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The role of an adhesive gel-forming polymer coated on separator for rechargeable lithium metal polymer cells

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Abstract

The gel-forming polymer of different thicknesses was coated on both sides of polyethylene separator. The porous polymer coated on the separator was gelled by soaking in an electrolyte solution and encapsulated a larger amount of electrolyte solution. Adhesive gel formed on both sides of PE separator provided an efficient transport of lithium ion through the solid electrolyte interphase, and the electrolyte solution absorbed in the separator gave an acceptable ionic conductivity. By using the separators with adhesive gel layer, lithium metal polymer cells composed of a lithium anode and $LiCoO_2$ cathode were assembled and their cycling performances were evaluated. The effect of thickness of gel polymer layer on cycling performances of the rechargeable lithium-metal polymer cells was investigated.

PACS: 72.80.L Polymers; Electrical conductivity

Keywords: Cycling performance; Gel-forming polymer; Lithium metal polymer cell; Polymer-coated separator; Solid electrolyte interphase

1. Introduction

Rechargeable lithium battery using lithium metal as an anode is the most attractive candidate for high energy density power sources for portable electronic devices, electric vehicles and load leveling systems. The major problem that prevents the lithium metal battery to achieve a comparable success is the risk associated with the reactivity of lithium metal that can affect cycle life of the battery and its safety. In order to solve this problem, polymer electrolytes have been introduced as a novel electrolyte material in the field of lithium metal batteries [1–6]. The concept is to stabilize the lithium electrode interface by the use of dry solid polymer electrolyte or gel polymer electrolyte. In particular, gel polymer electrolyte consisted of matrix polymer, organic solvent and salt exhibit high ionic conductivity exceeding 10^{-3} S/cm at room temperature [7], which is necessary for battery applications. When the gel polymer electrolyte is applied as an electrolyte in rechargeable lithium batteries, it also enables to utilize a flexible pouch rather than a metal can to package the battery, resulting in increased form factor such as battery size and shape. However, such gel polymer electrolyte suffers from poor mechanical strength, making assembly difficult and increasing the incidence of shorting between electrodes. In order to overcome this problem, the polyolefin separators impregnated with gel polymer electrolytes have been developed as an electrolyte material [8–10]. By Abraham et al. [8], a solution consisting of ethylene carbonate, propylene carbonate, tetraethylene glycol dimethyl ether, tetraethylene glycol diacrylate, $LiAsF_6$ and a small amount of a photopolymerization initiator was impregnated into the porous polyolefin membrane and polymerized to form a solid electrolyte. Numerous small dots comprising 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 [10]. Such membrane-supported gel polymer electrolytes show excellent mechanical strength for the fabrication of batteries and can therefore help in reducing the overall thickness of the electrolyte layer when compared to conventional gel polymer electrolytes. However, despite a considerable number of reports on the studies about the separators impregnated with gel polymer electrolytes, few studies have been conducted on the role of gel-forming polymer coated on separator on the lithium metal battery performances.

With the aim of developing highly conductive polymer electrolyte that can be handled like conventional separators,

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we tried to coat gel-forming porous polymer onto a microporous polyethylene (PE) separator. Gelation of polymer on PE separator occurred by soaking the polymer-coated separator in an electrolyte solution. In the polymer-coated separator, gel-forming polymer coated on both sides of the separator is adapted to encapsulate an electrolyte solution in the porous PE separator and to further assist in adhering the electrodes to the separator. In our work, separators with different thicknesses of gel layer are prepared, and the cycling performances of lithium polymer batteries composed of a metallic lithium anode and a lithium-cobalt oxide cathode are presented. More attention will be paid to the influence of the thickness of gel layer formed onto polyolefin separator on cycling performances of the rechargeable lithium metal polymer cells.

2. Experimental

2.1. Preparation of polymer-coated separators

The gellable polymer coated on PE separator in this work is acrylonitrile (AN)–methyl methacrylate (MMA) copolymer (hereafter called the AM copolymer). The AM copolymer was synthesized by emulsion polymerization with a small amount of potassium persulfate as an initiator, as previously reported [11]. From the ^{1}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 concentrations (1, 2, 3 and 4 wt.%) in an anhydrous dimethylformamide (DMF). A microporous PE separator (Asahi Kasei, thickness: 25 μm, porosity: 40%) was then immersed in the polymer solution for 3 h. The separator was taken out and immersed in a water bath in order 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 °C for 24 h. The polymer-coated separator was transferred into a glove box and soaked in either 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) or 1 M $LiClO_4$ in EC/propylene carbonate (PC) (1:1 by volume) for 1 h. The separator with gel polymer layer was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The ac impedance measurement was performed using Zahner Elektrik IM6 impedance analyzer.

2.2. Li/$LiCoO_2$ cell

The cathode was prepared by coating the NMP-based slurry of $LiCoO_2$ (Japan Chemical), PVdF and super-P carbon on an aluminum foil. The thickness of cathode was about 55 μm after roll-pressing, and its active mass loading corresponded to the capacity of about 2.4 mA h/cm^2. The anode consisted of 50-μm-thick Li foil (Cyprus Foote Mineral) pressed onto copper current collector. Lithium metal polymer cell was assembled by sandwiching the separator with gel polymer layer between lithium anode and $LiCoO_2$ 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. In order to investigate the interfacial phenomena of Li/SGP/$LiCoO_2$ cell (SGP: separator with gel polymer), ac impedance measurement was performed using an impedance analyzer over the frequency range of 0.001 Hz to 100 kHz with an amplitude of 10 mV. The charge and discharge cycling tests of lithium metal polymer cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U). To measure the discharge capacities at low temperature, the cells were charged at 0.2 C rate (0.48 mA/cm^2) at room temperature, equilibrated at the test temperature for 6 h, and then discharged with a constant current of 0.2 C at the test temperature.

3. Results and discussion

As the AM copolymer was coated on the PE separator by dip coating and phase inversion, micropores were formed and the distribution of pores was observed to be uniform, as has been reported previously [12]. The presence of pores in the gel-forming polymer coated on PE 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. Thickness and weight of gel-forming polymer coated on both sides of PE separator are linearly increased with polymer concentration, as given in Table 1. The polymer-coated separators with different thicknesses of coating layer were soaked in $LiClO_4$ in EC/DMC for 1 h. The porous polymer coated on both sides of PE separator was gelled and became sticky in contact with the electrolyte solution. After soaking in the electrolyte solution, thickness of gel layer on PE separator, amount of an electrolyte

Table 1
Physical properties of the polymer-coated separators

Polymer concentration (wt.%)	1	2	3	4
Thickness of polymer coated (μm)	4.2 (29.2)[a]	8.9 (33.9)	13.6 (38.6)	18.5 (43.5)
Weight of polymer coated (mg/cm^2)	0.10	0.18	0.25	0.31
After soaking in $LiClO_4$ in EC/DMC (1:1)				
Thickness of gelled layer (μm)	2.1 (27.1)[a]	4.3 (29.3)	6.1 (31.1)	7.9 (32.9)
Amount of electrolyte solution (%)	84.6	89.0	90.2	90.9
Ionic conductivity (S/cm)	7.7×10^{-4}	9.1×10^{-4}	1.1×10^{-3}	1.0×10^{-3}

[a] The value in parentheses is the thickness including the PE separator.

solution absorbed, and ionic conductivity are summarized in Table 1. It can be seen that the thickness of polymer-coated PE separator was decreased after gelation by soaking in electrolyte solution. This result is due to the fact that the porous gel-forming polymer layer is changed to the dense gel polymer layer by destruction of pores in the polymer coated on PE separator. With increasing the thickness of the gel-forming polymer layer, uptake of an electrolyte solution is increased and eventually reaches a steady-state value. As described above, the gel-forming layer on both sides of PE separator is consisted of porous AM copolymer. Therefore, an increase of uptake with thickness of gel-forming layer is due to a high affinity of AM copolymer for electrolyte solution, which results from the presence of polar functional groups in AM copolymer. On the other hand, an increase in thickness of gel-forming polymer more than 13.6 µm has little effect on both the uptake of electrolyte solution and the ionic conductivity.

Fig. 1 shows the charge–discharge curve of the first two cycles of Li/SGP/$LiCoO_2$ cell, which is obtained at a constant current density of 0.24 mA/cm^2. In this cell, SGP was prepared by soaking the polymer-coated separator in $LiClO_4$-EC/DMC. The voltage drop in passing from charge to discharge is observed to be small, which means lower resistance of the cell. It is evaluated that coulombic efficiencies of the first two cycles are 96.2% and 99.1%, respectively. After the initial few cycles, the coulombic efficiencies gradually approach to unity (about 99.5%).

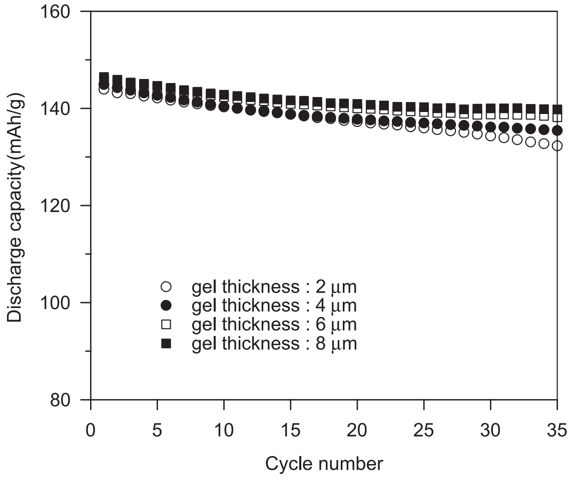

Fig. 2. Discharge capacities as a function of cycle number for the Li/$LiCoO_2$ cells prepared with the separator of different gel thicknesses. Cycling was carried out at constant current density of 0.24 mA/cm^2 between 3.0 and 4.2 V.

Fig. 2 shows the discharge capacities as a function of cycle number in the cells prepared with the separators of different gel thicknesses. It should be noted the cycling tests obtained in this figure are performed without applying external pressure to the cell. Initial discharge capacities of the cells ranged from 144 to 146 mA h/g based on $LiCoO_2$ active material in the cathode, and the values are observed to be slightly increased with the thickness of gel layer on PE separator. Cycling characteristics of the cells also seem to depend on the thickness of gel layer on PE separator. The use of separator with thicker gel layer allowed better cycling characteristics to be reached. These results are due to the fact that the adhesive gel formed on PE separator provides a strong interfacial contact between PE separator and electrodes such that applying external pressure is not necessary.

In order to clarify the reason that the cell prepared with the separator of thicker gel layer shows better cycling performances, we measured the ac impedance of the cells after the repeated charge and discharge cycles (35 cycles). Although the resistance includes contribution from both the cathode and the anode in the lithium cells, the contribution of the resistance of the anode solid electrolyte interphase (SEI) is the major one [13,14]. Since an equivalent circuit for SEI is extremely complex and can be represented by a very large number of series and parallel distribution of RC elements, a rigorous identification of a combination of many

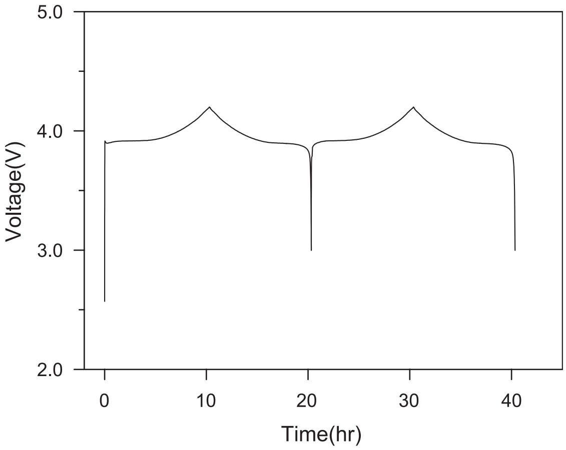

Fig. 1. Charge–discharge curve of the first two cycles of the Li/$LiCoO_2$ cell employing separator with gel polymer layer (thickness: 6.1 µm), which was measured at 0.24 mA/cm^2.

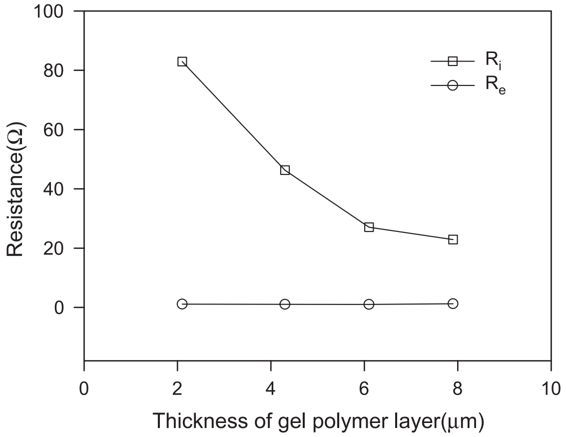

Fig. 3. Variation of R_e and R_i in the Li/$LiCoO_2$ cells with thickness of gel layer after the repeated 35 cycles.

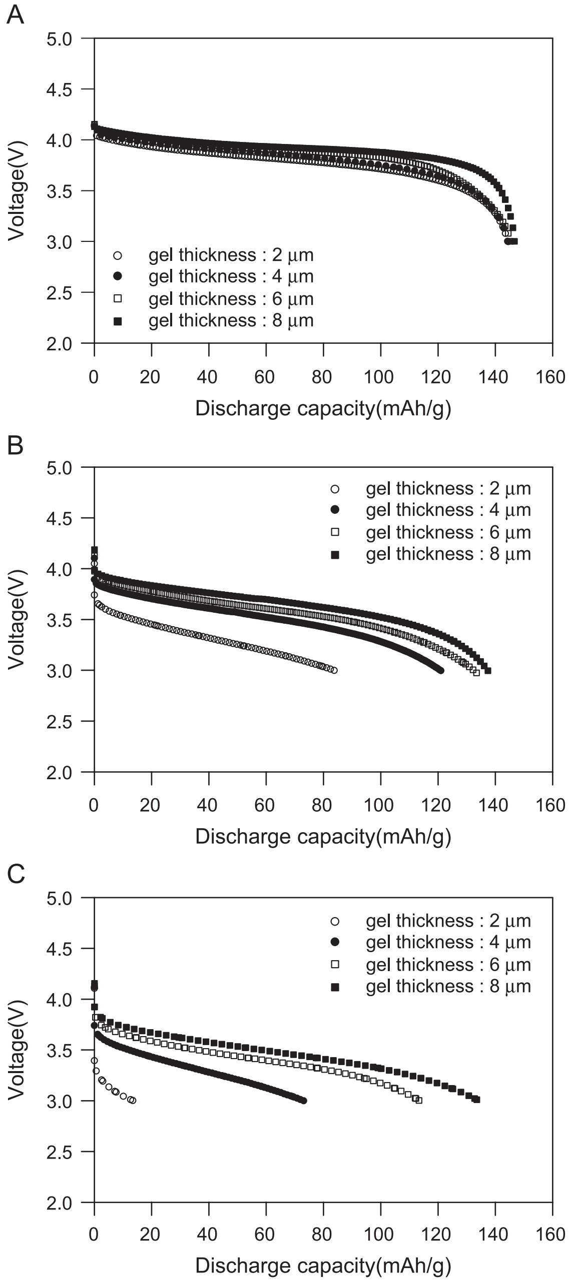

Fig. 4. Discharge profiles of the Li/LiCoO$_2$ cells prepared with the separator of different gel thicknesses, which are obtained at different current rates: (A) 0.48, (B) 1.20 and (C) 2.40 mA/cm^2.

poorly separated semicircles is beyond the scope of this work. Of particular interest in the ac impedance spectra is the total interfacial resistance, which is related to the migration of Li$^+$ and charge transfer. The results are presented in Fig. 3, which represents a variation of electrolyte resistance (R_e) and interfacial resistance (R_i) with thickness of gel layer. It is found that there is little dependence of thickness of gel layer on the value of R_e. However, the value of R_i is decreased with the gel layer thickness. As discussed above, it is plausible that the thicker the gel layer on both sides of PE separator, the higher is the electrolyte uptake and the easier is the lithium-ion transport through the SEI, which results in a decrease of R_i with thickness of gel layer. Good interfacial contact between the adhesive gel layer on separator and lithium electrode can also contribute to the suppression of dendrites. Therefore, we can say that stable cycling characteristics of the lithium metal polymer cell prepared with the polymer-coated separator of thicker gel layer can be ascribed to the efficient charge transfer reaction and the formation of less resistive SEI.

The rate capability of the lithium metal polymer cell was evaluated. The discharge curves obtained at different current rates are given in Fig. 4. The charge current was 0.48 mA/cm^2 for all the measurements. It is found that the discharge capacity is almost the same at low current density, regardless of the thickness of gelled polymer layer. This may be due to the fact that the current rate tested (0.48 mA/cm^2, 0.2 C) is not high enough to reflect the difference in the interfacial resistances. However, with increasing current rate to 1.20 or 2.40 mA/cm^2, the cell prepared with separator of thicker gel layer not only shows lower polarization but also delivers higher discharge capacity. High rate performance of the cell prepared with separator of thicker gel layer is likely encouraged by the fast kinetics of the charge transfer reaction and the less resistive SEI film, as expected and already discussed.

The Li/SGP/LiCoO$_2$ cell was prepared with separator of thick gel layer (gel thickness: 8 μm) in order to evaluate low temperature performance. In the test, SGP was prepared by soaking the polymer-coated separator in LiClO$_4$-EC/PC, because PC can effectively suppress the crystallization of EC. Fig. 5 shows the discharge curves obtained at different temperatures. In the figure, the relative capacity is defined as the ratio of the discharge capacity at test temperature to the discharge capacity delivered at room temperature. Both the voltage and the capacity are found to decrease gradually

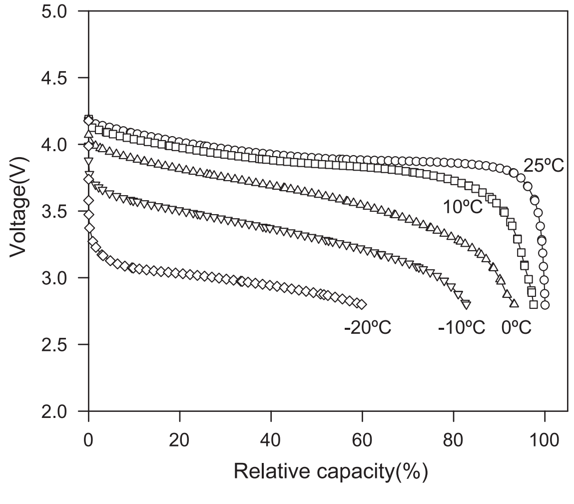

Fig. 5. Discharge profiles of the Li/LiCoO$_2$ cells prepared with the separator of 8 μm gel thickness, which are obtained at different temperatures. Charge rate is 0.2 C with 4.2 V cutoff at room temperature, and discharge rate is 0.2 C with 2.8 V cutoff at test temperature.

with decreasing temperature, which caused by both the high polarization due to the increase of the internal resistance of the cell and the reduced lithium ion diffusivity in the electrode. Cell resistance includes both electrolyte resistance and interfacial resistance (resistance of SEI, charge transfer resistance). At -20 °C, the discharge capacity of the cell was 60% compared with that obtained at room temperature. This result is not sufficient as a low temperature performance of the cell, and must be improved further by optimizing the solvents and the salts used in preparing SGP. Further research is being conducted in the author's laboratory to improve the cycle life, high rate performance and low temperature performance for the rechargeable lithium metal polymer cells.

4. Conclusions

The gel-forming porous polymer coated on both sides of PE separator was gelled in contact with the electrolyte solution and encapsulated a larger amount of electrolyte solution. Gel layer formed on both sides of PE separator promoted strong interfacial adhesion between electrodes and separator, and the intimate contact was proved to be essential for good capacity retention in the cell. Cycling performances of the Li/$LiCoO_2$ cells were shown to be dependent on the thickness of gel layer on PE separator, when tested as packed in a flexible plastic pouch without applying external pressure. The cell prepared with the separator of thicker gel layer exhibited a less capacity fading and better high rate performance. Better performance of the cell prepared with separator having thick gel layer can be ascribed to both the higher electrolyte uptake and the easier lithium-ion transport through the SEI.

Acknowledgements

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