Fabrication and Properties of Crosslinked Poly(propylene carbonate maleate) Gel Polymer Electrolyte for Lithium-Ion Battery

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ABSTRACT: The poly(propylene carbonate maleate) (PPCMA) was synthesized by the terpolymerization of carbon dioxide, propylene oxide, and maleic anhydride. The PPCMA polymer can be readily crosslinked using dicumyl peroxide (DCP) as crosslinking agent and then actived by absorbing liquid electrolyte to fabricate a novel PPCMA gel polymer electrolyte for lithium-ion battery. The thermal performance, electrolyte uptake, swelling ratio, ionic conductivity, and lithium ion transference number of the crosslinked PPCMA were then investigated. The results show that the T_g and the thermal stability increase, but the absorbing and swelling rates decrease with increasing DCP amount. The ionic conductivity of the PPCMA gel polymer electrolyte firstly increases and then decreases with increasing DCP ratio. The ionic conductivity of the PPCMA gel polymer electrolyte with 1.2 wt % of DCP reaches the maximum value of 8.43×10^{-3} S cm^{-1} at room temperature and 1.42×10^{-2} S cm^{-1} at 50°C. The lithium ion transference number of PPCMA gel polymer electrolyte is 0.42. The charge/discharge tests of the Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell were evaluated at a current rate of 0.1C and in voltage range of 2.8–4.2 V at room temperature. The results show that the initial discharge capacity of Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell is 115.3 mAh g^{-1}. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2078–2083, 2010

Key words: gel polymer electrolyte; lithium-ion battery; electrochemical properties; poly(propylene carbonate)

INTRODUCTION

The development of lithium batteries has gained an unprecedented significance in the last two decades as the demand for portable telecommunication devices, computers, and eventually hybrid electric vehicles has been an ever-increasing one.[1,2] The advantages such as no leakage of polymer electrolyte, higher energy density, flexible geometry, and improved safety hazards have drawn the attention of many researchers on the development of lithium polymer batteries.[3,4] The development of polymer electrolytes has gone through three stages namely[5–7]: (i) dry solid polymer electrolyte, (ii) gel polymer electrolytes, and (iii) composite polymer electrolytes. Among these various types of polymer electrolytes, gel polymer electrolytes are one of the most promising ways to improve the ionic conductivity and electrochemical properties of polymer electrolyte in lithium-ion batteries.[8–11] Due to the wide variety of polymers available in the market, a great number of GPEs was described in the literature, generally based on polymethylmethacrilate (PMMA), polyethylene oxide (PEO), polyvinilidenefluoride (PVdF), poly(vinylidene fluoridehexaflour-propylene) (PVDF-HFP).[12–15]

However, the properties of currently used polymer electrolytes are still not satisfied enough to meet the applicable requirement. Because, the gain in ionic conductivity is accompanied by a loss of mechanical strength adversely and also leads to poor compatibility with the lithium electrodes and this high reactivity of lithium metal results in serious problems in terms of battery cyclability and eventually safety.[16–18] To retain the mechanical properties of polymer gel electrolytes, the gel films have to be hardened either by chemical or by physical curing (high energy radiation) and these results in high processing costs. Intensive efforts have been devoted to modify the structure and properties of polymer electrolyte.[19–23]

Poly(propylene carbonate) (PPC) is a cheap and biodegradable polymer. In our laboratory, we

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selected MA as the third monomer to be introduced into the copolymerization of CO_2 and PO to produce poly(propylene carbonate maleate) (PPCMA), and the introduction of small amount of crosslinkable moiety provides a very effective way to improve the thermal stability and to extend its application area.[24,25] Here in this study, a novel crosslinked PPCMA-based gel polymer electrolyte was prepared and its thermal stability, ionic conductivity, lithium ion transference number, and charge/discharge performance were also investigated. The PPCMA gel polymer electrolyte has superior ionic conductivity even at room temperature because of the encapsulation of a higher amount of organic liquid electrolyte in the polymer host.

EXPERIMENT

Preparation of PPCMA gel polymer electrolyte

The PPCMA polymer matrix was synthesized by the terpolymerization of carbon dioxide (CO_2), propylene oxide (PO), and maleic anhydride (MA), as reported in a previous work.[25] The molar ratio of PO/MA is 15 : 1 in this experiment. The PPCMA polymer matrix was then crosslinked by thermal pressing process in semiautomatic molding pressing machine under pressure of 20 MPa and at 170°C for 10 min. The ratios of DCP crosslinking agent and PPCMA (DCP: PPCMA) were 0.5, 0.8, 1.0, 1.2, 1.5, and 2.0 wt %, respectively. Finally, the crosslinked PPCMA dry membranes were actived by soaking in 1.0*M* $LiClO_4$ electrolyte solution of EC and DMC (1 : 1 v/v ratio) to prepare PPCMA gel polymer electrolyte.

Synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material was synthesized by the conventional high temperature solid-state reaction. The experiment was performed by utilizing electrolyzed MnO_2 (EMD), NiO, Co_3O_4, and Li_2CO_3 as the raw materials. A stoichiometric mixture of the raw materials was mixed by ball-milling for 12 h, using zirconia milling media, in alcohol, followed by drying. Then the mixed powder was heated at 480°C for 6 h and finally calcined at 950°C for 16 h in air.

Characterization

Differential scanning calorimetry (DSC) examination of PPCMA polymer electrolyte membranes was carried out on a NETZSCH DSC-200PC instrument at a heating rate of 20°C min^{-1} from −50 to 100°C in the heating cycle and from 100 to −50°C in the cooling cycle under nitrogen atmosphere. The second scan was immediately initiated after the sample was cooled to −50°C.

The thermal stability of PPCMA polymer electrolyte membranes ranging from 70 to 600°C was determined with a PerkinElmer TGA/DTA 6300 (thermogravimetric analyzer (TGA)/differential thermal analysis (DTA)) under nitrogen atmosphere. The heating rate was 10°C min^{-1}.

The uptake electrolyte and swelling ratio of PPCMA polymer electrolyte was determined as follows: The membrane was dried under vacuum at 60°C for 24 h. The weighed membrane was immersed in electrolyte at room temperature for 24 h. Wet membrane was weighed quickly upon wiping up its surface water with tissue paper. The electrolyte uptake of membrane was calculated according to the following eq. (1):

$$\text{water uptake } (\%) = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\% \quad (1)$$

where, W_{wet} and W_{dry} are wet and dry the weights of the membrane, respectively.

The dimensional stability of the membrane was characterized by swelling ratio. The swelling ratio was assessed from the following eq. (2):

$$\text{swelling ratio} = (L_w - L_d)/L_d \times 100\% \quad (2)$$

where, L_w and L_d are the lengths of the cross of the wet membrane and dry membrane (test radium 1.0 cm), respectively.

Electrochemical properties

The ionic conductivity of the PPCMA gel polymer electrolyte was determined by electrochemical impedance spectroscopy (EIS) method and calculated using the following eq. (3):

$$\sigma = \frac{d}{R_b S} \quad (3)$$

Where σ is the ionic conductivity, d is the thickness (cm) of the polymer electrolyte, the resistance R_b (Ω) can be estimated from the impedance spectra at the point where the line intercepted the real part in the high frequency region, and S is the area of the polished gold electrode (cm^2).

The impedance tests were performed with a Solartron 1255B frequency response analyzer functioning with the an oscillating voltage of 5 mV from 1 MHz to 1 Hz frequency range at various temperatures ranging from 298 to 353 K. The PPCMA gel polymer electrolyte membranes were sandwiched between two polished gold disks with a diameter of 1.0 cm that acted as ion blocking electrodes in a specially designed cell setup for conductivity studies. The cell

TABLE I
Thermal Properties of PPCMA Gel Polymer Electrolytes as a Function of DCP

DCP content	5 wt %	8 wt %	10 wt %	12 wt %	15 wt %	20 wt %
T_g (°C)	33.8	34.2	34.8	35.3	34.9	35.0
$T_{(-5\%)}$	264.1	264.2	263.4	263.3	265.0	266.4
$T_{(-50\%)}$	289.9	289.8	290.2	290.9	297.8	297.9

was placed into a self-designed oven coupled with a temperature controller. For each temperature, at least 30 min were waited before the impedance response was recorded.

The measurement of lithium ion transference number (t_+) was suggested by Bruce et al.[26,27] Briefly, a well sealed symmetrical Li/polymer electrolyte/Li test cell was assembled in an argon-filled Mikrouna Super(1220/750/900)glove box and tested by combining the AC impedance method and the DC-polarization method using EG&G Electrochemical Analyzer (Solartron 1255B) to determine the transference number (t_+) using the following eq. (4):

$$T_{\mathrm{Li}^+} = \frac{I_s}{I_0}\left(\frac{\Delta V - I_0 R_0}{\Delta V - I_s R_f}\right) \tag{4}$$

Where, V is the applied DC-potential difference, I_o and I_s represent the initial and steady state currents flowing through the test cell respectively. Finally, R_o and R_f give the initial and steady state resistance of the interface. In this study, the membrane radium is 1.0 cm, and the applied DC-potential difference is fixed to10 mV. The resistance needed in eq. (4) was estimated from the impedance spectra obtained in the frequency ranging from 1 to 100 kHz.

The Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ lithium polymer cells were assembled in an argon-filled glove box, using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as cathode material, a lithium foil as anode and PPCMA gel polymer electrolyte as electrolyte and separator, respectively, and the galvanostatic charge–discharge studies were performed in the voltage range of 2.8–4.2 V at 0.1C rate on LAND-CT2001A battery program-control test system, as reported in our previous work.[28]

RESULTS AND DISCUSSION

Thermal stabilities of crosslinked PPCMA polymer

The thermal stabilities of crosslinked PPCMA were determined by DSC and TGA techniques. The glass transition temperature (T_g), the 5 and 50% weight loss temperature ($T_{-5\%}$, $T_{-50\%}$) of the PPCMA-base gel polymer electrolytes with different DCP ratio are tabulated in Table I. It can be seen that T_g, $T_{-5\%}$, and $T_{-50\%}$ of the PPCMA electrolyte tend to slightly increase with increasing DCP ratio. This indicates that the DCP can increase effectively the crosslinking ratio of PPCMA. The increased crosslinking content then leads to the improvement of the thermal stability of PPCMA. From Table I, we can conclude that the crosslinked PPCMA polymer electrolyte film is thermally stable up to 260°C.

Electrolyte uptake and swelling ratio

Figures 1 and 2 show the liquid electrolyte uptake and swelling ratio plots of PPCMA gel polymer electrolyte with different DCP ratio. It is apparent that

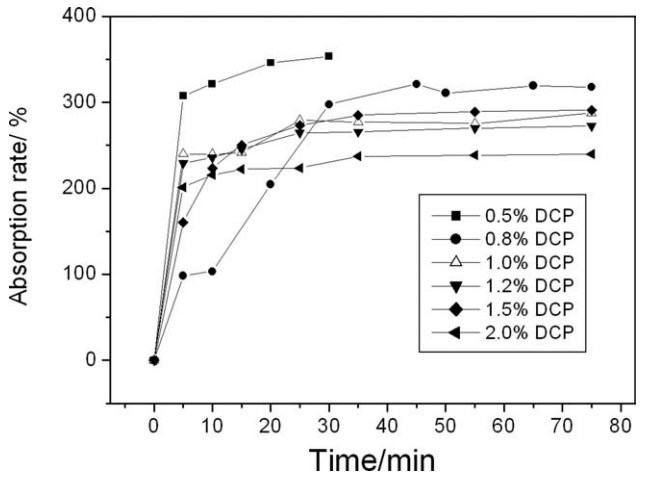

Figure 1 Electrolyte uptake of PPCMA gel polymer electrolytes as a function of DCP content.

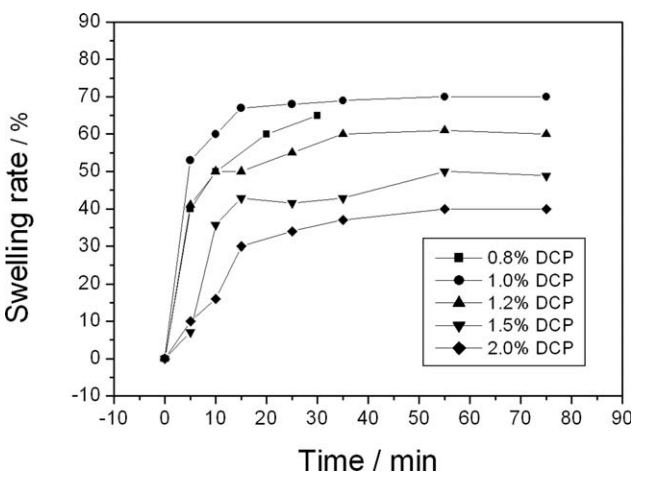

Figure 2 Swelling rates of PPCMA gel polymer electrolytes as a function of DCP content.

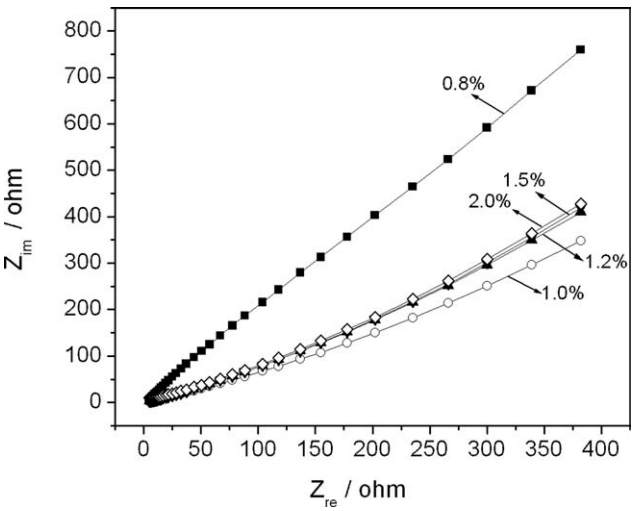

Figure 3 Nyquist plots for PPCMA gel polymer electrolyte with different DCP content at 25°C.

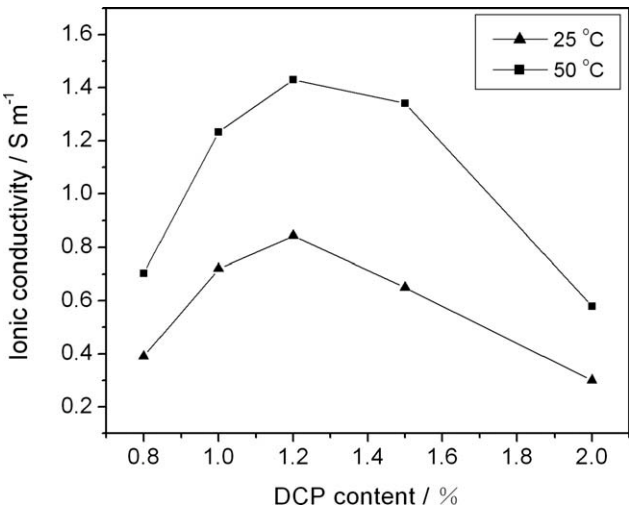

Figure 4 Ionic conductivities of PPCMA gel polymer electrolytes as a function of DCP content at 25 and 50°C.

the liquid electrolyte uptake of PPCMA polymer electrolytes matrix decrease with increasing DCP ratio. This is due to the decrease in the solubility of PPCMA matrix subjected to crosslinking. The PPCMA gel polymer electrolyte with 2.0% DCP ratio shows the highest electrolyte uptake after 3–4 min together with a maximum weight uptake ratio of 210%. However, the dimensional stability can be greatly improved because of the crosslinking of PPCMA matrix. These phenomena are easier to understand in terms of the change of polymer solubility.

Ionic conductivity

The ionic conductivity of a polymer electrolyte is a crucial performance factor for lithium-ion battery. The ionic conductivity was determined by electrochemical impedance spectroscopy (EIS) analysis in this work. Figure 3 shows the Nyquist plots of PPCMA gel polymer electrolyte at room temperature. The impedance spectra of all PPCMA gel polymer electrolytes are almost linear along with the real x-axis. The disappearance of semicircular portion in the high frequency range as shown in the inset of Figure 3 suggests that the current carriers are ions according to theoretical analysis.[29] This behavior was often observed in the impedance response of polymer electrolytes.[30,31]

Figure 4 shows the variations of the ionic conductivity of PPCMA gel polymer electrolytes versus DCP ratio at room temperature and 50°C, respectively. The ionic conductivity of the PPCMA gel polymer electrolyte increases with increasing DCP ratio, upto a maximum value at 1.2 wt % DCP used. The highest ionic conductivities of PPCMA gel polymer electrolyte with 1.2 wt % DCP ratio are 8.45×10^{-3} S cm^{-1} at room temperature and 1.42×10^{-2} S cm^{-1} at 50°C in turn. The ionic conductivity then decreased with further increasing DCP ratio. The results indicate that the matrix structure in polymer electrolyte medium can be modified by crosslinking reaction, and the interaction between polymer chain and lithium ion facilitates ionic conductivity enhancement. The interaction is generally influenced by the mobility of polymer chains. At low DCP ratio, the ion transport can be promoted with increasing DCP ratio because of the structural stability enhancement and solvent maintaining capability of polymer electrolyte. At higher DCP ratio, the conductivity decreases due to the decrease in the mobility of polymer chains.

The typical plot of ionic conductivity versus inverse temperature ($1000/T$) for PPCMA gel polymer electrolyte with different ratio DCP is depicted in Figure 5. In general, the ionic conductivities of all

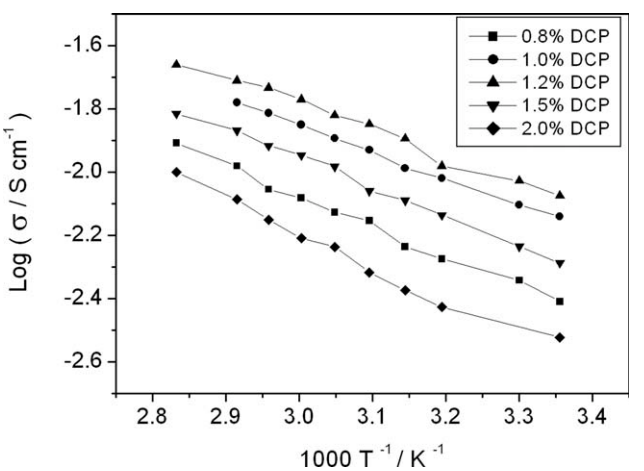

Figure 5 Temperature dependence of ionic conductivities for the PPCMA gel polymer electrolyte.

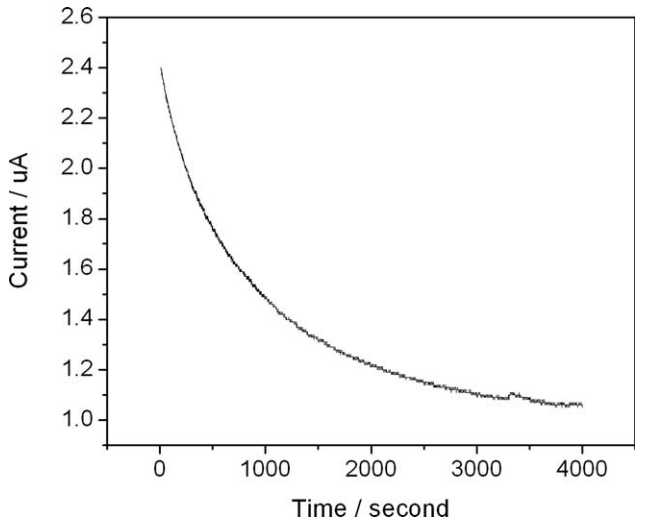

Figure 6 Variation of current with time during polarization of PPCMA gel polymer electrolytes with total applied potential difference of 10 mV.

samples increase with the increase of temperature, obeying the Arrhenius plot of conductivity, which suggests that the conductivity is thermally activated. From this data, the activation energy (E_0) for the movement of Li^+ ions in GPEs can be calculated by using the following Arrhenius expression:

$$\sigma = \sigma_0 \exp\left(\frac{-E_0}{RT}\right) \quad (5)$$

where σ_0 is a pre-exponential factor, which may be related to ion mobility and ion association. E_0 is the activation energy.

The activation energy E_0 calculated from eq. (5) are 18.87, 17.23, 16.69, 16.79, 21.10 kJ mol^{-1} for the GPEs with 0.8, 1.0, 1.2, 1.5, 2.0% DCP, in their turns. The result suggests that the DCP ratio have significant effect on the ion transportation energy, which is related to the ionic conductivity. This is because the DCP ratio can directly affect on the stability of PPCMA polymer matrix.

Lithium transference number

Figures 6 and 7 show the direct-current (DC) polarization profile and AC impedance spectra of PPCMA-based gel polymer electrolyte with 1.2% DCP ratio at room temperature, and the impedance measurements were obtained before and after DC-polarization measurements. It can be seen that the initial current (I_o) and the steady state current (I_s) are measured as 2.45×10^{-6} and 1.06×10^{-6A}, respectively. The initial resistance of interface (R_o) and steady state resistance of interface (R_f) are calculated as 3.21×10^3 Ω and 7.53×10^3 Ω, respectively, and the lithium ions transference number is therefore calculated to be 0.42. In addition, there is no obvious difference in the impedance spectrum of PPCMA gel polymer electrolyte membrane of the test cell before and after dc-polarization studies. In other words, the interfacial resistance caused by the formation of a new passive film and the bulk resistance did not change significantly during dc-polarization. Presumptively, it is may be due to the unique stability of the passive film formation.

Charge/discharge performance

According to the above results on electrolyte uptake, ionic conductivity, and lithium transference number, the prepared GPEs exhibit superior potential in the rechargeable lithium batteries application. Among these polymer electrolytes, the PPCMA GPE with 1.2 wt % DCP displays simultaneously high ionic conductivity and lithium ion transference number. It was therefore used to fabricate a series of Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ lithium polymer cell using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as cathode materials, a lithium metal foil as the anode and PPCMA gel polymer electrolyte with 1.2 wt % DCP linkage as electrolyte and the separator, respectively. Figure 8 shows the charge–discharge curves for the Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell at a current rate of 0.1C and in voltage range of 2.8–4.2 V at room temperature. As seen in Figure 8, the cell with PPCMA gel polymer electrolyte delivered the initial discharged capacity of 115.3 mAh g^{-1} at room temperature, which is slightly lower than the conventional liquid electrolyte. From these results, it can be concluded that the PPCMA-based gel polymer electrolyte has an enough potential for the use in Lithium-ion polymer battery. However, for practical

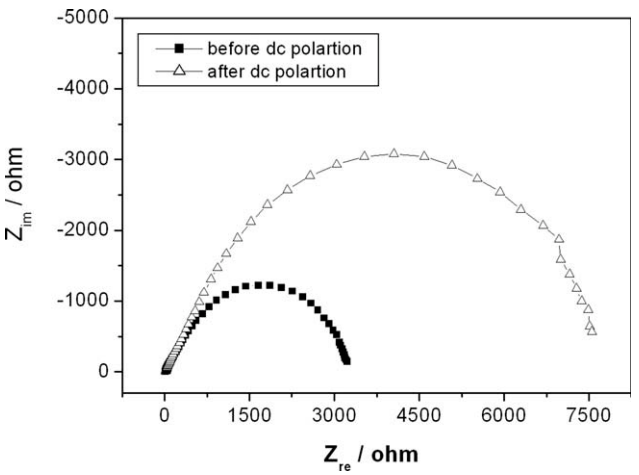

Figure 7 Nyquist plots of the PPCMA gel polymer electrolyte before and after polarization.

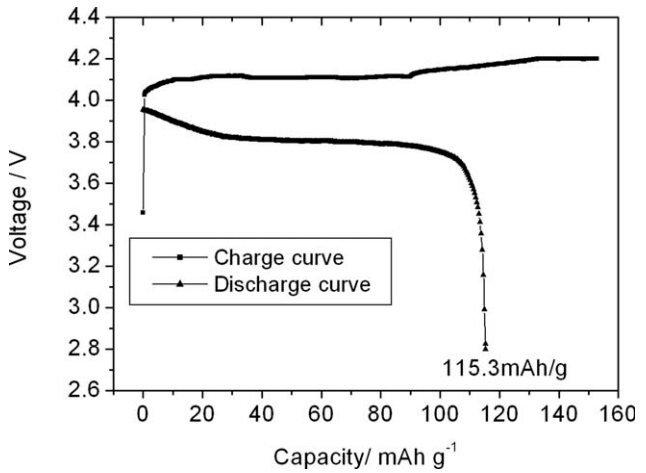

Figure 8 Charge and discharge curves of the Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell in the voltage range of 2.8–4.2V at 0.1C rate.

application of this polymer electrolyte, much more attention should be paid to the interfacial adhesion between polymer electrolyte film and electrodes in the future.

CONCLUSIONS

The crosslinked PPCMA gel polymer electrolyte developed in this work shows the superior electrochemical performances. The ionic conductivity of the PPCMA gel polymer electrolyte firstly increased and then decreased with increasing DCP ratio. The ionic conductivity of the PPCMA gel polymer electrolyte with 1.2% of DCP reached the maximum value of 8.43×10^{-3} S cm^{-1} at room temperature and 1.42×10^{-2} S cm^{-1} at 50°C. The Lithium ions transference numbers of the said polymer electrolyte is 0.42. The charge–discharge results show that the initial discharge capacity of Li/PPCMA GPE/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell is 115.3 mAh g^{-1} at a current rate of 0.1C and in voltage range of 2.8–4.2 V at room temperature. The as-prepared gel polymer electrolytes are considered to be a promising candidate material for lithium-ion battery applications.

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