Synthesis and Electrochemical Properties of Redox Active Polyurethanes with Ferrocene Units in Polyether Soft Segments

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ABSTRACT: Electrochemical active segmented polyurethane with ferrocene units in polyether soft segments (PU-S-Fc) has been originally synthesized and identified by ^{1}H-NMR spectra. Electrochemical behaviors of PU-S-Fc blending with lithium perchlorates were investigated by cyclic voltammetry. In *N,N'*-dimethyl formide solution, PU-S-Fc exhibited normal cathodic and anodic peaks of the ferrocene/ferricinium (Fc/Fc$^+$) couple. Compared with that of ferrocene molecules blended in ordinary polyurethane (PU-B-Fc), redox peaks of ferrocene units in PU-S-Fc were found to be broader, which may be ascribed to the weak adsorption of the polyurethane on the electrode surface. The influence of lithium perchlorate concentration on peak potentials indicated that supporting electrolytes played an important role in electrochemical redox of PU-S-Fc. In the solid state, PU-S-Fc/Li$^+$ showed discernible redox peaks at temperatures higher than 60°C, and an exponential increase curve of electrochemical response with an increase of temperature was found. Temperature variations of the solid-state ionic conductivity for PU-S-Fc/Li$^+$ can be interpreted by the Arrhenius equation. The similarity between the temperature dependence of ionic conductivity and electrochemical response revealed that transport mechanism of ionic and redox species in the polyurethane matrix was controlled by the mobility of polyether chains. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2674–2680, 1999

Key words: redox active polyurethane; ferrocene; electrochemical behaviors; cyclic voltammetry; electrochemical response

INTRODUCTION

Electrochemical systems mutually convert chemical energy and electrical energy, and take an important role in the artificial and biological systems. Electroactive species that can be electrochemically reduced and/or oxidized and ion-containing media that provide the reaction fields of electron transfer are essential to construct electrochemical systems. Aqueous solutions and organic solutions of alkali–metal salts are the most common ion-containing media. Meanwhile, ionic conductive polymers or polymer electrolytes, such as poly(ethylene oxide) (PEO) with alkali metal salts (LiClO$_4$ or LiCF$_3$SO$_3$, etc.) that allows fast and selective transport of ions in the solid state, can readily incorporate many electroactive molecules to build up electrochemical active polymer system.[1–9]

Electrochemical active polymers can be shaped as thin films and confine reagents near the electrode surface. Therefore, solid-state cells can be readily miniaturized for attractive application as solid-state sensors or electrode materials. Diffu-

sion coefficients of ferrocenecarboxylic acid dissolved in polyethers increased when volatile organic vapors partition into the polymer phase. A solid-state electrochemical gas chromatography detector was prepared on the basis of this so-called polymer plasticization effect.[5] The enzyme electrode was fabricated by the use of a redox polymer, poly(N-isopropylacrylamide-co-vinylferrocene), which functioned as a charge transfer mediator between enzyme and electrode.[6]

There are two different ways to obtain electrochemical active polymers: blending electroactive small molecules with polymers,[1–5] and chemically fixing redox species to the side or end of polymer chain.[6–9] The second approach may circumvent problems related to dispersion stability or insufficient solubility of many interesting redox species in solid polymer matrices. Electrochemical reactions of the vinylferrocene–MEO$_9$ copolymers,[7] PEO–hemin in ionic conductive PEO matrices,[8] and a linear monotagged redox polymer, Fc-MePEG[9] have been studied by solid-state voltammetry.

In this article, we originally described a novel type of electrochemical active polymers. Redox-active segmented polyurethane with covalently linked ferrocene groups in PEO soft segments was prepared. Incorporating ferrocene units to PEO main chains can avoid the physical loss of admix redox molecules by migration. At the same time, because the flexible PEO chain would not unfavorably alter the mobility and access of ferrocene units, the original redox properties of ferrocene would be maintained to a certain extent. The polyurethane functions as a binder, as well as an ion-containing media. The advantage of using the polyurethane is related to its solubility in organic solvent for thin-film coating, excellent mechanical properties, and a strong attachment to the electrode surface. Another important fact is that polyether polyurethane electrolytes with ionic conduction species either in a hard domain[10] or in a soft domain[11] have high ionic conductivities at moderate temperature, and may be suitable media for redox of the electroactive solute.[12]

We illustrated the application of cyclic voltammetry to the study of redox couples in the present system. Electrochemical redox reactions in the bulk polymer medium and in fluid solvent are different in that transportation of redox and ionic species in the bulk polymer phase is dependent on the segmental motion of polymer chains. Therefore, the characteristic of the electron transfer reaction of ferrocene units covalently linked to PEO main chains in solid-state and conventional organic solvent (DMF) will be described separately. We aimed to obtain a chemically reversible and detectable redox polyurethane system for practical use.

EXPERIMENTAL

Materials

1,1′-Diacetylferrocene (I) was synthesized by the Friedel-Crafts acylation reaction of ferrocene with $CH_3COCl/AlCl_3$ in anhydrous methylene chloride at room temperature.[13] The crude product was separated by dry column chromatography on neutral aluminum oxide with CH_2Cl_2 as the developing solvent,[14] and purified by recrystallization from benzene. The absence of ferrocene and acetylferrocene was proven by thin-layer chromatography on silica gel. The R_f values of ferrocene, acetylferrocene,[15] and diacetylferrocene in benzene are 0.87, 0.28, and 0.05, respectively. Melting point (m.p.): 127.5–128.5°C (Lit.) 124–125°C (Found, uncorrected).

Ferrocene-1,1′-dicarboxylic acid (II) was prepared by oxidation of diacetylferrocene (I) with NaOBr in H_2O/dioxane.[16] The reaction temperature was lower than 0°C to avoid decomposition of ferrocene nuclei. Sodium bisulfate was added to remove residual sodium hypobromite at the end of reaction. Purification was performed by reprecipitating with dilute hydrochloric acid after dissolving crude acid in a sodium bicarbonate solution. The impurity was found to be less than 5% by the titration method.

1,1′-Ferrocenedicarbonyl chloride (III) was prepared from a mixture of (II) and phosphate pentachloride in anhydrous benzene,[17] followed by recrystallization from benzene–petroleum ether. m.p.: 94–96°C (Lit.) 93–94°C (Found).

4,4′-Methylenebis(phenyl isocyanate) (MDI, Aldrich Chemical Co.), dibutyltin dilaurate (catalyst, Aldrich), and lithium perchlorate were used as received. Poly(ethylene oxide) (PEO MW = 600, 1000) was dried in a vacuum oven for 48 h at 70°C. 1,4-Butanediol (BD) was treated by sodium and purified by distillation. N,N′-dimethyl formide (DMF) was treated by calcium hydride, dried with molecular sieves, and purified by vacuum distillation.

Sample Preparation

Poly(ethylene oxide) having ferrocene groups (PEO-Fc) (IV) was synthesized by reaction of 1,1′-

ferrocenedicarbonyl chloride (III) with PEO (MW = 600) (Scheme 1). A solution of 1,1′-ferrocenedicarbonyl chloride in anhydrous benzene was added dropwise over 24 h to a refluxing solution of PEO in benzene under nitrogen atmosphere. The reaction mixture was gently refluxed for 48 h. All of the solvents were removed under reduced pressure to obtain the product.

Polyurethane with ferrocene units in soft segments (PU-S-Fc) was prepared by typical two-step condensation reaction of MDI, PEO-Fc (IV), and BD with molar ratio 3/1/2. The synthetic route was outlined in Scheme 2. The PEO-Fc/DMF solution was added to the MDI/DMF solution containing 0.05% dibutyltin dilaurate. After 1.5 h at 60°C, BD/DMF solution was added dropwise. Chain extension required 2 h at 65°C followed by 4 h at 80–85°C. The product was obtained by precipitation from distilled water, washed by ethanol, and further extracted by Soxhlet's apparatus with benzene to remove any small molecular weight residual. The polyurethane was dried under vacuum at 60°C for 72 h.

Segmented polyether polyurethane from MDI, PEO (MW = 1000), and BD with a molar ratio of 3/1/2 blending with ferrocene (PU-B-Fc) was also obtained.

Polyurethanes with redox and ionic species were obtained by blending ferrocene-containing polyurethanes with lithium perchlorates. Sample nomenclature, PU-S-Fc/Li$^+$ 10/1, represents polyurethane with a ethylene oxide/Li$^+$ molar ratio 10/1.
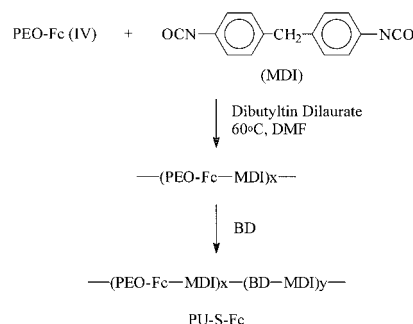
Characterization

^{1}H-NMR spectra were obtained with Me$_4$Si as internal standard, and recorded on a Bruker AM-500 spectrometer.

A three-electrode system was used in electrochemical analysis. Redox potentials of K$_3$Fe(CN)$_6$
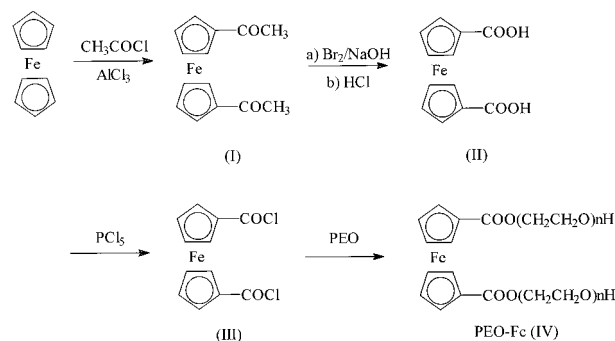
Scheme 1   Preparation of ferrocene derivatives.

Scheme 2   Synthetic route to PU-S-Fc.

in water were recorded and compared with the literature result to prove validity of the electrode system. The experiments were carried out on an EG & G Princeton Applied Research Potentiostat Model 273. When test was performed in solution, working and auxiliary electrodes were Pt wires (geometric areas are 4×10^{-3} cm^2) and potentials were referred to a saturated calomel electrode (SCE). DMF was used as the solvent and lithium perchlorate as the supporting electrolyte. Absence of any peak in cyclic voltammogram of DMF in the range from -1.0 to 1.0 V means that DMF is a suitable solvent for electrochemical analysis of the present system. When potentials were measured in the solid state, polymer-coated Pt/Pt/Ag electrodes were produced by casting polyurethane/DMF solution onto the electrode surface. The solvents were removed under an infrared lamp, then dried in a vacuum oven at 60°C for 24 h to remove the residue solvent. The reference electrode was Ag electrode.

Complex impedance and ionic conductivity measurements with alternating current were carried out with a 378 Electrochemical Impedance System (EG & G Princeton Applied Research) in the frequency range from 10 to 10^6 Hz. The test film was cut to a required size and then painted with silver paste on both sides to form two Ag electrodes. The cell was kept in a temperature-controlled dry box, and the conductivity was measured at each temperature after equilibrium for 30 min.

RESULTS AND DISCUSSION

Sample Identification

Proton magnetic resonance spectra of PEO-Fc in CDCl$_3$ and PU-S-Fc in Me$_2$SO-d$_6$ were shown in Figure 1. The spectrum of PEO-Fc exhibited sub-
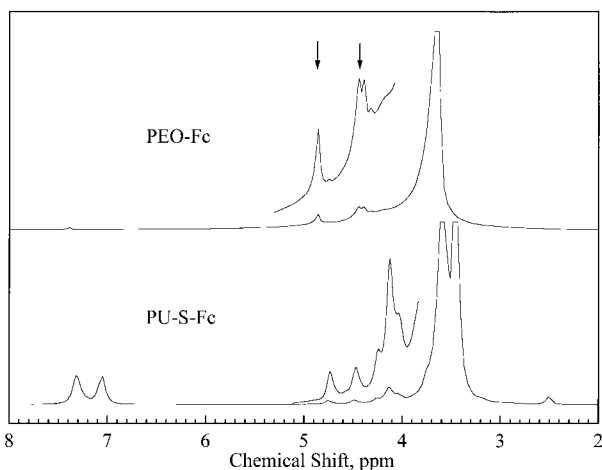
Figure 1 ^{1}H-NMR of PEO-Fc and PU-S-Fc.

stituted cyclopentadienyl ring proton signals at 4.8 and 4.4 ppm. Chemical shifts for Fc-Hα and Fc-Hβ of PU-S-Fc are 4.7 and 4.5 ppm, respectively.
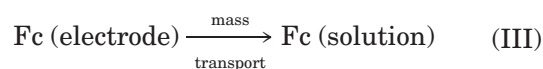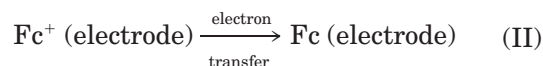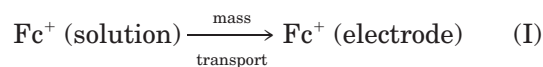
Electrochemical Analysis in Solution

Cyclic voltammograms for the DMF solution of PU-B-Fc and PU-S-Fc containing LiClO$_4$ as a supporting electrolyte were shown in Figure 2. Electrochemical process of ferrocene, dissolved in ordinary polyether polyurethane, was studied as control system. Cathodic and anodic potentials (E_p^c and E_p^a) of the ferrocene/ferricinium (Fc/Fc$^+$) couple in PU-B-Fc were 496 and 338 mV (scan rate 20 mV/s), respectively. Apparent formal potentials, which were defined as the average of cathodic and anodic peak potentials, were found to be almost independent of the scan rate. Normal cathodic and anodic peaks of PU-S-Fc were observed at 674 and 116 mV (scan rate 20 mV/s) and apparent formal potentials were similar with that of PU-B-Fc. It demonstrated our prediction that original redox property of ferrocene would be maintained to a great extent when it was covalently linked to the flexible PEO main chain. Nevertheless, it was notable that PU-S-Fc gave greater peak separation and broader peaks than PU-B-Fc.

As the electron transfer reactions in these samples are close to each other, i.e.,

$$Fe(C_5H_4R)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} [Fe(C_5H_4R)_2]^+,$$
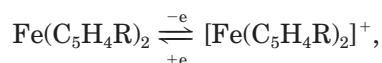
the difference of redox behaviors may be explained by the nature of electrode reaction. In a

typical cyclic voltammetry process when ferricinium is reduced to ferrocene, the simplest electrode reactions must include three steps:

$$Fc^+ \text{ (solution)} \xrightarrow[\text{transport}]{\text{mass}} Fc^+ \text{ (electrode)} \quad \text{(I)}$$

$$Fc^+ \text{ (electrode)} \xrightarrow[\text{transfer}]{\text{electron}} Fc \text{ (electrode)} \quad \text{(II)}$$

$$Fc \text{ (electrode)} \xrightarrow[\text{transport}]{\text{mass}} Fc \text{ (solution)} \quad \text{(III)}$$

If electron transfer rates are significantly greater than the rate of mass transfer, values of the cathodic peak potential and peak separation are independent of the scan rate. When the rate of mass transfer becomes comparable to electron transfer rates, the most notable effect is the increase of peak separation.[18] Because the polyether chains in PU-S-Fc exerted a stronger restriction on mobility of ferrocene species on the
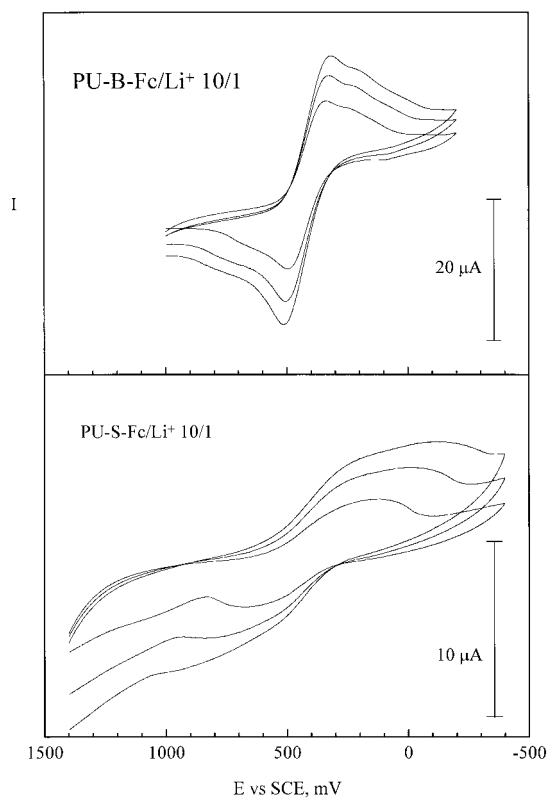

Figure 2 Cyclic voltammograms of PU-B-Fc and PU-S-Fc in DMF solution with LiClO$_4$ as the supporting electrolyte at a scan rate of 60, 40, and 20 mV/s (from top to bottom).

surface of electrode, electrochemical redox of ferrocene units was more difficult than that in PU-B-Fc; a greater peak separation was found as expected in the former.

The broadening of the peaks in PU-S-Fc may be ascribed to the existence of the adsorption process of the sample on the electrode surface:

$$Fc^+ \text{ (solution)} \underset{\text{adsorption}}{\rightleftharpoons} Fc^+ \text{ (electrode)} \quad (IV)$$
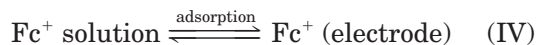
If the adsorption of Fc^+/Fc couple is equal, the adsorption peaks will appear at the same potentials as the normal diffusion-controlled peaks. If adsorption of one species is different from the other, adsorption prepeak or postpeak will be found.[18] Therefore, the separation between the adsorption and diffusion peak reflects the relative strength of adsorption. Because the adsorption peaks are not discernible apart from the broaden of peaks, a weak adsorption process may exist in the electrochemical reaction of PU-S-Fc. A possible adsorption mechanism is the electron sharing of the aromatic ring of the polyurethane with metal atoms of the electrode.[19]

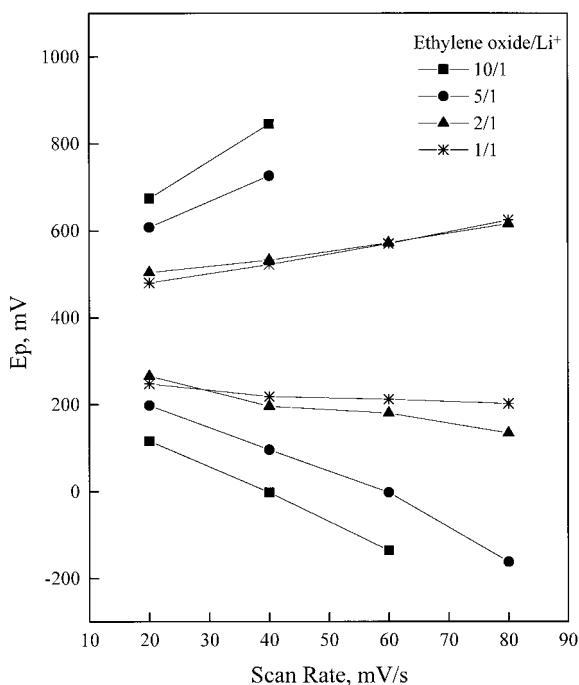PU-S-Fc with different concentrations of supporting electrolytes exhibits notable behaviors. As

Figure 3 Influence of the scan rate and concentration of the supporting electrolyte on peak potentials in the PU-S-Fc/DMF solution.
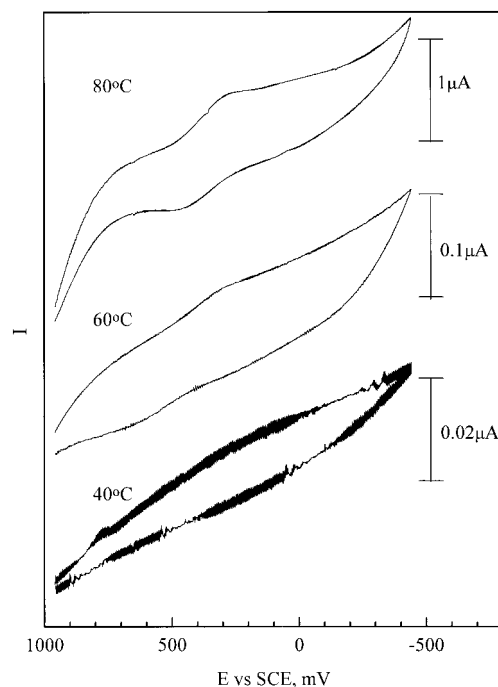

Figure 4 Cyclic voltammogram of PU-S-Fc/Li$^+$ 10/1 in a solid state.

shown in Figure 3, cathodic peak potential of sample with stoichiometric ratio 10 : 1 lies in the more positive position with respect to others. When the content of Li^+ increases, peak separation decreases until a certain molar ratio (2/1) between ethylene oxide/Li^+ is reached. No further change can be found when the molar ratio of ethylene oxide to Li^+ is 1/1. This phenomenon is expected, because the presence of the supporting electrolyte can reduce the potential error due to the uncompensated solution resistance, transportation of a large majority of the charge through the solution, and effective elimination of migration as a mode of mass transport for the electroactive species.

Electrochemical Response in Solid State

Figure 4 shows cyclic voltammogram of PU-S-Fc/Li$^+$ 10/1 in a solid state over a temperature range from room temperature to 80°C. At a temperature lower than 60°C, no electrochemical response can be observed, although both cathodic and anodic peaks were found at temperatures higher than 60°C.

The experimental I versus E response was differentiated. The peaks on the plot of dI/dE versus E can be measured accurately in contrast to conventional I versus E plot where uncertainty over

the baseline causes difficulty in the measurement of peaks. An exponential increase curve of electrochemical response (peak height) with an increase of temperature was shown in Figure 5. In the film, reduction/oxidation rates of Fc^+/Fc and peak currents are controlled by such processes as motion of the polymer chain, diffusion of ferrocene groups to the electrode surface, and diffusion of counter ions. Mobility is inversely proportion to viscosity, and strongly dependent on temperature. The probability that polymer segments jump by micro-Brownian motion from one position to a neighboring position is closely related to an average of free volume. Slow relaxation of chain segments at lower temperature is unfavorable to the transport of redox species, and is responsible for the absence of an electrochemical response. Free volume increases with increasing the temperature. Higher mobility of polymer chain, redox species, and counter ions is advantageous for redox at a higher temperature. From the plot of logarithm response versus the reciprocal of the absolute temperature, apparent activation energy of 156 kJ/mol was found.

Figure 6 shows the temperature dependence of ionic conductivity for PU-S-Fc/Li$^+$ 20/1, which can be interpreted by the Arrhenius equation, and apparent activation energy was 77KJ/mol.

Conductivity refers to the transport of charge carriers through a media under the influence of an electronic field or temperature gradient, and is thus, dependent on the number of charge carriers and their mobility. The ionic conductivity in polymeric materials can be attributed to the diffusion of ionic charge carriers. The similarity between the temperature dependence of ionic conductivity
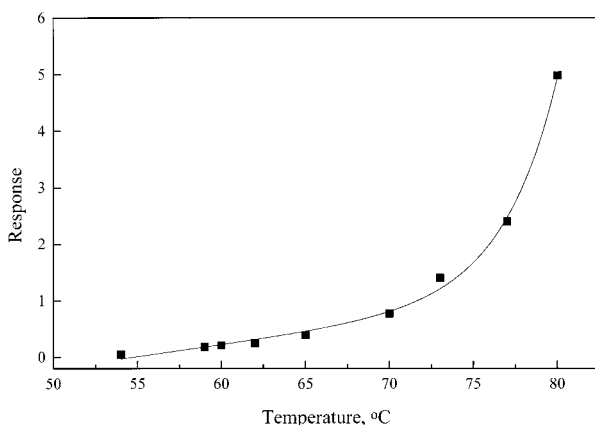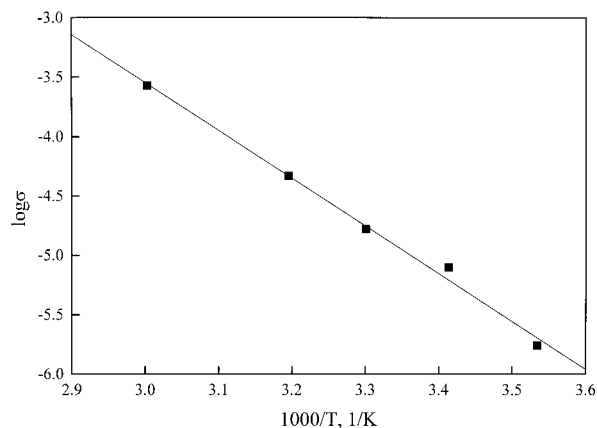

Figure 6 Temperature dependence of ionic conductivity.

and electrochemical response of redox moiety reveals that the transport mechanism of ionic and electronic species in polyurethanes is controlled by the mobility of polyether chains.

CONCLUSIONS

1. Polyurethane with ferrocene groups in soft segments has been synthesized based on polycondensation reaction of MDI, PEO-Fc, and BD with molar ratio 3/1/2. PU-S-Fc exhibited substituted cyclopentadienyl ring proton signals in ^{1}H-NMR spectra.
2. In *N,N′*-dimethyl formide solution, PU-S-Fc exhibited normal cathodic and anodic peaks of the ferrocene/ferricinium (Fc/Fc^+) couple apart from the broading of the redox peaks, which may be ascribed to the adsorption of the polyurethane on the electrode surface. The influence of lithium perchlorate concentration on peak potentials indicates that supporting electrolytes played an important role in the electrochemical redox of PU-S-Fc.
3. In the solid state, PU-S-Fc/Li$^+$ shows cathodic and anodic peaks at a temperature higher than 60°C, and an exponential increase curve of electrochemical response with an increase of temperature was found. Temperature variations of solid-state ionic conductivity for PU-S-Fc/Li$^+$ can be interpreted by the Arrhenius equation. The similarity between the temperature dependence of ionic conductivity and electrochemical response reveals that transport

Figure 5 Temperature dependence of electrochemical response.

mechanism of ionic and redox species in polyurethanes is controlled by the mobility of polyether chains.

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