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A preliminary study on a new LiBOB/acetamide solid phase transition electrolyte

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ABSTRACT

New solid electrolytes containing acetamide and lithium bioxalato borate (LiBOB) with different molar ratios have been investigated. Their melting points (T_m) are around 42 °C. The ionic conductivities and activation energies vary drastically below and above T_m, indicating a typical feature of phase transition electrolyte. The ionic conductivity of the LiBOB/acetamide electrolyte with a molar ratio of 1:8 is 5×10^{-8} S cm^{-1} at 25 °C but increases to 4×10^{-3} S cm^{-1} at 60 °C. It was found that anode materials, such as graphite and $Li_4Ti_5O_{12}$, could not discharge and charge properly in this electrolyte at 60 °C due to the difficulty in forming a stable passivating layer on the anodes. However, a Li/$LiFePO_4$ cell with this electrolyte can be charged properly after heating to 60 °C, but cannot be charged at room temperature. Although the LiBOB/acetamide electrolytes are not suitable for Li-ion batteries due to poor electrode compatibility, the current results indicate that a solid electrolyte with a slightly higher phase transition temperature than room temperature may find potential application in stationary battery for energy storage where the electrolyte is at high conductive liquid state at elevated temperature and low conductive solid state at low temperature. The interaction between acetamide and LiBOB in the electrolyte is also studied by Raman and FTIR spectroscopy.

1. Introduction

In amide type organic compounds ($RCONH_2$), such as acetamide (CH_3CONH_2) or urea molecule (NH_2CONH_2), the O atom is partially negatively charged and the N atom is partially positively charged. The dipolar property produces a resonance structure with a zwitterion form [1–3]. When amide compounds are mixed with lithium salt (LiX), the association of Li and X in the LiX lattice and hydrogen bonds (–C=O·H–N–) among $RCONH_2$ molecules are weakened due to a columbic interaction between Li^+ and the $O^{\delta-}$ atom in $RCONH_2$ and the interaction between X^- and the $N^{\delta+}$ atom. Consequently, a new group of liquid electrolytes can be produced [4–10]. The eutectic temperature of lithium bis(trifluoromethane sulfone)imide ($LiN(SO_2CF_3)_2$, LiTFSI) and acetamide system is as low as −67 °C [6,7]. The LiX–$RCONH_2$ liquid electrolytes show potential application in lithium ion batteries [2–9] and electrochemical double layer capacitors [10–12]. Up to now, LiTFSI [6,7], lithium bis(perfluoroethysulfonyl) imide ($LiN(SO_2C_2F_5)_2$, LiBETI) [8], lithium perchlorate ($LiClO_4$) [12] and lithium triflate ($LiCF_3SO_3$) [12–14] have been studied as lithium salts in this series of electrolytes.

Lithium bis(oxalato)borate (LiBOB) has attracted much attention as a lithium salt or additive in nonaqueous electrolytes for lithium ion batteries, due to its high solubility in organic solvents, low toxicity, and high chemical and electrochemical stability [15–20]. Therefore, it is interesting to investigate the LiBOB–$RCONH_2$ electrolyte system. In this paper, the electrolytes composed of lithium bis(oxalato)borate (LiBOB) and acetamide are investigated for the first time. Different from reported LiX–$RCONH_2$ systems, the melting points (T_m) of the new electrolytes are around 42 °C. The ionic conductivity and activation energy show a large difference below and above T_m. Consequently, the electrochemical activity of the lithium batteries using these new solid electrolytes is influenced strongly by the temperature.

2. Experimental

2.1. Preparation of the electrolyte

The electrolytes were prepared by mixing anhydrous LiBOB (Shanghai Topsol, 99%) and acetamide (Aldrich, 99%) powder with the required molar ratio in an argon-filled glove box first, the mixture was heated until a homogeneous melt was formed and then cooled down to room temperature naturally.

2.2. Thermal behavior measurement of the electrolyte

The thermal behavior was investigated using a NETSCH STA 449C differential scanning calorimeter. About 10 mg sample was sealed in a special aluminum pan in the glove box. Then the aluminum pan was transferred onto the DSC's sample holder. The pan containing the mixture was first cooled down to −50 °C and then heated to 100 °C at a rate of 5 K min^{-1}.

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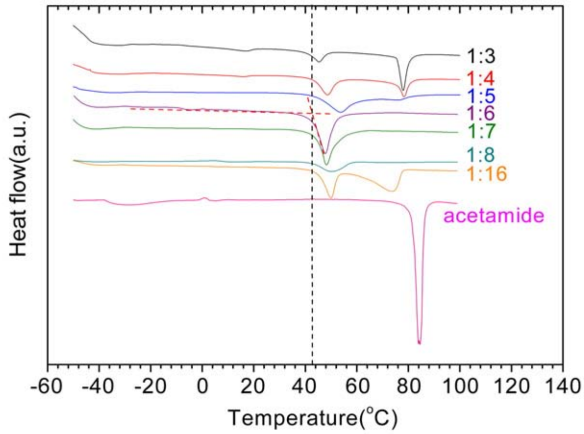

Fig. 1. DSC curves of pure acetamide and LiBOB/acetamide with different molar ratios.

2.3. Conductivity measurement

The ac conductivity was measured by a HP4192A impedance analyzer in the frequency range of 5 Hz–13 MHz with 5 mV amplitude. The sample had been kept at each temperature for an hour before each measurement.

2.4. Spectroscopic investigation

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Bruker vector200 FTIR spectrometer. The electrolyte sample was mixed with dried KBr powder and was compressed into a pellet for IR measurement. Raman spectroscopy measurements were performed by a Bruker RFS 100 FT-Raman spectrometer. The samples were sealed in disposable optical glass test-tubes. The wavelength of the laser was 1.064 µm. The resolution of the IR and Raman spectrometers were both set to 4 cm^{-1}. All of the above samples were prepared and sealed in the argon-filled glove box.

2.5. Electrochemical test

The $LiFePO_4$ electrode was composed of 85 wt.% $LiFePO_4$ (lab-made), 8 wt.% polyvinylidene fluoride (PVDF), and 7 wt.% carbon black. The graphite electrode was composed of 95 wt.% graphite (CMS, 15 µm, graphitized at 2600 °C, Shanghai Shanshan, China) and 5 wt.% PVDF. The $Li_4Ti_5O_{12}$ electrode was composed of 85 wt.% $Li_4Ti_5O_{12}$ (lab-made), 8 wt.% PVDF and 7 wt.% carbon black. Al foil was used as cathode current collector and Cu foil was used as anode current collector. The discharge–charge experiment was carried out by a Land battery test system at certain temperature. The cells had been kept at each temperature for 12 h before test.

Electrochemical impedance spectra were recorded by a BAS-Zahner IM6e impedance analyzer in the frequency range of 5×10^{-3} Hz–100 kHz with 5 mV amplitude. The cell was kept at each temperature for 12 h before measuring.

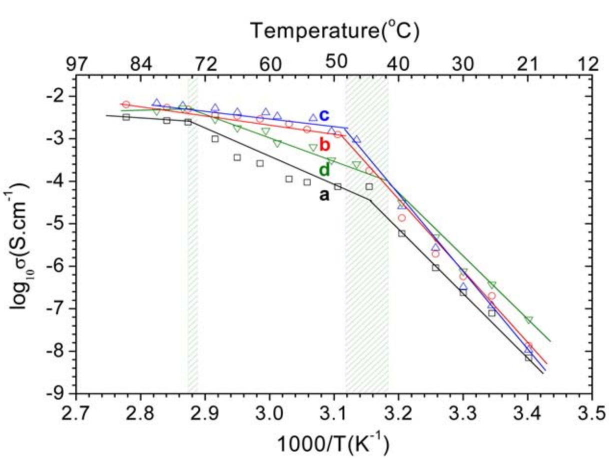

Fig. 2. Arrhenius plots of the LiBOB/acetamide electrolytes with different molar ratios: a: LiBOB/acetamide (1:4); b: LiBOB/acetamide (1:6); c: LiBOB/acetamide (1:8); d: LiBOB/acetamide (1:16).

Table 1
*E*a comparison of different electrolytes in high and low temperature ranges.

No.	Electrolyte	Ea (kJ mol^{-1}) (eV)		
		High temperature	Middle temperature	Low temperature
a	LiBOB–acetamide (1:4)	22.9 (0.24)	109 (1.13)	299 (3.10)
b	LiBOB–acetamide (1:6)	40.8 (0.42)		313 (3.24)
c	LiBOB–acetamide (1:8)	29.0 (0.30)		327 (3.39)
d	LiBOB–acetamide (1:16)	26.5 (0.27)	94.0 (0.97)	265 (2.75)

3. Results and discussion

3.1. Thermal properties and ionic conductivity of the electrolytes

Fig. 1 shows the DSC curves of the electrolytes. Beyond the molar ratio range of 1:6 to 1:8 for LiBOB to acetamide, two endothermic peaks can be observed, indicating the existence of liquid–solid coexistence regime between 40 and 80 °C. Within this molar ratio range, only one endothermic peak is observed. The melting points for LiBOB/acetamide (1:6 to 1:8) are around 42 °C. It is much higher than the eutectic temperature of −67 °C for LiTFSI/acetamide (1:4) [7], −57 °C for $Li[N(SO_2C_2F_5)_2]$(LiBETI)/acetamide (1:4) [8] and −52 °C for $LiCF_3SO_3$/acetamide (1:5) [12].

Fig. 2 shows the conductivities of the electrolytes in a temperature range from 20 °C to 90 °C. When the LiBOB/acetamide molar ratio is 1:16 or 1:4, the Arrhenius curve shows three slopes, and when the LiBOB/acetamide molar ratio is 1:8 or 1:6, the Arrhenius curves show two slopes. The appearance of two or three slopes is consistent with the liquid–solid phase transition shown in the DSC curves. The activation energies of the electrolytes over different temperature ranges are listed in Table 1. It can be seen that low activation energy and high conductivity are achieved in the liquid phase region and the liquid–solid coexistence region.

3.2. Interaction between LiBOB and acetamide

LiBOB starts to decompose at 300 °C before melting and the melting temperature of acetamide is 81.2 °C. The melting temperatures of the

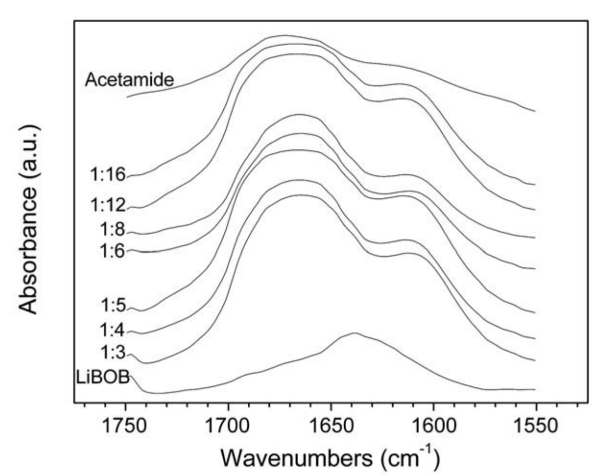

Fig. 3. IR spectra of the LiBOB/acetamide electrolytes with different molar ratios.