



Short communication

Study on γ -butyrolactone for LiBOB-based electrolytesJia-yuan Huang^a, Xing-jiang Liu^b, Xiao-li Kang^a, Zhao-xin Yu^a, Ting-ting Xu^a, Wei-hua Qiu^{a,*}^a Beijing Key Lab. of New Energy Materials and Technologies, School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China^b China Electronics Technology Group Corporation, Tianjin Institute of Power Sources, Tianjin 300381, China

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ABSTRACT

To solve the problems of LiBOB-based electrolytes, small salt solubility and low conductivity, a sort of cyclic carboxylate, γ -butyrolactone (GBL) was applied in the lithium-ion battery electrolyte as the main solvent of lithium bis(oxalate)borate (LiBOB). LiBOB–GBL electrolyte exhibits good electrochemical stability, which is suitable to be the candidate of the lithium-ion battery electrolyte. Using GBL as the solvent of the LiBOB salt can increase the solubility and conductivity dramatically. At room temperature, LiFePO₄/LiBOB–GBL/Li half cell shows satisfying cycle performance with no capacity fading in the first 50 cycles and promising capacity performance with stable discharge capacity of about 125 mAh g⁻¹. EA is mixed with GBL to get lower viscosity solvent. In LiFePO₄/Li half cell with 0.5 C discharge rate, 0.2 M LiBOB–GBL/EA (1:1, wt) electrolyte exhibits best at room temperature and 0.7 M LiBOB–GBL/EA (1:1, wt) electrolyte exhibits best at elevated temperature.

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1. Introduction

Nowadays, lithium bis(oxalate)borate (LiBOB) has been reported as a promising candidate for lithium salt used as electrolyte solute in lithium-ion batteries [1,2]. LiBOB has the advantages that the producing cost is low [3], the potential window is wide, the structure is hydrogen and fluorine free, and the thermal stability is good [4]. LiBOB is attractive also because of its particular properties. LiBOB-based electrolyte can passivate and protect aluminum current collector [5], and can form solid electrolyte interface (SEI) to stabilize the graphitic anode structure even in pure propylene carbonate (PC) solvent [6]. In addition, LiBOB is environmentally friendly with simple fabrication process [3].

However, compared to lithium hexafluorophosphate (LiPF₆) salt used in commercial electrolytes, LiBOB has smaller solubility and lower conductivity in typical carbonate mixtures, which could render electrolytes with poor low-temperature performance and low rate capability. LiBOB has a very poor solubility in low dielectric constant solvents such as linear carbonates [7]. For example, the EC/DEC (1:1) mixture is saturated with only 0.8 M LiBOB at room temperature. To solve these problems, a proper solvent mixture that is tailored for LiBOB needs to be formulated.

γ -Butyrolactone (GBL) is a sort of cyclic carboxylate once used in primary lithium batteries. The physical properties of GBL and its counterpart, ethyl carbonate (EC) are displayed in Table 1 [8]. The melting point and the boiling point of GBL are -43.53°C and

204°C , respectively, which form a wider liquid region than EC. The melting point of GBL is far below the room temperature, which may improve the lower temperature performance of the electrolyte. The flash point and bubble point of GBL are relatively high, not as high as EC, but can meet the requirement of most usage condition. Cyclic carboxylate GBL and the commonly used organic carbonate EC are structurally similar. EC differs from GBL in the molecule structure only by an oxygen atom replacing of the carbon on the carboatomic ring and the two hydrogen atoms connecting to the carbon atom. Ethyl acetate (EA) is a sort of linear carboxylate with low viscosity (0.426 mPa s, at 25°C) and higher dielectric constant (6.02, at 25°C) than most linear carbonates. The physical properties of EA are displayed in Table 1 too. It has been reported [9] that the electrolyte conductivity can be increased by introducing GBL and EA to the LiBOB–EC/DMC system. However, the study on using GBL as the main solvent of LiBOB-based electrolyte is rare.

In this paper, we report our recent effort in optimizing the LiBOB-based electrolytes by changing the main solvents from the conventional carbonic esters to the carboxylic esters. The work aims at finding a sort of organic solvent that can replace carbonic esters to solve the problem of small salt solubility and low conductivity.

2. Experimental

2.1. Sample preparation and chemical used

LiBOB salt was prepared and purified in our lab through the procedures as described in our previous publications [3,10]. Battery level LiPF₆ was purchased from Merck and EC, DEC solvents were from Beijing Institute of Chemical Reagent. GBL and EA were

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Table 1

The physical properties of GBL, EC and EA (at 25 °C).

	m.p. (°C)	b.p. (°C)	f.p. (°C)	ε	η (mPa s)
GBL	−43.53	204	98.3	39	1.7
EC	37	248	160	89.6 ^a	1.86 ^a
EA	−83	77.1	7.2	6.02	0.426

^a At 40 °C.

obtained from Tianjin Jinniu. The positive electrode in the T-type cell was LiFePO_4 (0.5 cm^2) and the fabrication procedure is mentioned in the prior paper [11]. The anode materials used in T-type cell was lithium foil (2 cm^2). Celgard 2400 microporous membrane was used as separator. In the three electrode system, stainless steel (SS) was used as the counter electrode and working electrode. Separator filled with electrolyte was assembled between two SS electrodes. Li foil was used as the reference electrode. Thus the decomposition voltage of the electrolyte (vs. Li) can be obtained through the cyclic voltammetry (CV) test.

2.2. Instruments

The testing cells and the electrolyte used were all assembled and sealed in an argon-filled glove box. The T-type cell utilized in the galvanostatic cycling test was cycled on LAND CT2001C tester (Wuhan, China). The cut-off voltage was 2.6–4.25 V. The three-electrode system utilized in the CV test was tested on the CHI 660A electrochemical workstation (Shanghai, China). Rex DDST-308A conductivity meter was involved in the measurement of ionic conductivity of the electrolyte.

3. Results and discussion

3.1. Electrochemical properties of GBL

3.1.1. The electrochemical stability test

The solvents for the lithium-ion batteries must have good electrochemical stability. The decomposition voltage of the electrolyte should be over 4.2 V. Fig. 1 shows the CV test results of 1.0 M LiBOB-GBL electrolyte and 1.0 M LiPF_6 -GBL with the scan rate of 5 mV s^{-1} . According to Xu et al. [12], 0.1 mA cm^{-2} can act as an indicator of decomposing of electrolytes at this scan rate. However, the current density in Fig. 1 does not reach the criteria. Fig. 1 shows that the current density (of the order of magnitude of $10^{-2} \text{ mA cm}^{-2}$) is much smaller than the current generated by the electrode reaction (always of the order of magnitude of 10^0 mA cm^{-2} , at 0.05 mV s^{-1}). Because the positive area (S1) and negative area (S2) are identical, it can be concluded that the tiny reactions are reversible. No negative reaction occurs, which is indicated by the good repeatability of the CV curves. The test results reveal that 1.0 M LiPF_6 -GBL electrolyte and 1.0 M LiBOB-GBL electrolyte are stable in the voltage range of 0–5 V. Both electrolytes tested have good electrochemical stability, which is appropriate to be used as the lithium-ion battery electrolyte.

3.1.2. The solubility and conductivity measurement

In the study, the maximum solubility of LiBOB in pure GBL is about 2.5 M at room temperature, much higher than that in the cyclic carbonate EC or PC-based system. Fig. 2 shows the conductivities of the solvents of 1.5 M LiBOB/ LiPF_6 in pure GBL at different temperatures ranged from 2 to 80 °C. The conductivity of 0.7 M LiBOB in EC/DEC (1:1, wt) system is also given in Fig. 2 as a contrast. The conductivity at room temperature is higher than all the binary carbonate solvent systems tested in our lab [13], but not as high as assumed, which may be attributed to the high viscosity of the electrolyte. At 30 °C, the conductivity of 1.5 M LiBOB-GBL electrolyte is

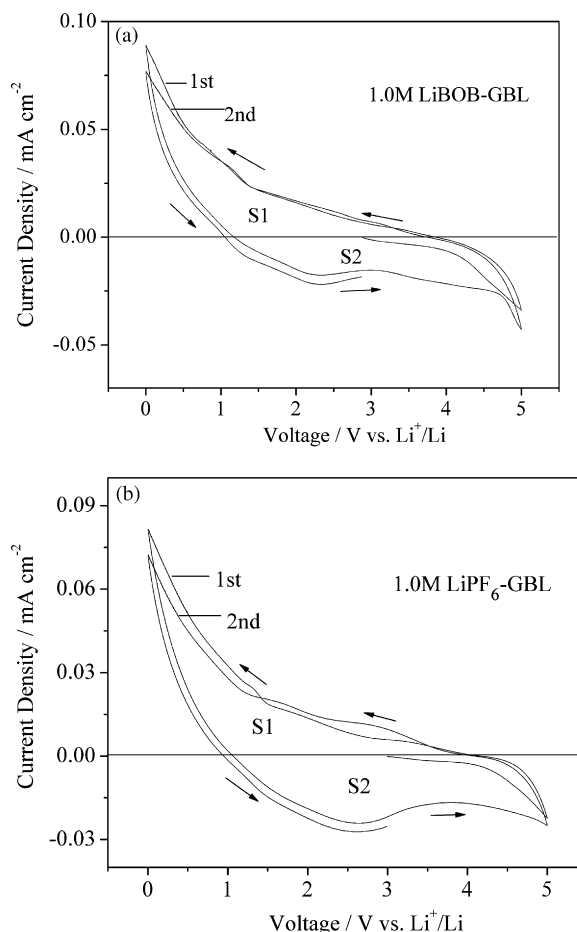


Fig. 1. The current–potential curve at the scan rate of 5 mV s^{-1} (a) 1.0 M LiBOB-GBL and (b) 1.0 M LiPF_6 -GBL.

7.45 mS cm^{-1} while conductivity of 0.7 M LiBOB-EC/DEC electrolyte is 4.79 mS cm^{-1} . At 60 °C, the conductivities of the two electrolytes referred above are 12.98 mS cm^{-1} and 7.76 mS cm^{-1} , respectively. The conductivity difference value between LiBOB-GBL system and LiBOB-EC/DEC system increases with the increasing temperature and reaches the highest value of 5.58 mS cm^{-1} at 80 °C.

The test results indicate that the solubility and conductivity of LiBOB-based electrolyte can be enhanced dramatically by chang-

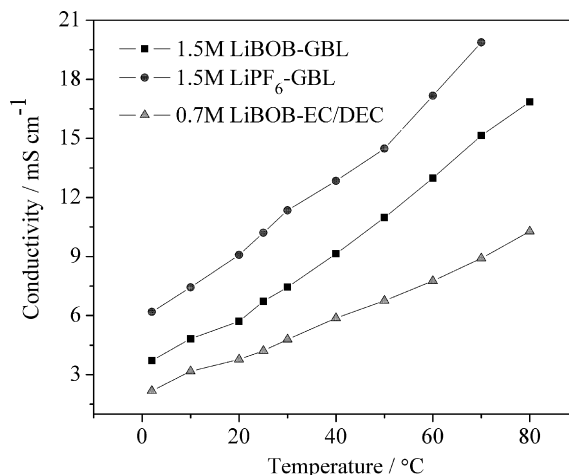


Fig. 2. Change of conductivity with temperature for 1.5 M LiBOB-GBL, 1.5 M LiPF_6 -GBL, and 0.7 M LiBOB-EC/DEC (1:1, wt) solution.

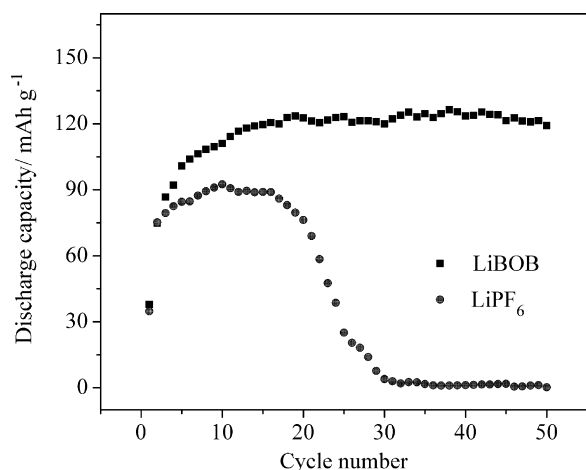


Fig. 3. Cycling performances of LiFePO₄/Li half cells using 1.5 M LiBOB-GBL, 1.5 M LiPF₆-GBL as electrolyte at 0.5 C (30 °C).

ing the solvent to GBL. The initial purpose of the work has been accomplished.

3.1.3. The application of GBL as the solo solvent in lithium-ion battery electrolyte

Both 1.5 M LiBOB-GBL mixture and 1.5 M LiPF₆-GBL mixture are used as the electrolyte of Li/LiFePO₄ half cell in the test. The testing cells are cycled at room temperature with 0.5 C discharge rate. The cycle performances of cells with two different electrolytes are shown in Fig. 3. Cells with LiPF₆-GBL electrolyte exhibit poor cycle performance. The discharge capacity starts to decay after 15 cycles and falls down to less than 10 mAh g⁻¹ after 30 cycles. These phenomena reveal the fact that LiPF₆-GBL electrolyte is not suitable for lithium battery. However, the internal mechanism which causes the bad cell performance is still unclear. Further study will carry on to explain it. Whereas, cells with LiBOB-GBL electrolyte represents much better cycle performance. The initial discharge capacity is 38.0 mAh g⁻¹, which is quite close to the one of cell with LiPF₆-GBL electrolyte (34.8 mAh g⁻¹). In the first 10 cycles, the discharge capacity increases steadily, which is probably because that the high viscosity and large interface resistance prolong the activation procedure. The discharge capacity gets to a stable value of about 120 mAh g⁻¹ after 10 cycles and remains to be 125.4 mAh g⁻¹ after 50 cycles with no fading. The results referred indicate that LiBOB-GBL electrolyte shows good compatibility with LiFePO₄ cathode.

3.2. Electrochemical properties of GBL/EA mixture

Based on the results above, it can be concluded that LiBOB-GBL system can be used as lithium-ion battery electrolyte. However, because of its high viscosity, GBL is not suitable to be the only solvent of the lithium salt in lithium battery electrolyte.

Linear carbonate or carboxylate should be mixed with GBL to attain electrolyte with lower viscosity. While screening the potential solvent candidate, EA is considered to be a good choice. Physical properties of EA have been referred in Table 1. Linear carboxylate EA can be introduced in LiBOB-GBL-based electrolyte because of its three merits. First of all, EA has a low viscosity, which can render the GBL-based electrolyte with a much lower viscosity. Secondly, a trace of EA has been discovered in the decomposing products of GBL, which will be described in detail in our other papers. It is expected that mixing EA with GBL can depress the decomposition reaction of GBL and electrolyte with better electrochemical stability can be obtained. Thirdly, LiBOB is almost insoluble in sol-

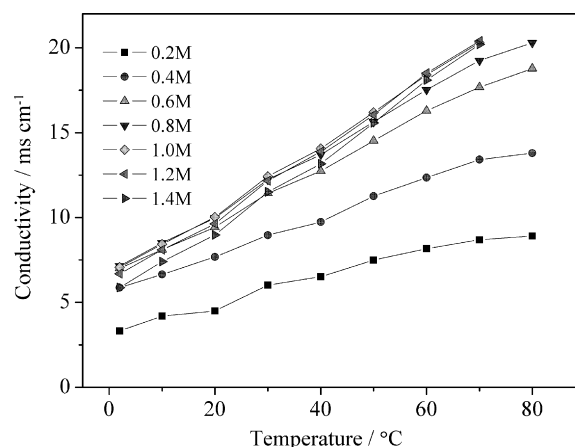


Fig. 4. Change of conductivity with temperature for LiBOB-GBL/EA (1:1, wt) system.

vents of low dielectric constant such as linear carbonates [7]. EA has higher dielectric constant than most linear carbonate. Solvent with higher dielectric constant could facilitate lithium salt dissolving and conductivity increasing, both of which are the key problems to be solved in LiBOB-based electrolytes. In the following work, the electrolyte is optimized by mixing EA with pure GBL to get a mixture of GBL/EA (1:1, wt).

3.2.1. The solubility and the conductivity measurement

The LiBOB salt concentration in the saturated solution of LiBOB-GBL/EA (1:1, wt) at room temperature is about 2.0 M. Different electrolytes composed of different LiBOB salt concentrations ranged from 0.2 M to 1.4 M were fabricated and their conductivities were tested (Fig. 4). At 30 °C, conductivity of 1.0 M LiBOB-GBL/EA (1:1, wt) solution is 12.43 ms cm⁻¹, which is the highest of all the electrolytes with different salt concentration. It can be concluded that adding EA to pure GBL, though the solubility is decreased, the conductivity increases significantly because decreased viscosity.

3.2.2. The application of GBL/EA system as mixed solvent in lithium-ion battery electrolyte

LiBOB salt concentration of a low concentration 0.2 M, an intermediate concentration 0.7 M, and a high concentration 1.2 M were chosen to dissolve in the solvent of GBL/EA (1:1, wt). The electrolytes with three different LiBOB salt concentrations were used in Li/LiFePO₄ half cells tested.

The cycle performances are shown in Fig. 5. Compared to pure GBL system, the initial discharge capacity is improved in the mixed solvent system at room temperature of 20 °C. The activate procedure is still a long term. Discharge capacity increases steadily in the 50 cycles tested. The initial discharge capacity of cell with 0.2 M LiBOB-GBL/EA (1:1, wt) electrolyte is 69.4 mAh g⁻¹, which is the highest of the three types cells. Cell with the low salt concentration electrolyte also exhibits the best capacity performance. After 50 cycles, the discharge capacity of cell with 0.2 M LiBOB is 126.4 mAh g⁻¹. The capacity performance of cell with high salt concentration electrolyte is the poorest. The initial discharge capacity is only 44.5 mAh g⁻¹ and maintains 92.6 mAh g⁻¹ after 50 cycles. In the first 50 cycles, no capacity fading is observed in any of the three types cells. It can be seen that at low discharge rate of 0.5 C, the low ion concentration shows no negative effect on the capacity property, though the conductivity is relatively low.

At elevated temperature of 50 °C, LiBOB-GBL/EA (1:1, wt) system presents wonderful cell performance. The activate procedure is obvious shorten to 3 cycles. The discharge capacity does not fade after 50 cycles. Cell using intermediate concentration of 0.7 M electrolyte possesses the best capacity performance. The initial dis-

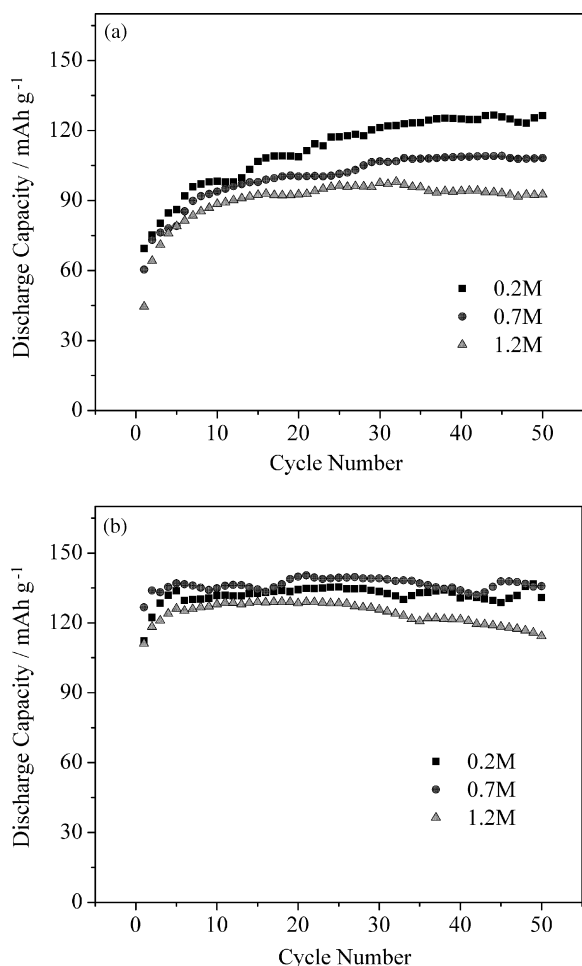


Fig. 5. Cycling performances of LiFePO₄/Li half cells with different LiBOB salt concentration dissolved in GBL/EA (1:1, wt) solution at 0.5 C (a) at room temperature (20 °C); (b) at elevated temperature (50 °C).

charge capacity is 126.7 mAh g⁻¹. After the third cycle, discharge capacity reaches 135–140 mAh g⁻¹. Cell with high concentration of 1.2 M still has the worst capacity property with the discharge capacity of about 125 mAh g⁻¹.

It can be concluded that at elevated temperature, the best electrolyte formula contains more LiBOB salt than at room temperature. At room temperature, viscosity is the key factor that influences the cell capacity most. Electrolyte with more LiBOB salt has high viscosity since the large BOB⁻ anion increase the viscosity of solution. Due to the high viscosity of electrolyte, the interface impedance is relatively high and the separator wettability is poor. Thus cell with low salt concentration performs best despite of the low conductivity. At elevated temperature, viscosity of electrolyte decreases and conductivity becomes the key factor. Thus cell with higher conductivity electrolyte (0.7 M) performs best. However, cell with 1.2 M salt concentration has the worst capacity performance at both temperatures. It can be seen from Fig. 5 that high concentration electrolyte conductivity and low concentrate one are identical at

the temperature ranged from 20 °C to 50 °C. In other word, if the salt concentration is over 0.7 M, the conductivity does not increase with increasing concentration but the viscosity gets higher. Therefore the intermediate salt concentration of 0.7 M is the best choice. It should be noticed that when temperature is over 50 °C, conductivity of 1.2 M electrolyte exceeds the one of 0.7 M electrolyte and the difference between them increases with the increasing temperature. That means at a high temperature of 80 °C or even higher, cell with high salt concentration probably performs better.

4. Conclusion

Using cyclic carboxylate GBL in lithium-ion battery electrolyte as the main solvent of the LiBOB can solve the problems of small solubility and low conductivity. LiBOB–GBL electrolyte exhibits good electrochemical stability in the voltage range of 0–5 V, which is suitable to be the candidate of the lithium-ion battery electrolyte. At room temperature, LiFePO₄/Li half cells with LiBOB–GBL electrolyte have good cycle performances with no capacity fading in the first 50 cycles. The discharge capacity is stabilized at about 120 mAh g⁻¹. GBL is not compatible with LiPF₆, which can be concluded from the poor cycle performance. The reason is still unclear and further study is needed.

Linear carboxylate EA was mixed with pure GBL to get a lower viscosity mixture of GBL/EA (1:1, wt). LiBOB–GBL/EA system was tested. LiBOB–GBL/EA (1:1, wt) system also has high conductivity. In the cell test, LiBOB salt concentration of a low concentration 0.2 M, an intermediate concentration 0.7 M, and a high concentration 1.2 M were chosen to dissolve in the solvent of GBL/EA (1:1, wt) to form the electrolytes. It can be concluded that at a low discharge rate of 0.5 C, cell with 0.2 M LiBOB–GBL/EA (1:1, wt) electrolyte exhibits the best capacity performance at room temperature and 0.7 M LiBOB–GBL/EA (1:1, wt) electrolyte performs best at elevated temperature.

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