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Cycling performances of Li/LiCoO$_2$ cell with polymer-coated separator

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Abstract

Gel polymer electrolyte (GPE) was prepared with the porous polymer-coated separator by soaking in an electrolyte solution. The porous polymer coated on both sides of polyethylene separator was gelled in contact with the electrolyte solution and encapsulated a larger amount of electrolyte solution. The gel polymer electrolyte exhibited high ionic conductivity in order of 10^{-3} S/cm and was electrochemically stable up to 4.9 versus Li. With the gel polymer electrolyte, lithium metal polymer cell composed of a lithium anode and LiCoO$_2$ cathode was assembled and its cycling performances were evaluated.

Keywords: Cycling performance; Gel polymer electrolyte; Lithium cobalt oxide; Lithium polymer battery; Polymer-coated separator

1. Introduction

There has been an increasing need for high energy density rechargeable batteries for portable electronic equipments. Among them, lithium polymer batteries are now being widely studied and developed, because they can be produced in a variety of forms, thus permitting portable batteries of the required shapes to be produced readily, and enabling customization of portable power driven electronic equipment to be produced [1–4]. Conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes have been the most commonly studied, but they exhibited ionic conductivities ranging from 10^{-8} to 10^{-5} S/cm at room temperature, which is not enough for practical application at ambient temperature. In this respect, most of recent research works have been directed to the preparation and characterization of gel polymer electrolytes (GPE) that exhibit higher ionic conductivity at ambient temperature [5]. Such GPEs exhibit high ionic conductivities in excess of 10^{-3} S/cm, but the mechanical properties of the material are not enough to produce thin films, because the impregnation of liquid electrolyte into a polar polymer resulted in softening of the polymer.

In this study, with the aim developing highly conductive polymer electrolyte that can be handled like conventional separators, we tried to coat gellable porous polymer onto a microporous polyethylene (PE) separator. With the polymer-coated separator, gel polymer electrolyte supported by PE separator was prepared by soaking in an electrolyte solution. In the polymer-coated separator, polyethylene separator can give mechanical integrity to the electrolyte system and offers the enhanced safety of exhibiting thermal shutdown under severe abuse condition, while gellable polymer-coated on both sides of the separator is adapted to encapsulate an electrolyte solution in the porous PE separator and to further assists in adhering the electrodes to the separator. The electrochemical characteristics of the gel polymer electrolyte prepared with polymer-coated separator are reported, and the cycling performances of lithium polymer batteries composed of a metallic lithium anode and a lithium-cobalt oxide cathode are presented.

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2. Experimental

2.1. Preparation of polymer-coated separators and electrodes

The gellable polymer-coated on PE separator in this work is acrylonitrile (AN)–methyl methacrylate (MMA) copolymer (hereafter called the AM copolymer). In the copolymer, AN is considered due to its chemical stability for use in lithium batteries [6] and MMA is considered due to its ability to be easily wetted by the polar solvents [7]. Molar ratio of AN and MMA in the AM copolymer was 84:16. To prepare the polymer-coated separator, AM copolymer was dissolved 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 for 5 h 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 80 °C for 24 h. The cathode was prepared by coating the NMP-based slurry of $LiCoO_2$ (Japan Chemical), PVdF and super-P carbon on an aluminum foil. Electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of cathodes ranged from 50 to 65 μm, and their active mass loading corresponded to capacity of about 2.4 mAh/cm^2. The anode consisted of a 50 μm thick Li foil pressed on to a copper current collector.

2.2. Electrical measurements

The polymer-coated separator was transferred into a glove box and soaked in 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) for 1 h. The wetted separator was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The ac impedance measurement was performed using Zahner Elektrik IM6 impedance analyzer. A linear sweep voltammetry was performed on a SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV/s. Lithium metal polymer cell was assembled by sandwiching the activated polymer-coated separator 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. The charge and discharge cycling tests of lithium-metal polymer cells were conducted in the voltage range of 3.0–4.2 V with Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

Scanning electron micrographs (SEM) of surface for the porous PE separator and the polymer-coated separator are presented in Fig. 1. The PE separator shows a uniform submicron pore structure. 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 PE separator reflect an effective exchange between the organic solvent (DMF) and water during phase inversion process. The phase inversion method has been shown to be effective for producing a porous structure [8]. 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. Since some of AM copolymer is penetrated into the pores of PE separator, the coated polymer can be physically affixed to the PE separator. Thickness of polymer layer coated on both sides of PE separator was about 18 μm. The mechanical strength of the polymer-coated separator was of the same order as that of the PE separator itself.

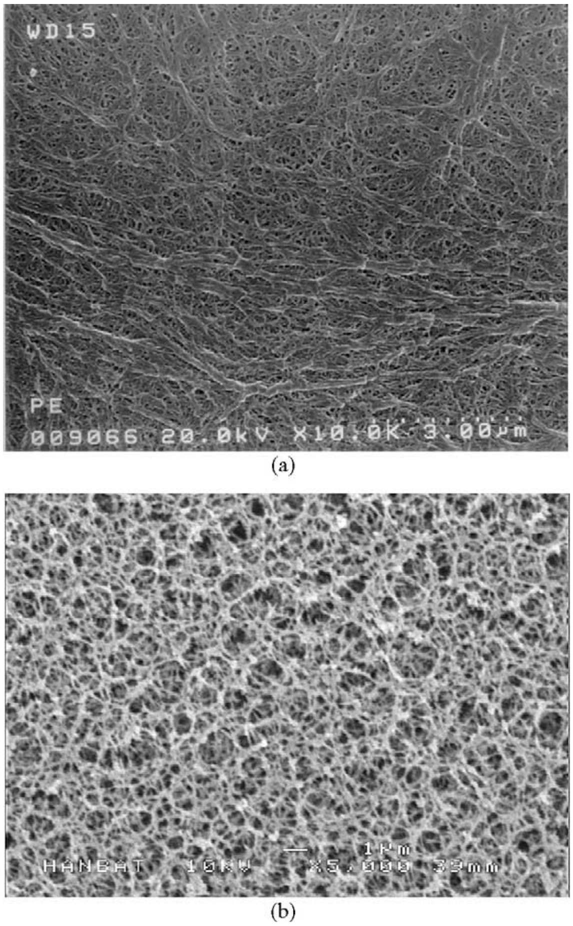

Fig. 1. SEM images of surface for the PE separator (a) and the porous polymer-coated separator (b).

The polymer-coated separator was soaked in $LiClO_4$-EC/DMC for 1 h. The polymer coated on both sides of PE separator was gelled in contact with the electrolyte solution. Amount of an electrolyte solution and ionic conductivity after soaking in the electrolyte solution are 91 wt.% and 1.0

× 10^{-3} S/cm, respectively. High value of uptake of electrolyte solution is due to a high affinity of AM copolymer for electrolyte solution, which results from the presence of polar functional groups in AM copolymer. Gelled polymer layer on PE separator became very sticky after physical gelation by electrolyte solution, thus it is expected that it could promote a strong interfacial adhesion between PE separator and electrodes. From the linear sweep voltammetric measurement, the current onset of the polymer-coated separator gelled by $LiClO_4$-EC/DMC was detected over 4.9 V versus Li, which can be assigned to the decomposition voltage of the gelled polymer electrolyte.

Li/PE/$LiCoO_2$ cell was fabricated with the above polymer electrolyte. Fig. 2a shows the charge–discharge curves with number of cycles, which are obtained at a constant current density of 0.24 mA/cm^2. The cell has a first charge capacity of 150 mAh/g followed by reversible discharge capacity of 146 mAh/g based on $LiCoO_2$ active cathode material. The initial coulombic efficiency of the cell is 97.3%. The voltage drop in passing from charge to discharge was observed to be small, which means lower resistance of the cell. As previously described, the gel layer on both sides of PE separator could promote strong interfacial adhesion between electrodes and separator, and the intimate contact may contribute to lower the interfacial resistance of the cell. Fig. 2b shows the discharge capacities of the cell as a function of cycle number. This figure shows good capacity retention with the repeated cycling. This is a convincing indication of a good interfacial contact between electrodes and separator. The coulombic efficiency of the cell is maintained to be higher than 99.5% through cycling after the initial few cycles. An increase of coulombic efficiency is associated with an improved interfacial property during charge–discharge cycles of the cell. This presumption was confirmed by ac impedance analysis of the Li/PE/$LiCoO_2$ cell with the repeated cycling [9].

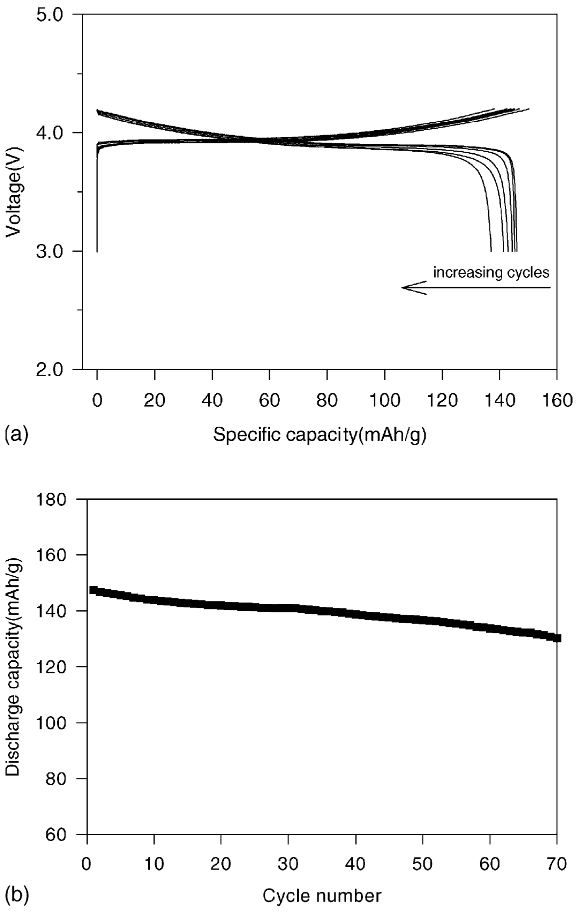

Fig. 2. (a) Charge and discharge curves (1, 2, 5, 10, 20, 50th cycle) and (b) variation of discharge capacity with cycle number for Li/PE/$LiCoO_2$ cell prepared with polymer-coated separator. Cycling was carried out at constant current density of 0.24 mA/cm^2 between 3.0 and 4.2 V.

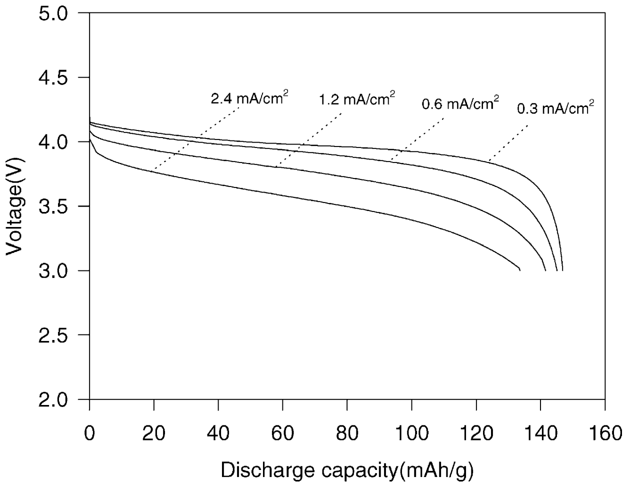

Fig. 3. Discharge profiles of a Li/PE/$LiCoO_2$ cell as a function of current rate.

The rate capability of the lithium metal polymer cell was evaluated. The discharge curves obtained at different current rates are given in Fig. 3. It is found that the voltage profiles remain almost unchanged on increasing the current rate from 0.3 to 2.4 mA/cm^2, with a slight decrease in both average discharge voltage and discharge capacity. At 2.4 mA/cm^2 (1.0 C rate), the cell could deliver a fairly high discharge capacity of 134 mAh/g based on $LiCoO_2$ material in the cathode. Good performance at high current rate may be ascribed to the efficient ionic conduction in the polymer-coated separator and the favorable interfacial charge transport between electrodes and electrolyte in the cell.

4. Conclusions

We have demonstrated that the polymer-coated separator could be a good candidate for use in lithium metal polymer batteries. The 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 on both sides of PE separator promoted strong interfacial adhesion between electrodes and separator, and the intimate contact was proven to be essential for good capacity retention in the cell. The Li/GPE/$LiCoO_2$ cell prepared with the polymer-coated separator exhibited a stable high discharge capacity and good rate performance even though packed in a flexible plastic pouch without applying external pressure. These results lead us to conclude that the polymer-coated separator is a promising electrolyte material for rechargeable lithium metal polymer batteries.

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References

[1] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Review, vol. 1–2, Elsevier Applied Science, London, 1987–1989.
[2] J.S. Tonge, D.F. Shriver, in: J.H. Lai (Ed.), Polymers for Electronic Applications, CRC Press Inc., Boca Raton, FL, 1989, Chapter 5.
[3] F.M. Gray, Polymer Electrolytes, The Royal Society of Chemistry, Cambridge, 1997.
[4] W.A. Van Schalkwijk, B. Scrosati (Eds.), Advances in Lithium-Ion Batteries, Kluwer Academic/Plenum Publishers, New York, 2003.
[5] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Sources 77 (1999) 183.
[6] H. Akashi, K. Tanaka, K. Sekai, J. Electrochem. Soc. 145 (1998) 881.
[7] D.W. Kim, Y.R. Kim, J.K. Park, S.I. Moon, Solid State Ionics 106 (1998) 329.
[8] A. Bottino, G. C-Roda, G. Capannelli, S. Munari, J. Membr. Sci. 57 (1991) 1.
[9] Y.B. Jeong, S.M. Lee, D.W. Kim, Poster No MO-058, in: Proceedings of the 1st International Conference on Polymer Batteries and Fuel Cells, JeJu Island, Korea, 2 July, 2003.