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Polymeric Electrolytes for Ambient Temperature Lithium Batteries: Final Report

G.C. Farrington

September 1987

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**POLYMERIC ELECTROLYTES FOR
AMBIENT TEMPERATURE LITHIUM BATTERIES**

Final Report

September 1987

by

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SUMMARY

During this reporting period a number of novel solid polymer electrolytes formed by salts of multivalent cations and poly(ethylene oxide) [PEO] have been prepared and characterized. These materials are of interest not only because of their potential ionic conductivities, but also because some of them may have electronic conductivity and oxidizing power which would be useful for novel electrode materials in all-solid-state batteries.

Two broad classes of materials were investigated: PEO solutions of Zn(II), Cd(II), and Pb(II), all of which are potential electrolytes for solid-state batteries, and PEO solutions of transition metal salts, which are of interest as possible cathode materials. Mixed compositions containing both divalent cations and lithium ions were also prepared.

Electrolytes formed with small, highly-polarizing ions, such as Mg(II) and Ca(II), are essentially pure anion conductors. Electrolytes containing Zn(II) behave similarly, unless they are hydrated, in which case the Zn(II) ions are quite mobile. Electrolytes formed with larger, more polarizable cations, such as Pb(II) and Cd(II), conduct both anions and cations. Solutions of salts of transition metal cations form a third group of electrolytes. Of the electrolytes investigated so far, those formed with Ni(II) salts are the most unusual. It appears as if the transport number of Ni^{++} and the electrolyte conductivity can be greatly enhanced by controlling the hydration and dehydration of the polymer.

revised: 7/28/87

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I. INTRODUCTION

Since Wright et al. [1] and Armand [2] demonstrated that solutions of alkali metal salts in PEO have significant ionic conductivities, there has been considerable interest in the potential use of these materials as solid electrolytes in solid-state batteries. Previous investigations have principally focussed on PEO electrolytes that conduct lithium ions, because of the attractiveness of Li in lightweight, high specific energy electrodes.

It is now well-established that, in fact, many different ionic salts dissolve in PEO to form solid polymer electrolytes. Recent work has shown that PEO dissolves a variety of halides of divalent cations and that many of these polymeric electrolytes have appreciable ionic conductivities [3-7]. This work is, in part, based on earlier reports of James et al. [8,9] who showed that the divalent halides of Zn, Co, Fe, and Cu dissolve in poly(propylene oxide) and Blumber et al. [10, 9] who prepared complexes of CdCl_2 and HgCl_2 with PEO.

All of these investigations make it clear that the electrochemical properties of PEO electrolytes are more closely related to those of nonaqueous organic electrolytes than to crystalline solid electrolytes. Like liquid electrolytes, PEO dissolves a wide variety of ionic salts, and many of the solutions have significant transport numbers for both anions and cations. PEO electrolytes just happen to behave physically like solids. The electrochemistry and potential applications of these new electrolytes have received relatively little investigation. Yet, it is clear that they are unusual materials with properties in between those of truly liquid and truly solid electrolytes.

Most existing battery technologies are based on the use of liquid electrolytes or solid electrolytes that are cation conductors. Aqueous liquid electrolytes have only a small range of electrochemical stability, which precludes their use in high-specific-energy batteries. Nonaqueous electrolytes are more stable towards highly reactive electrodes, but their complex interfacial electrokinetics complicates their use in rechargeable cells. Solid electrolytes are generally far more stable than liquid electrolytes, but they typically conduct only a few ions,

suffer from low conductivities at moderate temperatures, and are difficult to successfully fabricate into electrochemical cells.

Solid polymer electrolytes based on PEO as a 'solvent' appear to be intriguing materials that combine many of the advantages of the more traditional liquid and solid electrolytes. Like nonaqueous and solid electrolytes, they are stable enough to permit the use of highly reactive anodes and cathodes. But, unlike inorganic solid electrolytes, they are relatively easy to fabricate and form interfaces with solid electrode materials that withstand electrochemical cycling without loss of electrode/electrolyte contact.

The first applications of PEO electrolytes that have been proposed are rather traditional, (i.e.) PEO-based solution of Li salts as a Li^+ conductor in a Li-anode cell. The cathode is a heterogeneous mixture of an oxidizing agent, such as TiS_2 or V_6O_{13} and polymer electrolyte. Efforts to develop this cell into a commercial battery are underway in a number of laboratories around the world and in the United States. It should be emphasized that PEO-based batteries use conventional reactants and are capable of very high specific energies. In this way they differ from most of the so-called, polymer batteries that have received extensive publicity over the past several years. For example, it has been widely proposed to use polyacetylene, an electronically conductive polymer, as the oxidant and reductant in a rechargeable battery. Unfortunately, the polyacetylene available to date is quite unstable and is not capable of high specific energy applications. In fact, none of the battery designs that use electronically conductive polymers as electrodes has yet been shown to have an energy density or specific energy comparable to the PEO system.

In spite of the attractiveness of the Li-based PEO battery, it is a technology that is closely related to more traditional battery designs. However, for some time it has been clear that PEO-based electrolytes might be much more versatile and make it possible to construct electrochemical cells that are very different from those traditionally proposed. For example, one characteristic of PEO electrolytes that is unusual and has not been exploited technologically is the ability of certain PEO electrolyte compositions to behave as nearly-pure anion conductors. It should be possible to exploit this property in a number of novel electrochemical cells that use high-energy-density reactants linked by fast

anion transport. Another unusual characteristic of PEO as a 'solvent' is the possibility of using it to dissolve salts of transition metal cations. It is reasonable to expect that some of the resulting solutions will combine fast anion transport with reasonable electronic conductivity and oxidizing power. Mixed electrolytes of this sort are intriguing alternate anodes and cathodes for all-polymer batteries.

Fig. 1: Novel Battery Based on Solid Anion Conductor.

All of these new PEO-based electrolytes are similar in that they are formed with salts of di- and tri-valent cations. Materials of this sort received very little attention before this program was initiated. The objective of this project is to explore a number of unconventional electrode and electrolyte possibilities made possible by the use of PEO as a 'solid electrochemical solvent' for salts of multivalent cations. Of particular interest are electrolytes that are pure anion conductors and solutions of multivalent transition metal cations.

We have succeeded in preparing and characterizing a wide variety of new electrolyte and electrode materials using PEO to dissolve salts of multivalent cations. One group of new electrolytes, formed with salts of Mg(II) and Ca(II) , are essentially pure anion conductors, which may make it possible to operate unusual electrochemical cells using Mg or Ca (or possibly Al) as high energy density anode materials. Such a cell (Fig. 1) would use a PEO solution of, for example, MgCl_2 , to separate a composite anode formed from PEO electrolyte, Mg , and MgCl_2 , from a composite cathode, which would be similar to the anode but would have, for example, a $\text{Co(III)}/\text{Co(II)}$ chloride couple as the oxidant. Although many other oxidant couples are available, the cobalt couple is very attractive because of its high oxidation potential. The two electrodes would be linked by anion transport in the electrolyte.

Electrochemical cells of this type present an intriguing alternative to cells containing lithium as an anode material. Lithium is almost universally used as a high-energy density anode because it is reasonably stable in nonaqueous solvents and its salts are quite soluble in them. The salts of alternate anodes, such as Mg and Ca, are generally insoluble in the same electrolytes, so these anode materials have received relatively little attention. Yet, a soluble anion conductor might make it possible to use Mg, Ca, and Al as anodes, and thus avoid problems posed by the cost and scarcity of lithium.

A number of PEO electrolytes that are conductors of divalent cations, including Cd(II), Pb(II), and perhaps Zn(II) were formed. Representatives of another group of PEO-based electrolytes that are not only ionic conductors but also electronic conductors were prepared. These mixed electrolytes are formed by dissolving salts of transition metals, such as Ni, Mn, and Co, in PEO. Several of these materials are virtually pure anion conductors, yet the presence of the transition metal cations gives them electronic conductivity and oxidizing power. The divalent cation conductors might be used as electrolytes for novel solid-state batteries based on Cd, Pb, and Zn anodes, materials which have been used extensively with aqueous electrolytes but essentially never with solid electrolytes. The mixed ionic/electronic conductors are interesting as potential homogeneous polymer cathodes.

Two broad classes of electrolytes are discussed in this report: PEO solutions of Zn(II), Cd(II), and Pb(II), all of which are conductors of divalent cations, and PEO solutions of transition metal salts. Mixed compositions containing both divalent cations and lithium ions as well as pure anion conductors, were prepared. The monovalent/divalent cation conductors are not discussed here nor are the pure anion conductors based on solutions of alkaline earth ions because they were described in several previous reports listed later in this document.

All of the new electrolytes were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), variable-temperature microscopy, UV-visible spectroscopy, complex ac impedance analysis, and dc polarization studies in order to characterize their composition, stability, crystallinity, hydration/dehydration reactions, conductivity, and transport properties.

• II. SAMPLE PREPARATION

With the exception of the Pb(II) electrolytes, all of the PEO electrolytes discussed in this report were prepared by solution casting from a mixed ethanol/acetonitrile solvent. The salts were first dissolved in ethanol and PEO was dissolved in acetonitrile. Since lead salts are insoluble in ethanol, DMSO was used instead of ethanol. The solutions were then mixed and cast. After the solvent evaporated, the resulting films were dried under vacuum at 120-130°C.

Electrolytes of NiBr₂ dissolved in PEO were prepared by solution casting as previously described. As cast, the samples were green. After the films were heated to 140°C in vacuum to remove residual solvent, their color changed from green to brown.

In the remainder of this report, the following terms will be used to denote the origins of various samples: 'as cast' denotes a sample that has been cast and then de-solvated at room temperature in a desiccator; 'as cast and dried' means the sample was cast and de-solvated by slow heating to 140°C in vacuum or dry gas; 'modified' means the sample was heated to 140°C, cooled to room temperature, hydrated in moist gas, and then dehydrated by heating to 140°C in a flow of dry argon or nitrogen.

III. DISCUSSION OF RESULTS

III.1 Electrolytes Containing Zn(II), Cd(II), and Pb(II): Electrolytes containing ZnX₂, in which X is Cl, Br, I, and ClO₄, were prepared and studied over a wide range of composition, typically from ZnX₂·(PEO)₄ to ZnX₂·(PEO)₃₀. Fig. 2 shows typical plots of the ionic conductivities of ZnX₂·(PEO)_n as a function of composition. The conductivities of PEO solutions of LiCF₃SO₃ and MgCl₂ are shown for comparison. The best ionic conductors of each anion type are ZnCl₂·(PEO)₂₄, ZnBr₂·(PEO)₂₀, ZnI₂·(PEO)₁₆, and Zn(ClO₄)₂·(PEO)₂₀. Of these, ZnI₂·(PEO)₁₆ has the highest conductivity, 3.6×10^{-4} (ohm-cm)⁻¹ at 140°C.

Most of the PEO-based electrolytes are complex mixtures of several phases and compositions. The relative fraction of each constituent depends on the type of salt dissolved, its gross concentration, the thermal history of the electrolyte, and the temperature. Analysis by optical microscopy shows that most electrolytes below about 65°C consist of mixtures of spherulitic crystalline regions separated by amorphous solutions of salt in PEO. Ionic conductivity occurs principally in the amorphous regions.

DSC studies of the ZnX_2 compositions indicate a close relationship between their ionic conductivity and morphology. Lower temperatures favor the crystallization of specific PEO-salt complexes and of unreacted PEO, and higher temperatures produce an increase in the fraction of the amorphous, conducting materials. In most systems, if the polymer electrolyte is heated to about 100°C and then immediately cooled, the high-temperature, amorphous electrolyte can be quenched and the crystallization of poorly-conducting crystalline complexes are suppressed. This produces a metastable electrolyte that is highly conductive at room temperature.

Transport number measurements show that dry ZnX_2 electrolytes are essentially pure anion conductors. They behave similarly to PEO solutions of $Mg(II)$ salts. The divalent cations are apparently trapped in strong electrostatic bonds with the ether linkages on the polymer chains. However, ZnX_2 electrolytes that have been prepared from hydrated salts have been reported to have transport numbers for $Zn(II)$ as high as 0.9.

PEO electrolytes containing $Cd(II)$ ions were also prepared and characterized. These tend to be rather good conductors of cations. For example, the transport number of $Cd(II)$ in $CdBr_2 \cdot (PEO)_8$ is about 0.8 at 140°C and nearly 1 at 150°C. To the best of our knowledge, it is the only PEO electrolyte that is virtually a pure cation conductor at this temperature.

PEO also forms complexes with PbX_2 salts, where X is Cl, Br, and I. Compositions of $PbBr_2 \cdot (PEO)_n$ (n is 8-30), $PbI_2 \cdot (PEO)_n$ (n is 6-40), and $PbCl_2 \cdot (PEO)_{16}$ were prepared and characterized. In general, these materials are thermally stable up to about 300°C in vacuum or inert gas. They absorb moisture at room temperature, but the reaction is completely reversible on

heating in vacuum or dry gas at 140°C. As with the Zn(II) electrolytes, the specific compositions with the highest conductivities vary with the anion. Fig. 3 shows the relationship between composition and conductivity for the $\text{PbBr}_2 \cdot (\text{PEO})_n$ group of electrolytes. Of the three electrolytes containing Pb halides studied in this work, those formed with PbBr_2 have the highest conductivities, as shown in Fig. 4.

Like the PEO electrolytes containing Cd(II), those formed with Pb(II) salts are reasonably good conductors of Pb(II). Transport number measurements were made at 140°C using complex ac impedance analysis and non-blocking Pb electrodes. The results show that the transport number of Pb(II) is in the range of 0.6-0.7 under these conditions. Separate dc analysis with Pb electrodes found a transport number for Pb(II) of 0.6-0.7 over a potential range of 10-100 mV.

III.2 Electrolytes Containing Transition Metal Cations: PEO solutions of salts of transition metal cations were quite surprising because electrolytes containing salts of Ni(II) appears to activate the transport of the cation by a careful process of hydration and dehydration carried out after an electrolyte film has been cast. This result was completely unexpected.

Sample Characterization: Polymer film conductivities were measured in two ways. In the first, a sample of polymer film was sandwiched between blocking Pt electrodes and the complex impedance/admittance spectrum of the cell recorded from 10^2 to 10^6 Hz. The second method used non-blocking Ni electrodes and complex impedance/admittance measurements over the frequency range of 10^{-2} to 10^6 Hz. The values of bulk conductivity determined were the same with either type of electrode, but the use of Ni electrodes made it possible to estimate the Ni^{2+} transport number.

Thermogravimetric Analysis: A typical TGA trace for $(\text{PEO})_8\text{NiBr}_2$ is shown in Fig. 5. During the initial heating of a freshly prepared film, there was a gradual loss in weight between room temperature and 80°C but no further weight loss before heating was discontinued at 200°C. When the sample was then cooled in dry nitrogen and re-heated, the low-temperature weight loss observed during the first heating did not re-appear, and the sample weight was stable until decomposition commenced around 330°C.

TGA also showed that sample films rapidly hydrate when exposed to water vapor at room temperature. For example, when a sample of $(\text{PEO})_8\text{NiBr}_2$ was allowed to hydrate in moist air for 24 hours at room temperature, it absorbed about 30 molecules of water per $(\text{PEO})_8\text{NiBr}_2$ unit. When the sample was then exposed to flowing dry nitrogen at room temperature for 24 hours, it lost all but 6 molecules of water per $(\text{PEO})_8\text{NiBr}_2$. The remainder of the water could be removed by heating to 140°C .

These results clearly indicate that there are at least two types of water in hydrated samples of $(\text{PEO})_8\text{NiBr}_2$. The tightly bound water, which can only be removed upon heating to 140°C , corresponds to water in the hexaaquo complex $(\text{PEO})_8\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$. The existence of this complex was confirmed by optical spectroscopy measurements (discussed in a later section of this report).

The results obtained by TGA measurements on as-cast samples of $(\text{PEO})_8\text{NiBr}_2$ and on rehydrated samples are clearly different. The TGA trace for an as-cast sample is shown in Fig. 6A, and that for the same sample after it had been purposely hydrated is shown in Fig. 6B. As Fig. 6A shows, the trace water that remains in the films after initial casting from non-aqueous solution is readily lost by 80°C , but the water in a sample that has been purposely-hydrated (Fig. 6B) is not lost until 130°C - 140°C . Therefore it appears that water is bound more tightly in the hydrated sample. Note, however, that such a sample returns to its original dried weight. Hence purposeful hydration appears to be completely reversible upon heating.

Optical Microscopy: Samples of $(\text{PEO})_8\text{NiBr}_2$ with different water contents have very different appearances. A sample that had been exposed to moist air for 24 hours and therefore contained a large excess of water [composition of $(\text{PEO})_8\text{NiBr}_2 \cdot x\text{H}_2\text{O}$, $x \sim 30$] was nearly colorless. A sample that had been exposed to moist air and then dried in flowing nitrogen at room temperature has a composition of about $(\text{PEO})_8\text{NiBr}_2 \cdot x\text{H}_2\text{O}$, $x \sim 6$ and is light green in color, characteristic of hexa-aquo $\text{Ni}(\text{II})$. Finally, light green samples of $(\text{PEO})_8\text{NiBr}_2 \cdot x\text{H}_2\text{O}$, $x \sim 6$ that were completely dehydrated underwent a sharp color change from green to brown between 128 - 130°C .

The degree of crystallinity, as qualitatively observed with cross-polarized light, also changes with temperature. At room temperature, samples with compositions of about $(\text{PEO})_8\text{NiBr}_2 \cdot x\text{H}_2\text{O}$ are highly crystalline. Around 60°C , they become far less crystalline, because the crystalline PEO phase melts. Then, during complete dehydration at $128\text{--}130^\circ\text{C}$, the samples appear to become more crystalline again as the color changes from green to brown.

Conductivity Measurements: The conductivity of $(\text{PEO})_8\text{NiBr}_2$ during heating and cooling is shown in Fig. 7. Before the data were taken, the sample was dried *in situ* at 140°C . The data represent the bulk conductivity and were the same whether they were measured with blocking (Pt) or non-blocking (Ni) electrodes. The conductivity knee around 60°C is a feature generally expected in these materials because of melting of the uncomplexed PEO. In addition, the conductivity undergoes an unexpected dip around 130°C and then gradually increases at higher temperatures. DSC analysis shows a marked endotherm around 130°C , optical microscopy shows an apparent increase in transmission under cross-polarized light due to perhaps liquid crystal formation at the same temperature, and the color of hydrated samples changes abruptly from green to brown from 128 to 130°C .

The state of hydration strongly influences the conductivity of $(\text{PEO})_8\text{NiBr}_2$ (see Fig. 8) which illustrates in a qualitative way the correlation between conductivity and degree of hydration. The dry sample is brown. Upon exposure to water vapor, it first changes to dark green and then to progressively lighter and lighter green as the water content of the sample increases. The green color is characteristic of the $\text{Ni(II)} \cdot 6\text{H}_2\text{O}$ complex. As the water content of the sample increases, its conductivity at 23°C increases by about ten orders of magnitude as the dry sample becomes fully hydrated.

This increase in conductivity upon hydration is not surprising and, in fact, has been observed with many other PEO electrolytes. What is quite surprising is the effect that the process of hydration and dehydration has on the Ni^{2+} transport number in $(\text{PEO})_8\text{NiBr}_2$. For the purposes of the following discussion, 'as-cast/dried' describes a sample that has been freshly prepared, never purposely exposed to water vapor, and dried at 140°C for 4 hours. The sample called 'modified' is a sample that has been prepared, dried at 140°C and purposely

hydrated at room temperature in moist Ar flow to a composition of about $(\text{PEO})_8\text{NiBr}_2 \cdot x\text{H}_2\text{O}$ ($x \sim 30$). Then it is dehydrated, first at room temperature overnight by stream of dry argon, followed by slow heating to 140°C . So far as it can be determined, the modified samples are as dry as the as-cast samples; even after they had been thoroughly hydrated before drying.

As Fig. 9 shows, there is a dramatic difference between the conductivities of the as-cast/dried and modified samples at temperatures above 60°C . The most intriguing change is that the modified samples are not only more conductive than the as-cast/dried samples, they also have much higher transport numbers for Ni^{2+} .

Transport Number Measurements: The transport numbers of Ni^{2+} in as-cast/dried and modified samples were estimated using complex ac impedance analysis and dc polarization with non-blocking Ni electrodes. It is quite clear that the Ni^{2+} transport number in the as-cast/dried sample is quite low, even at 140°C , whereas the modified sample shows appreciable Ni^{2+} transport even at 123°C . The ac results were confirmed by dc polarization studies. Table 1 summarizes the transport number for as-cast/dried and modified samples during ac and dc polarization. The data show that the as-cast/dried film is almost a pure anion conductor, while the modified sample has considerable Ni^{2+} mobility. This effect was reproducible on every sample.

There was no evidence that the films, once modified, revert to their as-cast/dried state. The hydration/dehydration process can be repeated on a modified sample but no further change in the conduction properties is observed.

IV. CONCLUDING REMARKS

The properties of the various materials prepared in this study clearly demonstrate the wide variety of transport properties of PEO-based electrolytes. Electrolytes formed with small, highly polarizing ions, such as $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$, are essentially pure anion conductors. The cations are presumably trapped in strong electrostatic interactions with the ether oxygens on the polymer chains. Electrolytes containing $\text{Zn}(\text{II})$ behave similarly, unless they are hydrated, in

which case the Zn(II) ions are liberated from strong ion/chain interaction and are quite mobile.

Electrolytes formed with larger, more polarizable cations, such as Pb(II) and Cd(II), conduct both anions and cations. These divalent cations form much weaker associations with the polymer chains than do Mg(II) and Ca(II). The electrolytes are predominantly cation conductors above about 130°C, and at lower temperatures they are simultaneous anion and cation conductors.

Solutions of salts of transition metal cations form a third group of electrolytes. Of the two types investigated so far, the electrolytes formed with Ni(II) salts are the most unusual. It appears as if the transport number of Ni²⁺ can be switched on and off, or at least enhanced, by a process of controlled hydration and dehydration. According to UV-visible spectra the hydration peaks disappear when the electrolyte is heated to 140°C. The same process also produces a dramatic increase in conductivity above 60°C. For example, an as cast/dried film has a conductivity of about 10⁻⁶ (ohm-cm)⁻¹ at 150°C. After modification by hydration and dehydration, its conductivity increases to about 10⁻³ (ohm-cm)⁻¹ at the same temperature. This increase in conductivity is far more than would be expected from a simple increase in the Ni²⁺ transport number.

It is not fully understood why these changes in conductivity and transport number occur. An extensive study of the optical spectroscopy of the complexes is underway at this time. Preliminary measurements of the UV-visible spectroscopy of (PEO)₈NiBr₂ show that during hydration water preferentially complexes with Ni(II) to form the hexa-aquo complex. TGA data indicate that essentially all of the Ni(II) forms the complex. Presumably, the complex formation liberates the Ni(II) from coordination with the ether groups in the PEO chains and from anion complexation. The structure of the electrolyte must be very different after dehydration than before, since there is such a large increase in conductivity. Other techniques are being utilized to characterize this difference more thoroughly.

In spite of the unclear origins of the unusual conduction properties of (PEO)₈NiBr₂, it is obvious that PEO electrolytes formed with transition metal salts are an interesting family of materials. Spectroscopy should be a powerful

tool for investigating the local ion/ion and ion/PEO interactions which influence their conductivity and ion transport behavior. It also appears possible to prepare PEO solutions of ions with mixed valence states. Of particular interest are solutions of Co(II) and similar ions that have high oxidation states, such as Co(III), that are vigorous oxidants. It may be possible to form these species by direct electrochemical oxidation in the polymer solution. The resulting PEO electrolytes should then have both ionic conductivity and electronic conductivity, as well as being relatively powerful oxidants. These materials should be of interest as novel homogeneous cathodes for all-solid-state polymer batteries.

V. PRESENTATIONS AND PUBLICATIONS

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3. "Thermal and Transport Properties of First Transition Series Divalent Cation Salts with PEO Complexes," R. Huq and G.C. Farrington, Electrochemical Society Fall Meeting, San Diego, October 1986.
4. "Characterization of Polymer Electrolytes: Poly(ethylene oxide)/Transition Metal Salts," H. Yang, G.C. Farrington, and A.R. McGhie, Proc. 15th NATAS Conf., Cincinnati, September 1986, 447.
5. "Ionically-Conductive Polymers," G.C. Farrington and R. Huq, presented at the Workshop on Conducting Polymers, Sintra, Portugal, July 1986.
6. "Poly(ethylene oxide) Complexes of Lead Halides: New Polymeric Conductors of Pb(II) ," R. Huq, G. Chiodelli, P. Ferloni, A. Magistris, and G.C. Farrington, **J. Electrochem. Soc.**, **134** (1987) 364.

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Table 1

Ni⁺⁺Transference Number: (PEO)₈NiBr₂ Ni Electrodes

AC Impedance Measurements

T(°C)	t _{Ni2+}	Condition
123	3.2x10 ⁻²	dried
145	9.9x10 ⁻²	as-cast/dried film
151	1.5x10 ⁻¹	
87	0.21	
100	0.24	
125	0.41	
127	0.45	modified
130	0.55	
140	0.61	
142	0.66	
95	0.22	
104	0.29	repeat
119	0.33	after seven days
140	0.62	
141	0.64	

DC Measurements

T(°C)	Potential mV	t _{Ni2+}	
120	100	0.54	
123	100	0.57	
123	250	0.63	modified
123	300	0.65	
123	350	0.66	
123	400	0.66	

Figure Captions

- Figure 2. Ionic conductivity as a function of temperature for electrolytes of ZnCl_2 , ZnBr_2 , ZnI_2 , and $\text{Zn}(\text{ClO}_4)_2$ dissolved in PEO. Data for electrolytes containing LiCF_3SO_3 and MgCl_2 are included for comparison.
- Figure 3. Isotherm of $\log(\text{conductivity})$ as a function of composition for $\text{PbBr}_2 \cdot (\text{PEO})_n$ for the temperature range of 80 to 200°C.
- Figure 4. Conductivity of $\text{PbBr}_2 \cdot (\text{PEO})_8$, $\text{PbI}_2 \cdot (\text{PEO})_{24}$, $\text{MgCl}_2 \cdot (\text{PEO})_{16}$, and $\text{LiCF}_3\text{SO}_3 \cdot (\text{PEO})_9$
- Figure 5. Typical TGA trace for $(\text{PEO})_8\text{NiBr}_2$ at 5°C/min. during heating from room temperature to the decomposition temperature.
- Figure 6. A) TGA trace for as-cast, dried sample of $(\text{PEO})_8\text{NiBr}_2$; B) TGA trace for same sample after hydration and dehydration at room temperature for 24 hours under dry nitrogen flow.
- Figure 7. Conductivity of $(\text{PEO})_8\text{NiBr}_2$, as-cast/dried sample during heating and cooling.
- Figure 8. Change of conductivity with hydration time at room temperature for $(\text{PEO})_8\text{NiBr}_2$.
- Figure 9. Conductivity of as-cast/dried sample of $(\text{PEO})_8\text{NiBr}_2(0)$ and modified sample (X).

Figure 2

Figure 3

Figure 4

Figure 5

- A. AS CAST DRY SAMPLE
B. HYDRATED & DEHYDRATED
FOR 24hrs UNDER
N₂ FLOW

Figure 6

Figure 7

Figure 8

Figure 9

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