Electrochemical studies of gel polymer electrolytes based on methyl methacrylate-styrene copolymers

Soo Ik Jo[a], Hun-Joon Sohn[a], Dong-Wan Kang[b], Dong-Won Kim[b],[*]

[a]*School of Materials Science and Engineering, College of Engineering, Seoul National University, 56-1 Shinrim-Dong, Kwanak-Gu, Seoul 151-742, South Korea*
[b]*Department of Chemical Technology, Hanbat National University, San 16-1, Dukmyung-Dong, Yusung-Gu, Taejon 305-719, South Korea*

Abstract

Gel polymer electrolytes (GPEs) composed of porous methyl methacrylate-styrene copolymer membrane and electrolyte solution were prepared. The electrochemical characteristics of these polymer electrolytes were investigated in terms of copolymer composition and content of liquid electrolyte. The ionic conductivity reached 1.0×10^{-3} S/cm in the gel polymer electrolyte prepared with porous methyl methacrylate-styrene copolymer membrane of which methyl methacrylate composition is 77 mol%. This system showed good mechanical properties and a sufficient electrochemical stability to allow operation in the rechargeable lithium-ion polymer batteries (LIPBs).
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

In the past two decades, the progress of the portable consumer electronic devices has made it an urgent need to develop new batteries with a high energy density and design flexibility. Among them, lithium-ion polymer batteries (LIPBs) 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 [1,2]. In LIPBs, gel polymer electrolytes (GPEs) exhibit high ionic conductivity at ambient temperature and thus can be a good candidate for practical use. Though the GPEs show high ionic conductivities that are comparable to those of liquid electrolytes, other properties such as mechanical strength, solvent retention ability and sub-ambient temperature conductivity should be further improved for practical applications.

Poly(methyl methacrylate) (PMMA) is one of the matrix polymers commonly used in preparing the gel polymer electrolytes [3]. It has been reported that PMMA-based gel polymer electrolytes showed high ionic conductivity of about 1×10^{-3} S/cm at ambient temperature [4]. How-

ever, they could not form free-standing films at high content of liquid electrolyte. One of the approaches to solve this problem was to blend PMMA with other polymers such as poly(vinyl chloride) (PVC) [4] and acrylonitrile-butadiene-styrene (ABS) terpolymer [5]. Another way to enhance the mechanical strength is the use of a copolymer as a matrix polymer [6,7]. In our previous work [7], we synthesized poly(methyl methacrylate-co-styrene) (PMS) copolymers for preparing the gel polymer electrolytes by solution casting method. In the copolymer, it is considered that the styrene unit can improve the mechanical strength of gel polymer electrolyte due to its low affinity for liquid electrolyte. In this work, the porous PMS membranes are prepared, and the gel polymer electrolytes are prepared by soaking them in liquid electrolyte. The electrochemical characteristics of these gel polymer electrolytes are investigated in terms of copolymer composition.

2. Experimental

2.1. Characterization

PMS copolymer was synthesized by emulsion polymerization, as previously reported [7]. Molar composition of the PMS copolymer was determined by ^{1}H NMR spectroscopy.

---

¹H NMR spectra were obtained in CDCl$_3$ solvent on a Bruker-DRX-300 NMR spectrometer with tetramethyl silane (TMS) as an internal standard reference. PMS copolymers synthesized are designated PMS(x/y) for brevity, where x and y indicate the mol% of MMA and ST units, respectively, in the copolymer. Gel permeation chromatography (GPC) was carried out to know the molecular weight of the copolymer by using a Waters CV-150 instrument equipped with three μ-Styragel columns (10^3, 10^4, and 10^5 Å), and the system was calibrated with the monodisperse polystyrene standards in THF.

2.2. Preparation of the gel polymer electrolytes

PMS was dissolved in an anhydrous tetrahydrofuran. After the polymer was completely dissolved, the solution was cast on a glass plate. It was then immersed in a water bath to form the porous structure by phase inversion. After drying the porous membrane in a vacuum oven at 80 °C for 24 h, it was soaked in 1 M LiClO$_4$–ethylene carbonate (EC)/ dimethyl carbonate (DMC) solution (1:1 by volume, Samsung Cheil Industries, battery grade) to make the gel polymer electrolyte. The film thickness was in the range of 30–35 μm. Scanning electron microscopy (SEM) measurements were carried out to investigate the degree of gelation of GPEs. Gel polymer electrolyte was broken by using liquid N$_2$ to observe cross-sectional SEM images.

2.3. Electrical measurements

GPE was cut into squares of 4 cm^2 and sandwiched between two stainless steel (SS) electrodes for conductivity measurement. The ac impedance measurements were performed using Zahner Elektrik IM6 impedance analyzer over the frequency range of 100 Hz to100 kHz with amplitude of 10 mV. Each sample was allowed to be equilibrated for 1 h at each temperature before impedance measurement. In order to investigate the electrochemical stability of GPEs, linear sweep voltammetry experiments were carried out on a stainless steel working electrode with lithium electrodes as counter and reference electrodes at a scanning rate of 1 mV/s.

## 3. Results and discussion

The molar composition of PMS was determined by the ¹H NMR spectrum, as given in our previous work [7]. The calculated molar compositions of the PMS copolymers are summarized in Table 1. The copolymers produced have random distribution of monomer units. The average molecular weights of PMS copolymers are also given in Table 1. The molecular weights are measured to be high, and the polydispersity indexes range from 2.1 to 3.0.

Fig. 1 shows the cross-sectional SEM images of GPEs prepared by soaking the porous PMS membranes with

Table 1
Molar composition and average molecular weight of PMS

Polymer	Molar composition	Molecular weight	
		M_n	M_w
PMS(50/50)	50/50	880000	2180000
PMS(64/36)	64/36	1120000	2384000
PMS(77/23)	77/23	700000	2000000
PMS(82/18)	82/18	680000	2060000

different copolymer composition in LiClO$_4$–EC/DMC. As the content of MMA increases from 50 to 77 mol%, the porous structure of membrane collapses and becomes a homogenous gel, which means that the degree of gelation for the porous PMS membrane is increased with MMA content in the PMS copolymer. It can be also found that the films obtained by soaking in electrolyte solution become transparent in appearance, as the MMA content increases. These results suggest that liquid electrolyte swells the polar
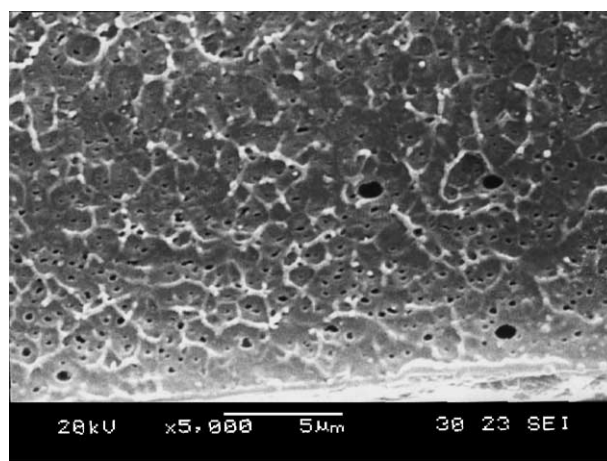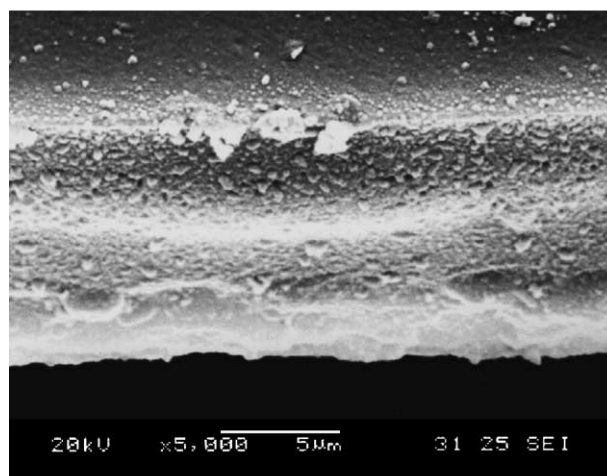
Fig. 1. SEM cross-sectional images of GPEs prepared with: (a) porous PMS(50/50) membrane, and (b) porous PMS(77/23) membrane.
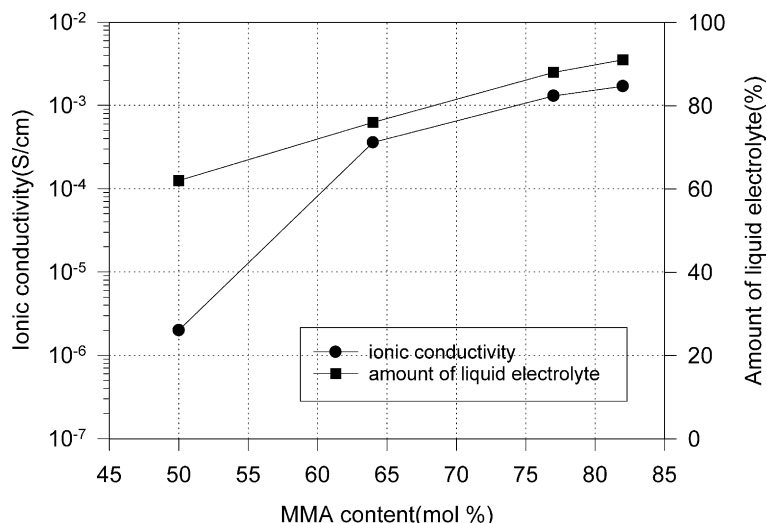
Fig. 2. Ionic conductivity and amount of the electrolyte solution absorbed by the porous membrane as a function of the MMA content. Soaking electrolyte solution is LiClO$_4$–EC/DMC.

MMA unit to form ion conductive channels and the non-polar ST unit forms a supporting structural phase, thereby giving a free-standing film.

Fig. 2 illustrates ionic conductivity and amount of the electrolyte solution absorbed by the porous membrane after soaking of the porous membrane in the electrolyte solution, as a function of MMA composition in the porous PMS membrane. It can be seen that an increase of MMA content in the PMS copolymer enabled the porous membranes to absorb more electrolyte solution. This result is due to the fact that the MMA unit is more compatible with the carbonate-based liquid electrolyte as compared to the ST unit, as previously explained. Gel polymer electrolyte prepared with PMS(82/18) membrane exhibited the highest ionic conductivity. However, it was sticky and difficult to handle, because the membrane prepared with PMS(82/18) easily swelled by imbibing the electrolyte solution. In consideration of both

ionic conductivity and mechanical strength, the gel polymer electrolyte prepared with PMS(77/23) has the best combination of characteristics, namely, acceptable ionic conductivity and good mechanical strength. It is a free-standing film which exhibits an ambient temperature conductivity of 1.0×10^{-3} S/cm.

Fig. 3 shows an Arrhenius plot of ionic conductivities for GPEs prepared with different PMS membranes. The temperature dependency of ionic conductivity is found to be non-Arrhenius type, which shows a slight positive curvature. It can be described by the Vogel–Tamman–Fulcher (VTF) equation based on free-volume theory of ion mobility [8], so the ion transport mechanism is governed by the free-volume-related characteristic.

The electrochemical stability of GPE was evaluated by linear sweep voltammetric measurements, as shown in Fig. 4. Experiments performed by applying an anodic voltage to a
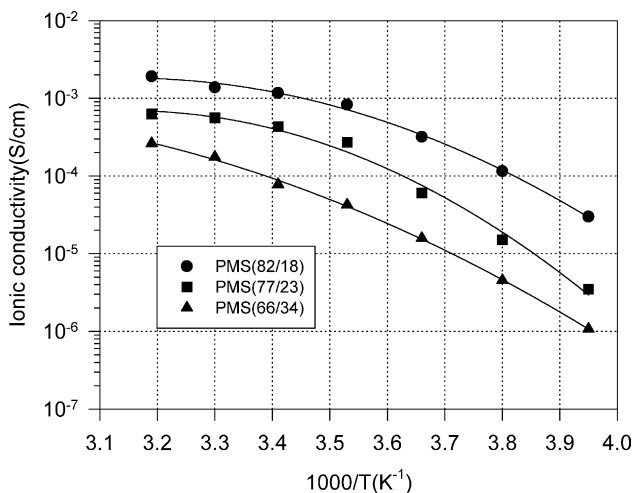

Fig. 3. Temperature dependence of ionic conductivity for GPEs prepared with different PMS membranes.
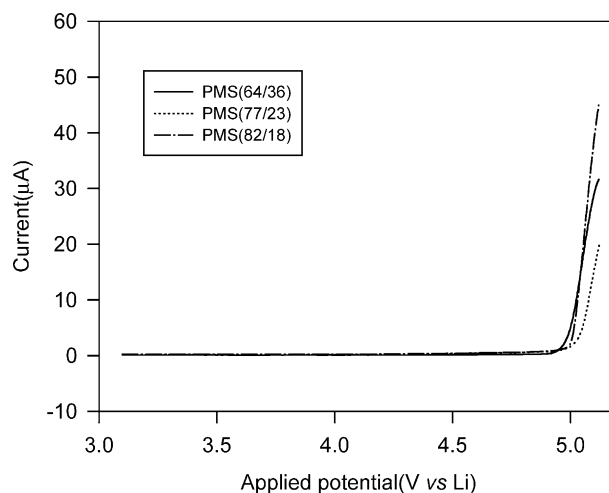

Fig. 4. Current–voltage curves of Li/GPE/SS cell at 25 °C (scan rate: 1 mV/s).

cell composed of the GPEs sandwiched between a lithium electrode and an inert SS electrode. The voltage was swept from the open-circuit potential of the cell towards more anodic values until a large current change due to the electrolyte decomposition at the inert electrode interface occurred. For all systems studied, the current onsets are observed around 4.9 V, which can be assigned to decomposition voltages of GPEs. From these results, it is concluded that the gel polymer electrolytes prepared with PMS membranes are stable over a large electrochemical voltage window.

4. Conclusions

Electrochemical characteristics of the gel polymer electrolytes based on the porous PMS membranes were investigated. Physicochemical properties such as ionic conductivity, mechanical strength, and uptake of liquid electrolyte depended on the molar composition of PMS copolymer. GPE prepared with PMS(77/23) and $LiClO_4$–EC/DMC exhibited a high conductivity of 1.0×10^{-3} S/cm at ambient temperature and a good mechanical strength. Anodic decomposition voltage of GPEs was found to be about 4.9 V (versus Li^+/Li).

References

[1] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, vols. 1 and 2, Elsevier, London, 1987 and 1989.
[2] F.M. Gray, Polymer Electrolytes, The Royal Society of Chemistry, Cambridge, 1997.
[3] G.B. Appedtedcchi, F. Croce, B. Scrosati, Electrochim. Acta 40 (1995) 991.
[4] N.S. Choi, J.K. Park, Electrochim. Acta 46 (2001) 1453.
[5] X. Hou, K. Siow, Polymer 41 (2000) 8689.
[6] D.-W. Kim, Y.R. Kim, J.K. Park, S.I. Moon, Solid State Ionics 106 (1998) 329.
[7] D.-W. Kang, D.-W. Kim, S.I. Jo, H.-J. Sohn, J. Power Sources 112 (2002) 1.
[8] M.B. Armand, K.M. Chabagno, M.J. Duclot, P. Vashishta, J.N. Mundy, G.K. Shenoy (Eds.), Fast Ion Transport in Solids, North-Holland, Amsterdam, 1979, p. 131.