Short communication

Electrochemical properties of the Li-ion polymer batteries with P(VdF-co-HFP)-based gel polymer electrolyte

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Abstract

Gel polymer electrolytes consisting of 25 wt.% P(VdF-co-HFP), 65 wt.% ethylene carbonate + propylene carbonate and 10 wt.% $LiN(CF_3SO_2)_2$ are prepared using by a solvent-casting technique. The electrodes are for use in lithium-ion polymer batteries. The electrochemical characteristics of the gel polymer electrolytes are evaluated by means of ac impedance and cyclic voltammetry. The charge–discharge performance of lithium polymer and lithium-ion polymer batteries is examined. A $LiCoO_2$ | gel polymer electrolyte (GPE) | mesocarbon microbeads (MCMB) cell delivers a discharge capacity of 146.8 and 144.5 mAh g^{-1} on the first and the 20th cycle, respectively. The specific discharge capacity is greater than 140 mAh g^{-1} for up to 20 cycle at all the current densities examined.
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1. Introduction

Lithium-ion batteries have been widely used as power sources for modern portable electronic devices such as laptop computers, cellular phones, and video cameras. These batteries use liquid electrolytes with organic solvents, which are flammable and easy to ignite on exposure to high temperatures. To solve this safety problem, there is a strong desire to non-flammable electrolytes. Inorganic solid electrolytes are essentially non-flammable and are thus the most promising candidates. Many academic and industrial laboratories have been engaged in the development of ion-conducting polymer batteries [1–4]. Moreover, the use of polymer electrolytes allows lithium secondary batteries to be thin and flexible in addition to having high safety [5,6].

Conventional poly(ethylene oxide) (PEO)-based polymer electrolytes have been the most commonly studied and exhibit ionic conductivity from 10^{-8} to 10^{-5} S cm^{-1} at room temperature. In order to enhance the conductivity at room temperature, several types of gel polymer electrolytes have been developed and characterized. Gel polymer electrolytes are prepared by incorporating liquid electrolytes into a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP), poly(vinyl sulfone) (PVS), poly(ethylene oxide) (PEO), and poly(methyl methacrylate) (PMMA) [7–12]. The ionic conductivities of these systems exceed 10^{-4} S cm^{-1} at room temperature, which is necessary for commercial battery applications. Most processes for preparing gel polymer electrolytes require a moisture-free environment because of the high water-sensitivity of the lithium salt. The co-polymer poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-co-HFP)] (Kynar-Flex 2801) has received particular attention since it has shown excellent safety in battery applications. Gel polymer electrolytes with improved cathode materials are also of great interest as components in advanced secondary lithium batteries because of their high specific energy, high cell voltage, flexible geometry, and no memory effect [13–15].

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In this study, a gel polymer electrolyte is made from P(VdF-co-HFP), ethylene carbonate (EC)/propylene carbonate (PC) and $LiN(CF_3SO_2)_2$ salt. Gel polymer-coated electrodes are then prepared using $LiCoO_2$ and mesocarbon microbeads (MCMB) powders. Lithium-ion polymer cells are assembled with these materials and their electrochemical performances.

2. Experimental

Gel polymer electrolyte films were prepared from a mixture of 25 wt.% P(VdF-co-HFP) (Kynar-Flex 2801), 65 wt.% EC + PC and 10 wt.% $LiN(CF_3SO_2)_2$ salt with acetone at room temperature for 30 min. The resulting homogeneous and viscous solution was poured on to a polyethylene terephthalate (PET) sheet and the desired thickness was obtained with a doctor blade. The resulting film was dried for 24 h. A dimensionally stable and solvent-free polymer electrolyte film with a thickness of 75 μm was obtained.

Positive electrodes (cathodes) were prepared from a slurry of 85% active material and 5% super-P carbon, and negative electrodes (anodes) from 87% MCMB and 3% Super-P. The resulting powders were separately added to 10% P(VdF-co-HFP) binder in acetone and blended by means of a mixing machine. The blended pastes were coated uniformly on to aluminum and copper mesh with a doctor blade. Finally, the gel electrolyte was coated on both electrodes by a solution casting process, again using a doctor blade, in order to impregnate the polymer solution into the porous electrodes.

The ionic conductivity of the gel polymer electrolytes was measured by ac impedance analysis. The thin-film gel polymer electrolyte was sandwiched between two blocking electrodes of stainless steel (SS). The conductivity was measured using an IM6 electrochemical impedance analyzer in the frequency range of 1 Hz–100 kHz at room temperature.

The electrochemical stability window of the gel polymer electrolyte was studied by linear sweep voltammetry and cyclic voltammetry. A cell configuration of SS | gel polymer electrolyte | Li was used. The transference number was determined through a combination of complex impedance and potentiostatic polarization measurements; the gel polymer electrolyte films were sandwiched between two metallic lithium electrodes. The charge–discharge behaviour of the cells was studied at a current density of 0.25 mA cm⁻².

3. Results and discussions

The ionic conductivity of the gel polymer electrolyte was determined from Cole–Cole plots of the impedance data. The ac impedance diagram is presented in Fig. 1. Only a slanted spike displaced from the origin is observed in the plot of the imaginary part and real part of the impedance. This spike represents a resistor in a series with a capacitor. The resistance of the gel polymer electrolyte is measured from the intercept
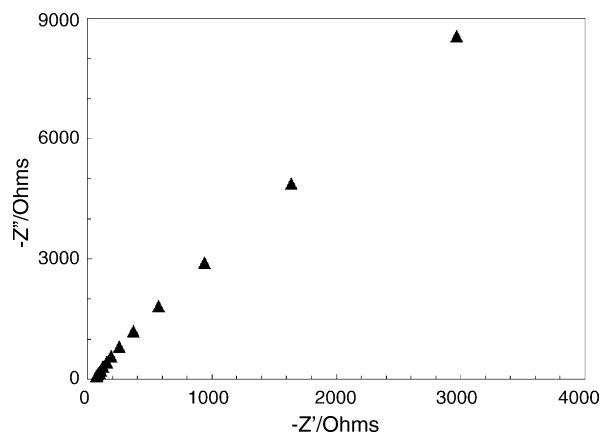

Fig. 1. Typical impedance plot of gel polymer electrolyte consisting of 25 wt.% P(VdF-co-HFP), 65 wt.% EC + PC and 10 wt.% $LiN(CF_3SO_3)_2$ at room temperature.

on the real axis in the high-frequency range. The ionic conductivity of the gel polymer electrolyte is calculated from the measured resistance, surface area and thickness of the film. The ionic conductivity of 25 wt.% P(VdF-co-HFP) containing 65 wt.% EC + PC is 1.2×10^{-3} S cm⁻¹.

One of important parameters in the characterization of the gel polymer electrolyte is the electrochemical stability window in lithium-ion polymer batteries. This parameter can be determined by means of a linear sweep voltammetry (LSV). The resulting voltammogram a SS | P(VdF-co-HFP), EC + PC and $LiN(CF_3SO_2)_2$ | Li cell is shown in Fig. 2. The onset voltage for anodic current is detected at around 4.8 V versus Li/Li⁺, which is assumed to be the decomposition voltage of the membrane. This means that the membrane has good electrochemical stability for use in lithium secondary cells that are typically cycled at around 4.2 V [16]. The cyclic voltammogram of the lithium deposition–stripping process for the gel polymer electrolyte at room temperature is given in Fig. 3. During the negative-going scan, the voltage required to de-
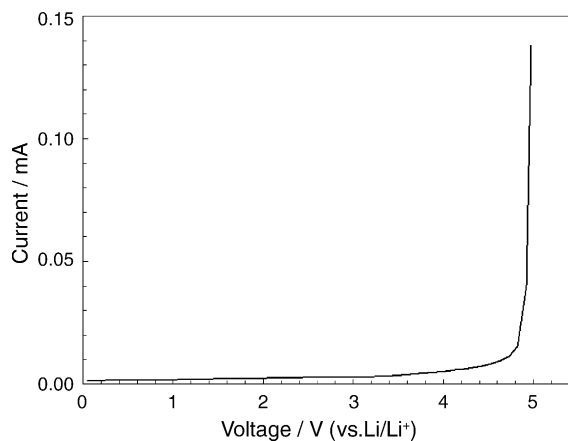

Fig. 2. Linear sweep voltammetry of gel polymer electrolyte consisting of 25 wt.% P(VdF-co-HFP), 65 wt.% EC + PC and 10 wt.% $LiN(CF_3SO_3)_2$ obtained at sweep rate of 10 mV s⁻¹ at room temperature.
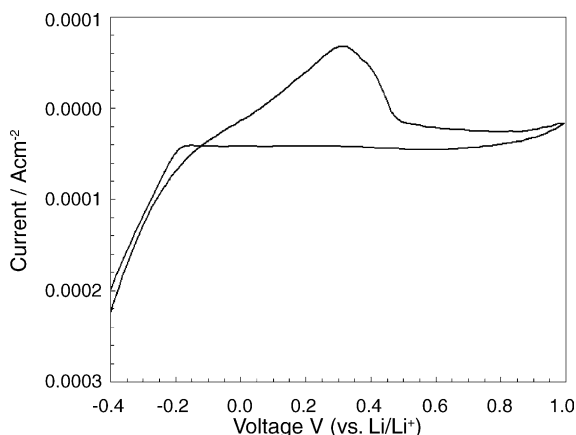
Fig. 3. Cyclic voltammetry of lithium deposition–stripping process in gel polymer electrolyte consisting of 25 wt.% P(VdF-co-HFP), 65 wt.% EC + PC and 10 wt.% LiN(CF$_3$SO$_3$)$_2$ obtained at sweep rate of 10 mV s^{-1} at room temperature.

posit lithium metal on the surface of SS is a few millivolts negative, probably because of the overpotential for polymer electrolyte crystallization. Similar behaviour has been found [17,18] for Li deposition in polymer electrolyte cells. Once a monolayer is formed, further plating can occur at any potential below zero volts with respect to the lithium counter elec-
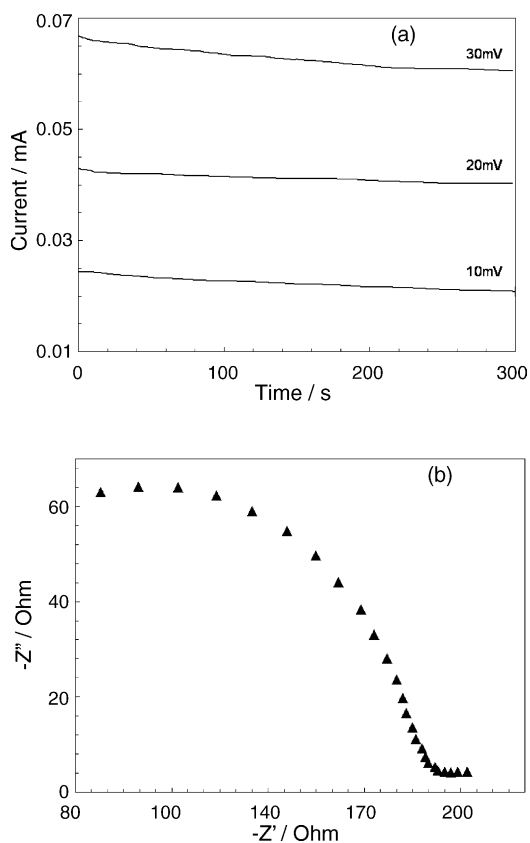

Fig. 4. (a) Polarization current as function of time and (b) impedance spectrum of Li | 25 wt.% P(VdF-co-HFP)–65 wt.% EC + PC–10 wt.% LiN(CF$_3$SO$_3$)$_2$ | Li.
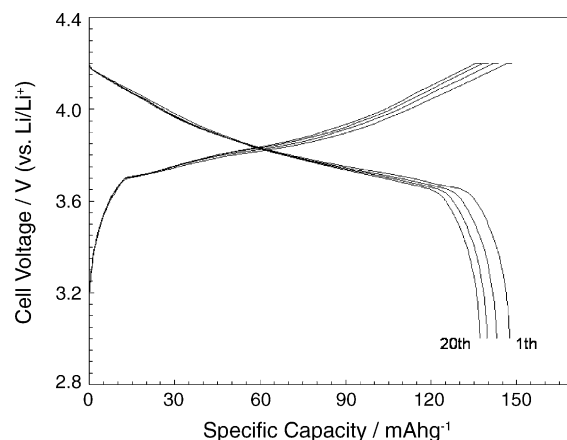

Fig. 5. Charge–discharge behaviour of LiCoO$_2$ | gel polymer electrolyte | lithium cells cycled between 3.0 and 4.2 V at current density of 0.25 mA cm^{-2}.

trode. Finally, the current peak in the positive-going scan of the cyclic voltammogram indicates that plated lithium can be reversibly stripped from the SS substrate, which demonstrates the applicability of the membranes for lithium rechargeable batteries [19].

For intercalation–de-intercalation of lithium ions throughout the host compound lattice, electrolytes with a Li$^+$ transference number that approaches unity are desirable in order to avoid a concentration gradient during charge–discharge cycling [20]. Therefore, evaluation of the transference number is important for characterizing electrolyte materials for lithium polymer battery applications. Scrosati and coworkers [20] have proposed various methods for the determination of t_{Li^+} in polymer electrolytes. These include dc polarization, ac impedance spectroscopy, potentiometric analysis, and classical Turbandt gravimetric analysis. Warren et al. [21] have recently reported a method based on a combination of dc polarization and ac impedance analysis for the determination of t_{Li^+}. This method is based on calculation of the transference number of gel polymer electrolyte films. Under a constant
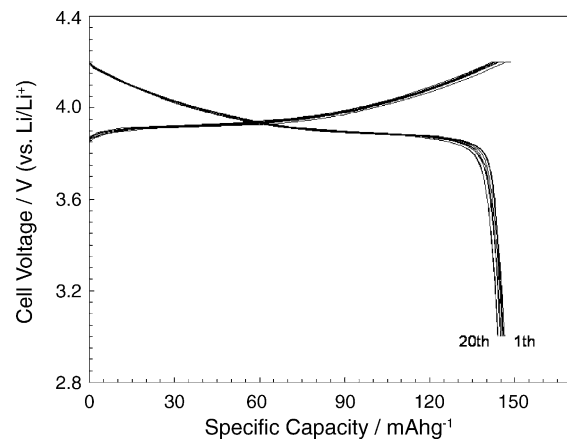

Fig. 6. Charge–discharge behaviour of LiCoO$_2$ | gel polymer electrolyte | MCMB cells cycled between 3.0 and 4.2 V at current density of 0.25 mA cm^{-2}.
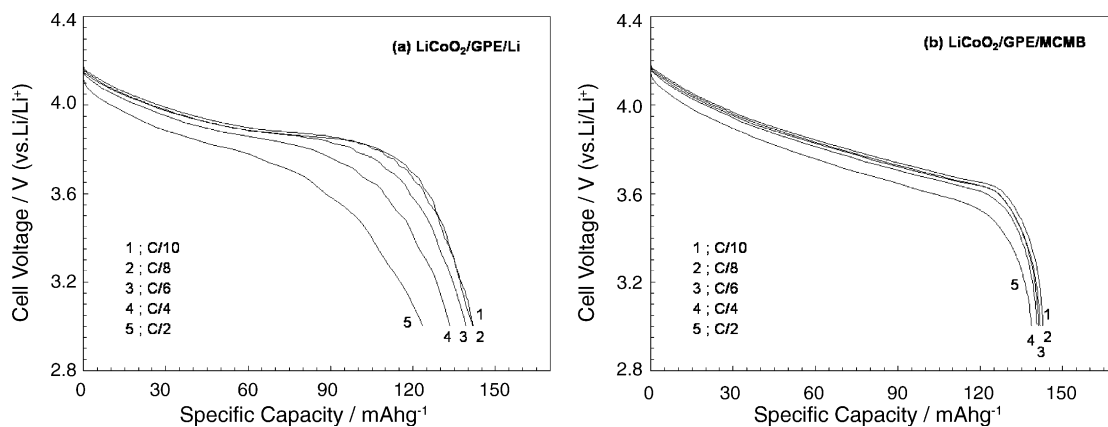
Fig. 7. Voltage profiles for (a) $LiCoO_2$ | GPE | Li and (b) $LiCoO_2$ | GPE | MCMB cell with charge–discharge cycling at various current rates.

potential, the transient current $I(t)$ of a Li | 25 wt.% P(VdF-co-HFP)–65 wt.% EC + PC–10 wt.% LiN (CF$_3$SO$_2$)$_2$ | Li cell can be expressed by $I(t) = V/(R_b + R_i)$, where V is a constant applied potential and R_b and R_i are the bulk resistance and interfacial resistance, respectively [22]. The values of these parameters can be calculated from complex impedance measurements. At $t = 0$, cation and anion migration takes place, but when 't' tends to infinity, the current reaches an equilibrium state which is denoted by $I(\alpha)$. At this time, the cations are the only mobile carriers. Then, t_{Li^+} can be easily derived from Fig. 4(a) that represents the current as a function of time for the cell at 10, 20 and 30 mV. The impedance spectrum for the low- and high-frequency semicircle is shown in Fig. 4(b). The transference number t_{Li^+} of the gel polymer electrolyte can be calculated from $t_{Li^+} = R_b/[V/I(\alpha) - R_i]$ and is found to have a value of to 0.4.

Charge–discharge curves for a $LiCoO_2$ | GPE | Li cell cycled between 3.0 and 4.2 V at a current density of 0.25 mA cm^{-2} are given in Fig. 5. The cell delivers a specific discharge capacity of 147.6 and 136.7 mAh g^{-1} with a coulombic efficiencies of 99.8 and 99.2% on the first and the 20th cycle, respectively. The cell shows good capacity retention due to the good interfacial contact in the composite electrode with gel polymer electrolyte.

In order to evaluate the electrochemical performance of lithium-ion polymer cells, the cells consisting of $LiCoO_2$, the P(VdF-co-HFP)-based gel polymer electrolyte and MCMB were prepared. The cells were charged and discharged between 3.0 and 4.2 V at the 0.1C rate; the results at a current density of 0.25 mA cm^{-2} are presented in Fig. 6. The cell delivers a discharge capacity of 146.8 and 144.5 mAh g^{-1} with a coulombic efficiency of 99.0 and 98.5% on the first and the 20th cycle, respectively. The slight decrease in capacity might be due to physical changes in the active materials and the interfaces, which gradually increase the internal resistance of the cell during cycling. Nevertheless, the data indicate that lithium-ion polymer cells using P(VdF-co-HFP)-based gel polymer electrolyte have a good capacity retention. Akashi et al. [15] have reported that most of the porous electrode

materials for Li-ion batteries have narrow and deep cavities thus the solution-casting method is also effective method for applying the gel polymer electrolyte to the surface of an electrode active-material.

The rate performance of the lithium-ion polymer battery was measured using $LiCoO_2$ | GPE | Li and $LiCoO_2$ | GPE | MCMB cells at various current densities. The voltage profiles of the cells charged at the 0.1C rate and discharged at 0.1, 0.125, 0.166, 0.25 and 0.5C rates are given in Fig. 7 (a) and (b), respectively. The rate capability of the $LiCoO_2$/GPE/MCMB cell is better than that of the $LiCoO_2$/GPE/Li cell, and its specific discharge capacity is higher than 140 mAh g^{-1} for up to 20 cycles at all current densities.

4. Conclusions

A homogeneous viscous solvent-free gel polymer electrolyte consisting of 25 wt.% P(VdF-co-HFP), 65 wt.% EC + PC and 10 wt.% LiN(CF$_3$SO$_2$)$_2$ has been prepared and its ionic conductivity is 1.2×10^{-4} S cm^{-1}. A $LiCoO_2$ | gel polymer electrolyte | Li cell delivers a specific discharge capacity of 147.6 and 136.7 mAh g^{-1} with a coulombic efficiencies of 99.8 and 99.2% on the first and then 20th cycle, respectively. By contrast, a $LiCoO_2$ | gel polymer electrolyte | MCMB cell gave a discharge capacity of 146.8 and 144.5 mAh g^{-1} with a coulombic efficiency of 99.0 and 98.5% on the first and the 20th cycle, respectively. The specific discharge capacity of a $LiCoO_2$ | GPE | MCMB cell is greater than 140 mAh g^{-1} for up to 20 cycles at all current densities.

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