

Electrochemical Properties of Cross-linked Polyurethane Acrylate-Based Gel Polymer Electrolyte

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Abstract. In this study, a gel polymer electrolyte was prepared from urethane acrylate and its electrochemical performances were evaluated. And, LiCoO₂/GPE/graphite cells were prepared and their performances depending on discharge currents and temperatures were evaluated. The precursor containing 5 vol% curable mixture had a low viscosity relatively. Ionic conductivity of the gel polymer electrolyte at room temperature and -20°C was ca. $5.9 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and $1.7 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, respectively. GPE showed electrochemical stability up to potential of 4.5 V vs. Li/Li⁺. LiCoO₂/GPE/graphite cell showed a good high-rate and a low-temperature performance.

Key words : Polyurethane acrylate, Lithium-ion polymer battery, Gel polymer electrolyte, Curable mixture, Ionic conductivity

1. Introduction

Lithium ion battery has a good high-rate and a low-temperature performance, but has a relatively low safety due to leakage of a liquid electrolyte. A probability of the leakage of lithium ion polymer battery is very low because of adopting a solid type or a gel type electrolyte, but the high-rate and the low-temperature performance decrease because its ionic conductivity is low. Therefore, a new type advanced lithium-ion battery with a gel polymer electrolyte are developing to complement their demerits and to use their merit, i.e. high power density and no leakage of electrolyte¹⁾.

Many research results on membrane type gel polymer electrolytes have been reported. Kono et al.²⁾ prepared gel polymer electrolyte consisting of poly(alkylene oxide) macro-monomer, LiClO₄, and propylene carbonate (PC). And, many kinds of polymeric hosts such as polyacrylonitrile (PAN)³⁾, poly(vinylidene fluoride) (PVdF)⁴⁾, poly(ethylene oxide) (PEO)⁵⁾, poly(methylmethacrylate) (PMMA)⁶⁾, poly(vinyl chloride) (PVC)⁷⁾ have been proposed as frameworks for gel polymer electrolyte. Their ionic conductivities were reported between 10^{-4} and 10^{-3} Scm^{-1} at room temperature. Hybrid polymer electrolytes based on P(VdF-HFP)^{8,9)} copolymers exhibited high ionic conductivity and good mechanical performances.

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, photo-polymerization, and electron beam radiation polymerization. If crosslinkable urethane

acrylate were used in a gel polymer electrolyte, the cell might exhibit good electrochemical and mechanical performance.

In this study, precursor for the GPE was prepared from polyurethane acrylate (PUA) oligomer, hexanediol dimethacrylate (HDDA) and tri(ethylene glycol) dimethacrylate (TEGDMA) as a reactive modifier, benzoyl peroxide (BPO) as a thermal initiator, and 1.0 M LiPF₆/EC-DEC (1:1 vol%) as an electrolyte. The LiCoO₂/GPE/graphite cells are prepared and their electrochemical properties were evaluated at various current densities and temperatures.

2. Experimental

2.1. Preparation of gel polymer electrolyte and cell

A precursor for the gel polymer electrolyte of lithium-ion polymer battery consists of a liquid electrolyte, a monomer/oligomer/macromonomer, a reactive modifier, and an initiator. In this study, curable mixture consisted of an oligomer, a reactive modifier, and an initiator except for a liquid electrolyte. Chemical structure of PUA has been shown the previous literature¹⁰⁾.

Battery grade solution of 1.0 M LiPF₆/EC-DEC (1:1 vol%) was obtained from Cheil Industries. 1,6-hexanediol dimethacrylate (HDDA) and tri(ethylene glycol) dimethacrylate (TEGDMA) were used as a reactive modifier to improve mechanical properties of gel polymer electrolyte. Benzoyl peroxide (BPO) [C₁₄H₁₀O₄, Aldrich Chemical Co.] was used as a thermal initiator. A precursor containing of 95 vol% electrolyte and 5 vol% curable mixture with 2 phr of BPO was polymerized by a thermal reaction at 80°C for 40 minutes. HDDA and TEGDMA was added about 50-300 phr. All procedures for preparing the precursor were carried out in a

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dry-box filled with argon gas.

Lithium cobalt oxide electrodes were prepared by mixing 93 wt% LiCoO_2 (Osaka Gas) 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) 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 40 minutes in an oven.

2.2. Characterization of electrochemical properties of GPE and cell

Ionic conductivity, viscosity and electrochemical stability window of the gel polymer electrolyte were evaluated. Viscosity of the precursor was measured by a viscometer DV-II⁺ (Brookfield Co.). The ionic conductivity of gel polymer electrolyte 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 the technique of cyclic voltammetry (CV). CV 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 in the potential range of -0.5 V to 4.3 V vs. Li/Li^+ at a sweep rate of 5 mVs^{-1} .

The electrochemical properties of the obtained cell were evaluated using an AC impedance analyzer and a cycler. AC impedance measurements were performed using by Zahner Elektrik IM6 impedance analyzer over a frequency range of 700 mHz to 2 MHz for interface investigation of the cells. The charge and discharge cycling tests of LiCoO_2 /gel polymer electrolyte/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

The ionic conductivity is one of the important factors in the gel polymer electrolyte. It has been reported that the ionic conductivity²⁻⁴⁾ of the membrane-type gel polymer electrolyte is about 10^{-3} Scm^{-1} . The ionic conductivity of gel polymer electrolyte was measured using an AC impedance analyzer with a stainless steel blocking electrode. Figure 1 shows the AC impedance spectra of the gel polymer electrolytes polymerized at 80°C for 40 minutes. There was only a spike, which represents a resistor in series with a capacitor, at the plot. The intercept on the real axis gives the resistance

of the gel polymer electrolyte. The ionic conductivity at 20°C was calculated to be $5.9 \times 10^{-3} \text{ Scm}^{-1}$ from the electrolyte resistance with thickness and surface area of the gel polymer electrolyte.

The electrolyte of the cell should also allow low temperature performances, because the commercial batteries are sometimes used at low temperature. 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 having the liquid electrolyte. Figure 2 shows the ionic conductivity of the gel polymer electrolyte containing 5 vol% monomer obtained at various temperatures. The ionic conductivity of GPE at 20°C was around $5.9 \times 10^{-3} \text{ Scm}^{-1}$. And, it increased with increase in temperature. This behavior can be rationalized by recognizing the free-volume model¹¹⁾. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules, or polymer segments can move into the free volume. The resulting conductivity, represented by the overall mobility of ion

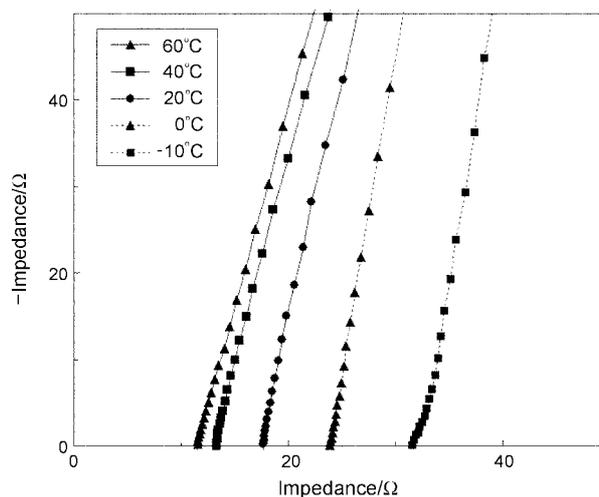


Fig. 1. AC impedance spectra of SS/GPE/SS cell with gel polymer electrolyte.

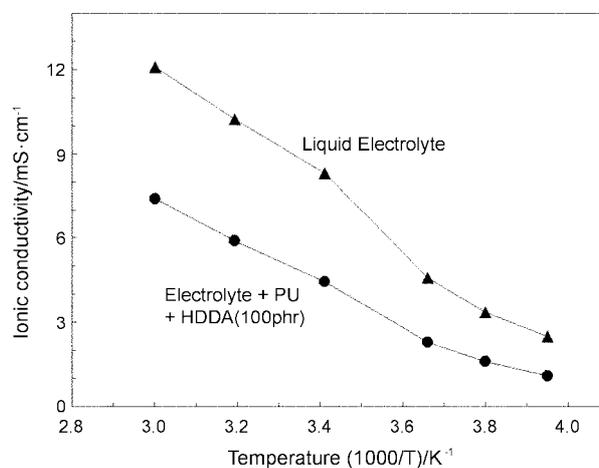


Fig. 2. Ionic conductivity of polymer gel electrolyte at various temperatures.

and polymer, is determined by the free volume around the polymer chains. Therefore, as temperature increases, the free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds.

One should consider its mechanical property as well as mobility of lithium ion in lithium-ion polymer battery using a gel polymer electrolyte. Polyurethane acrylate has a merit that its property can be easily modified from blending with reactive modifier. Figure 3 shows the relationship between the ionic conductivity of lithium ions and the contents of HDDA. HDDA as a reactive modifier was used to obtain a dense network structure and to decrease the viscosity of polyurethane acrylate. The ionic conductivity did not change so much with the contents of HDDA, but maximum ionic conductivity was observed at 200 phr HDDA. The reason why the maximum value was obtained in Figure 3 is not clear, however it is thought that it is attributed to miscibility of electrolyte and curable mixture. We observed that whitening phenomena appeared at tube test, when the contents of HDDA increased. Figure 4 shows the relationship between

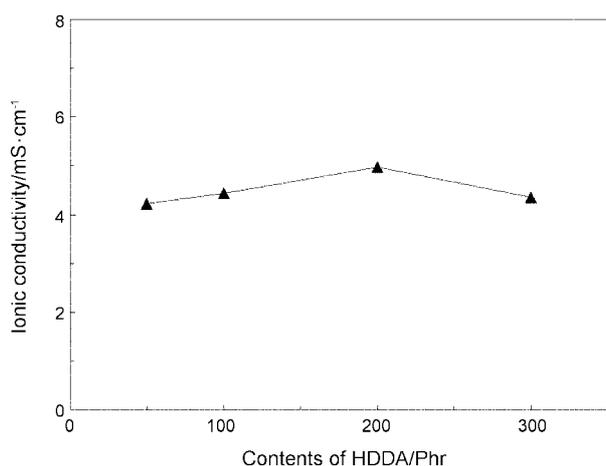


Fig. 3. Relationship between the ionic conductivity and the contents of HDDA.

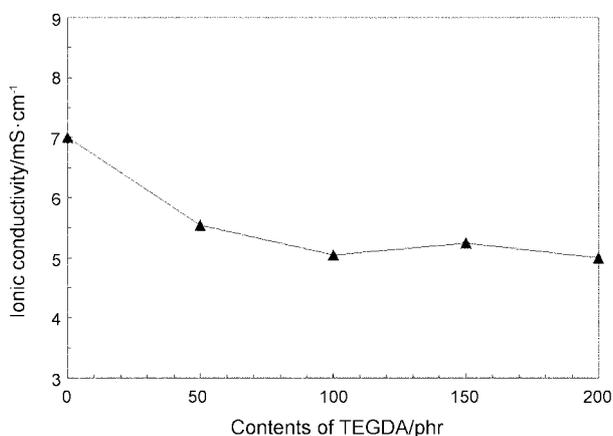


Fig. 4. Relationship between the ionic conductivity and the contents of TEGDMA.

the ionic conductivity of lithium ions and the contents of TEGDMA. The ionic conductivity decreased with increasing the contents of TEGDMA. TEGDMA could act as a cross-linking agent to improve mechanical stability. However ionic conductivity decreased a little because the ionic conductivity and the mechanical stability were in trade-off relationship.

Two types of polyurethane acrylate having two and three active sites were blended to improve properties of the gel polymer electrolyte. Figure 5 shows the ionic conductivity with contents of polyurethane acrylate having two active sites. It was expected that the ionic conductivity increased with mixing each other, because network structure was developed less in polyurethane having two active sites. However, lithium ions moved fast in three active sites.

The electrochemical stability of the gel polymer electrolyte was studied using a cyclic voltammetry. Figure 6 shows the cyclic voltammograms of the gel polymer electrolyte on the stainless steel electrodes measured between -0.5 and 5.0 V vs. Li/Li⁺. No peak was observed up to 4.5 V except at potential range of -0.5~0.5 V. There is no problem in the electrochemical stability, because charging voltage for lithium ion battery

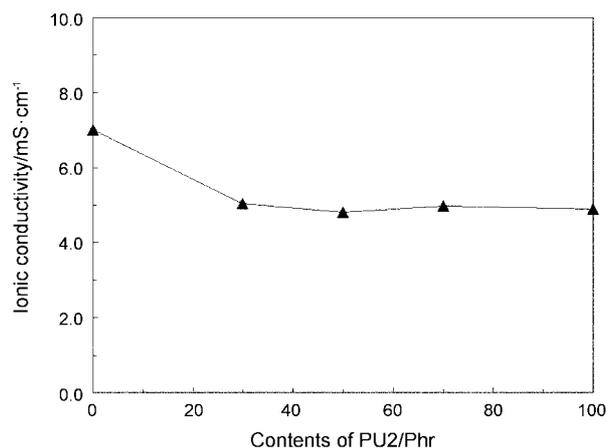


Fig. 5. Relationship between the ionic conductivity and the contents of PU2.

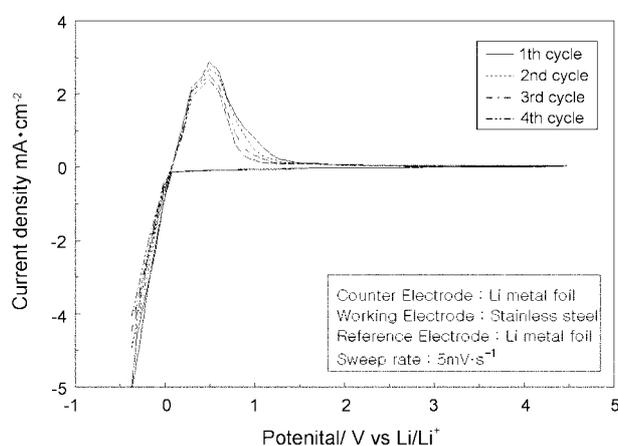


Fig. 6. Cyclic voltammogram of stainless steel/GPE/Li cell at 25°C

using lithium cobalt oxide is about 4.2 V. On scanning the electrode in a negative direction, a cathodic peak is observed at about -0.45 V, which corresponds to the plating of lithium on to the STS electrode. On the reverse scan, stripping of lithium is observed at about 0.37 V. The voltammograms ascribed to lithium deposition/dissolution are highly reversible, because the peak currents remain fairly constant with repeated cycling.

Figure 7 shows the AC impedance spectra of the $\text{LiCoO}_2/\text{GPE}/\text{graphite}$ cell. The impedance spectrum of the cell was obtained after filling of the precursor and after 1st cycling. Only one semicircle was observed at higher frequency in the cell that was not cycled. The intercept on the real axis is related to the bulk resistance (R_b) of the gel polymer electrolyte. The ionic conductivity at 20°C was calculated to be $5.9 \times 10^{-3} \text{ Scm}^{-1}$ from the electrolyte resistance with thickness and surface area of the gel polymer electrolyte. 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 resis-

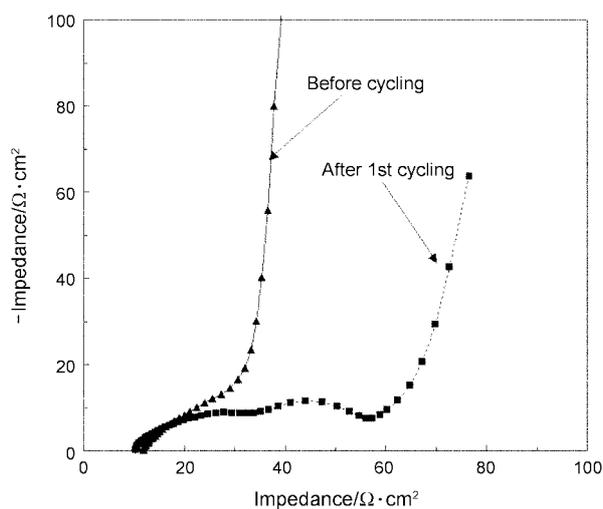


Fig. 7. AC impedance spectra of $\text{LiCoO}_2/\text{GPE}/\text{graphite}$ cell at 20°C.

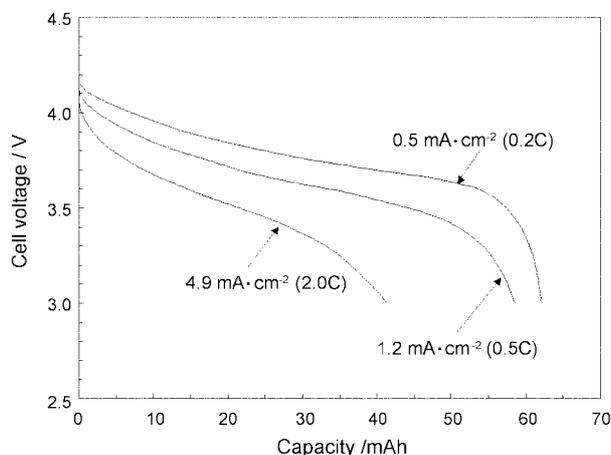


Fig. 8. Typical discharge curves for $\text{LiCoO}_2/\text{GPE}/\text{MCF}$ cell at various current densities at 20°C.

tance (R_b) of the gel polymer electrolyte. The semicircle was assumed to be associated with a parallel combination of interfacial resistance (R_{int} electrode/electrolyte interface) and the constant-phase element of the multipassivation films on both electrode surfaces¹²). The diameter of the semicircle is related to the interfacial resistance (R_{int}) between the electrode and the gel polymer electrolyte¹³). The semicircle at medium frequency is assigned to the parallel combination of the charge transfer resistance (R_{ct}) (as indicated by the diameter of the medium-frequency semicircle) 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 polymer cell using the gel polymer electrolyte, a $\text{LiCoO}_2/\text{GPE}/\text{graphite}$ cell was fabricated. The gel polymer electrolyte consisted of 5 vol% curable mixture and 95 vol% 1.0 M $\text{LiPF}_6/\text{EC-DEC}$. 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 mAcm^{-2}). 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^{14,15}). 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 at different current densities. Their discharge curves obtained at different current rates are given in Figure 8. The cell delivered a discharge capacity of ca. 63 mAh at current density of 0.5 mAcm^{-2} (0.2C rate). The discharge capacity slowly decreased with current rate, which was due to polarization. A useful capacity of ca. 59 mAh was obtained at 0.5C rate, which was 94% of the discharge capacity at 0.2C rate. The capacity of ca. 42 mAh was available even at 2.0C rate, which was 67% of the discharge capacity at 0.2C rate. The reduced capacity in the $\text{LiCoO}_2/\text{GPE}/\text{graphite}$ cell at high rate may be related to the lower diffusion rate of lithium ions in the gel polymer electrolyte¹⁶). Performance at high-rate discharge is, however, better than membrane-type gel polymer electrolyte.

The performances of the $\text{LiCoO}_2/\text{GPE}/\text{graphite}$ cell at various temperatures were also evaluated. The discharge curves obtained at current density of 1.2 mAcm^{-2} at various temperatures are given in Figure 9. The discharge capacity of the cell was ca. 63 mAh at 20°C. The discharge capacity slowly decreased with decreasing the temperature. A useful capacity of ca. 57 mAh was obtained at 0°C, which was 90% of the discharge capacity at 20°C. The capacity of ca. 43 mAh was available even at temperature of -10°C, which was 68% of the discharge capacity at 20°C. The cells, furthermore, will be able to deliver discharge capacity much more, when discharge cut-off voltage become 2.7 or 2.5 V. And, performances of the lithium-ion cells at low temperature, therefore, can be improved more using such solvents having low freezing point.

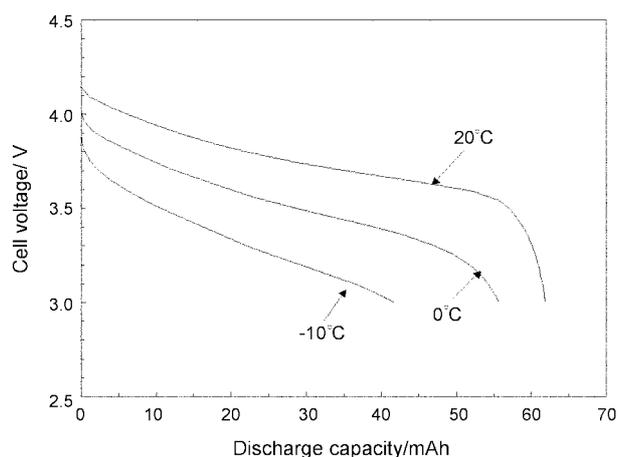


Fig. 9. Typical discharge curves for LiCoO₂/GPE/MCF cell at various temperatures.

4. Conclusions

Gel polymer electrolyte was obtained using liquid electrolyte, PUA oligomer, reactive modifier, and initiator. The ionic conductivity of the gel polymer electrolyte at 20°C was around $5.9 \times 10^{-3} \text{ Scm}^{-1}$. The gel polymer electrolyte had good electrochemical stability up to 4.5 V vs. Li/Li⁺. The capacity of the cell at 2.0C rate was 67% 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 was 68% of the discharge capacity at temperature of 20°C.

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