Electrochemical properties of poly(tetra ethylene glycol diacrylate)-based gel electrolytes for lithium-ion polymer batteries

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Abstract

The precursor for a gel polymer electrolyte (GPE) consisted of tetra (ethylene glycol) diacrylate monomer, benzoyl peroxide, and 1.1 M $LiPF_6$/EC:PC:EMC:DEC (30:20:30:20 wt.%). $LiCoO_2$/graphite cells were prepared and their electrochemical properties were evaluated at various current densities and temperatures. The viscosity of the precursor containing 5 vol.% tetra (ethylene glycol) diacrylate monomer was around 4.6 mPa s. The ionic conductivity of the gel polymer electrolyte at 20 °C was around 6.34×10^{-3} S cm^{-1}. The gel polymer electrolyte had good electrochemical stability up to 4.5 V versus Li/Li$^+$. The capacity of the cell at 2.0 C rate was 74% of the discharge capacity at 0.2 C rate. The capacity of the cell at temperature of −10 °C was 81% of the discharge capacity at temperature of 20 °C. Discharge capacity of the cell with gel polymer electrolyte was stable with charge–discharge cycling.
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Keywords: Gel polymer electrolyte; Cell; Tetra (ethylene glycol) diacrylate; Benzoyl peroxide; Lithium-ion polymer battery; Advanced lithium-ion battery

1. Introduction

An advanced lithium-ion battery (ALB) with a gel polymer electrolyte has been developing to obtain high performances of the cell, i.e. high power density and no leakage of electrolyte [1–4]. Many research results on the gel polymer electrolytes have been reported. Kono et al. [2] prepared gel polymer electrolyte consisting of poly(alkylene oxide) macromonomer, $LiClO_4$, and propylene carbonate (PC). Its ionic conductivity is around 10^{-3} S cm^{-1}. Also 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} S cm^{-1} at room temperature. Hybrid polymer electrolytes based on P(VdF-HFP) [8,9] copolymers exhibited high ionic conductivity and good mechanical performances. These polymers can be obtained from monomers with relatively low molecular weight and prepared by methods such as UV, thermal radiation, photopolymerization, and electron beam radiation polymerization. When an acrylate or a methacrylate monomer was used

in a gel polymer electrolyte, the precursor can be easily infiltrated into the electrodes and the separator because it has relatively low viscosity. The resulting polymer network has high mechanical properties.

In this study, a precursor for the GPE was prepared using tetra (ethylene glycol) diacrylate (TEGDA) as a monomer, benzoyl peroxide (BPO) as a thermal initiator, and 1.1 M $LiPF_6$/EC:PC:EMC:DEC (30:20:30:20 wt.%) as an electrolyte, respectively. The $LiCoO_2$/GPE/graphite cells are prepared and their electrochemical properties were evaluated at various current densities and temperatures.

2. Experimental

A precursor for the gel polymer electrolyte of lithium-ion cell consists of a liquid electrolyte, a monomer, and an initiator. Battery grade solution of 1.1 M $LiPF_6$/EC:PC:EMC:DEC (30:20:30:20 wt.%) was obtained from Cheil Industries. TEGDA (CH_2=CHCOO(CH_2CH_2O)$_4$OCCH=CH_2, Aldrich Chemical Co.) and BPO ($C_{14}H_{10}O_4$, Aldrich Chemical Co.) were used as a monomer and a thermal initiator, respectively. A precursor containing of 95 vol.% electrolyte and 5 vol.% monomer was polymerized by a thermal reaction at 80 °C for 40 min. All procedures for preparing the precursor were carried out in a dry-box filled with argon gas.

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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 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 with a cyclic voltammetry (CV). It 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 cm × 5 cm was swept in the potential range of −0.5 to 4.5 V versus Li/Li$^+$ at a sweep rate of 10 mV s^{-1}.

Lithium cobalt oxide electrodes were prepared by mixing 93 wt.% LiCoO$_2$ (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.% milled carbon fiber (MCF, 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 40 min in an oven.

The electrochemical properties of the obtained cell were evaluated using an ac impedance analyzer and a cycler. The 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-3100 K). 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

3.1. Properties of the gel polymer electrolytes

To some extent, mechanical strength is required at the interface between a gel polymer electrolyte and electrodes to obtain low internal resistance in lithium-ion polymer battery. Polymers having crosslinked structures can be used for good mechanical strength. In this case, network structure, after thermal polymerization, is formed to provide a good mechanical strength, but the precursor appears not to infiltrate easily a separator and electrodes due to its high-viscosity. Fig. 1 shows the relationship between the contents
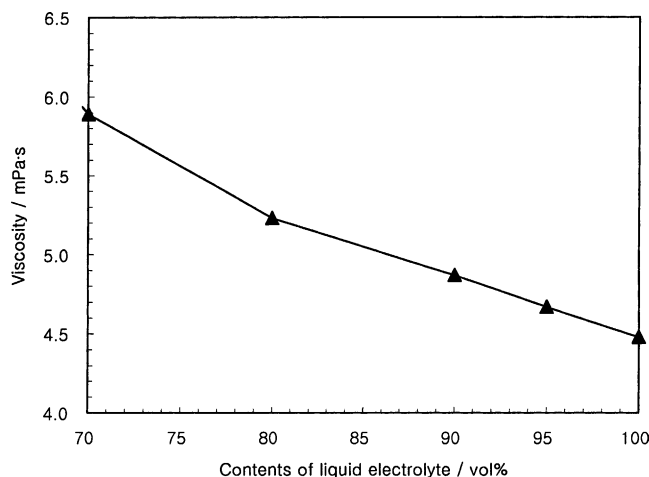

Fig. 1. Relationship between the viscosity and the contents of TEGDA monomer in the precursor.

of the electrolyte and the viscosity of the precursor. The viscosity of the precursor containing 30 vol.% monomer was ca. 5.9 mPa s, and it decreased with increasing the contents of the electrolyte. The viscosity of the precursor containing 5 vol.% monomer was around 4.7 mPa s. It is, therefore, thought that its value is enough practically for separator to be infiltrated fully.

One of the important factors in the gel polymer electrolyte is the ionic conductivity. It has been reported that the ionic conductivity [2–4] of gel polymer electrolyte is about 10^{-3} S cm^{-1}. The ionic conductivity of gel polymer electrolyte was measured using an ac impedance analyzer with a stainless steel blocking electrode. Fig. 2 shows the ac impedance spectra of the gel polymer electrolytes polymerized at temperature of 80 °C for 40 min. 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
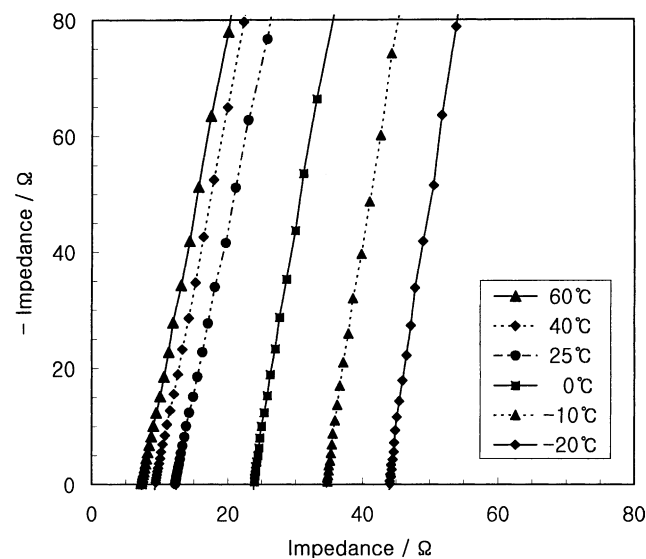

Fig. 2. The ac impedance spectra of SS/GPE/SS cells with gel polymer electrolyte.
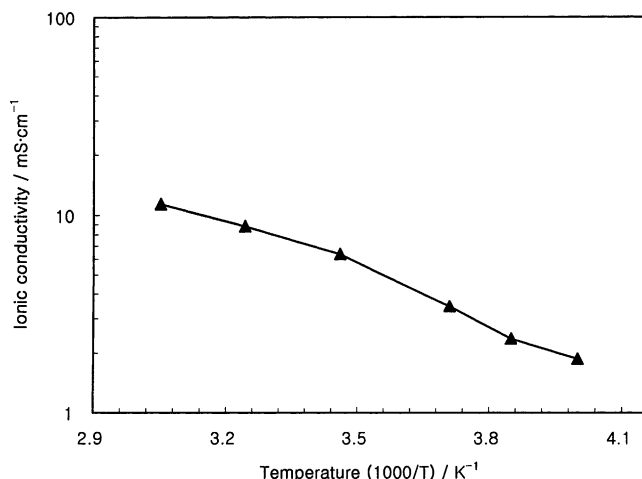
Fig. 3. Arrhenius plots of the ionic conductivity of the gel polymer electrolyte.

Fig. 5. The ac impedance spectra of LiCoO$_2$/GPE/graphite cell at 20 °C.

of the gel polymer electrolyte. The ionic conductivity at 20 °C was calculated to be 6.34×10^{-3} S cm^{-1} from the electrolyte resistance with thickness and surface area of the gel polymer electrolyte. Fig. 3 shows the ionic conductivity of the gel polymer electrolyte containing 5 vol.% monomer at various temperatures. The ionic conductivity of GPE at 20 °C was around 6.34×10^{-3} S cm^{-1}. And, it increased with increase in temperature. It is thought that the mobility of a lithium ion is governed with a liquid phase in the gel-type polymer electrolyte.

The electrochemical stability of the gel polymer electrolyte was studied using a cyclic voltammetry. Fig. 4 shows the cyclic voltammograms of the gel polymer electrolyte on the stainless steel electrodes measured between −0.5 and 4.5 V versus Li/Li$^+$. No peak was observed up to 4.5 V except at potential range of −0.5 to 0.5 V. There is no problem in the electrochemical stability, because charging voltage for lithium-ion battery using lithium cobalt oxide is about 4.2 V. On scanning the electrode in a negative direction, a cathodic
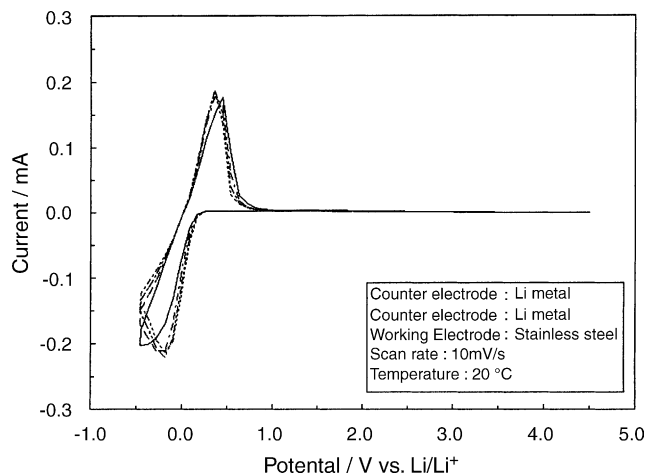
peak is observed at about −0.45 V, which corresponds to the plating of lithium on to the stainless steel electrode. On the reverse scan, stripping of lithium is observed at about 0.37 V. The voltammograms ascribed to lithium deposition/dissolution are highly reversible, because the peak currents remain fairly constant with repeated cycling.

3.2. Performances of the cells

Fig. 5 shows the ac impedance spectra of the LiCoO$_2$/GPE/graphite cell. The impedance spectrum of the cell was measured at potential of 3.6 V and obtained after filling of the precursor, first cycling, and zeroth 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 gel polymer electrolyte. After first cycling, the impedance spectroscopy of the cell exhibited a high-frequency depressed semicircle and also a medium-frequency semicircle. The Z' intercept of the semicircle on the real axis at higher frequency is related to the bulk resistance of the gel polymer electrolyte [10,11]. 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, a narrow Warburg region followed by a steep sloping line. The Warburg region is assigned to solid-state diffusion of Li ions into the bulk cathode/anode materials, while the slanted line reflects capacitive behavior at the very low frequencies. The diameter of two depressed semicircles increased with cycling. It meant that the interfacial resistance and the charge transfer resistance increased with charge–discharge cycling.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using the gel polymer electrolyte, a LiCoO$_2$/GPE/graphite cell was fabricated. 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 0.2 C rate (0.5 mA cm^{-2}). An irreversible capacity was observed in the

Fig. 4. Cyclic voltammograms of the gel polymer electrolyte on SS working electrode at potential scan rate of 10 mV s^{-1}.
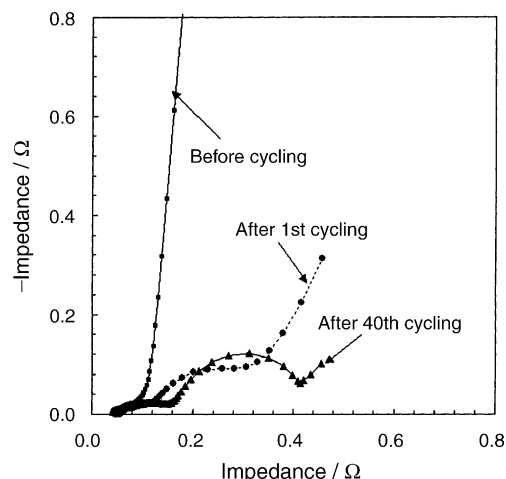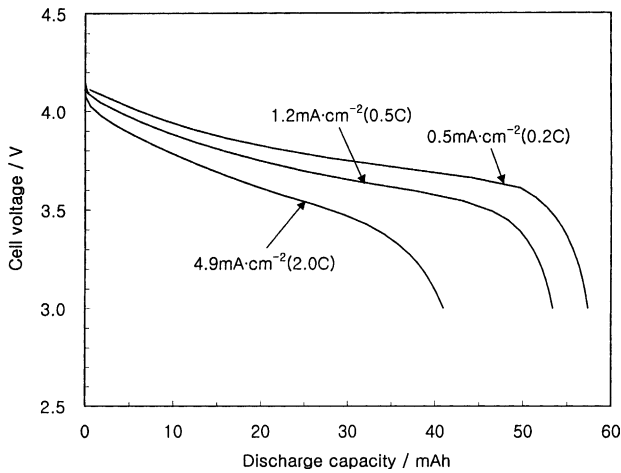
Fig. 6. Typical discharge curves for LiCoO₂/GPE/graphite cells at various current densities at 20 °C.

Fig. 8. Capacity change upon cycling at current density of 1.2 mA cm^{-2} (0.5 C rate) for LiCoO₂/GPE/graphite cell at 20 °C.

first 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 [12,13]. 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 rate capability of the LiCoO₂/GPE/graphite cell was evaluated. The discharge curves obtained at different current rates were given in Fig. 6. The cell delivered a discharge capacity of ca. 57 mAh at current density of 0.5 mA cm^{-2} (0.2 C rate). The discharge capacity slowly decreased with current rate, which was due to polarization. A useful capacity of ca. 42 mAh was obtained at 2.0 C rate, which was 74% of the discharge capacity at 0.2 C rate. The reduced capacity in the LiCoO₂/GPE/graphite cell at high rate may be primarily related to the lower diffusion rate of lithium ions in the gel polymer electrolyte [14] and to
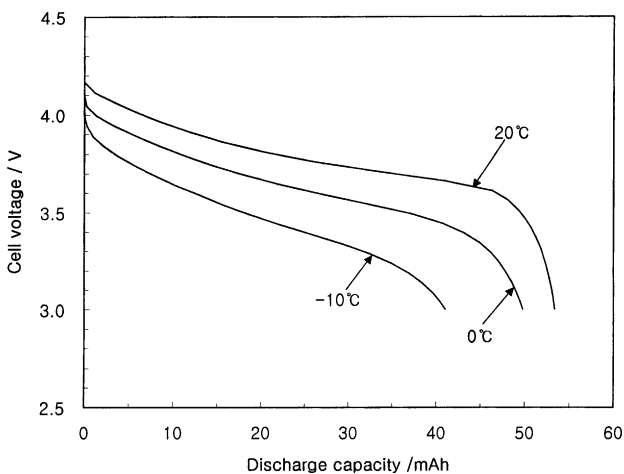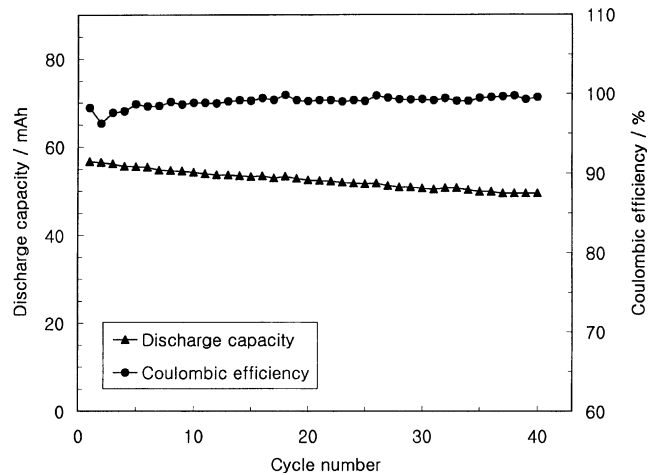
the lower wetting. Further research is being conducted to improve the high-rate performance of the lithium-ion polymer batteries.

The performances of the LiCoO₂/GPE/graphite cell at various temperatures were also evaluated. The discharge curves obtained at current density of 1.2 mA cm^{-2} at various temperatures were given in Fig. 7. The discharge capacity of the cell was ca. 57 mAh at 20 °C. The capacity of ca. 42 mAh was available even at temperature of −10 °C, which was 81% 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). Performances of the lithium-ion cells at low temperature, therefore, can be improved using such solvents having low freezing point.

Fig. 8 shows the discharge capacity with cycling for LiCoO₂/GPE/graphite cell at current density of 1.2 mA cm^{-2}. Discharge capacity of the cell with gel polymer electrolyte was stable with charge–discharge cycling. It is also expected that crossliking polymer after curing decrease the interface resistance between the electrode and the gel polymer electrolyte.

4. Conclusions

The viscosity of the precursor containing 5 vol.% tetra-(ethylene glycol) diacrylate monomer was around 4.6 mPa s. The ionic conductivity of the gel polymer electrolyte at 20 °C was around 6.34×10^{-3} S cm^{-1}. The gel polymer electrolyte had good electrochemical stability up to 4.5 V versus Li/Li$^+$.

The capacity of the LiCoO₂/GPE/graphite cell at 2.0 C rate was 74% of the discharge capacity at 0.2 C rate. The discharge capacity slowly decreased with decreasing the temperature. The capacity of the cell at temperature of −10 °C was 81% of the discharge capacity at temperature

Fig. 7. Typical discharge curves for LiCoO₂/GPE/graphite cell at current density of 1.2 mA cm^{-2} at various temperatures.

of 20 °C. Discharge capacity of the cell with gel polymer electrolyte was stable with charge–discharge cycling.

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