



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

ARTICLE INFO

Article history:

Received 30 June 2008

Received in revised form 21 December 2008

Accepted 22 December 2008

Available online 30 December 2008

Keywords:

Lithium-ion battery

Electrolyte

LiBOB

 γ -Butyrolactone

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

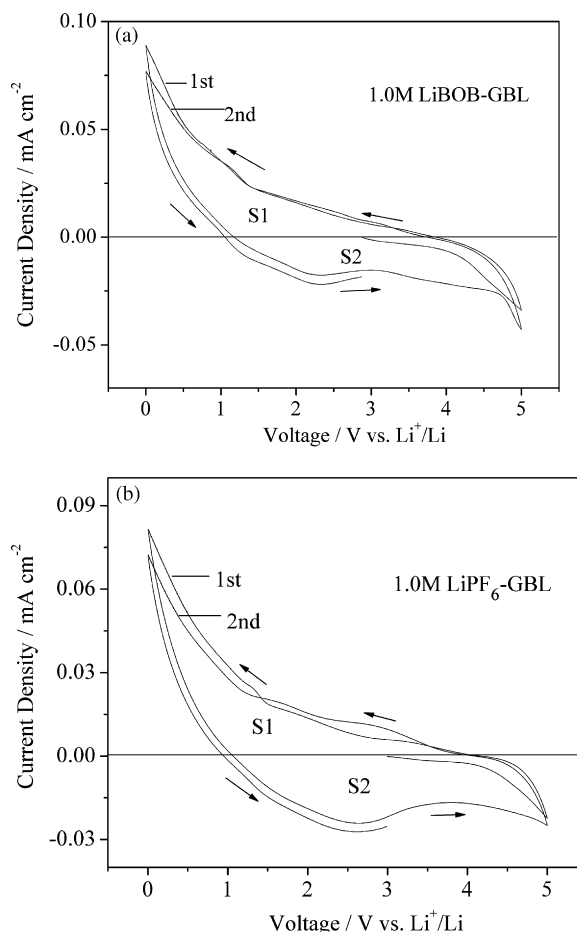


Fig. 1. The current–potential curve at the scan rate of 5 mV s^{-1} (a) 1.0 M LiBOB-GBL and (b) 1.0 M LiPF_6 -GBL.

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-

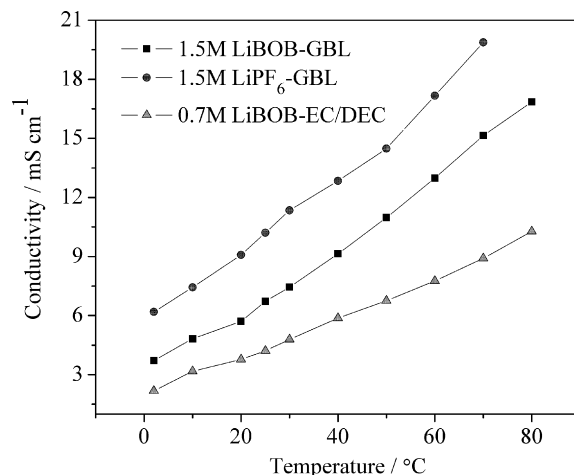


Fig. 2. Change of conductivity with temperature for 1.5 M LiBOB-GBL, 1.5 M LiPF_6 -GBL, and 0.7 M LiBOB-EC/DEC (1:1, wt) solution.

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