Preparation and electrochemical performance of gel polymer electrolytes using tri(ethylene glycol) dimethacrylate

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Abstract

A gel polymer electrolyte (GPE) is prepared from tri(ethylene glycol) dimethacrylate monomer, benzoyl peroxide, and 1.0 M $LiPF_6$/ethylene carbonate:diethyl carbonate (1:1 vol.%). The $LiCoO_2$|graphite cells are assembled and their electrochemical properties are evaluated at various current densities and temperatures. The viscosity of the precursor containing 5 vol.% tri(ethylene glycol) dimethacrylate monomer is around 4.6 mPa s. The ionic conductivity of the gel polymer electrolyte at 20 °C is around 5.9×10^{-3} S cm^{-1}. The gel polymer electrolyte has good electrochemical stability up to 4.5 V versus Li/Li$^+$. The capacity of the cell at the 1.0 C rate is 89% of the discharge capacity at the 0.2 C rate. The capacity of the cell at temperature of -10 °C is 81% of the discharge capacity at 20 °C. The discharge capacity of the cell with gel polymer electrolyte is stable with charge–discharge cycling.
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1. Introduction

The lithium-ion battery has a good high-rate and a low-temperature performance, but has relatively low safety due to the possibility of leakage of liquid electrolyte. A probability of leakage from a lithium-ion polymer battery is very low because of the use of a solid or gel type of electrolyte, but the high-rate and the low-temperature performance decrease because the ionic conductivity of such electrolytes is low. Therefore, new types of advanced lithium-ion battery with gel polymer electrolytes are underdevelopment to provide high power density and take advantage of the leak-free characteristics [1–4].

Many studies on membrane-type gel polymer electrolytes have been reported. Kono et al. [2] prepared a gel polymer electrolyte which consisted of a poly(alkylene oxide) macromonomer, $LiClO_4$, and propylene carbonate (PC). The ionic conductivity at 30 and 80 °C was $\sim 10^{-5}$ and 10^{-4} S cm^{-1}, respectively. Many kinds of polymeric hosts, such as poly-acrylonitrile (PAN) [3], poly(vinylidene fluoride) (PVdF) [4], poly(ethylene oxide) (PEO) [5], poly(methylmethacrylate) (PMMA) [6] and poly(vinyl chloride) (PVC) [7] have been proposed as frameworks for gel polymer electrolytes.

Their ionic conductivities were reported to be between 10^{-4} and 10^{-3} S cm^{-1} at room temperature. Hybrid polymer electrolytes based on P(VdF-HFP) copolymers [8,9] exhibited high ionic conductivity and good mechanical performance. Cross-linked polymers were found to reduce the solubility of the polymers in 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 are prepared by methods such as UV, thermal radiation, photo-polymerization, and electron beam radiation polymerization.

Recently, a new-type gel polymer electrolyte has been suggested; a precursor consisting of a curable monomer/macromer and a liquid electrolyte was wetted into a cell and then cured to form a polymer network. When an acrylate or a methacrylate monomer is used in a gel polymer electrolyte, the precursor can be easily wetted into the electrodes and the separator because it has relatively low viscosity. The resulting polymer network has high mechanical properties.

In this study, the precursor for the GPE is prepared using tri(ethylene glycol) dimethacrylate (TEGDMA) as a monomer, benzoyl peroxide (BPO) as a thermal initiator, and 1.0 M $LiPF_6$/EC:DEC (1:1 vol.%) as an electrolyte. $LiCoO_2$|GPE|graphite cells are prepared and their electrochemical properties are evaluated at various current densities and temperatures.

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2. Experimental

2.1. Preparation of GPE

The precursor for a gel polymer electrolyte for use in a lithium-ion cell consists of a liquid electrolyte, a monomer, and an initiator. Battery grade solution of 1.0 M $LiPF_6$/ ethylene carbonate:diethyl carbonate (1:1 vol.%) was obtained from Cheil Industries. TEGDMA [$CH_2=C(CH_3)COO(CH_2CH_2O)_3COC(CH_3)=CH_2$, Aldrich] and BPO [$C_{14}H_{10}O_4$, Aldrich] were used as a monomer and a thermal initiator, respectively. A precursor containing 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.

2.2. Characterization of GPE

The ionic conductivity, viscosity and electrochemical stability window of the gel polymer electrolyte were evaluated. The viscosity was measured by means of a viscometer DV-II+ (Brookfiel 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 between -20 and 60 °C. A potential difference of 5 mV was applied to the sample for frequencies that ranged from 100 Hz to 2 MHz.

The electrochemical stability of GPE was studied with the technique of cyclic voltammetry (CV). This was carried out using a potentiostat (model 273, EG&G Co.) and a three-electrode system. Stainless-steel was used as the working electrode, and lithium was used for the counter and the reference electrodes. A stainless-steel electrode with an area of 3 cm × 5 cm was scanned in the potential range -0.5 to 4.3 V versus Li/Li$^+$ at a sweep rate of 5 mV s^{-1}.

2.3. Preparation of the cell

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 then coating the mixture on an aluminum foil. The graphite electrodes were prepared with 95 wt.% milled carbon fiber (MCF) and 5 wt.% PVdF. Celgard 2500 was used as a separator. The electrodes were stacked and inserted into an aluminum laminated 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 80 °C for 40 min in an oven. The fabrication procedure of the cell is described in Fig. 1.

2.4. Evaluation of cell performance

The electrochemical properties of the assembled cells were evaluated by means of ac impedence spectroscopy.
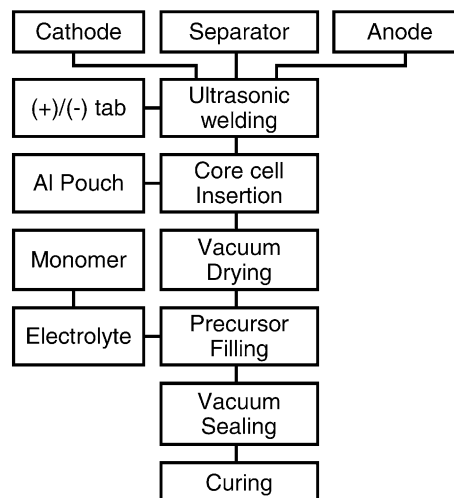

Fig. 1. Fabrication procedure of lithium-ion polymer battery with curing type gel polymer electrolyte.

The measurements were performed with a Zahner Elektrik IM6 impedance analyzer over a frequency range of 700 mHz to 2 MHz. The charge and discharge cycling tests were conducted galvanostatically with a Toyo battery test system (TOSCAT-3100 K). The discharge curves were obtained at different current rates to obtain the rate capabilities of the cells and also at various temperatures.

3. Results and discussion

3.1. Properties of the gel polymer electrolyte

To some extent, mechanical strength is required at the interface between a gel polymer electrolyte and electrodes to obtain intimate contact in lithium-ion polymer battery. Polytri(ethylene glycol) dimethacrylate has a cross-linked structure and, therefore, good mechanical strength. On the other hand, the precursor of liquid electrolyte and monomer appears not to wet the separator and electrodes due to its high viscosity. The viscosity can be controlled to some extent, because it depends on the contents of the electrolyte, the type of electrolyte, the concentration of salt, the temperature, etc. The relationship between the contents of the electrolyte and the viscosity of the precursor is shown in Fig. 2. The viscosity of the precursor containing 30 vol.% monomer is 6.2 mPa s and decreases with increasing amount of the contents of the electrolyte. The electrodes and separator have to be wetted sufficiently with electrolyte to provide the cell with good performance. The viscosity of the precursor containing 5% monomer is around 4.6 mPa s. It is thought that this value is sufficient for the separator to be wetted fully.

One of the important factors in the gel polymer electrolyte is ionic conductivity. It has been reported [2–4] that the ionic conductivity of the membrane-type gel polymer electrolyte is about 10^{-4} S cm^{-1}. The ac impedance spectra of the gel
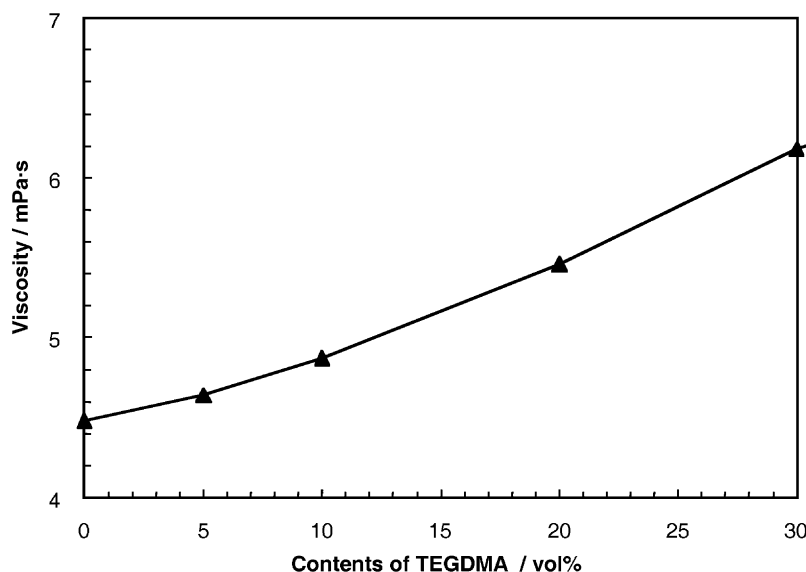
Fig. 2. Relationship between viscosity and contents of TEGDMA monomer in precursor.

polymer electrolytes polymerized at temperature of 80 °C for 40 min are presented in Fig. 3. There is only a spike, which represents a resistor in series with a capacitor. The intercept on the real axis gives the resistance of the gel polymer electrolyte. The ionic conductivity at 25 °C is calculated to be 5.9×10^{-3} S cm^{-1} from the electrolyte resistance with thickness and surface area of the gel polymer electrolyte.

The relationship between the contents of the liquid electrolyte and the ionic conductivity of the gel polymer electrolyte is given in Fig. 4. The ionic conductivity of a GPE containing 60 vol.% electrolyte is 5.6×10^{-4} S cm^{-1}, and it increases with increasing the contents of the liquid electrolyte. It is, therefore, thought that a high conductivity of the

gel polymer electrolyte is due mainly to the liquid electrolyte.

The electrolyte of the cell should also allow low-temperature performance, because the commercial batteries are sometimes used in these conditions. It is especially pointed out that performance of lithium-ion polymer batteries at low temperature and high current is low compared with lithium-ion batteries having the liquid electrolyte. The ionic conductivity of a gel polymer electrolyte containing 5 vol.% monomer obtained at various temperatures is shown in Fig. 5. The ionic conductivity of GPE at 20 °C is around 5.9×10^{-3} S cm^{-1} and it is quite high, i.e. 1.4×10^{-3} S cm^{-1}, at temperature of -20 °C. This behavior can be understood in terms of the free-volume model [10]. 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 ions and the 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.

The electrochemical stability of the gel polymer electrolyte was evaluated by means of cyclic voltammetry. Cyclic voltammograms for the gel polymer electrolyte on the stainless-steel electrodes measured between -0.5 and 5.0 V versus Li/Li$^+$ are presented in Fig. 6. No peaks were observed up to 4.5 V except in potential range -0.5 to 0.5 V. There is no problem with 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 plating of lithium on to
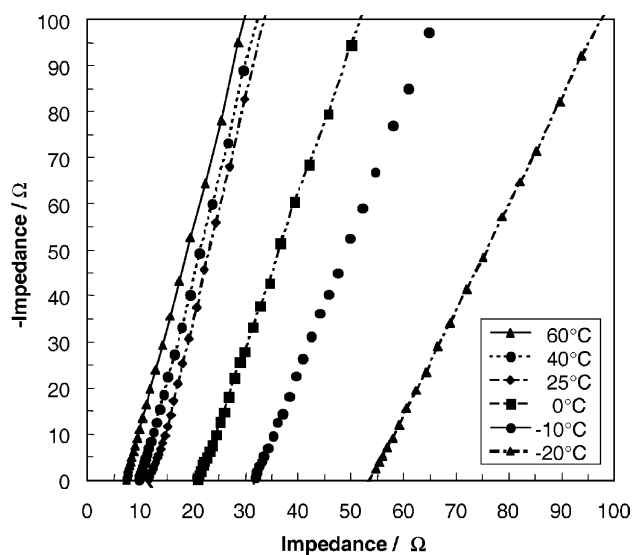

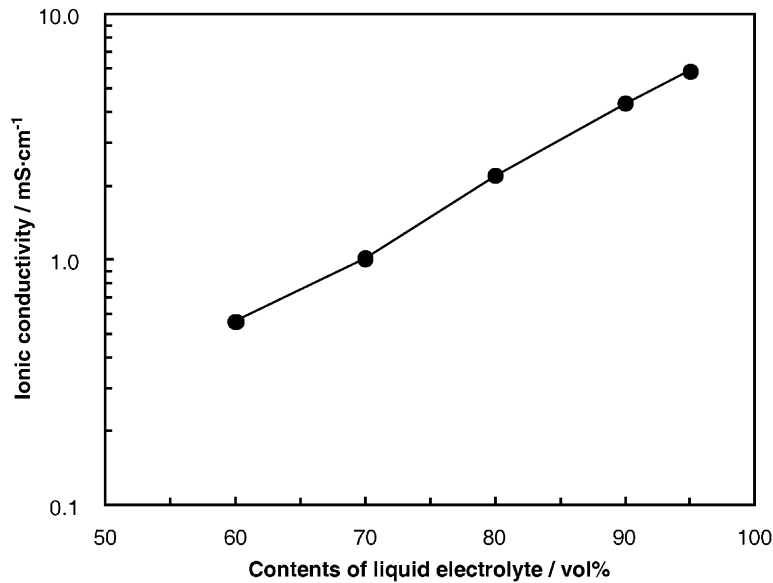Fig. 3. The ac impedance spectra of SS/GPE/SS cell with gel polymer electrolyte.

Fig. 4. Isothermal ionic conductivity at 20 °C for gel polymer electrolyte as function of contents of liquid electrolyte.
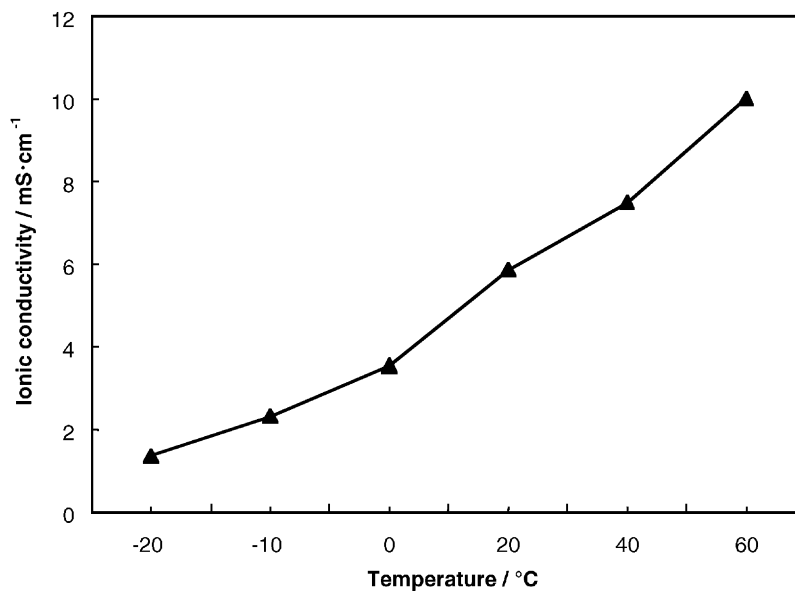

Fig. 5. Ionic conductivity of gel polymer electrolyte at various temperatures.

the Ni 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. Cell performance

Fig. 7 shows the ac impedance spectra for the LiCoO$_2$|G-PE|graphite cell. The impedance spectrum of the cell was obtained after filling of the precursor and after the first cycle. Only one semicircle is observed at higher frequency in the cell that was not cycled. This is related to the bulk resistance (R_b) of the gel polymer electrolyte. With further cycling, the impedance spectroscopy of the cell exhibits two depressed semicircles. The Z' intercept of the semicircle on the real axis at higher frequency is related to the bulk resistance (R_b) of the gel polymer electrolyte. The semicircle is 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 surfaces [11]. The diameter of the semicircle is related to the interfacial resistance (R_{int}) between the electrode and the gel polymer electrolyte [12].The semicircle at
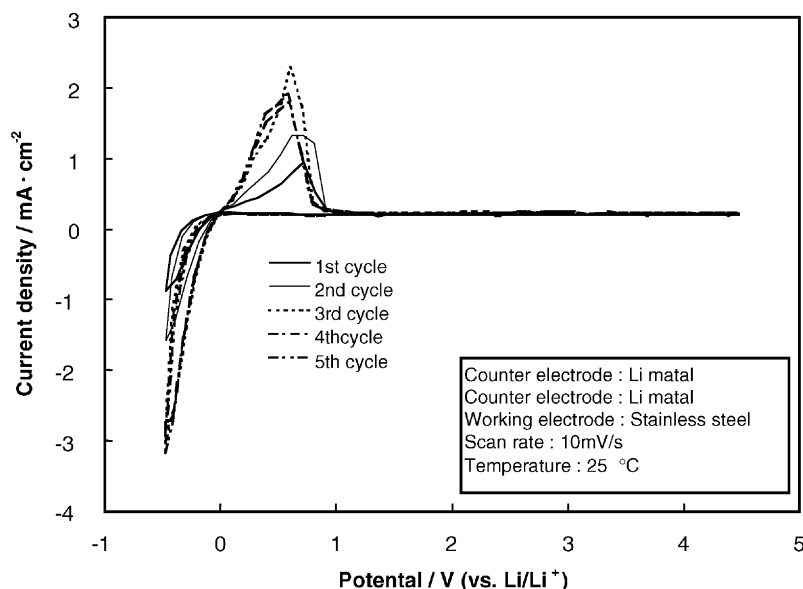
Fig. 6. Cyclic voltammograms of gel polymer electrolyte on stainless-steel working electrode at potential scan rate of 10 mV s^{-1}.

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 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 LiCoO$_2$|GPE|graphite cell was fabricated. The gel polymer electrolyte consisted of 5 vol.% monomer and 95 vol.% 1.0 M LiPF$_6$/EC:DEC. The assembled cell was pre-conditioned with a cut-off voltage of 4.2 V as the upper limit and 3.0 V as the lower limit at the 0.2 C rate (1.5 mA cm^{-2}). An

irreversible capacity was observed on the first cycle and this is caused by the formation of passivation film on the surface of the carbon electrode due to decomposition of electrolyte, as reported by other authors [13,14]. The development of a passivation film on the surface during 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 pre-conditioning cycle, the cell was charged at a current density of 1.5 mA cm^{-2} up to cell voltage of 4.2 V. This was followed by a constant-voltage charge with a decline in current until the final value reached 20% of the charging current. The cell was then discharged to a cut-off voltage of 3.0 V at the same current density. Charge and discharge curves of the cell at the current density of 1.5 mA cm^{-2} are given in Fig. 8. The plot shows a well-defined charge–discharge voltage profile, which indicates a reversible cycling process. The small voltage drop, obtained from the cycle test, confirms the low internal resistance of the lithium-ion polymer cell. The coulombic efficiency in the pre-conditioning cycle is calculated to be ~100%.

The rate capability of the LiCoO$_2$|GPE|graphite cell was evaluated. The discharge curves obtained at different current rates were given in Fig. 9. The cell delivered a discharge capacity of 675 mAh at current density of 0.6 mA cm^{-2} (0.2 C rate). The discharge capacity slowly decreases with current rate, which is due to polarization. A useful capacity of 660 mAh is obtained at the 0.5 C rate, which is 98% of the discharge capacity at the 0.2 C rate. The capacity of 600 mAh is available even at the 1.0 C rate, which is 89% of the discharge capacity at the 0.2 C rate. The reduced capacity in the cell at high rate may be primarily related and
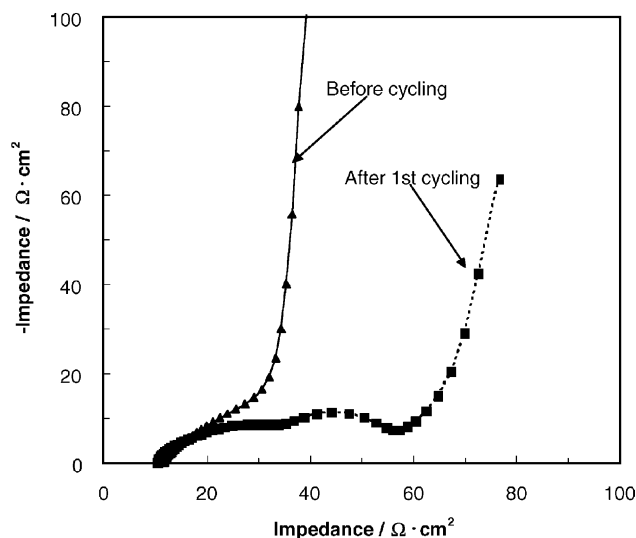

Fig. 7. The ac impedance spectra of LiCoO$_2$|GPE|graphite cell at 25 °C.
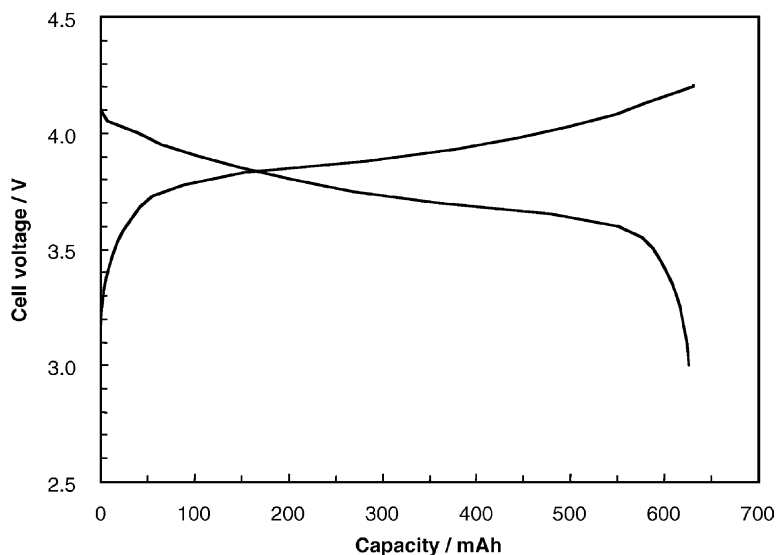
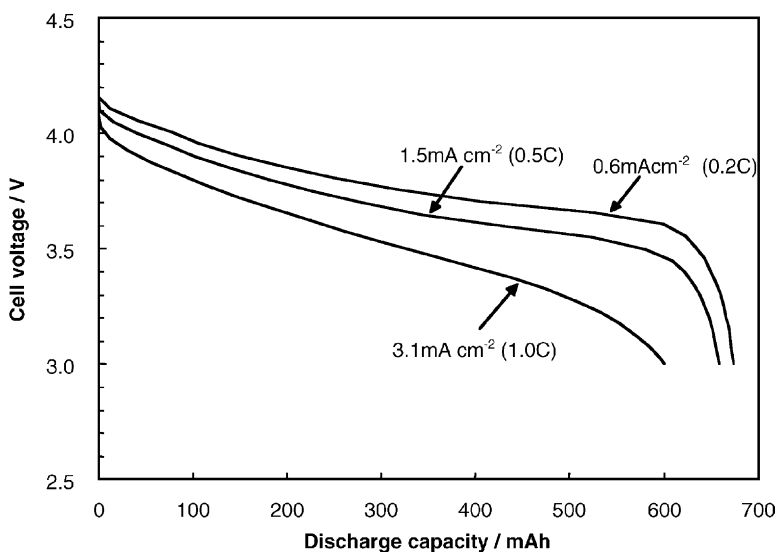Fig. 8. Charge and discharge curves of $LiCoO_2$|GPF|graphite cell at current density of 0.6 mA cm^{-2}.

Fig. 9. Typical discharge curves for $LiCoO_2$|GPE|graphite cell at various current densities at 25 °C.

to the lower wetting and to the lower diffusion rate of lithium ions in the gel polymer electrolyte [15]. Further research is being conducted to improve the high-rate performance of the lithium-ion polymer batteries.

The performance of the $LiCoO_2$|GPE|graphite cell at various temperatures were also evaluated. Discharge curves obtained at a current density of 1.5 mA cm^{-2} at various temperatures are given in Fig. 10. The discharge capacity of the cell is 643 mAh at 20 °C. The discharge capacity slowly decreases with decreasing temperature. A useful capacity of 630 mAh is obtained at 0 °C which is 98% of the discharge capacity at 20 °C. A capacity of 522 mAh is even available at −10 °C, i.e. 81% of the discharge capacity at 20 °C. Recently, ethyl methyl carbonate (EMC) has been found to

be a useful co-solvent in binary solutions with propylene carbonate and ethylene carbonate because of its low freezing point (−55 °C). The performance of lithium-ion cells at low temperature can therefore be improved by using solvents with such a low freezing point.

Fig. 11 shows the change in discharge capacity with cycling for a $LiCoO_2$|GPE|graphite cell at a current density of 1.5 mA cm^{-2}. The discharge capacity of the cell with gel polymer electrolyte remains stable with cycling. Kono et al. [16] have reported that the improved cycleability may be related to the fact that gel polymer electrolytes restrain the dendritic deposition of Li. It is also expected that a cross-linked polymer after curing decreases the interface resistance between the electrode and the gel polymer electrolyte.
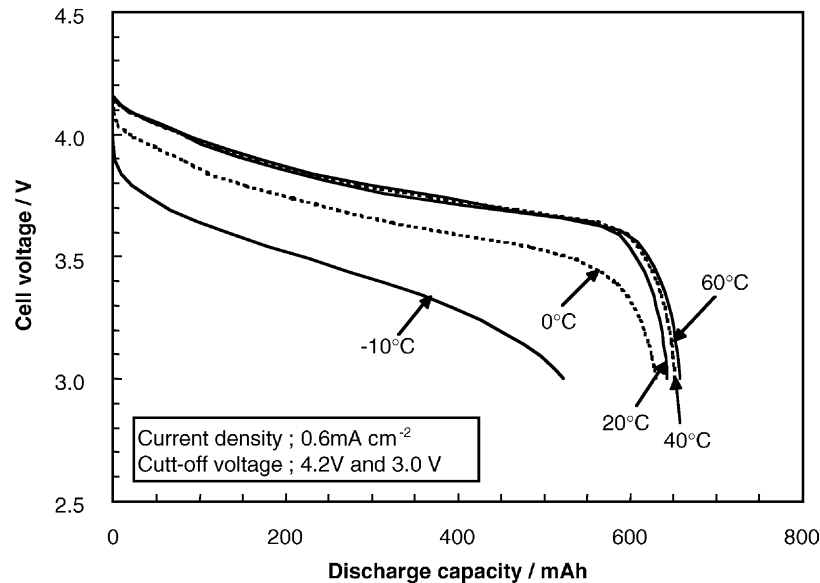
Fig. 10. Typical discharge curves for LiCoO$_2$|GPE|graphite cell at current density of 1.5 mA cm^{-2} at various temperatures.
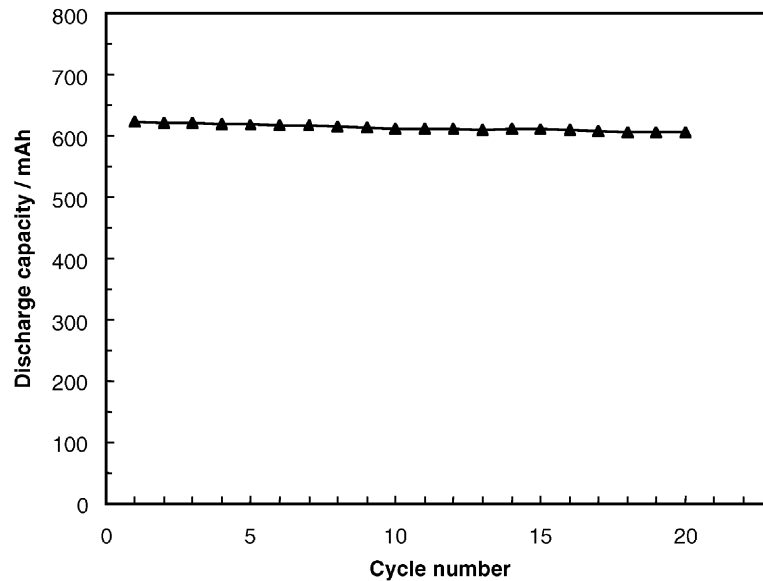

Fig. 11. Discharge capacity upon cycling at current density of 1.5 mA cm^{-2} for LiCoO$_2$|GPE|graphite cell at 20 °C.

4. Conclusions

The viscosity of the precursor containing 5 vol.% tri(ethylene glycol) dimethacrylate monomer is around 4.6 mPa s, which is sufficient for separator and electrodes to be wetted practically. The ionic conductivity of the gel polymer electrolyte at 20 °C is around 5.9×10^{-3} S cm^{-1}. The gel polymer electrolyte had good electrochemical stability up to 4.5 V versus Li/Li$^+$.

Charge and discharge curves of LiCoO$_2$|GPE|graphite cells exhibit well-defined voltage profiles, which indicate a reversible cycling process. The cells also have good rate capability. The capacity at the 1.0 C rate is 89% of the discharge capacity at the 0.2 C rate. The discharge capacity slowly decreased with decreasing the temperature. The capacity of the cell at −10 °C is 81% of the discharge capacity at 20 °C. The discharge capacity of the cell with gel polymer electrolyte is stable with charge–discharge cycling.

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