

# Highly conductive polymer electrolytes supported by microporous membrane

Dong-Won Kim\*, Kun Ae Noh, Jong-Han Chun, Sang-Hern Kim, Jang-Myoun Ko

*Department of Chemical Technology, Hanbat National University, San 16-1, Dukmyung-Dong, Yuseong-Gu, Taejeon 305-719, South Korea*

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## Abstract

Highly conductive polymer electrolytes supported by a microporous separator were prepared and characterized. These polymer electrolytes were prepared by coating poly(ethylene oxide) (PEO) and poly(ethylene glycol dimethacrylate) (PEGDMA) onto a microporous polyethylene membrane, and soaking them in an electrolyte solution. The relative weight ratio of PEO and PEGDMA coated on the microporous membrane proved to play a critical role in determining uptake of an electrolyte solution and ionic conductivity. The electrolyte optimized in this work displayed a high ionic conductivity and electrochemical stability, exhibiting no solvent leakage. An encapsulation of electrolyte solution within the porous membrane diminished the passivation of lithium electrodes. With these electrolytes, lithium-ion polymer cells composed of a carbon anode and LiCoO<sub>2</sub> cathode were assembled, and their electrochemical performances were evaluated. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium-ion polymer battery; Microporous separator; Poly(ethylene glycol dimethacrylate); Poly(ethylene oxide); Polymer-coated membrane; Polymer electrolyte

## 1. Introduction

Polymer electrolytes are receiving considerable attention as solid electrolyte materials in advanced applications such as rechargeable lithium batteries and electrochromic devices [1–3]. Though conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes have been the most commonly studied, their low conductivity at room temperature excluded practical application at ambient temperature [4]. To enhance ionic conductivity at room temperature, several classes of gel polymer elec-

trollytes have been developed and characterized. Most gel polymer electrolytes encapsulate high amounts of an electrolyte solution, and their ionic conductivities exceed 10<sup>-3</sup> S/cm, which is necessary for battery application [5]. Gel polymer electrolyte films are usually prepared by casting a solution of the electrolyte solution and a matrix polymer in a low-boiling-point solvent. However, this process requires a moisture-free environment because of the higher water sensitivity of the lithium salt. Besides, their mechanical properties were often very poor, and the films had to be hardened by either chemical or physical curing. To overcome these problems, microporous membranes of polyolefins such as polyethylene and polypropylene, impregnated with gel polymer electrolytes, have been developed as an

\* Corresponding author. Tel.: +82-42-821-1550; fax: +82-42-822-1562.

*E-mail address:* dwkim@hanbat.ac.kr (D.-W. Kim).

electrolyte material for lithium batteries. Morigaki et al. [6] manufactured a lithium secondary battery using a microporous polyolefin separator, the pores of which were filled with gel polymer electrolyte. In another example, a solution consisting of ethylene carbonate, propylene carbonate, tetraethylene glycol dimethyl ether, tetraethylene glycol diacrylate,  $\text{LiAsF}_6$  and a small amount of a photopolymerization initiator is impregnated into the porous polyolefin membranes and polymerized to form a solid electrolyte [7]. Recently, a membrane-supported gel polymer electrolyte was also prepared and characterized by Kim et al. [8], which was prepared by coating a gel polymer electrolyte onto a porous polyethylene membrane. Properties that must be considered for selection of the polymer impregnated into the porous membranes include: capability to absorb an electrolyte solution without its leakage, chemical compatibility with electrode materials, and adhesive property for adhering the electrodes to the porous separator.

With the aim of developing highly conductive polymer electrolyte supported by a porous separator, we tried to coat PEO and poly(ethylene glycol) dimethacrylate (PEGDMA) onto a microporous polyethylene membrane. With these polymer-coated membranes (PCM), highly conductive polymer electrolytes without solvent exudation were prepared by soaking them in an electrolyte solution. In these polymer-coated PE membranes, PE membrane could give mechanical integrity to the electrolyte system, while PEO and PEGDMA coated on both sides of

the membrane were adapted to encapsulate an electrolyte solution in the porous membrane and to further assist in adhering the electrodes to the separator. The electrochemical characteristics and performance of these polymer electrolytes are presented, and we discuss the possibility of them as an electrolyte material for lithium-ion polymer batteries.

## 2. Experimental

### 2.1. Preparation of PCMs and electrodes

Appropriate amounts of PEO ( $M_n$ : 600 000, Aldrich Chemical), PEGDMA ( $M_n$ : 350, Aldrich Chemical) and azobisisobutyronitrile (AIBN) were dissolved in an anhydrous acetonitrile. AIBN was used as a free-radical initiator for chemical cross-linking of PEGDMA. In this formulation, the weight ratio of two polymers (PEO/PEGDMA) was varied with compositions of 10/0, 8/2, 6/4, 4/6, 2/8 and 0/10. A microporous PE separator (Asahi Kasei, thickness: 25  $\mu\text{m}$ , porosity: 40%) was then immersed in the polymer solution for 1 h. The membrane was taken out on a Teflon plate and left to evaporate to the solvent slowly at room temperature in a dry box. After evaporation of acetonitrile, the membrane was cured and vacuum dried at 80°C for 24 h. Weight increase after coating and curing of two polymers on the PE membrane is given in Table 1. For brevity, the PCM prepared as above is designated as PCM ( $x/y$ ) in the following discussion, where  $x$  and  $y$  indicate the weight ratio of PEO and

Table 1  
DSC results of PEO, PE membrane and polymer-coated PE membranes

Polymer	Melting of PEO		Melting of PE		Weight increase after coating (%) <sup>a</sup>
	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	
PEO	73	153			–
PE membrane			139	165	–
PCM (10/0)	69	141	137	152	153
PCM (8/2)			137	156	170
PCM (6/4)			137	157	177
PCM (4/6)			137	158	183
PCM (2/8)			137	156	200
PCM (0/10)			137	149	223

<sup>a</sup> Defined as the weight ratio of the polymers (PEO and PEGDMA) coated to the PE membrane.

PEGDMA coated on PE membrane, respectively. Differential scanning calorimetry (DSC) thermal analysis was carried out to measure the thermal properties of PEO, PE membrane and polymer-coated PE membranes, with a heating rate of  $10^{\circ}\text{C}/\text{min}$  from 25 to  $250^{\circ}\text{C}$ . The carbon anode was prepared by coating the slurry of mesophase carbon fiber (MCF, Petoca), poly(vinylidene fluoride) (PVdF) and super-P carbon on a copper foil. The cathode contained the same binder (PVdF) and super-P carbon along with  $\text{LiCoO}_2$  (Japan Chemical) cathode material, which was cast on aluminum foil. The thickness of electrodes ranged from 100 to  $120\ \mu\text{m}$ , and their active mass loading corresponded to a capacity of about  $3.5\ \text{mA h}/\text{cm}^2$ .

## 2.2. Electrical measurements

The polymer-coated PE membrane was transferred into a glove box and soaked in either 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) or 1 M  $\text{LiBF}_4$  in EC/DMC (1:1 by volume, Samsung Cheil Industries Inc., battery grade) for 1 h, to activate the polymer-coated PE membrane. After activation, it was taken out from the electrolyte solution and an excess electrolyte solution on the surface of membrane was wiped with filter paper. The wetted membrane was cut into  $4\text{-cm}^2$  squares and sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The cell was enclosed in an aluminum plastic pouch and sealed to permit testing outside of a glove box. The a.c. impedance measurement was performed using Zahner Elektrik IM6 impedance analyzer over a frequency range from 10 Hz to 100 kHz. A linear sweep voltammetry experiment was carried out on a SS working electrode with lithium electrode as the counter and reference electrode at a scanning rate of  $1.0\ \text{mV}/\text{s}$ . Lithium-ion polymer cell (electrode area:  $4\ \text{cm}^2$ ) was assembled by sandwiching the activated polymer-coated PE membrane between MCF anode and  $\text{LiCoO}_2$  cathode. The cell was then enclosed in a metallized plastic bag and vacuum sealed. All assemblies of the cells were carried out in a dry box filled with argon gas. The charge and discharge cycling tests of lithium-ion polymer cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000 U).

## 3. Results and discussion

Fig. 1 shows typical DSC thermograms of PEO, PE membrane and PEO-coated PE membrane, and their DSC results are summarized in Table 1. PEO and PE membrane show an endothermic peak at 73 and  $139^{\circ}\text{C}$ , respectively, which are attributed to their melting. For PCMs, it can be seen that the melting temperature and heat of fusion of PE are not very dependent on the composition of PEO and PEGDMA coated on PE membrane. The crystallinity of PE in the PCM, which imparts the mechanical strength to PCM, is found to be almost maintained. On the contrary, melting transition of PEO can be observed only in the PCM (10/0), which means that the crystallizing tendency of PEO is significantly reduced by chemical cross-linking of PEGDMA in the PEO/PEGDMA blend.

Fig. 2 presents scanning electron micrographs of the PCMs with different PEO/PEGDMA composition. It can be clearly observed that the surface morphology of PCM is dependent on PEO/PEGDMA composition. When the PEO content exceeds about 40 wt.% (Fig. 2(a)–(d)), the pores of the membrane becomes fully covered by two polymers, and the PCMs revealed a pore-free morphology. With less than 40 wt.% PEO, the PCMs show voids of small size on their surface. When PEO/PEGDMA solution is coated on the porous PE separator, PEGDMA is a viscous liquid. With poly-

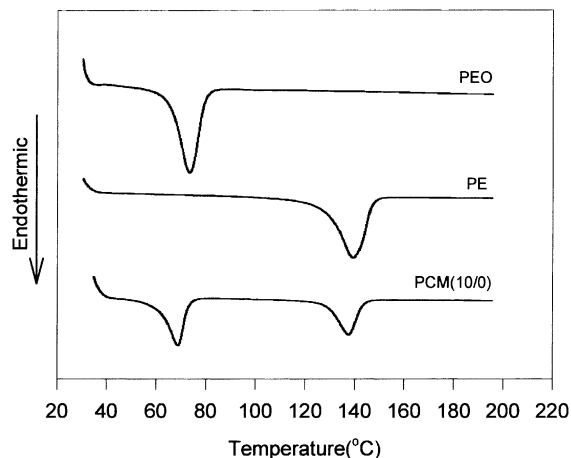


Fig. 1. DSC thermograms of PEO, PE membrane and PEO-coated PE membrane.

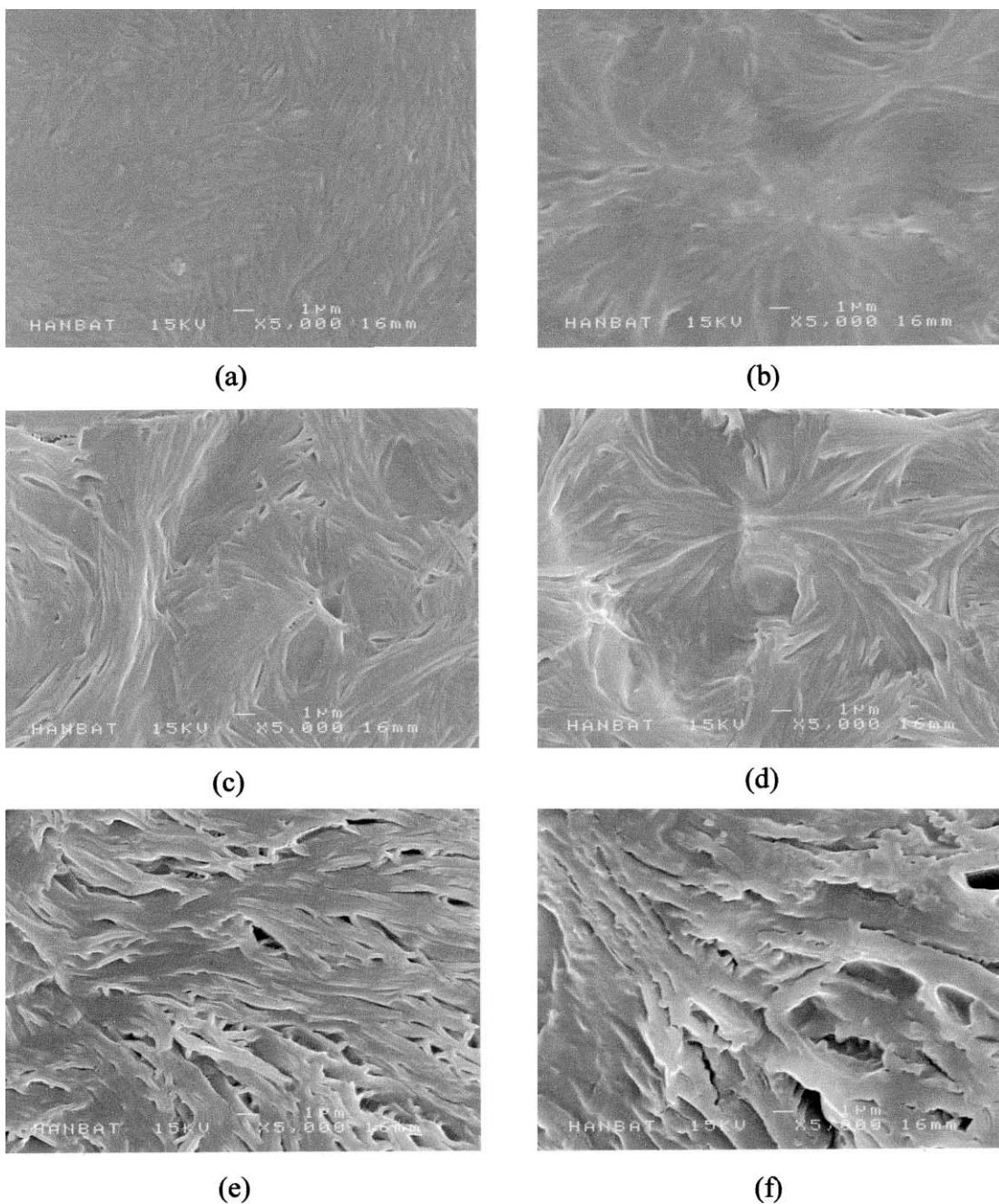


Fig. 2. Scanning electron micrographs of the PCMs with different PEO/PEGDMA composition. (a) PCM (10/0), (b) PCM (8/2), (c) PCM (6/4), (d) PCM (4/6), (e) PCM (2/8), (f) PCM (0/10).

merizing of PEGDMA by free radical initiator (AIBN), liquid PEGDMA is changed to a chemically cross-linked solid network. The polymerization of

PEGDMA is believed to cause a shrinkage of polymer coating on PE membrane. Thus, the pores of membrane could not be fully covered by polymers,

in case of higher amount of PEGDMA, as shown in Fig. 2(e) and (f).

PCMs were soaked in either  $\text{LiPF}_6$  in EC/DMC or  $\text{LiBF}_4$  in EC/DMC for 1 h. Uptake of an electrolyte solution and room temperature conductivity of the PCMs after soaking in the electrolyte solution are given in Table 2. In this table, uptake of an electrolyte solution was determined as follows:

$$\text{uptake (\%)} = (W - W_0) / W \times 100$$

where  $W$  and  $W_0$  are the weights of the wet and dried PCM, respectively. It is clearly found that both uptake of an electrolyte solution and ionic conductivity decrease with content of PEGDMA in the polymer (PEO/PEGDMA)-coated membrane. This result is due to the fact that the formation of network by chemical cross-linking of PEGDMA on PE membrane hinders penetration of an electrolyte solution into the microporous membrane. For PCM (0/10), the amount of an electrolyte solution absorbed by PCM is not more than 32%. Ionic conductivity of PCM (0/10) could not be measured, because its resistance exceeded the detection limit of our impedance analyzer. From the table, it can be also seen that a type of salt ( $\text{LiPF}_6$  or  $\text{LiBF}_4$ ) dissolved in EC/DMC little affects the uptake of electrolyte solution. However, the PCM soaked by  $\text{LiPF}_6$ -EC/DMC exhibits a higher ionic conductivity. The difference in conductivity arises from the difference in the ionic conductivity of an electrolyte solution. When comparing the ionic conductivities of two electrolyte solutions added to the PCM,  $\text{LiPF}_6$ -EC/DMC ( $1.1 \times 10^{-2}$  S/cm) exhibits higher ionic conductivity than  $\text{LiBF}_4$ -EC/DMC ( $5.2 \times 10^{-3}$  S/cm). After soaking PCM in the electrolyte solution, its thickness is increased to about 19%, and the value is not very dependent on the polymer composi-

tion. With increasing PEO content, a soaking of PCM in the electrolyte solution rendered its surface to be more glutinous. Thus, PCM (10/0)-based electrolyte shows the best adhesion properties among the PCM systems studied. In further experiments, the composition of PEO/PEGDMA coated on PE membrane will be restricted to 10/0, 8/2 and 6/4, in consideration of ionic conductivity and adhesion property.

For a lithium-ion polymer battery, the cell potential can approach as high as 4.5 V vs.  $\text{Li}/\text{Li}^+$ , implying that the polymer electrolyte should be electrochemically stable up to at least 4.5 V. The electrochemical stability of polymer electrolyte was evaluated by linear sweep voltammetric measurement. An experiment was performed by applying an anodic voltage to a cell consisting of a polymer electrolyte sandwiched between a lithium electrode and an inert SS electrode. The voltage was swept from the open circuit potential of cell towards more anodic values until a large current due to the electrolyte decomposition at the inert electrode interface occurred. The decomposition voltage limit was defined as the potential at which a rapid rise in current was observed and continued to increase as the potential was swept, since the onset of the current flow may be associated with the decomposition of the given electrolyte. Fig. 3 shows the linear sweep voltammetry curves of the cell prepared with PCM containing an electrolyte solution of  $\text{LiPF}_6$ -EC/DMC. It should be noted that the small oxidation peak is observed at about 4.3 V. The origin for this oxidation peak is unclear at this time, but it may be thought to correspond to the oxidative breakdown of coating polymers (PEO or PEGDMA) by  $\text{LiPF}_6$ . In this figure, the mixture ratio between PEO and PEGDMA seems to have no obvious effects on the anodic stability. The oxidation stability of PCM-based electrolyte could be extended

Table 2  
Uptake of electrolyte solution and room temperature ionic conductivity

Soaking electrolyte		PCM					
		10/0	8/2	6/4	4/6	2/8	0/10
1 M $\text{LiPF}_6$ , EC/DMC	Uptake (%)	84	71	60	52	41	31
	Ionic conductivity (mS/cm)	2.2	1.1	1.0	0.8	0.6	–
1 M $\text{LiBF}_4$ , EC/DMC	Uptake (%)	75	68	56	49	40	32
	Ionic conductivity (mS/cm)	1.0	0.6	0.5	0.4	0.4	–

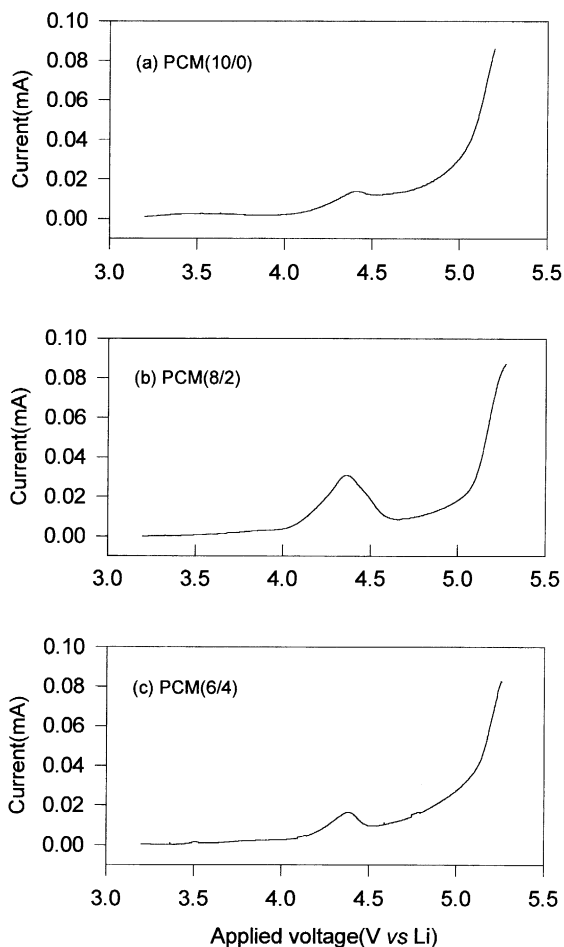


Fig. 3. Linear sweep voltammetry curves of the cell prepared with PCM containing an electrolyte solution of  $\text{LiPF}_6$ -EC/DMC (sweep rate: 1.0 mV/s).

to  $> 4.5$  V by replacing the  $\text{LiPF}_6$  with  $\text{LiBF}_4$ , as shown in Fig. 4. In the cell prepared with PCM containing  $\text{LiBF}_4$ -EC/DMC, no additional peaks appeared at a potential lower than 4.5 V. The potential dependence of electrolyte oxidation on different salt suggests that degradation of polymer by salt is a major factor contributing to the apparent stability limit. From these results, PCM soaked by  $\text{LiPF}_6$ -EC/DMC is thought not to be acceptable for high-voltage cathode materials, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ . Therefore, PCM soaked by  $\text{LiPF}_6$ -EC/DMC was excluded in further discussions.

We tried to investigate the interfacial behavior of a lithium electrode in contact with the PCM contain-

ing  $\text{LiBF}_4$ -EC/DMC. Fig. 5 shows the time evolution of the a.c. impedance spectrum of a Li/PCM (6/4)-based electrolyte/Li cell under open-circuit potential conditions at 25°C. The spectra showed a combination of many poorly separated semicircles. A rigorous identification of the depressed semicircles is beyond the scope of this work. Of particular interest in the depressed semicircles is the total interfacial resistance ( $R_i$ ), which can be calculated from the difference between the intercept at low frequency and bulk resistance ( $R_b$ ). Time evolution of interfacial resistance is shown in Fig. 6. For PCM (10/0) and PCM (8/2), the interfacial resistance slightly increases with time and reaches a steady-state value.

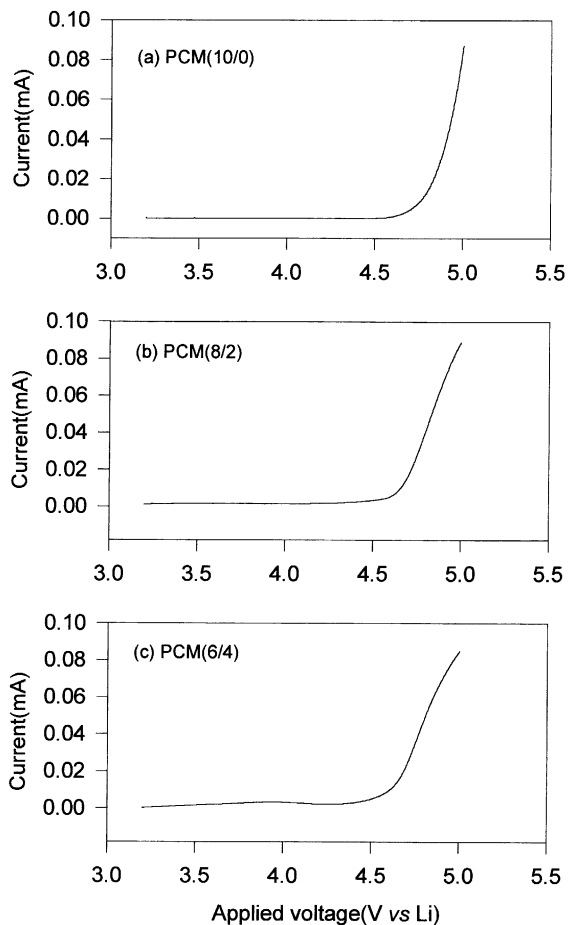


Fig. 4. Linear sweep voltammetry curves of the cell prepared with PCM containing an electrolyte solution of  $\text{LiBF}_4$ -EC/DMC (sweep rate: 1.0 mV/s).

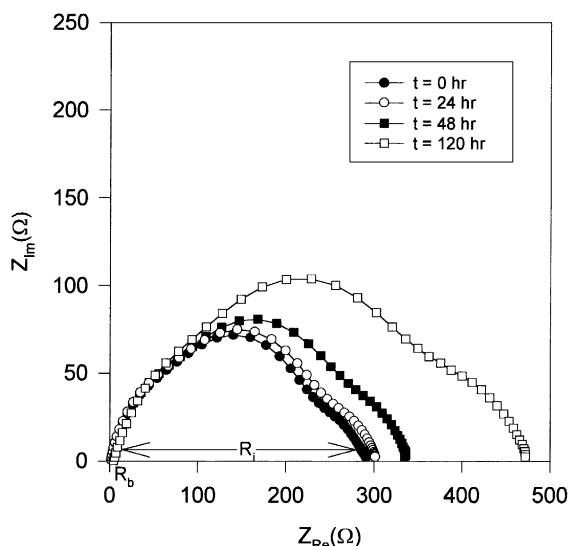


Fig. 5. a.c. impedance spectra of Li/PCM (6/4) containing  $\text{LiBF}_4\text{-EC}$ , DMC/Li cell as a function of storage time at  $25^\circ\text{C}$ .

The initial increase can be attributed to the formation of a passive layer, due to the reactivity of an electrolyte solution toward the lithium electrode. Aprotic solvents such as EC and DMC are well known for forming a passivating layer on lithium metal [9–11]. The final steady-state value of  $R_i$  suggests the absence of further growth of the passive film. It should be noted that the initial and steady-state value of interfacial resistance is low compared to those of

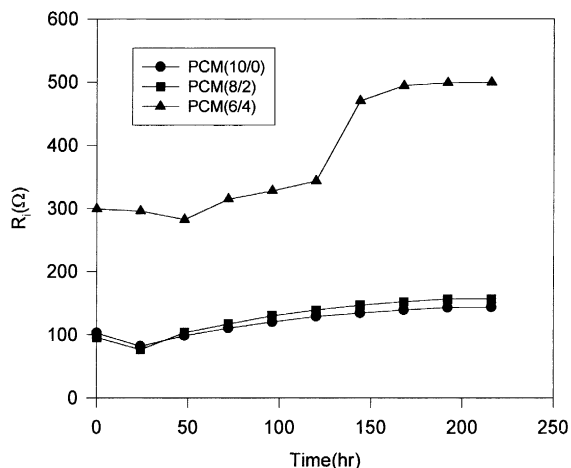


Fig. 6. Variation of  $R_i$  with storage time in the Li/PCM containing  $\text{LiBF}_4\text{-EC}$ , DMC/Li cells.

other gel polymer electrolyte systems [5]. This result means that thin passivation layer is formed at an early stage, and there is no flow of corrosive solvents to the lithium surface afterwards, which is attributed to the immobilization of an electrolyte solution within the porous membrane. For PCM (6/4), the initial and steady-state values of interfacial resistance are higher than the former two systems. The result is believed to be due to the lower capacity of PCM (6/4) to retain an electrolyte solution in the microporous membrane.

To evaluate the electrochemical performance of a lithium-ion polymer cell using the PCM (10/0) containing  $\text{LiBF}_4\text{-EC/DMC}$ , a MCF/PCM-based electrolyte/ $\text{LiCoO}_2$  cell was fabricated. The assembled cell was subjected to the cycle tests in the following order: preconditioning with cutoff voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at C/10 rate (1.4 mA) for the first cycle and subsequent C/5 rate (2.8 mA) cycles. Fig. 7 shows a preconditioning charge–discharge cycle of the lithium-ion polymer cell at C/10 rate, and subsequent two charge–discharge cycles at C/5 rate. This cell delivered a discharge capacity of 14.7 mA h during the first preconditioning cycle. This value is equivalent to the capacity of 142 mA h/g for an active  $\text{LiCoO}_2$  material in the cathode. The coulombic efficiency, which is defined as the ratio of the discharge capacity to charge capacity, is 93% at the first preconditioning cycle. The low coulombic effi-

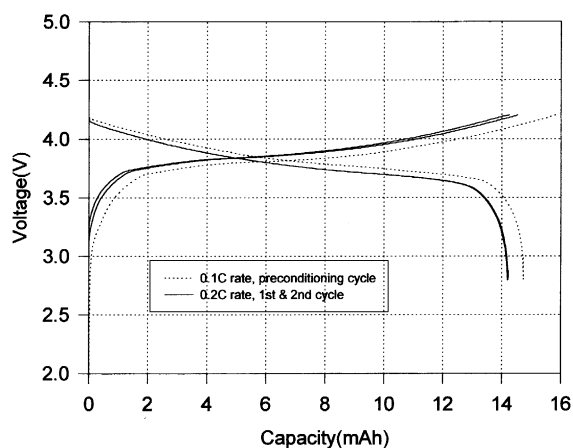


Fig. 7. Charge and discharge curves of a lithium-ion polymer cell (cell size:  $2 \times 2 \text{ cm}^2$ ).

ciency observed during the first preconditioning cycle is caused by the formation of a passivating film on the surface of the carbon electrode due to the decomposition of an electrolyte, as previously reported [12,13]. With further charge–discharge cycles at C/5 rate, an increase of cycling efficiency can be clearly seen. The values of cycling efficiency are 97.9% and 99.3% for the first and second cycles, respectively. Fig. 8 shows the charge and discharge capacities as a function of cycle number at C/5 rate. The cell initially delivered 14.2 mA h and the discharge capacity of the cell was decreased with cycling. The charge–discharge efficiency was maintained to be more than 99.5% through cycling after two cycles.

We tried to determine the rate capability of the lithium-ion polymer cell. Fig. 9 shows the discharge curves of the cell obtained at different current rates. Both the voltage and the capacity are found to be gradually decreased with increasing current rate, which reflects the large polarization. The large polarization resulted in a reduction of the discharge capacity. It showed a good performance at 1.0 C rate (3.5 mA/cm<sup>2</sup>), whose discharge capacity was 94% compared to that obtained at 0.2 C rate. However, the discharge capacity is found to drop at 2.0 C rate. At a current rate of 2 C, the cell retained 43% of its discharge capacity at 0.2 C. This result is not sufficient as a high-rate performance of lithium-ion polymer cell, and has to be improved. Further research is

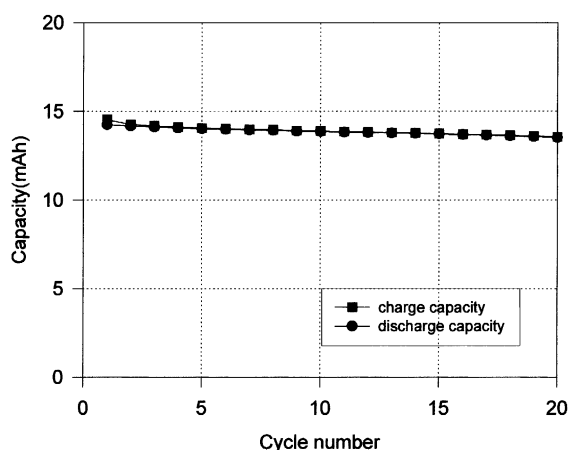


Fig. 8. Charge and discharge capacities of a lithium-ion polymer cell as a function of cycle number at C/5 rate.

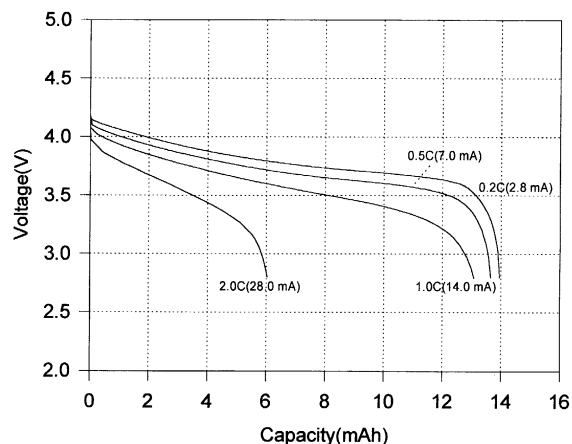


Fig. 9. Discharge profiles of a lithium-ion polymer cell. Charge rate is 0.2 C with 4.2 V cutoff.

being conducted in the authors' laboratory to improve the high-rate performance of the lithium-ion polymer cell. Improvements in the battery performance will be reported soon.

#### 4. Conclusions

Polymer-coated PE membranes were prepared by coating PEO and PEGDMA with different weight ratios onto a microporous polyethylene membrane. With these PCMs, highly conductive polymer electrolytes without solvent exudation were prepared by soaking them in an electrolyte solution. In these polymer-coated PE membranes, PE membrane gave mechanical integrity to the electrolyte system, and PEO coated on both sides of the microporous membrane encapsulated an electrolyte solution within the porous membrane. Uptake of an electrolyte solution and ionic conductivity were increased with content of PEO in the PCM. The ionic conductivity and electrochemical stability window of PCM (10/0) containing an electrolyte solution of LiBF<sub>4</sub>-EC/DMC were measured to be  $1.0 \times 10^{-3}$  S/cm and 4.5 V vs. Li/Li<sup>+</sup>, respectively. Lithium-ion polymer cells composed of MCF anode, PCM-based electrolyte and a LiCoO<sub>2</sub> cathode showed a high discharge capacity of 142 mA h/g based on active LiCoO<sub>2</sub> material, their charge–discharge efficiencies were proven to be about 100%. At a current rate of



1.0 C, the cell retained 94% of its discharge capacity at 0.2 C. Further improvements in cycle life and high-rate performance are essential for portable electronic applications.

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