

Solid polymer electrolytes: attempts to improve conductivity

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To attempt to improve conductivity in solid polymer electrolytes, we have examined several approaches. These include the preparation of new polymer-salt complexes, the use of soluble additives that would provide conduction pathways and the use of certain insoluble additives that might also tend to improve electrical properties. In this paper we report on these attempts and the effect that such materials have on conductivities. Metal-ion complexes of poly(vinyl acetate), a polyphosphinate, and a crown ether containing polymer were prepared and evaluated. All exhibited significant conductivity but the best result was obtained when the polymeric crown ether was combined with poly(vinylene carbonate). Conductivity near 10^{-3} Scm^{-1} close to room temperature was observed. Silver(I) and mercury (II) salts were also shown to form conducting complexes with poly(ethylene oxide) with the silver complexes having about 100 times better conductivities than the mercury complexes. Addition of high surface area materials, for example silica gel, microcrystalline cellulose and carbon black, to polymeric electrolytes did not improve conductivities.

(Keywords: polymer electrolytes; conductivity; polymer-salt complexes)

INTRODUCTION

Not very many years ago organic chemicals were universally believed to be electrical insulators. Of course, various types of rubber, polyethylene and other polymers were commonly used as dielectric barriers on wire conductors. In the late nineteen-sixties and early nineteen-seventies a revolution took place, one that is still having effect. Those decades saw the discovery of new organic materials and combinations of materials that exhibited unique and quite remarkable electrical properties culminating in the first report of an organic superconductor in 1980¹. Not only were the electronic properties of organic materials being examined at that time but also current carrying by ionic species. The discovery of fast ion conductivity in polymer-salt complexes² was followed a few years later by the suggestion that such materials might be useful in batteries as solid electrolytes³.

Once it was realized that polymers might be useful as electrolytes, intense research aimed at increasing ionic conductivity and at improving stability in a rechargeable battery environment began. For some time research concentrated on a few polymer systems because there were no adequate mechanistic explanations of how ions could move in the solid polymer matrix, and therefore it was unclear what types of polymers might be useful. Poly(ethylene oxide) [PEO] was the prototypical substance used in most of these studies because of its affinity for alkali metal ions, its ready solubility and the attractive character of films made from the complex.

Since uncomplexed PEO was known to be in a helical structure⁴, its properties were believed similar to the crown ethers⁵ and an explanation for ionic transport in PEO, based on that analogy, was invoked^{6,7}. To explain higher conductivity found in amorphous complexes and the ionic transport found in systems of rather complicated

phase mixtures two general mechanisms have been proposed. One involves cation migration in the helical tunnel existing in crystalline polymer-salt complexes⁸, and cation motion by a free volume mechanism in amorphous materials¹. Refinements on these original suggestions for ion transport were based on thermodynamic arguments and include an intrahelical jumping process in the crystalline regions and ionic mobility in the amorphous regions which depends on motion of the polymer chains^{9,10}.

As understanding of the physics and chemistry of solid polymer electrolytes progressed so too did thinking on methods of improving conductivity and stability of these new materials. Some of the approaches to these goals involve preparing complexes of different polymers. For example, polyitaconates¹¹, poly(vinylene carbonate)¹², derivatized poly(phosphazenes)¹³, poly(ethylene succinate)^{14,15} and other polymers¹⁶ have been examined as potential solid electrolytes. Some workers have attempted to add inert fillers, e.g. α -alumina, to improve both electrochemical and mechanical properties¹⁷. Since both cation and anion contribute to conductivity in polymer electrolytes, and anion reactions with electrodes are thought to be detrimental to good cell operation, polymers have been prepared where only the cation can be mobile¹⁸. Because there is interest in metals of various kinds for battery applications some new research has gone into looking at the electrical properties of complexes with cations other than alkali ions^{19,20}. These are only examples of the many avenues being investigated to define the limits and to improve the properties of solid polymer electrolytes.

The purpose of this paper is to report some of our own results in this arena. In addition to working with some different types of polymers, we have explored the efficacy of several additives, both soluble and insoluble, we have studied the complexes of polymers with several cations

other than alkali metal ions and finally, we have made some attempt to find mixed polymer systems that would result in enhanced electrical properties.

EXPERIMENTAL

All salts used in these studies were purchased in their anhydrous form or dried in a vacuum oven prior to use. The following polymers were purchased and used as supplied from the manufacturers: PEO (M_w 5×10^6 , Aldrich Chemical Co.) and Polycrown DB-186-F (Parish Chemical Co.). Other polymers were prepared by standard free radical polymerization methods, e.g. poly(vinyl acetate) and poly(vinylene carbonate). Acetonitrile, reagent grade, was distilled from anhydrous potassium carbonate under a dry nitrogen atmosphere and stored in a glove box until used. The glove box was used to store all reagents, polymers and solvents under an atmosphere of dry nitrogen. All manipulations required to prepare samples were performed in this equipment. Most films were prepared by casting an acetonitrile solution of the polymer-salt complex on a PTFE plate and permitting the solvent to evaporate into the dry-box atmosphere.

The film samples were removed from the plate and loaded into ceramic dies. Stainless steel screws with flat polished ends were inserted into both ends of the dies and tightened against the films with a force of approximately 10 Kpsi. The loaded dies were removed from the dry box in sealed glass bottles, then loaded into a dry-nitrogen purged computer controlled furnace. Wire leads were attached to each electrode and a thermocouple imbedded into a hole in the ceramic die near the film sample.

Complex impedance measurements were made every 2 to 3 degrees between about 30°C and 130°C. The sample was allowed to equilibrate for 20 min at each new temperature. Impedance measurements were made from 5 to 13 MHz using a computer-controlled Hewlett-Packard 4192A impedance analyser. The d.c. resistance was calculated from the intersection of the electrode characteristic with the real axis in the complex impedance plane plot. As a check on the method, examination of representative examples of the complex impedance plane plots showed the presence of a depressed arc representing a distributed samples capacitance and resistance and a low frequency line due to the electrode processes.

Because it is now well recognized that polymer-salt complexes are composed of multiphase mixtures, we plotted all conductivity data using the straightforward Arrhenius relationship:

$$\sigma = A \exp(-E_a/kT)$$

This treatment permitted avoidance of the problem of trying to distinguish between several microscopic models of conductivity without having sufficient data to do so. At the same time we were able to obtain useful information that allowed us to compare the various samples.

RESULTS AND DISCUSSION

One of the main issues of concern in studies of polymer electrolytes is the question of what types of polymers might be useful. As pointed out above¹⁶ examples of different polymer classes have been examined. In our own

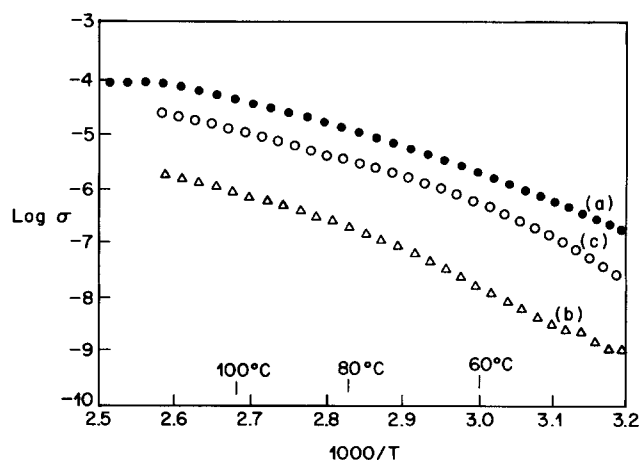
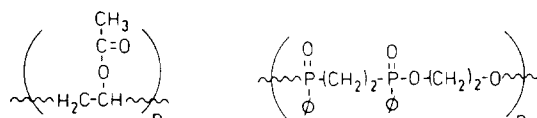


Figure 1 Arrhenius plots of conductivity for polymer-LiCF₃SO₃ complexes: (a) PVAc; (b) polyphosphinate; and (c) polyphosphinate plus crown ether

work, we have prepared ionic conductors from a range of polymer types that might be suspected of forming complexes with cations. These materials were chosen because they have a large amount of oxygen and/or phosphorus available whose electron lone pairs are conveniently disposed for complex formation.

Varying the polymer

For example, a solution of poly(vinyl acetate) and LiCF₃SO₃ in acetonitrile was cast on glass and the solvent permitted to evaporate. The ratio of the concentration of monomer units to salt was 9:1. Poly(vinyl acetate) [PVAc] is a polymer with a fairly low glass transition temperature ($T_g = 30^\circ\text{C}$). This is an important requirement for materials that exhibit high ionic conductivity since most of the conductivity occurs in the amorphous regions of these complexes²¹. PVAc is also known to possess primarily a head-to-tail structure which means that the ester groups are bound to a hydrocarbon backbone at alternate carbons, and are in positions available to surround nearby cations. *Figure 1* shows the results of complex impedance plane conductivity measurements for PVAc. For a salt concentration that in PEO would result in relatively high conductivity, in PVAc only moderate conductivity is observed. Such a result may be due to an increase in the T_g of the complex as compared to the pure polymer, an effect well known in polyether-metal salt complexes^{23,24} (*Scheme 1*).



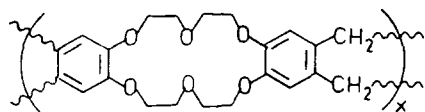
Scheme 1 Poly(vinyl acetate) and polyphosphinate

Another class of polymers that has not been explored are phosphate esters, an example of which are the polyphosphinates. In order to examine at least one of these materials, we prepared the monomer 2-phenyl-1,3,2-dioxaphospholane following published procedures²⁵, and polymerized it using Lewis Acid catalysis²⁶. It was purified by precipitation of a chloroform solution of the polymer in cyclohexane. For

electrical measurements the complex was prepared by casting a film from an acetonitrile/chloroform solution of the polymer containing LiCF_3SO_3 with a ratio of monomer unit to Li^+ of 10:1. The resulting film was clear and quite brittle. Nevertheless, conductivity measurements were undertaken and the results shown in *Figure 1*. Even at 110°C the conductivities are quite low, in the order of $2 \times 10^{-6} \text{ Scm}^{-1}$.

Since we have enjoyed some success in improving the electrical properties of another solid polymer electrolyte by the addition of crown ethers to the complex¹² the same approach was used here. As can be seen in *Figure 1*, when a molar amount of 15-crown-5 equal to the Li salt was added and new films prepared the conductivities achieved were an order of magnitude higher. These results show that, under the conditions used here, this material even with the help of the crown compound has conductivities that are too low to make it useful as a battery electrolyte.

The final polymer discussed here is one that incorporates the crown compound in the polymer backbone, a commercial polymer of a dibenzo-18-crown-6 type (*Scheme 2*). Acetonitrile containing LiCF_3SO_3 was



Scheme 2 Polymeric crown ether

permitted to stand in contact with the insoluble crown polymer powder and then solvent was removed by evaporation. The ratio of crown to Li^+ was 1:1. Impedance measurements were performed and resulted in a conductivity value between 10^{-8} and 10^{-9} Scm^{-1} , on the borderline of being an insulator. However, the crown polymer, LiCF_3SO_3 , and vinylene carbonate were mixed in the ratio 1:1:20. The vinyl compound was polymerized and data derived from electrical measurements. These results are shown in *Figure 2*. The conductivity of this particular mixture was very close to that previously published for the crown ether/poly(vinylene carbonate) system¹². Conductivities such as these, i.e. about 10^{-3} Scm^{-1} , near room temperature, are among the highest reported for polymer-salt complexes.

One additional experiment was performed to determine what level of conductivity could be expected when a polymer mixture containing a crown ether, known to form a good conductor with a soluble lithium salt contained, instead, an insoluble salt with a polymeric anion. This experiment was performed so that we could examine a solid electrolyte that contained only one mobile ionic species, the cation. We chose lithium poly(styrene sulphonate) for this test and found that reasonable conductivities were obtained. Similar work¹⁸ using plasticized sodium poly(styrene sulphonate) concluded that under these conditions a Na^+ conductor could be prepared. Levels of conductivity were about the same as with our Li^+ superionic conductor, 10^{-5} Scm^{-1} .

Varying the cation

While it has been known for some time that certain polymers form complexes with some divalent metal ions^{27,28}, it is only recently that the phenomenon of ionic conductivity has been addressed in these systems^{29,30}. The

conductivities of Mg^{+2} and Pb^{+2} PEO complexes have been shown to be comparable to those reported for some alkali metal salt-PEO complexes. Preliminary transport numbers for Pb^{+2} complexes were shown to be about 0.6³⁰. Complexes of PEO with Ca^{+2} were found to exhibit only moderate ionic conductivity^{29,30}. Other divalent cations (including Hg^{+2}) have been shown to be adsorbed by polyamides having oligo(oxyethylene) segments in the repeat unit, but no conductivity measurements were performed³¹. In this work we report on the transport of Hg^{+2} and Ag^{+1} in PEO complexes.

Three different mercury-PEO complexes were prepared. Mercuric acetate and PEO, in the molar ratio 1:10, were stirred overnight in dry CH_3CN . The resulting pale yellow-orange solution contained a small amount of solid. Films were prepared and the conductivity measured. These results are shown in *Figure 3*. The data exhibit two straight line Arrhenius regions of a curve where one part, at low temperature, has a much higher activation energy than the part at higher temperatures. The point of intersection occurs at about 60°C for the acetate and at about 55°C for the cyanide, which is near the melting point of crystalline PEO, and clearly has to do with a distinct morphological change in the complexes¹⁶.

Mercuric cyanide also formed a complex with PEO and films of it were prepared in the usual way. Impedance measurements were performed and conductivity plots are

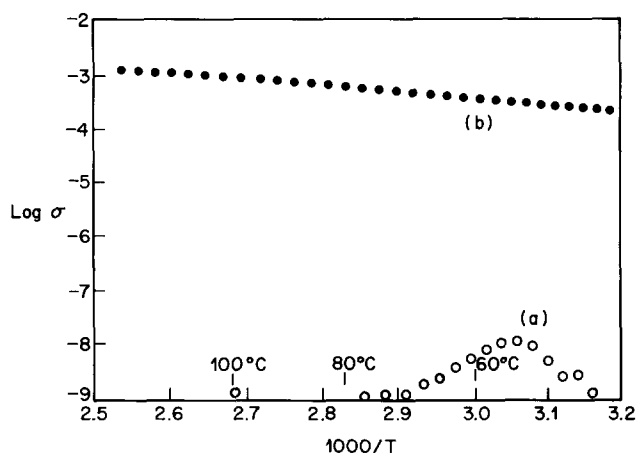


Figure 2 Arrhenius plots of conductivity of LiCF_3SO_3 complexes of (a) polycrown DB-186 and (b) polycrown DB-186 plus poly(vinylene carbonate)

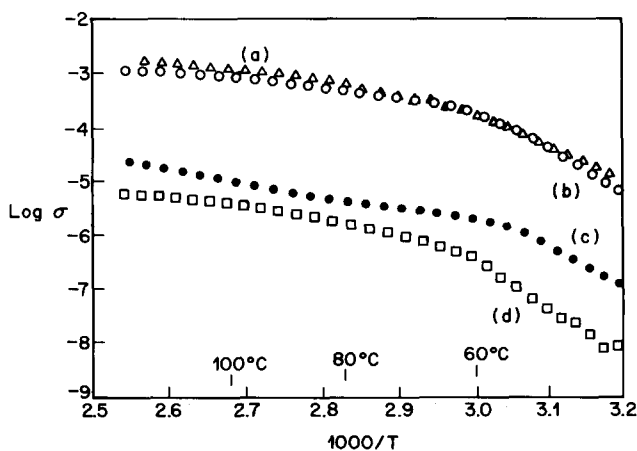


Figure 3 Arrhenius plots of conductivity of PEO complexes of (a) AgBF_4 ; (b) AgCF_3SO_3 ; (c) $\text{Hg}(\text{CN})_2$ and (d) $\text{Hg}(\text{OAc})_2$

shown in Figure 3. The cyanide salt appears to be a better conductor than the acetate over the entire temperature range. The break in the curve comes at a lower temperature in the case of the cyanide (54°C), perhaps indicating a greater affinity of this salt for the PEO than the acetate. Whether this higher conductivity can be attributed to more facile movement of the Hg^{+2} or of the CN^- , or both, is not known.

An attempt was made to form a PEO complex with HgI_2 . The initially red acetonitrile solution on stirring at room temperature soon became colourless and deposited a thick white precipitate, presumably an insoluble complex of some sort. No further work was done with this material.

Silver salts have also been of interest in our studies of polymer electrolytes. We have prepared complexes of PEO with both AgCF_3SO_3 and AgBF_4 and measured their conductivities. Data are given in Figure 3 for a ratio of salt to monomer unit of 1:10. We have measured, but not plotted here, data which show the conductivity of the same complexes except with 15-crown-5 added at a concentration equal to that of the salt. The conductivities of the samples without crown ether present exhibit a smooth curve which starts at about 40°C and 10^{-5}Scm^{-1} and rises to about 10^{-3}Scm^{-1} at 120°C. The addition of the crown compound seems to affect the ionic transport, especially at lower temperatures. At high temperature all the lines converge. These results compare favourably with those previously obtained by another group for AgNO_3 complexes with poly(alkylene sulphides)¹⁹. In that earlier study a high transference number, 0.9, was found for Ag^+ in one of the complexes, but conductivities were only marginal, in the 10^{-8}Scm^{-1} range at 45°C in their best case, poly(pentamethylene sulphide). No comparison with silver salts in PEO was reported.

Effect of an insoluble additive

Attempts to improve the mechanical and electrical properties of polymer-alkali metal salt complexes in one case involved the addition of inert fillers to the polymer-salt mixture⁷. With α -alumina the ionic conductivity of a Li^+ electrolyte was only negligibly affected; also, when filter paper was impregnated with a FeCl_3 -pyrrole combination the conductivity was raised to 10^{-2}Scm^{-1} . While most of the conduction was believed to be electronic in nature, there was no appropriate measurement to determine this. These authors did recognize that a significant component of the conductivity was ionic³². One final piece of information that led us to attempt to increase ionic transport through the addition of insoluble particles are the reports of 1 to 3 orders of magnitude increase in conductivity of LiI-alumina or LiI-silica composites compared to LiI alone^{33,34}.

In the present work we hypothesized that ionic conduction in PEO-salt complexes might be enhanced if additional channels or sites could be provided for cations to travel through or move to. Since previous work indicated that α -alumina was ineffective⁷, but that filter paper might be useful³², our approach was to incorporate microcrystalline cellulose, carbon black or silica gel into a PEO complex to act as high surface area particles that cations might have an affinity for, and yet move easily to and from.

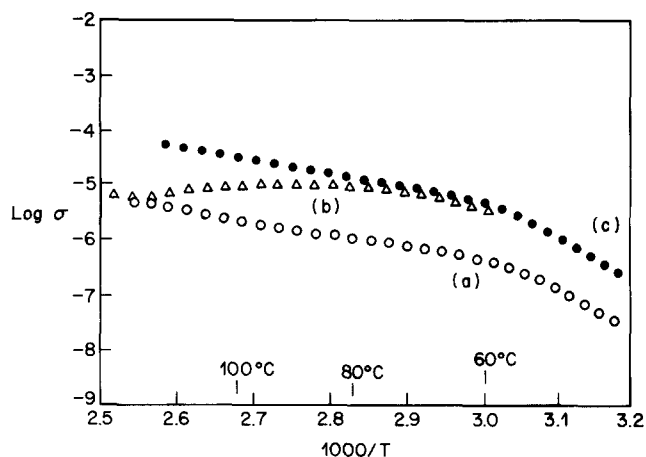


Figure 4 Arrhenius plots of conductivity of PEO- LiBF_4 complexes: effect of (a) microcrystalline cellulose; (b) silica gel and (c) salt alone

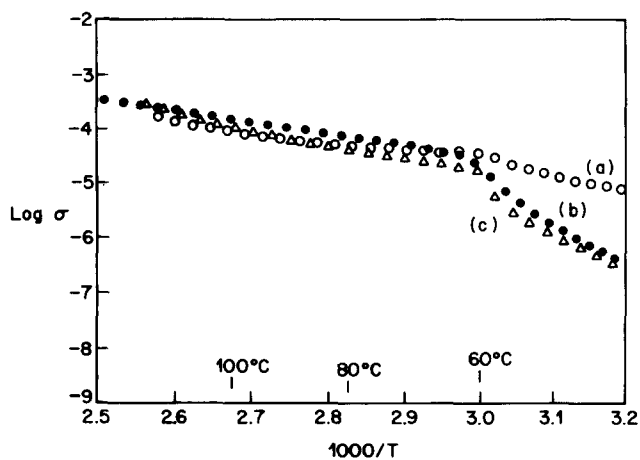


Figure 5 Arrhenius plots of conductivity of PEO- LiCF_3SO_3 complexes: effect of (a) carbon black; (b) salt alone; (c) carbon black and crown ether

Samples of PEO containing LiBF_4 in the ratio of 4.5:1 monomer units to salt, and each containing 10 times, by weight, either microcrystalline cellulose (1–2 μm particle size) or silica gel (100–200 mesh) were prepared. There was no improvement in conductivity noted over that for the pure polymer-salt complex at the same polymer/salt ratio (Figure 4). A similar experiment was undertaken using PEO and LiCF_3SO_3 in the ratio of 10:1 with added carbon black (Norit A) at a level of 1/10 of the weight of the PEO. Experiments were done both with and without crown ether present. Again, no increase in conductivity was observed except at the low temperature end of the plot with carbon black alone. These data are summarized in Figure 5.

CONCLUSIONS

Three different approaches have been taken to enhance the ionic conductivity of solid polymer electrolytes. In the first instance some novel polymer types were examined including poly(vinyl acetate), a polyphosphinate and a crown ether containing polymer. While all exhibited significant ionic conductivity when complexed with lithium salts, the best result (about 10^{-3}Scm^{-1} , at room temperature) was obtained when the polymer-crown ether was combined with poly(vinylene carbonate).

Therefore, it seems that a ripe area for continued work would be combinations of polymers that work synergistically to bring about desirable electrical properties.

The second subject that was examined involved preparation of various polymer-salt complexes that did not include the alkali metal salts. Most work in the area of solid polymer electrolytes concentrates on alkali metals, particularly lithium. The reason for this is the great potential that is envisioned for thin film fast ion conductors in secondary lithium batteries. Other power sources have been neglected. However, some interest has been awakened recently in the alkaline earths and in silver and mercury. In this work we have reported our results in the case of the latter two metal complexes with PEO. The materials prepared had reasonable conductivities; however, how much of the current was carried by the cation relative to the anion is still open to question.

The final area of this research included looking at what effect the addition of certain insoluble additives had on the electrical properties of polymeric fast ion conductors. Previous workers had found that α -alumina and silica enhanced the conductivity of the inorganic lithium ion conductor, LiI. This led us to try silica gel, carbon black and microcrystalline cellulose in polymer-salt complexes to see if any improvements could be found. In the experiments performed no enhancement of electrical properties was noted. Thus, we believe that insoluble additives will not be useful except, perhaps, to change the mechanical properties of the polymeric electrolytes.

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