

Solid polymer electrolytes based on cross-linked polysiloxane-*g*-oligo(ethylene oxide): ionic conductivity and electrochemical properties

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Abstract

Poly(siloxanes-*g*-oligo(ethylene oxide)) with acrylate groups at the terminal position were prepared and examined for the solid polymer electrolyte (SPE) by curing them. Poly(ethylene glycol) dimethyl ether (PEGDME) was added as a plasticizer. Conductivity of the resulting polymer electrolytes was greatly enhanced with increasing amounts of low molecular weight PEGDME. Maximum conductivity was found to be 8×10^{-4} S/cm at 30 °C with an [EO]/[Li] ratio of about 8. These electrolytes showed oxidation stability up to 4.95 V against the lithium reference electrode. Reversible electrochemical plating/stripping of lithium was observed on the nickel electrode. The plating/stripping efficiency of lithium on nickel was measured to be about 53%.

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1. Introduction

A solid polymer electrolyte (SPE) based on polyethylene oxide (PEO) is one of the promising electrolytes for high energy-density secondary lithium batteries such as lithium–sulfur batteries and lithium metal batteries [1,2]. Since SPEs are less reactive with lithium than liquid electrolytes, SPEs have advantages in safety over liquid electrolytes. But conductivity of the PEO-based SPE at ambient temperature is still below the practically useful range ($\sim 10^{-3}$ S/cm) although PEO can dissolve lithium salts in high concentration by the cooperative interaction of ether oxygens and lithium ions. The ionic conductivity in SPE is closely related to the ion mobility, which in turn is related to the segmental motion of the polymer chain. Thus, preparation of SPE with a low glass transition temperature (T_g) is important. To decrease T_g of polymer, studies have been conducted on the preparation of oligo(ethylene oxide) grafted comb-shaped and network solid polymer electrolytes using the different polymer backbones such as polyphosphazene [3,4], polyacrylate [5–7] and polysiloxane [8–10].

Among them, polysiloxanes, due to the very low T_g (-123 °C for poly(dimethylsiloxanes)) and the chemical

inertness, are a good candidate for the SPE backbones and several promising results have been already published. Ionic conductivity about 10^{-5} S/cm at room temperature was achieved using the oligo(ethylene oxide) grafted comb-shaped polysiloxane prepared from the reaction of poly(methylhydrogensiloxane) and poly(ethylene glycol) monomethyl ether ($M_w = 350$) with catalytic amounts of zinc octanoate [11]. More recently, Hooper et al. have reported that the double-comb type polysiloxane compounds prepared from the condensation of bis-[oligo(ethylene glycol) ether propyl] dichloro silane showed conductivity of 4.5×10^{-4} S/cm [12]. The conductivity of these polymers are very close to the conductivity of the practical use ($\sim 10^{-3}$ S/cm) but these materials may suffer from the low mechanical strength as most low T_g polymers do.

Cross-linking or networking of polysiloxane may improve the mechanical stability. The hydroxy functionalized ethylene oxide grafted polysiloxane prepolymer was prepared from the hydrosilylation of poly(methylhydrogensiloxane) and monoallyl ether of poly(propylene oxide-co-polyethylene oxide). This hydroxy functionalized prepolymer was cross-linked together with toluene diisocyanate and tri(hydroxymethyl)propane and the resulting networked polymer showed a conductivity of about 10^{-4} S/cm at 25 °C [10]. Kuo et al. have reported the conductivity of thermal cross-linked polysiloxanes prepared from the curing

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of epoxy grafted poly(methylsiloxane) and amine terminated poly(propylene oxide) to be about 10^{-7} S/cm at 25 °C [13]. But the thermal curing of diisocyanate and epoxy produced reactive group such as an urethane and a hydroxy group which can react with lithium. Also, the temperature was relatively high and curing time was relatively long.

In this study, we synthesized a new cross-linker based on the oligo(ethylene oxide) grafted polysiloxane at which end the acrylate functional group was attached. The acrylate is a suitable functional group for thermal and photochemical preparation of cross-linked polymer electrolytes [5–7]. Ionic conductivity and electrochemical properties of the SPEs were examined with varying the chain length of the grafted oligo(ethylene oxide) and the amounts of the added plasticizer, PEGDME.

2. Experimental

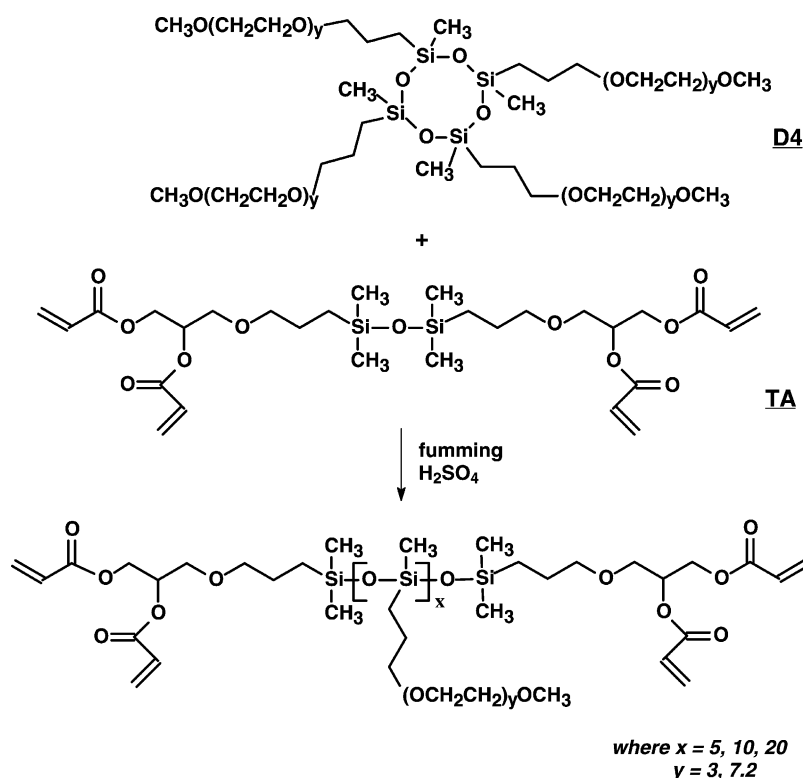
Poly(ethylene glycol) dimethyl ether (PEGDME, $M_w = 250$, Aldrich), 2,2'-dimethoxy-2-phenylacetophenone (DMPA, Aldrich), benzoyl peroxide (BPO, Aldrich) and LiCF_3SO_3 (Aldrich) were dried in vacuum before use.

The acrylate end-capped polysiloxane cross-linker was synthesized by polymerization of a cyclic monomer (D4) and a termination agent (TA) as shown in Scheme 1. The cyclic monomer (D4) was synthesized by the hydrosilylation reaction using tetramethylsiloxane and poly(ethylene glycol) (EO = 3 or 7.2) methyl allyl ether. Similarly, the

terminating agent (TA) was synthesized from the hydrosilylation of tetramethyldisiloxane and 3-allyloxy-propane-1,2-diol followed by the acryloylation. By changing the feeding ratio of the D4 and TA, the chain length of the cross-linker (x) was controlled to be between 5 and 20 (see Table 1). The molecular weight of the polysiloxane cross-linker was calculated to be between 2150 ($x = 5$, $y = 3$) and 9680 ($x = 20$, $y = 7.2$) by the end group analysis using ^1H NMR spectroscopy. Synthetic details of the polysiloxane cross-linkers will be published elsewhere.

Cross-linked solid polymer electrolytes were prepared by UV-radiation or thermal curing using a homogeneous solution of an acrylate end-capped polysiloxane cross-linker, a lithium salt (LiCF_3SO_3), an initiator (DMPA or BPO) and PEGDME ($M_w = 250$) according to the method described previously [7,14]. The photo curing was carried out using a 350 nm light source for 10–30 min and thermal curing in a heating oven at 100 °C for 15 min under the argon atmosphere.

The conductivity measurement was carried out by coating the polymer electrolytes onto the pre-patterned ITO cell that has been developed by our laboratory [7,14,15]. The thickness of the polymer layer was about 100 μm . The ac impedance was recorded using an impedance analyzer (Zahner Elektrik, model IM6) in the frequency range of 1 Hz to 1 MHz. The temperature of the sample was controlled by means of the programmable hot plate (Mettler, model FP82HT). The electrochemical stability of the solid polymer electrolytes was examined by means



Scheme 1. Synthetic scheme of polysiloxane-g-oligo(ethylene oxide) cross-linker.

Table 1
Chemical composition of synthesized cross-linkers

Reagents		Degree of polymerization (x)		Calculated molecular weight	Sample code
Mole ratio (TA:D4)	Side chain length (y)	Expected	Measured		
4:5	3	5	5.80	2150	Ta3-05
2:5	3	10	11.98	3780	Ta3-10
1:5	3	20	23.87	6920	Ta3-20
4:5	7.2	5	5.34	3020	Ta7-05
2:5	7.2	10	13.37	6630	Ta7-10
1:5	7.2	20	20.14	9680	Ta7-20

of cyclic voltammetry using an EG&G model 270 potentiostat. The electrochemical cell was a typical two-electrode system using a nickel working electrode and a lithium foil electrode for a counter and a reference electrode. All samples for the electrical measurements were prepared in argon gas filled glove box, and samples were sealed with a metallized polyethylene bag using vacuum sealer.

3. Results and discussion

3.1. Preparation of polymer electrolyte

The polymer electrolyte was blended in any portions with PEGDME without phase separation. The cross-linked polymer electrolyte was transparent and amorphous at room temperature. The dimensional stability of the prepared polymer electrolyte film depended on the side chain ethylene oxide length (y), the number of the repeating unit of the main chain (x) and the content of PEGDME. When main chain length (x) was 10 and side chain EO unit (y) was 3 (Ta3-10) and 7 (Ta7-10), a good self-supportive film was obtained up to 70% of PEGDME by weight. But a gel-like film was obtained when x was 20 (Ta3-20 and Ta7-20) and PEGDME content was larger than 30%. When we used diacrylate substituted siloxanes instead of tetraacrylate or longer main chain polymer, it was very difficult to obtain good films. Thus, maintaining higher cross-linking density was important to produce a film with better dimensional stability.

3.2. Ionic conductivity

The conductivity of the polymers without additional PEGDME was in the range from 1.6×10^{-5} to 5.8×10^{-5} S/cm at 30 °C. These values were of a similar order of magnitude to those for branched and cross-linked PEO polymer electrolytes [3–7]. The conductivity for different main chain length and side chain was examined and results are shown in Fig. 1. It was observed that ionic conductivity of the polymer electrolytes increased with the increase of the main chain length. The improved conductivity for the higher

molecular weight of cross-linker may be explained by the increased chain flexibility of the main chain. As the main chain length (x) increases, the cross-linking density of the resulting polymer electrolyte decreases, therefore, the higher degree of freedom for polymer segmental motion is expected. The polymer electrolytes with 7.2 EO units showed better ionic conductivity than those with 3 EO. The maximum conductivity was measured to be 5.8×10^{-5} S/cm at 30 °C for the polymer obtained from Ta7-20 without adding PEGDME.

The results of the added PEGDME contents on the ionic conductivity and glass transition temperature are shown in Fig. 2. Conductivity of the polymer was gradually increased with increasing the content of PEGDME. The maximum conductivity at 30 °C was measured to be 8×10^{-4} S/cm at 30 °C (cross-linker: Ta3-20, PEGDME content: 70%). The plasticizing effect of the PEGDME was clearly demonstrated by the decrease of T_g of the polymer electrolytes with increase of the PEGDME content. The conductivity increase can be well related to the decrease of T_g . A similar

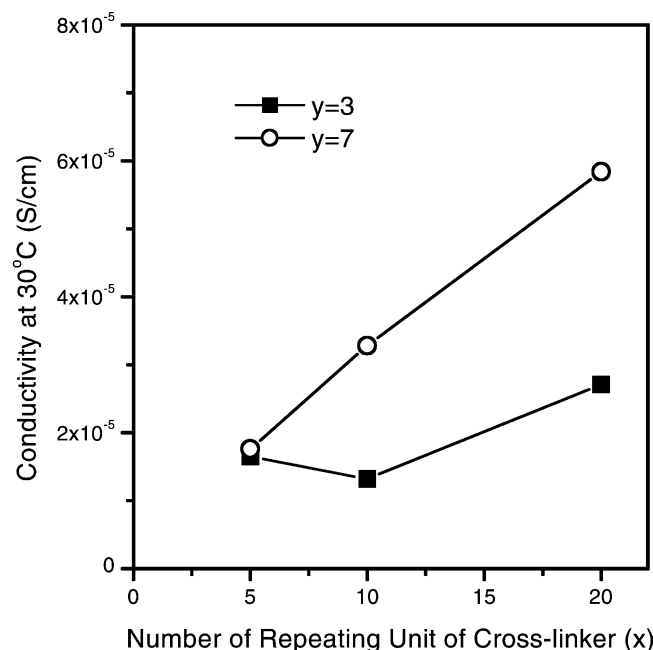


Fig. 1. Changes of ionic conductivity at 30 °C for different cross-linkers.

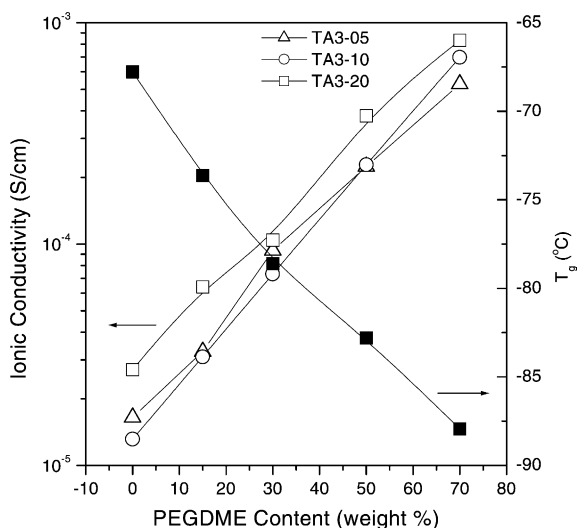


Fig. 2. Changes of ionic conductivity (open symbol) at 30 °C and glass temperature (closed symbol) as a function of PEGDME contents. Lithium salt, LiCF_3SO_3 ; $[\text{EO}]/[\text{Li}^+]$, 20.

increase in conductivity and a decrease of T_g have been reported for a PVdF-HFP [16] and cross-linked PEO polymer electrolytes plasticized with PEGDME [7,15].

In Fig. 3, the dependence of conductivity on the temperature (40–130 °C) is shown for the SPEs prepared from Ta3-10 with various PEGDME contents. The ionic conductivity was increased as the ion mobility was enhanced with the increased segmental motion of the siloxane main chain and the PEO side chain at the elevated temperature. Conductivity–temperature (σ – T) curves are deviated from Arrhenius behavior. These curves show a typical Vogel–

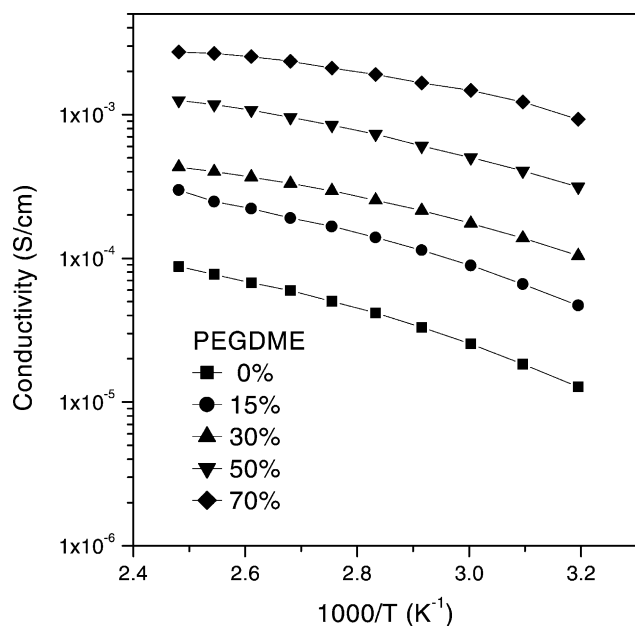


Fig. 3. Temperature dependence of conductivity at the different PEGDME content. Cross-linker, Ta3-10; lithium salt, LiCF_3SO_3 and $[\text{EO}]/[\text{Li}^+]$, 20.

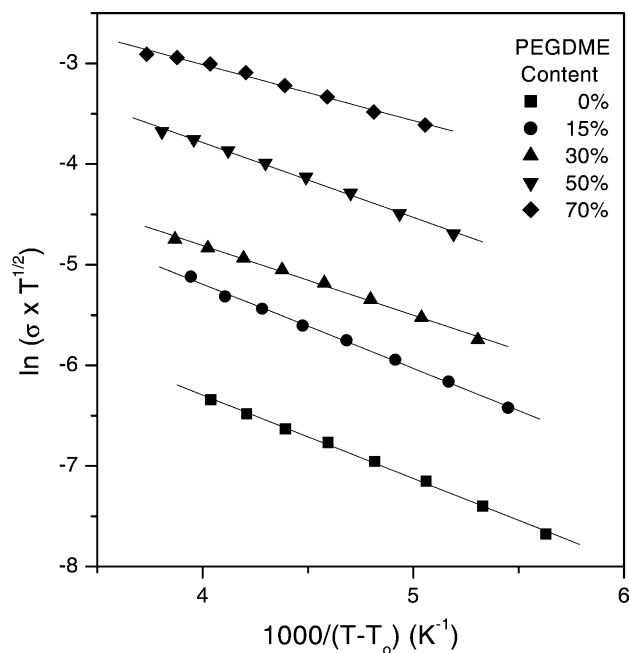


Fig. 4. VTF plots of ionic conductivity at the different PEGDME content. Cross-linker, Ta3-10; lithium salt, LiCF_3SO_3 and $[\text{EO}]/[\text{Li}^+]$, 20.

Tamman–Fulcher (VTF) relationship (Eq. (1)) in the temperature range from 30 to 120 °C.

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

where A , E_a , R and T_0 are fitted parameters which are related to the carrier density, pseudo activation energy, gas constant and zero configuration entropy of the polymer chain, respectively. The VTF expression implies that the main mechanism of ion conduction may be related to the free volume theory [1,17]. In Fig. 4, VTF plots for different PEGDME contents are shown where T_0 is taken 50° below the T_g . The fitted VTF parameters are listed in Table 2. The E_a of the polymer electrolyte without PEGDME was calculated to be 6.9 kJ/mol, which was similar to the reported value for the cross-linked poly(ethylene oxide) [7] and PEO block copolymers [18]. As the PEGDME content increased, the E_a gradually decreased. The decrease of E_a is well correlated to the decrease of T_g , which elucidated the promotion of the polymer chain segmental motion with an increase of the

Table 2
Fitted VTF parameters

PEGDME content (wt.%)	VTF parameters		T_g (°C)
	A ($\text{S K}^{0.5}/\text{cm}$)	E_a (kJ/mol)	
0	0.051	6.90	–67.8
15	0.159	6.97	–73.6
30	0.131	5.76	–78.6
50	0.443	6.18	–82.8
70	0.458	4.64	–87.9

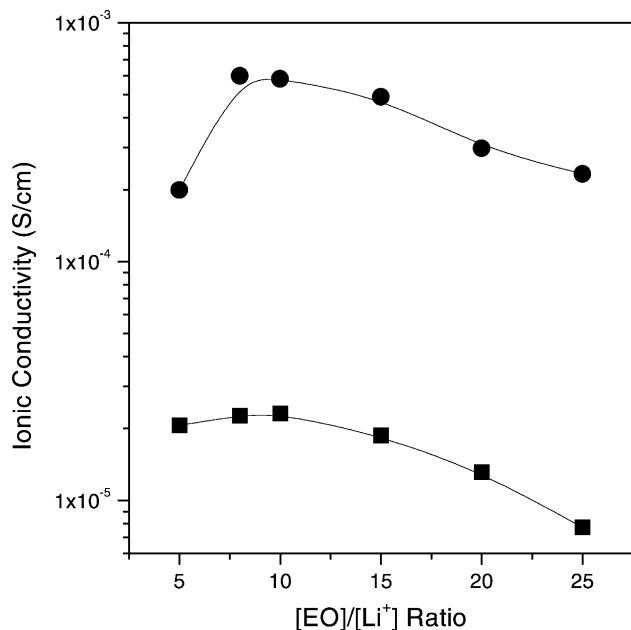


Fig. 5. Conductivity at 30 °C as a function of [EO]/[Li⁺] ratio for the polymer electrolyte containing (■) 0 wt.% and (●) 50 wt.% PEGDME. Cross-linker, Ta3-10; lithium salt, LiCF₃SO₃ and [EO]/[Li⁺], 20.

PEGDME content. However, the *A* parameter, which usually correlates to the ion carrier density, increased significantly when the PEGDME content was larger than 50 wt.%. This implied that the ionic conduction through the entrapped PEGDME phase is probably dominant at the high PEGDME content. The similar feature was also reported for the EC-PC plasticized Kynar polymer electrolyte [19].

The dependence of the ionic conductivity on the salt concentration is shown in Fig. 5 for SPEs prepared from Ta3-10 with and without PEGDME (50 wt.%). The ionic conductivity increased, passed a maximum about [EO]/[Li⁺] = 8, and then decreases with increasing salt concentration. The number of charge carriers increases with increasing salt concentration in the beginning. At the higher concentration of salts, due to the increased inter- and intramolecular coordination of ether dipoles with lithium ions, which may act as transient cross-linking points in the polymer electrolytes, chain mobility decreases and the resulting increase of *T_g* yielded the maximum of conductivity [20]. This kind of ionic conductivity variation with lithium salts concentration was also reported for the comb-shaped [21] and cross-linked polymer electrolytes [7].

3.3. Electrochemical properties

Electrochemical stability of the solid polymer electrolyte containing 70 wt.% of PEGDME was examined at 30 °C by means of cyclic voltammetry. Fig. 6 shows the cyclic voltammograms of this polymer electrolyte (Ta7-05, PEGDME 70 wt.%, LiCF₃SO₃, [EO]/[Li] = 20) sandwiched between Ni and lithium metal electrode. Significant oxidative degradation of the polymer electrolyte started around

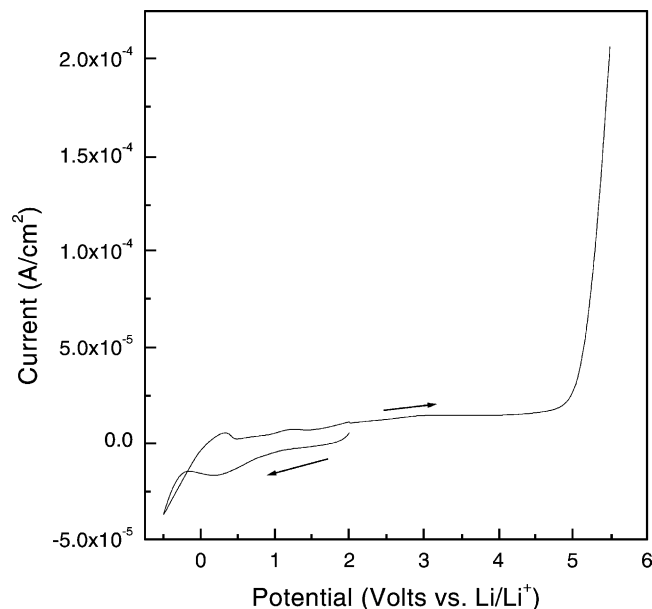


Fig. 6. Cyclic voltammogram for the polymer electrolyte containing 70 wt.% PEGDME at 30 °C. Working electrode, nickel; counter and reference electrode, lithium; initial potential, 2.0 V and scan rate, 5 mV/s. Cross-linker, Ta7-05; lithium salt, LiCF₃SO₃ and [EO]/[Li⁺], 20.

4.95 V. The potential window of the resulting polymer electrolyte was large enough to be useful for the lithium-polymer battery.

As shown in Fig. 7, reversible plating/stripping of lithium was also examined in the potential range of -0.5 to 0.5 V (versus Li/Li⁺) with a sweep rate of 5 mV/s. The variation of

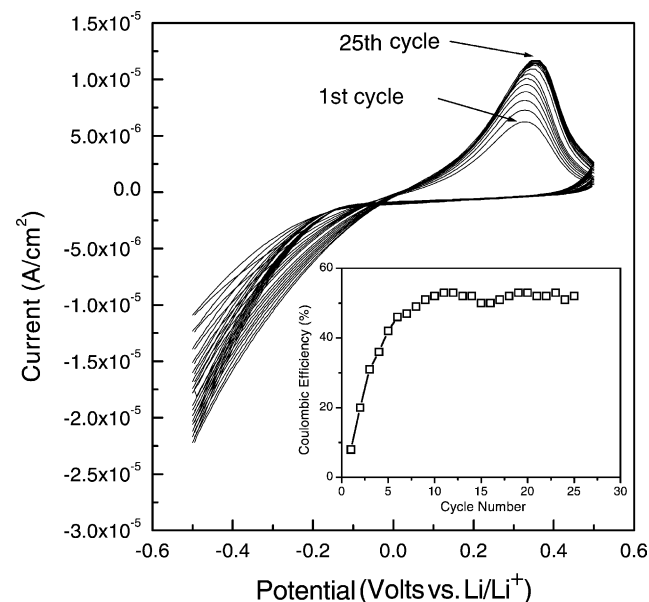


Fig. 7. Cyclic voltammogram of lithium plating/stripping on the nickel electrode for the polymer electrolyte containing 70 wt.% PEGDME at 30 °C. Working electrode, nickel; counter and reference electrode, lithium; initial potential, 0.0 V and scan rate, 5 mV/s. Cross-linker, Ta7-05; lithium salt, LiCF₃SO₃ and [EO]/[Li⁺], 20.

coulombic efficiencies calculated from the voltammogram at a different cycle number is also shown in the inset of Fig. 7. The calculated coulombic efficiency is about 53% on the Ni electrode at 30 °C. The coulombic efficiency of lithium plating/stripping measured by this method was relatively low compared with that measured for a PEO based polymer electrolyte at high temperature [22]. This poor efficiency was explained by the fact that the rapid corrosion of the freshly deposited lithium surface resulted in the passivation of the electrode surface [23,24].

4. Summary

Oligo(ethylene oxide) grafted polysiloxane with acrylate functional groups at the end of polymer was synthesized. The network polyethylene oxide (PEO) based solid polymer electrolyte (SPE) was prepared by curing of the synthesized poly(siloxane-*g*-oligo(ethylene oxide)) tetraacrylate. The conductivity of the polymer without plastisizer was in the range from 1.6×10^{-5} to 5.8×10^{-5} S/cm at 30 °C depending on the structure of the polymer. Conductivity was greatly enhanced by adding low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME). Maximum conductivity was found to be 8×10^{-4} S/cm at 30 °C. These electrolytes showed oxidation stability up to 4.95 V against a lithium reference electrode. Partially reversible electrochemical plating/stripping of lithium was observed on the nickel electrode.

Acknowledgements

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