

Preparation and characterization of high salts polymer electrolyte based on poly(lithium acrylate)^①

TANG Aì-dong(唐爱东), HUANG Kè-long(黄可龙),

PAN Chun-yue(潘春跃), LU Cui-hong(卢翠红)

(School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China)

Abstract: Novel polymer electrolytes were prepared by highly mixing poly(lithium acrylate) (PPALi) with eutectic lithium salts of lithium acetate and lithium nitrate. Poly(lithium acrylate) was prepared by inverse emulsion polymerization from acrylic acid and LiOH. Phase transition temperatures were measured for all the eutectic lithium of binary system samples as a function of the concentration of Li(CH₃COO), and the mixtures exhibit the lowest phase transition temperatures of (448 ± 2) K at about 50% (mass fraction) Li(CH₃COO). Thermogravimetry(TG) and X-ray diffraction(XRD) analysis indicate the formation of a novel polymer-salt complex. The highest conductivity (approximately $4.97 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$) is found at room temperature with the electrolyte composition of eutectic mixture of about 80% (mass fraction), poly(lithium acrylate) 20% under quickly cooling condition, which is 150% higher than that under natural cooling condition.

Key words: polymer electrolyte; thermal stability; ionic conductivity

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1 INTRODUCTION

Worldwide research and efforts are currently underway to fabricate all-solid-state, rechargeable Li and Li-ion batteries utilizing Li⁺-conductive polymer electrolytes^[1]. Solid polymer electrolytes possesses many advantages including high ionic conductivity, high specific surface energy, solvent free, wide electrochemical stability windows, light and easy processability^[2]. Apart from polyethylene oxide (PEO)^[3], poly(vinyl alcohol) (PAV)^[4], poly(tetramethylene glycol) (PTG)^[5], poly(vinyl difluoride) (PVDF)^[6], poly(trimethylene carbonate) (PTMC)^[7] and poly(acrylonitrile) (PAN)^[8], poly(lithium acrylate) (PPALi) has also been used as the polymer host material. In most solid polymer electrolytes, the polymer host is doped with inorganic salts and one or more plasticizers in order to improve the conductivity. The conductivity is highly related to the species of polymer and additive salts. The main purpose of the present work is to discuss the effects of the extremely salt-riched concentration and different cooling mode on ionic conductivity of polymer electrolyte, and also to determine the structure of novel polymer-in-salt mixture based on poly(lithium acrylate). Although a certain amount of general information is available on the thermal behavior of the nitrate and acetate^[9], we have also re-measured these salts for the sake of completeness

in order to make comparisons with the other investigated substances measured under the same experimental conditions.

2 EXPERIMENTAL

2.1 Preparation of binary lithium salts sample

All reagents used in this experiment were analytical grade. The Li(CH₃COO) and LiNO₃ were dried to constant mass at 150 °C, and stored over silica gel in desiccator before used. The binary lithium salts were prepared by mixing appropriate amounts of Li(CH₃COO) and LiNO₃, the obtained binary lithium salts were milled in an agate mortar to form fine powders. The samples were done in quartz crucible to melt (no chemical reaction between the quartz and lithium salts was observed) and stored over silica gel in desiccator until used for further experiments.

2.2 Preparation of poly(lithium acrylate) (PLA)

50 mL acrylic acid monopolymer solution (0.02 mol/ mL) was slowly added to 100 mL LiOH solution, stirring at 40 °C for 30 min, the solution was then heated at 70 °C for 1 h. After adding 100 mL NH₄S₂O₄ (0.1 mol/ mL) and methyl alcohol, the precipitate, poly(lithium acrylate) (PLA) was obtained by filtered and washed three times by methyl alcohol, the product was dried in vacuum at 90 °C for 48 h.

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Correspondence: PAN Chun-yue, Professor; + 86-731-8876099; E-mail: panchunye@sina.com

2.3 Preparation of polymer electrolyte

Samples of lithium nitrate and lithium acetate were dried at 90 °C for 4h before used. After thoroughly mixing PLA, LiNO_3 , LiOAc in the desired proportions at proper temperature, polymer electrolyte films were prepared by quick cooling in liquid nitrogen or natural cooling with oven to ambient temperature, then stored over silica gel in desiccators for use.

2.4 Thermal analysis

Thermal analysis of the polymer electrolyte film and lithium salts were carried out using a WRT-3P Micro-Thermalbalance and SCRKZ220-5 Differential Thermal Analysis (DTA) apparatus in a quiescent air atmosphere at heating rate of 8 °C/min, with $\alpha\text{Al}_2\text{O}_3$ used as a reference material. Time, temperature and temperature differences were recorded simultaneously during the experiment.

2.5 Conductivity measurement

The total ionic conductivities at ambient temperature were obtained in a sandwich format cell (INOX/electrolyte/INOX) by electrochemical impedance spectroscopy using an electrochemical working station (CHI660A, made in china) in 0.01 Hz ~100 kHz.

2.6 X-ray diffraction (XRD)

The structure of the materials were characterized using the X-ray power diffraction (SIMENS-D500 XRD) using $\text{Cu K}\alpha$ irradiation ($\lambda = 1.5406 \text{ \AA}$) at 50 kV at room temperature. The data were collected at rate of $0.5(^{\circ})/\text{min}$ in the diffraction angle range of 8° to 47° .

3 RESULTS AND DISCUSSION

3.1 FTIR studies

The IR spectra of acrylate lithium and poly(lithium acrylate) are shown in Fig. 1.

The vibrational bands at 3405 cm^{-1} and 1440 cm^{-1} in Fig. 1(a) were assigned to C—H asymmetric stretching and bending vibrations of acrylate lithium^[10], respectively. The frequencies 1645 and 996 cm^{-1} were due to C=C stretching and bending vibrations of acrylate lithium in Fig. 1(a). The peaks at 1572 , 1278 and 845 cm^{-1} may be assigned to stretching vibrations of C=O, C—O and symmetrical stretching of C—O—C of acrylate lithium and poly(lithium acrylate). The absorption peak at 640 cm^{-1} in Fig. 1(b) may be attributed to the amorphous poly(lithium acrylate). The spectra shows that there is no absorption bands of C=C at 1645 and 996 cm^{-1} , indicating no existence of C=C in PPALi.

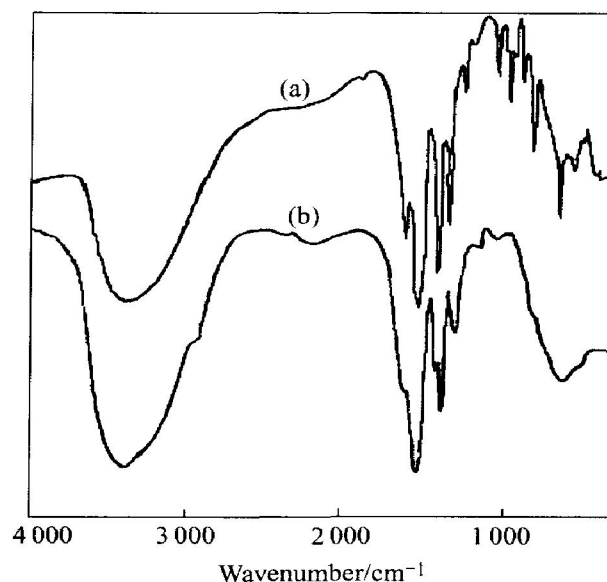


Fig. 1 IR spectra of acrylate lithium(a) and poly(lithium acrylate) (b)

3.2 DTA analysis and phase diagram of binary $\text{Li}(\text{CH}_3\text{COO})$ - LiNO_3 system

Based on DTA curves for all the compositions during the heating process, the phase diagram of $\text{Li}(\text{CH}_3\text{COO})$ - LiNO_3 system is shown in Fig. 2. The change of phase state is answer for the law of binary simple eutectic mixture. $\text{Li}(\text{CH}_3\text{COO})$ and LiNO_3 formed the eutectic mixture at about 50% $\text{Li}(\text{CH}_3\text{COO})$ with the melting temperature of $(175 \pm 2) ^{\circ}\text{C}$. The melting point reduces about $77 - 112 ^{\circ}\text{C}$ compared with the melting point of single composition.

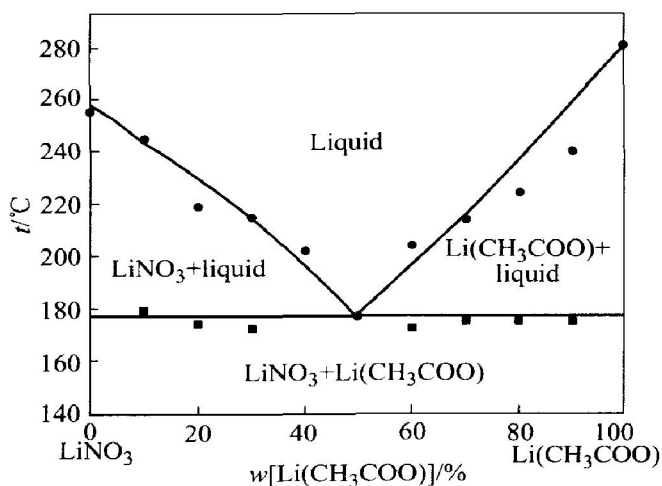


Fig. 2 Phase diagram of $\text{Li}(\text{CH}_3\text{COO})$ - LiNO_3 system

The conductivities at room temperature for various $\text{Li}(\text{CH}_3\text{COO})$ concentration of binary system are shown in Fig. 3. The lowest conductivity of LiNO_3 - $\text{Li}(\text{CH}_3\text{COO})$ mixtures is observed when the content of $\text{Li}(\text{CH}_3\text{COO})$ increases to 50%.

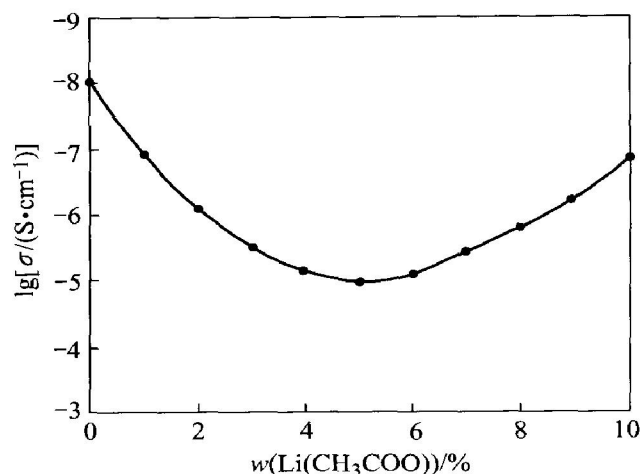


Fig. 3 Plot of $\lg \sigma$ versus concentration of $\text{Li}(\text{CH}_3\text{COO})$ at room temperature

3.3 TG analysis of $\{\text{CH}_2\text{CHOOli}\}_n$, polymer electrolyte and lithium salts

Thermal characterization of polymer electrolyte and various salts are shown in Table 1. The sample of $\{\text{CH}_2\text{CHOOli}\}_n$ starts to lose mass below 200 °C. This initial mass loss results from residual solvent evaporation. The second mass loss happens around 405 °C. This may be due to the decomposition of sample. The third mass loss begins around 722 °C, which can be attributed to the decomposition of the residual.

The TG data of poly(lithium acrylate)/salts complex shows that mass loss of 4.86% exists below 100 °C, which may be due to the absorbed moisture. The polymer electrolyte decomposes around 313 °C with mass loss of 11%, and around 354 °C just 20.35%. The final mass loss of 24.37% around 766 °C results from decomposition of the residual polymer electrolyte.

The anhydrous lithium acetate shows a theoretical mass loss of 39.24%, expected in the temperature from 358 °C. Corresponding to decomposition of $\text{Li}(\text{CH}_3\text{COO})$, the result in excellent agreement with the experimental value of 39.48%. At 802 °C, decomposition with the generation of Li_2CO_3 takes place. A mass loss of 28.46% is expected (observed mass loss, 28.13%).

The thermolysis of $\text{LiNO}_3 \cdot n\text{H}_2\text{O}$ is rather simple. Water is given off from 65 °C to 201 °C (experimental mass loss 10.57%, calculated for loss of 0.45 mol water, 10.50%). A mass loss of 63.00% is expected (mass loss observed, 63.07%). The results of thermal behavior of $\text{Li}(\text{CH}_3\text{COO})\text{-LiNO}_3$, PLA and SPE show that polymer/salts complex was formed after poly(lithium acrylate) dissolving in lithium salts because of no single thermal characterization of raw material ($\text{Li}(\text{CH}_3\text{COO})$ -, LiNO_3 and PLA).

The presence of some extent of water content was characterized by TG of about 1% – 5%, even after careful drying procedures in the range of the salt studied. This water content could give an additional contribution to the dissolution and thus increases the conductivities. So, polymer electrolytes can be obtained by dissolving the appropriate polymers and lithium salts in solvent, then evaporating the solvent and drying of the samples at high vacuum.

3.4 XRD

Fig. 4 shows XRD patterns of polymer/salts complexes under different cooling conditions.

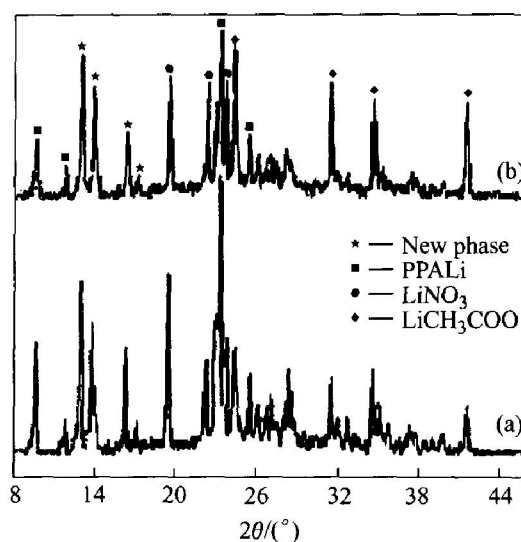


Fig. 4 X-ray diffraction spectrum of complex with poly(lithium acrylate) (20)- $[\text{Li}(\text{CH}_3\text{COO})\text{-LiNO}_3]$ (80) under natural cooling (a) and quick cooling (b)

Table 1 Thermal decomposition parameters of polymer electrolyte and salts

Sample	Step 1		Step 2		Step 3		Step 4	
	$t_{pl}/\text{°C}$	Mass loss/ %	$t_{pl}/\text{°C}$	Mass loss/ %	$t_{pl}/\text{°C}$	Mass loss/ %	$t_{pl}/\text{°C}$	Mass loss/ %
LiOAc	134	7.57	499	39.48			802	28.13
$\text{LiNO}_3 \cdot n\text{H}_2\text{O}$	66	3.58	201	7.07			650	63.07
Poly(lithium acrylate)	192	27.66	405	37.10			722	18.53
SPE	75	4.86	313	11.00	354	20.35	766	24.37

There are peaks corresponding to the pure $\text{Li}(\text{CH}_3\text{COO})$ and LiNO_3 appeared in the complex which indicates the incomplete dissolution of high concentration salt in poly(lithium acrylate) matrix.

There was a decrease in the relative intensity of the peaks under quickly cooling condition. This result can be interpreted by considering the Hodge et al's Criterion that establishes a correlation between the height of the peak and the degree of crystallinity^[11]. The X-ray diffraction analysis reveals that the quickly cooling sample consisting of $[\text{Li}(\text{CH}_3\text{COO}) (40)\text{-LiNO}_3(40)]\text{-poly}(\text{lithium acrylate}) (20)$ shows less crystallinity compared to the natural cooling sample^[10].

3.5 Ionic conductivity

The typical impedance plot (Z' and Z'') for the electrolyte composition $\text{LiNO}_3(40)\text{-LiCH}_3\text{COO} (40)\text{-poly}(\text{lithium acrylate}) (20)$ is shown in Fig. 5. In the impedance response behaviour, the disappearance of the high frequency semicircular portion leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction^[5]. The conductivity was calculated according to the value of R in the complex impedance plot and the known area and thickness of the SPE film. The room temperature conductivity of the quickly cooled sample is $4.97 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, which is 150% higher than that obtained under natural cooling condition^[10].

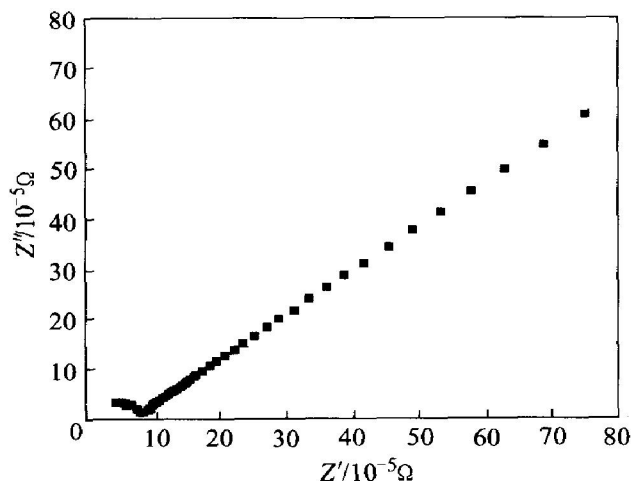


Fig. 5 Impedance diagram of $\text{LiNO}_3(40)\text{-LiCH}_3\text{COO}(40)\text{-poly}(\text{lithium acrylate})(20)$ polymer complex at room temperature under quick cooling condition

4 CONCLUSIONS

The phase diagram of binary $\text{Li}(\text{CH}_3\text{COO})\text{-LiNO}_3$ system is suggested, there is a eutectic at $(175 \pm 2)^\circ \text{C}$ and with 50% $\text{Li}(\text{CH}_3\text{COO})$, so the highest conductivity (approximately $4.97 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$) is found at room temperature with $\text{LiNO}_3(40)\text{-LiCH}_3\text{COO}(40)\text{-poly}(\text{lithium acrylate})(20)$ polymer complex under quick cooling condition, which is 150% higher than that obtained under natural cooling condition.

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