ELSEVIER

Electrochemistry Communications 3 (2001) 535–538

electrochemistry communications

www.elsevier.com/locate/elecom

Electrochemical performances of lithium-ion cells prepared with polyethylene oxide-coated separators

Dong-Won Kim [a,*], Jang-Myoun Ko [a], Jong-Han Chun [a], Sang-Hern Kim [a], Jung-Ki Park [b]

[a] *Department of Chemical Technology, Hanbat National University, San 16-1, Dukmyung-Dong, Yusung-Gu, Taejon 305-719, Republic of Korea*
[b] *Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Taejon 305-701, Republic of Korea*

Received 3 May 2001; received in revised form 11 July 2001

Abstract

Poly(ethylene oxide) (PEO)-coated separators were prepared by coating PEO onto a microporous polyethylene (PE) separators. Highly conductive electrolytes were prepared by soaking them in an electrolyte solution. The uptake of the electrolyte solution and the ionic conductivity of the PEO-coated separator (PCS) after soaking in $LiBF_4$–ethylene carbonate (EC)/dimethyl carbonate (DMC) were measured to be 76% and 1.0×10^{-3} S/cm, respectively. With these PCSs, lithium-ion cells composed of mesocarbon microbead (MCMB) anode and $LiCoO_2$ cathode were assembled, and their electrochemical performances were evaluated.

Keywords: Electrochemical performance; Lithium-ion cell; Microporous separator; PEO-coated separator

1. Introduction

Polymer electrolytes have been actively studied and developed for application in rechargeable lithium batteries, because the use of a polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility [1–3]. Attempts to obtain solid polymer electrolytes, consisting of a matrix polymer and a lithium salt, so far have been producing materials with limited ionic conductivity at ambient temperature [4]. It was found that the addition of polar solvents could significantly increase the ionic conductivity of those materials. Such gel polymer electrolytes exhibit high ionic conductivities in excess of 10^{-3} S/cm [5–8]. However, their mechanical properties are often very poor, which is one of the most important deficiencies preventing them from being used in practical cells. In order to overcome this problem, the microporous polyolefin separators impregnated with gel polymer electrolytes have been developed as an electrolyte material for lithium batteries. For example, 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 separators and polymerized to form a solid electrolyte [9]. Recently, a membrane-supported gel polymer electrolyte was also prepared and characterized by author, which was prepared by coating a gel polymer electrolyte onto a porous polyethylene (PE) membrane [10]. Such membrane-supported polymer electrolytes show excellent mechanical strength for the fabrication of lithium-ion polymer batteries.

To develop highly conductive polymer electrolytes supported by a porous separator, we tried to coat poly(ethylene oxide) (PEO) onto a microporous PE separator. Highly conductive electrolytes were then prepared by soaking the PEO-coated membrane in electrolyte solution. With these materials, we assembled lithium-ion cells composed mesocarbon microbead (MCMB) anode and lithium-cobalt oxide cathode. The electrochemical performances of these lithium-ion cells are presented.

* Corresponding author. Tel.: +82-42-821-1550; fax : +82-42-822-1562.
E-mail address: dwkim@hanbat.ac.kr (D.-W. Kim).

1388-2481/01/$ - see front matter
PII: S1388-2481(01)00214-4

2. Experimental

2.1. Preparation of PEO-coated membranes and electrodes

Appropriate amounts of PEO (MW: 600 000, Aldrich Chemical) was dissolved in an anhydrous acetonitrile. A microporous PE separator (Asahi Kasei, thickness: 25 μm, porosity: 40%) was then immersed in the polymer solution for 1 h. The separator was taken out on Teflon plate and left to evaporate to the solvent slowly at room temperature. After evaporation of acetonitrile, the separator was vacuum dried at 80 °C for 24 h. The thickness of PEO-coated separator (PCS) was 26 μm. The carbon anode was prepared by coating the slurry of MCMB (Osaka gas), 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 $LiCoO_2$ (Japan Chemical) cathode material, which was cast on aluminum foil. Electrodes were roll pressed to enhance particulate contact and adhesion to foils. The thickness of electrodes ranged from 50 to 65 μm, and their active mass loading corresponded to capacity of about 2.4 mAh/cm^2.

2.2. Electrical measurements

The PCS was transferred into a glove box and soaked in 1 M $LiBF_4$ in ethylene carbonate(EC)/dimethyl carbonate(DMC) (1:1 by volume, 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 an excess electrolyte solution on the surface of separator was wiped with filter paper. The wetted separator was cut into 4 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 Zahner Elektrik IM6 impedance analyzer over a frequency range from 10 Hz to 100 kHz. Lithium-ion cell was assembled by sandwiching the activated PCS between MCMB 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-ion cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

Ionic conductivity of the PCS after soaking in the electrolyte solution was measured as a function of storage time in the sealed cell. For comparison, the microporous PE separator used in preparing the PCS was also soaked in the same electrolyte solution. Fig. 1 illustrates the time dependence of the ionic conductivity for the electrolyte prepared with PCS and the PE separator, which are soaked in $LiBF_4$–EC/DMC. It is observed that an electrolyte prepared with the PCS exhibits a higher ionic conductivity over time periods measured. The difference in ionic conductivity between two systems arises from the difference in the quantity of electrolyte solution encapsulated in the separator. For the PCS, the amount of electrolyte solution absorbed (76%) is greater than that (51%) absorbed by the PE separator. This result arises from the fact that the PEO-coated membrane is able to trap a large amount of electrolyte solution due to the good compatibility between PEO and organic solvents. On the other hand, the PE separator without PEO has poor affinity for electrolyte solution. Ion conduction behavior with time is also found to be different for each parent membrane. Gradual decrease in the ionic conductivity for PE separator may be related to the solvent exudation upon long storage, which also arising from poor compatibility with electrolyte solution, as described above. After ac impedance measurements, liquid electrolyte exuding from the PE separator was observed in the cell. On the contrary, constant value (1.0×10^{-3} S/cm) of ionic conductivity for the PCS for a long period of time suggests that the electrolyte solution is well encapsulated in the PCS, which gives no leakage problem in this system.

In order to evaluate the electrochemical performance of a lithium-ion cell using the PCS, we fabricated a MCMB/PCS/$LiCoO_2$ cell. The assembled cell

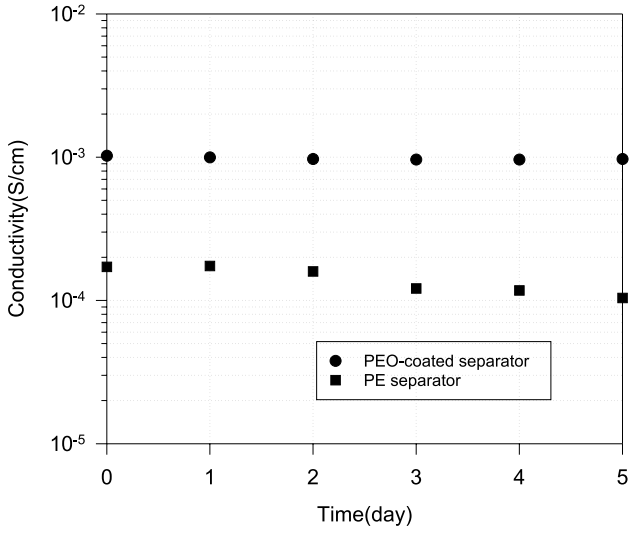

Fig. 1. Time evolution of the room temperature ionic conductivity of the PCS and the PE separator containing an electrolyte solution of $LiBF_4$–EC/DMC.

was subjected to the cycle tests in the following order: preconditioning with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at C/10 rate (0.24 mA/cm^2) for the first cycle and subsequent C/5 rate (0.48 mA/cm^2) cycles. Fig. 2(a) shows the repeated charge/discharge cycles of the lithium-ion cell at C/5 rate after a preconditioning cycle, which is a plot of the voltage profiles after 1, 2, 5, 10, 20, 30 cycles. This cell initially delivered a discharge capacity of 145 mAh/g based on $LiCoO_2$ material in the cathode. The coulombic efficiency, which is defined as the ratio of the discharge capacity to charge capacity, is shown to be increased with cycles. The low coulombic efficiency observed during the initial cycles is caused by the formation of a passivating film on the surface of the carbon electrode due to the decomposition of an electrolyte. The discharge capacity vs cycle number for a cell subjected to 30 cycles is shown Fig. 2(b). It should be noted that the cycling tests obtained in this figure are performed without applying external pressure to the cell. The use of PCS allows good cycling characteristics to be

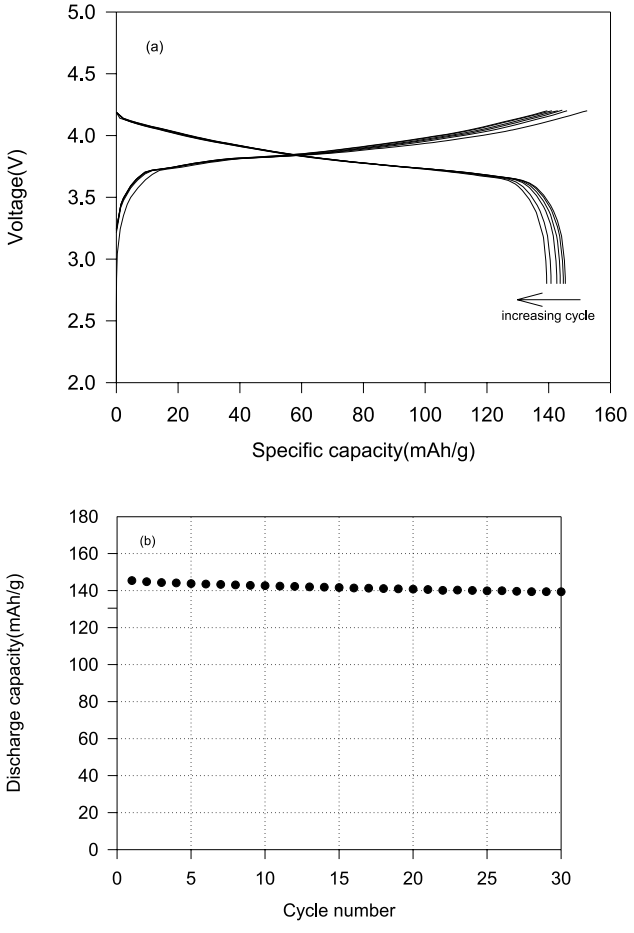

Fig. 2. (a) Charge and discharge curves of lithium-ion cell prepared with the PCS at C/5 rate; (b) discharge capacity vs cycle number for the lithium-ion cell prepared with the PCS.

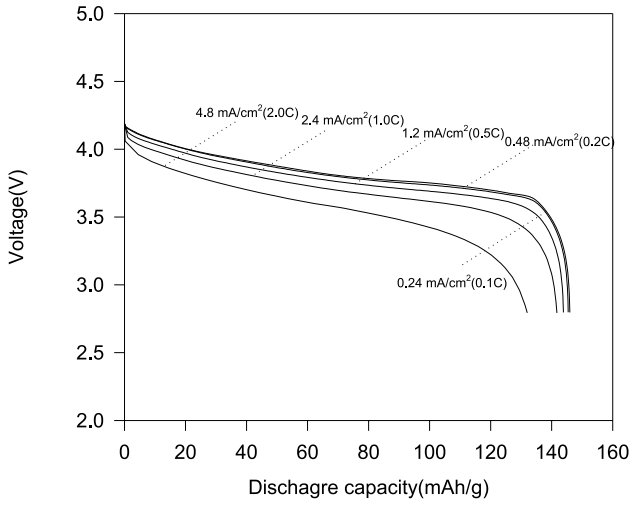

Fig. 3. Discharge profiles of a lithium-ion cell prepared with the PCS as a function of current rate. Charge rate is 0.2 C with 4.2 V cut-off.

reached. PEO-coated on both sides of the PE separator can adapt to encapsulate an electrolyte solution in the porous separator and further assist in adhering the electrodes to the separator, which result in good capacity retention. This result is a convincing evidence of the good capacity retention of a lithium-ion cell employing the PCS, even without applying any external pressure to the cell.

We tried to determine the rate capability of the lithium-ion cell prepared with PCS. Fig. 3 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. However, it showed a good performance at high current rate (2.0 C), whose discharge capacity was 132 mAh/g based on $LiCoO_2$ material in the cathode. It corresponds to 90% compared to that obtained at 0.1 C rate. From the results described above, it is expected that the PCS is a promising electrolyte material for rechargeable lithium-ion batteries packed in a plastic pouch without applying external pressure.

4. Conclusions

We have demonstrated that the PCS could be a good candidate for use in lithium-ion batteries packed in a plastic pouch. The PCS after soaking in electrolyte solution exhibited a high ionic conductivity, excellent mechanical and good adhesive properties. Lithium-ion cells composed of MCMB anode, PCS and $LiCoO_2$ cathode showed a high discharge capacity of 145 mAh/g based on active $LiCoO_2$ material, their capacity retention was proven to be good. It also showed the attractive discharge capacity of 132 mAh/g at 2.0 C.

Acknowledgements

This work was supported in part by the Korea Science and Engineering Foundation (KOSEF) through the Advanced Materials Research Center for Better Environment (AMAREN) at Hanbat National University (HNU).

References

[1] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Review, vols. 1–2, Elsevier Applied Science, London, 1987, 1989.
[2] B. Scrosati, Applications of Electroactive Polymers, Chapman & Hall, London, 1993.
[3] F.M. Gray, Polymer Electrolytes, Royal Society of Chemistry, Cambridge, 1997.
[4] F.M. Gray, Solid Polymer Electrolytes, VCH, New York, 1991.
[5] Z. Jiang, B. Carroll, K.M. Abraham, Electrochim. Acta 42 (1997) 2667.
[6] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Source 77 (1999) 183.
[7] G. Appetecchi, F. Croce, P. Romagnoli, B. Scrosati, U. Heider, R. Oesten, Electrochem. Commun. 1 (1999) 83.
[8] C.S. Kim, S.M. Oh, Electrochim. Acta 46 (2001) 1323.
[9] K.M. Abraham, M. Alamgir, D.K. Hoffman, J. Electrochem. Soc. 142 (1995) 683.
[10] D.W. Kim, B. Oh, J.H. Park, Y.K. Sun, Solid State Ionics 138 (2000) 41.