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Ion conducting polyurethane electrolyte with fixed ferrocene groups as redox active sites

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Summary

Ion conducting polyurethane electrolyte with redox active ferrocene groups which are fixed to the polymer backbone by covalent bonds was prepared. It has been found that the resulting polyurethane electrolyte has high conductivity even at lower temperature. And the temperature dependence of conductivity follows well the Arrhenius equation. Solid state electrochemical property was measured by cyclic voltammetric method with microdisk electrodes at different temperature. The results indicated that the polyurethane electrolyte has good redox stability, as well as reiteration, and show electrochemical activity in the solid state.

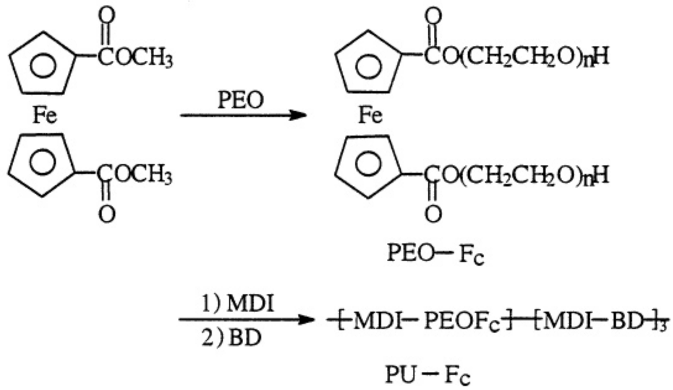
Introduction

In recent years there has been a growing interesting in redox active ion-conducting copolymers. These copolymers include poly[ω-methoxyocta(oxyethylene) methacrylate-block-4-vinylpyridine](1) and poly[methoxy-nona(ethylene oxide)methacrylate-block-vinylferrocene](2) . Besides their applications as solid state sensors materials, they also supply a new sort object of studying solid state electrochemistry. However, the conductivity and mechanical strength of these copolymers should be improved for practical use. And the mechanisms of electron transfer reaction still need to be studied further. We have synthesized a series of sulfonated polyurethane ionomers which have the advantage of good mechanical behavior and high ionic conductivity at moderate temperature(3) and have studied the solid state electrochemical properties of redox active solutes in the ionomer media(4). In this report, a polyurethane elastomer is used as ion conductive matrix which has superior characteristics in chemical resistance, weatherability, durability and mechanical strength. The redox active sites are fixed to the polymer backbone by covalent bonds. The ionic conductive property and solid state electrochemical property are measured by complex impedance analysis and voltammetric method with microelectrode respectively. The preliminary experimental results indicate that these materials has high conductivity at lower temperature and show electrochemical activity in the solid state.

Experimental

Synthesis of polyurethane with fixed redox sites

A toluene solution of poly(ethylene oxide) (PEO, Mn = 1000, Aldrich), dimethyl ferrocenedicarboxylate, and zinc acetate as catalyst was refluxed for 48 h under nitrogen gas. Part of the toluene was replaced by an equivalent of fresh solvent every 2h. Then N,N-dimethyl formamide (DMF) was added to reaction mixture after removal all of toluene. The polyurethane containing ferrocene group (PU-Fc) was a condensate of methylene diphenyl-dicyanate (MDI, Eastman Kodak Chemical co.), PEO-Fc and 1,4-butanediol (BD, 99%, Aldrich) with molar ratio 4/1/3. MDI/DMF solution was added to PEO-Fc solution containing 0.05% dibutyltin dilaurate. After 1.5h at 60 °C, BD was added dropwise. Chain extension required 2h at 65°C followed by 4h at 80-85°C. The product was obtained by precipitation from toluene/petroleum ether 50/50 (V/V), washed by ethanol, and further extracted by Soxhlet apparatus with toluene to remove any small molecular residual. The polyurethane with fixed ferrocene group was dried under vacuum at 60°C for 72h. The synthetic route was outlined in Scheme 1.



Scheme 1. Synthetic route of polyurethane containing ferrocene units in soft segments (PUFc)

Sample Preparation

The polyurethane matrices containing Ferrocene groups are doped with $LiClO_4$, which provides the carriers in ionic conducting. The molar ratio of Li^+/ethylene oxide is 1/20. Samples for ionic conductivity measurements were prepared by solution casting at 60°C in DMF on a Teflon plate. After the solvent evaporated at 60-70°C, the film was dried further 140°C for 0.5h. The film was cut to a required size and then painted with conductive Ag paste at both sides to form two Ag electrodes. The painted films were dried at 60°C in a vacuum oven for 48h before ionic conductivity measurements.

The microelectrode consisted of two Pt wires with 10μm diameter and one Ag wires, serving as working, auxiliary, and reference electrodes, respectively. The electrode was soaked in the DMF solution of polyurethane-$LiClO_4$ electrolyte containing redox active sites and the solvent was removed under an infrared lamp. After the operation had been repeated for several times, the electrode was dried in a vacuum oven at 60°C for at least 48h to remove the residual solvent.

Measurement

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 10^6Hz. The cell was kept in a temperature-controlled dry box and the conductivity was measured at each temperature after equilibration for 30 min. The ionic conductivity is calculated by

$$\sigma = (1/R_B)d/S$$

where d is the thickness of the sample, measured before the film was painted, S is the area of the Ag electrode. R_B is the bulk resistance of the sample obtained from the complex impedance spectra. Cyclic voltammetric measurements were carried out with Electrochemical Analyzer BAS 100B (American BS Co.). The electrode was kept in a superthermostat and the cyclic voltammetric curve was measured at each temperature after equilibration for 30 min.

Results and Discussion

Ionic Conductivity

Fig 1 shows the typical complex impedance spectrum for the polyurethane electrolyte. There are a high-frequency semicircle arc and low-frequency sharp slope.

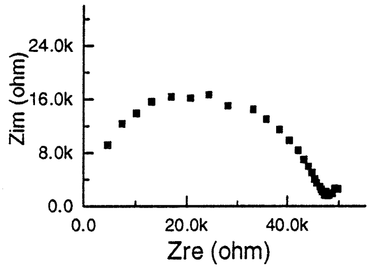


Fig. 1 Complex impedance spectra of polyurethane electrolyte at 283K

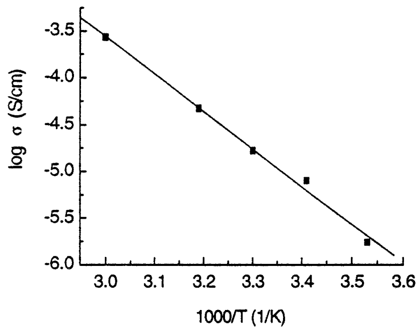


Fig.2 Temperature dependence of ionic conductivity

The temperature dependence of the ionic conductivity polyurethane electrolyte with fixed redox sites was shown in Fig. 2.

The data of ionic conductivity indicated that the resulting polyurethane electrolyte has high conductivity even at lower temperature. Considering of the chemical resistance, weatherability, durability and mechanical strength of polyurethane elastomer, this polyurethane electrolyte with electroactive sites has potential application for solid state sensors. The temperature dependence of conductivity follows well the Arrhenius equation. Ea calculated from the slope is equal to 76.9 J/mol. The low value of Ea reflects high ionic conductivity. The result is interesting. In general, the temperature dependence of conductivity of many polymer electrolytes reported does not follow the Arrhenius equation, however, could be interpreted by using the Voyel-Tamman-Fulcher (VTF) equation. The mechanism

Solid State Electrochemical Properties

The cyclic voltammetric curves of the resulting polyurethane electrolyte at different temperatures is shown in Fig. 3.

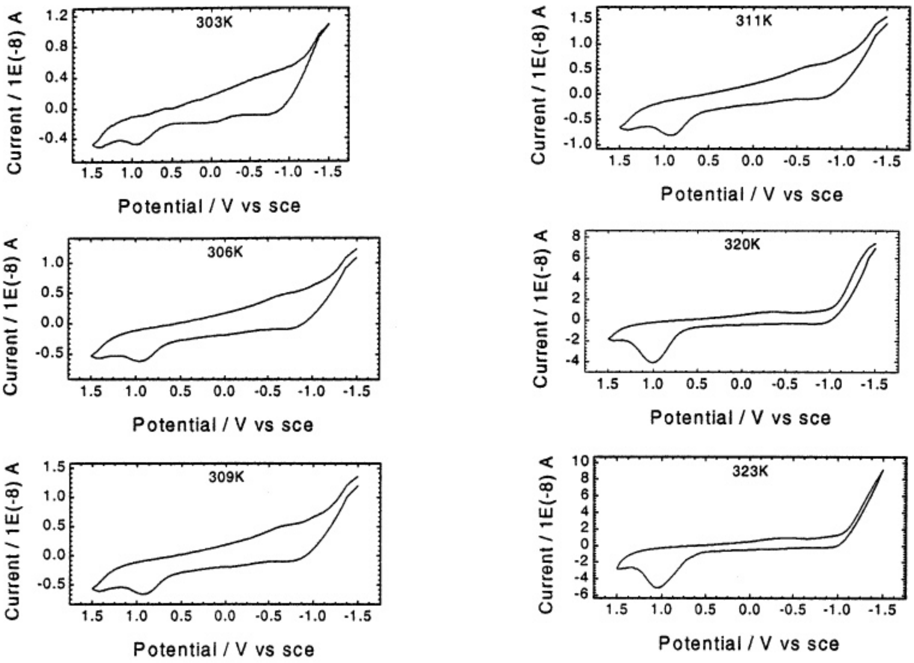


Fig.3 Cyclic voltammograms on the microelectrode for the polyurethane electrolyte with fixed redox sites recorded at 10mV/s

There is only a anodal peak at the temperature below 40°C. The potential of the range from room temperature to 40°C. However, the potential of the anodal peak increases at the temperature above 40°C and there appears an cathodic peak. The peak current increases with temperature. This reflects the mobility of ferrocene groups depend on segmental motions of polyurethane chains. Fig. 4 shows the temperature dependence of peak current.

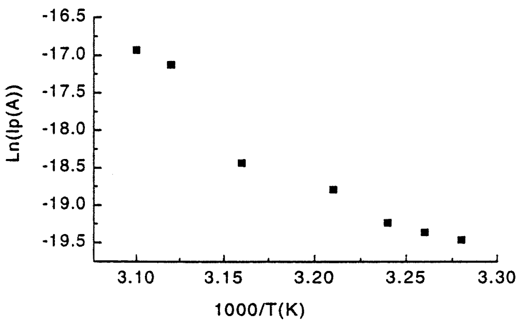


Fig. 4 The temperature dependence of peak current

Introducing redox sites into ionic conductive matrix will raise the response speed of solid state sensors, such as display device and enzyme electrode. More attention is paid to develope the materials have ionic conductivity as well as electronic properties. The preliminary experimental results showed that polyurethane electrolyte with fixed ferrocene group has electrochemical activity in the solid state. Further research will give more information on the electrochemical properties and applications of these materials. The molecular mechanism is being studied.

Conclusion

Ion conducting polyurethane electrolyte with fixed redox active sites on the polymer backbone has high conductivity at lower temperature and shows electrochemical activity in the solid state as well as redox stability. This sort of polymer electrolyte has potential application in solid state sensors.

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