Application of Lithium Oxalate Borate of a Preformed the Solid-state Interface in Lithium ion Batteries

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Abstract. Lithium bis(oxalato)borate (LiBOB) is a promising salt for Li-ion batteries owing to its excellent characteristics, and its most outstanding performance is SEI film-forming ability. Here, we use the film-forming properties of LiBOB, cells with LiBOB electrolyte system first run 3-5 cycles in battery tester, making the formation of a robust SEI film on the MCMB surface, then use the pre-filming MCMB electrode and LiPF6 electrolyte to assemble new cells and to conduct electrochemical test. The pre-film was found to effectively retard the re-decomposition of the solvent.

1. Introduction
Electrolytes play the role of ions’ transmission between positive and negative electrodes, and hold important implications for battery’s capacity, circulation and security properties[1]. At present, the mixture of LiPF6 salt and organic carbonate (EC/DEC) is the most essential and widely used ingredient of commercial electrolytes. However, the use of LiPF6 raises severe safety problems, because of its limited thermal stability and sensitivity to trace moisture in the air.

Recently, lithium bis(oxalato)-borate (LiBOB) is regarded as the most promising one for the lithium-ion batteries[2,3]. When compared with LiPF6, LiBOB has several advantages: It is thermally more stable, it is friendlier to the environment because its hydrolytic decomposition products are less toxic and corrosive, and it actively takes part in the formation of a stable solid electrolyte interface (SEI) film on the graphite electrode[4]. In addition, the solubility and ion conductivity restricted the extensive use of LiBOB, and the thick SEI layer easily formed in LiBOB-based electrolytes dramatically increased the interfacial impedance and deteriorated the power capability of the lithium ion batteries.

In this study, combining with the advantages and disadvantages of LiPF6 and LiBOB electrolyte salt, we used the cell with the electrolyte of 0.7 mol L−1 LiBOB-sulfolane (SL) / dimethyl sulfite (DMS) (1:1 by volume) to run in advance firstly 3-5 cycles in battery tester, forming a superior SEI film on the graphite electrode surface. Then we use the the pre-filming graphite electrode to compose a new cell with the electrolyte of 0.7 mol L−1 LiPF6-SL/DMS(1:1 by volume). We expect that the SEI film is able to obviously enhance the cyclic capability of the graphite electrode and effectively hinder the erosion of HF to electrode surface and further electrolyte decomposition.
2. Experimental

2.1. Materials
LiBOB was synthesized in our laboratory by employing a solid-state reaction, and purified to above 99.9% by repeating recrystallizations with anhydrous CH$_3$CN several times. Electrolyte system was prepared in an argon atmosphere glove box by dissolving 0.7 mol L$^{-1}$ LiBOB - SL/DMS and 1 mol L$^{-1}$ LiPF$_6$ - SL/DMS was produced in an argon atmosphere glove box. The negative electrode was composed of 92 wt.% MCMB and 8 wt.% poly (vinylidenefluoride) (PVDF).

2.2. Instruments
Electrochemical properties tests of cells were carried out on a land cell tester CT2001A (Wuhan, China) in the voltage range of 0.01-2 V with a constant current density of 0.02 mA cm$^{-2}$ at room temperature. Cyclic voltammetry (CV) were tested through a CHI660C Electrochemical Workstation (Shanghai, China) at the scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0 - 3.0 V. The surface morphology and chemical components of the electrode were observed by scanning electron microscopy (SEM, JSM-5600, Japan) and X-ray photoelectron spectroscopy (XPS, GG 314-JPS-9200) techniques, respectively.

3. Results and discussion

3.1. Electrochemical characteristics of the first cycles of Li / MCMB cells

![Fig. 1. The first discharge–charge curves of Li / MCMB cells.](image)

The first discharge–charge curves of Li / MCMB half cells with different electrolyte systems are given in Fig. 1. The first capacity of the Li/MCMB cell with LiBOB-containing electrolyte is 187.1 mAh g$^{-1}$. However, the first capacity of the Li/MCMB cell with 1 mol L$^{-1}$ LiPF$_6$-containing electrolyte is 451.4 mAh g$^{-1}$. The following trend is detected as the decomposition potential drop: LiPF$_6$ (1.49 V) < LiBOB (1.78 V). It is suggested that the LiBOB-SL/DMS electrolyte can significantly improve the capacity stability, which may be ascribed that the LiBOB can priority reduction to form SEI layers.

3.2. XPS analysis of the SEI layer

![Fig.2. XPS spectra of MCMB electrodes](image)

The O 1s spectrum of two MCMB electrodes surface extracted from cells contains a broad peak characteristic of C–O and C=O containing components at 532–533.5 eV are shown in the O 1s spectra. This suggests the deposition of carbonate salts on the surface of the electrode, resulting from the decomposition of the salt$^{[5]}$. As for B 1s spectra, no peak appears in the B 1s spectrum for the MCMB surface of LiPF$_6$-based cell, but cells cycled with LiBOB-SL/DMS electrolyte show peaks in the B1s spectra around 192.5–193.8 eV, which can be combined with reductive products of solvents (RCO$_3$Li...
for example) and will improve stability of the SEI film, and provide the SEI film tenacity, uniformity and densification [6,7]. The broad peak around 284–287 eV is a group of superimposed peaks including the C-C (MCMB, sp2) at 284.4 eV, C-O/amorphous carbon at 285 eV, C-OH at 286 eV and C=O at 287 eV. In addition, there is an abundance of ROO\textsubscript{2}Li characterized by the peak at 289 eV in C1 s due to the ring-opening of the BOB\textsuperscript{−} anion [8]. The peak at 289 eV is assigned to the composition of ROCO\textsubscript{2}Li and the peak at 290.4 eV is assigned to Li\textsubscript{2}CO\textsubscript{3}. Electrodes cycled with LiPF\textsubscript{6} peaks at 287.5 and 290 eV, characteristic of CH\textsubscript{2}-O, and O-(C=O)-O containing species, such a lithium alkyl carbonates. Generally, sulfurous compounds are better conductors of Li\textsuperscript{+} ions than analogical carbonates, existences of these sulfurous compounds in SEI film are very helpful for impedance reduction [9]. However, the peak positions and contents of S in LiBOB and LiPF\textsubscript{6}-based cell are different, indicating that the reaction is different during the film formation. After 1 cycle, two peaks obviously emerge at 168.6 and 169.3 eV of LiBOB-based cell, which are characteristic peaks of Li\textsubscript{2}SO\textsubscript{3} and Li\textsubscript{2}SO\textsubscript{4}, respectively. 167.9 eV peak of LiPF\textsubscript{6}-based cell is characteristic peak of RSO\textsubscript{3}Li. The products and its valencies of two MCMB surfaces are different, indicating there are interaction between salts and solvents, and the interaction of LiBOB with the solvent makes the film formation better.

3.3. SEM measurement of MCMB surface in Li / MCMB cells

The SEM images of the MCMB surface extracted from three different Li / MCMB cells shown in Fig. 3. In Fig. 3 (a), surfaces of MCMB materials are covered by uniform SEI layers, arising from reductions of both LiBOB and organic solvents. Morphological of MCMB with LiBOB-containing electrolyte observation shows uniform while well stability of SEI is formation. In Fig. 3 (b), Morphological LiPF\textsubscript{6}-containing electrode observation shows not only rough and irregular but also many defects. After changing electrode (Fig. 3 (c)), there still are some electrolyte decomposition products attached to MCMB surface after 1 cycle, but it has the same morphological as MCMB with LiBOB-containing electrolyte. These results suggest that the pre-filming of LiBOB protects MCMB electrode and effectively prevents the further decomposition of electrolyte.

3.4. Cyclic voltammetry

Fig. 4. The CV test results of Li / MCMB half-cells: (a) 0.7 mol L\textsuperscript{−1} LiBOB-SL/DMS; (b) after changing electrode; (c) 1 mol L\textsuperscript{−1} LiPF\textsubscript{6}-SL/DMS

Fig.4. shows the cyclic voltammogram (CV) test results for Li / MCMB half-cells, the current – voltage curves at 25 °C with the scanning speed of 0.1 mV s\textsuperscript{−1}. The reduction peak of the DMS solvent on the
MCMB anode is observed at ~2.5 V, as shown in Fig.4 (a) and (c). The reduction current peak of 1.5 V arises from BOB\(^{-}\) anion and SL, which are attributed to the SEI formation. However, Fig.4 (b) just have ~ 0.1V lithiation reaction, it means that solvents did not reduce at MCMB surface. From these results, LiBOB produces a robust interface film compared with LiPF\(_6\) thus inhibiting electrolyte decomposition and protecting MCMB electrode.

4. Conclusions
LiBOB is a promising salt for lithium ion batteries owing to its unique characteristics, especially SEI film-forming ability. We use LiBOB to form a robust SEI film on MCMB surface and take it to apply LiPF\(_6\) electrolyte system and consequently enhance electrochemical performance of LiPF\(_6\) electrolyte system. The SEM and CV test result shows LiBOB achieve pre-filming effect.

Acknowledgements
This work is supported by the Natural Science Foundation of China (No. 51502124 and 21766017), the Gansu Province Science and Technology Major Project (17ZD2GC011).

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