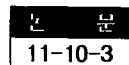


# Electric and Electrochemical Characteristic of PMMA-PEO Gel Electrolyte for Rechargeable Lithium Battery



박수길\*, 박종은\*, 이홍기\*\*, 이주성\*\*\*

(Soo-Gil Park, Jong-Eun Park, Hong-Ki Lee, Ju-Seong Lee)

## Abstract

The new type polymer electrolyte composed of polymethyl methacrylate(PMMA) - polyethyleneoxide(PEO) contain  $\text{LiClO}_4$ -EC/PC was developed for the weightless and long or life time of lithium polymer battery system with using polyaniline electrode. The gel type electrolytes were prepared by PMMA with PEO at different lithium salts in the glove box. The minimum thickness of PMMA-PEO gel electrolyte for the slim type is about  $<400\sim 450\mu\text{m}$ . These gel electrolyte showed good compatibility with lithium electrode. The test cell of Li/polymer electrolyte/polyaniline solid state cell which was prepared by different lithium salt was researched by electrochemical technique.

**Key Words** : Polymer electrode, Lithium battery, Polymer cathode

## 1. Introduction

A large number of studies to date have been carried out on the solid state batteries utilizing the plasticized polymer electrolytes in which the liquid electrolyte solution has been immobilized by incorporation into a matrix polymer. These plasticized polymer electrolytes combine the best features of both liquid and solid electrolytes for lithium polymer battery is an employment of statistical copolymers as a matrix polymer. Poly(methyl methacrylate) is one of the host polymers previously used in plasticized polymer electrolyte, first reported by Iijima et al.<sup>4)</sup> and even more recently by Bohnke et al.<sup>2)</sup> The PMMA based plasticized polymer electrolyte showed the high ionic conductivity of  $1 \times 10^{-4}\text{S/cm}$  at  $25^\circ\text{C}$  and at the content of 45%.

However, this electrolyte suffers from a gel-like mechanical property; it does not form a free-standing film at a high plasticizer content. For the reason, an improvement in the mechanical property of the PMMA-based plasticized electrolyte is required to be useful in commercial application.

In this paper, we recently studied the new plasticized polymer electrolyte composed of the PEO/PMMA blend as a host polymer, the mixture of EC and PC as a plasticizer, and  $\text{LiClO}_4$  as a salt try to improve mechanical property. This approach allows to optimize the physical-chemical properties such as ionic conductivity, mechanical properties, compatibility with plasticizing electrolyte solution, and stability towards lithium electrode. Polymer electrolytes consist of polyethyleneoxide(PEO), polymethylmethacrylate(PMMA), 1M  $\text{LiClO}_4$ , in ethylene carbonate (EC), propylene carbonate(PC).

## 2. Experimental

### 2.1 Materials

PEO (molecular weight: 5,000,000 Aldrich

\* : 충북대학교 공대 화학공학부 공업화학과

(충북 청주시 흥덕구 개신동 산 48, Fax: 0431-273-8221

E-mail : sgpark@trut.chungbuk.ac.kr

\*\* : 우석대학교 공대 화학공학과

\*\*\* : 한양대학교 공대 화학공학과

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Chemical Co Inc), PMMA (molecular weight: 350,000 Aldrich Chemical Co Inc), ethylene carbonate(EC), propylene carbonate(PC) were purchased from Aldrich and used without further purification(>99.9%).  $\text{LiClO}_4$  supplied from Aldrich was used after drying at  $150^\circ\text{C}$  under vacuum for 24h.

## 2.2 Synthesis of Polyaniline

Aniline(0.50 mol) was dissolved in 500ml 1M HCl. A solution of ammonium peroxy disulfate (171.2g:0.75mol) dissolved in distilled water(130ml) was added dropping to the aniline solution under a  $\text{N}_2$  atmosphere. Ammonium peroxy disulphate solution is added very slowly to prevent the warming of the solution. The mixture was stirred for 2 hours at  $-4^\circ\text{C}$ . The time of initial colouration on mixing of reagents depends upon the temperature and protonic acid used. When HCl is used as a protonic acid, the colouration of solution occurs almost after 1 minute at  $-4^\circ\text{C}$ . The sequence of colouration is light blue  $\rightarrow$ blue green  $\rightarrow$ coppery tint  $\rightarrow$ green precipitates. The precipitate was filtered and washed repeatedly with distilled water until the filtered is colourless. The precipitated is then washed with methyl alcohol and filtered and dried under dynamic vacuum oven at  $60^\circ\text{C}$  for 8 hours. This product was suspended in 0.1 mole ammonium hydroxide and stirred for 6 hours. The pH of this solution should be kept around 9 by adding drops of 1M  $\text{NH}_4\text{OH}$ . The blue emeraldine base obtained after filtration is dried dynamic vacuum. The composite cathode electrode was prepared by N-methyl -2-pyrrolidone (NMP) solution of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and chemically polymerized PAn. The concentrated (DMcT + PAn)/NMP solution has a high viscosity like ink. DMcT(2g) was dissolved in NMP(5g), and then chemically polymerized PAn(1g) was dissolved in the viscous DMcT/NMP solution. The viscous ink was spread on Al foil and then dried  $80^\circ\text{C}$  for 1 hour. Fig 1 exhibits diagram of synthesis of polyaniline.

## 2.3 Preparation of polymer electrolyte

All the electrolyte were prepared by the solution casting technique. The solution for film cast were prepared by dissolving appropriate

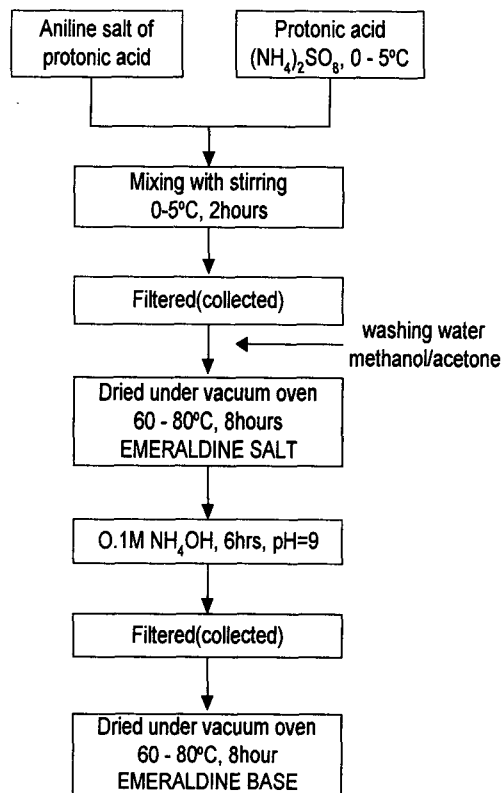


Fig. 1. Synthesis diagram of polyaniline

amounts of the PEO, the PMMA, the plasticizer EC, PC as organic solvent and  $\text{LiClO}_4$  together in acetonitrile. The solution was poured into Teflon molder and evaporating acetonitrile in an Ar atmosphere at room temperature. After evaporation of the acetonitrile, mechanically stable free standing film and the thickness( $450\mu\text{m}$ ) was obtained and peeled from the molder

## 2.4 Electrochemical measurement

Ionic conductivity measurement was prepared by sandwiching the polymer electrolyte with two SUS electrode SUS/gel-SPE/SUS and lithium yield measurement was prepared by sandwiching the polymer electrolyte with two lithium electrode Li/gel-SPE/Li,  $2\text{cm} \times 2\text{cm}$  cell by using Impedance /Gain Phase Analyzer 4194A at a frequency range  $100\text{Hz} \sim 4\text{MHz}$ .

Cyclic voltammetry were measured EG&G 273A by using Li/gel-SPE/Li, and PAn/SPE/Li cell.

The voltage range from 0 to 4V, scan rate 10mV/s.

Charge discharge test were performed coin type cell which the polymer electrolyte film was sandwiched with the composite cathode film and a lithium foil as an anode, and then sandwiched with current collectors to give a test cell. Fig 2. show coin type cell.

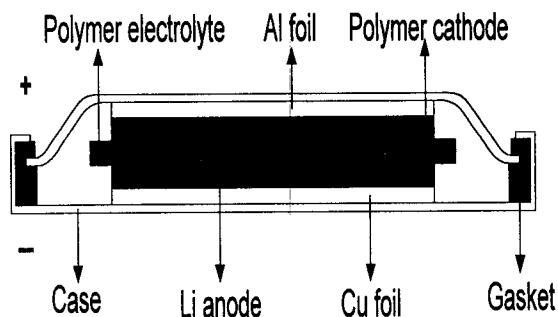


Fig. 2. Apparatuses of coin type cell

### 3. Results and Discussion

#### 3.1 Electric conductivity of polymer electrolyte

We measured the resistance of lithium by ac impedance measurement. Figures 3 and 4 show Cole-Cole plots of polymer electrolyte with non-blocking electrode and blocking electrode. It is clear that a depressed semicircle appear in each plot. We consider that this semicircle correspond to the interfacial impedance, including the charge transferrer resistance of lithium deposition and the surface layer formed by side reaction with PC, EC, PEO, PMMA and LiClO<sub>4</sub>. Fig. 3 show ionic conductivity using blocking electrode system. The bulk resistance of polymer electrolyte was about 39.5Ω and area of polymer electrolyte was 4cm<sup>2</sup>. The polymer electrolyte which was using equation (1) was  $0.24 \times 10^{-4}$  S/cm electric conductivity at room temperature. Fig. 4 shows ionic conductivity using non-blocking(between two lithium electrode Li/gel-SPE/Li) electrode system. The bulk resistance(Rb) and interface resistance(Re) was 45.5Ω, 53.6Ω respectively. ΔV was 5mV and I<sub>∞</sub> (A/cm) was  $4.65 \times 10^{-5}$ . The lithium yield was calculated using equation (2). The yield was 0.44.

$$\sigma \text{ (S/cm)} = T(\mu\text{m}) / \{R_b(\Omega) \cdot A(\text{cm}^2)\} \quad (1)$$

- σ : Ionic conductivity
- T : Thickness of polymer electrolyte
- R<sub>b</sub> : Bulk resistance
- A : Area of polymer electrolyte.

$$t_{Li^+} = \frac{R_b}{(\Delta V / I_{\infty}) - R_e} \quad (2)$$

- t : Yield
- R<sub>b</sub> : Bulk resistance
- R<sub>e</sub> : Interface resistance
- I<sub>∞</sub> (A/cm) : Equivalent Conductance

#### 3.2 Electrochemical property of polymer electrode

Fig 5 show electrochemical property of polymer electrode. We use a test cell which consist of Li/gel-SPE/PAn and reference electrode Li tip.

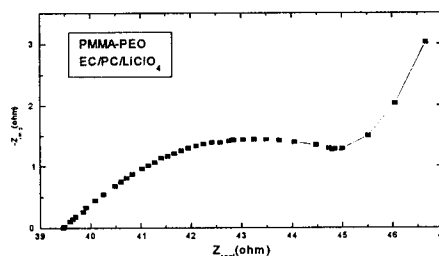


Fig. 3. Impedance diagram of SUS/gel-SPE/SUS cell

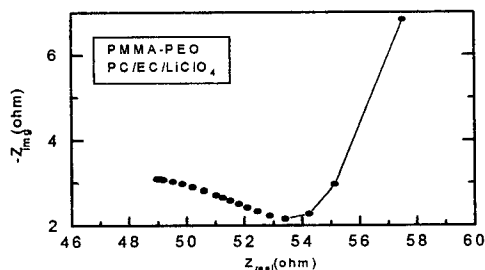


Fig. 4. Impedance diagram of Li/gel-SPE/Li cell

We measure of electrochemical stability windows from 0~4V. It show that oxidation peak

appeared 2.4V. It means that  $\text{ClO}_4^-$  anion which used lithium salt in electrolyte move toward the backbone of polymer composite cathode. When the cycle numbers are increase, the current density was increase. By cycling surface resistance are increased between polymer cathode and electrolyte because passivation layer is formed polymer cathode surface. That caused capacitance loss and cycle number. Oxidation peak at 2.3V correspond with cyclic voltammogram of polymer electrolyte second oxidation peak at 2.3V in Fig. 6.

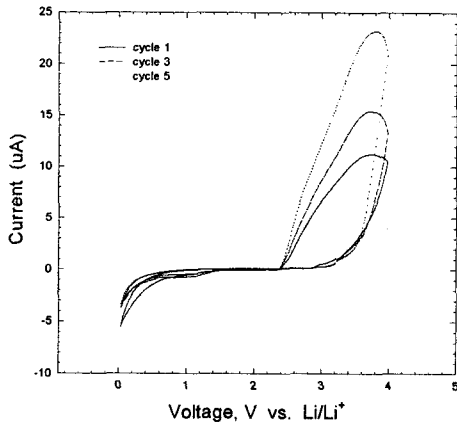


Fig. 5. Cyclic voltammogram of Li/gel-SPE/PAN cell scan rate 10mV/s

### 3.3 Electrochemical property of polymer electrolyte

Fig 6 show electrochemical property of polymer electrolyte. We use a test cell which consist of Li/gel-SPE/SS and reference electrode Li. Polymer electrolyte has wide electrochemical stability window from 0~4V. Oxidation peak about 1.2V decomposition of water, and second oxidation peak at 2.3V  $\text{ClO}_4^-$  anion reacted on polyaniline cathode. The reduction peak was shifted more minus voltage range. This peak intensity are increase by cycling. at first cycle polymer electrolyte was formed passivation layer on lithium surface. So that the current density more higher than second and 10th cycle. After 10th cycle the current density are stabilized between first and second cycle.

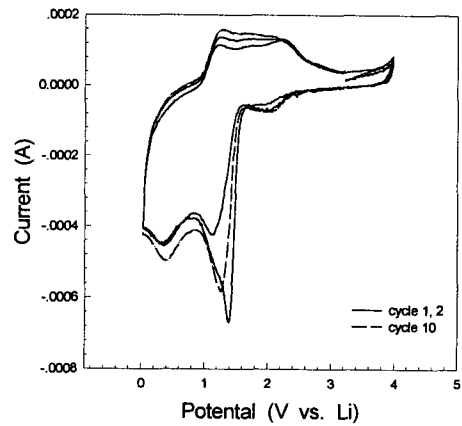


Fig. 6. Cyclic voltammogram of Li/gel-SPE/SS cell scan rate 10mV/s

### 3.4 Dielectric property of polymer electrolyte

The polarization peak at the high frequency region above  $10^5$ Hz is more clearly found, which is strong evidence for the stopping of the transported ion at the interface. As the stress induced by electric field cannot be dissipated by the ionic transport at interface, so the polarization peak is generated

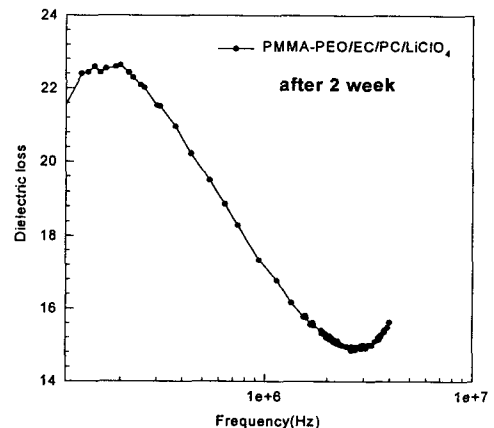


Fig. 7. Dielectric loss spectra of the electrolytes

### 3.5 Charge-Discharge performances of cell

Fig. 8 show charge discharge property of coin cell. This coin type battery was charged at a

constant voltage(4.5V) until the current  $<0.1\text{mA}/\text{cm}^2$ . The discharge was performed at  $0.1\text{mA}/\text{cm}^2$  and cut off 2.25V. Both charge and discharge were performed at  $20^\circ\text{C}$ . When the charging voltage was 4.5V, average discharge voltage 4.5V during the 8hour. It has  $13.3\text{mAh/g}$  weight energy density.

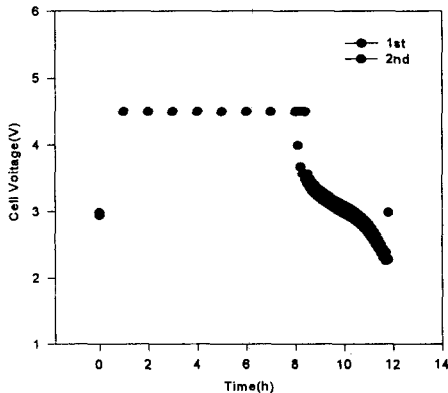


Fig. 8. Charge discharge curve coin type cell.

#### 4. Conclusion

The polymer electrolyte has  $0.24 \times 10^{-4}\text{S}/\text{cm}$  ionic conductivity at room temperature. The yield of polymer electrolyte was 0.44 in the non-blocking electrode system. It has electrochemical stability windows from 0~4V. it show that oxidation peak appeared 2.3V cause by  $\text{ClO}_4^-$  which used lithium salt in electrolyte move toward the backbone of polymer composite cathode. The polarization peak at the high frequency region above  $10^5\text{Hz}$ . The stress induced by electric field cannot be dissipated by the ionic transport at interface, so the polarization peak is

generated. The energy density of polyaniline lithium ion cell show about  $70\text{mAh/g}$ . In our experimental The coin type polyaniline lithium polymer battery has  $13.3\text{mAh/g}$  weight energy density.

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#### References

1. Liu, M., Visco, S.J. & L.C. *J. electrochem. Soc.* 138, 1896-1895(1991)
2. Oyama, N. et al. Proc. New Sealed Rechargeable Batteries Supercapacitors 379 -388
3. F. Coowar et al. *J. Power Sources* 179-186 (1996)
4. L. Yang et al., *Solid State Ionic*, 40/41, 616 (1990)
5. D. Peramunage, D. M. Pasquariello and K. M. Abraham, *J. Electrochem. Soc.* 142, 1789(1995)
6. S. J. Visco, C. C. Mailhe, L.C.De jonghe, and M.B. Armand, *J. Electrochem. Soc.*, 136, 661(1989)
7. I. D. Raistic, *Sloid State Ionics*, 18/19, 40(1984)
8. C. Tubandt, Handbuch der Experimental Physik, Bd. x II, Akademische Verlag (1932)
9. J. Mizusaki, K. Arai, K. Fueki, *Sloid State Ionics*, 11, 203(1983)
10. K. Kiukkola, C. Wagner, *J. Electrochem. Soc.* 104, 308, 379(1957)
11. C. Wagner, Proc. CITCE 7th p.361(1955)
12. J.Mizusaki, K. Fueki, Rev. Chim. Minerale, 17, 356(1980)
13. J.Mizusaki, K. Fueki, T. Mukaibo, Bull. Chem, Soc, Jpn., 51, 694(1978)