

---

---

## Development of Gel-Type Pouch Cell

---

---

**Dr. Hyunsoo Kim**

(Korea Electrotechnology Research Institute)



# Development of Gel-Type Pouch Cell

Hyun-Soo Kim and Seong-In Moon

Korea Electrotechnology Research Institute, Changwon 641-120, KOREA

## 1. Introduction

Lithium-ion polymer battery with a gel polymer electrolyte (GPE) has been underdeveloping in order to obtain leakage-free batteries. Many kinds of polymeric hosts such as polyacrylonitrile (PAN)<sup>1)-4)</sup>, poly(vinylidene fluoride) (PVdF)<sup>5)</sup>, poly(ethylene oxide) (PEO)<sup>6)-8)</sup>, poly(methylmethacrylate) (PMMA)<sup>9)-10)</sup>, poly(vinyl chloride) (PVC)<sup>11)</sup> have been proposed as frameworks for gel polymer electrolyte. Their ionic conductivities were reported between  $10^{-4}$  and  $10^{-3}$  S·cm<sup>-1</sup> at room temperature. Hybrid polymer electrolytes based on P(VdF-HFP)<sup>12)-13)</sup> copolymers exhibited high ionic conductivity and good mechanical performances.

Recently, a cure-type gel polymer electrolyte has been studied to apply an advanced lithium battery. Cross-linked polymers were found to reduce the solubility of the polymers with the organic solvents and also helped to trap the liquid electrolyte within the polymer matrix. These polymers can be obtained from monomers, which have relatively low molecular weight, and prepared by methods such as UV, thermal radiation and electron beam radiation polymerization.

In this study, four kind of monomer/oligomer such as tri(ethylene glycol) dimethacrylate (TEGDMA, tetra(ethylene glycol) diacrylate (TEGDA), methylmethacrylate interpenetrating polymer network(IPN), and urethane acrylate(UA) oligomer were used. The GPE and LiCoO<sub>2</sub>/GPE/graphite cells are prepared and their electrochemical properties were evaluated at various current densities and

temperatures.

## 2. Experimental

TEGDMA and TEGDA were obtained from Aldrich and used as a monomer. The UA was synthesized by an additional reaction (Fig. 1). A polyol (Mw = 2000, GP2000) was obtained from Hankook Polyol Co. and dehydrated under reduced pressure at 80°C for 24 h before use. The polyol was random copolymer of propylene glycol and ethylene glycol. Hydrogenised 4, 4'-methylene bis (phenyl isocyanate) (HMDI) was obtained from Aldrich and used as received. The prepolymer was prepared by allowing the mixture of HMDI and the polyol to react at 60 °C for 2h with stirring under a dried nitrogen blanket. After the prepolymer was synthesized, its contents of NCO groups were characterized with dibutyl amine back titration method. And required amount of hydroxyethyl acrylate (HEA) was slowly added to the NCO terminated prepolymer. HEA was obtained from Aldrich and used as received. The reaction was allowed to continue 3 hours and then it was terminated by addition of small amounts of methanol. PMMA IPN system was prepared by dropping methylmethacrylate (MMA) into PMMA at 60 °C in oxygen atmosphere. The ratio of PMMA : MMA was 30:70 wt%. Hexanediol dimethacrylate (HDDA) was used as a cross-linker.

A precursor for the gel polymer electrolyte of lithium ion cell consisted of a liquid electrolyte, a macromonomer, a reactive modifier, and an initiator. A curable mixture consisted of a macromonomer, reactive modifier, and an initiator except for a liquid electrolyte. Battery grade solution of 1.0 M LiPF<sub>6</sub>/EC-DEC (1:1 vol%) was obtained from Cheil Industries. TEGDMA were used as a reactive modifier to improve

mechanical properties of gel polymer electrolyte. BPO (C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>, Aldrich Chemical Co.) was used as a thermal initiator. All procedures for preparing the precursor were carried out in a dry-box filled with argon gas. Properties of the monomer and initiator were summarized in Table 1.

Lithium cobalt oxide electrodes were prepared by mixing 93wt% LiCoO<sub>2</sub> (Umicore Korea Co.) with 4 wt% super P black and 3 wt% PVdF and coated on an aluminum foil. Graphite electrode were prepared using 95 wt% MCF (milled carbon fiber, Petoca Materials Co.) and 5 wt% PVdF. Celgard 2500 was used as a separator. The electrodes were stacked and inserted into an aluminum laminate film. The precursor was filled into the assembled cell in a dry-box filled with argon gas and then it was vacuum-sealed. The assembled cells were polymerized at the temperature of 80 °C for 1 hour in an oven. The fabrication procedure of the cell was shown in Fig. 2.

Films for infrared analysis were prepared by casting GPE on the potassium. The films were stored in an argon-filled dry box and transferred to the holder in the spectrometer. FTIR spectra were collected using Burker IFS 66/FRA 106 system at a resolution of 4 cm<sup>-1</sup>. Viscosity of the precursor was measured by DV-II<sup>+</sup> system (Brookfiel Co.). The ionic conductivity of GPE was measured using an AC impedance analyzer (IM6, Zahner Elektrik) with a stainless steel blocking electrode cell. Ionic conductivity was measured for temperatures ranging from -20 °C to 60 °C. A potential difference of 5 mV was applied to the sample for frequencies ranging from 100 Hz to 2 MHz.

The electrochemical stability of the GPE was studied using a linear sweep voltammetry (LSV). LSV was carried out using a potentiostat(model 273, EG&G Co.). A three-electrode system was used for all measurement. A stainless steel was used the working

electrode and a lithium electrode was used as the counter and the reference electrode, respectively. A stainless steel electrode with an area of  $3 \times 5 \text{ cm}^2$  was swept at a sweep rate of  $5 \text{ mV}\cdot\text{s}^{-1}$ . The electrochemical properties of the cell were evaluated using an AC impedance analyzer and a cycler. AC impedance measurements were performed over a frequency range of 700 mHz to 2 MHz for interface investigation of the cells. The charge and discharge cycling tests of  $\text{LiCoO}_2/\text{GPE}/\text{graphite}$  cells were conducted galvanostatically using Toyo battery test system (TOSCAT-3100K). The discharge curves were obtained at different current rates to get the rate capability of the cell and also at various temperatures.

### 3. Results and discussion

Typical IR spectrum obtained from polyurethane acrylate was shown in Figure 3. There are many peaks such as N-H stretching region at wavenumber of ca.  $3,600 \text{ cm}^{-1}$ , aliphatic C-H stretching region at wavenumber of ca.  $3,000\sim 2,900 \text{ cm}^{-1}$ , and carbonyl group's peak at wavenumber of ca.  $1,800\sim 1,700 \text{ cm}^{-1}$  on the spectrum.

Viscosity of precursor is one of important factor to consider in a gel-type lithium-ion polymer battery, because electrodes and separator have to be wetted sufficiently to show a good performance as the cell. Figure 4 showed the relationship between the contents of the liquid electrolyte and the viscosity of PUA-based precursor. The viscosity of the precursor containing 40 vol% monomer was ca.  $32 \text{ mPa}\cdot\text{s}$ , and it decreased with decreasing the contents of the curable mixture. The viscosity of the precursor containing 5 vol% curable mixture was around  $4.5 \text{ mPa}\cdot\text{s}$  and it was nearly same level in the liquid electrolyte.

Ionic conductivity is most important factor in the gel polymer electrolyte. It has been reported that the ionic conductivity<sup>2)-4)</sup> of the membrane-type gel polymer electrolyte is about  $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ . Figure 5 showed the AC impedance spectra of the PUA-based GPEs polymerized at temperature of 80 °C for 1 hour. There was only a spike, which represents a resistor in series with a capacitor<sup>14)</sup>. The intercept on the real axis gives the resistance of the GPE. The ionic conductivity at 20 °C was calculated to be  $5.9 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  from the electrolyte resistance with thickness and surface area of the GPE. The full linearity in the high frequency region is convincing evidence of the integrity of the gel polymer. If phase separation and/or crystallization had been present, these would have been evidenced by the appearance of semicircles or, more generally, by deviation from linearity in the high frequency region of the impedance spectra<sup>15)</sup>. It was, therefore, thought that crystallization in the gel polymer was occurred at around -20 °C because deviation from linearity in the high frequency region was observed.

It is especially pointed out that performance of lithium-ion polymer batteries at low temperature and high current is low compared to lithium-ion batteries with liquid electrolyte. Figure 5 showed the ionic conductivity of PUA-based GPE containing 5 vol% curable mixture obtained at various temperatures. The ionic conductivity of the liquid electrolyte was also plotted to be compared. The ionic conductivity of GPE at 20 °C was around  $4.5 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  and it was even  $1.1 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at temperature of 20 °C. And, it increased with increase in temperature. Other GPE such TEGDMA-, TEGDA-, and PMMA IPN-based has nearly same ionic conductivity; i.e. about  $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ . As mentioned above, 95 vol% liquid electrolyte was contained in this system. It is therefore that ionic behavior is seem to be same in a lithium-ion battery.

It is required to consider its mechanical property as well as mobility of lithium ion in lithium ion polymer battery with a GPE. TEGDMA and HDDA was used to obtain a dense network structure and to decrease the viscosity of polyurethane acrylate. Figure 7 showed the relationship between the ionic conductivity of lithium ions and the contents of TEGDMA and HDDA. The ionic conductivity decreased with increasing the contents of TEGDMA and HDDA. Gelation time decreased and whitening phenomena was observed at gelation test, when the contents of TEGDMA and HDDA increased. Mechanical stability might be enhanced by adding the reactive modifier because the ionic conductivity and the mechanical stability were in trade-off relationship, but mechanical strength test was not performed in this study.

The electrochemical stability of the GPE was studied using by a cyclic sweep voltammetry. The cyclic sweep voltammograms of the GPE on the stainless steel electrodes were shown in Fig. 8. The decomposition voltage was not observed up around 4.5 V vs. Li/Li<sup>+</sup>. There is no problem in the electrochemical stability, because charging voltage for lithium ion battery using lithium cobalt oxide is about 4.2 V.

The AC impedance spectra of the LiCoO<sub>2</sub>/TEGDMA-based GPE/graphite cell were shown in Fig. 9. The impedance spectrum of the cell was obtained after filling of the precursor and 1st cycling. Only one semicircle was observed at higher frequency in the cell that was not cycled, which is related to the bulk resistance ( $R_b$ ) of the GPE. After 1st cycling, the impedance spectroscopy of the cell exhibited two depressed semicircles. The  $Z'$  intercept of the semicircle on the real axis at higher frequency is related to the bulk resistance of the GPE. The semicircle was assumed to be associated with a parallel combination of interfacial resistance ( $R_{int}$ ) and the constant-phase element of the multi-passivation films on both electrode surfaces<sup>16), 17)</sup> The diameter of the semicircle is related to the interfacial resistance



between the electrode and the GPE<sup>18)</sup>. The semicircle at medium frequency is assigned to the parallel combination of the charge transfer resistance ( $R_{ct}$ ) in the electrodes and the double-layer capacitance ( $C_{dl}$ ) contributed by both the cathode and the anode. At a lower frequency there is a slanted line due to solid-state diffusion of Li ions within the bulk cathode/anode materials.

In order to evaluate the electrochemical performance of a lithium ion, a LiCoO<sub>2</sub>/GPE/ graphite cell was fabricated. The GPE consisted of 5 vol% curable mixture and 95 vol% 1.0M LiPF<sub>6</sub>/EC-DEC. The assembled cell was preconditioned with a cut-off voltage of 4.2 V for the upper limit and 3.0 V for the lower limit at the 0.2C rate (0.5 mA·cm<sup>-2</sup>). An irreversible capacity was observed in the 1st cycle and this is caused by the formation of passivation film on the surface of the carbon electrode due to the decomposition of electrolyte, as reported previously by other authors<sup>19), 20)</sup>. The process of passivation film on the surface during the initial cycling is referred to as the formation period. The film can prevent the electrolyte from further reduction by the active lithium and thus limits the degradation of electrolytes.

After the preconditioning cycle, the cell was charged and discharged at various current densities and temperatures. Charge and discharge curves of the cell showed well-defined charge-discharge voltage profile, which indicates a reversible cycling process. The small voltage drop in the cycle test confirms the low internal resistance of the lithium-ion polymer cell. The coulombic efficiency in the cycle test was ca. 100 %. The discharge curves, obtained at different current rates, of LiCoO<sub>2</sub>/TEGDMA-based GPE/graphite cell were given in Figure 10. The cell delivered a discharge capacity of ca. 506 mAh at current density of 0.5 mA·cm<sup>-2</sup> (0.2C rate). The discharge capacity slowly decreased with current rate, which was due to polarization. A useful capacity of ca. 488 mAh was obtained at 0.5C rate, which was 96 % of

the discharge capacity at 0.2C rate. The capacity of ca. 444 mAh was available even at 1.0C rate, which was 88 % of the discharge capacity at 0.2C rate. Other cells also have shown nearly same rate capability. The reduced capacity in the cell at high rate may be primarily related to the lower diffusion rate of lithium ions in the gel polymer electrolyte<sup>21</sup>.

The performances of the LiCoO<sub>2</sub>/GPE/graphite cell at various temperatures were also evaluated. The discharge curves obtained at current density of 1.2 mA·cm<sup>-2</sup> (0.5C rate) at various temperatures were given in Figure 11. The discharge capacity of the cell was ca. 488 mAh at 20 °C. The discharge capacity slowly decreased with decreasing the temperature. A useful capacity of ca. 415 mAh was obtained at 10 °C, which was 85 % of the discharge capacity at 20°C. Recently, ethyl methyl carbonate (EMC) was found to be a useful co-solvent in binary solutions with propylene carbonate and ethylene carbonate because of its low freezing point (-55 °C). And propylene carbonate (PC) is also one of solvent that shows good low-temperature performance. Performances of the lithium-ion cells at low temperature, therefore, can be improved using such solvents having low freezing point.

#### 4. Conclusions

TEGDA-, TEGDMA-, PMMA IPN-, and PUA-based GPE was prepared. The viscosity of the precursor containing 5 vol% curable mixture was around 4~5 mPa·s. The ionic conductivity of the GPE at 20°C was around 4~5 x 10<sup>-3</sup> S·cm<sup>-1</sup>. The GPE had good electrochemical stability up to 4.5 V vs. Li/Li<sup>+</sup>. The capacity of the LiCoO<sub>2</sub>/GPE/graphite cell at 1.0C rate was about 80 % of the discharge capacity at 0.2C rate. The discharge capacity slowly decreased with decreasing the temperature. The capacity of the cell at temperature of

-10 °C was ca. 80 % of the discharge capacity at temperature of 20°C.

## References

- 1) K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 136 (1990) 1657.
- 2) D. Kim, K. Noh, H. Min, D. Kang, and Y. Sun, *Electrochem. & Solid-State Letters*, 5 (2002) A63.
- 3) H. Akashi, K. Tanaka, and K. Sekai, *J. Power Sources*, 104 (2002) 241.
- 4) S. Panero, D. Satolli, A. D'Epifano, and B. Scrosati, *J. Electrochem. Soc.*, 149 (2002) A414.
- 5) F. Boudin, X. Andrieu, C. Jehoulet, and I. I. Olsen, *J. Power Sources*, 81-82 (1999) 804.
- 6) B. Scrosati, F. Croce, and L. Persi, *J. Electrochem. Soc.*, 147 (2000) 1718.
- 7) Y. Aihara, G. B. Appetecchi, and B. Scrosati, *J. Electrochem. Soc.*, 149 (2002) A849.
- 8) M. Kono, E. Hayashi, and M. Watanabe, *J. Electrochem. Soc.*, 146 (1999) 1626.
- 9) E. Quartarone, C. Tomasi, P. Mustarelli, G. B. Appetecchi, and F. Croce, *Electrochimica Acta*, 43 (1998) 1435.
- 10) S. Kuwabata and M. Tomiyori, *J. Electrochem. Soc.*, 149 (2002) A988.
- 11) M. Alamgir, K.M. Abraham, *J. Electrochem. Soc.*, 140 (1993) L96.
- 12) V. Arcella, A. Sanguineti, E. Quartane, and P. Mustarelli, *J. Power Sources*, 81-82 (1999) 790.
- 13) H. Huang and S. L. Wunder, *J. Electrochem. Soc.*, 148 (2001) A279.
- 14) G. G. Kumar and N. Munichandraiah, *J. Power Sources*, 102 (2001),

46.

15) W. A. van Schalkwijk and B. Scrosati (Eds), *Advances in Lithium-Ion Batteries*, Kluwer Academic / Plenum Publishers, New York (2002)

16) S. Rajendran and T. Uma, *J. Power Sources*, 88 (2000) 282.

17) M. D. Levi, G. Salitra, B. Makovsky, H. D. Abache, U. Heider, and L. Heider, *J. Electrochem. Soc.*, 146 (1999) 1279.

18) H. Wang, H. Huang, and S. L. Wunder, *J. Electrochem. Soc.*, 147 (2000) 2853.

19) R. Fong, U. von Sacken, J. R. Dahn, *J. Electrochem. Soc.*, 137 (1990) 2009.

20) J. M. Rarascon and D. Guyomard, *J. Electrochem. Soc.*, 138 (1991) 2864.

21) D. Kim, *J. Power Sources*, 87 (2000) 78.

22) D. Kim and Y. Sun, *J. Power Sources*, 102 (2001) 41.

23) M. Kono, E. Hayashi, M. Nishiura, and M. Watanabe, *J. Electrochem. Soc.*, 147 (2000) 2517.

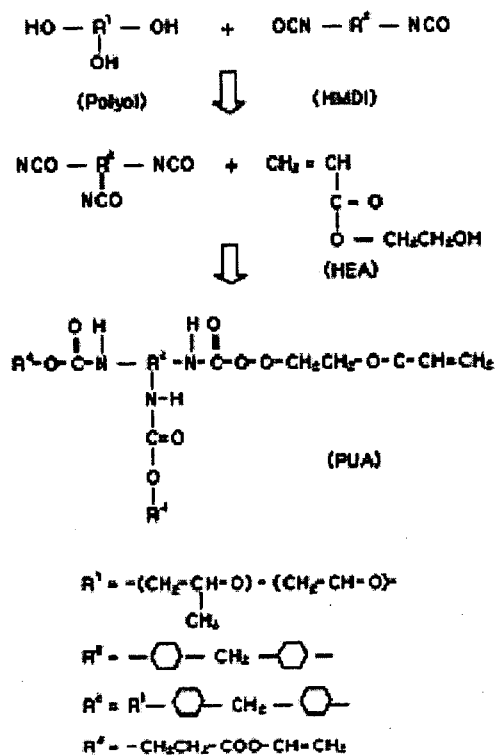


Fig. 1. Schematic of synthesis for urethane acrylate oligomer.

Table 1 Properties of a monomer and an initiator.

Materials	Tri (ethylene glycol) dimethacrylate	Tetra (ethylene glycol) diacrylate	Methyl methacrylate	1,6-Hexandiol Dimethacrylate	Benzoyl peroxide
Maker	Aldrich Chemical Company	Aldrich Chemical Company	Aldrich Chemical Company	Aldrich Chemical Company	Acros organics
State	Liquid	Liquid	Liquid	Liquid	Powder
Molecular weight (FW)	286.33	302.22	100.12	254.33	242.23
Specific gravity (25°C)	1.092	1.110	0.936	0.995	-
Chemical structure					

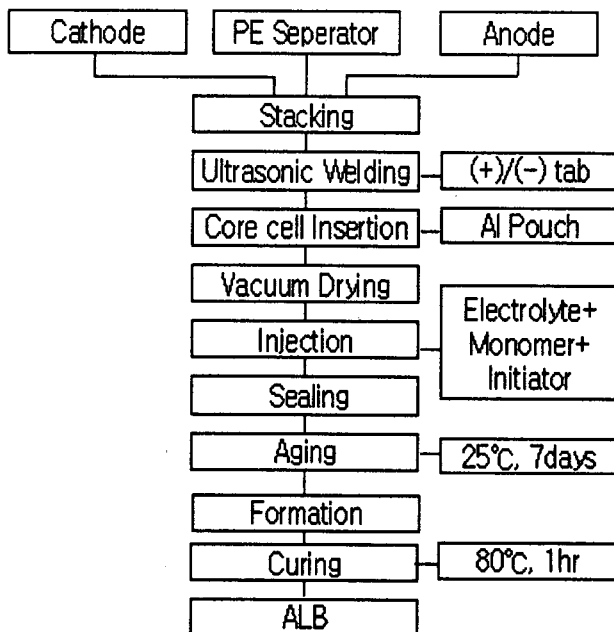


Fig. 2 Fabrication procedure of gel-type pouch cell.

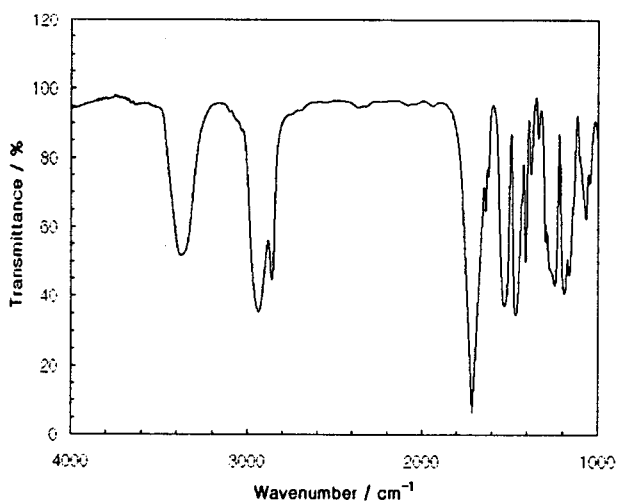


Fig. 3 FTIR spectrum of polyurethane acrylate macromonomer.

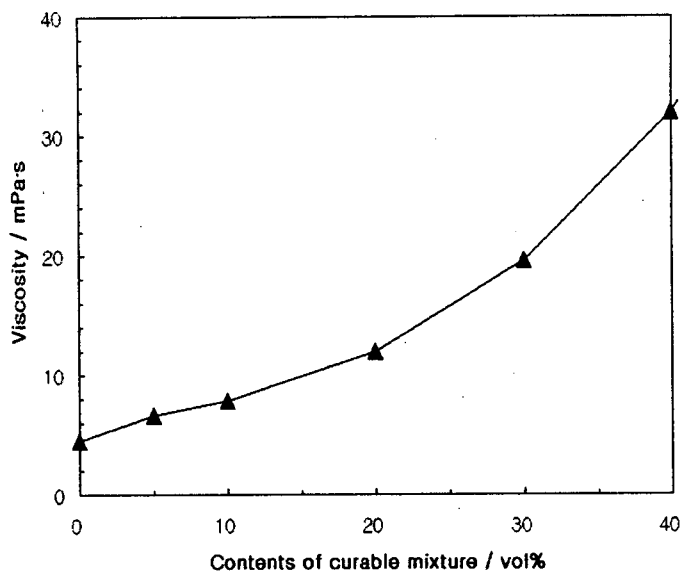


Fig. 4 Relationship between the viscosity of the PUA-based precursor and the contents of the curable mixture.

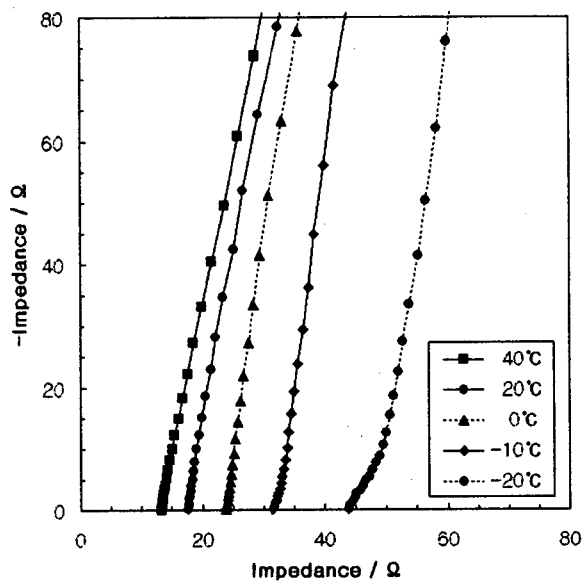


Fig. 5 AC impedance spectra of SS/PUA-based GPE/SS cell with gel polymer electrolyte.

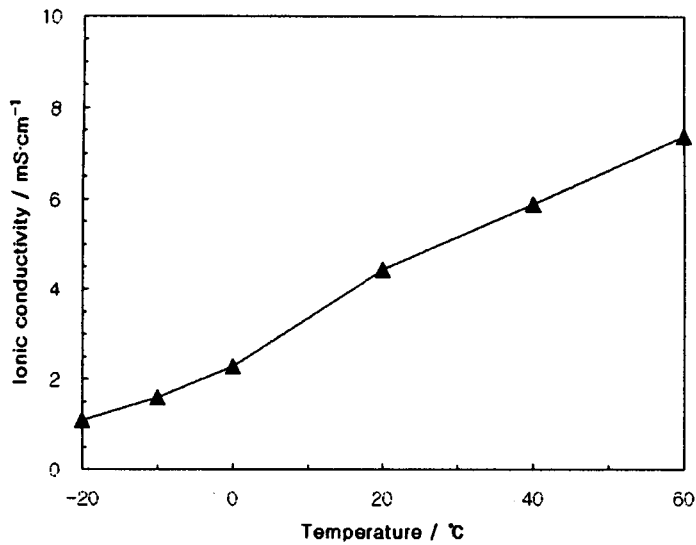


Fig. 6 Ionic conductivity of PUA-based gel polymer electrolyte obtained at various temperatures.

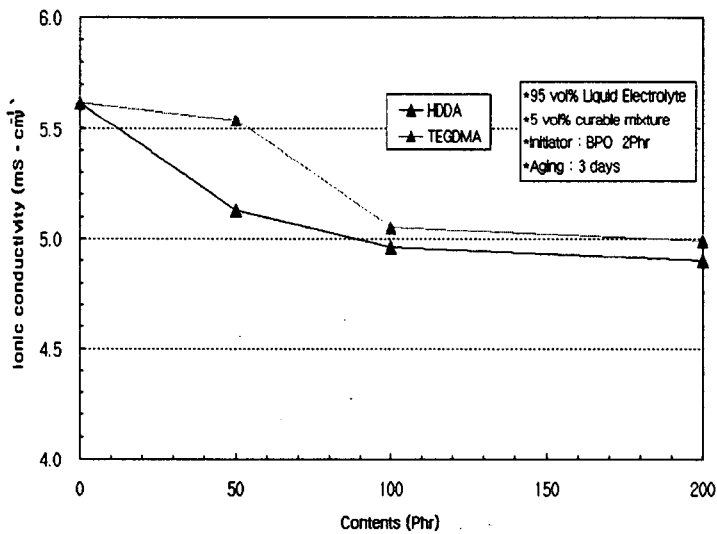


Fig. 7 Ionic conductivity of PUA-based gel polymer electrolyte obtained at various temperatures.



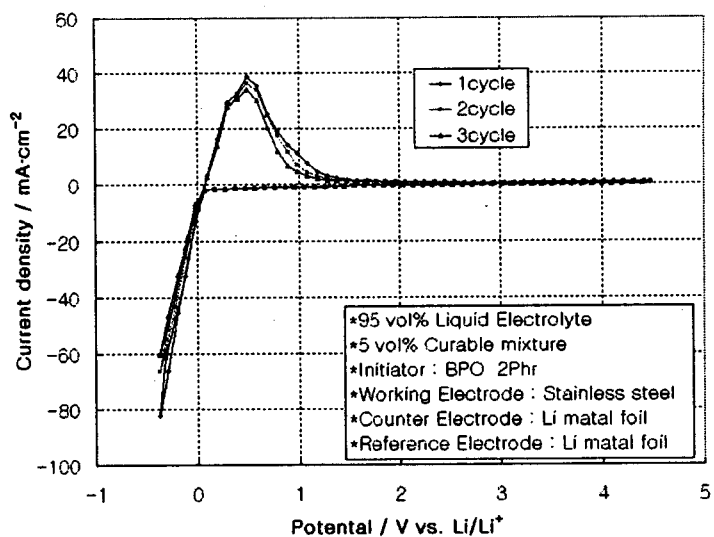


Fig. 8 Cyclic sweep of stainless steel/PUA-based GPE/Li cell at 20°C.

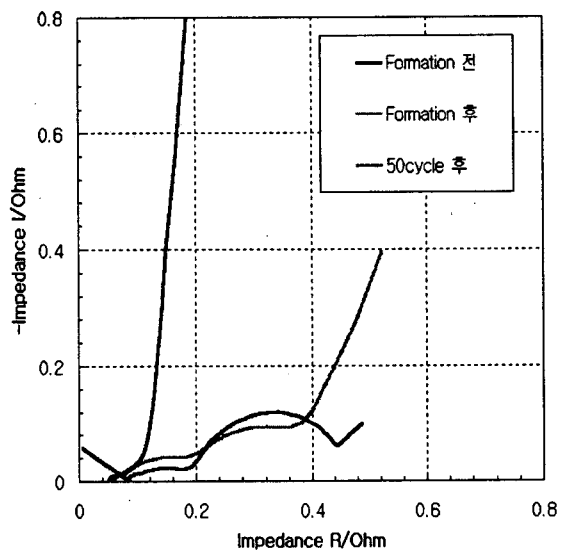


Fig. 9 AC impedance spectra of  $\text{LiCoO}_2$ /TEGDMA-based GPE/graphite cell at 20°C.

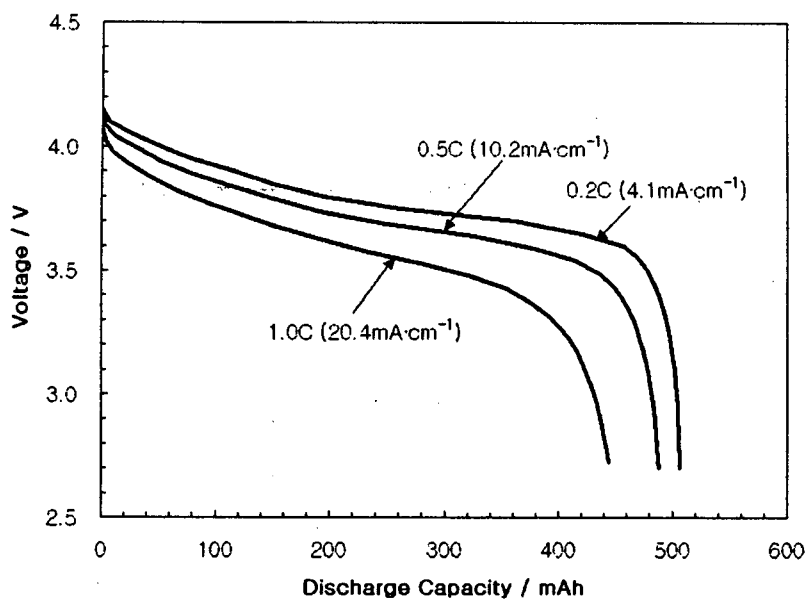


Fig. 10 Typical discharge curves for LiCoO<sub>2</sub>/TEGDMA-based GPE/MCF cell at various current densities at 20°C.

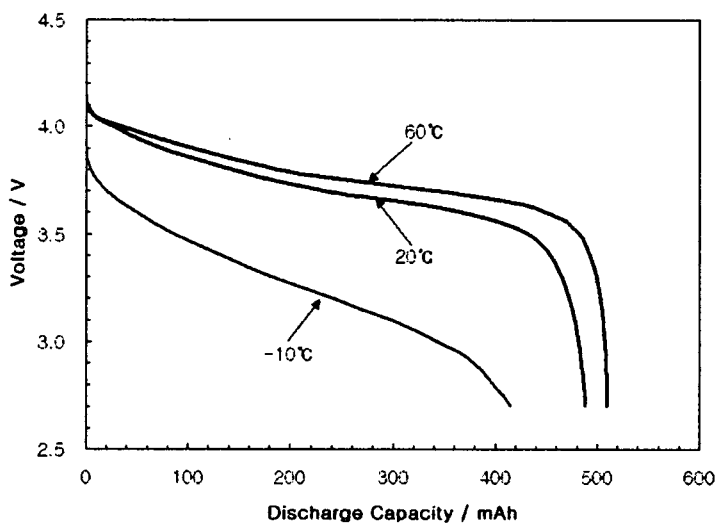


Fig. 11 Typical discharge curves for LiCoO<sub>2</sub>/TEGDMA-based GPE/MCF cell at various temperatures.