

# Effect of thickness of coating layer on polymer-coated separator on cycling performance of lithium-ion polymer cells

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Received 6 August 2003; accepted 30 September 2003

## Abstract

Porous polymer-coated separators with different thicknesses of coating layer have been prepared by a dip coating and phase inversion method. Polymer-coated separators soaked with electrolyte solution exhibit high ionic conductivity in the order of  $10^{-3} \text{ S cm}^{-1}$  at room temperature and are electrochemically stable up to 5.0 V against  $\text{Li}^+/\text{Li}$ . Lithium-ion polymer cells each composed of a mesocarbon microbead anode and a lithium–cobalt oxide cathode and separated with a polymer-coated separator, have been assembled and their charge–discharge cycling performance has been evaluated in terms of the thickness of the gelled polymer layer that is coated on the polyolefin separator.

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**Keywords:** Cycling performance; Gelled polymer electrolyte; Lithium-ion polymer cell; Polymer-coated separator; Ionic conductivity

## 1. Introduction

Polymer electrolytes have been actively studied and developed for application in rechargeable lithium-ion polymer batteries. The use of a polymer electrolyte enables fabrication of safe batteries and permits the development of thin batteries with design flexibility. In addition, lithium-ion polymer batteries do not require metal cans that are required to ensure stack pressure between electrodes and separator, and this allows cells to be packaged in plastic material and thus achieve an improvement in specific energy. To date, attempts to obtain solid polymer electrolytes, consisting of a matrix polymer and a lithium salt, have only produced materials with limited ionic conductivity at ambient temperature [1,2]. It has been found that the addition of polar solvents can significantly increase the ionic conductivity of these materials [3]. Such gel polymer electrolytes exhibit high ionic conductivities in excess of  $10^{-3} \text{ S cm}^{-1}$ . On the other hand, mechanical properties are often very poor, which is one of the most important deficiencies preventing them from being used in practical cells. For example, the poor mechanical strength of gel polymer electrolytes can lead to internal short-circuits and safety hazards. In order to overcome the above problem, microporous polyolefin

separators impregnated with gel polymer electrolytes have been developed as an electrolyte material for lithium-ion batteries [4–6]. Abraham et al. [4] prepared a solution which consisted of ethylene carbonate, propylene carbonate, tetraethylene glycol dimethyl ether, tetraethylene glycol diacrylate,  $\text{LiAsF}_6$  and a small amount of a photopolymerization initiator. This solution was impregnated into the porous polyolefin membranes and polymerized to form a solid electrolyte. Recently, a gel polymer electrolyte supported by a microporous polyethylene separator was also prepared and characterized by Kim et al. [5]. Numerous small patches which comprised a fluid adhesive mastic of poly(vinylidene fluoride) (PVdF) in *N*-methyl-pyrrolidinone (NMP) have been applied to both sides of a microporous polyolefin separator [6]. Such membrane-supported polymer electrolytes display excellent mechanical strength for the fabrication of lithium-ion polymer batteries and can therefore help in reducing the overall thickness of the electrolyte layer when compared with gel polymer electrolytes. Despite the considerable number of studies of separators impregnated with gel polymer electrolytes, few have examined the influence on battery performance of the thickness of the gel layer coated on the separator.

With the aim developing highly conductive polymer electrolyte that can be handled like conventional separators used in lithium-ion batteries, this study has attempted to coat gellable porous polymer with different thicknesses on to a microporous polyethylene (PE) separator. Gel polymer

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electrolytes supported by PE separator are prepared by soaking in an electrolyte solution. In these separators, the polyethylene separator can give mechanical integrity to the electrolyte system and offers enhanced safety by exhibiting thermal shutdown under condition of severe abuse, while gellable polymer coated on both sides of the separator is adapted to encapsulate an electrolyte solution in the porous PE separator and to assist further in adhering the electrodes to the separator. The electrochemical characteristics of these polymer electrolytes prepared with polymer-coated separators are reported, and the electrochemical performances of lithium-ion polymer cells composed of a mesocarbon microbead (MCMB) anode and a lithium–cobalt oxide cathode are presented. More attention is paid to the influence of the thickness of the coating polymer layer applied to polyolefin separator on the cycling performance of the cells.

## 2. Experimental

### 2.1. Preparation of polymer-coated separators and electrodes

The gellable polymer coated on the PE separator was acrylonitrile (AN)–methyl methacrylate (MMA) copolymer (hereafter called ‘AM copolymer’). In the copolymer, AN is chosen due to its chemical stability for use in lithium batteries [7], and MMA due to its ability to be easily wetted by polar solvents [8]. The AM copolymer was synthesized by emulsion polymerization with a small amount of potassium persulfate as an initiator, as previously reported [9]. From the  $^1\text{H}$  NMR spectroscopy, the molar composition of AN and MMA was determined to be 84:16. To prepare the polymer-coated separators, AM copolymer was dissolved with different polymer concentration (1, 2, 3 and 4 wt.%) in anhydrous dimethylformamide (DMF). A microporous PE separator (Asahi Kasei, thickness: 25  $\mu\text{m}$ , porosity: 40%) was then dip coated in the polymer solution. The separator was taken out and immersed in a water bath to induce phase inversion. After the exchange of DMF and water by phase inversion, a substantial number of pores were formed in the polymer layer coated on PE separator. The resulting polymer-coated separator was washed with deionized water and vacuum dried at 100  $^\circ\text{C}$  for 24 h. Dried separators with thicknesses that varied from 30 to 45  $\mu\text{m}$ , depending on the polymer concentration of the dipping solution, were obtained. The carbon anode was prepared by coating the NMP-based slurry of MCMB (Osaka gas), 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 electrodes were roll pressed to enhance particulate contact and adhesion to the foils. The thickness of the electrodes ranged from 50 to 65  $\mu\text{m}$ , and their active mass loading corresponded to capacity of about 2.4  $\text{mAh cm}^{-2}$ .

### 2.2. Electrical measurements

The polymer-coated separator was transferred to a glove box and soaked in 1 M  $\text{LiClO}_4$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v, Samsung Cheil Industries, battery grade) for 1 h, to activate the polymer-coated PE separator. After activation, it was taken out from the electrolyte solution and the excess electrolyte solution on the surface of the separator was wiped with filter paper. The wetted separator 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 in order to permit testing outside of a glove box. The AC impedance measurement was performed using a Zahner Elektrik IM6 impedance analyzer. Linear sweep voltammetry was performed on a SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0  $\text{mV s}^{-1}$ . A lithium-ion polymer cell was assembled by sandwiching the activated polymer-coated separator between the MCMB anode and the  $\text{LiCoO}_2$  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 which was filled with argon gas. Charge and discharge cycling tests of lithium-ion cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U).

## 3. Results and discussion

Typical scanning electron micrographs (SEM) of surface of the polymer-coated separator are presented in Fig. 1. As the AM copolymer is coated on the PE separator by dip coating and phase inversion, micropores are formed and the distribution of pores is observed to be uniform. The pores formed in the polymer coated on the PE separator reflect an effective exchange between the organic solvent (DMF) and water during the phase inversion process. The phase inversion method has been shown to be effective for producing a porous structure [10]. An increase in the polymer concentration of the dipping solution gives rise to a decrease in the pore size, as can be seen in Fig. 1. The presence of micropores on the surface of the polymer-coated separator can lead to efficient uptake of the liquid electrolyte when it is soaked in an electrolyte solution, which may finally result in gelation of the coated polymer. The thickness of the polymer layer coated on both sides of the PE separator linearly increases with the polymer concentration of the dipping solution. The thickness ranges from 4 to 19  $\mu\text{m}$ .

Polymer-coated separators with different thicknesses of coating layer were soaked in  $\text{LiClO}_4$  in EC/DMC for 1 h. The polymer coated on both sides of PE separator was gelled in contact with the electrolyte solution. The uptake of electrolyte solution and room temperature conductivity after soaking in the electrolyte solution are summarized in

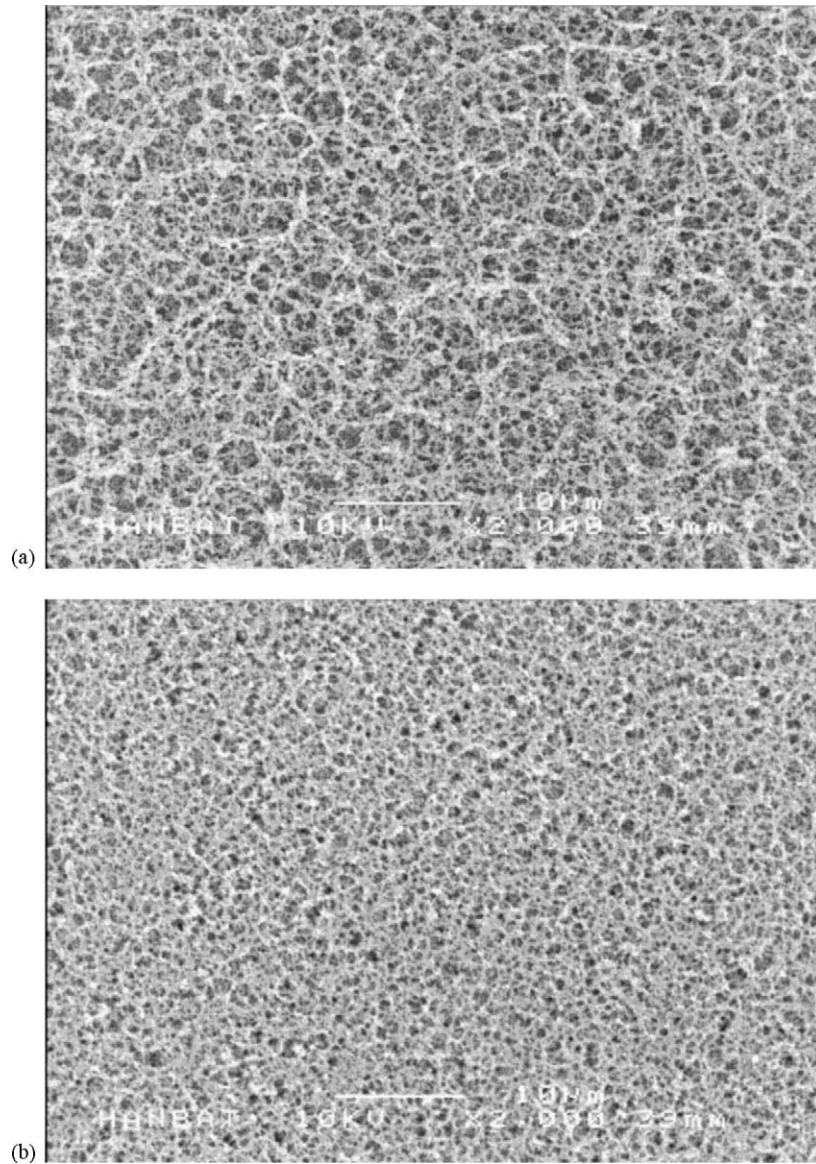


Fig. 1. Scanning electron micrographs of polymer-coated separators prepared with different polymer concentration: (a) 1 wt.%, (b) 3 wt.%.

**Table 1.** The table, uptake was determined as follows:

$$\text{uptake (\%)} = \frac{W_g - W_d}{W_g} \times 100 \quad (1)$$

where  $W_g$  and  $W_d$  are the weights of the gelled and dried polymer-coated separator, respectively. It is found that up-

take of electrolyte solution increases slightly with thickness of the coating layer. As described above, the coating layer on both sides of PE separator consists of AM copolymer. Therefore, an increase of uptake with thickness of coating layer is due to a high affinity of AM copolymer for electrolyte solution, which results from the presence of polar

Table 1

Uptake of electrolyte solution and ionic conductivity of polymer-coated separators with different thickness of coating layer after soaking in electrolyte solution

Polymer concentration in dipping solution (wt.%)	Thickness of coating layer ( $\mu\text{m}$ )	Uptake of electrolyte solution (%)	Ionic conductivity ( $\text{S cm}^{-1}$ )
1.0	4 (30) <sup>a</sup>	85	$7.7 \times 10^{-4}$
2.0	9 (35)	89	$9.1 \times 10^{-4}$
3.0	14 (40)	90	$1.1 \times 10^{-3}$
4.0	19 (45)	91	$1.0 \times 10^{-3}$

<sup>a</sup> Value in parentheses is thickness of polymer-coated separator including PE separator.

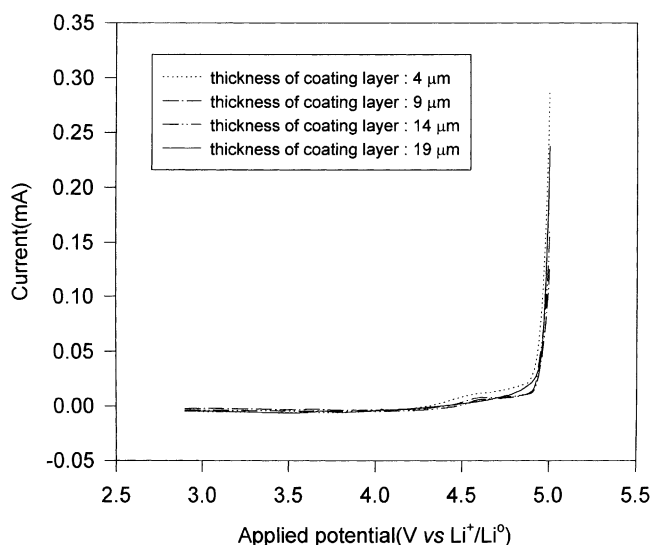


Fig. 2. Linear sweep voltammetry curves of cells prepared with polymer-coated separators soaked with  $\text{LiClO}_4\text{-EC/DMC}$  (scan rate:  $1 \text{ mV s}^{-1}$ ).

functional groups in the AM copolymer. On the other hand, increase in the thickness of the coating layer to more than  $14 \mu\text{m}$  has little effect on the ionic conductivity. From these results, the proper thickness of coating layer to ensure both high uptake of electrolyte solution and good ionic conductivity is thought to be about  $14 \mu\text{m}$  for the systems under study.

The electrochemical stability of the polymer-coated separators soaked by electrolyte solution was evaluated by linear sweep voltammetry. Voltammograms for cells prepared with the polymer-coated separator gelled by an electrolyte solution of  $\text{LiClO}_4\text{-EC/DMC}$  are shown in Fig. 2. The decomposition voltage is found to be high, with no electrochemical oxidation occurring until a potential of  $4.9 \text{ V}$ . This suggests that polymer-coated separator soaked by  $\text{LiClO}_4\text{-EC/DMC}$  is acceptable for high voltage cathode materials, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ . It appears that the decomposition voltage is not influenced by the thickness of the gel layer on the PE separator, as shown in the Fig. 2.

The electrochemical performance of lithium-ion polymer cells prepared with the polymer-coated separators has been evaluated. The assembled cells were initially subjected to a pre-conditioning cycle with a cut-off voltage of  $4.2 \text{ V}$  for charge and  $2.8 \text{ V}$  for discharge at a constant current of  $0.24 \text{ mA cm}^{-2}$  ( $C/10$  rate). The pre-conditioning charge–discharge cycles of the lithium-ion polymer cells prepared with polymer-coated separators having different thickness of gelled coating layer are given in Fig. 3. It can be seen that the discharge capacities of the cells are almost the same, regardless of the thickness of the gel layer. The AC impedance spectra of the lithium-ion polymer cells prepared with the polymer-coated separators of different coating layer thickness, are shown in Fig. 4. The spectra were obtained at a fully discharged state after the pre-conditioning cycle. It has been reported [11,12] that the AC impedance spectrum

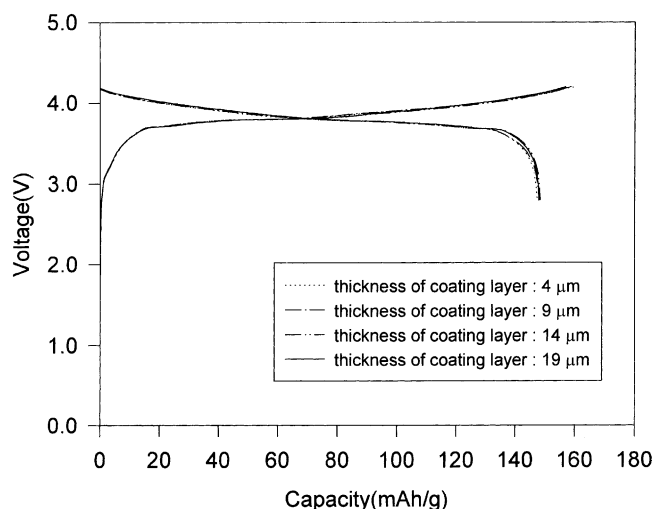


Fig. 3. First pre-conditioning charge–discharge cycles of lithium-ion polymer cells prepared with polymer-coated separators of different coating layer thickness.

of a lithium-ion cell depends on the state-of-charge. For a fair comparison, a study was made of the cell in a fully discharged state. According to previous work [11], the AC impedance spectrum of a lithium-ion cell is composed of three partially overlapping semicircles in high, medium and low frequency regions, and a straight sloping line at the very low frequency region. After the pre-conditioning cycle in the present work, the AC impedance spectra showed a combination of poorly separated semicircles and a Warburg line related to the diffusion of  $\text{Li}^+$  within the electrodes. From other investigations [11,13], the overlapping semicircles

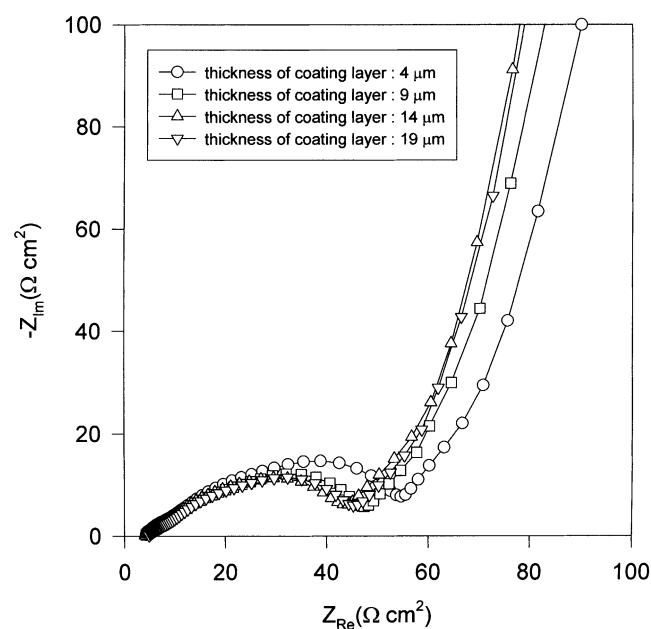


Fig. 4. AC impedance spectra of lithium-ion polymer cells prepared with polymer-coated separators of different coating layer thickness. Spectra measured after pre-conditioning cycle.



Table 2

Electrolyte resistance ( $R_e$ ) and interfacial resistance ( $R_i$ ) in lithium-ion polymer cells prepared with polymer-coated separator with different thickness of coating layer

Thickness of coating layer ( $\mu\text{m}$ )	$R_e$ ( $\Omega \text{ cm}^2$ )	$R_i$ ( $\Omega \text{ cm}^2$ )	$R_t$ ( $\Omega \text{ cm}^2$ ) <sup>a</sup>
4	4.3	50.4	54.7
9	4.2	43.2	47.4
14	4.0	40.1	44.1
19	4.9	40.4	45.3

<sup>a</sup> Value of  $R_t$  means total resistance of cell ( $R_e + R_i$ ).

observed from high to low frequency regions correspond to the SEI film impedance and the charge transfer process. Of particular interest in the depressed semicircles is the total interfacial resistance ( $R_i$ ), which is the sum of the resistance of the SEI ( $R_{\text{SEI}}$ ) and the charge transfer resistance ( $R_{\text{ct}}$ ). The electrolyte resistance ( $R_e$ ) and the total interfacial resistance ( $R_i$ ), determined from the AC impedance spectra in Fig. 4, are listed in Table 2. When comparing the electrolyte resistance, the cell prepared with polymer-coated separator of 14  $\mu\text{m}$  coating layer has the lowest resistance. The larger value of electrolyte resistance in the polymer-coated separator with a 19  $\mu\text{m}$  layer is attributed to the higher thickness of the polymer-coated membrane. It can be also seen from Table 2 that the interfacial resistance decreases with the thickness of the coating layer on the PE separator in the cell. The gel layer on both sides of the PE separator has an adhesive property, and thus a thick adhesive layer can achieve efficient interfacial bonding of the separator to the electrodes. Such intimate contact can give favorable interfacial properties, which results in lowering of the interfacial resistance. During the pre-conditioning cycle (Fig. 3), the voltage drop in passing from charge to discharge is observed to be lowest in the cell prepared with the polymer-coated separator with a 14  $\mu\text{m}$  layer. This result indicates that this cell has the lowest internal cell resistance, which is consistent with the AC impedance results discussed above.

After the pre-conditioning cycle, the cells were subjected to a cycle test at a constant current of  $0.48 \text{ mA cm}^{-2}$  (C/5 rate) with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit. The resulting discharge capacities are shown in Fig. 5 as a function of cycle number. It should be noted that the cycling tests were performed without applying external pressure to the cells. As in the pre-conditioning cycle, the initial discharge capacities depend little on the thickness of the gel layer on PE separator. Cells initially deliver about  $147 \text{ mAh g}^{-1}$  based on  $\text{LiCoO}_2$  active material in the cathode. The cycling characteristics of the cells appear to depend on the thickness of the gel layer. The use of polymer-coated separators with a thick gel layer allows good cycling characteristics to be reached. This result is due to the fact that the AM copolymer coated on both sides of the PE separator can adapt to encapsulate an electrolyte solution in the porous PE separator and can further assist in adhering

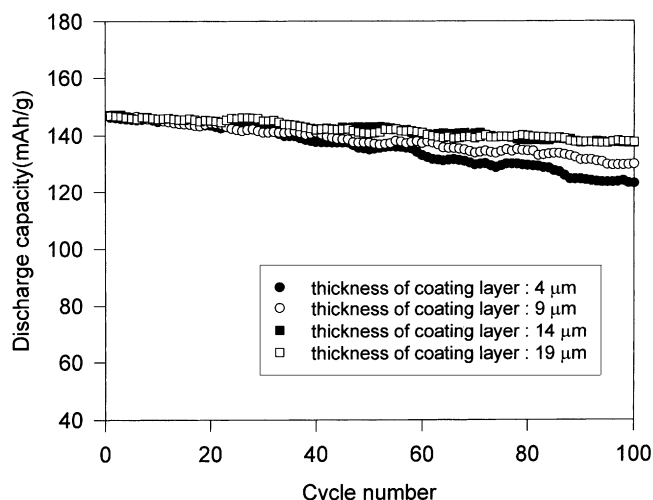


Fig. 5. Discharge capacities as a function of cycle number in the cells prepared with the polymer-coated separators of different gel layer thickness.

the electrodes to the separator, which result in good capacity retention. Cells prepared with a polymer-coated separator with a 14 or 19  $\mu\text{m}$  layer retain about 94% of the initial discharge capacity after 100 cycles.

In order to clarify the reason why a cell using a polymer-coated separator with a thick gel layer shows better cycling performance, measurement was also made of the AC impedance of the cell after repeated charge and discharge cycles. Spectra of lithium-ion polymer cells in a fully-discharged state after 100 cycles are presented in Fig. 6. The spectra are clearly composed of two semicircles, which can be assigned to the impedance of the SEI

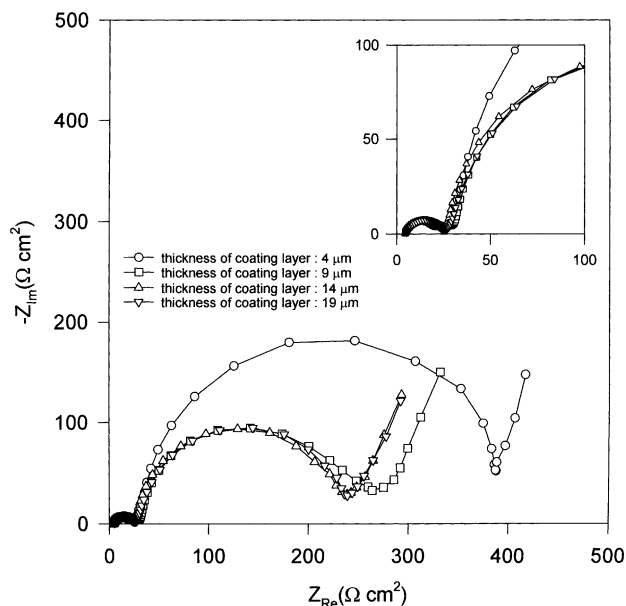


Fig. 6. AC impedance spectra of lithium-ion polymer cells prepared with polymer-coated separators of different coating layer thickness. Spectra measured after repeated 100 cycles.

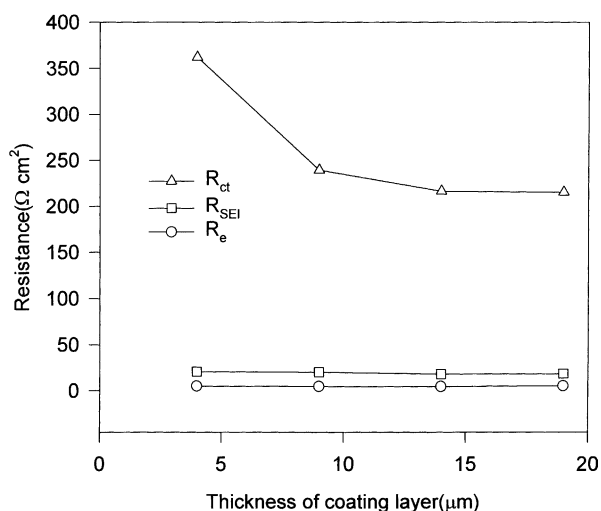


Fig. 7. Variation of  $R_e$ ,  $R_{SEI}$  and  $R_{ct}$  with thickness of gel layer in cells after repeated 100 cycles.

( $R_{SEI}$ ) and the charge transfer process ( $R_{ct}$ ), respectively, with a slopping straight Warburg line at low frequency. The variation of  $R_e$ ,  $R_{SEI}$  and  $R_{ct}$  with the thickness of the gel layer, which are extracted from the AC impedance spectra given in Fig. 6, are shown in Fig. 7. Clearly, there is little dependence of the thickness of the gel layer on the values of  $R_e$  and  $R_{SEI}$ . By contrast, the value of  $R_{ct}$  is significantly decreased with the coating layer thickness. In other words, the impact of  $R_b$  and  $R_{SEI}$  on the cycling performance of the cell is rather small compared with that of  $R_{ct}$ . It is plausible that the thicker the gel layer on both sides of PE separator, the stronger is the interfacial bonding between the electrodes and the separator, which is essential for efficient charge transport during repeated cycling. Therefore, it can be concluded that stable cycling characteristics of the lithium-ion polymer cell prepared with the polymer-coated separator of thicker gel layer can be ascribed to an efficient charge-transfer reaction in the cell, which originates from the good interfacial properties.

The voltage profiles of a cell prepared with a polymer-coated separator with a 14 μm gel layer are presented in Fig. 8; the profiles are obtained at different current rates. It is found that the voltage profiles remain almost unchanged on increasing the current rate from a 0.2 to a 2.0 C rate, with a slight decrease in both average discharge voltage and discharge capacity. At the 2.0 C rate, the cell could deliver a discharge capacity of 137 mAh g<sup>-1</sup> based on LiCoO<sub>2</sub> material in the cathode, which corresponds to 94% of the capacity delivered at the 0.2 C rate. Good performance at a high current rate may be ascribed to efficient ionic conduction in the polymer-coated separator and favorable interfacial charge transport between electrodes and electrolyte in the cell. The relative capacities of lithium-ion polymer cells prepared with polymer-coated separators of different coating layer thickness are given in Fig. 9, as a function of cur-

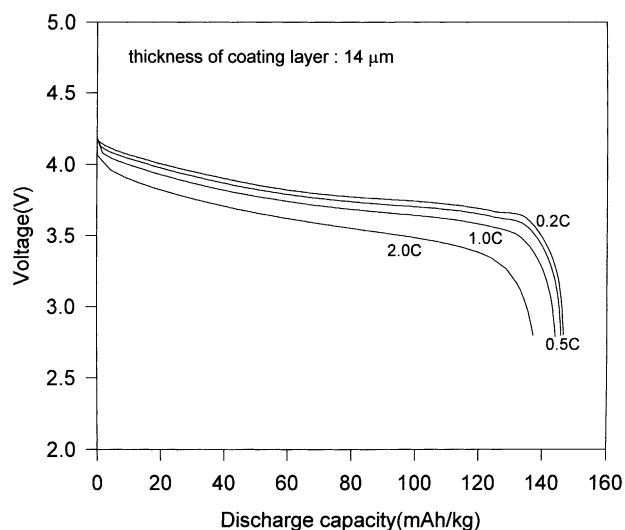


Fig. 8. Discharge profiles of lithium-ion polymer cell prepared with polymer-coated separator with 14 μm gel layer, as function of current rate. Charge rate is 0.2 C with 4.2 V cut-off.

rent rate. The relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge capacity delivered at the 0.2 C rate. The cell prepared with the polymer-coated separator with a 14 μm gel layer exhibits the best rate performance. Increasing the thickness of the gel layer can facilitate the charge transfer reaction, but cannot lower the electrolyte resistance, as discussed above. Therefore, it is concluded that the better rate performance of the cell with a 14 μm gel layer compared with that with a 19 μm gel layer is due to the reduced electrolyte resistance, since these two cells have similar  $R_{SEI}$  and  $R_{ct}$  values. From these results, the optimum thickness of coating layer on PE separator to ensure both good capacity retention and excellent rate performance is thought to be about 14 μm.

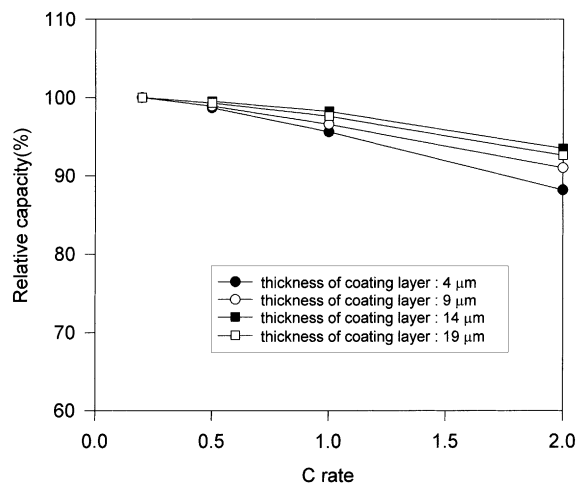


Fig. 9. Relative capacities of lithium-ion polymer cells prepared with polymer-coated separators of different coating layer thickness, as function of current rate.

#### 4. Conclusions

It has been demonstrated that a polymer-coated separator could be a good candidate for use in lithium-ion polymer batteries. The porous polymer coated on both sides of PE separator is gelled in contact with the electrolyte solution and encapsulates a larger amount of electrolyte solution. A gel layer on both sides of the PE separator promotes strong interfacial adhesion between the electrodes and the separator, and the intimate contact is found to be essential for good capacity retention. Lithium-ion polymer cells using a polymer-coated separator with a 14  $\mu\text{m}$  coating layer display a stable high discharge capacity and excellent rate performance even though packed in a flexible plastic pouch without applying external pressure. These results suggest that a polymer-coated separator with a proper thickness of gel layer is a promising electrolyte material for rechargeable lithium-ion polymer cells.

#### Acknowledgements

This work has been supported in part by the Ministry of Information & Communication of Korea. (“Support Project of University Information Technology Research Center” supervised by KIPA.).

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