Photocured PEO-based solid polymer electrolyte and its application to lithium–polymer batteries

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Abstract

A solid polymer electrolyte (SPE) based on polyethylene oxide (PEO) is prepared by photocuring of polyethylene glycol acrylates. The conductivity is greatly enhanced by adding low molecular weight poly(ethylene glycol) dimethylether (PEGDME). The maximum conducticity is 5.1×10^{-4} S cm^{-1} at 30°C. These electrolytes display oxidation stability up to 4.5 V against a lithium reference electrode. Reversible electrochemical plating/stripping of lithium is observed on a stainless steel electrode. Li/SPE/LiMn$_2$O$_4$ as well as C(Li)/SPE/LiCoO$_2$ cells have been fabricated and tested to demonstrate the applicability of the resulting polymer electrolytes in lithium–polymer batteries. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solid polymer electrolytes based on polyethylene oxide (PEO) have become very important materials for solid lithium–polymer battery technology. The advantages of such polymer electrolytes are: (i) volatile solvent is not incorporated; (ii) dendrite formation at the lithium electrode can be minimized. The high crystallinity of PEO at ambient temperature, however, restricts the polymer chain movement and this results in a relatively low ionic conductivity at room temperature [1]. Grafting low molecular weight PEO into the side chain of polymers is a well-known method to minimize the crystallinity. PEO has been grafted into various polymers such as branched copolymers [2–6] and cross-linked copolymers [7–10]. Recently, oligomeric poly(ethylene glycol) dimethylether (PEGDME) was used as plasticizer to enhance the ionic conducitivity [11–13]. The PEGDME was entrapped in poly(vinylidene fluoride)-hexafluoropropylene copolymers (PVdF-HFP) up to 65 wt.% and its maximum conductivity was reported to be 2×10^{-4} S cm^{-1} at room temperature [12,13].

This work evaluates PEO grafted polyacrylate network polymers as a matrix to entrap PEGDME. The polymer can be easily blended with PEGDME because of their similarity in chemical structure. The PEO grafted polyacrylate network polymers have also been successfully used for liquid solvent plasticized gel-type polymer electrolytes. [14,15].

In this paper, PEGDME incorporated polyacrylate network polymer electrolytes are prepared by means of ultra violet (UV) radiation curing. The change in conductivity as a function of PEGDME content is studied. The applicability of these solid polymer electrolytes is demonstrated by fabricating and characterizing lithium–polymer batteries.

2. Experimental

Methoxy poly(ethylene glycol) methacrylate. (MPEGM, $M_w = 400$, Poly science), poly(ethylene glycol) dimethacrylate (PEGDMA, Poly Science), (PEGDME, $M_w = 250$, Aldrich), 2,2′-dimethoxy-2-phenylacetophenone (DMPA, Aldrich), LiCF$_3$SO$_3$ (Aldrich) and LiN(SO$_2$CF$_3$)$_2$ (3M Co.) were dried in vacuum before use.

Solid polymer electrolytes were prepared by UV radiation curing of a homogeneous mixture solution of PEG-based acrylates (MPEGM and PEGDMA), lithium salts, a photo

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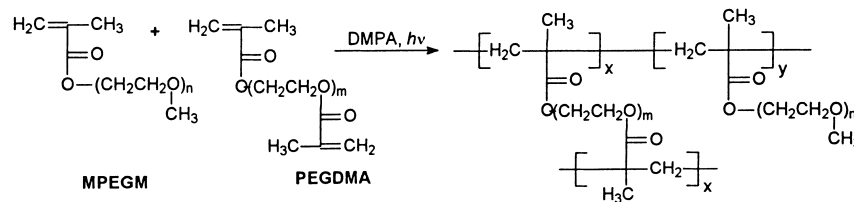*E-mail address*: ykang@pado.krict.re.kr (Y. Kang).

Fig. 1. Schematic diagram of photocross-linked polymer electrolyte.

initiator (DMPA), and low molecular weight PEGDME. The details of the preparation were similar to those described elsewhere [16]. The typical structure of the polymer electrolyte is shown in Fig. 1.

The conductivity measurement was carried out with the polymer coated on to a pre-patterned Indium-Tin Oxide (ITO) cell that had been developed by our laboratory [16,18]. The thickness of the polymer layer was about 100 μm. The ac complex impedance was recorded with an impedance analyzer (Zahner Elektrik, model IM5d) in the frequency range 1 Hz to 1 MHz. The temperature of the sample was controlled by means of a programmable hot plate (Mattler, model FP82HT). All samples were prepared in an argon-gas filled glove-box.

The electrochemical stability of the solid polymer electrolytes was examined by means of cyclic voltammetry using an EG&G model 270 potentiostat. Stainless steel was used as a working electrode and lithium foil as a counter and a reference electrode. Battery performance was characterized with an Arbin model B-2000 battery tester. Test cells were assembled in the glove box and sealed in vacuum using a metallized polyethylene bag.

3. Results and discussion

3.1. Ionic conductivity

The photocross-linked polymer electrolyte was transparent and amorphous at room temperature. The polymer electrolyte was freely blended with PEGDME without phase separation. The PEGDME content, however, was larger than 70 wt.% of the total polymer. The polymer electrolyte showed gel-type characteristics and a self-supportive film was not obtained.

The change in the measured conductivity and in the glass temperature, T_g, as a function of PEGDME content is shown in Fig. 2(a). The conductivity of the polymer without PEGDME is about 10^{-5} S cm^{-1} at 30°C. This value is of a similar order of magnitude as those for branched [2–6] and cross-linked PEO polymer electrolytes [7–10].

The conductivity of the polymer gradually increases with increase in the content of PEGDME. By contrast, the T_g decreases.

A similar increase in conductivity has been reported [12,13] for a PVDF-HFP polymer electrolyte plasticized with PEGDME. The plasticizing effect of PEGDME is

clearly demonstrated by the decreasing value of T_g of the polymer electrolytes with increasing content of PEGDME.

The temperautre dependence of the ionic conductivity, σ, for the polymer is shown in Fig. 2(b). The curves show a typical Vogel–Tamman–Fulcher (VTF) relationship (Eq. (1)) in the temperature range 30–120°C, i.e.

$$\sigma = AT^{1/2} \exp\left(\frac{-B}{(T - T_0)}\right) \qquad (1)$$

where A, B and T_0 are fitted parameters which are related to the carrier density, pseudo activation energy and zero configuration entropy of the polymer chain, respectively. The VTF expression implies that the main mechanism of ion
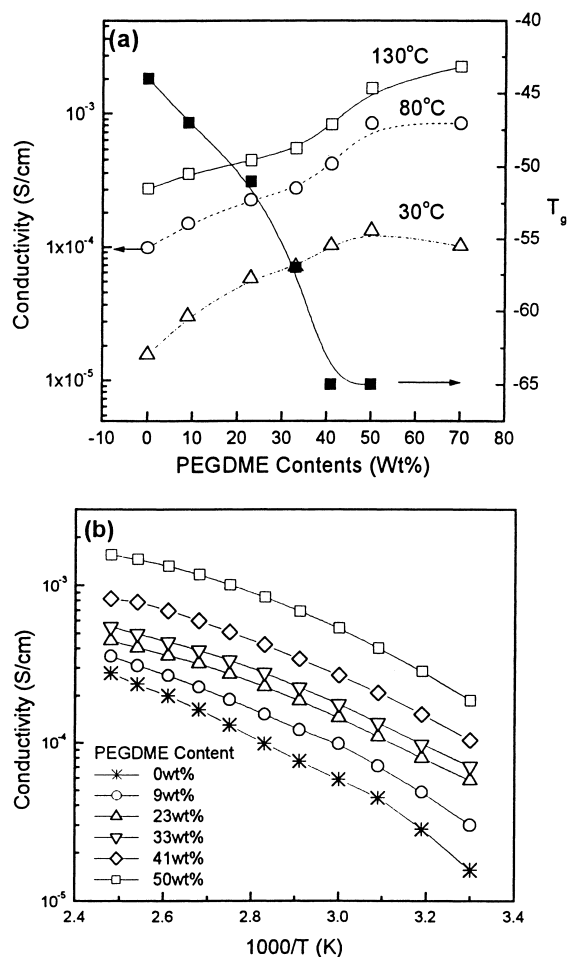

Fig. 2. (a) Conductivity and glass temperature (T_g) as a function of PEGDME content; (b) Temperature dependence of conductivity at various PEGDME contents. Lithium salt = LiCF$_3$SO$_3$. [EO]/[Li] = 15.

Table 1
Activation energy for ionic conduction in polymer electrolytes with different PEGDME contents

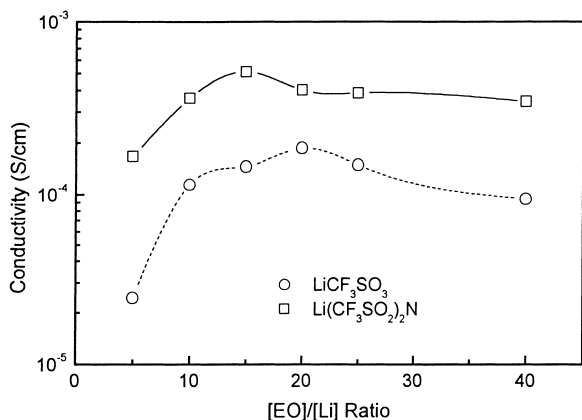|	PEGDMe content (wt.%)					
	0	9	23	33	41	50
E_a (kcal/mol)	6.06	5.02	4.32	4.32	4.38	4.06

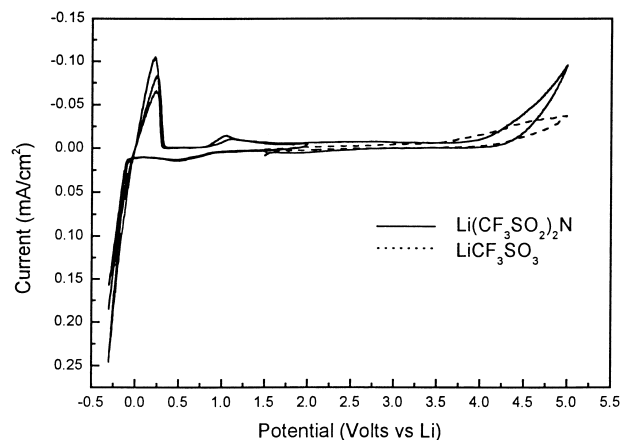Fig. 3. Conductivity at 30°C as function of [EO]/[Li] ratio.

Fig. 4. Cyclic voltammogram for polymer electrolyte containing 50 wt.% PEGDME at 30°C. Sweep rate = 1 mV s^{-1}.

conduction may be related to the free volume theory [17]. The activation energies of ion conduction (E_a) calculated from the Arrhenius relationship are listed in Table 1. The E_a of the polymer electrolyte without PEGDME is calculated to be 6.06 kcal/mol and that of PEGDME plasticized polymer electrolytes gradually decreases with increasing content of PEGDME.
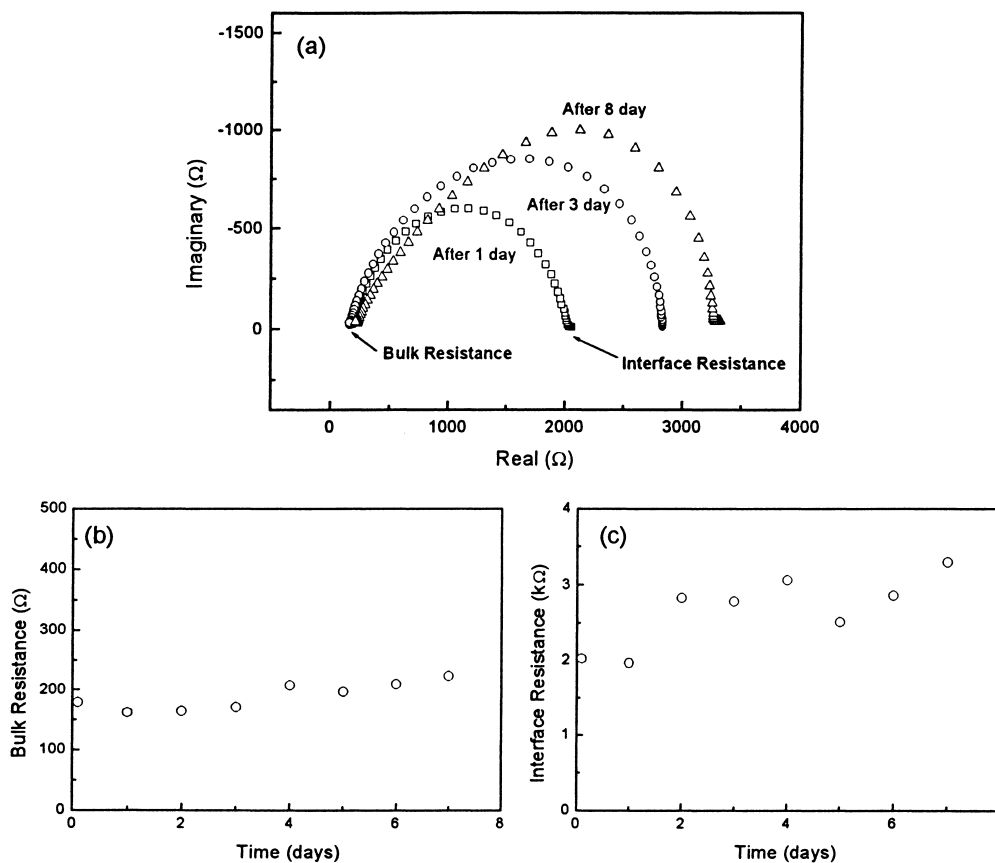

Fig. 5. (a) Niquist plots of polymer electrolyte containing 50 wt.% PEGDME stored 30°C change in (b) bulk resistance and (c) interfacial resistance with storage time.

A similar decrease of E_a has been reported [12,13,18] for PEGDME plasticized polymer electrolytes. Although the ethylene oxide units in PEGDME, as well as in branched PEO, can complex with lithium salt, a higher mobility of lithium ion is expected in the former because of the higher degree of freedom for polymer chain movement. Thus, the E_a of conduction decreases and the conductivity increases with increase in PEGDME content. This implies that a new ion conduction path is formed by adding PEGDME, and that ion conduction through this path is probably dominant at high contents of PEGDME. A similar phenomenon has been observed [19] for a liquid solvent plasticized PVdF-HFP polymer electrolyte.

The influence of the [EO]/[Li] ratio on the conductivity is shown in Fig. 3. The maximum conductivity is found to be at [EO]/[Li] = 15 and 20 for $LiN(SO_2CF_3)_2$ and $LiCF_3SO_3$, respectively. Over the salt concentration range, the conductivity of the polymer electrolyte containing $LiN(SO_2CF_3)_2$ is about four times larger than that of the polymer electrolyte containing $LiCF_3SO_3$. The maximum conductivity of the polymer electrolyte containing $LiN(SO_2CF_3)_2$ is 5.1×10^{-4} S cm^{-1} at 30°C.

3.2. Electrochemical stability

The cyclic voltammogram for a polymer electrolyte containing 50 wt.% PEGDME is shown in Fig. 4. Significant oxidative degradation of the polymer electrolyte is not observed until a potential of 4.5 V (versus Li) is reached, reversible electrochemical plating/stripping lithium takes place on the stainless steel electrode in the potential range −0.3–0.5 V. Plating of lithium starts at about −0.1 V and the maximum anodic peak is at about 0.25 V.

The stability of the lithium electrode and polymer electrolyte interface was evaluated by measuring the ac impedance of a Li/SPE/Li cell stored at 30°C under open-circuit potential condition. The change in the bulk resistance (R_{bulk}) and the interface resistance (R_{intf}) as a function of storage time is shown in Fig. 5. The value of R_{bulk} changes little during the experiment. On the other hand, R_{intf} increases initially and reaches a steady value after 2 days. The initial increase in R_{intf} may be explained by the formation of a passivation film on the surface of the lithium electrode due to residual impurities in the polymer electrolyte.

3.3. Battery performances

The applicability of the photocross-linked polymer tor-lithium cells was demonstrated by fabricating and characterizing Li/SPE/LiMn$_2$O$_4$ and C(Li)/SPE/LiCoO$_2$ systems. The composite LiMn$_2$O$_4$ electrode for the Li/SPE/LiMn$_2$O$_4$ cell was prepared by mixing 50 wt.% of polymer electrolytes as well as electroactive materials. Typical carbon and LiCoO$_2$ electrodes, which are usually employed for Li-ion polymer technology, were chosen for the C(Li)/SPE/LiCoO$_2$ cell. Typical charge–discharge curves, coulombic efficiency,

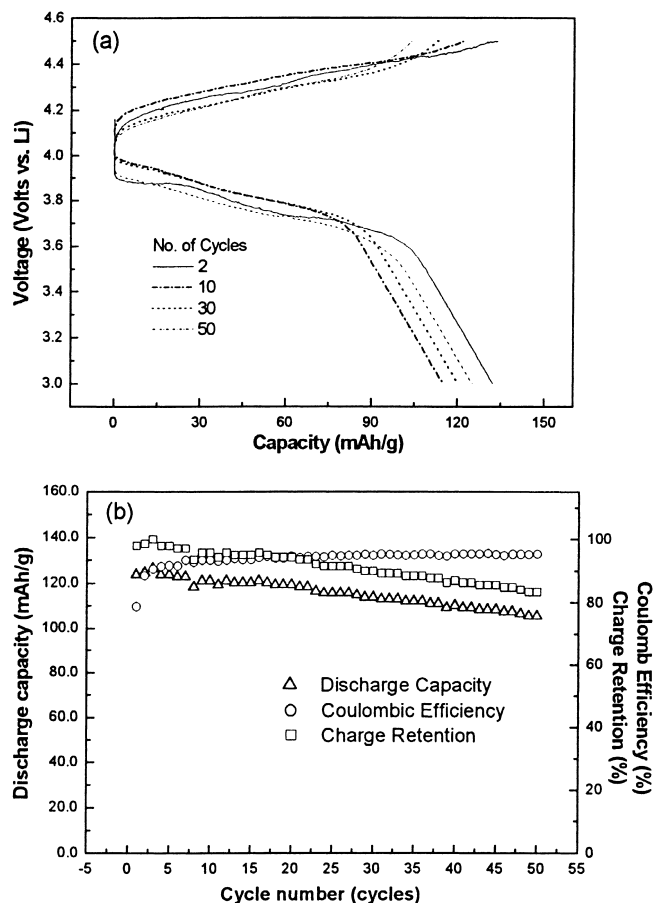Fig. 6. (a) Charge–discharge curves of Li/SPE/LiMn$_2$O$_4$ cell; (b) Discharge capacity, coulombic efficiency and charge retention as a function of cycle number. Discharge rate = 0.1 mA cm^{-2}.

charge retention and discharge capacity of the Li/SPE/LiMn$_2$O$_4$ cell at room temperature are shown in Fig. 6.

The charging and discharging current density was 0.1 mA cm^{-2}. The initial discharge capacity is $\sim$130 mA h g^{-1} based on the electroactive materials. The discharge capacity gradually decreases with cycling. For example, the discharge capacity after 50 cycles is $\sim$115 mA h g^{-1}. The charge retention at this stage is 85% of the initial capacity. The coulombic efficiency is better than 95% during cycling.

The discharge capacity, coulombic efficiency and charge retention of the C(Li)/SPE/LiCoO$_2$ cell at 50°C are presented in Fig. 7(a). The charge and discharge rate was 0.1 C. The discharge capacity is $\sim$110 mA g^{-1} based on the LiCoO$_2$ during the initial five cycles. The coulombic efficiency is better than 98%. The discharge rate dependence of the capacity retention with respect to the theoretical capacity is given in Fig. 7(b). The capacity retention is $\sim$90% at 0.1 C and 0 2 C, but it gradually decrease to 58, 39 and 20% at a discharge rate of 0.5, 1 and 2 C, respectively. The decrease in the capacity at the high discharge rate may be due to the slow diffusion rate of the ions in the electrode and the low ionic conductivity of the polymer electrolyte.
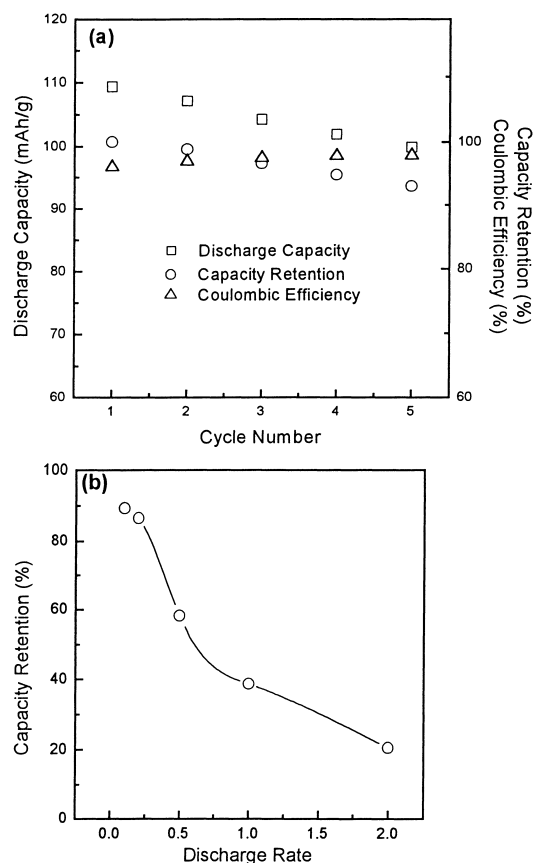
Fig. 7. (a) Discharge capacity, coulombic effieciency and capacity retention C(Li)/SPE/LiCoO$_2$ cell at discharge rate of 0.2 C (0.15 mA cm^{-2}; (b) Discharge rate dependence of capacity retention.

4. Summary

A solid polymer electrolyte containing low molecular weight PEGDME was prepared by photocuring of PEG-based acrylates. The maximum conductivity is 5.1×10^{-4} S cm^{-1} at room temperature. The electrolyte shows oxidation stability up 4.5 V versus a lithium reference electrode. Reversible electrochemical plating/stripping of lithium is observed on a stainless steel electrode. The initial discharge capacity is ~130 and 110 mA h g^{-1}, based on the electroactive materials, for a Li/SPE/LiMn$_2$O$_4$ cell and a C/SPE/LiCoO$_2$ cell, respectively. The PEGDME incorporated polymer electrolyte may be applicable to solid lithium–polymer batteries which operate at ambient temperature.

Acknowledgements

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