

## Short Communication

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# Rechargeable lithium batteries with a polymeric single-ion conductor

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### Abstract

A polymeric single-cation conductor has been found to be a more stable electrolyte than a polymeric bi-ion conductor. The discharge/charge characteristics of Li/polymeric single-cation conductor/ $V_3O_8Li_{1-x}$  cell have been investigated. A hysteresis in the discharge voltage exists during the initial discharge of the battery. Nevertheless, the battery exhibits good discharge/charge characteristics and long shelf life.

### Introduction

In previous publications [1–5], the conduction and transport mechanisms of polymeric single-ion conductors have been reported. This work examines the characteristics of a polymeric single-ion conductor as the electrolyte membrane for a rechargeable lithium battery. The performance of the battery is compared with that of a system using a bi-ion conductor.

### Experimental

#### Materials

A polymeric single-ion conductor (PSC) and a polymeric bi-ion conductor (PBC) were prepared according to methods reported previously [1]. The ambient ionic conductivity of the PBC, a complex of poly[methoxy oligo(oxyethylene) methacrylate-co-acrylamide] and lithium perchlorate (i.e.,  $P(MEO_{16}-AM) \cdot LiClO_4$ ) is  $6.5-7.0 \times 10^{-5} S cm^{-1}$ . A PSC, a blend of poly(ethylene glycol) dimethyl ether (DMEO<sub>16</sub>), poly(sulfohexyl methacrylate lithium) (PSHMLi) and  $P(MEO_{16}-AM)$  (i.e.,  $P(MEO_{16}-AM)/DMEO_{16}/PSHMLi$ ) has an ionic conductivity of  $3.5-5.5 \times 10^{-6} S cm^{-1}$  at room temperature. The cathode material was the complex membrane of the polymeric ion conductor and the electroactive compound,  $V_3O_8Li_{1-x}$ . Assembly of the test cells was carried out in moistureless glove box that was filled with argon.

#### Measurements

A linear voltage scanning method (scan rate:  $1.0 mV s^{-1}$ ) was employed to study the decomposition voltage. An inert electrode was used as the measurement electrode.

A constant-voltage procedure was employed to evaluate the d.c. polarization characteristics of the polymeric ion conductor when sandwiched between lithium electrodes. The apparent d.c. conductivity was calculated from the current for a balanced d.c. polarization curve. Discharge/charge cycling of the test batteries was conducted galvanostatically at 30 °C with an electrode area of 0.785 cm<sup>2</sup>.

## Result and discussion

### *D.c. polarization characteristics and decomposition voltage*

Figure 1 presents the time dependence of the polarization current of the PSC and the PBC when sandwiched between lithium electrodes at a d.c. polarization voltage of 3.0 V. Although the initial conductivity of PSC is about one order of magnitude lower than that of PBC, the conductivity of the latter decays rapidly. The conductivity of each conductor reaches the same value after about 8 min. After polarization for 2 h, the conductivity of the PBC falls to  $\sim 10^{-7}$  S cm<sup>-1</sup>, a decline of nearly two orders of magnitude. By contrast, the conductivity of the PSC decreases by less than half an order of magnitude, and is even higher than that of PBC.

The difference in the d.c. polarization characteristics of PSC and PBC arises from differences in their molecular structure and composition. The PBC is composed of LiClO<sub>4</sub> and the ether-oxygen group of the polymer. Under the solvolytic influence of the ether-oxygen group, LiClO<sub>4</sub> dissociates into ClO<sub>4</sub><sup>-</sup> and Li<sup>+</sup>. Li<sup>+</sup> forms complexes with the ether-oxygen group. Therefore, two kinds of carriers, Li<sup>+</sup> and ClO<sub>4</sub><sup>-</sup>, exist in PBC. These carriers exhibit opposite transport behaviour in an electric field.

Due to the high viscosity of the solid polymeric media, it is difficult for the ions to be transported by thermal diffusion. As a result, a concentration gradient of ClO<sub>4</sub><sup>-</sup> appears near the surface of the cathode during the polarization. This leads to the formation of an electric potential difference due to concentration polarization. The electric potential difference is opposite to the outside electric field and increases with

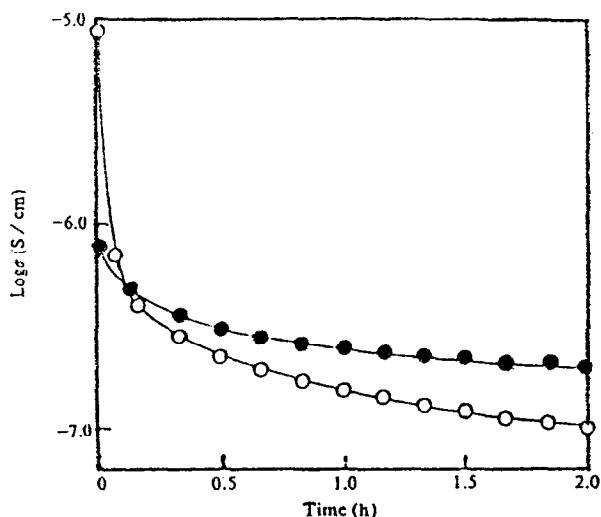


Fig. 1. Time dependence of d.c. polarization current of (●) PSC and (○) PBC measured with lithium electrodes (polarization voltage: 3.0 V; temperature: 30 °C).

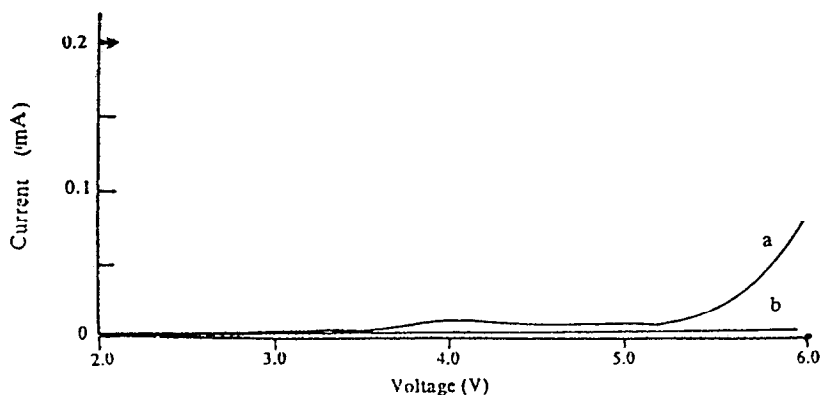


Fig. 2. Decomposition voltage of (a) PBC and (b) PSC.

polarization time. Meanwhile, the accumulation of ions forms a salt-rich phase because of the partial decomposition characteristics of the salt in polymer media [6]. This causes the decrease in polarization current. When a kinetic equilibrium is reached in the polarized sample, the polarization current no longer decreases and, thereby, reaches a constant value. The PSC is a ternary complex composed of poly(sulfohexyl methacrylate lithium), a polymer containing an ether–oxygen group, and an oligo-ether with a high molecular weight. Anchored on a macromolecular chain through covalent bonds, the anions cannot be transported in an electric field. Thus, only  $\text{Li}^+$  dissociated by the action of the ether–oxygen group is mobile. The cationic transference number  $t_+$  in this system is close to 1 [1]. As a result, there is no formation of a concentration polarization of the anion group around the cathode surface, and a stable polarization current is observed.

Figure 2 shows the decomposition voltage of the polymeric ion conductor. In the range of 0 to 6 V, no decomposition voltage appears for the PSC, while the decomposition voltage of the PBC is greater than 5.5 V. Both polymeric ion conductors, especially PSC, exhibit remarkable electrochemical stability.

#### *Discharge/charge characteristics of lithium batteries*

The current curve for short-circuit discharge of lithium batteries using PSC and PBC is presented in Fig. 3. It is obvious that the two batteries display a difference in the short-circuit discharge. The instantaneous short-circuit current density of the PBC lithium battery is more than  $8.8 \text{ mA cm}^{-2}$ , but decreases rapidly with short-circuit time and becomes  $0.2 \text{ mA cm}^{-2}$  after 20 min. By contrast, although the instantaneous short-circuit current density of the PSC lithium battery is only  $0.1 \text{ mA cm}^{-2}$ , it increases gradually with short-circuit time and reaches a maximum value of  $0.4 \text{ mA cm}^{-2}$  after 15 min, and then decreases.

The sharp fall in the short-circuit current density of the PBC battery is caused by a rapid increase in the internal polarization overvoltage of the battery due to the concentration polarization of anions. This concentration polarization does not exist with the PSC, with the result that the PSC battery exhibits a different short-circuit discharge behaviour. The initial, gradual increase in the current density of PSC may be the result of a reaction between PSC and the cathode material surface.

The lower current at the start of discharge is caused by the higher cathode/PSC interface resistance. The reactive electric resistance decreases with discharge time and,

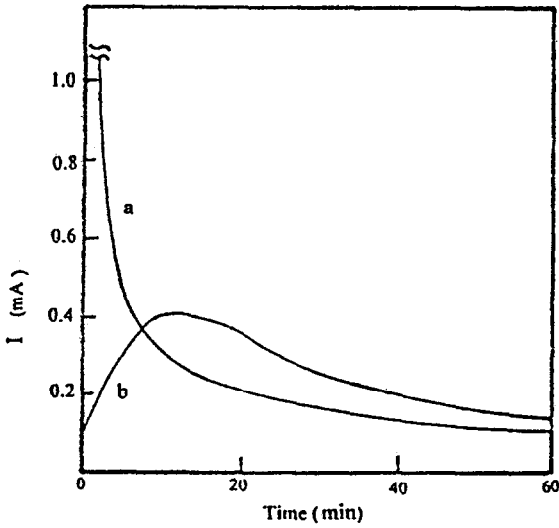


Fig. 3. Short-circuit discharge curves of (a) PBC and (b) PSC lithium batteries (temperature: 30 °C).

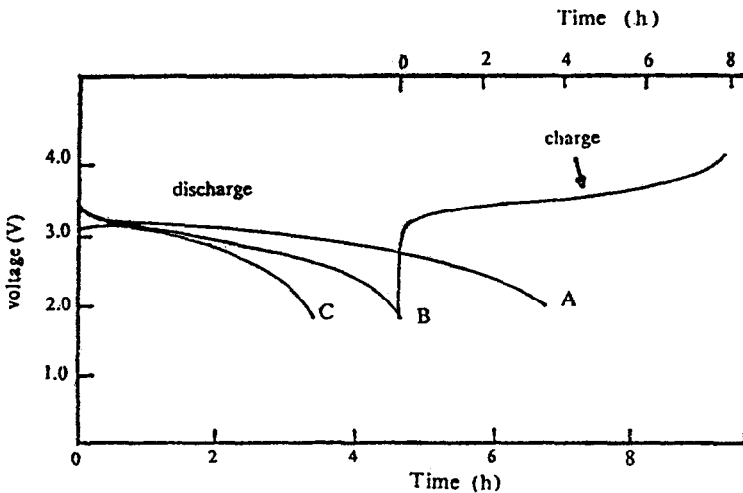


Fig. 4. Discharge/charge curves for PSC lithium batteries (discharge current density: A:  $50 \mu\text{A cm}^{-2}$ ; B:  $75 \mu\text{A cm}^{-2}$ , and C:  $100 \mu\text{A cm}^{-2}$ . Charge current density = 50% discharge current density).

consequently, the current gradually increases and reaches a maximum. As calculated from the data in Fig. 3, the total amount of discharge within 60 min are  $610 \mu\text{Ah}$  and  $560 \mu\text{Ah}$  for PSC and PBC batteries, respectively. Although both the conductivity and the instantaneous short-circuit current density of the PSC are lower than that of the PBC, they deliver the same discharge quantity for the same period of time. This implies that the PSC is superior to the PBC as a lithium battery electrolyte.

TABLE 1

Influence of discharge/charge cycle number of PSC lithium battery on discharge performance<sup>a</sup>

Discharge/charge number		1	3	4	6	7
Discharge	Initial voltage (V)	3.36	4.00	3.95	3.90	3.96
	Terminal voltage (V)	2.40	1.97	2.06	1.96	1.95
	Discharge time (h)	6.20	5.63	5.20	4.05	4.15
	Discharge quantity (mAh)	0.31	0.28	0.26	0.20	0.21
Charge	Initial voltage (V)	2.80	3.00	2.66	3.00	
	Terminal voltage (V)	4.00	3.95	4.01	3.96	
	Charge time (h)	13.8	12.0	15.5	17.0	
	Charge quantity (mAh)	0.23	0.20	0.26	0.28	

<sup>a</sup>Discharge current density:  $50 \mu\text{A cm}^{-2}$ ; charge current density:  $1/3$  discharge current density; weight of cathode material: about 0.03 g; temperature:  $30^\circ\text{C}$ .

TABLE 2

Influence of shelf life of PSC lithium battery on discharge quantity<sup>a</sup>

Storage time	Initial	2 months	6 months
Open-circuit voltage (V)	3.36	3.54	3.47
Discharge quantity (mAh)	0.31	0.28	0.23

<sup>a</sup>Discharge current density:  $50 \mu\text{A cm}^{-2}$ ; end-of-discharge voltage: 2.00 V; weight of cathode material: 0.03 g; temperature:  $30^\circ\text{C}$ .

Discharge/charge curves for the PSC battery are shown in Fig. 4. Because of the low conductivity of PSC and the high internal electric resistance of the battery, PSC lithium batteries can only discharge a small current. When the discharge current density is higher than  $100 \mu\text{A cm}^{-2}$ , the cell voltage falls dramatically and then rises gradually, that is to say, there is a voltage hysteresis. The initial decrease in cell voltage is related to the discharge current density. When the batteries are discharged at  $150 \mu\text{A cm}^{-2}$ , the instantaneous voltage drops to 2.5 V, and then gradually rises to about 3.1 V. After a discharge/charge cycle, the voltage hysteresis no longer exists when the batteries are discharged at the same discharge current density. These results suggest that the cathode/PSC interface has been improved after a discharge/charge cycle.

The influences of discharge/charge cycle number and shelf life of the PSC battery on the discharge performance are shown in Tables 1 and 2. It can be seen that the batteries have excellent discharge/charge characteristics and shelf stability. When the batteries were opened after a year's storage, no change in the lustre of the lithium surface was observed.

## Conclusions

The PSC, with no diffusion transference of anions, has a stable polarization current under an electric field and behaves with excellent electrochemical stability. On the other hand, the reaction at the interface between PSC and the  $\text{V}_3\text{O}_8\text{Li}_{1-x}$  cathode is poor. A hysteresis of voltage exists initially under high current density, but is improved

to some degree after a discharge/charge cycle. Lithium batteries using the PSC exhibit excellent discharge/charge characteristics and shelf stability.

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