Highly Conductive PEO-like Polymer Electrolytes

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Polymer electrolyte membranes comprising poly(vinylidene fluoride)−hexafluoropropene (PVdF−HFP) copolymer plasticized with a solution of $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$, or $LiPF_6$ in oligomeric poly(ethylene glycol) dimethyl ethers (PEGDME, $M_w = 250$, 400, and 500) were prepared by hot-melt-rolling or solvent-casting techniques. Since the electrolytes containing PEGDME400 and PEGDME500 are "dry" with essentially no volatile components up to 150 °C, we have dubbed them PEO-like. Their thermal stability, mechanical strength, conductivity, electrochemical stability window, and Li/electrolyte interface stability were characterized. Plasticizing PVdF−HFP with the PEGDME/LiX solutions disordered the polymer structure leading to polymer electrolytes having lower crystallinity than the polymer host itself. The mechanical strength of the electrolyte membranes varied depending on the PVdF content. Tensile strength (stress) as high as 420 psi at an elongation-at-break value (strain) of 75% was observed. The conductivities of the electrolytes correlated with the molecular weights of PEGDME as well as the concentration of the Li salt, and most of the electrolytes prepared showed room-temperature conductivities of greater than 10^{-4} S/cm. The high room-temperature conductivity of these electrolytes compared to PEO-based electrolytes is attributed to the high mobility of the ionic charge carriers. The Li/electrolyte interface stability under open-circuit conditions was found to be good as assessed from the small change in the interfacial impedance for the measured case of the PVdF−PEGDME500−$LiN(SO_2CF_3)_2$ electrolyte. This electrolyte also showed oxidation stability up to 4.5V versus Li^+/Li on Al, Ni, and stainless steel (SS) and reduction stability down to 0.0V versus Li^+/Li on both Ni and SS. The applicability of these electrolytes in batteries was demonstrated by the fabrication and testing of Li/oxygen and Li/$LiMn_2O_4$ cells.

Introduction

Polymer electrolytes formed by encapsulating organic electrolyte solutions in polymer hosts have shown room-temperature conductivities of $>10^{-3}$ S/cm and have enabled the development of solid-state Li and Li ion batteries with performance reminiscent of their liquid electrolyte counterparts.[1] Polymers found to be useful to form such electrolytes include polyacrylonitrile (PAN), poly(vinyl chloride) (PVC), poly(vinyl sulfone) (PVS), poly(vinylpyrrolidinone) (PVP), poly(ethylene glycol diacrylate) (PEGDA), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride) (PVdF). As for the organic solvents, those having low molecular weights and high dielectric constants, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), *N*-methylpyrrolidinone (NMP), sulfolane (SL), and γ-butyrolactone (BL) are the usual choices. Low lattice energy Li salts (LiX) such as $LiPF_6$, $LiAsF_6$, and $LiN(SO_2CF_3)_2$ have been used to form the electrolyte solutions.

Our recent study[2] has revealed that PVdF−EC/PC−LiX polymer electrolytes lose solvent by evaporation when they are exposed to an open atmosphere. For example, an electrolyte containing 30 wt % (w/o) PVdF-30 w/o EC/30 w/o PC-10 w/o $LiN(SO_2CF_3)_2$ lost 12.3%, 42.0%, and 51.4% of its mass after being stored in a drybox ($T = \sim 25$ °C) for 1, 5, and 11 days, respectively. Solvent loss leaves an electrolyte not only with indeterminate composition but also with low ionic conductivity. We have found that this is a general behavior of polymer electrolytes containing low molecular weight solvents such as those mentioned above, although the extent to which solvent is lost varies from one electrolyte to the other. Solvent evaporation is of little concern for most practical use of these electrolytes since Li batteries are almost always hermetically sealed. An exception is the Li/O_2 polymer electrolyte battery[3] in which oxygen is accessed from the environment. For the practical implementation of this battery, a polymer electrolyte with high conductivity and little or no volatility is desired. The key to the development of such a polymer electrolyte is to identify an organic plasticizer solvent that has little or no volatility at ambient temperatures and to identify a polymer host in which a substantial amount of the organic solution can be incorporated.

Here, we report on a class of nonvolatile (dry) polymer electrolytes, obtained by plasticizing a PVdF−HFP (HFP = hexafluopropylene) copolymer with solutions of lithium salts in oligomeric poly(ethylene glycol) dimethyl ethers (PEGDME). The use of PEGDME to plasticize poly(ethylene oxide) (PEO)-based electrolytes was attempted before,[4,5] but the thermal properties of these polymer electrolytes, especially their volatility, were not

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(1) Alamgir, M.; Abraham, K. M. In *Lithium Batteries, New Materials, Developments and Perspectives*; Pistoia, G., Ed., Elsevier: Amsterdam, 1994; Chapter 3, Vol. 5.

(2) Jiang, Z.; Carroll, B.; Abraham, K. M. *Electrochim. Acta,* in press.

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studied. Furthermore, fine ceramic particles had to be added to the PEO-based electrolytes in order to achieve good mechanical strength.[5] Unlike those, the PEGDME plasticized PVdF−HFP-based electrolytes, reported for the first time here, have excellent mechanical strength and may be considered the long-sought room-temperature analogues of PEO-based electrolytes. They have very low volatility, good ambient-temperature conductivity, and excellent dimensional and electrochemical stability. The factors affecting the structure and conductivity of the electrolytes are discussed together with the performance of Li/O_2 and $Li/LiMn_2O_4$ battery cells.

Experimental Section

Reagent Sources and Purification. PVdF−HFP copolymer (Elf Atochem Kynar 2822 with PVdF to HFP molar ratio of about 88:12; denoted as PVdF2822) was dried under vacuum at 50 °C for 24 h. Both $LiSO_3CF_3$ (triflate) and $LiN(SO_2CF_3)_2$ (imide) were obtained from 3M and were dried under vacuum at 100 °C for 24 h before use. Poly(ethylene glycol) dimethyl ethers (PEGDME, Fluka) having the molecular weights of 250, 400, and 500 daltons were dried over 5 Å, activated molecular sieves. Dimethyl carbonate (DMC, Aldrich Chemical Co., 99%) was distilled before use. Ethylene carbonate (EC), propylene carbonate (PC) (Grant Chemical, 99.98% pure and battery grade), Li (Cyprus Foote Mineral Company), and $LiPF_6$ (Advance Research Chemicals, Inc.) were used as-received. All the experiments were carried out in a Vacuum Atmospheres Corp. drybox filled with argon.

Preparation of Polymer Electrolyte Films. The PVdF−PEGDME−LiX polymer electrolyte films were prepared using two methods. The $LiSO_3CF_3$ or $LiN(SO_2CF_3)_2$-containing electrolytes were prepared by rolling a hot precursor melt. In this procedure, a mixture of PVdF2822, PEGDME, and the Li salt were heated in a Pyrex bottle at 135 °C for 30−60 min. The resulting homogeneous, viscous solution was poured between two Teflon film-coated stainless steel plates, and rolled into thin membranes by passing the plates through two rollers. On cooling, dimensionally stable, free-standing electrolyte membranes, 100−200 μm thick, were formed. A few samples of electrolytes containing a solution of the Li imide in a 1:1 by weight mixture of EC and PC or EC and DMC were also prepared using this method.[2] The $LiPF_6$-containing electrolytes were prepared by a solvent-casting method. In a typical procedure, a mixture containing appropriate amounts of PVdF2822, PEGDME, and $LiPF_6$ was dissolved in tetrahydrofuran (THF) and the resulting solution was poured into a glass dish. A free-standing electrolyte film was formed when the THF was evaporated at room temperature. All electrolyte compositions are given as weight percent, denoted by a number preceding the electrolyte component.

Characterization of PVdF and the Electrolytes. X-ray diffraction patterns of PVdF2822 and the electrolytes were obtained with the aid of a Rigaku X-ray diffractometer using Cu Kα_1 radiation. The thermal stabilities of PVdF2822 and the polymer electrolytes were studied using a Perkin-Elmer thermal gravimetric analyzer (TGA) and a Perkin-Elmer differential scanning calorimeter (DSC). The freezing points of PEGDMEs were also measured using the DSC. Sealed SS (stainless steel) pans were used as sample containers for all DSC measurements. The mechanical strength of the polymer electrolytes was determined from stress−strain measurements using an Instron Model 4204 universal testing instrument. The tensile tester was equipped with a 20 lb load cell and interfaced to an IBM-compatible computer for data collection. The SPE samples having the dimensions of 1 in. × 6 in. were pulled at a constant rate of 2 in./min.

Ionic conductivity of the polymer electrolytes was determined from complex impedance spectra measured using an EG&G Princeton Applied Research (PAR Model 273) potentiostat/galvanostat in combination with an EG&G lock-in analyzer (Model 5208) in the frequency range of 0.1 Hz to 100 kHz. A conductivity cell containing two stainless steel blocking electrodes was used. The conductivities of the liquid electrolytes were also measured from impedance spectra. A Yellow Springs Instrument, Inc. model conductivity cell with a cell constant of about 1 was used. The cell constant was determined using a KCl conductivity standard solution purchased from Fischer Scientific.

The lithium ion transference numbers, T^+, of the electrolytes were measured by the technique described by Evans et al.[6] This method consists of measuring the resistance and the current across a symmetric Li/electrolyte/Li cell polarized by a dc voltage. The Li/electrolyte interfacial and electrolyte bulk resistances and the current are used to solve the expression for T^+ (see Results and Discussion). The Li/electrolyte/Li cells had areas of ~10 cm^2. The resistances were determined from the impedances of the cells measured in the same way as described earlier.

Cyclic voltammetric studies of the polymer electrolytes were carried out on several metal working electrodes in a three-electrode cell in which Li served as both the counter and the reference electrodes. A Solartron SI 1287 electrochemical interface was used to perform the voltammetric experiments. The stability of the Li/electrolyte interface was studied by monitoring the impedance of a Li/polymer electrolyte/Li cell stored at room temperature as a function of storage time.

Infrared spectra were recorded on a Nicolet Magna-IR 700 spectrometer with the sample sandwiched between KBr windows.

Viscosities of the plasticizer solvents and their $LiN(SO_2CF_3)_2$ solutions were measured with the aid of a Cannon-Fenske viscometer (Model 100, International Research Glassware). The temperature of the samples was maintained at 25 °C using a Haake E52 water bath. The kinematic viscosities (in centistokes) were obtained by multiplying the efflux time in seconds by the viscometer constant.

Evaluation of the Polymer Electrolytes in Li/Polymer Electrolyte/$LiMn_2O_4$ and Li/Polymer Electrolyte/Oxygen Cells. The applicability of the PVdF polymer electrolytes to batteries was studied in Li/polymer electrolyte/$LiMn_2O_4$ and Li/polymer electrolyte/oxygen cells. The $LiMn_2O_4$ composite electrodes for the former cells were prepared by pasting a slurry of spinel $LiMn_2O_4$, the polymer electrolyte and Chevron acetylene black, prepared in THF, onto an aluminum foil current collector. When the THF was evaporated at room temperature, $LiMn_2O_4$ electrodes having a composition of 50 w/o $LiMn_2O_4$−42 w/o polymer electrolyte−8 w/o carbon black were obtained. The spinel $LiMn_2O_4$ was prepared according to our recently reported procedure.[7] The carbon cathode for the Li/oxygen cell was fabricated by heating a 20 w/o Chevron carbon−80 w/o polymer electrolyte mixture at 135 °C and pressing it onto a Ni screen current collector. The Li/$LiMn_2O_4$ and Li/oxygen cells were fabricated as described in refs 7 and 3, respectively. The electrochemical performance of the cells was evaluated galvanostatically using an Arbin battery test system (Bryan, TX).

$$-\!\!\left[CH_2CF_2\right]_n\!\!- \qquad -\!\!\left[CH_2CF_2\right]_{0.88}\!\!-\!\!\left[CF_2CF(CF_3)\right]_{0.12} \qquad CH_3O-\!\!\left[CH_2CH_2O\right]_n\!\!-CH_3$$

I, PVdF II, PVdF-HFP III, PEGDME

Results and Discussion

Poly(vinylidene fluoride) (I) is a fluoropolymer that can be considered as being formed by replacing two of the hydrogens in polyethylene with fluorines. It is a chemically resistant polymer with good mechanical strength and has a relatively high dielectric constant (ϵ; ϵ = 7.2−13.5 versus 2.2−2.3 for polypropylene). Its copolymer with hexafluoropropylene has the structure II. The PEGDME plasticizers are oligomeric poly(ethylene glycol) dimethyl ethers of the general struc-

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(7) Jiang, Z.; Abraham, K. M. *J. Electrochem. Soc.* **1996**, *143*, 1591.

ture III where $n = 4.6$, 8, and 10.3 when the molecular weights are 250, 400, and 500 daltons, respectively.

The thermoplastic PVdF homopolymer melts between 160 and 170 °C, while the copolymers of PVdF and HFP are characterized by lower crystallinity, lower melting and glass transition temperatures, and higher solubility in organic solvents.[8] These properties make the copolymer a better host for forming polymer electrolytes.

Preparation of PVdF Polymer Electrolytes. PVdF−HFP polymer electrolytes plasticized with solutions of Li salts in organic carbonates had been prepared before using either a solvent-casting[9] or a hot-melt-rolling method.[2,10] The latter method used in our laboratory[2,10] appears to be simpler and faster and is especially suitable for the continuous, large-scale production of electrolyte membranes, provided that the electrolyte is stable at the extrusion temperature.

In the present study, Li imide- and Li triflate-containing electrolytes with PEGDME plasticizers were prepared by rolling. At 135 °C, it took 30−60 min to form a homogeneous melt containing PVdF2822, PEGDME, and the Li salt suitable for the extrusion of thin films. The time it took to form this melt is rather short when compared to the 2 days it took to obtain a homogeneous PEO−imide−PEGDME melt at 120−130 °C.[5] These PEO electrolyte films were reported to be very sticky and difficult to handle,[11] and a ceramic filler such as γ-LiAlO$_2$ had to be added to improve their mechanical strength.[5,11] On the contrary, the PVdF electrolytes we have prepared exhibited good homogeneity and excellent dimensional stability and were easy to handle. Thus, from the point of view of processibility, PVdF2822 offers significant advantages over PEO as a polymer host for the PEGDME plasticizer.

To gain an understanding of their processibility by hot-rolling, PVdF−PEGDME−LiX electrolytes with a variety of compositions were prepared and their homogeneity, dimensional stability, and ability to be rolled into thin films from precursor melts were compared. The results are illustrated by means of triangular composition diagrams. For example, Figure 1 illustrates the composition diagram for the electrolytes containing PVdF2822, PEGDME500, and the imide. How this diagram gives the composition of an electrolyte is illustrated with the 30 PVdF2822-60 PEGDME-10 imide electrolyte. The intercepts on the three axes of the three arrows directed from the point representing this electrolyte composition gives the weight percent of PVdF-2822, PEGDME, and imide. All the compositions shown in Figure 1 gave homogeneous solutions at 135 °C. However, those containing >35 PVdF2822 were too viscous to be cast into thin films, and those containing <22.5 PVdF2822 yielded films that were too fragile to be useful as separators in practical batteries. The compositions containing 22.5−35 PVdF2822 in combination with 5−25 w/o imide, represented by the shaded area, gave the best electrolytes, capable of forming free-standing, 75−100 μm thick, membranes. As will be seen from the mechanical properties discussed later, electrolytes thinner than these can be prepared, but we made no attempt in this work to optimize electrolyte thickness, and, consequently, very thin electrolytes were not prepared.

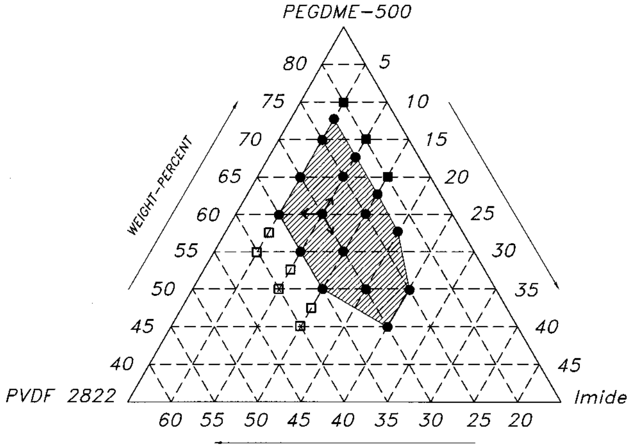

Figure 1. Composition diagram for polymer electrolytes containing PVdF2822, PEGDME500, and the imide in various ratios by weight. (●) dimensionally stable electrolyte, (■) mechanically fragile electrolyte, and (□ highly viscous solution which cannot be cast into thin films.

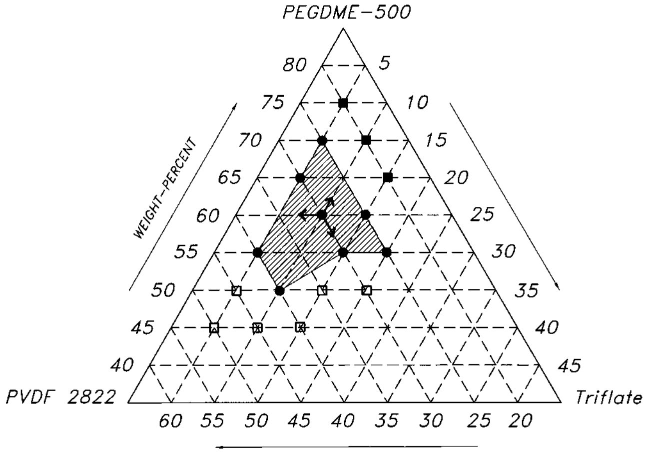

Figure 2. Composition diagram for the polymer electrolytes containing PVdF2822, PEGDME500, and LiCF$_3$SO$_3$ in various ratios by weight. (●) dimensionally stable electrolyte, (■) mechanically fragile electrolyte, (□) highly viscous solution which cannot be cast into thin films.

Figure 2 displays the composition diagram for polymer electrolytes composed of PVdF2822, PEGDME500, and LiSO$_3$CF$_3$. Since LiSO$_3$CF$_3$ has a relatively low molecular weight (Mw = 156), precursor mixtures containing 35−45 w/o PVdF and 15−20 w/o LiSO$_3$CF$_3$ produced melts with high concentrations of the salt and too viscous to be processed into thin films. The dimensionally stable electrolytes prepared with this salt are those falling in the shaded area in Figure 2.

The preparation of LiPF$_6$-containing electrolytes by melt-rolling was attempted without success; the precursor mixture decomposed when heated to 135 °C. The problem was traced to PEGDME. It was observed that heating a mixture of LiPF$_6$ and PEGDME500 at 135 °C yielded a dark-brown solution unlike when a solution of LiPF$_6$ in an EC/PC mixture was heated at the same temperature.[2] Apparently, LiPF$_6$ catalyzes the decomposition of PEGDME. In fact, this reaction of the PEGDME/LiPF$_6$ solution resembles the LiAsF$_6$-cata-

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(8) Gozdz, A. S.; Tarascon, J. M.; Schmutz, C. N.; Warren, P. C.; Gebizlioglu, O. S.; Shokoohi, F. K. Abstract No. 117, *Extended Abstracts*, Vol. 94−2, ECS Fall Meeting, Miami, FL; Oct 1994.

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(10) Choe, H. S.; Giaccai, J.; Alamgir, M.; Abraham, K. M. *Electrochim. Acta* **1995**, *40*, 2289.

(11) Borghini, M. C.; Mastroagostino, M.; Passerrini, S.; Scrosati, B. *J. Electrochem. Soc.* **1995**, *142*, 2118.

lyzed decomposition of diethyl ether we have reported elsewhere.[12] In the latter case, the decomposition was initiated by AsF_5 produced from the dissociation of $LiAsF_6$, and the products were ethylene and intractable As-containing materials. A similar mechanism involving PF_5 is possible here since it is known that $LiPF_6$ dissociates into LiF and PF_5. The most probable reactions leading to the decomposition are those shown in eqs 1−3, where R_2O stands for PEGDME. The ionic

$$LiPF_6 \leftrightarrow LiF + PF_5 \qquad (1)$$

$$R_2O + PF_5 \rightarrow R_2O{:}PF_5 \qquad (2)$$

$$R_2O{:}PF_5 + PF_5 \rightarrow [R_2O - PF_4]^+PF_6^- \qquad (3)$$

complex formed in reaction 3 decomposes to alkenes, HF, and phosphorus-containing products. Indeed, reactions similar to those in eqs 1−3 may be a general occurrence in solutions of alkali-metal salts derived from a Lewis acid and an alkali-metal halide, such as $LiBF_4$, $LiPF_6$, and $LiAsF_6$, in ether solvents. The Lewis basicity of the solvent is apparently important to promote this reaction since EC/PC−$LiPF_6$ solutions do not decompose even when heated to 180 °C. The reason appears to be that the carbonate solvents EC and PC are less basic than ethers, and as a result they do not take part in a reaction of the type shown in eq 2 which promotes the dissociation of $LiPF_6$ into PF_5 and LiF.

Dimensionally stable $LiPF_6$-containing electrolytes were prepared by solvent-casting using THF as the solvent vehicle. A typical electrolyte composition prepared was 30 PVdF2822−60 PEGDME500−10 $LiPF_6$, a colorless transparent film which showed no change after 48 h at 70 °C.

Polymer Electrolyte Structure. Depicted in Figure 3a,b are the XRD patterns for PVdF2822 and the 30 PVdF2822−60PEGDME500−10 imide electrolyte, respectively. Both the PVdF and the polymer electrolyte are poorly crystalline materials, but the PVdF exhibits an additional loss of its crystallinity upon incorporation of the solution with the result that the electrolyte is even more disordered than the polymer. Apparently PVdF−HFP undergoes structural reorganizations to acquire conformations suitable for accommodating the PEGDME/LiX solution. The differential scanning calorimetric (DSC) data (Figure 4) appears to substantiate this. It shows several endothermic transitions, most probably related to the melting of the PVdF associated with several different polymer electrolyte aggregates.

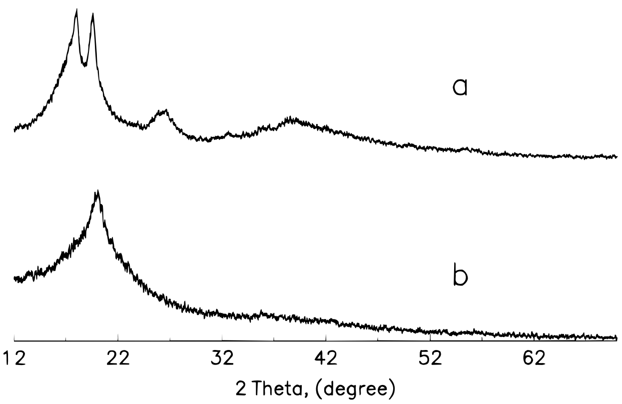

Figure 3. XRD patterns of (a) PVdF2822 and (b) 30 PVdF2822−60 PEGDME500−10-imide.

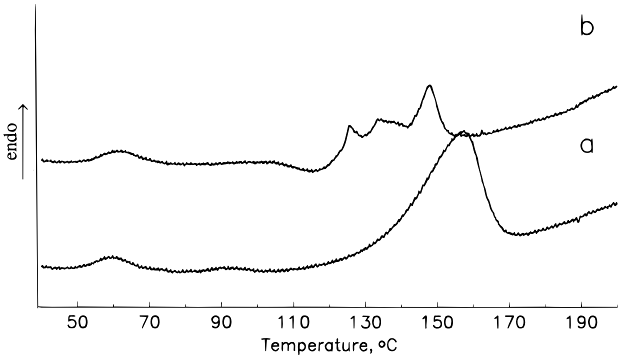

Figure 4. DSC plots for (a) PVdF2822 and (b) 30 PVdF2822−60 PEGDME500−10-imide.

Figure 4a,b display the DSC plots for PVdF2822 and the 30 PVdF2822−60 PEGDME500−10 imide electrolyte, respectively. The former shows a broad endothermic peak between 130 and 170 °C, which is attributed to the melting of PVdF2822. The polymer electrolyte, on the other hand, begins to melt at 125 °C, and shows a broad endotherm with at least three peaks between 125 and 150 °C. We speculate that the peaks may correspond to the melting of different polymer electrolyte aggregates formed when the electrolyte is extruded from the precursor solution. The small endothermic peak at around 60 °C shown in Figure 4a,b is ascribed to the melting of some low-molecular-weight component of PVdF2822.

Both the X-ray data, which show a decrease in the polymer crystallinity, and the DSC results, which suggest the formation of several polymer electrolyte aggregates, are consistent with the formation of gels by absorption of the organic electrolyte solutions into the polymer structure. A structural model consistent with experimental results is one in which the PEGDME complexes with the Li salt and this complex in turn interacts with the PVdF chain, probably through interactions between the fluorines and Li^+. Infrared spectra of PEGDME400 and its Li salt solutions have indicated a broadening of the C−O stretching vibrational peaks in PEGDME at about 1100 cm^{-1}, probably indicative of $C{-}O \rightarrow Li^+$ complexation. The C−H stretching vibrations of the CH_2 groups in PEGDME400-Li salt complexes at 2920 cm^{-1} appeared to be split also. In a previous publication[13] we showed that the (PEO)−$LiClO_4$ complexes could be distinguished from PEO by means of their IR spectra. Despite the close structural similarities between PEGDME and PEO, such clear distinction is lacking in the PEGDME−LiX liquid complexes. Further evidence for the structural model discussed above comes from the freezing points of PEGDMEs and their electrolytes, determined from the DSC cooling curves. The data are summarized in Table 1. The higher freezing point of the PEGDME500/$LiN(SO_2CF_3)_2$ solution is most probably indicative of a complex formed between this ether and the Li salt. The freezing of the PEGDME in the polymer electrolyte occurs at a lower temperature than either the neat

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(12) Abraham, K. M.; Goldman, J. L.; Natwig, D. L. *J. Electrochem. Soc.* **1982**, *129*, 2404.

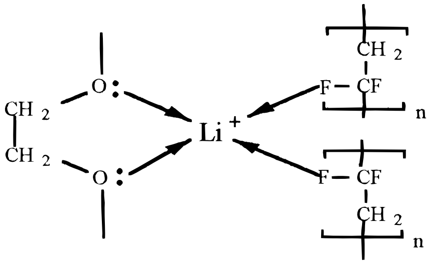
(13) Abraham, K. M.; Alamgir, M. *Chem. Mater.* **1991**, *3*, 345.

Table 1. Freezing Point of PEGDME, PEGDME/Imide Solutions, and Polymer Electrolytes Determined from DSC Curves

sample	freezing point (°C)
PEGDME500	20.8
PEGDME500/imide[a] (6:1 in weight)	26.5
30 w/o PVdF2822−60 w/o PEGDME500−10 w/o imide	10.0
PEGDME400	8.0
PEGDME400/imide (6:1 in weight)	8.0
30 w/o PVdF2822−60 w/o PEGDME400−10 w/o imide	−3.0
PEGDME250	−19.5
PEGDME250/imide (6:1 in weight)	−17.0
30 w/o PVdF2822−60 w/o PEGDME250/10 w/o imide	<−50[b]

[a] Imide is $LiN(SO_2CF_3)_2$. [b] Measurements made down to −50 °C only.

solvent or the corresponding liquid electrolyte, and it suggests that there are strong interactions between the polymer and the PEGDME/$LiN(SO_2CF_3)_2$ complex. The PEGDME to Li salt mole ratio in the electrolyte with a 6:1 by weight ether to salt is about 3.5:1, and the oxygen to Li^+ mole ratio at this salt concentration is about 36:1. Clearly, there is sufficient amount of oxygen in PEGDME to fully complex Li^+ with a coordination number of 4. How the $LiN(SO_2CF_3)_2$/PEGDME complex interacts with the PVdF polymer chain is not clear. One possibility is that Li^+ serves as a cross-link between PEGDME and PVdF with the Li^+ bonding the former via oxygens and the latter via fluorines as shown here:



The DSC cooling curves of PEGDME400, PEGDME250, and their imide solutions showed similar trends. The behavior of the shortest chain PEGDME is particularly interesting in that the melting point of the PEGDME250−$LiN(SO_2CF_3)_2$ liquid electrolyte is about 2.5 °C higher than that of PEGDME250, while the solid polymer electrolyte prepared with it does not show a freezing point down to −50 °C.

The stress−strain data, plotted in Figure 5, provide information on the mechanical strength of the PVdF2822−PEGDME500−imide electrolytes. Stresses between 120 and 420 psi at an elongation-at-break value (strain) close to 70% are indicative of their good mechanical strength. The PVdF content is the dominant factor that determines the electrolyte's ultimate tensile strength; a higher PVdF content in the electrolyte yields a stronger film. The elastic property measured by the strain value, on the other hand, is much less sensitive to the PVdF content.

Depicted in Figure 6a is the thermal gravimetric analysis (TGA) plot for the 30 PVdF2822−60PEGDME500−10-imide electrolyte, showing that heating this polymer electrolyte from 20 to 150 °C (under a flow of argon) results in a weight loss of only 1.1%. Even more revealing is the isothermal TGA data obtained by heating the same electrolyte at 70 °C for 24 h. A weight loss of only 1.7% (Figure 7a) is observed. Heating the 30 PVdF2822−60PEGDME400−10-imide electrolyte, in which the PEGDME has a molecular weight of 400 daltons, resulted in weight losses of 2.1 and 2.7%, respectively (Figures 6b and 7b) at the same conditions. The small weight losses observed for these electrolytes, primarily in the initial stages of heating, are presumably caused by the evaporation of some low molecular weight components in the PEGDME samples. We

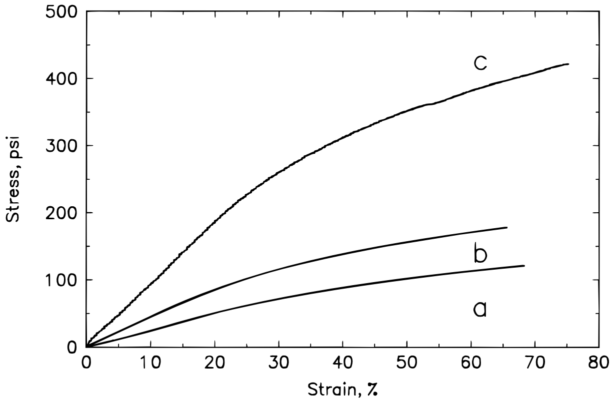


Figure 5. Stress−strain plots for (a) 22.5 PVdF2822−67.5 PEGDME500−10-imide, (b) 30 PVdF2822−60 PEGDME500−10-imide, and (c) 35 PVdF2822−50 PEGDME500−15-imide.

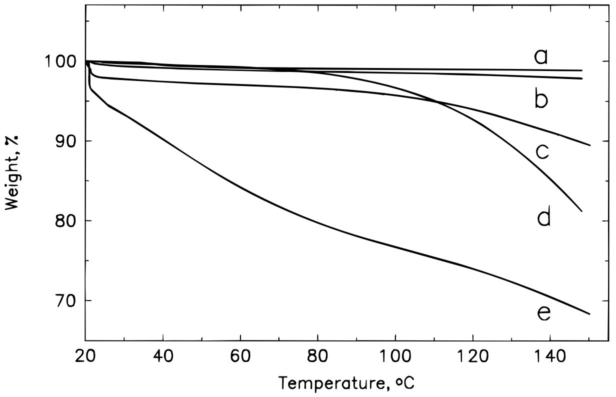


Figure 6. TGA data for (a) 30 PVdF2822−60 PEGDME500−10-imide, (b) 30 PVdF2822−60 PEGDME400−10-imide, (c) 30 PVdF2822−60 PEGDME250−10-imide, (d) 30 PVdF2822−30 EC/30 PC−10-imide, and (e) 30 PVdF2822−30 EC/30 DMC−10-imide between 20 and 150 °C. The polymer electrolytes were heated at 5 °C/min under a flow of argon.

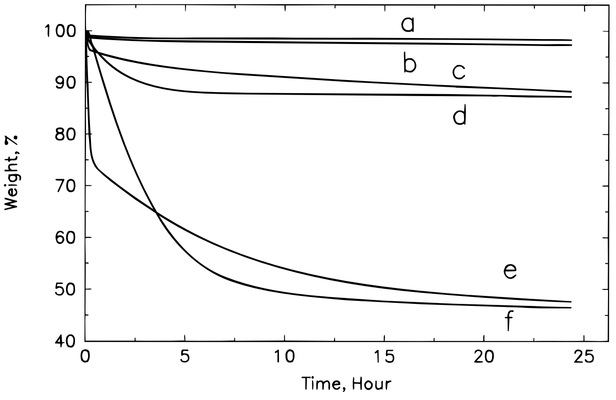


Figure 7. Isothermal TGA plots for (a) 30 PVdF2822−60 PEGDME500−10-imide, (b) 30 PVdF2822−60 PEGDME400−10-imide, (c) 30 PVdF2822−60 PEGDME250−10-imide, (d) 30 PVdF2822−44.3 PEGDME400/10.7 PC−15-imide, (e) 30 PVdF2822−30 EC/30 DMC−10-imide, and (f) 30 PVdF2822−30 EC/30 PC−10-imide. The samples were kept at a constant temperature of 70 °C for 24 h under flowing argon.

Table 2. TGA Results of Various PVdF-Based Electrolytes

	weight loss (%)	
electrolyte	heated from 20 to 150 °C	heated at 70 °C for 24 h
30 PVdF−60 PEGDME500−10 imide[a]	1.1	1.7
30 PVdF−60 PEGDME400−10-imide	2.1	2.7
30 PVdF−60 PEGDME250−10-imide	10.5	11.7
30 PVdF−44.3 PEGDME400/10.7 PC−15-imide		12.7
30 PVdF−30 EC/30 PC−10-imide	18.8	53.5
30 PVdF−30 EC/30 DMC−10-imide	31.7	52.4

[a] The number preceding an electrolyte component is its weight percent.

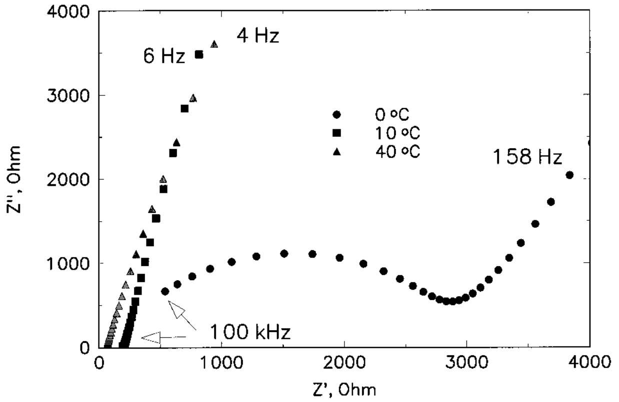


Figure 8. Impedance spectra of the 30 PVdF2822−60 PEGDME500−10 $LiSO_3CF_3$, at different temperatures, recorded between stainless steel blocking electrodes.

conclude that the polymer electrolytes containing PEGDME500 and PEGDME400 are essentially nonvolatile at ambient temperature and pressure.

The TGA plots shown in Figures 6c and 7c for the 30PVdF2822−60 PEGDME250−10-imide electrolyte indicate that PEGDME250 is volatile. Weight losses of 10.5 and 11.7%, were observed in the variable temperature and isothermal TGA tests, respectively. For comparison, Figures 6 and 7 also display the TGA plots for polymer electrolytes containing EC, PC, and/or DMC as the plasticizer. Significant weight losses are observed for electrolytes containing all the three carbonates. From weight loss data summarized in Table 2, the volatility order of the solvents appears to be DMC > PC/EC > PEGDME250.

Ionic Conductivity and Lithium Ion Transference Number. Conductivities of the electrolytes were calculated from the membrane resistances determined from complex impedance spectra. Typical impedance spectra obtained at different temperatures are depicted in Figure 8. Two types of spectrum, dependent on the temperature, were observed for the Cole−Cole plots of the PVdF2822−PEGDME500−triflate electrolyte. Above about 10 °C, the spectra are characterized by slanted straight lines intercepting the real axis on the high-frequency side. This represents an equivalent circuit in which a resistor is in series with a capacitor, i.e., the electrolyte resistance in series with the electrode capacitance. The intercept on the real axis gives the resistance from which the conductivity of the electrolyte is calculated (vide infra). At and below 0 °C, the spectrum consists of a depressed semicircle with a slanted line (spur) at low frequencies. This spectrum represents an equivalent circuit in which the electrode resistance is in series with a parallel combination of electrolyte resistance and capacitance. The electrolyte resistance was calculated from the intercept of the spur extrapolated to the real axis. Conductivity (σ) was obtained from, $\sigma = l/RA$, where l is the thickness of the electrolyte film (in cm), R is its resistance (in Ω), and A is its area (in cm^2). The data in Table 1 indicate that the plasticizer in this electrolyte freezes at about 8 °C, and consequently the impedance spectrum at 0 °C is representative of a “frozen” electrolyte. Clearly, the impedance spectrum in the 1 Hz to 100 kHz range for a “frozen” electrolyte is distinctly different from that of a “fluid” electrolyte. It appears that in the “frozen” electrolyte, the capacitance component becomes significant in the 1 Hz−100 kHz range due to slower dielectric relaxation times. In fact, this behavior is similar to that we previously observed[13] for the MEEP/PEO−LiX mixed polymer electrolytes in which the room-temperature spectra were similar in shape to the 0 °C spectrum in Figure 8, while above 55 °C , where PEO melted to form an amorphous phase, the spectra resembled the 10 and 40 °C spectra in Figure 8. Clearly, impedance spectrum is useful to assess the morphology of gel polymer electrolytes, i.e., to determine whether they are “frozen” or “solid” versus “fluid” or “plastic”. The conductivity data for several imide-containing polymer electrolytes are shown in Table 3, and plots of the temperature dependence of the conductivity are displayed in Figure 9. Our prior results on the PVdF−EC/PC−LiX electrolytes indicated that the ratio of PVdF to plasticizer solvent was a key factor determining their conductivities.[2] In the present study, all the electrolytes had a PVdF to the plasticizer solvent ratio of ~0.5, which fixed the effect of this ratio on conductivity while preserving the good mechanical strength of the electrolyte. The electrolytes plasticized with PEGDME500/imide solutions exhibited conductivities between 0.82×10^{-5} and 3.2×10^{-4} S/cm from 20 to 40 °C. The 20 °C conductivities of the 30 PVdF2822−60PEGDME500−10-imide and 30PVdF2822−55PEGDME500−15-imide electrolytes are about 2−3 times higher that of the previously reported PEO−PEGDME500−imide−γ-$LiAlO_2$ electrolytes.[5] The conductivities of the 30 PVdF2822−60 PEGDME500−10 $LiPF_6$ and 30 PVdF2822−60 PEGDME500−$LiSO_3CF_3$ electrolytes are tabulated in Table 4 along with a graphical representation in Figure 10. At 20 °C, both electrolytes have a conductivity of $\sim 10^{-4}$ S/cm, slightly lower than that of the 30 w/o PVdF2822−60 PEGDME500−10-imide electrolyte.

The conductivity of the PEGDME500-containing electrolytes exhibited a sharp drop when they were cooled below room temperature. For example, for the 30 PVdF2822−65 PEGDME500−5-imide electrolyte it decreased from 8.15×10^{-5} S/cm at 20 °C to 3.36×10^{-6} S/cm at 10 °C and further to 5.38×10^{-11} S/cm at −10 °C. For the 30 PVdF2822−60 PEGDME500−10-imide and the 30 PVdF2822−55 PEGDME500−15-imide electrolytes, a significant drop in the conductivity occurred when the temperature was lowered from 10 to 0 °C. As alluded to earlier, these sharp drops associated with the freezing of the electrolytes were reflected in the shapes of the impedance spectra. This behavior was also observed with the 30PVdF2822−60PEGDME500−10$LiPF_6$ and the 30PVdF2822−60PEGDME500−10$LiSO_3CF_3$ electrolytes; they began to freeze at 0 °C. It appears that the concentration of the Li salt has a direct impact on the temperature at which this occurs.

Table 3. Conductivity Data for PVdF2822−PEGDME−Imide at Various Temperatures

electrolytes	weight ratio of PVdF/(PEGDME)	conductivity (S/cm) −10 °C	20 °C	40 °C
30 PVdF2822−65[a] PEGDME500−5-imide	0.46	5.38×10^{-11}	8.15×10^{-5}	1.73×10^{-4}
30 PVdF2822−60 PEGDME500−10-imide	0.50	1.47×10^{-10}	1.21×10^{-4}	2.90×10^{-4}
30 PVdF2822−55 PEGDME500−15-imide	0.55	3.91×10^{-10}	1.41×10^{-4}	3.24×10^{-4}
30 PVdF2822−60 PEGDME400−10-imide	0.50	3.3×10^{-5}	2.08×10^{-4}	4.26×10^{-4}
30 PVdF2822−60 PEGDME250−10-imide	0.50	1.16×10^{-4}	4.24×10^{-4}	7.88×10^{-4}
30 PVdF2822−44.3 PEGDME400−10.7 EC−15-imide	0.50	6.68×10^{-5}	3.74×10^{-4}	8.58×10^{-4}
30 PVdF2822−44.3 PEGDME400−10.7 PC−15-imide	0.55	6.80×10^{-5}	3.90×10^{-4}	8.31×10^{-4}

Table 4. Conductivity Data for $LiPF_6$ and $LiSO_3CF_3$-Containing Electrolytes

electrolytes	weight ratio of PVdF/(PEGDME)	conductivity (s/cm) −10 °C	20 °C	40 °C
30 PVdF2822−60 PEGDME500−10 $LiPF_6$	0.50	3.70×10^{-9}	0.93×10^{-4}	2.33×10^{-4}
30 PVdF2822−60 PEGDME500−10 $LiSO_3CF_3$	0.50	5.80×10^{-10}	1.00×10^{-4}	2.20×10^{-4}

[a] The number preceding an electrolyte component is its weight percent.

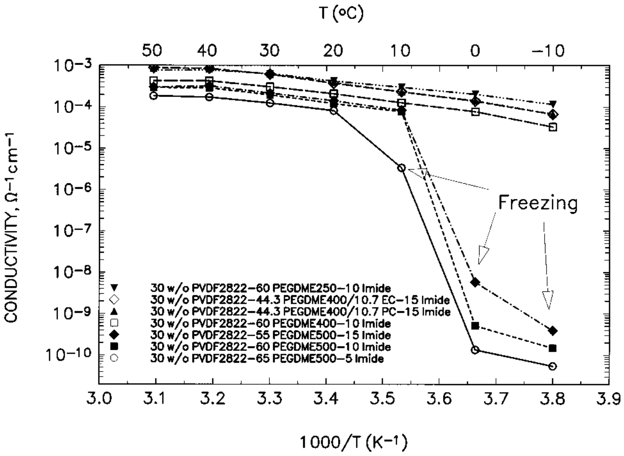


Figure 9. Conductivity versus temperature plots for the PVdF2822−PEGDME−imide electrolytes.

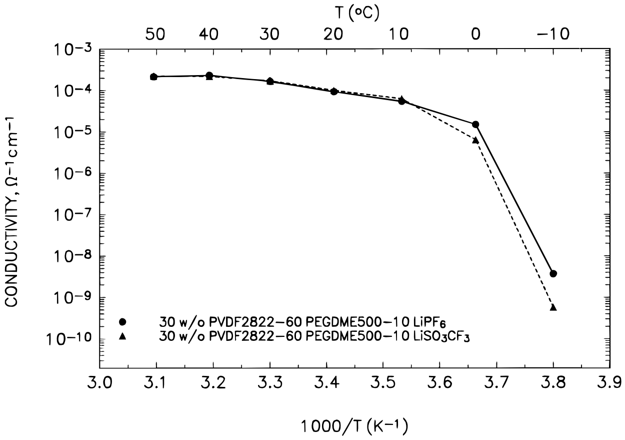


Figure 10. Conductivity versus temperature plots for the 30 PVdF2822−60 PEGDME500−10 $LiPF_6$ and 30 PVdF2822−60 PEGDME500−10 $LiSO_3CF_3$ electrolytes.

Table 5. Activation Energy of Polymer Electrolytes

electrolyte	activation energy, E_a[a] (kcal/mol)
30 PVdF−60 PEGDME500−10-imide	7.8
30 PVdF−55 PEGDME500−15-imide	8.0
30 PVdF−60 PEGDME400−10-imide	7.3
30 PVdF−60 PEGDME250−10-imide	5.7
50 PVdF−40 EC/PC−10-imide	5.7
30 PVdF−60 EC/PC- 10-imide	4.8
28 PVdF−59 EC/PC−13-imide	4.3
20 PVdF−75 EC/PC−5-imide	3.6
PEO-$(LiBF_4)_{0.13}$	20[b]

[a] Calculated from the Arrhenius equation, $\sigma = \sigma\, e^{-E_a/RT}$. [b] From ref 15. This value calculated from conductivities above 60 °C.

For example, compared with the 30PVdF2822−65PEGDME500−5-imide electrolyte, the higher salt concentrations in the 30PVdF2822−60PEGDME500−10-imide, and 30PVdF2822−55PEGDME500−15-imide electrolytes appeared to have delayed the freezing by at least 10 °C. Replacing PEGDME500 with PEGDME400 or PEGDME250 increased the conductivity. For example, conductivities of the 30 PVdF2822−60 PEGDME400−10-imide and the 30 w/o PVdF−60 PEGDME250−10 imide electrolytes at 20 °C are 1.7 and 3.5 times, respectively, higher than that of their counterpart containing PEGDME500. The conductivities of both the PEGDME400 and PEGDME250-containing electrolytes showed a monotonous drop when going from 50 to −10 °C, suggesting that these imide electrolytes do not freeze down to −10 °C.

Some insight into mechanism of ionic conductivity in these electrolytes can be obtained from an examination of the activation energies for conduction given in Table 5. These data were obtained from analyses of the conductivity−temperature (σ−T) behavior according to the Arrhenius equation. Before examining these data, we concede that the temperature dependence of the conductivities of polymer electrolytes are probably best described by the Vogel−Tanaman−Fulcher (VTF) equation:

$$\sigma = AT^{-1/2}e^{-E_a/R(T-T_0)} \tag{4}$$

where T_0 is the temperature at which the segmental mobility of the polymer backbone ceases to exist and is usually the same as the glass transition temperature (T_g). The VTF equation is also believed to describe more accurately the σ−T behavior of highly concentrated (i.e., greater than ~0.1 M) liquid electrolytes and molten salts.[14] Nevertheless, the activation energies calculated from the Arrhenius plots provide information useful to assess the relative roles of ionic mobility and charge carrier concentration on the conductivity of these PEO-like electrolytes. The values of E_a vary from 5.7 to 7.8 kcal/mol and increase as the molecular weight of the PEGDME increases. More importantly, these values are only 30−40% of that of PEO−LiX (E_a = ~20 kcal/mol above 60 °C) and are close to the 8−9 kcal/mol

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(14) Smedley, S. I. *The Interpretation of Conductivity in Liquids*; Plenum Press: New York, 1980; p 82.

Table 6. Kinematic Viscosity of Various Plasticizers and Their $LiN(SO_2CF_3)_2$ Solutions

plasticizer/plasticizer solution	viscosity (cSt)
PC	2.2
PC/imide (6:1 weight)	4.2
PEGDME250	6.6
PEGDME250/imide (6:1 in weight)	11.1
PEGDME400	14.7
PEGDME400/imide (6:1 weight)	25.8
PEGDME500	26.5
PEGDME500/imide (6:1 in weight)	44.3

Table 7. Ionic Conductivities of PEGDME/Imide Solutions

	conductivity (S/cm)	
electrolyte	20 °C	30 °C
86 w/o PEGDME500/14 w/o imide	3.94×10^{-4}	5.96×10^{-4}
86 w/o PEGDME400/14 w/o imide	5.81×10^{-4}	8.31×10^{-4}
86 w/o PEGDME250/14 w/o imide	1.23×10^{-3}	1.64×10^{-3}

observed for the plasticized poly(vinyl sulfone) electrolytes and the 3.5−5 kcal/mol observed for PAN/EC−PC/LiX electrolytes.[16] The implication is that the high room-temperature conductivities of the PVdF−PEGDME−LiX electrolytes are predominately associated with high ionic mobilities. Furthermore, these PVdF electrolytes have about 10^5 times higher room temperature conductivities than PEO−LiX, although the dielectric constants of PEO and PEGDME are rather similar with a value of about 5, implying similar charge carrier concentrations in both of these electrolytes for the same concentrations of the Li salt. The decreasing conductivity with increasing molecular weight of PEGDME can be attributed to the increasing viscosity of the plasticizers (see Table 6), again demonstrating the overriding importance of ionic mobility for the high conductivities of these electrolytes. In fact, the conductivities of the polymer electrolytes follow the same trend as that of the PEGDME/$LiN(SO_2CF_3)_2$ liquid electrolytes (Table 7). The major difference is that the conductivity decreases 2−3 times when the liquid electrolytes are encapsulated into the polymer matrix.

Compared with PVdF/PEGDME−LiX, the carbonate solvent-based PVdF−EC/PC−LiX have about 10 times higher conductivity[2] which can be ascribed to the lower viscosity of the carbonate solvents (Table 6), as well as to the higher charge carrier concentrations owing to the significantly higher dielectric constants (ϵ) of EC and PC; ($\epsilon = 89.6$ for EC at 40 °C and 64.4 for PC at 25 °C). Partial replacement of the PEGDME in the polymer electrolyte by PC would increase its conductivity, since PC has both a higher dielectric constant and a lower viscosity, both beneficial to increase conductivity. Indeed, the 30 PVdF2822−44.3 PEGDME400−10.7 PC−15-imide electrolyte possessed almost twice as high a conductivity as the 30 PVdF2822−60 PEGDME400−10 imide electrolyte in the temperature range of −10 to 50 °C. When PC in the 30 PVdF2822−44.3 PEGDME400−10.7 PC−15-imide electrolyte was replaced with EC, the conductivity did not change.

The transference number (T^+) of the electrolytes were measured according to the method of Evans et al.[6] According to them, for small electrode potential polarizations, the initial (I_0) and steady-state (I_s) currents are given by

$$I_0 = \Delta V/\left(R_1^\circ + \frac{k}{\sigma}\right) \tag{5}$$

$$I_s = \Delta V/\left(R_1^s + \frac{k}{T^+\sigma}\right) \tag{6}$$

where ΔV is the potential applied across the Li/polymer electrolyte/Li cell, k is the cell constant, T^+ is the cationic transference number, σ is the conductivity of the electrolyte, R_1° and R_1^s are the initial and steady-state resistances of the passivating layers on the Li electrode. If R_i and R_f represent initial and final resistances of the electrolytes, then eqs 5 and 6 will become

$$I_0 = \frac{\Delta V}{R_1^\circ + kR_i} \tag{6}$$

$$I_s = \frac{\Delta V}{R_1^s + \frac{kR_f}{T^+}} \tag{7}$$

From eqs 7 and 8

$$T^+ = \frac{I_s R_f}{I_0 R_i}\left[\frac{\Delta V - I_0 R_1^\circ}{\Delta V - I_s R_1^s}\right] \tag{9}$$

Note that this equation is a slightly modified version of the original Evans et al. equation in that it takes into account the changes in the resistance of the polymer electrolyte also. We have used potential steps of 70−130 mV (Table 8), large enough to overcome the INTLINITiR drops due to the large resistances of the passivation layers on Li. Recently, in connection with the transport number measurements of PAN-based electrolytes we have discussed[16] the importance of using an appropriately large potential step in order to obtain accurate transference numbers.

The Li-ion transference numbers for three electrolytes are presented in Table 8. These electrolytes contained the imide salt, and the three different PEGDME plasticizers. The transference number of ∼0.3 is comparable to the ∼0.3 reported for a PEO−PEGDME500-imide−γ-$LiAl_2O_3$ electrolyte.[5] Apparently, the anionic species are the main contributors to the total ionic conductivity. This behavior is reminiscent of conventional organic liquid electrolytes as well as of the PAN−EC/PC−LiX polymer electrolytes for which we obtained values of 0.2−0.3, and it illustrates the similarity in the conductivity mechanisms of plasticized polymer electrolytes and conventional liquid electrolytes.

Electrochemical Stability. The electrochemical stability of the 30 w/o PVdF−60 PEGDME500−10-imide electrolyte was studied using cyclic voltammetry. Figure 11 shows the cyclic voltammograms measured between 2 and 4.5 V on Al, SS^{304} and Ni electrodes. Judging by the magnitude of the current responses, the oxidation stability of the electrolyte is excellent on all the electrodes up to 4.5 V. The high electrochemical stability shown by this electrolyte is unique since both Al and Ni electrodes showed corrosion currents at lower potentials in all the other currently known ambient-temperature polymer electrolytes containing LiN(SO$_2$-

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(15) Abraham, K. M.; Alamgir, M.; Reynolds, R. K. *J. Electrochem. Soc.* **1989**, *136*, 3576.

(16) Choe, H. S.; Carroll, B. G.; Pasquariello, D. M.; Abraham, K. M. *Chem. Mater.* **1997**, *17*, 369.

Table 8. Results of Lithium Ion Transference Number Measurements

electrolyte	expt no	$R_{\rm I}^{\rm o}$(Ω)	$R_{\rm I}^{\rm s}$(Ω)	$R_{\rm b}^{\rm o}$(Ω)	$R_{\rm b}^{\rm s}$(Ω)	$I^{\rm o}$(mA)	$I_{\rm s}$(mA)	V(mV)	T^+
30 w/o PVdF−60 PEGEME500−10-imide	a	77.9	121.8	8.8	8.5	1.25	0.60	130	0.27
	b	89.5	125.6	10.5	11.4	1.19	0.58	130	0.22
30 w/o PVdF−60 PEGDME400−10-imide	a	38.3	49.1	4.8	4.6	1.57	0.79	110	0.34
	b	56.1	108.7	7.3	6.2	1.42	0.65	120	0.32
50 w/o PVdF−45 PEGDME250−5-imide	a	49.3	89.9	8.5	9.2	0.72	0.24	70	0.26

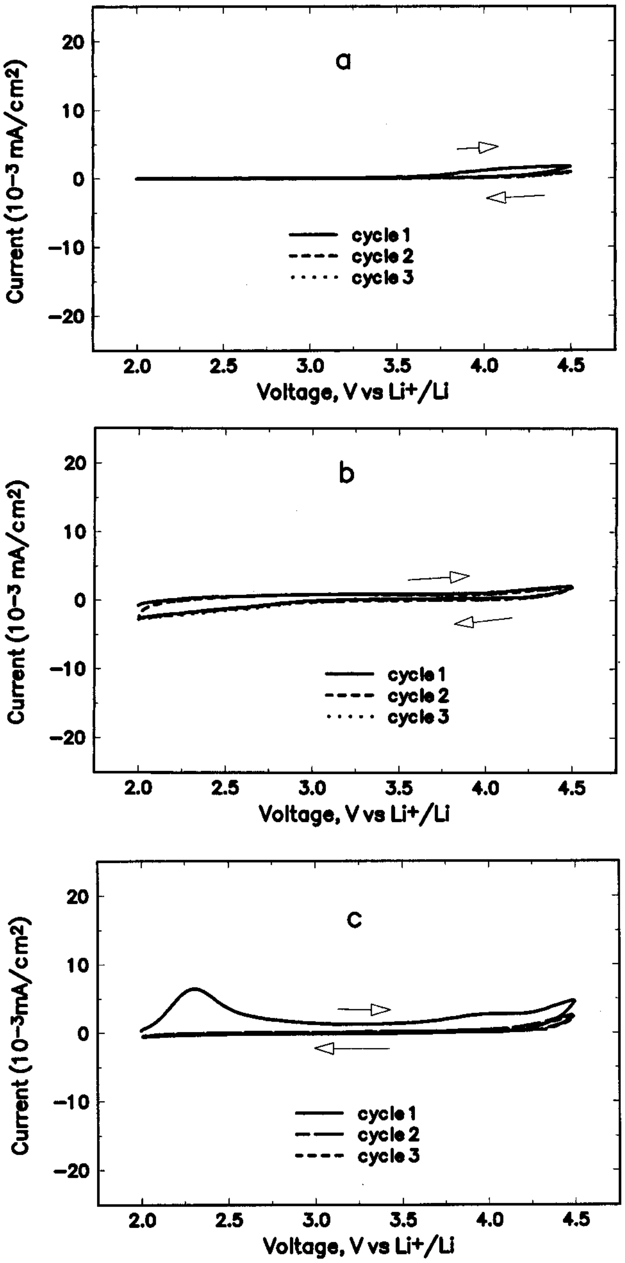

Figure 11. Cyclic voltammograms for the 30 PVdF2822−60 PEGDME500−10-imide electrolyte on a working electrode of (a) Al between 2 and 4.5 V, (b) SS between 2 and 4.5 V, and (c) Ni between 2 and 4.5 V. The potential was swept at a scan rate of 1 mV/s.

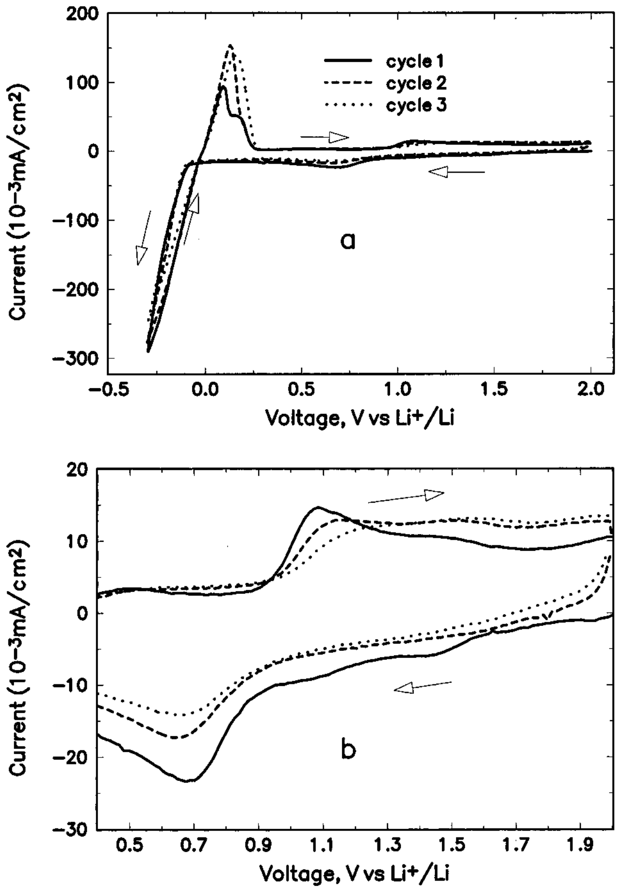

Figure 12. Cyclic voltammograms for the 30 PVdF2822−60 PEGDME500−10-imide electrolyte on Ni (a) in the voltage range between 2 and −0.3 V and (b) in the voltage range between 2 and 0.4 V at a smaller current scale. The potential was swept at a scan rate of 1 mV/s.

$CF_3)_2$.[2,16] For example, cycling the 30 PVdF2822−30 EC/30 PC−10-imide electrolyte on Al resulted in high anodic currents[2] at about 4.0V vs Li^+/Li attributed to the oxidation breakdown of the passivation layer on this electrode. In 14.2 w/o PAN−39.3 EC/39.3 PC−7.1 imide,[16] Al corroded at ∼3.7 V vs Li^+/Li. When the PAN−EC/PC−LiX electrolytes with LiX = Li imide, $LiPF_6$, Li triflate, $LiAsF_6$ were cycled on Ni, only the $LiAsF_6$-containing electrolyte showed stability beyond 4 V.[16] The high oxidation stability of the PEGDME electrolytes containing $LiN(SO_2CF_3)_2$ on Al and Ni may be attributed to stability afforded by passivation films formed from oxidation reactions, probably of PEGDME.

Depicted in Figures 12a and 13a are the voltammograms of the same PEGDME-containing electrolyte on Ni and SS in the voltage range of 2 to −0.3 V. The peaks observed between −0.3 and 0.3 V in both voltammograms are attributed to the plating and stripping of Li. Interestingly, we notice two Li stripping steps in the first cycle. This phenomenon was observed previously in the MEEP−PEO−$LiBF_4$ electrolyte[13] and was attributed to the environments of the plated Li. Apparently, Li is plated on the Ni and SS electrodes in two different environments; a first layer adjacent to the electrode and strongly adsorbed onto it, and a second fraction that is plated on the first layer. Consequently, the second fraction is stripped at a potential closer to the formal Li^+/Li potential than the first fraction which is stripped at a slightly more positive potential. The Li stripping/plating efficiency calculated from the voltammograms are 30−39% and 18−34%, on Ni and

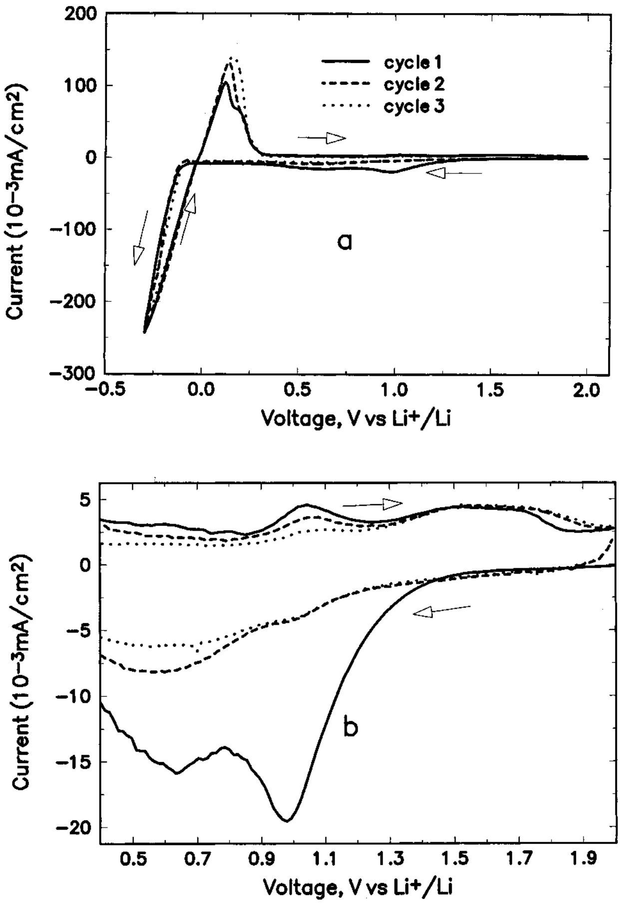

Figure 13. Cyclic voltammograms for the 30 PVdF2822−60 EC/PC−10-imide electrolyte on SS (a) in the voltage range between 2 and −0.3 V and (b) in the voltage range between 2 and 0.4 V at a smaller current scale. The potential was swept at a scan rate of 1 mV/s.

SS, respectively, in the first three cycles. These poor cycling efficiencies may be attributed to the rapid corrosion of fresh Li surface leading to passivation.

In Figures 12b and 13b, the voltammograms in the 0.4−2.0 V range are presented with the current in a more sensitive scale on the *y*-axis. The reduction of the electrolyte on the Ni electrode, reflected by the small cathodic peak at about 1.0 V, was irreversible. This probably represents the formation of a passivation layer on the metal electrodes. On the other hand, the cathodic peak at 0.7 V in both voltammograms appeared to be reversible as reflected by the anodic peak at 1.0 V. This reversible reaction is probably associated with a redox process involving electrode surface species, such as oxides.

Li/Polymer Electrolyte Interface Stability. The stability of the Li interface in the PVdF−PEGDME−LiX polymer electrolytes was studied by monitoring the impedance response of a symmetrical Li/30 PVdF2822−60 PEGDME500−10-imide/Li cell, which was stored at room temperature under the open-circuit condition for a period of 95 days. The impedance spectra displayed in Figure 14 are characterized by a large, skewed, semicircle whose diameter increases as the storage time is increased. On the basis of our model presented[17] before for the Li/electrolyte interfacial behavior of a polymer electrolyte cell, the intercept at the high-frequency side corresponds to the ohmic resistance of the cell which is predominantly the electrolyte resistance (R_{bulk}). The diameter of the semicircle has two contributions: (i) the resistance of the passivation film (R_{film}) formed on the Li electrode by its reaction with the electrolyte and (ii) the charge-transfer resistance. It can be seen that R_{bulk} remained at about 10 Ω, suggesting that the composition of the polymer electrolyte did not change, either through plasticizer loss or through reactions with the Li electrode. On the other hand, R_{film} increased from 101 to 119 Ω during the first 8 days of storage, indicating that the film probably grew slightly in thickness during that period of time. Thereafter, R_{film} stabilized at values between 110 and 119 Ω. The small initial increase in R_{film} followed by its stabilization suggest that the film formed at the Li/polymer electrolyte interface has excellent passivation characteristics. This is further supported by the Li/O_2 and Li/$LiMn_2O_4$ cell data discussed below.

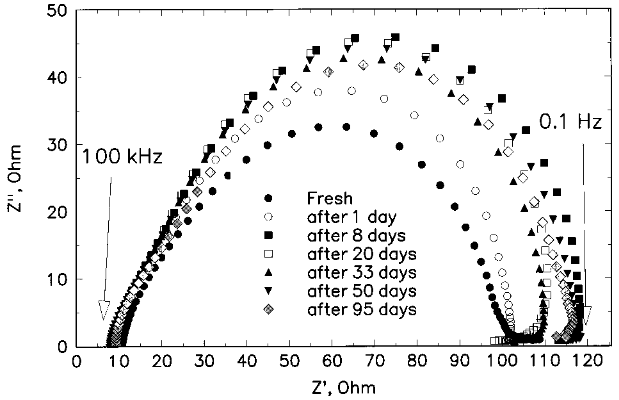

Figure 14. Impedance plots of a Li/30 PVdF2822−60 PEGDME500−10-imide/Li cell stored at room temperature. The cell was stored in a metallized bag. The electrode area was 10 cm2.

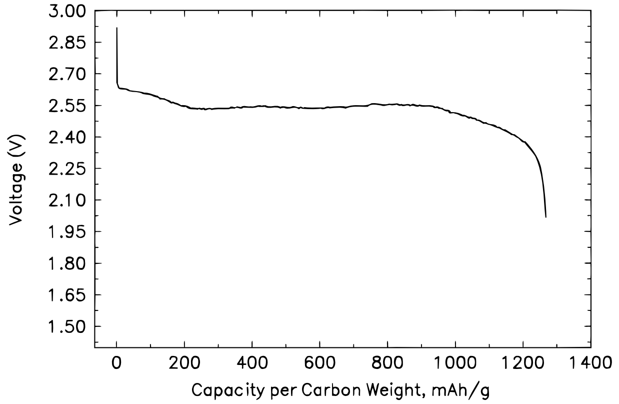

Figure 15. Discharge curve of a Li/30 PVdF2822−60 PEGDME400−10-imide/oxygen cell at 0.1 mA/cm^2. The cell was discharged at room temperature in an atmosphere of oxygen.

Performance of the Electrolytes in Li/Polymer Electrolyte/Oxygen and Li/Polymer Electrolyte/$LiMn_2O_4$ Cells. The low volatility exhibited by the PVdF−PEGDME−LiX electrolytes makes them applicable not only in sealed batteries but also in unsealed batteries such as the solid-state Li/polymer electrolyte/oxygen battery,[3] where both the electrolyte and the carbon cathode are exposed to an oxygen atmosphere during battery operation. Figure 15 shows the discharge curve for a Li/oxygen cell containing the 30

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(17) Alamgir, M.; Abraham, K. M. *J. Power Sources* **1995**, *54*, 40.

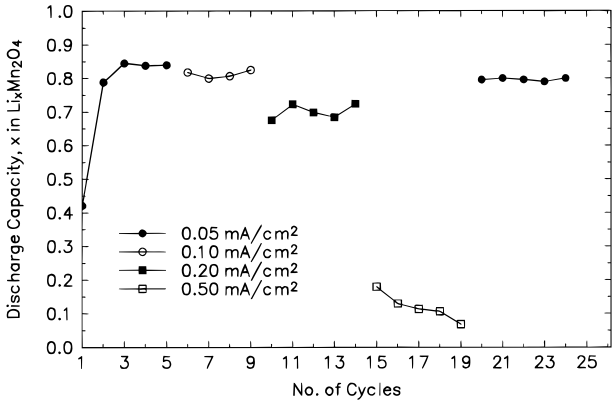

Figure 16. Discharge capacity vs cycle number of a Li/30 PVdF2822−60 PEGDME500−10-imide/$LiMn_2O_4$ cell cycled at room temperature and various current densities.

PVdF2822−60 PEGDME400−10-imide electrolyte. The cell had an open-circuit voltage of 2.95 V. Discharged at 0.1 mA/cm^2 in an oxygen atmosphere, it showed an average load voltage of ~2.5 V, which is ascribed to the reduction of oxygen on the carbon electrode. At the voltage cutoff of 2.0 V, a capacity of 1262 mAh/g of carbon in the cathode was obtained, which is close to that obtained from the cells using a PAN−EC/PC−$LiPF_6$ electrolyte.[3] The capacity of the cell is expressed as milliampere hour (mAh) per gram (g) of carbon (mAh/g) since it appears that the end-of-discharge of the cell is reached when the pores of the carbon electrode are choked by the deposition of Li_2O_2, the reduction product of oxygen in these cells.

The high electrochemical oxidation stability of the PVdF−PEGDME−LiX electrolytes makes them useful in high-voltage batteries utilizing 4 V cathode materials such as $LiMn_2O_4$, $LiNiO_2$, and $LiCoO_2$. Depicted in Figures 16 and 17, respectively, are the discharge capacity vs cycle number and the corresponding cycling curves of a Li/30PVdF2822−60PEGDME500−10-imide/$LiMn_2O_4$ cell. At 0.05 and 0.1 mA/cm^2, the cell delivered a reversible capacity equivalent to 0.8−0.83 Li/$LiMn_2O_4$ (~120 mAh/g) with an average load voltage of 3.9 V. At 0.2 mA/cm^2, the capacity decreased slightly to 0.7 Li/$LiMn_2O_4$. The rate capability of the cell was low. For example, when the cell was cycled at 0.5 mA/cm^2, it showed a capacity of 0.2 Li per $LiMn_2O_4$ in the first cycle and it steadily declined thereafter so that at the fifth cycle at this rate only 0.075 Li/$LiMn_2O_4$ was obtained. This low capacity, however, was a rate-related phenomenon because it increased to 0.8 Li/$LiMn_2O_4$ when the current was lowered to 0.05 mA/cm^2. The low rate performance of these cells is consistent with the lower conductivity of these electrolytes compared to PAN−EC/PC−LiX and conventional organic liquid electrolytes.

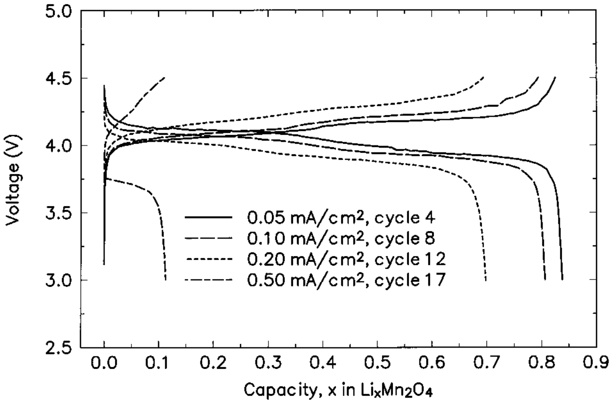

Figure 17. Representative cycling curves of the Li/$LiMn_2O_4$ cell showed in Figure 16. The current densities are shown on the curves.

Conclusions

PEO-like electrolytes with conductivities as high as 2×10^{-4} S/cm at room temperature have been prepared by encapsulating PEGDME−$LiN(SO_2CF_3)_2$ solutions in poly(vinylidene fluoride)−hexafluoropropene copolymers. We have dubbed them PEO-like because of the structural similarities between PEO−LiX and PEGDME−LiX, and the good thermal stabilities of PVdF−PEGDME500 (400)−$LiN(SO_2CF_3)_2$ in the 20−100 °C range. These properties essentially make them solid electrolytes despite the presence of liquid plasticizers. Their high conductivities should make them suitable for room-temperature applications for which PEO electrolytes are not suitable because of poor conductivity.

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