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Preparation and characterization of gel polymer electrolytes based on methyl methacrylate–styrene copolymers

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

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

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Abstract

Gel polymer electrolytes (GPEs) are prepared with methyl methacrylate (MMA)–styrene (ST) copolymers and $LiPF_6$ or $LiBF_4$ in ethylene carbonate/dimethyl carbonate. Depending on the molar composition of the copolymer, these gel polymer electrolytes exhibit a different range of mechanical and electrical properties. On the aspect of ionic conductivity and mechanical property, the copolymer comprising about 33 mol% MMA is found to be most desirable. Lithium-ion polymer cells employing GPE containing different electrolyte solution are assembled and their cycling performances are evaluated.

Keywords: Cycling performance; Gel polymer electrolyte; Ionic conductivity; Lithium-ion polymer cell; Methyl methacrylate–styrene copolymer

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 high specific energy and design flexibility. Among them, lithium-ion 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 [1,2]. After the first suggestion of the use of poly(ethylene oxide) (PFO) as a polymer-based solid electrolyte by Armand et al. [3], a solid polymer electrolyte has been considered as ideal alternative to the liquid electrolyte. Much work has been performed to develop practical all-solid state batteries based on solid polymer electrolytes [1–5]. A major problem with solid polymer electrolytes, however, is the low ionic conductivity at ambient temperature. This is due to the low segmental mobility of the polymer chain incorporated with lithium salt. In this respect, most of the research has focused on the preparation and characterization of gel polymer electrolytes (GPEs) which exhibit higher ionic conductivity at ambient temperature. Even if the GPEs show a high ionic conductivity comparable to that of liquid electrolytes, other properties such as mechanical strength, solvent retention ability and sub-ambient temperature conductivity should further be improved for practical applications.

Poly(methyl methacrylate) (PMMA) is one of the matrix polymers commonly used in the gel polymer electrolytes [6], and has been proposed for lithium battery application [7]. PMMA-based gel polymer electrolytes show high ionic conductivity of about 1×10^{-3} S cm^{-1} at ambient temperature [8]. They cannot, however, form free-standing films with a high content of organic solvents such as ethylene carbonate (EC) and dimethyl carbonate (DMC). One of the approaches to solve this problem has been to blend PMMA with other polymers such as poly(vinyl chloride) (PVC) [9] and acrylonitrile–butadiene–styrene terpolymer (ABS) [10]. Another way to enhance the mechanical strength is to use a copolymer as a matrix polymer. When the polymer–solvent affinity is controlled by a proper selection of the molar composition of the copolymer, the gel polymer electrolytes possess reasonable mechanical strength.

In our work, in order to prepare highly conductive polymer electrolytes with sufficient mechanical strength, methyl methacrylate (MMA)–styrene (ST) copolymer has been synthesized as a matrix polymer for preparing gel polymer electrolytes. In the copolymer, it is considered that the styrene unit can improve the mechanical strength of gel polymer electrolyte due to the low affinity for liquid electrolyte. The copolymers differ in molar composition and, thereby, carry a different degree of affinity for electrolyte solution. Gel polymer electrolytes composed of methyl

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

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methacrylate–styrene copolymer and liquid electrolyte are prepared, and their electrochemical properties are studied. With these materials, lithium-ion polymer cells composed of a mesocarbon microbead (MCMB) anode and a $LiCoO_2$ cathode are assembled, and their electrochemical performances are evaluated.

2. Experimental

2.1. Polymer synthesis and characterization

P(methyl methacrylate–co-styrene), PMS, was synthesized via emulsion polymerization with distilled water at 60 °C in a glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel, and a mechanical stirrer. The molar ratio of co-monomers in the reaction feed was varied with a total monomer concentration of 1 mol l^{-1}. Potassium persulfate ($K_2S_2O_8$) was used as a free-radical water-soluble initiator, and sodium lauryl sulfate was used as an emulsifier. The polymerization was continued for 5 h with vigorous agitation. The polymer was isolated by filtration and washed successively with distilled water at 80 °C to remove any impurities such as residual monomers and initiator. The product was then dried in a vacuum oven at 100 °C for 24 h. White powder was obtained as a final product. ^{1}H NMR spectra were obtained in $CDCl_3$ solvent by means of a Bruker-DRX-300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference. Differential scanning calorimetry (DSC) thermal analysis, with a heating rate of 10 °C min^{-1}, was performed to measure the thermal properties of polymers.

2.2. Preparation of gel polymer electrolytes

GPEs were prepared by the solution casting method. PMS was first dissolved in anhydrous tetrahydrofuran (THF). After the polymer was completely dissolved, an appropriate amount of 1.0 M $LiPF_6$ or 1.0 M $LiBF_4$ in EC/DMC (1:1 (v/v), Samsung Cheil Industries, battery grade) was added and solution was further stirred. The amount of electrolyte solution added was changed from 70 to 90 wt.% based on the total weight of the gel polymer electrolyte. The resulting viscous solution was cast with a doctor blade on to a glass plate, and then left to allow the solvent to evaporate slowly at room temperature. After evaporation of the THF, GPE films were obtained. The thickness of films was in the range 40–80 μm. GPE was confirmed to be free of THF by means of ^{1}H NMR. All procedures for preparing GPEs were carried out in a dry box filled with argon gas (99.999%).

2.3. Electrical measurements

GPE was cut into 4 cm^2 squares and sandwiched between two stainless-steel (SS) electrodes for conductivity measurement. An ac impedance measurement was performed using a Zahner Elektrik IM6 impedence analyzer over the frequency range 100 Hz–100 kHz with an amplitude of 10 mV. Each sample was allowed to equilibrate for 1 h at each temperature before measurement. Ionic conductivity was calculated from the bulk resistance obtained from the impedance spectrum. In order to investigate the electrochemical stability of GPEs, linear sweep voltammetry experiments were carried out on a SS working electrode with lithium electrodes as the counter and reference electrodes at a scanning rate of 1 mV s^{-1}.

2.4. Lithium-ion polymer cells

The carbon anode was prepared by coating a slurry of MCMB (Osaka gas), poly(vinylidene fluoride) (PVdF) and super-P carbon on a copper foil. The cathode comprised the same binder (PVdF) and super-P carbon along with $LiCoO_2$ (Japan Chemical) and was cast on an aluminum foil. The 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 a capacity of about 2.4 mAh cm^{-2}. A lithium-ion polymer cell was assembled by sandwiching the gel polymer electrolyte between a MCMB anode and a $LiCoO_2$ cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All assemblies of 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

The molar composition of the PMS copolymer was determined from a ^{1}H NMR spectrum, a typical example of which is shown in Fig. 1. In the ^{1}H NMR spectrum for PMS copolymer, the methine protons in the benzene ring of the ST unit appear separately at $\delta = 6.97$–7.16 ppm, and the methoxy protons of the MMA unit are observed at $\delta = 3.60$ ppm. On the other hand, the peaks of the methine, methylene and methyl protons in MMA and ST units observed at a higher field overlap one another. The relative intensities of the methylene and methine protons in the ST unit can be calculated by multiplying the intensity of the methine proton in benzene ring by 3/5. The intensities of the methylene and methyl protons in MMA unit can also be estimated by multiplying the intensity of the methoxy proton which appears at $\delta = 3.60$ ppm by 5/3. The molar composition of the co-monomer unit can thus be estimated from the total intensity of the corresponding monomer unit. The molar composition of MMA and ST was determined to be 66:34 from the ^{1}H NMR spectrum shown in Fig. 1. The molar compositions of copolymers synthesized in our work are listed in Table 1. The PMS copolymers are designated PMS (x/y) for brevity, where x and y indicate the mol% of the MMA and the ST units in the copolymer, respectively.

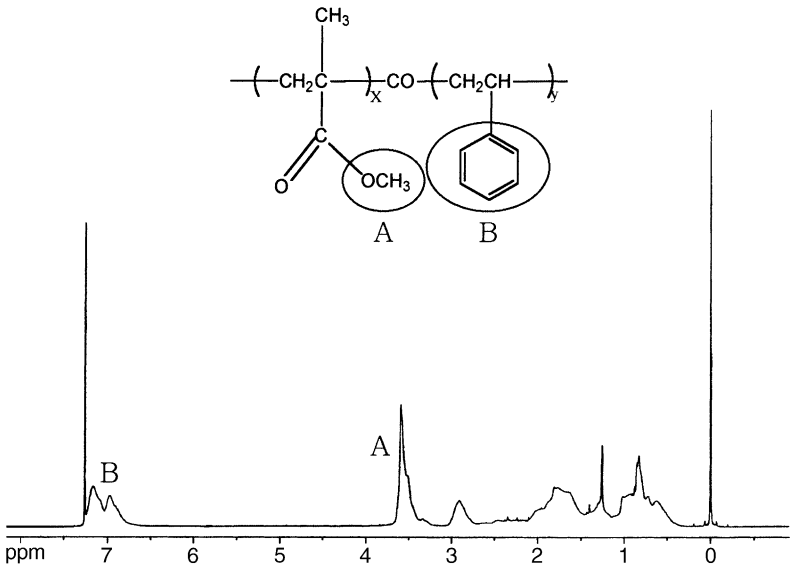

Fig. 1. ^{1}H NMR spectrum of PMS copolymer in $CDCl_3$ at 25 °C.

Table 1
Molar composition and glass transition temperatures of PMS

Copolymer	Molar composition (MMA:ST)	T_g (°C)
PMS (11/89)	11:89	104.6
PMS (33/67)	33:67	107.3
PMS (66/34)	66:34	111.5

The DSC thermograms of PMS copolymers are shown in Fig. 2 and the results are summarized in Table 1. From the literature [11,12], it is known that the glass transition temperature, T_g, of PMMA is 113 °C, while that of PS is 100 °C. The glass transition for each PMS copolymer is observed in the temperature range of 100–113 °C, and the T_g value is found to increase with MMA content in the copolymer. This is consistent with the glass transition behavior observed in random copolymers [13,14].

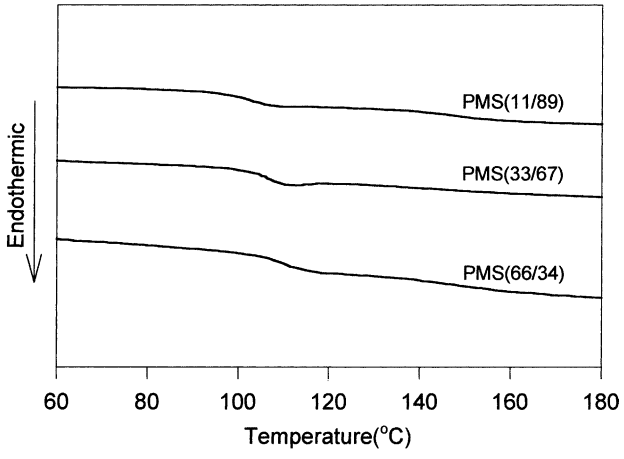

Fig. 2. DSC curves of PMS copolymers with different molar composition.

The ionic conductivities of GPEs prepared with $LiPF_6$-EC/DMC are presented in Fig. 3 as a function of the content of the electrolyte solution. The ionic conductivity increases with the amount of electrolyte solution in the gel polymer electrolyte. An increase in the ionic conductivity with the content of liquid electrolyte is due to enhancement of the ionic mobility and the number of carrier ions, as many previous workers have reported [15]. From the data in Fig. 3, it is also found that the ionic conductivity increases as the molar composition of the MMA in the copolymer increases. The difference in ionic conductivity with molar composition of copolymer may be caused by the degree of encapsulation of liquid electrolyte in the matrix polymer. Since the MMA unit has a carbonyl group (–COO–) in the

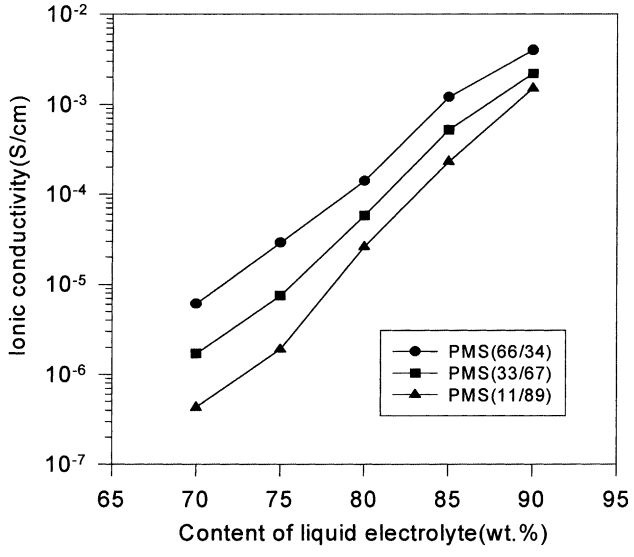

Fig. 3. Ionic conductivities of PMS-based GPEs as function of content of electrolyte solution. Electrolyte solution is $LiPF_6$-EC/DMC.

side chain, it can be concluded that the MMA unit is more compatible with the carbonate-based electrolyte than with the ST unit. This speculation is confirmed by measuring the weight loss of electrolyte solution in GPE under open-atmosphere conditions. The weight loss of solvent increases with increasing ST content in the copolymer. Even though gel polymer electrolyte prepared with PMS (66/34) shows the highest ionic conductivity, it is sticky and difficult to handle. Because PMS copolymer with a high content of MMA easily swells by imbibing organic solvent, the gel polymer electrolyte becomes mechanically weak. The copolymer with about 33 mol% MMA is thought to be desirable in that it ensures both high ionic conductivity and good mechanical strength. With 90 wt.% liquid electrolyte solution, the gel polymer electrolytes prepared with PMS (33/67) have an ionic conductivity of 2.2×10^{-3} S cm^{-1}.

Arrhenius plots of ionic conductivities for GPEs containing 10 wt.% PMS (33/67) and 90 wt.% liquid electrolyte, which are prepared with different electrolyte solutions, are shown in Fig. 4. It is found that the temperature dependence of $LiBF_4$-based GPE is different from that of $LiPF_6$-based GPE. For GPE prepared with $LiBF_4$-EC/DMC, the ionic conductivity is lower than that of GPE prepared with $LiPF_6$-EC/DMC at all temperatures, and is observed to decrease suddenly at low temperature. It has been reported [16] that this abrupt decrease in ionic conductivity is related to crystallization of the organic solvent. This behavior of $LiBF_4$-based GPE indicates that $LiBF_4$-EC/DMC has poor affinity with PMS (33/67) and results in the freezing of organic solvent at low temperature. From the DSC results of GPE prepared with $LiBF_4$-EC/DMC, two endothermic peaks are observed at −9.9 and 16.6 °C, which are attributable to the melting of DMC and EC, respectively. Here, the polymer–solvent interaction discourages to a certain extent the crystallization of DMC and EC, and thereby lowers the melting temperatures compared with the values for pure DMC (3 °C) and EC (37 °C). On the other hand, GPE prepared with $LiPF_6$-EC/DMC does not exhibit any endothermic peaks at >−30 °C, which suggests that the solvents in the GPE are not frozen even at −30 °C, and that strong dipole–dipole interactions occur in the polymer–solvent–salt and hinder the ordering of solvent molecules. These results indicate that freezing of solvent in the GPE can be suppressed by a proper choice of salt.

The electrochemical stability of the GPE was evaluated by linear sweep voltammetric measurements. Experiments were performed by applying an anodic voltage to a cell which was composed of a GPE sandwiched between a lithium electrode and an inert SS electrode. The voltage was swept from the open-circuit voltage of the cell towards more positive values until a large current change due to electrolyte decomposition at the inert electrode interface occurred. Linear sweep voltammograms for cells prepared with GPE containing different electrolyte solutions are shown in Fig. 5. The current onsets are detected around 4.1–4.5 V versus Li, which can be assigned to the decomposition voltages of the GPEs. The decomposition behavior of the GPE is observed to be influenced by the type of salt. The decomposition voltage of GPE prepared with $LiBF_4$-EC/DMC is higher than that for GPE prepared with $LiPF_6$-EC/DMC electrolyte, which means a wider electrochemical stability of GPE prepared with $LiBF_4$-EC/DMC. From these results, the cycling performance of lithium-ion polymer cells employing high voltage $LiCoO_2$ cathodes is thought to be influenced by the type of salt used in preparing GPE.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using PMS-based GPE, cells with the configuration MCMB/GPE/$LiCoO_2$ were fabricated. The assembled cells were subjected to cycle tests in the following order: preconditioning with a cut-off voltage of

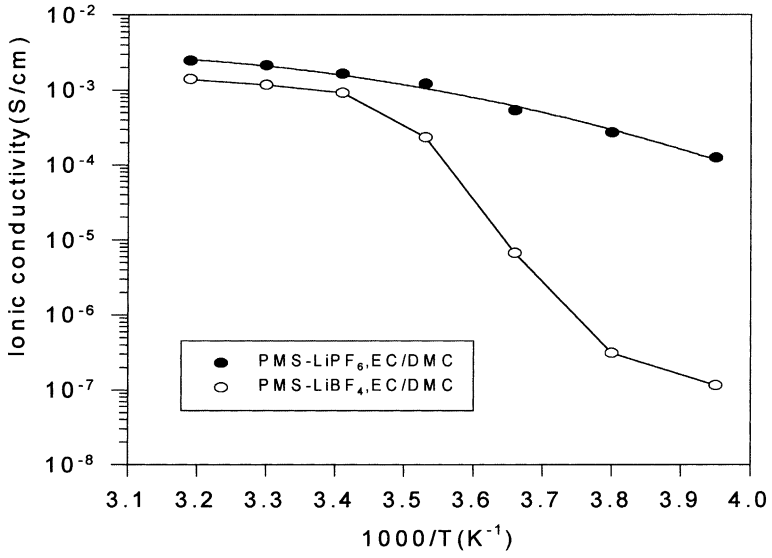

Fig. 4. Temperature dependence of ionic conductivity for GPE prepared with different electrolyte solutions, where GPE consists of 10 wt.% PMS (33/67) and 90 wt.% electrolyte solution. Electrolyte solution is either $LiPF_6$-EC/DMC or $LiBF_4$-EC/DMC.

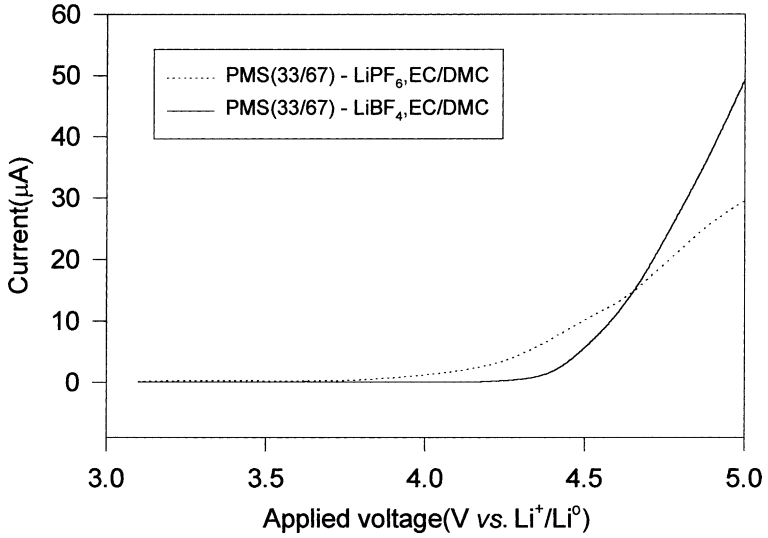

Fig. 5. Current–voltage curves of Li/GPE/SS cell, where GPE consists of 10 wt.% PMS (33/67) and 90 wt.% electrolyte solution. Electrolyte solution is either $LiPF_6$-EC/DMC or $LiBF_4$-EC/DMC.

4.2 V for the upper limit and 2.8 V for the lower limit at the *C*/10 rate for the first cycle and the *C*/5 rate for subsequent cycles. Preconditioning charge–discharge cycles of the lithium-ion polymer cells with GPEs containing different electrolyte solutions are shown in Fig. 6. It can be seen that both the discharge capacity and the cycling efficiency during preconditioning cycling are higher in $LiBF_4$-based GPE than in $LiPF_6$-based GPE. The large irreversible capacity and low discharge capacity in the cell prepared with $LiPF_6$-based GPE may be due to the decomposition of gel polymer electrolyte at the operating voltage of the cell. As shown in Fig. 5, $LiPF_6$-based GPE is found not to be sufficiently electrochemically stable up to an upper target voltage of 4.2 V. From these results, the gel polymer electrolyte consisting of PMS and $LiPF_6$-EC/DMC is inappropriate for application in batteries using high voltage cathode materials such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$.

The charge and discharge capacities as a function of cycle number after preconditioning of the cell with GPE containing $LiBF_4$-EC/DMC are presented in Fig. 7. The cell initially delivers a specific capacity of about 134 mAh g^{-1} based on the active $LiCoO_2$ material in the cathode. The cycling efficiency was maintained at more that 99.5%, which indicates that the use of GPF prepared with PMS and $LiBF_4$-EC/DMC has good cycling characteristics. On the other hand, the cell prepared with GPE containing $LiPF_6$-EC/DMC has short cycle-life, usually about 10. During the course of 10 cycles, the discharge capacity is lower than 80% of that

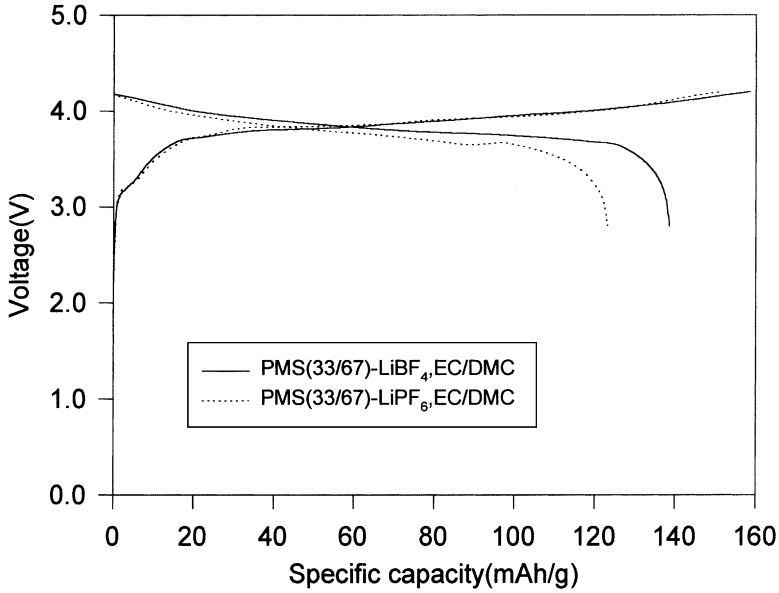

Fig. 6. Preconditioning cycles of lithium-ion polymer cells with GPEs containing different electrolyte solution.

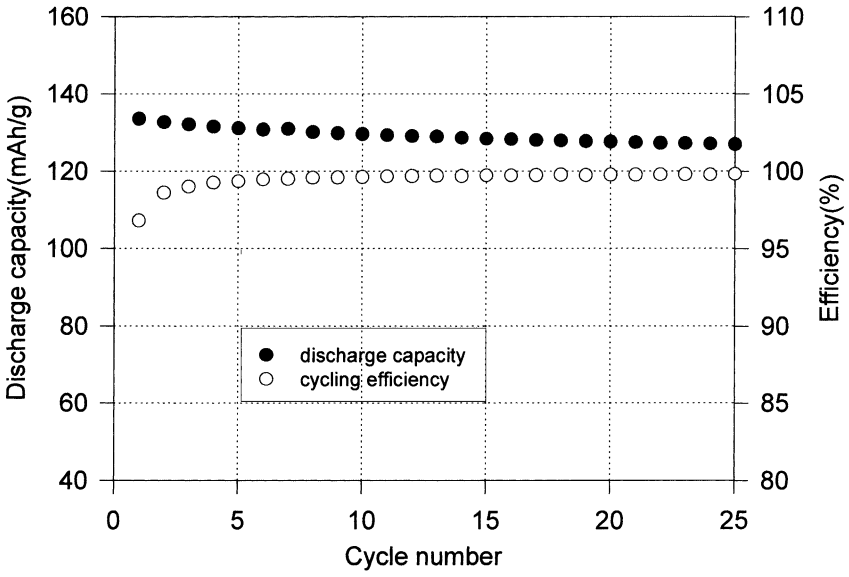

Fig. 7. Discharge capacity and cycling efficiency of lithium-ion polymer cell as function of cycle number at *C*/5 rate.

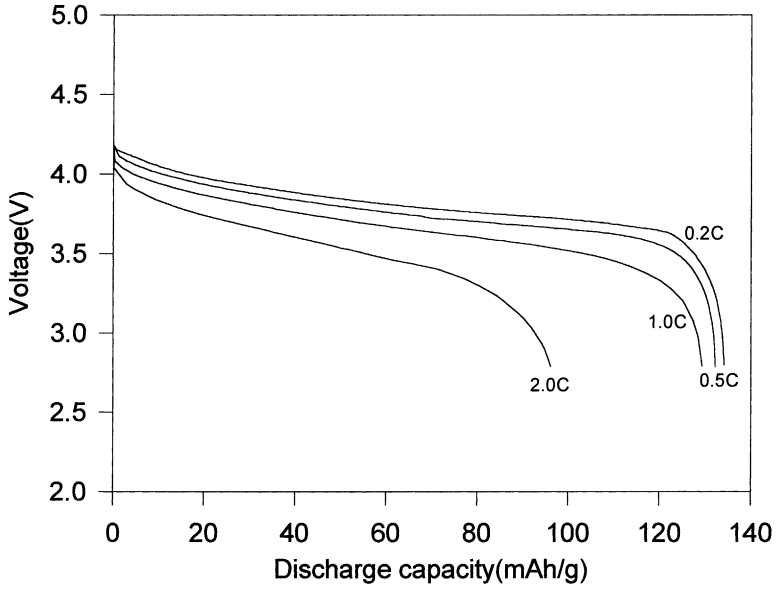

Fig. 8. Discharge profiles of lithium-ion polymer cell obtained at different current rates.

obtained during the preceding cycle, which may be caused by the decomposition of the gel polymer electrolyte. This means that wide electrochemical stability is a crucial requirement for guaranteeing acceptable performance when cell cycle ability is considered.

An attempt was made to determine the rate capability of the lithium-ion polymer cell. In this cell, GPE is prepared with PMS (33/67) and $LiBF_4$-EC/DMC. The discharge curves obtained at different current rates is shown in Fig. 8. The discharge capacity is found to gradually decrease with increasing current rate, which indicates a large polarization. The cell shows good performance at the 1.0 C rate (2.4 mA cm^{-2}), the discharge capacity is 96% compared with that obtained at the 0.2 C rate. At a current rate of 2 C, the cell retained 72% of its discharge capacity at 0.2 C. The reduced capacity at high rate can be related to the lower conductivity of the gel polymer electrolyte which employs $LiBF_4$-EC/DMC. Further research is being conducted in the authors' laboratory to improve the high-rate performance of lithium-ion polymer cells with PMS-based GPE.

4. Conclusions

PMS-based GPEs are prepared, and their electrochemical characteristics are investigated. With respect to ionic conductivity and mechanical properties, the most desirable composition of the PMS copolymer is PMS (33/67). GPE

prepared with PMS (33/67) exhibits high ionic conductivity which exceeds 1.0×1.0^{-3} S cm^{-1} at ambient temperature, and is obtained as a free-standing film. Though the ionic conductivity of GPE containing $LiPF_6$-EC/DMC is higher than that of GPE containing $LiBF_4$-EC/DMC over the temperatures measured, the latter cells give superior performance.

Acknowledgements

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