

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Single-Ion Conduction and Electrochemical Characteristics of Poly (Oxyethylene)/ Lithium Methoxy Oligo(Oxyethylene) Sulfate Blend

Hongming Chen<sup>a</sup>; Zhenghua Deng<sup>a</sup>; Yungui Zheng<sup>a</sup>; Wu Xu<sup>a</sup>; Guoxiang Wan<sup>a</sup>

<sup>a</sup> Chengdu Institute of Organic Chemistry Chinese Academy of Sciences, Chengdu, People's Republic of China

**To cite this Article** Chen, Hongming , Deng, Zhenghua , Zheng, Yungui , Xu, Wu and Wan, Guoxiang(1996) 'Single-Ion Conduction and Electrochemical Characteristics of Poly (Oxyethylene)/ Lithium Methoxy Oligo(Oxyethylene) Sulfate Blend', Journal of Macromolecular Science, Part A, 33: 9, 1273 – 1281

**To link to this Article:** DOI: 10.1080/10601329608010921

**URL:** <http://dx.doi.org/10.1080/10601329608010921>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# SINGLE-ION CONDUCTION AND ELECTROCHEMICAL CHARACTERISTICS OF POLY(OXYETHYLENE)/LITHIUM METHOXY OLIGO(OXYETHYLENE) SULFATE BLEND

HONGMING CHEN, ZHENGHUA DENG, YUNGUI ZHENG,  
WU XU, and GUOXIANG WAN\*

Chengdu Institute of Organic Chemistry  
Chinese Academy of Sciences  
P.O. Box 415, Chengdu 610041, People's Republic of China

## ABSTRACT

The ion conduction of a blend of poly(oxyethylene) (PEO) and lithium methoxy oligo(oxyethylene) sulfate (SAL<sub>8</sub>) and its electrochemical characteristics were studied. The maximum ambient conductivity of the blend reaches  $1.2 \times 10^{-6}$  S/cm. The blend exhibits single-ion conduction, excellent mechanical performance, and electrochemical stability. A battery of Li/PEO + SAL<sub>8</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> has a constant discharge capacity at different discharge current densities up to a certain voltage, while the discharge capacity of Li/P (MEO<sub>16</sub>-AM) + LiClO<sub>4</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> decreases with an increase of the discharge current density.

## INTRODUCTION

Polymer solid electrolyte (PSE) is getting more and more attention for its potential uses in solid lithium batteries, solid electrochromic display devices, capacitors, etc. [1–3]. In order to increase the conductivity of PSE, the method of blending liquid electrolyte with polymer to prepare gel electrolyte [4, 5] is used. The ambient conductivity of this kind of plasticized solid electrolyte exceeds  $10^{-3}$  S/cm. But it also has some disadvantages, such as poor electrochemical stability, low

cationic transference number, etc. Angell et al. put forward a new concept of blending a small amount of polymer with a large amount of low temperature molten salt to make a kind of "polymer in salt" solid electrolyte [6, 7]. In this kind of electrolyte the polymer supplies the mechanical properties and the molten salt supplies the carrier. This electrolyte has high ambient conductivity and single-ion conduction. In this paper we report the ion conduction and electrochemical characteristics of the elastic blend of poly(oxyethylene) (PEO) and the low temperature molten salt lithium methoxy oligo(oxyethylene) sulfate ( $\text{SAL}_8$ ).

## EXPERIMENTAL

### Materials

The molecular weight of PEO is  $6 \times 10^5$ . The synthesis of  $\text{SAL}_8$  was processed according to the literature [8].  $\text{SAL}_8$  and PEO were dissolved together in a solvent ( $\text{CH}_3\text{CN}$ ), and the electrolyte membranes were prepared by casting the solution. The membranes were dried under vacuum at  $100^\circ\text{C}$  for 24 hours before use.

The anode material of the lithium battery was lithium foil and the cathode materials were polyaniline/graphite and  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ /graphite. The assembly of the cells was carried out in a moistureless glove box filled with argon.

### Measurement

The ac conductivity measurements were carried out at 1100 Hz with the conductometer DDS-IIA and a temperature controlled apparatus. The dc conductivity measurements, in which a lithium electrode was utilized, were made by applying a constant voltage (3.0 V) over the cell and recording the current with a millivolt-ammeter. A polarization reversing method was employed to measure the lithium ion transference number of the sample [9]. A linear voltage scanning method (scan rate: 1.0 mV/s) was adopted to study the decomposition voltage by using inert electrodes. A constant-current procedure was used to study the discharge characteristics of the Li/solid electrolyte/cathode cell.

All measurements were carried out under dry conditions.

The thermal behavior was investigated with the Perkin-Elmer DSC-7 system in the temperature range of  $-100$  to  $200^\circ\text{C}$  with a temperature increase of  $20^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSIONS

### Relationship between Ionic Conductivity and Composition of the Blend

Figure 1 shows the composition dependence of the ion conductivity of PEO/ $\text{SAL}_8$ . The increase of ion conductivity at low  $\text{SAL}_8$  content is due to the increase of the carrier number and the decrease of the glass transition temperature ( $T_g$ ) by adding the  $\text{SAL}_8$  content. The decrease of  $T_g$  can be seen in Fig. 2. The  $T_g$ s of the blends with  $\text{SAL}_8$  contents of 50, 67, and 75% are  $-15$ ,  $-32$ , and  $-70^\circ\text{C}$ , respectively. This is because  $\text{SAL}_8$  is a noncrystalline liquid at room temperature [8].

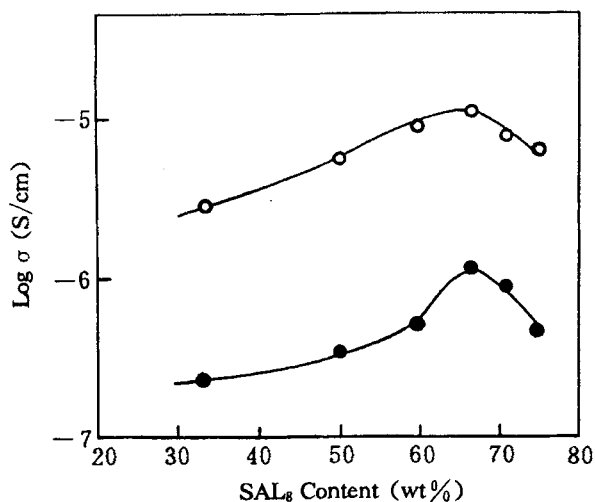


FIG. 1. Composition dependence of ion conductivity of PEO/SAL<sub>8</sub> blend. Temperature: 25°C (●), 50°C (○).

However, in the high salt concentration region, the conductivity decreases with an increase of SAL<sub>8</sub> content. This could be explained by the formation of ion pairs and ion clusters which results from excessive salt and which greatly impedes ion transference [10, 11], and this negative effect exceeds the favorable effect of the decrease of  $T_g$ . As a result, the conductivity of the blend is not benefited by the excessive salt. When the SAL<sub>8</sub> content is 67% (wt%), the ion conductivity reaches the maximum ( $\sigma_{25^\circ\text{C}} = 1.2 \times 10^{-6}$  S/cm,  $\sigma_{50^\circ\text{C}} = 1.1 \times 10^{-5}$  S/cm).

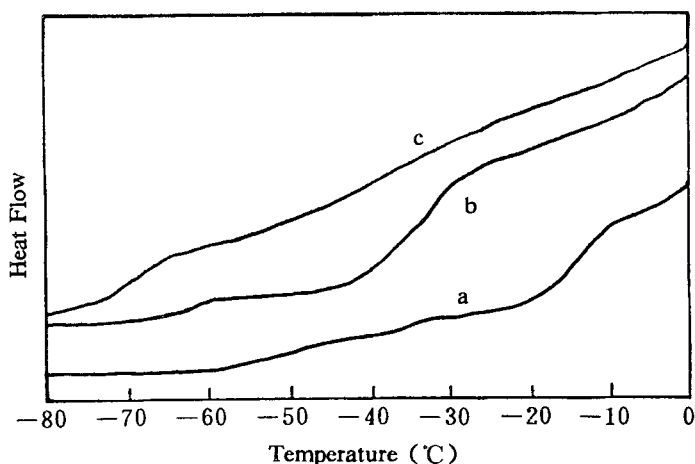


FIG. 2. DSC curves for PEO/SAL<sub>8</sub> blend: (a) PEO/SAL<sub>8</sub> (w/w) = 1:1, (b) PEO/SAL<sub>8</sub> (w/w) = 1:2, (c) PEO/SAL<sub>8</sub> (w/w) = 1:3.

Figure 3 shows that the temperature dependence of conductivity in the blend with a low salt content does not follow the Arrhenius equation, but at a high salt content it is of the Arrhenius type. This means that polymer segmental movement has a considerable effect on the ion conductivity in the blend with a low salt content. When the salt content is high, polymer segmental movement has an insignificant influence on the ion conductivity because of the low polymer content in the blend. The polymer acts mainly as a backbone of the blend.

### Polarization Characteristics and Ion Transference Number of the Blend

Figure 4 presents the dc polarization characteristics of the blend. As a comparison, the results of our previous works [12] are quoted. From Fig. 4 it can be seen that the dc conductivity of PEO/SAL<sub>8</sub> remains constant during polarization, which proves that the blend is a single-ion conductor. On the contrary, the dc conductivity of the bi-ion conductor P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub> drops sharply at the initial stage of polarization. When a dc voltage is applied to the blend of P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub>, Li<sup>+</sup> migrates to the cathode and is reduced to lithium while ClO<sub>4</sub><sup>-</sup> migrates to the anode and concentrates near the anode, which leads to the formation of concentration polarization and impedes the transference of Li<sup>+</sup>, so its dc conductivity decays rapidly. In PEO/SAL<sub>8</sub>, however, the methoxy oligo(oxyethylene) sulfate anion of SAL<sub>8</sub>, which has a huge volume, is very difficult to transfer and so only Li<sup>+</sup> can migrate in the electrolyte. When a lithium electrode is employed, Li<sup>+</sup> is reduced at the cathode and the lithium at the anode is oxidized to Li<sup>+</sup>. Therefore, no intrapolarization can form and the dc conductivity is constant. Thus, the single-ion conductor PEO/SAL<sub>8</sub> is an excellent electrolyte material for a solid-state lithium battery.

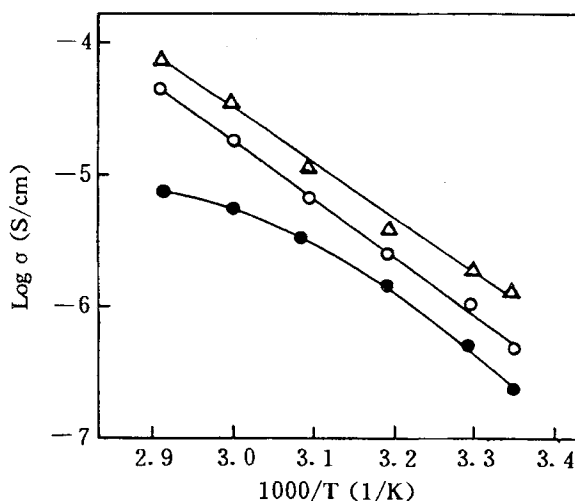


FIG. 3. Temperature dependence of ion conductivity of PEO/SAL<sub>8</sub> blend: (Δ) PEO/SAL<sub>8</sub> (w/w) = 1:2, (○) PEO/SAL<sub>8</sub> (w/w) = 1:3, (●) PEO/SAL<sub>8</sub> (w/w) = 1:0.5.

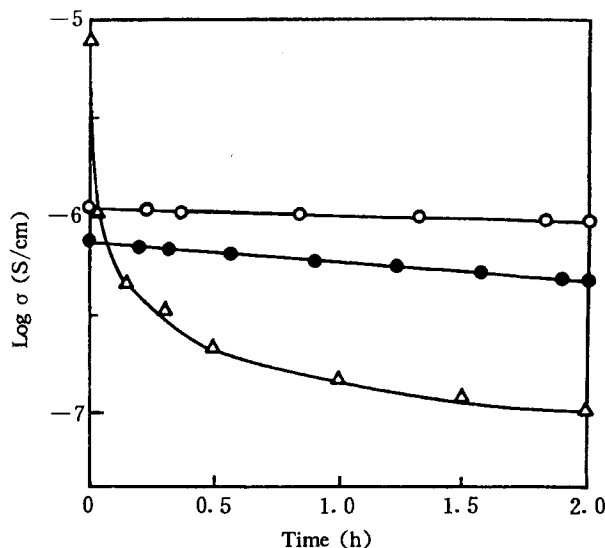


FIG. 4. Time dependence of dc ion conductivity: Temperature, 30°C; polarization voltage, 3.0 V; (○) PEO/SAL<sub>8</sub> (w/w) = 1:2, (●) PEO/SAL<sub>8</sub> (w/w) = 1:1, (△) P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub>.

In order to measure the ion transference number ( $t$ ) and the ion mobility ( $\mu$ ) of PEO/SAL<sub>8</sub>, a polarization reversing method is used. As seen in Fig. 5, after the bias polarization is reversed, two current peaks appear at 8 minutes ( $\tau_+$ ) and 335 minutes ( $\tau_-$ ), respectively. By means of the formulas  $\mu = d^2/(V\tau)$  and  $t_i = \mu_i/\Sigma\mu_i$ , where  $d$  is the thickness of the sample and  $V$  is the polarization voltage, the ion mobility ( $\mu_i$ ) and cation transference number ( $t_+$ ) were calculated as follows:

$$\mu_+ = d^2/(V\tau_+) = 8.3 \times 10^{-8} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$$

$$\mu_- = d^2/(V\tau_-) = 1.0 \times 10^{-9} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$$

$$t_+ = 0.98$$

These results mean that the transference of Li<sup>+</sup> plays a leading role in the ion conduction of the blend and that the PEO/SAL<sub>8</sub> blend acts as a single-ion conductor.

### Electrochemical Characteristics of the Blend

As seen in Fig. 6, the decomposition voltage of PEO/SAL<sub>8</sub> is 5.7 V, which satisfies the general requirement of a lithium battery. This means that the polymer solid electrolyte has excellent electrochemical stability.

Figure 7 shows the short-circuit discharge characteristics of the lithium battery using a single-ion conductor PEO/SAL<sub>8</sub> and a bi-ion conductor P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub> [12]. The short-circuit current of a bi-ion conductor falls rapidly from its initial current density of 8.8 mA/cm<sup>2</sup> to only 0.2 mA/cm<sup>2</sup> after 20 minutes, which is due to the intrapolarization caused by the migration of ClO<sub>4</sub><sup>-</sup>. The current density

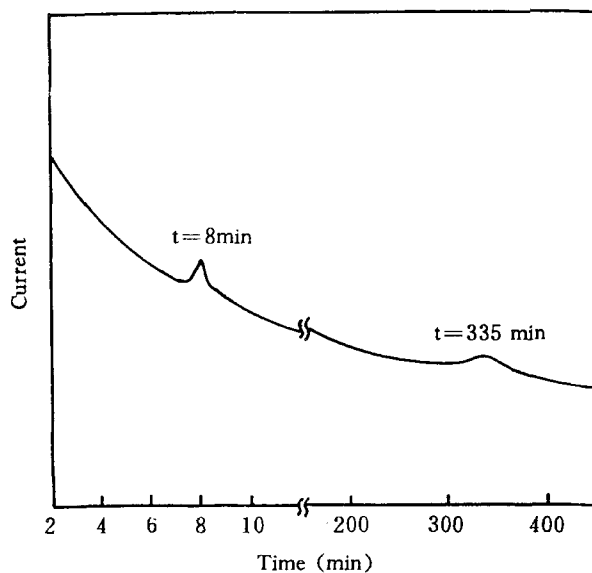


FIG. 5. Transient current curve of PEO/SAL<sub>8</sub> blend. Polarization voltage, 2.5 V; temperature, 50°C; PEO/SAL<sub>8</sub> (w/w) = 1:2.

of PEO/SAL<sub>8</sub>, on the contrary, increases slowly in the first stage and then decreases gradually after reaching a maximum. The variation of the short-circuit current in PEO/SAL<sub>8</sub> is smaller than that of the bi-ion conductor since no intrapolarization exists in PEO/SAL<sub>8</sub>. The initial increase of current in PEO/SAL<sub>8</sub> may be due to improvement of the cathode/electrolyte interface during discharge.

Under the constant current procedure, the discharge characteristics of lithium batteries with PEO/SAL<sub>8</sub> and P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub> are shown in Fig. 8 (A, B),

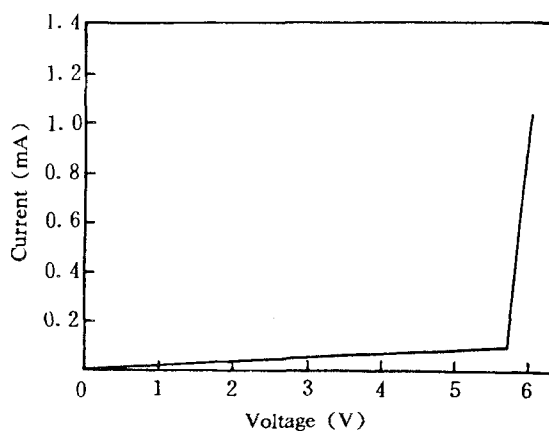


FIG. 6. Decomposition voltage of PEO/SAL<sub>8</sub>. Temperature: 30°C.

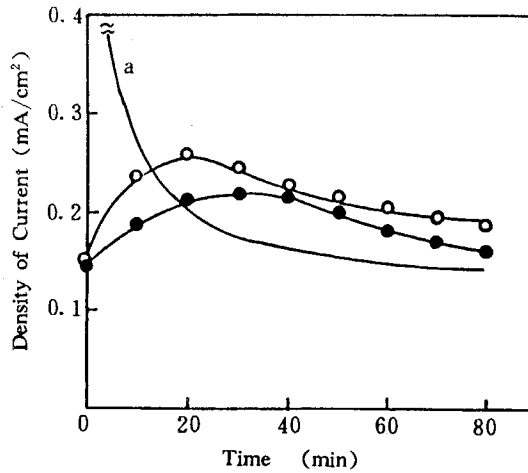


FIG. 7. Short-circuit discharge curves. Temperature, 30°C; PEO/SAL<sub>8</sub> (w/w) = 1:2; (○) Li/PEO + SAL<sub>8</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> cell, (●) Li/PEO + SAL<sub>8</sub>/PAN cell, (a) Li/P(MEO<sub>16</sub>-AM) + LiClO<sub>4</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> cell.

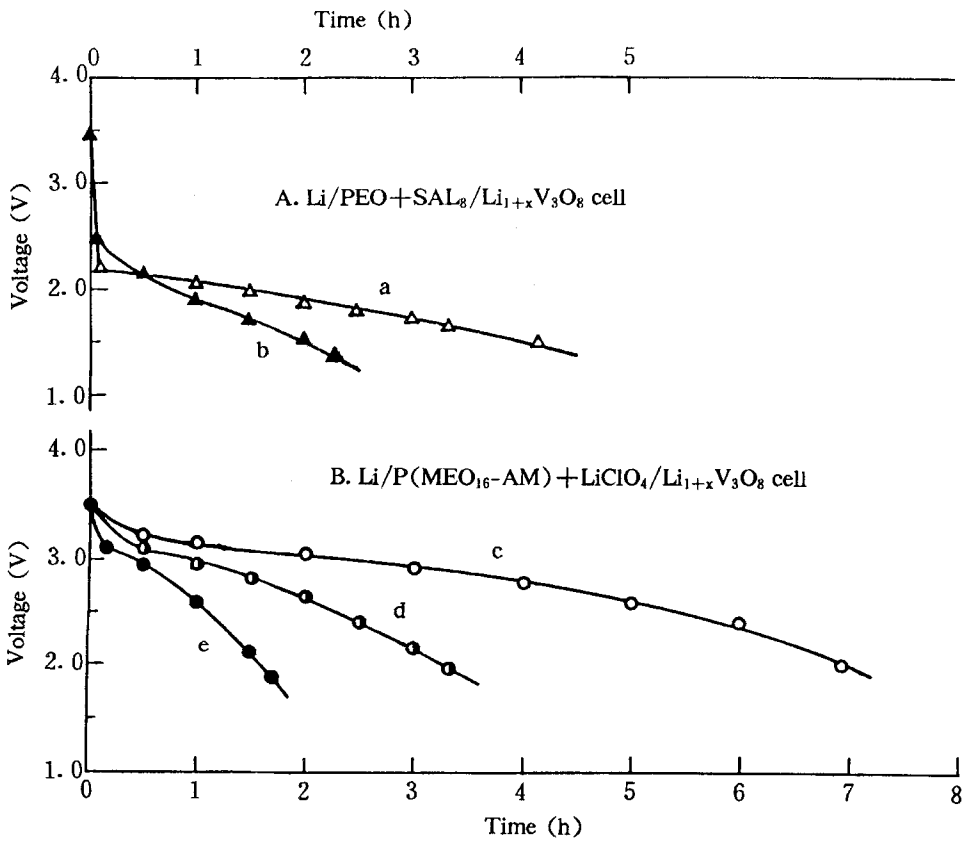


FIG. 8. Discharge curves for Li/polymer solid electrolyte/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> cells. Temperature: 30°C. Discharge current density in mA/cm<sup>2</sup>: (a) 0.05, (b, c) 0.10, (d) 0.15, (e) 0.20.



TABLE 1. Comparison of the Relationship of Discharge Capacity and Discharge Current Density for PEO + SAL<sub>8</sub> and P(MEO<sub>16</sub>-AM) + LiClO<sub>4</sub> Batteries

	Cell				
	Li/POE + SAL <sub>8</sub> / Li <sub>1+x</sub> V <sub>3</sub> O <sub>8</sub>		Li/P(MEO <sub>16</sub> - AM) + LiClO <sub>4</sub> /Li <sub>1+x</sub> V <sub>3</sub> O <sub>8</sub>		
	<i>Discharge Current Density (mA/cm<sup>2</sup>)</i>				
	0.05	0.10	0.10	0.15	0.20
	<i>Discharge Capacity (mA · h/cm<sup>2</sup>)</i>				
Discharge to voltage (V)					
2.5	—	—	0.553	0.350	0.224
2.0	0.075	0.075	0.692	0.490	0.320
1.5	0.208	0.208	—	—	—

lithium battery with PEO/SAL<sub>8</sub> initially descends sharply. This is due to the high interface resistance between the electrolyte and electrodes. When these lithium batteries are discharged to a certain voltage at different discharge current densities within the interfacial exchange current density (about 0.5 mA/cm<sup>2</sup>), the times needed differ greatly. The larger the discharge current density, the less time required. However, a much more interesting phenomenon has been discovered: The discharge capacity of the Li/PEO + SAL<sub>8</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> battery remains unchanged at different discharge current densities while the discharge capacity of the Li/P(MEO<sub>16</sub>-AM) + LiClO<sub>4</sub>/Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> battery decreases with an increase of the discharge current density (Table 1). This is ascribed to the difference between the single-ion conductor PEO + SAL<sub>8</sub> and the bi-ion conductor P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub>.

## CONCLUSION

The maximum ambient conductivity of the PEO/SAL<sub>8</sub> blend is  $1.2 \times 10^{-6}$  S/cm when the SAL<sub>8</sub> content reaches 67%. The blend has constant dc polarization characteristics and a high cationic transference number. It also has excellent electrochemical stability. A lithium battery with PEO/SAL<sub>8</sub> electrolyte has the same discharge capacity at different discharge current densities while the discharge capacity of a lithium battery with P(MEO<sub>16</sub>-AM)/LiClO<sub>4</sub> as the electrolyte degrades with an increase of the discharge current density.

## ACKNOWLEDGMENT

This project is supported by the State Key Laboratory of Polymer Materials Engineering in Sichuan Union University (Chengdu 610065).

## REFERENCES

- [1] M. B. Armand and D. Muller, US Patent 4,578,326.
- [2] K. Nagaoka and M. Watanabe, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 659 (1984).
- [3] D. J. Bannister, G. R. Danies, and I. M. Ward, *Polymer*, **25**, 1291 (1984).
- [4] M. Watanabe, K. Nagaoka, and I. Shinohara, *J. Appl. Polym. Sci.*, **27**, 4191 (1982).
- [5] I. Kelly, J. R. Owen, and B. C. H. Steele, *J. Power Sources*, **14**, 13 (1985).
- [6] C. A. Angell, C. Liu, and E. Sanches, *Nature*, **362**, 137 (1993).
- [7] C. A. Angell, J. Fan, C. Liu, and K. Xu, *Solid State Ionics*, **69**, 343 (1994).
- [8] Y. Zheng and G. Wan, *J. Macromol. Sci. – Pure Appl. Chem.*, **A30(5)**, 365 (1993).
- [9] M. Kosaki, H. Oshima, and M. Iede, *J. Phys. Soc. Jpn.*, **29**, 1012 (1970).
- [10] L. D. Pettit and S. Bruckenstein, *J. Am. Chem. Soc.*, **88**, 4783 (1966).
- [11] M. Matsumoto, T. Ichino, J. S. Rutt, and S. Nishi, *J. Electrochem. Soc.*, **141(8)**, 1989 (1994).
- [12] Z. Deng, Q. Xu, Y. Zheng, and G. Wan, *J. Power Sources*, **50(3)**, 369 (1994).

Received July 10, 1995

Revision received January 16, 1996