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Study on High Temperature Film Formation of LiBOB Lithium Salt

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Abstract: Lithium bis(oxalato)borate (LiBOB) has attracted much attention as a lithium salt or an additive in non-aqueous electrolytes for lithium-ion battery. In this work, the formation of a solid electrolyte interphase (SEI) film of MCMB (mesophase carbon microbeads) with LiBOB-sulfolane (SL)/ dimethyl sulfite (DMS) electrolyte is studied. The result shows that Li/MCMB cell with LiBOB-SL/DMS electrolyte at high temperature exhibits lower impedance than that at room temperature. The SEM images demonstrates that the LiBOB-SL/DMS electrolyte at high temperature shows more excellent film-forming characteristics. It suggests that LiBOB-SL/DMS electrolyte is a promising formation of the solid electrolyte interphase.

1. Introduction

It is well known that electrolyte decomposition accompanied by irreversible consumption of Li^+ ions takes place at the electrode/electrolyte interface in the initial charged state. The decomposition products would form a solid electrolyte interface (SEI) film on the surface of graphite anode. This process occurs mainly (but not exclusively) at the beginning of the initial cycle [1]. The formed SEI film can separate the graphite anode from the organic electrolyte and prevent the organic electrolyte for further intercalating into the graphite electrode [2]. It is critical to form a stable SEI film to the performance of lithium-ion battery. Therefore, it is necessary to investigate the role of the salt, solvents and conditions in the formation of an effective SEI film for further improvement of the performance of lithium-ion battery, including power capability, cycle performance, safety, etc [3].

The utilization of the LiBOB-SL/DMS electrolyte in lithium-ion batteries with excellent electrochemical performances have been reported in our previous studies [4-6]. The formation of the SEI film upon the anode surface is the most attractive achievement. On one hand, the impedance of SEI film based on LiBOB-SL/DMS electrolyte is lower than that of typical LiBOB-based electrolyte, which could overcome the bottleneck effect of high impedance of typical LiBOB-based cell. It is essential to improve the rate capability and low-temperature performance of lithium-ion battery absolutely. On the other hand, the SEI film shows good chemical and thermal stability even at elevated temperature, which is essential to improve the cycling performance of lithium-ion battery absolutely. It has also been proved that the reduction of impedance benefits from the rich sulfurous compounds in SEI film, which are better conductors for Li^+ than analogical carbonates. However, systematical analytical studies on the change of this SEI film with temperature have not been carried out so far.

In this study, we have focused on the formation of the SEI film with LiBOB-SL/DMS electrolyte at different temperatures to investigate the change in composition and performance of the SEI film with temperature.

2. Experimental Material Preparation

LiBOB was synthesized by a solid-state reaction [7,8]. Organic sulfites DMS was synthesized by the methods as reported previously [9]. SL was obtained from Liaoyang Guanghua Chemical Co, Ltd. Each kind of solvents was dried by 0.4 nm molecular sieves and alkali metals for at least two days until the water content was less than 20 mg L^{-1}, typically, determined by a Karl Fischer titration.

0.7 mol L^{-1} LiBOB-SL/DMS (1:1, by volume, the same below) was prepared in an argon atmosphere glove box.

3. Sample characterization

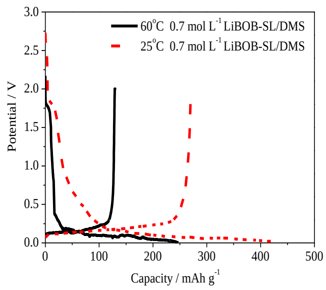
Electrochemical impedance spectroscopy (EIS) spectra of the negative electrode were measured at the fully delithiation state of 0.01 V for Li/MCMB half cells, in a three-electrode cell (the negative electrode was used as the working electrode, and lithium sheets were used as the counter electrode and the reference electrode, respectively) on a CHI660C electrochemical workstation (Shanghai, China). A sinusoidal AC perturbation of 5 mV was applied to the electrode with the frequency range of 100 kHz to 10 mHz. The morphology of SEI film on anode material surface was observed by scanning electron microscopy (SEM) (JSM-5600).

4. Electrochemical tests

Li/MCMB half cells were assembled in an argon atmosphere glove box using a lithium sheet as the anode, the as-prepared electrode as the cathode, the solution of 0.7 M LiBOB-SL/DMS as the electrolyte, and a Celgard (2400) porous polypropylene as the separator. The negative electrode was composed of 92 wt% mesophase carbon microbeads (MCMB) and 8 wt% poly (vinylidene fluoride) (PVDF).

Electrochemical property tests of MCMB/Li cells were carried out on a land cell testerCT2001A (Wuhan, China) in the voltage range of 0.001-2 V.

5. Results and Discussion



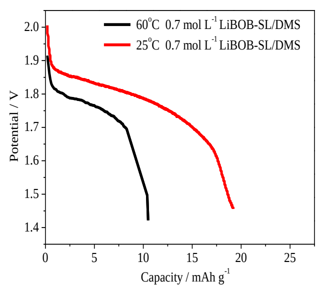


Figure 1. (a) The first discharge-charge curve of Li/MCMB cells.
(b) a clear transition reaction difference at the potential of 1.8 V of cells

Figure 1(a) shows the battery performance of the first charge-discharge curve on Li/MCMB cell at different temperatures. After first cycle, the discharge capacities of the cell are 434 mAh g^{-1} and 246.3 mAh g^{-1} for the electrolytes at 25 °C and 60 °C, respectively. Figure1(b) shows a clear transition reaction difference at the potential of 1.8 V of cells. However, compared them, the electrolyte at 60 °C exhibited a lower discharge platform. And the SEI film grows faster at a higher temperature, indicating that the new SEI film formed at 60 °C enhances the diffusivity of the Li ions leading to the intercalation into carbon quickly. The platform of 25 °C is longer than that of 60 °C, indicating that the reduction reaction consumes more lithium ions.

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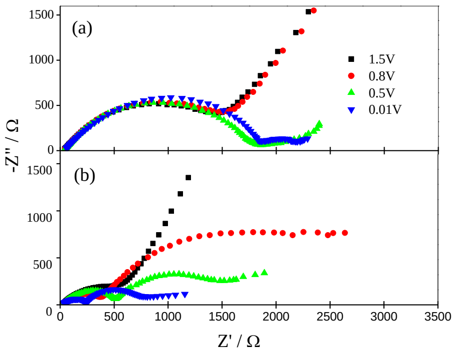

Figure 2. The impedance spectra during the first cycle of Li/MCMB half-cells with LiBOB-SL/DMS electrolyte at (a) 25 ºC and (b) 60 ºC, respectively.

Figure 2 shows the impedance spectra during the first cycle of Li/MCMB half-cells with 0.7 mol L^{-1} LiBOB-SL/DMS electrolyte at different temperatures. The semicircle in high frequency region represents the migration of the Li^+ at the electrode/electrolyte interface, while the semicircle in middle frequency range corresponds to the charge transfer process. The straight line in low frequency region is attributed to the diffusion of the lithium ions into the bulk of the electrode material or so-called Warburg diffusion [10]. It is obvious that the total impedance value of the cell at 25 ºC is much larger than that of at 60 ºC. The reduced impedance at elevated temperature leads to an enhanced electrochemical activity and improved electron diffusion in the Li^+ insertion and extraction processes, which are both favorable for improving the cycle performance.

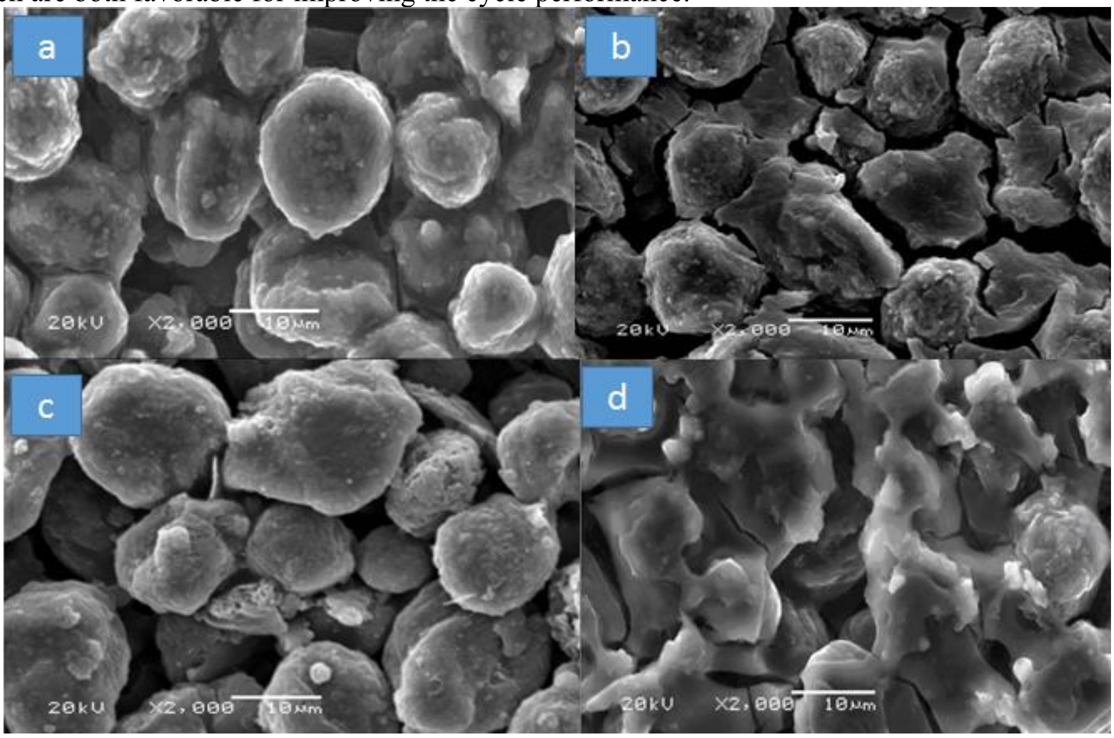

Figure 3. The SEM images of the surface of anode MCMB in Li/MCMB cells with LiBOB-SL/DMS electrolytes during the first lithiation process at different potential, (a) 1.5V and (b) 0.01V at room temperature, (c) 1.5 V and (d) 0.01 V at high temperature

Figure 3(a) and 3(b) show the typical SEM images of LiBOB-SL/DMS electrolyte at different potentials (1.5 V and 0.01V) at 25°C, Figure 3(c) and 3(d) show the typical SEM images of LiBOB-SL/DMS electrolyte in different potentials (1.5V and 0.01V) at 60 °C, respectively. In Figure 3(a) and 3(c) (the potential of 1.5 V), there is no obvious SEI film formed. However, , it can be observed in Figure 3(b) and 3(d) (the potential of 0.01V) that the MCMB electrode is clearly covered by a definite thickness SEI film. Figure 3(b) shows a coarse and inhomogeneous distribution, while Figure 3(d) shows a relatively smooth, compact and uniform film covered on the surface of electrode. The compact SEI film will impart more effective kinetic stability to prevent further reductions of the electrolyte during the successive cycle processes. As a result, the electrode exhibits good stability, safety, and fairly constant interface resistance. All of these phenomenon accord with results from Figure 2.

6. Conclusions

The formation of a solid electrolyte interphase of sulfolane (SL) with LiBOB is studied by using dimethyl sulfite (DMS) as mixed solvents. Li/ MCMB (mesophase carbon microbeads) cell with 0.7 mol L^{-1} LiBOB-SL/DMS (1:1) electrolyte at high temperature shows lower impedance than electrolyte at room temperature. The SEM shows that 0.7 mol L^{-1} LiBOB-SL/DMS (1:1) electrolyte at high temperature exhibits more excellent film-forming characteristics than electrolyte at room temperature. It suggests that LiBOB-SL/DMS electrolyte has an excellent ability of the formation of SEI film. It is believed that the reduced impedance is owing to both the rich existence of sulfurous compounds and the low content of Li_2S in SEI film.

Acknowledgements

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