Polyphosphazene Electrolytes for Lithium Batteries

Gholamabbas Nazri,* Donald M. MacArthur, and John F. Ogara

General Motors Research Laboratories, Warren, Michigan 48090-9055

Received January 11, 1989

Poly([2-(2-methoxyethoxy)ethoxy]phosphazene), MEEP, doped with lithium salts, is a useful electrolyte for a "solid-state" lithium battery. We report characterization of MEEP by conductivity measurements, NMR and FTIR spectroscopy techniques, and observations of electrochemical activity related to lithium batteries. The ^{31}P, ^{13}C, and ^{1}H NMR spectra show characteristic peaks related to polyphosphazene with etheric side chain with minor cross-linking. FTIR spectra show that lithium is weakly associated with ethoxide groups of the polymer and resides in an energy well ~0.045 eV deep. The conductivity of undoped MEEP was found to be $(2.5–5.0) \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ and of doped MEEP, at the level of 0.17 mol of $LiCF_3SO_3$ per mole of monomer equivalent, to be $\sim 2.5 \times 10^{-5}$, at ambient temperature. Cyclic voltammetry shows inefficiencies in the lithium redox reaction. The operation of $Li/MEEP(LiClO_4)/TiS_2$ cell at 30 $\mu A/cm^2$ charge and 50 $\mu A/cm^2$ on discharge indicates polarization during deintercalation of lithium from TiS_2.

Introduction

Lithium is a high specific energy material, and its use in batteries is attractive. High-energy, primary lithium batteries are widely available today in small sizes. Secondary, i.e., rechargeable, lithium batteries are the next frontier. A lithium battery using a solid electrolyte is particularly attractive since it offers new opportunities in design that are not available with liquid electrolytes.

There has been recent interest in solid materials that support fast ion transport, i.e., "good" electrolytes. These materials fall into broad classes, crystalline, glassy, or polymeric. Soft polymer materials are particularly attractive because of their elastomeric property (here considered as compliance to the shape of solid electrodes) and the (anticipated) ease of preparation. Fenton and coauthors[1] first described poly(ethylene oxide) (PEO) electrolytes. In 1979, Armand and coauthors[2] showed that PEO containing a dissolved lithium salt is a moderately good lithium ion conductor and noted the potential use in lithium batteries. Since then, research activities reported in the literature[3-12] have indicated major efforts on batteries. Optimistically, it has been proposed that these solid-state lithium cells could be scaled to a size suitable for electric vehicles.[4,5,8] Small cells using PEO electrolytes have been described. Tonge and Shriver[13] have reviewed the properties of PEO type electrolytes.

More recent reports have shown that polyphosphazenes, in which the —P=N— backbone supports ethoxides on side chains, also provide good lithium conductivity when doped with lithium salts.[14,15] Nazri and Meibuhr[16] have described some structure and conductivity measurements on such materials. Conductivity measurements have indicated that poly([2-(2-methoxyethoxy)ethoxy]phosphazene), MEEP, has a maximum conductivity at ambient temperature of about $10^{-4}\ \Omega^{-1}\ cm^{-1}$ while PEO has a conductivity, also at ambient temperature, of about $10^{-7}\ \Omega^{-1}\ cm^{-1}$ at the optimum salt concentration.[17] (A very recent report[18] has shown that oxymethylene-linked PEO may provide a conductivity of $\sim 5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 25 °C.) The salt concentration for maximum conductivity is not well-known; however, indications are that it occurs at one lithium from the salt to eight ethoxide oxygens in PEO[17] and one to sixteen for MEEP.[16] Communications describing observations of cells using MEEP electrolyte have appeared recently.[17,19] However, the stability of MEEP in contact with a lithium electrode is far from clear. This work describes the performance of a Li/TiS_2 cell using MEEP as the electrolyte and examine the interfacial resistance of lithium/MEEP interface as a function of time. The structure of MEEP was analyzed from NMR and IR spectroscopy.

Experimental Section

Preparation of MEEP. MEEP was prepared following the procedures published by Allcock and co-workers.[15] The trimer, 1, (Ethyl Corp.) was sublimed once before use. Polymerization was carried out in an evacuated, sealed glass tube at 250 °C for

---

(1) Fenton, B. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589.

(2) Armand, M.; Chabagno, J. M.; Duclot, M. In *Fast Ion Transport in Solids*; Vashishita, P., Mundy, J. N., Shenoy, G. K., Eds.; North-Holland: Amsterdam, 1979; p 131.

(3) Hooper, A.; North, J. M. *Solid State Ionics* **1983**, *9/10*, 1161.

(4) Sequeira, C. A. C.; North, J. M.; Hooper, A. *Solid State Ionics* **1984**, *13*, 175.

(5) Menetrier, M.; Levasseur, A; Delmas, C.; Audebert, J. F.; Hagenmuller, P. *Solid State Ionics* **1984**, *14*, 257.

(6) Ricoux, P. A.; Gauthier, J. M.; Armand, M. B. Communication EII-2 in EVS7 meeting, June, 1984.

(7) Gauthier, M.; Fauteux, D.; Vassort, G.; Belanger, A.; Duval, M.; Ricoux, P.; Chabagno, J. M.; Muller, D.; Rigaud, P.; Armand, M. B.; Deroo, D. *J. Electrochem. Soc.* **1985**, *132*, 1333; *J. Power Sources* **1985**, *14*, 23.

(8) Vassort, G.; Ricoux, P.; Gauthier, M.; Harvey, P. E.; Brochu, F. Characterization of Ambient Temperature Batteries with Polyether Based Electrolytes. Presented at the third Lithium Battery meeting, Kyoto, Japan, June, 1986.

(9) Gauthier, M.; Belanger, A.; Fauteux, D.; Duval, M.; Kapfer, B.; Robitaille, M.; Bellemare, R.; Giguere, Y. Preliminary Results on Scale-up Polymer Electrolyte Lithium Batteries: 10Wh Polyethylene Oxide Based Cells Operating at 80 to 100 °C (ref 8).

(10) Kapfer, B.; Gauthier, M.; Vassort, G.; Harvey, P. E.; Brochu, F. Assembly and Preliminary Results of a Polymer Electrolyte Solid-State Battery (1Wh) at Room Temperature. Presented at The Power Sources Conference, Brighton, England, September, 1986.

(11) Gauthier, M.; Belanger, A.; Fauteux, D.; Harvey, P. E.; Kapfer, B.; Duval, M.; Robitaille, C.; Vassort, G.; Muller, D.; Chabagno, J. M.; Ricoux, P. Recent Progress in the Development of Rechargeable Lithium Batteries Based on Polymer Electrolytes. Electrochem. Soc. meeting San Diego, October, 1986.

(12) Fauteux, D.; Gauthier, M. Lithium Electrode Behavior in Poly(ethylene oxide) Lithium Perchlorate Electrolytes (ref 11).

(13) Tonge, J. S.; Shriver, D. F. Solvent-Free Polymer Electrolytes. To be published as a chapter in *Polymers for Electronic Applications*, Lai, J. H., Ed.; CRC Press: Boca Raton, FL.

(14) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.*, **1984**, *106*, 6854.

(15) Allcock, H. R.; Austin, P. E.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

(16) Nazri, G. A.; Meibuhr, S. G. submitted to *J. Electrochem. Soc.*

(17) Abraham, K. M.; Alamgir, M.; Perrotti, S. J. *J. Electrochem. Soc.* **1988**, *135*, 535.

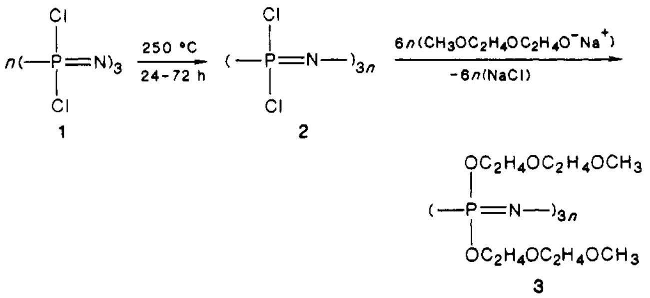
(18) Nicholas, C. V.; Wilson, D. T.; Booth, C.; Giles, J. R. M. Proc. Int. Symp. on Polymer Electrolytes, St. Andrews, Scotland, June 1987.

(19) Semkow, K. W.; Sammells, A. F. *J. Electrochem. Soc.* **1987**, *134*, 766.

(20) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(21) Palmer, D. N.; Brule, J. E.; Alexander, M. G.; O'Neill, J. K.; Miller, J. M. The Characteristics of Thin Film Poly(2[2-methoxyethoxy)ethoxy]phosphazene)-Lithium Aprotic Salt Ion Complexes as Electrolytes for Li Sec. Cell Applications. Paper presented at the Phosphazene Chemistry Workshop, Annapolis, MD, November, 1985.

0897-4756/89/2801-0370$01.50/0



$$n(-\mathrm{PCl_2}{=}\mathrm{N})_3 \ (\mathbf{1}) \xrightarrow[24-72\ \mathrm{h}]{250\ °\mathrm{C}} (-\mathrm{PCl_2}{=}\mathrm{N}-)_{3n} \ (\mathbf{2}) \xrightarrow[-6n(\mathrm{NaCl})]{6n(\mathrm{CH_3OC_2H_4OC_2H_4O^-Na^+})} (-\mathrm{P}(\mathrm{OC_2H_4OC_2H_4OCH_3})_2{=}\mathrm{N}-)_{3n} \ (\mathbf{3})$$

24–72 h. The chlorinated polymer, **2**, was separated from unreacted trimer by sublimation at 70 °C for 12 h. Polymer yield was 35–50%. The polymer was taken up in toluene that had been doubly distilled in contact with sodium under a nitrogen atmosphere. The polymer (5 g) was reacted with twice the stoichiometric amount of 2-(2-methoxyethoxy)ethanol in 1000 mL of toluene with 5 g of Na and 3 g of tetrabutylammonium bromide by refluxing under nitrogen at 110 °C for 24 h. The solvent was removed under vacuum, and MEEP, **3**, taken up into distilled water for removal of salt by dialysis, which was carried out over 5–7 days. The MEEP was dried under vacuum of at least 10^{-6} Torr before storage in a drybox. Lithium salts were predried before use and added to the MEEP by taking up into toluene or THF/toluene mixtures, which were subsequently evaporated.

Characterization of MEEP. NMR spectroscopy of MEEP dissolved in deuterated tetrahydrofuran (THF) was performed on an IBM NR270AF spectrometer operating at 270, 67.9, and 109.3 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Solid-state NMR experiments were performed on an IBM WP200SY spectrometer at 81 MHz for ^{31}P with a Doty Scientific magic-angle-spinning multinuclear probe. ^{31}P chemical shifts were referenced to 85% H_3PO_4 at 0 ppm and are reported taking downfield shifts as positive.

The MEEP and MEEP containing $LiCF_3SO_3$ salt were dissolved in toluene and cast as thin films on gold-plated stainless steel substrates. The spectra were collected by using an IBM-98 FT-IR spectrometer with the sample under vacuum. In the mid-IR region, an MCT nitrogen-cooled detector and a KBr beam splitter were used. A bare gold-plated stainless steel substrate was used as a reference in this work. The far-IR spectra were collected by using a DTGS detector, Mylar beam splitter, and mercury lamp light source. The spectra were collected in the reflection–absorption mode at 65° angle of incidence. The IR spectra in mid-IR and far-IR were collected at 320 and 640 scans, respectively.

The conductivity was measured by using a Solartron Model 1250 frequency analyzer and Model 1286 electrochemical interface instrument. The amplitude of the sign wave perturbation was 40 mV. The frequency range was 1 Hz to 60 kHz. Inside the drybox, about 0.1 g of MEEP was placed on a gold-plated nickel electrode held in a polypropylene cell case. Figure 1 shows the cell in cross section. The MEEP was confined by a polypropylene spacer, 0.78 mm thick, with a 1.15-cm-diameter opening providing a cross-sectional area for current transport of 1 cm^2. It was allowed to flow under its own weight to fill the space. This took a period of 12–24 h. The other gold electrode was then added. A spring provided compression on the electrodes, and the spacer prevented it from squeezing out the MEEP.

The MEEP was doped by dissolving a small quantity in toluene or toluene/THF and adding the predetermined amount of $LiCF_3SO_3$ or $LiClO_4$ to the solution. The solvent was then evaporated. Conductivity measurements of the doped MEEP were carried out as for the undoped material except that one electrode in contact with the MEEP was a lithium disk (Foote Mineral Company, lithium foil, 99.8%) supported on the gold-plated contact (Figure 1). This provided one electrode able to exchange lithium with the lithium ions in the polymer electrolyte.

Cell Construction and Testing. Lithium cells were constructed as above but by using TiS_2 as the counter electrode to the lithium. Alfa Products TiS_2 powder (99.5%) was compressed at 3.6×10^3 kg/cm^2 into a disk on the gold-plated current collector directly inside the cell case. The MEEP was placed on the pellet and confined by the washer. The lithium disk was added, and the gold plated electrode placed against this.

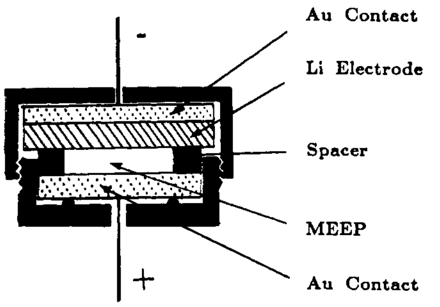


Figure 1. Schematic of cell construction showing arrangement for conductivity and voltammetry experiments. The bottom electrode was TiS_2 for cell tests.

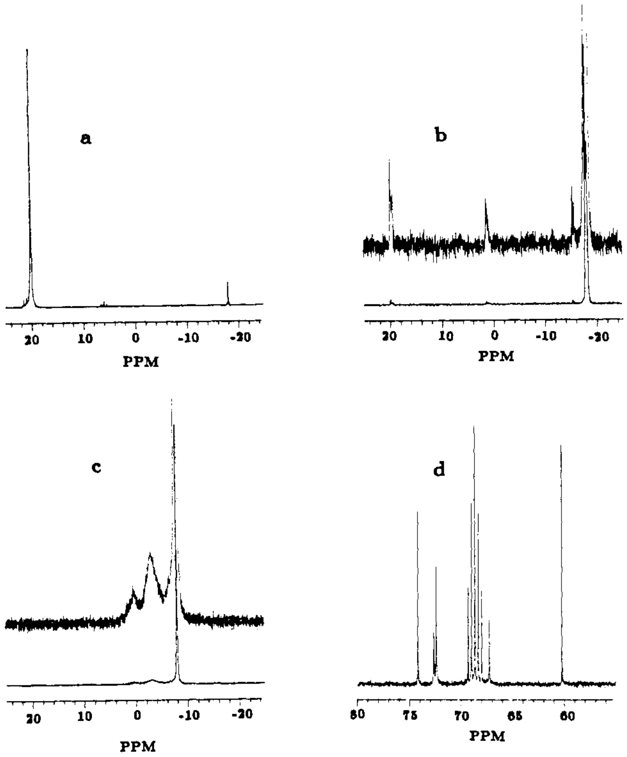


Figure 2. NMR results of ^{31}P for (a) the trimer in D-THF, (b) the chlorinated polymer in the solid state, (c) the substituted polymer in *d*-THF and, (d) ^{13}C for the substituted polymer in *d*-THF.

A PAR Model 173 potentiostat operating in the galvanostatic mode was used to cycle the cell. Cycle tests were run using cyclic voltammetry software on an Apple IIe computer with an Adalab interface.

Results and Discussion

MEEP Characterization. The MEEP had the appearance of a viscous gum. Yield from the starting material was ~25%. The polymerization reaction was difficult to control and required experience in carrying it out for the correct time period. Heating for too long a period resulted in cross-linking of the polymer. We find that a polymerization time of 48 h at 250 °C is optimal.

Figure 2 shows the ^{31}P NMR spectra of (a) the starting trimer material, (b) the chlorinated polyphosphazene in the solid state, (c) MEEP, and (d) the ^{13}C spectrum of MEEP. Analysis of the chlorinated polyphosphazene was hindered by trace water in the solvent, and therefore solid-state methods were used. The solid-state magic-angle-spinning direct-polarization NMR spectrum of the chorinated polyphosphazene, in addition to the main peak at −18 ppm, shows two lower intensity peaks at 20 and −15.5 ppm. The first peak is assigned to residual starting

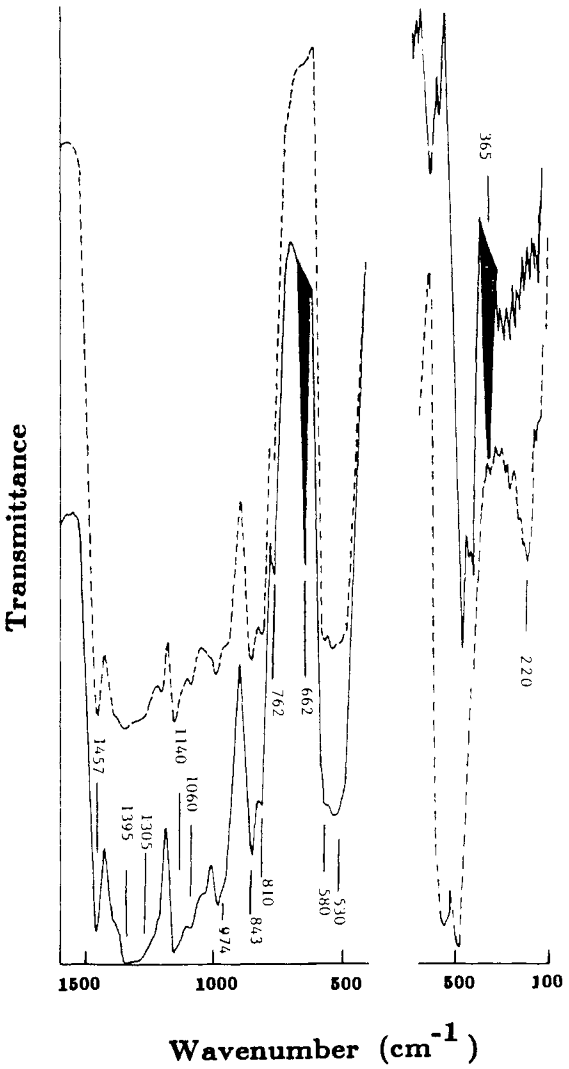


Figure 3. FT-IR spectra of MEEP containing $LiCF_3SO_3$ (solid line) and of undoped MEEP (dashed line) in mid-IR and far-IR regions.

material; the second peak may come from hydrolysis, end groups, or cross-links. The small peak at 1 ppm is assigned to a spinning sideband from the main peak. Analysis of the MEEP was accomplished by solution-state NMR. The major peak in the ^{31}P spectrum is associated with RO-P-OR units. In addition, two small broad peaks are observed at approximately −3.5 and 0 ppm. The peak at −3.5 ppm is assigned to hydroxide-substituted phosphorus, HO-P-OR, which may rearrange to the RO-P(O)-NH- form.[15,22] Integration reveals 17% of the repeat units are of this structure. The 0 ppm resonance may also be associated with these species or possibly end groups. Assuming a cyclic trimer group is on each end of the polymer chain, integration yields a molecular weight of 2.55×10^4 for this material. The ^{13}C spectrum of MEEP shows the expected chemical shifts of C(5) 65.0, C(4) 70.4, C(3) 70.3, C(2) 72.0, and C(1) 58.8 ppm, where $—N{=}P—[OC(5)H_2C(4)H_2O\text{-}C(3)H_2C(2)H_2OC(1)H_3]_2$.

The FT-IR spectra of a thin film of MEEP and of MEEP containing $LiCF_3SO_3$, cast on a gold substrate, are shown in Figure 3. The IR spectra did not show any residual water in the polymer. The IR band assignments are shown in Table I. The low-energy skeletal motion of PNP at 762 cm^{-1} is the indication of high flexibility of the backbone. This is related to the low glass transition temperature for this polymer (−80 °C). The POC deformation band occurs at 974 cm^{-1} and POC bending mode at 1305 cm^{-1}. The COC bending mode observed at 1060 cm^{-1} is similar to the COC bending mode of noncyclic etheric compounds. The IR bands at 530 and 580 are due to OCC bending mode and the vibrational modes related to SO_3 group. Some differences were observed in the far-IR spectra of MEEP and salt-doped MEEP. A new IR band was seen at 365 cm^{-1} (4×10^{-6} eV), which does not correspond to any absorption bands of MEEP or $LiCF_3SO_3$. Although the energy of this band is close to the band found in case of lithium ion trapped in crown ether cage, the definitive assignment of this band needs more work. We speculate that this may be due to the interaction of lithium ion with the ether chains attached to the MEEP backbone. The energy of this band is low, which can be interpreted in terms of the ionic nature of this interaction. This energy determines the mobility of the lithium ions trapped in the polymer, but the ionic interaction also will control the solubility of the salt in the polymer. A low energy of interaction provides the desired high mobility of the salt constituent ions in the polymer but is likely to result in the undesired low solubility of the salt. We are using far-IR spectroscopy to obtain the optimum mobility-solubility relationship for polymer salt doped electrolyte. It is also interesting to see that the skeletal motion of the ether side chain group, shown at 220 cm^{-1}, disappeared from the IR spectrum of the polymer containing lithium salt. We observed similar behavior for PEO and PEO doped with lithium salt.[23]

Table I. IR Band Assignments of MEEP and MEEP + $LiCF_3SO_3$

IR band posn, cm^{-1}	assignment
220	$(-CH_2CH_2O-)_n$ skeletal
360	Li^+-O
530	SO_3 and OCC bending
580	SO_3
662	CF deformation
762	PNP skeletal
810	PNP skeletal
845	PNP skeletal
974	POC deformation and COC bending
1060	POC, SO stretch
1140	CO stretch
1305	POC bend and P=N stretch
1395	OCH_2 bend symmetric
1457	OCH_3 bend symmetric

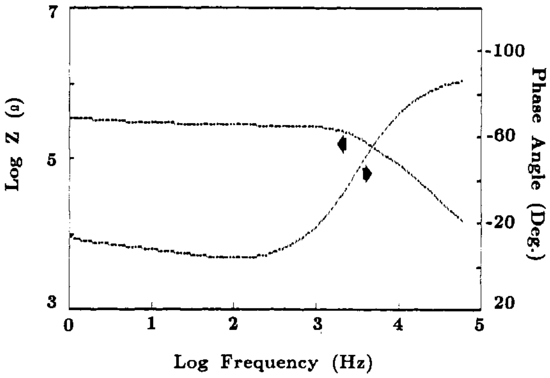


Figure 4. Impedance spectrum of undoped MEEP with Au_2 electrodes. The MEEP thickness was 0.8 mm and the area 1 cm^2.

The impedance spectrum, using gold electrodes, of MEEP with no lithium salt present is shown in Figure 4.

---

(22) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* 1982, *129*, 1694.

(23) Nazri, G.; MacArthur, D. M., to be published.

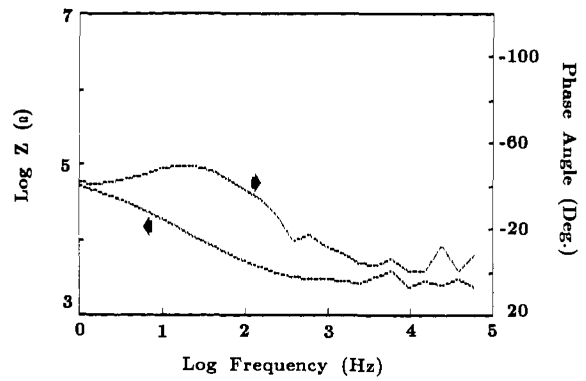


Figure 5. Impedance spectrum for doped MEEP, 0.17 mol of $LiCF_3SO_3$ per monomer unit.

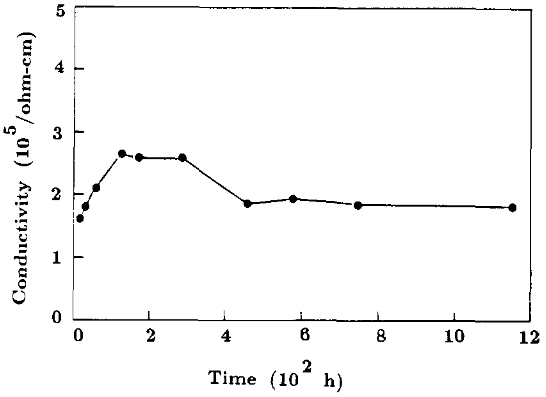


Figure 6. Conductivity at 1 kHz of the doped MEEP as a function of time on an open circuit stand.

The background conductivity, possibly electronic, is measured in this experiment. The spectrum shows low impedance and a 90° phase angle at high frequencies. At low frequencies and continuing out to about 1000 Hz, the impedance decreases only slightly and the phase angle approaches zero. The spectrum is characteristic of a simple parallel resistance–capacitance circuit and is the expected result. As a convenient reference frequency we take 1000 Hz; a frequency low enough to avoid double-layer capacitance effects and sufficiently high to avoid complications from concentration polarization of the electrodes. At 1000 Hz, a resistance of 250 kΩ was found, which translates to a conductivity of $3.0 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Palmer and coauthors[24] have reported a value of 2.8×10^{-6}. On several samples, we have observed resistance values between 200 and 400 kΩ. This value is a bit low for a good insulator. It is possible that the conductivity is slightly ionic from a trace of NaCl remaining in the MEEP. This residual conductivity is sufficiently low to not be a problem for self-discharge of a cell, but residual chloride in the electrolyte could have a deleterious chemical effect on the lithium electrode. Chemical analysis by X-ray fluorescence for chloride in the MEEP identified a very low chlorine content (0.005 wt %).

Figure 5 shows the impedance spectrum of a Li/MEEP($LiCF_3SO_3$)/Au cell with the MEEP doped at the level of 0.17 mol of lithium (trifluoromethyl)sulfonate per mole of MEEP monomer equivalent, $[(CH_3OC_2H_4OC_2H_4O)_2PN = 283.3]$, a ratio of 1 lithium to 12 ethoxide oxygens. (This concentration is near the maximum conductivity value observed by Blonsky and coauthors[5] using silver (trifluoromethyl)sulfonate at 70 °C.) The spectrum in the figure was obtained after the sample was 1 month on test and is typical of results obtained over a 2-month period. At 1000 Hz, the resistance found in the example was 38.6 kΩ cm, which gives an ionic conductivity of $2.6 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$. Figure 6 shows the conductivity found for this cell as a function of time on stand in the drybox. For the first 100 h, there was a decrease in resistivity observed. The reason for this is not known at the present time. A possible explanation is improved contact at the MEEP/electrode interface. The conductivity remained stable for more than 2 months, indicating that no highly resistive film formed at the lithium electrode interface during this period. If water were present or if there were a reaction between lithium and MEEP, a high-resistance film at the interface would be expected.

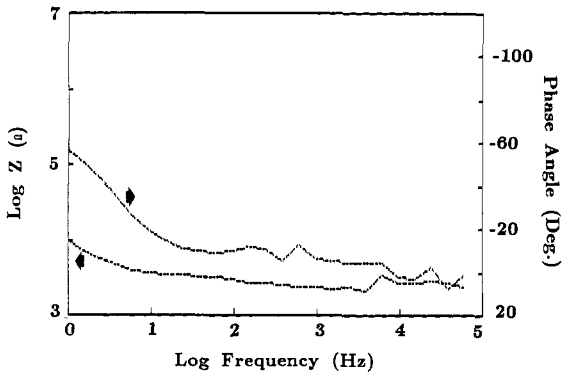


Figure 7. Impedance spectrum of doped MEEP at 60 °C.

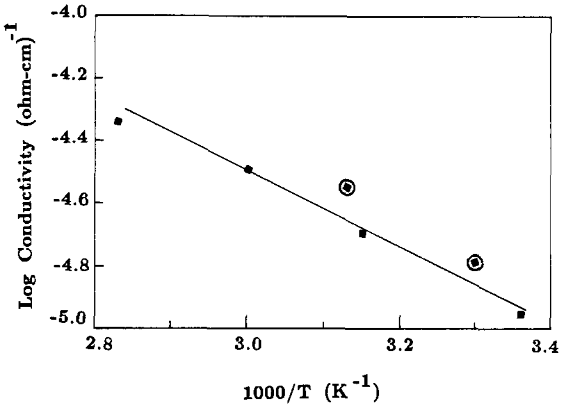


Figure 8. The log conductivity of the doped MEEP as a function of reciprocal temperature. Circled data points were obtained while decreasing the temperature.

Figure 7 shows, for another cell of the same construction, an impedance spectrum obtained at 60 °C. This spectrum may be compared to that in Figure 5 to note the effect of temperature. Figure 8 is a plot of log conductivity (at 1000 Hz) vs reciprocal temperature. Shown are data obtained on increasing and decreasing the temperature. The values obtained on decreasing the temperature are slightly higher, but the agreement is good indicating no major structural change of the sample within the temperature range examined. The relationship was found to be linear over the temperature range 25–80 °C. The slope of the plot ($2.8 \times 10^3\ K^{-1}$) provides an activation energy of 0.24 eV.

A model[22] frequently cited for ionic conductivity in these polymeric materials, the Vogel–Tamman–Fulcher model, is of the form

$$\sigma = AT^{1/2} \exp(-B/(T - T_0))$$

where σ is conductivity, A and T_0 are constants, B is closely related to activation energy, and T is the temperature. Within the range of our experiments, we cannot conclude that this model is more accurate than the Arrhenius relationship.

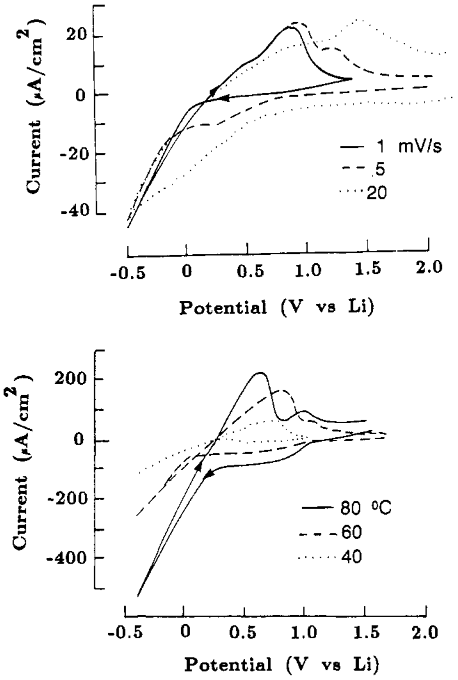


Figure 9. Cyclic voltammetry of the Au electrode vs Li as the counter electrode with doped MEEP as the electrolyte. Top curves show scans at 25 °C for different scan rates. Bottom curves show scans at 5 mV/s for different temperatures.

Table II. Resistance Values Obtained from Voltammetry Compared to Ac Impedance Values

temp, °C	slope of the I/E curve through $I = 0$, 10^3 Ω	impedance at 1000 Hz, 10^3 Ω
25	25	6.9
40	6.4	3.8
60	2.1	2.4
80	1.4	1.7

In Figure 9, potential scans of the cell, with the gold electrode as the working electrode, are shown. Reduction (negative) currents are lithium electrodeposition and oxidation (positive) currents are stripping the lithium off the gold electrode. The upper curves show the effect of different scan rates from 1 to 20 mV/s at ambient temperature. The lower curves show the effect of temperature. Note the change in the current scale for these curves. The lithium electrode was both counter and reference electrode in these experiments; therefore, the effects of electrolyte resistance and lithium electrode polarization are included in the observations. The polarization effect is expected to be small; however, the IR component from the electrolyte distorts the curves significantly. In Table II we provide the calculated resistance obtained from the slope of the $I-V$ curve in the figure (through zero current and scanning in the positive direction) and compare it to the value obtained from the impedance spectrum. At temperatures >40 °C, the two resistance values agree, indicating small polarization effects and a large exchange current. At lower temperatures, the $I-V$ resistance value is greater than the impedance value, indicating that polarization effects are significant (but not large) in this temperature range.

Table III. Ratio of Oxidized Area to Reduced Area in Voltammetry Curves

sweep rate, mV/s	Q(ox)/W(red) T = 25 °C	T = 40 °C	T = 60 °C	T = 80 °C
1	0.43			
5	0.61	0.43	0.59	0.37
20	0.76			

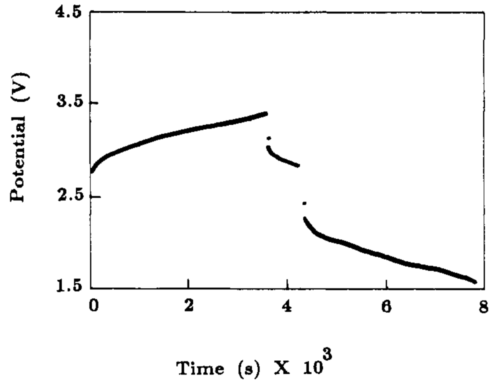


Figure 10. Cycle test of the Li/MEEP($LiCF_3SO_3$)/TiS_2 cell. Charge at 30 μA/cm² for 1 h, open circuit for 0.2 h, discharge at 50 μA/fcm² to 1.5-V cutoff.

Table III provides the areas under the curves that correspond to reduction and oxidation of lithium. The oxidation charge found (areas are proportional to charge) was less than the reduction charge. This result was unexpected and requires additional investigation. It suggests that either a reduction reaction other than lithium reduction occurred or the lithium was not completely oxidized back into solution.

Cell Tests. Figure 10 shows discharge and charge of a Li/MEEP($LiCF_3SO_3$)/TiS_2 cell. The charging current was 30 μA/cm² and the discharge was 50 μA/cm². The charge and discharge time was 1 h. The open circuit voltage after long term stand (>10 h) was 2.8–2.9 V. The midpoint of the charge and discharge occurred about 3.2 and 1.8 V, respectively. The cell operated at ~0.09 mW/cm² on discharge. Polarization of the electrodes was quite evident in these cells. Cells with a reference electrode indicated that much of the polarization occurred during the deintercalation of lithium from the TiS_2. It is known that the transference number of the anion is comparable to, or greater than, the transference number of Li^+ in these polymer electrolytes. The accumulation of anions at the electrode will lead to a high concentration of salt at the interface, which will lower conductivity of the electrolyte. It has been shown that polymers with high salt concentrations do have lower conductivity.[24]

Acknowledgment. We acknowledge Duward Shriver and Jim Tonge, Northwestern University, and Rafil Bashir, GM Research, for their assistance is preparative techniques. We thank Stephen Swarin and Patrick Hanley, GM Research, for chemical analyses.

Registry No. $LiCF_3SO_3$, 33454-82-9; $LiClO_4$, 7791-03-9.

---

(24) Blonsky, P. M. Ph.D. Dissertation, Chemistry Department, Northwestern University, 1986.