL = (a) 4:1, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 1:4 (v/v)]

In order to have a better understanding to the effect of electrolyte composition on the electrochemical performance, the impedance properties of lithium–sulfur batteries were studied. Figure 3 showed the impedance plots of lithium–sulfur batteries before discharge (a) and after the 20th discharge (b). From Fig. 3a, it could be seen the part overlapping of two compressed semicircles at high frequencies and medium frequencies. Two obvious semicircles were also shown in Fig. 3b of DME:DOL = 4:1, despite the one at high frequency was not complete. The corresponding equivalent electrical circuit was given in Fig. 3c. The R_b is bulk resistance of the cell, which reflects electric conductivity of the electrolyte, separator, and electrodes; R_s and C_s are resistance and capacitance of the solid-state interface layer formed on the surface of the electrodes, which correspond to the semicircle at high frequencies; R_{ct} and C_{dl} are faradic charge-transfer resistance and its relative double-layer capacitance, which correspond to the semicircle at medium frequencies; W is the Warburg impedance related to a combination of the diffusional effects of lithium ion on the interface between the active material particles and electrolyte, which is generally indicated by a straight sloping line at low frequency end.

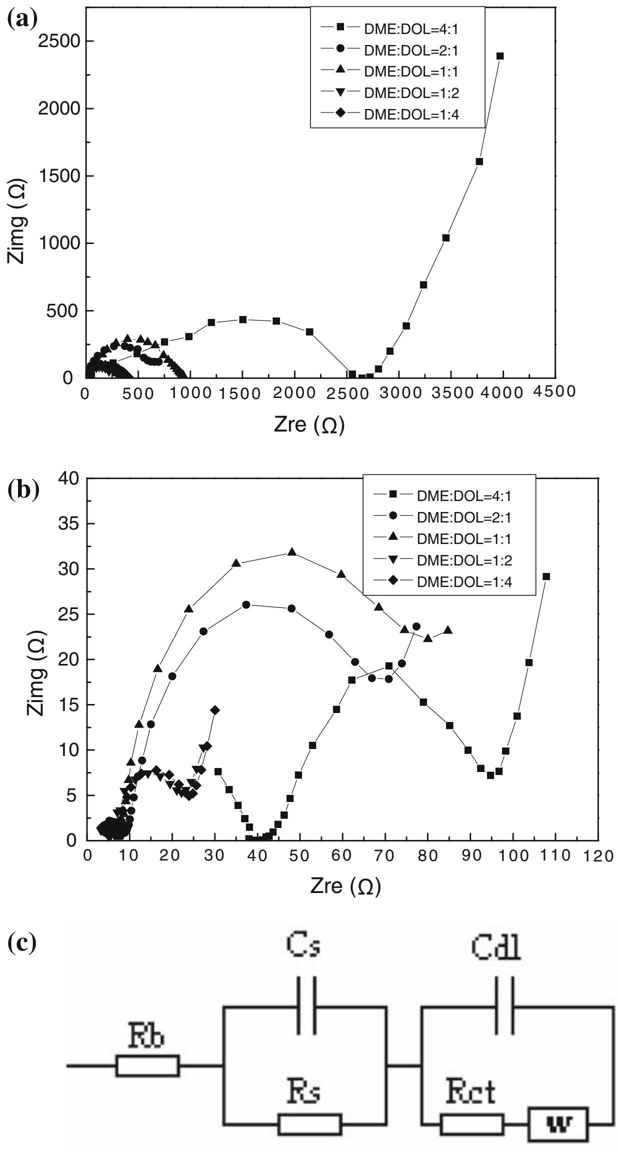

Fig. 3 The impedance plots of lithium–sulfur battery with different electrolyte composition: **a** initial and **b** after the 20th discharge, frequency range: 100 kHz–100 mHz, **c** the equivalent electrical circuit of **a** and **b**

In this case, it was presumed that the solid-state interface formed between electrodes and electrolyte was coming from the self-discharge process before discharge (Fig. 3a). Too high content of DME in electrolyte (DME:DOL = 4:1) would intensify the self-discharge process by dissolving the sulfur and polysulfide, causing the great increase of R_s and R_{ct} in Fig. 3a. After the 20th discharge, because of the disappearing of solid-state interface, the battery presented low R_s as shown in Fig. 3b except in the electrolyte with the composition of DME: DOL = 4:1. Maybe this is because the surface of the cathode was passivated by an impermeable layer over a large area compared to other composition electrolytes. The passivation layer was formed for the following reason: the better solubility of polysulfide in high content of DME electrolyte caused a high viscosity of electrolyte, which restricted the Li ions penetrating into inside of the cathode, hence the redox reactions were greatly localized on the surface of the cathode. Addition of DOL could improve the interfacial property between the electrodes and electrolyte, which led to a lower R_{ct}, but too high content of DOL in electrolyte was not beneficial to the cycle performance of batteries, as shown in Fig. 2. The results suggested that though the increase of DOL could decrease the interfacial resistance of batteries, but the suitable dissolving of polysulfide in electrolyte by DME was more critical to improve the electrochemical performance of lithium–sulfur batteries.

The surface morphologies of the sulfur cathode before discharge and after the 20th discharge were observed by SEM. $LiClO_4$, the electrolyte salt, was completely washed away by DME before SEM measurements. The cathode before discharge showed a homogenous morphology presenting uniform distribution of the active material, binder, and conducting agent (Fig. 4a). The images taken after 20 cycles showed the insoluble reduction products of sulfur depositing on the carbon matrix of the cathode [11, 12]. As shown in Fig. 4b, after the 20th discharge in the electrolyte of DME:DOL = 4:1, the surface of cathode was passivated by an impermeable layer over a larger area than those in other composition electrolytes. This result was consistent with the impedance result of Fig. 3 and the reason was

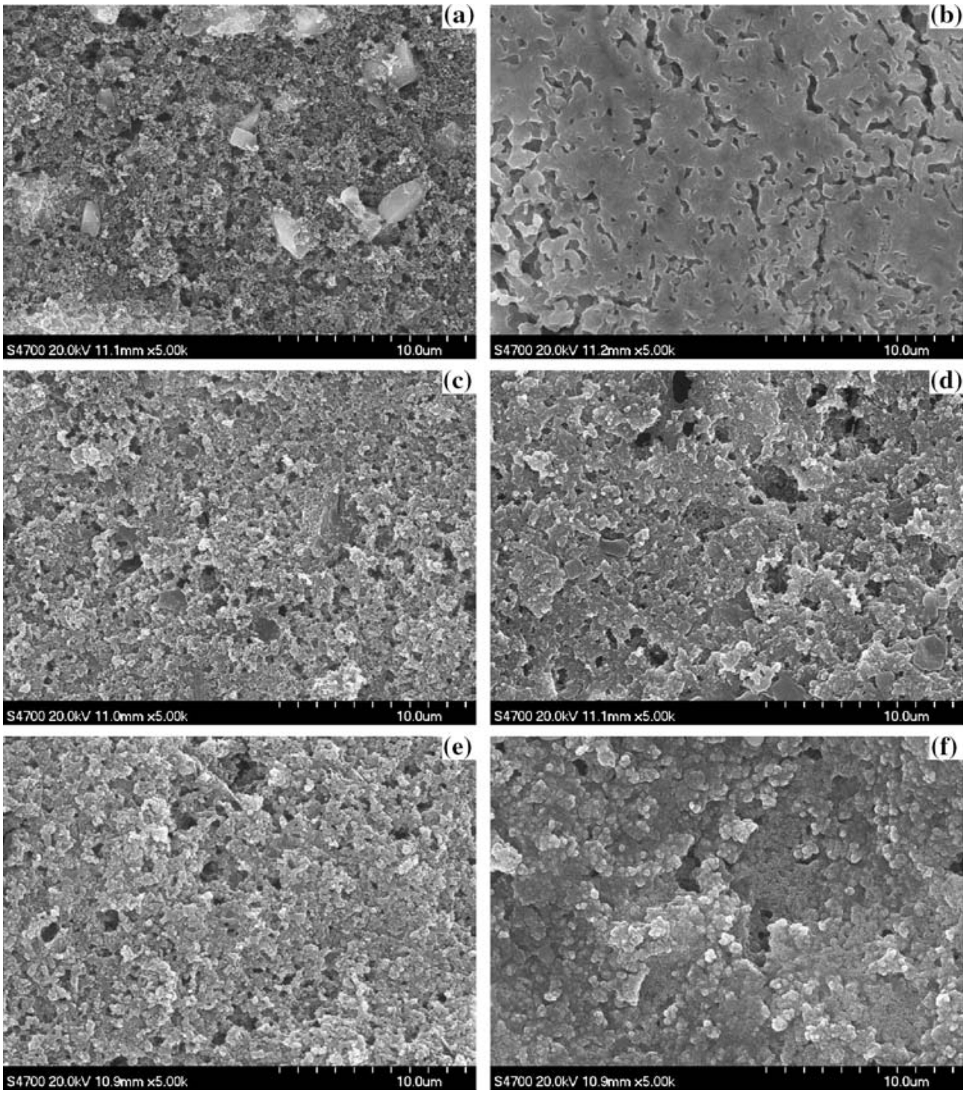

Fig. 4 SEM images of sulfur cathodes: **a** before discharge and **b**–**d** after the 20th discharge in electrolytes with different composition: DME:DOL = **b** 4:1, **c** 2:1, **d** 1:1, **e** 1:2, and **f** 1:4 (v/v)

mentioned above. This case caused a bad cycle electrochemical performance as shown in Fig. 2. However, the passivation became slightly with the decrease of DME. The most uniform and homogenous cathode morphology was achieved in the test battery with electrolyte composition of DME:DOL = 2:1 as shown in Fig. 4c, the cathode surface showed smaller particles of lithium sulfides. This results suggested the easy transportation of Li ions into interior of the cathode ensuring a higher utilization of sulfur during discharge process. Figure 4d–f exhibited the cathode surface changes after the 20th discharge in electrolytes with different composition of DME:DOL = 1:1, DME:DOL = 1:2 and DME:DOL = 1:4, respectively. It could be seen that the cathodes presented less homogenous morphology than Fig. 4c, but was better than Fig. 4b as increase of DOL, which correlated to the cycle performance results with different electrolyte composition as shown in Fig. 2.

4 Conclusions

For the lithium–sulfur batteries with $LiClO_4$ DOL/DME electrolyte, too high content of DME or DOL led to bad cycle performance. The DME could provide good surroundings for redox reaction but too high content in electrolyte would increase the resistance of the battery due to the high solubility of polysulfide. The DOL could improve the interfacial property between the electrodes and electrolyte, but too high content of DOL was not beneficial to the cycle performance of batteries. The results suggested that suitable dissolving of polysulfide in electrolyte by DME was more critical to improve the electrochemical performance of lithium–sulfur battery. The optimal composition of electrolyte was DME:DOL = 2:1. With this electrolyte, the lithium–sulfur battery obtained a high initial discharge capacity of 1,200 mA h g^{-1} and still remained 800 mA h g^{-1} even after 20 cycles.

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