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Properties of Lithium bis(oxatlato)borate (LiBOB) as a Lithium Salt and Cycle Performance in $LiMn_2O_4$ Half Cell

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Crystalline LiBOB which we prepared in our lab was observed by SEM method. Impurities of product were examined by XRD experiment. The decomposition voltage under a deoxidized current was 1V vs.Li+/Li, and under a oxidized current the electrochemical stabilities is up to 5V vs.Li+/Li. The conductivity of two kinds of LiBOB based electrolytes were both lower than that of $LiPF_6$ based electrolyte. Through galvanostatic cycling test of the half cells it could be observed that LiBOB cell has a better capacity retention than that of $LiPF_6$ cell.

Keywords: Lithium-ion battery , electrolyte, LiBOB

1. INTRODUCTION

Since a new lithium salt-lithium bis(oxalate)borate (LiBOB) was disclosed by Lischka et al[1] , in 1999 firstly, a series studies of its properties were carried on[2] . It meets the basic requirements for a salt to be used in lithium-ion cells: acceptable conductivity at ambient temperature, wide electrochemical window[3], the ability to form SEI layer on electrodes[4] and the ability to passivate aluminum current collector from anodic dissolution[5] . Though a thorough knowledge of this salt still hasn't been acquired, some unique properties especially for the thermal stability arouse much interesting. Unlike $LiPF_6$ decomposing to LiF and PF_5 at high temperature LiBOB is stable until 302°C. This unique property is regarded to solve capacity fading of $LiMn_2O_4$ spinel cathode cycling at high temperature. $LiMn_2O_4$ spinel degrades in $LiPF_6$ based electrolyte at high temperature and leads to a severe capacity fading during cycling[6].This phenomenon is attributed to Mn dissolution from the spinel cathode induced by HF acid generated by the reaction of $LiPF_6$ with trace water at elevated temperature[7].

In this paper, we investigated the general properties of LiBOB which we prepared in our lab and electrochemical characters of LiBOB based electrolyte firstly. Then we adopted two kinds of electrolyte systems ($LiPF_6$ based electrolyte and LiBOB based electrolyte) to compare the capacity performances of the $LiMnO_2$/Li cells at different temperature.

2. EXPERIMENTAL PART

LiBOB was prepared and purified in our lab through the procedures as described in our previous publications [8]. Battery level EC, DEC and EMC were purchased from Beijing Institute of Chemical Reagents. In an argon-filled glove box, the solution of 0.7M LiBOB in 1:1(v:v) ethylene carbonate(EC) and ethylmethyl carbonate(EMC) mixture or EC, Dimethyl Carbonate (DMC), EMC mixture were prepared. 1M $LiPF_6$ in 1:1:1(v:v:v) EC, DMC, EMC electrolyte was purchased from Beijing Institute of Chemical Reagents. $LiMn_2O_4$ was prepared in our lab through the procedures as described in our previous publications [9]. The positive electrode was fabricated with: $LiMn_2O_4$ as active material, acetylene black as conducting additive, and teflon as binder by a weight ratio of 85:10:5. The mixture was stirred, dried and then pressed into a thin film. Subsequently, the as-prepared electrode film was dried and degreased in a vacuum pipe for 24h at 120 ^oC to remove the surface solvents.

The cells were assembled and sealed in an argon-filled glove box with the electrode film as the cathode, lithium foil as the anode, Celgard 2400 polyethylene/ polypropylene as the separator and filled with either 0.7 M LiBOB/EC:EMC(1:1.v/v) or 1M $LiPF_6$/EC:EMC:DMC(1:1:1,v/v/v) as electrolyte. The cells were tested on a LAND BT-10 tester (Wuhan, China), and were charged/discharged galvanostatically at a current of 0.5C in the voltage window of 3.3-4.35V. The cells were cycled at room temperature (25 ^oC) or 65 ^oC in an oven to compared cycle performances at different temperature. X-ray diffraction (XRD) was carried out on LiBOB with a Rigaku D/max-A (Japan) machine. LiBOB powder was observed using Hitachi S3500N (Japan) scanning electron microscope (SEM). A three-electrode system was employed for solution conductivities and decomposition voltages with a CHI660A electrochemical workstation (Shanghai Chenhua) with Li foils as counter and reference electrodes.

3. RESULTS AND DISCUSSION

3.1 General properties of LiBOB

Figure 1 shows SEM micrograph of the purified crystalline LiBOB. From the image it can be observed that LiBOB has good crystalline form after purified procedure. Every needle-shape particle is about 10μm long and 2μm wide.

XRD patterns of unpurified LiBOB and purified counterpart were compared in Figure 2. The peak intensity of purified LiBOB was stronger than that of unpurified one. Some peaks which would be impurities disappeared after purified. Compared with the stander XRD pattern, the impurities could be identified to be HBO_2, HC_2O_4Li and Crystalline water. After being purified, the solubility of LiBOB in solvents increased to 0.7mol/L.

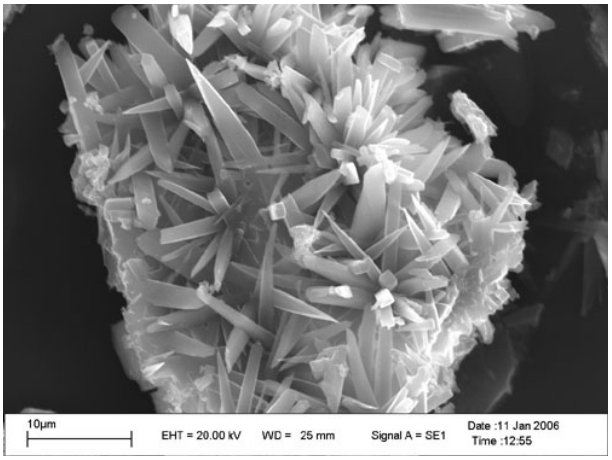

Figure 1. SEM image of purified LiBOB crystal.

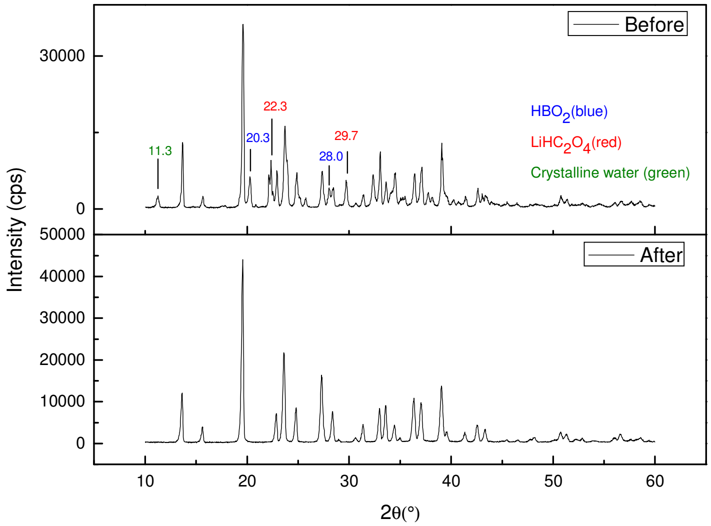

Figure 2. XRD patterns of LiBOB before and after being purified

3.2 Electrochemical analyzed of solution

Figure 3 shows cycle voltammogram of 0.7M LiBOB/EC:EMC(1:1,v;v), EMC, EMC and EC mixture (1:1,v:v) from 0V to 5V vs.Li+/Li. When the solvent only contained EMC, no current peak was observed. After adding EC or LiBOB into EMC solvent, the redox current occurred. After comparing the different of the CV between 0.7M LiBOB/EC:EMC(1:1,v:v) and EC+EMC solvent(1:1,v:v), the deoxidized current from 1.35V is attributed to the decomposition of LiBOB salt, and the decomposition voltage of LiBOB based electrolyte can be identified from 1.35V to 0V vs.Li+/Li under a deoxidized current. Under a oxidized current, the electrochemical stabilities is up to 5V vs.Li+/Li.

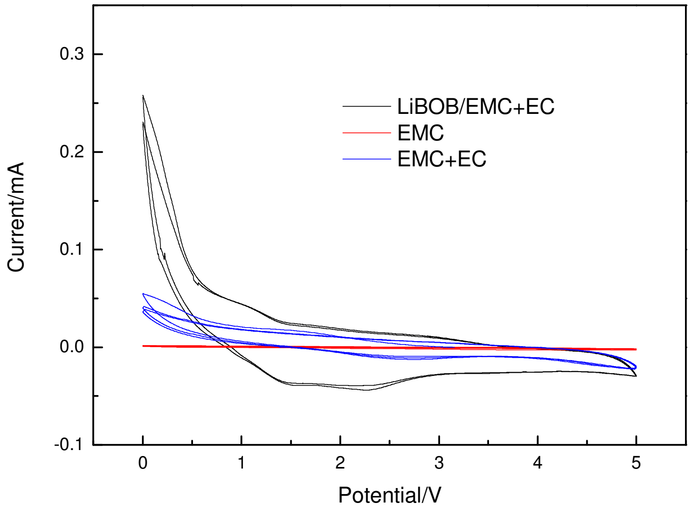

Figure 3. Cyclic voltammogram of 0.7M LiBOB/EC:EMC(1:1,v:v), EMC and EMC+EC(1:1,v:v) (scan rate: 5mV/s and 0-5V vs. Li+/Li) at room temperature

Figure 4 shows comparison of the conductivity among 1M $LiPF_6$/EC:EMC:DMC(1:1:1,v:v:v), 0.7M LiBOB/EC:EMC(1:1,v:v) and 0.7M LiBOB/EC:EMC:DMC(1:1:1,v:v:v). All of three increased with temperature gradually. LiPF6 based electrolyte shows much higher conductivity than LiBOB based electrolytes.

3.3 Galvanostatic cycling test of the half cells

Figure 5 shows comparison of the capacities between the testing cells cycled at room temperature (25 ^{o}C). The current density of charge and discharge were both 0.5C (70mA/g).The cell in LiBOB based electrolyte has an inferior capacity than the counterpart in LiPF6 based electrolyte during the first 20 cycles. But the cell containing LiBOB shows a higher efficiency (about 99% after formation cycles). The capacity retention of $LiPF_6$ cell is 73.88% which is much lower than 98.4% of LiBOB cell(30 cycles). Figure 6 shows the charge and discharge curves of the testing cells in two electrolytes (first three cycles). At first one or two cycles the gaps of median voltages of two cells were both relatively high (210mv at 55mAh/g of $LiPF_6$ cell and 370mv at 38mAh/g of LiBOB cell). After several cycles the gap became narrower prominently (102mv at 60mAh/g of $LiPF_6$ cell and 157mv at 55mAh/g of LiBOB cell). The difference between the gap of median voltage in two cells indicates the difference of resistance induced by different electrolytes.

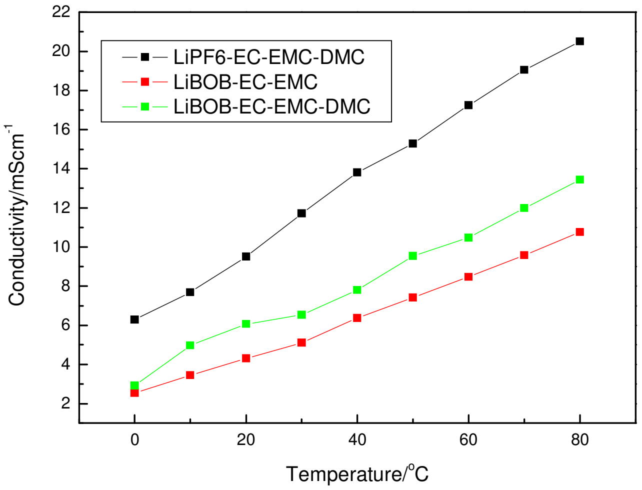

Figure 4. Change of conductivity with temperature for $1MLiPF_6/EC:EMC:DMC(1:1:1,v:v:v)$ □ 0.7MLiBOB/EC:EMC(1:1,v:v)□and 0.7MLiBOB/EC:EMC:DMC(1:1:1,v:v:v)

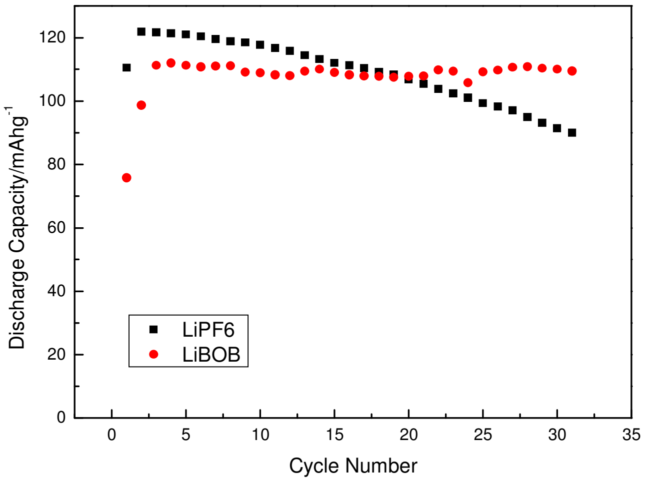

Figure 5. Cycle performace for $LiMn_2O_4$/Li cells using LiBOB- and $LiPF_6$-based electrolytes at room temperature

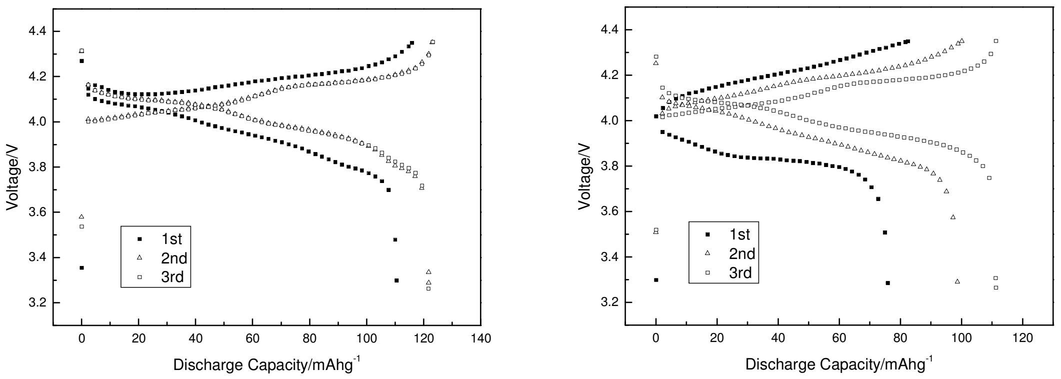

Figure 6. Charge and discharge profiles for $LiMn_2O_4$/Li cells using (a)$LiPF_6$- and (b)LiBOB-based electrolytes at room temperature

Cycle performances of two cells at elevated temperature are shown in Figure 7. Different from the performance at room temperature, LiBOB cell has better cycle performance than $LiPF_6$ counterpart.

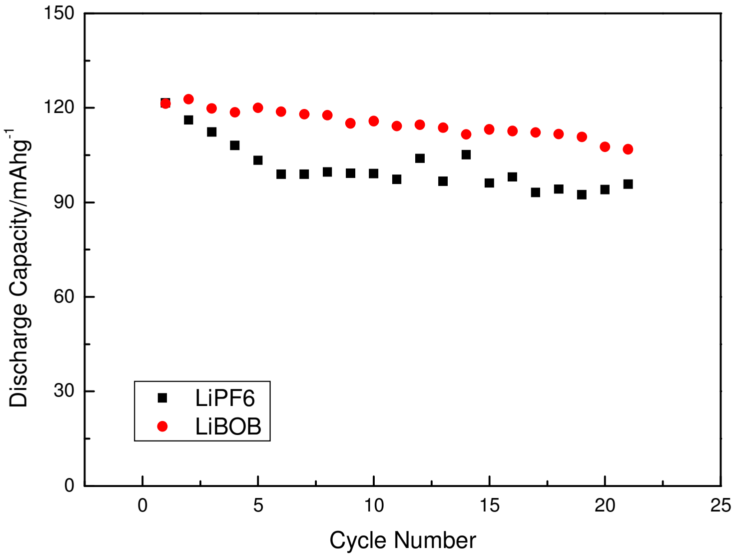

Figure 7. Cycle performance for $LiMn_2O_4$/Li cells using LiBOB- and $LiPF_6$-based electrolytes at 65 °C

Though $LiPF_6$ based electrolyte has higher conductivity than LiBOB counterpart, it is not induced higher capacity in half cell at elevated temperature in this current (40mA/g).At elevated temperature because of the increase of diffusion coefficient the discrimination of median voltages decreased (98mv at 55mAh/g of $LiPF_6$ cell and 73mv at 60mAh/g of LiBOB cell) which were shown in Figure 8. Especially in LiBOB based electrolyte the cell resistant decreased prominently. At the beginning of cycling, the cells in two kinds of electrolytes almost have the same capacity. But the cell in $LiPF_6$ based electrolyte exposed a lower durability. The capacity of $LiPF_6$ cell went down by 19% after 5 cycles and due to the dissolution of Mn in $LiPF_6$ based electrolyte at elevated temperature the cell capacity was unstable in cycling. Unlike $LiPF_6$, LiBOB is stable at high temperature and no HF is produced by salt decomposition. This character enabled LiBOB to have a stable cycle performance at high temperature.

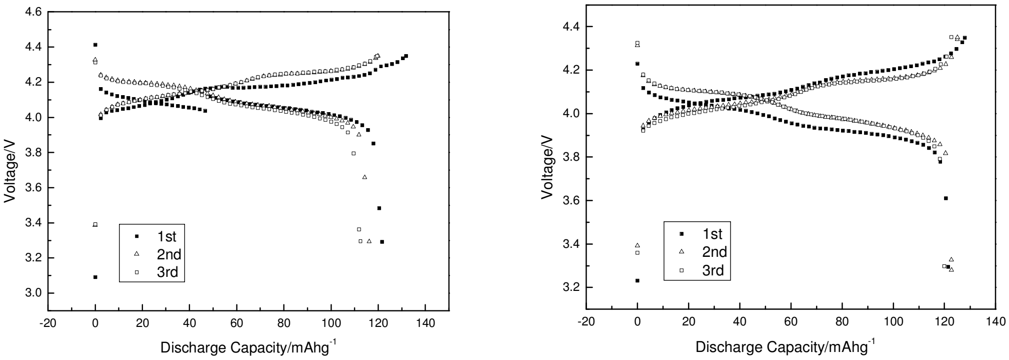

Figure 8. Charge and discharge profiles for $LiMn_2O_4$/Li cells using (a) $LiPF_6$- and (b)LiBOB -based electrolytes at 65 °C

4. CONCLUSIONS

After being purified, LiBOB formed a good crystalline phase and as shown in XRD patterns, the impurity reduced. The conductivity of LiBOB based electrolyte is the half of that of $LiPF_6$ counterpart from 0 °C to 80 °C. In half cell, LiBOB has a superior charge-discharge capacity at elevated temperaturethan that of $LiPF_6$, which could be result from the dissolution of $LiMn_2O_4$ in $LiPF_6$ at elevated temperature which induced a lower capacity retention.

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