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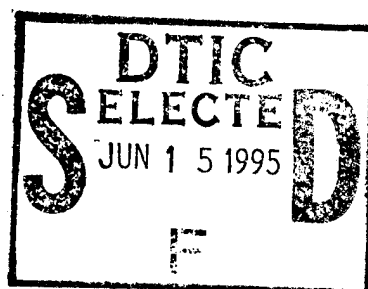# Plasticizers for Solid Polymer Electrolytes

Charles W. Walker, Jr. and Mark Salomon

ARL-TR-420   February 1995

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE February 1995	3. REPORT TYPE AND DATES COVERED Technical Report: May 93 to May 94

4. TITLE AND SUBTITLE

PLASTICIZERS FOR SOLID POLYMER ELECTROLYTES

5. FUNDING NUMBERS

6. AUTHOR(S)

Charles W. Walker, Jr. and Mark Salomon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

US Army Research Laboratory (ARL)
Physical Sciences Directorate (PSD)
ATTN: AMSRL-PS-CC
Fort Monmouth, NJ 07703-5601

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-TR-420

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The ionic conductivity of a solid polymer electrolyte based on a lithium salt dissolved in a poly(ethylene oxide) (PEO) host was significantly improved with the use of plasticizing agents and a lithium ion coordinating compound. Either a plasticizing salt, solvent or combinations of both were incorporated into freestanding solution-cast films of $(PEO)_x(LiCF_3SO_3)$. The greatest enhancement of conductivity was observed when the plasticizing salt ($LiN[CF_3SO_2]_2$) and a plasticizing solvent (diethyl phthalate, dimethyl phthalate, or dimethylglycol phthalate) were combined, with most notable improvement occurring below the melting temperature of PEO ($\approx 66°C$). Addition of a low concentration of 6,6-dibenzyl-14-crown-4, a lithium ion coordinating compound, also improved ionic conductivity. Electrochemical stability was determined by cyclic voltammetry, showing that plasticizers were generally stable between 4.3 V and 1.5 V versus lithium.

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14. SUBJECT TERMS

Electrochemistry; lithium battery; rechargeable battery; solid electrolyte; polymer electrolyte; plasticizers; ionic conductivity; nonaqueous electrolyte

15. NUMBER OF PAGES

36

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

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Introduction

In addition to high rate military applications, lithium batteries are gaining a place in low rate consumer applications (e.g., cameras and camcorders) where safety is imperative. Because lithium-based systems are more expensive than other (non-lithium) battery chemistries, a rechargeable lithium chemistry is more cost-competitive than a lithium primary system. Solid polymer electrolytes (SPE) containing dissolved metal salts have been proposed as an alternative to liquid electrolytes in rechargeable lithium batteries to address the need for low cost and enhanced safety. A solid polymer electrolyte system would also reduce other problems associated with (liquid) electrolyte leakage and corrosion of metallic lithium.

The most basic solid electrolyte is comprised of a polymer host containing dissolved lithium salt(s), allowing the movement of Li^+ and X^- ions between the electrodes. In the absence of liquids, batteries can be sealed in metallized plastic film pouches, eliminating the weight and volume that is wasted by metal cans which are required when using liquid electrolytes. In addition to its role as an electrolyte, an SPE film can also act both as a mechanical separator between the anode and cathode, and as a binder/adhesive to insure contact between electrodes. The SPE is also used as the binder in the preparation of the cathode. Elasticity allows the SPE to conform to electrode volume changes during cycling.

From a manufacturing viewpoint there are many advantages associated with the use of thin, freestanding, ionically conducting polymers. Production of thin films is easy since high speed film processing technology already exists. The shape of the battery is geometrically unrestricted, and many sizes could readily be cut from a single roll of film. SPE's are light weight, and there is minimal volume wasted when packaging batteries. If desired, bipolar construction would be rather simple since sophisticated seals between cells are not required.

One such polymer system is based on high molecular weight poly(ethylene oxide), PEO. PEO, $HO-CH_2CH_2(-O-CH_2CH_2-)_nOH$, has a glass transition (T_g) of -60°C, and a melting temperature (T_m) of 66°C. Solid electrolytes are readily prepared by dissolving PEO and an appropriate lithium salt in a volatile solvent such as acetonitrile. A solution cast film containing only PEO with dissolved salt yields a freestanding, flexible film of high mechanical strength. Lithium ions are coordinated by the PEO-oxygens and local segmental motion of the polymer chains permits ionic conduction of Li^+ ions. Extensive reviews discussing the formation, structure, morphology, and transport theory of PEO complexes have been published by Ratner (1) and Wright (2).

Unfortunately, at room temperature such films are highly crystalline, resulting in very low ionic conductivities ($\sigma \approx 10^{-7}$ S cm^{-1}). At the melting temperature of PEO the polymer becomes amorphous, and ionic conduction increases greatly. Increasing the amorphous nature of the polymer at ambient temperature can be achieved by the

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addition of plasticizing agents. In this study we explored the use of a plasticizing salt (LiN[CF$_3$SO$_2$]$_2$), plasticizing solvents (ethylene carbonate, propylene carbonate, dioctyl sebacate, dibutyl sebacate, diethyl phthalate, dimethyl phthalate, dimethyl isophthalate, dimethylglycol phthalate, tris(2-ethylhexyl)trimellitate), a solvent having a very high dielectric constant (2-cyanopyridine), and lithium ion coordinating agents (6,6-dibenzyl-14-crown-4, [Li$^+$15-crown-5]CF$_3$SO$_3^-$) to improve the ionic conductivity of (PEO)$_x$(LiCF$_3$SO$_3$) films.

Experimental

Film preparations and tests were conducted in an argon-filled glove box containing less than 5 ppm water vapor. PEO (Aldrich, average molecular weight 4 x 10^6 dried at 50°C under vacuum overnight) was dissolved in acetonitrile (Fluka, 99.5%, distilled under a stream of dry argon) along with the appropriate salts and solvents. Many plasticizers/solvents were chosen based on them having ester linkages. The oxygen molecules were expected to provide coordination sites for Li$^+$ ions and to assist ion transport, similar to the role of the oxygens in PEO. Some of the compounds were selected for their similarity to each other, differing only by the addition of a methyl group or by the ring position of the pendant groups (structures are given in Figures 1-4).

Lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$, Aldrich, 97%) and lithium trifluoromethanesulfonimide (LiN[CF$_3$SO$_2$]$_2$, 3M, 99.5%) were dried at 110°C overnight under vacuum. Dimethyl isophthalate (Fluka, 98%, mp 64-68°C) was dried at 56°C overnight under vacuum. Ethylene carbonate (Aldrich, 98%, mp 35-37°C) and propylene carbonate (Burdick and Jackson) were vacuum distilled and stored over 3Å molecular sieves. Bis(2-ethylhexyl) sebacate (Fluka, 97%), also called dioctyl sebacate, tris(2-ethylhexyl) trimellitate (Fluka, Selectophore), dibutyl sebacate (Fluka, Selectophore, bp 344°C), and 6,6-dibenzyl-14-crown-4 (Fluka, Selectophore) were used as received. Diethyl phthalate (Johnson Matthey, 99%), dimethyl phthalate (Fluka, 99%), dimethylglycol phthalate (Fluka, 90-95%, bp 230°C), were dried/stored over 3Å molecular sieves. A gift of [Li$^+$15-crown-5]CF$_3$SO$_3^-$, prepared by Angela F. Danil de Namor (University of Surrey, U.K.) was dried at 100°C overnight under vacuum. The 2-cyanopyridine (Lancaster, ≥ 98% pure, mp 28°C) was dried at 30°C over 3Å molecular sieves followed by vacuum distillation at 60-80°C.

Films were cast by pouring solutions into flat-bottomed teflon dishes and allowing the acetonitrile to completely evaporate. Mechanically stable freestanding films (25 to 300 μm thick) were peeled from the dishes. Initially, films were dried under vacuum overnight at 50°C to remove any traces of CH$_3$CN, but it was later found that results of conductivity measurements were no different if this procedure was omitted. Subsequently this extra drying step was discontinued. Films were placed between stainless steel blocking electrodes and conductivities determined from complex impedance measurements performed between 5 Hz to 100 kHz with an EG&G PAR Model 388 Electrochemical Impedance System.

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Dimethyl phthalate
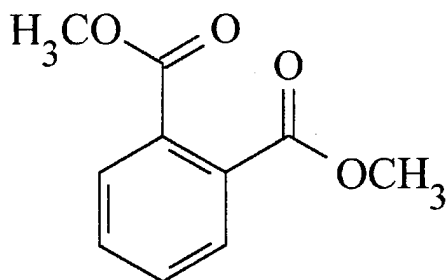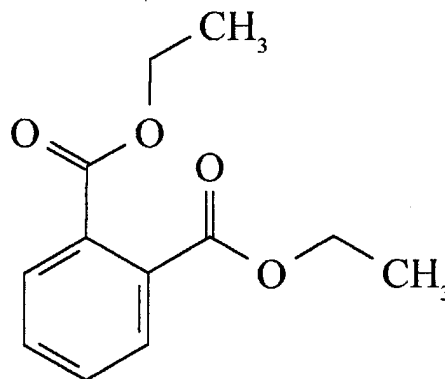
Diethyl phthalate

Dimethyl isophthalate
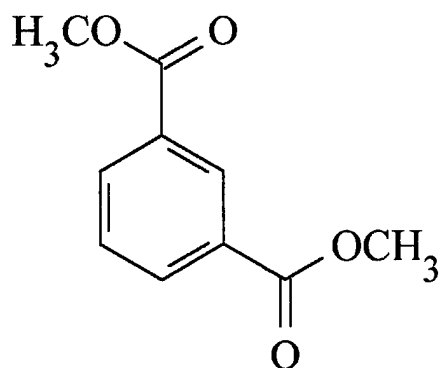
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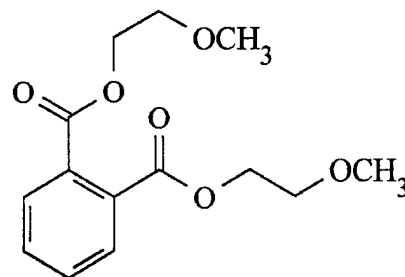
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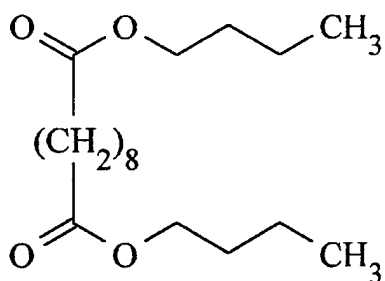
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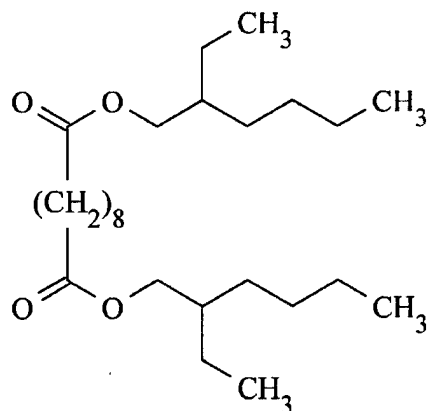
Figure 1. Chemical Structures of Plasticizers

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Tris(2-ethylhexyl)trimellitate
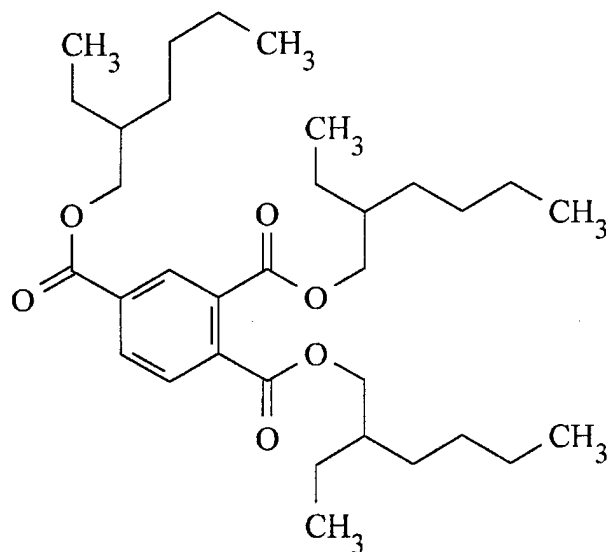
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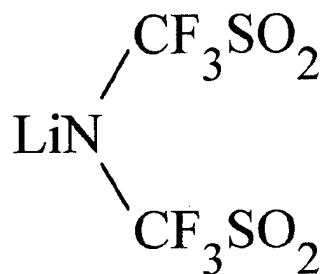
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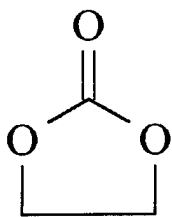
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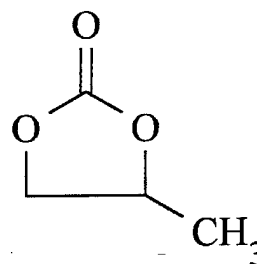
Figure 2. Chemical Structures of Plasticizers
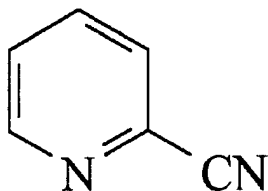
Figure 3. Chemical Structure of 2-Cyanopyridine

6,6-Dibenzyl-14-crown-4
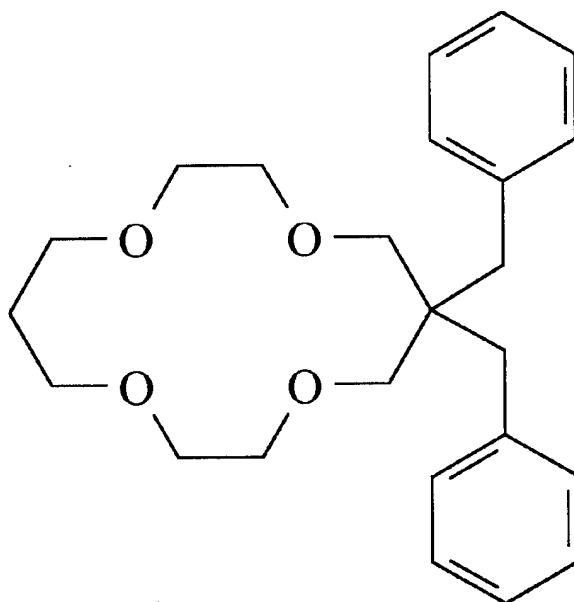
[Li⁺15Crown5]CF₃SO₃⁻

$[Li^+15Crown5]CF_3SO_3^-$
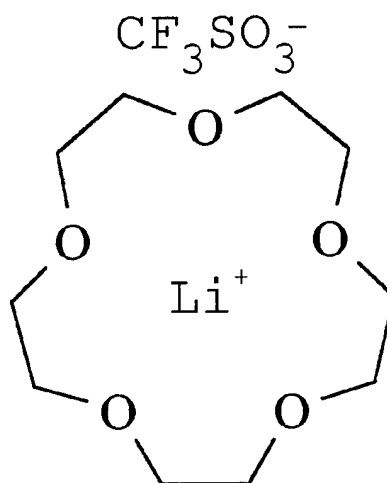
Figure 4. Chemical Structures of Coordinating Compounds

Results and Discussion

Ionic conductivity vs temperature for $(PEO)_{20}(LiCF_3SO_3)$ films is shown in Figure 5. As cast, these films are highly crystalline and have poor ionic conductivity between ambient temperature and T_m. However, once T_m is exceeded the polymer becomes amorphous and segmental motion is increased, leading to a sharp increase in conductivity that rises with temperature. Phase equilibria for this and other PEO-salt complexes have been reviewed by Fauteux (3). After the first temperature cycle, the cell was allowed to cool to ambient, and measurements repeated. With the second temperature cycle, conductivities were higher between ambient and T_m compared to the first cycle, while above T_m there was no change. The amorphous character of the polymer imparted by exceeding T_m in the first cycle was conserved, at least over a short time (days), implying slow crystallization kinetics. Subsequent to the first temperature cycle, conductivity did not change as temperature cycling was repeated. Thermal cycling improved conductivity at 20°C from 7.7×10^{-7} S cm^{-1} (as cast) to 1.3×10^{-6} S cm^{-1}.

We could not simulate thermal cycling simply by heating and slowly cooling films in a flat dish, as conductivity of "heat-treated" films was determined to be identical to untreated films. Enhanced conductivities below T_m were observed only when films were thermally cycled while being held between the electrodes of the conductivity cell.
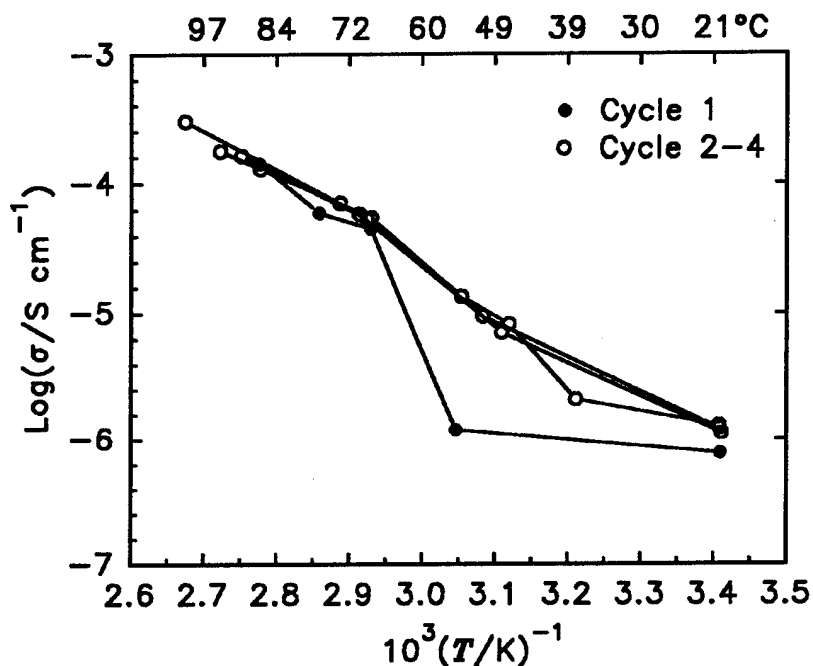
Figure 5. The effect of thermal cycling on the conductivity of $(PEO)_{20}(LiCF_3SO_3)$ solid polymer electrolyte.

Plasticizing Solvents. Initially we employed a combination of two solvents extensively studied as liquid electrolytes for lithium rechargeable cells. Propylene carbonate (PC) was chosen as a plasticizer partly because it is electrochemically stable above 4 V, and ethylene carbonate (EC) because of its high dielectric constant ($\epsilon \approx 90$). Also, a combination of PC and EC has shown good conductivity in poly(acrylonitrile) gel electrolytes (4-8). A PEO-PC-EC-LiCF$_3$SO$_3$ electrolyte containing a 20:10:10:1 mole ratio showed much higher conductivity than the (PEO)$_{20}$(LiCF$_3$SO$_3$) baseline, especially at room temperature, during the first temperature cycle (Figure 6). However, phase separation most likely occurred at high temperature as virtually all benefit was lost on the second temperature cycle, where conductivities were similar to those for films without the PC-EC additive.

Bis(2-ethylhexyl) sebacate, also known as dioctyl sebacate (DOS, bp=170°C), is a known plasticizing agent, and has been used to plasticize PVC membranes used in ion selective electrodes (9-11). DOS was of interest because of the two ester linkages in the molecule. The multiple oxygen sites provide coordination sites for Li$^+$ ions to assist Li$^+$ conduction. (PEO)$_{20}$(LiCF$_3$SO$_3$) films containing 0.3 and 1.0 mole ratio DOS were prepared and tested. Films containing 0.3 mole ratio DOS showed no significant improvement in conductivity. DOS at a concentration of 1.0 mole ratio showed an improvement (Figure 7) in conductivity below T$_m$ (on the first cycle) comparable to that seen in temperature-cycled films without DOS (Figure 5). Above T$_m$, conductivity of films containing DOS was equal to or slightly better than films without DOS. Subsequent temperature cycles showed no further change in conductivity. The advantage of adding DOS is primarily that it decreases the crystallinity of PEO, and cast films behave as if they had been thermally cycled. This was a modest improvement, but did not satisfy the requirement to raise ionic conductivity over all temperatures. Increasing the DOS concentration to increase the amorphous character of the polymer was considered impractical because films containing DOS mole ratios ≥1.0 are slightly oily on the surface, indicating solubility limitations. Dibutyl sebacate, structurally similar to DOS was used in concert with a plasticizing salt, and will be discussed later.

Another ester, diethyl phthalate (DEP, bp=295°C), was chosen for study for the same reasons cited for DOS. Films with two concentrations of DEP were prepared: (PEO)$_{20}$(LiCF$_3$SO$_3$)(DEP)$_x$ where x = 1 or 5. Unlike films with a 1.0 mole ratio of DOS which tended to be slightly oily, these films were "dry." For x(DEP)=1, the conductivity was equal to but no better than films containing DOS. For x(DEP)=5, significant improvement in conductivity was observed from room temperature up to 97°C (Figure 7) compared to the baseline as well as DOS-containing films. As with DOS, results for the first temperature cycle and subsequent cycles showed no change in conductivity.

Dimethylglycol phthalate (DMGP) is similar to DEP, varying in structure by the addition of a methyl group on the pendant chains (see Figure 1). Added at a lithium salt to DMGP ratio of 1:5 produced a film with a very oily surface, indicating that the solubility limit was exceeded. Even though the actual concentration of DMGP was less

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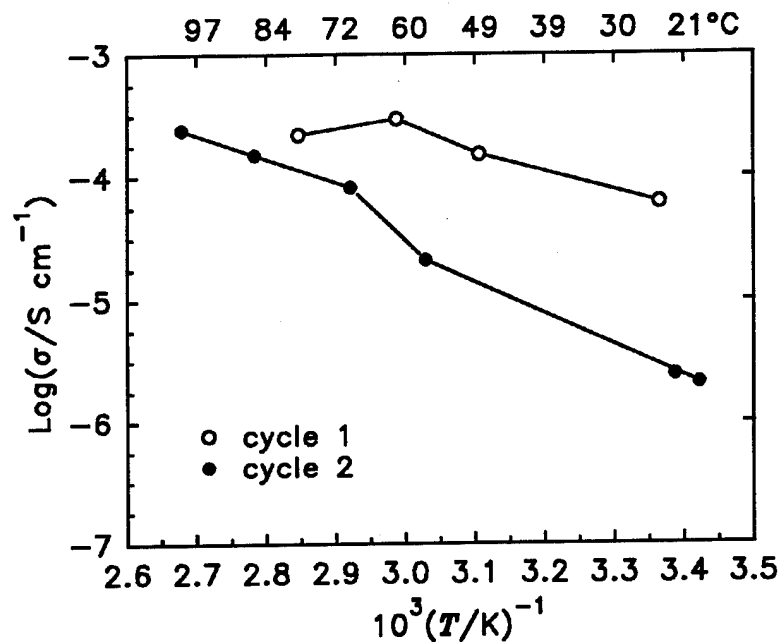
Figure 6. The effect of thermal cycling on the conductivity of solvent-plasticized $(PEO)_{20}(EC)_{10}(PC)_{10}(LiCF_3SO_3)$.
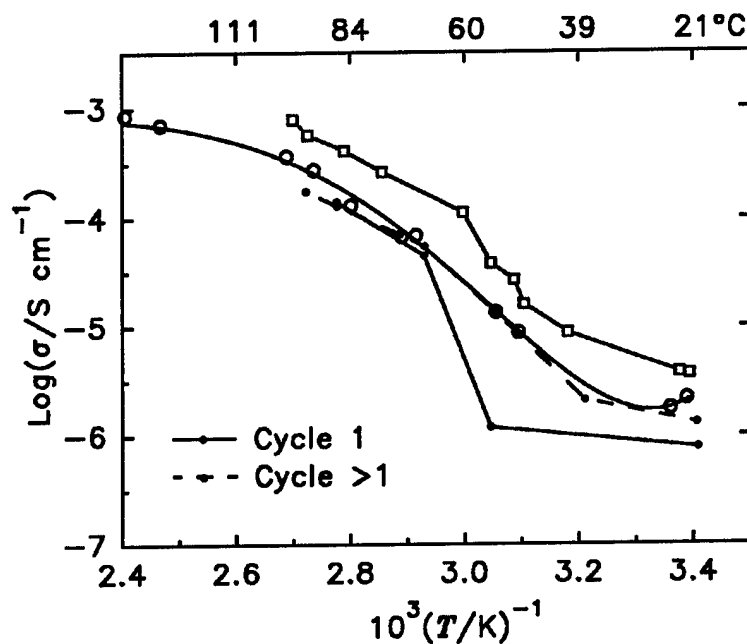
Figure 7. Conductivity vs temperature for $(PEO)_{20}(LiCF_3SO_3)$ with the addition of plasticizing esters, ● no plasticizer; ○ $(DOS)_1$; □ $(DEP)_5$.
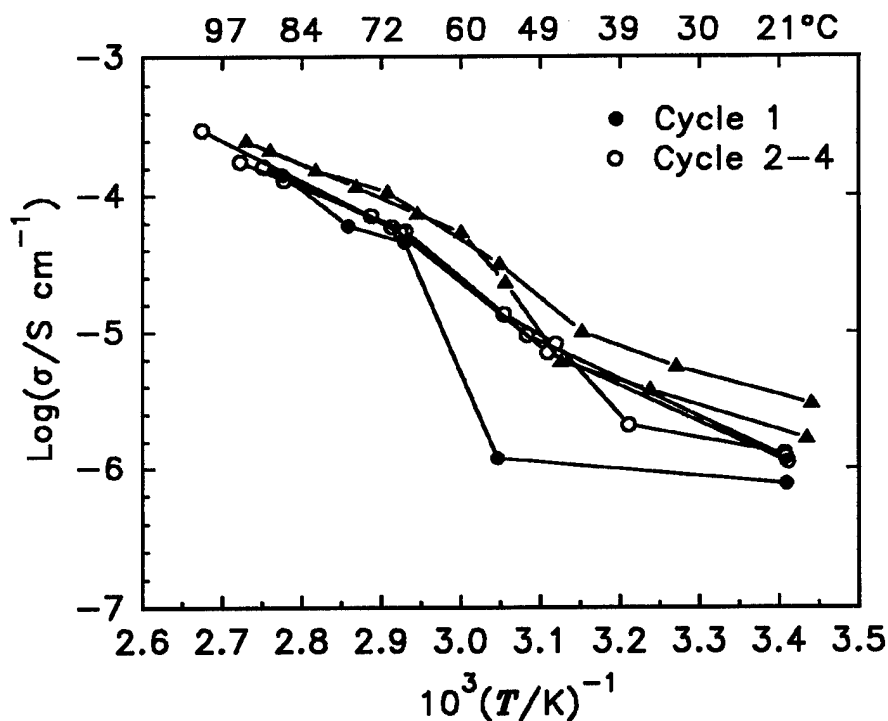
Figure 8. Conductivity of $(PEO)_{20}(LiCF_3SO_3)_1$ on first ($\bullet$) and subsequent ($\bigcirc$) thermal cycles, and the first two thermal cycles ($\blacktriangle$) with the addition of $(DMGP)_5$.

than 5, conductivity was determined. Between room temperature and T_m, conductivity of $(PEO)_{20}(LiCF_3SO_3)(DMGP)_{5-x}$ was as good or better than thermally cycled $(PEO)_{20}(LiCF_3SO_3)$ (Figure 8). Above T_m, conductivity was slightly better than films without DMGP. Another film was prepared with $x(DMGP)=1$ and with the addition of $LiN(CF_3SO_2)_2$, a plasticizing salt. With the lower fraction of DMGP the oily quality of the surface was eliminated. Conductivity of this film will be discussed later under "Combinations of Plasticizers."

Although dimethyl isophthalate (DMIP) is solid at room temperature (mp 64°C), it was used to prepare $(PEO)_{20}(LiCF_3SO_3)(DMIP)_5$. It was chosen as a candidate plasticizer based on its structural similarity to dimethyl phthalate, diethyl phthalate and dimethylglycol phthalate (see Figure 1). The conductivity of this film (not shown) was comparable to film containing DOS. That is, conductivity was as good but no better than thermally cycled polymer without DMIP. However, conductivity of the first thermal cycle was actually lower with DMIP added.

2-cyanopyridine (2CNP) was considered an attractive potential plasticizer since it has a dielectic constant (ϵ = 93.77 at 30°C (ref. 12)) that is greater than both water and PC, and a viscosity (1.832 cP at 30°C (ref. 12)) lower than PC. We hoped that the

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addition of 2CNP would reduce ion association thereby increasing ion mobility. However, conductivity of PEO films was actually worse when using a concentration of 2CNP corresponding 1:1 with the concentration of lithium triflate salt. Where 2CNP was added at levels five times that of the lithium salt, several samples were tested showing either small or no improvement.

Although disappointing, results for films containing 2CNP were not surprising based on concurrent studies in liquid electrolyte by Salomon and Hefter (12-13). Despite the very high permittivity of 2CNP, they observed weak to moderate ion association in solution, concluding that 2CNP is a poor solvent but noting that solution conductivity could be improved with the addition of a low viscosity co-solvent such as acetonitrile. They also found that single ion molar conductance of lithium-crown ether complexes in 2CNP was greater than that of the uncomplexed cation. This suggests that PEO-based films might show improved conductivity if 2CNP were used in conjunction with another plasticizer or a crown ether. However, when used alone, 2CNP was detrimental to ionic conductivity.

Plasticizing Salt. An alternative approach to decrease polymer crystallinity is the use of a plasticizing lithium salt. This would be preferred over liquid plasticizers since films would truly be solid state, eliminating the possibility of solvent reacting with the lithium electrode, and resulting in increased storage capability.

Armand (14) developed an imide salt, lithium trifluoromethanesulfonimide $(LiN(CF_3SO_2)_2)$, which increased ionic conductivity to about 5×10^{-5} S cm^{-1} at 25°C in PEO. In solution studies, Dominey (15) found conductivities to be higher than most lithium salts and determined the anion to be electrochemically stable between 0V and 4.5V. Weber (16) showed that the imide salt was much more conductive than lithium triflate, $LiCF_3SO_3$, despite the higher viscosity of the imide electrolyte. Others have recently reported limiting molar conductivities and association constants in liquid electrolytes (17), prepared phase diagrams and determined T_g-composition relationships in PEO (18), evaluated the effect of the imide salt on lithium plating/stripping in liquid electrolytes (19), followed the rise in impedance at the Li/SPE interface over extended time periods (20), and evaluated its use in other polymer hosts (21).

In the PEO-based SPE, we (22) found that $LiN(CF_3SO_2)_2$ was a better plasticizer at all temperatures than the solvents we explored (e.g., see Figure 9). However, the $(PEO)_8(LiN[CF_3SO_2]_2)$ film was extremely difficult to work with, being very tacky and tending to stick to itself, unable to be pulled apart. Addition of a second lithium salt might diminish this problem without jeopardizing the gain in conductivity, so a binary salt electrolyte, $(PEO)_{20}(LiCF_3SO_3)(LiN[CF_3SO_2]_2)$, was prepared. The sticky quality disappeared, leaving an easily handled freestanding film. A decline in conductivity midway between the single-salt systems was expected, but was observed to be only slightly lower than $(PEO)_8(LiN[CF_3SO_2]_2)$ (Figure 9).

Although the conductivities of $(PEO)_x(LiCF_3SO_3)$ films are highly dependent upon salt concentration, those of PEO-based films containing the imide salt were shown to be nearly independent of concentration (14). When using the plasticizing imide salt in a binary salt electrolyte, we found the effect of salt concentration to be small. Figure 10 shows that the conductivity of a 1:1 mixture of the triflate and imide salts was affected slightly (lower) as total lithium salt concentration was increased.
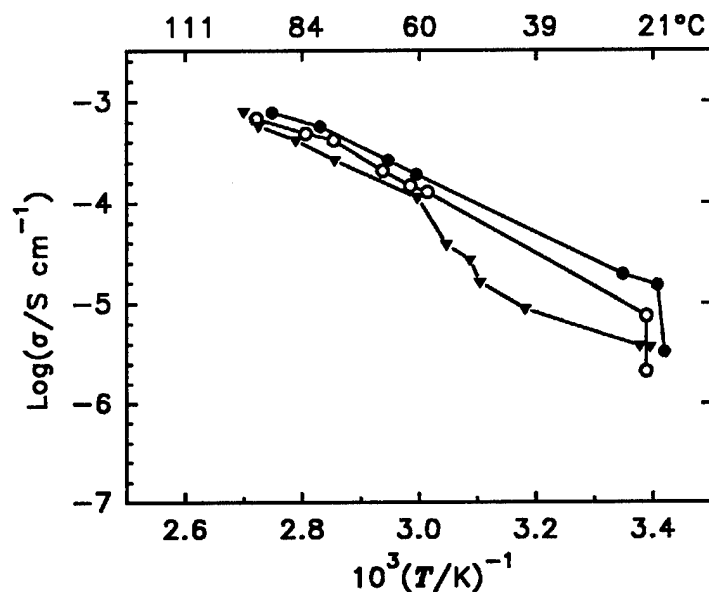

Figure 9. Conductivity effects with the addition of a plasticizing imide salt compared to a plasticizing solvent (DEP). ▼ $(PEO)_{20}(LiCF_3SO_3)(DEP)_5$; ● $(PEO)_8(LiN[CF_3SO_2]_2)$; ○ $(PEO)_{20}(LiCF_3SO_3)(LiN[CF_3SO_2]_2)$.
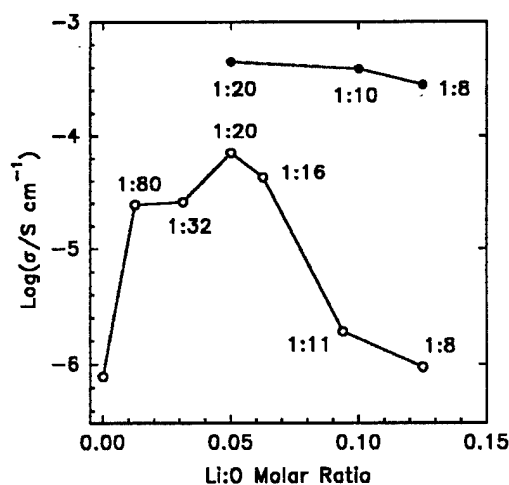
Figure 10. The dependence of conductivity on salt concentration at 74°C. ○ $(PEO)_x(LiCF_3SO_3)$; ● $(PEO)_x(LiCF_3SO_3)(LiN[CF_3SO_2]_2)$ (salts 1:1).

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Coordinating Compounds. Crown ethers are macrocyclic ligands that can be used effectively for ion-specific coordination of cations. They have been found useful in ion-selective polymer membranes (23), for solvent extraction of cations (24) and for cation selectivity (25), and in improving the ionic conductivity of both liquid electrolytes (13,26) and solid state (polymer) electrolytes (27-28).

The addition of $[Li^+15\text{-crown-5}]CF_3SO_3^-$ (1:1 with $LiCF_3SO_3$) showed slight improvement (in most cases) in conductivity over films without the additive between room temperature and 65°C (not shown). However, results were not consistent; in some cases conductivity was poorer than films without $[Li^+15\text{-crown-5}]CF_3SO_3^-$. Above 65°C, conductivity was the same or worse than films without the additive. After the first thermal cycle, conductivity remained better up to 60°C, but was worse above 60°C. The reason for the erratic data was clear upon disassembly of each cell, as a large amount of precipitated salt was observed on the stainless steel electrodes after peeling the polymer film away. Obviously there is a problem with solubility, and salt is coming out of the polymer upon heating and cooling.

Because only a small amount of material was on hand, 6,6-dibenzyl-14-crown-4 was added at a concentration equal to one tenth that of lithium triflate in preparing a film of $(PEO)_{20}(LiCF_3SO_3)_1(6,6\text{-dibenzyl-14-crown-4})_{0.1}$. During the first cycle, between ambient and 65°C, conductivity showed improvement intermediate beween the first and subsequent thermal cycles of films without the additive (Figure 11). After the first cycle, films containing 6,6-dibenzyl-14-crown-4 had conductivities that were better than thermally cycled films without 6,6-dibenzyl-14-crown-4.

Above the T_m of PEO, conductivity was unchanged compared to films without the additive. Perhaps if the concentration of 6,6-dibenzyl-14-crown-4 could be increased to 1.0 or greater the improvement in conductivity would be more striking, and might even show improvement of conductivity at temperatures above T_m.
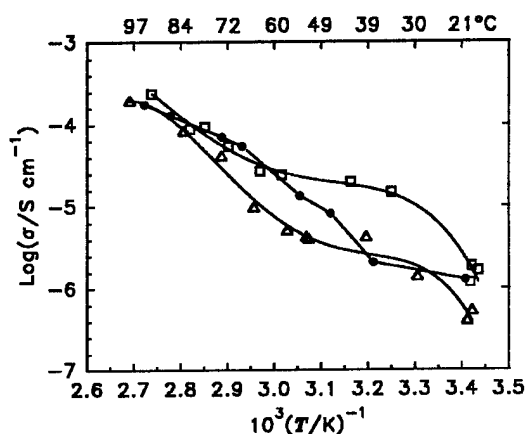
Figure 11. Conductivity vs temperature for thermally cycled $(PEO)_{20}(LiCF_3SO_3)_1$ (●), and with $(6,6\text{-dibenzyl-14-crown-4})_{0.1}$ for thermal cycle 1 (△) and subsequent cycles (□).

Combinations of Plasticizers. The combination of the plasticizing imide salt with a plasticizing solvent was also explored to see if an additive improvement in conductivity could be achieved. An electrolyte composed of $(PEO)_{20}(EC)_{10}(LiN[CF_3SO_2]_2)$ provided better conductivity (Figure 12) than any plasticizing solvent or salt alone. It was interesting to notice that this film was not sticky, and handled easily. However, in some (but not all) instances conductivity dropped off after the first temperature cycle. A waxy material believed to be EC (perhaps with dissolved salt) separated from the film. Since the melting point of EC is 36°C, a probable explanation is that as the electrolyte is cooled from high temperature the EC may or may not crystallize out depending on cooling rate and/or concentration of the electrolyte.

We then evaluated $(PEO)_{20}(DEP)_5(LiN[CF_3SO_2]_2)$, finding films to be "dry" but rubbery and very tacky. Because it readily stuck to itself, these films were difficult to handle. Conductivity was equal to that of the analogous film containing EC (Figure 12). At room temperature, however, conductivity was better, perhaps due in part to the lower melting point of DEP (-3°C).

Based on previous experience (discussed above), lithium triflate was added to reduce the tacky quality of the film. A film of $(PEO)_{40}(DEP)_5(LiN[CF_3SO_2]_2)(LiCF_3SO_3)$ (keeping the Li^+:O ratio constant at 1:20) was only slightly tacky, yet conductivity was indistinguishable from the electrolyte without lithium triflate (Figure 12).
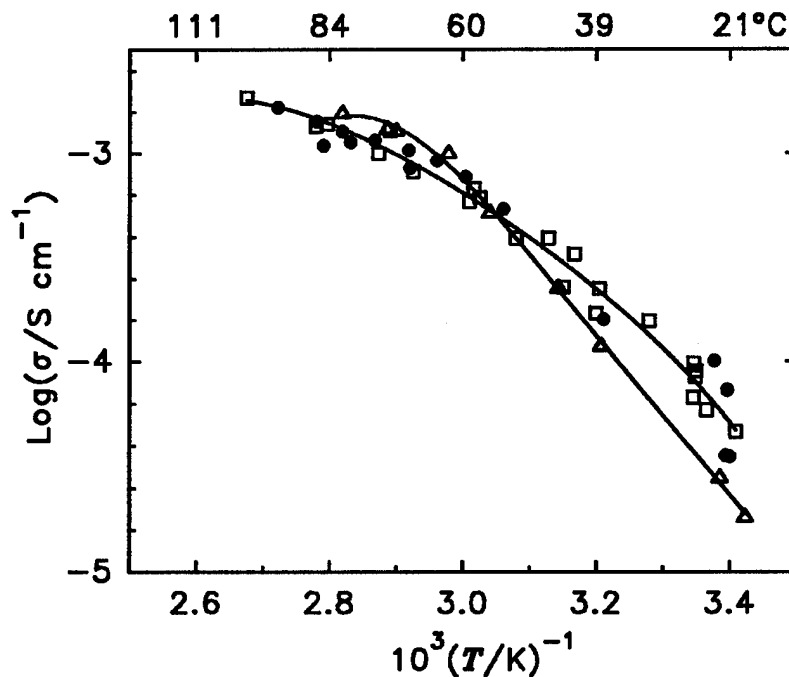
Figure 12. Conductivity vs temperature for PEO-based electrolytes containing combinations of a plasticizing solvent and a plasticizing salt. △ $(PEO)_{20}(EC)_{10}(LiN[CF_3SO_2]_2)$; ● $(PEO)_{20}(LiN[CF_3SO_2]_2)(DEP)_5$; □ $(PEO)_{40}(LiCF_3SO_3)(LiN[CF_3SO_2]_2)(DEP)_5$.

The improvement in conductivity with the imide-DEP additives is significant compared to our baseline electrolyte containing only lithium triflate. As cast, $(PEO)_{20}(LiCF_3SO_3)$ had a conductivity of 7.7 x 10^{-7} S cm^{-1} at 20°C (Figure 5), while electrolyte containing the imide salt and DEP was 4.6 x 10^{-5} S cm^{-1}. Even after thermally cycling $(PEO)_{20}(LiCF_3SO_3)$, conductivity increased to only 1.3 x 10^{-6} S cm^{-1}. At 38°C, a greater than 100-fold improvement in conductivity is observed (Figure 13) in films containing both plasticizers (2.3 x 10^{-4} S cm^{-1} versus 2.1 x 10^{-6} S cm^{-1}). The role of these plasticizers in enhancing conductivity is more than a simple reduction of polymer crystallinity since the conductivity of electrolyte without plasticizers is much less, even at temperatures above T_m where the polymer is completely amorphous.

To determine whether a sharp drop in conductivity would occur at or below the melting point of DEP (-3°C), impedance measurements were made down to -20°C. There was no change in the slope of the line, and, in fact, the conductivity at -20°C (2.3 x 10^{-6} S cm^{-1}) remained high enough to be comparable to that of thermally cycled $(PEO)_{20}(LiCF_3SO_3)$ at 38°C (Figure 13).

Dimethyl phthalate (DMP) resembles DMIP except for the ring position of the pendant groups (see Figure 1). Two concentrations of DMP were used in combination with the imide salt, forming films of $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1(DMP)_X$, where X is equal to 1 or 5. When X was 1, conductivity was much improved, but not as much as films with $(DEP)_5$. Room temperature conductivity was about 10^{-5} S cm^{-1}, and 10^{-6} S cm^{-1} at 0°C. Improvement was about equal to that seen with films containing $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1$.

When X was 5, conductivity was only slightly less than films with $(DEP)_5$, but fell off below -10°C (Figure 14). Conductivity at -20°C was slightly better than 10^{-6} S cm^{-1}.
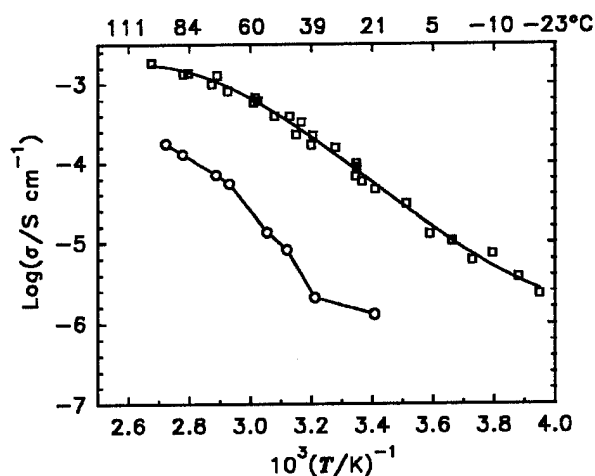
Figure 13. Conductivity vs temperature for "baseline" and plasticized PEO-lithium triflate. O $(PEO)_{20}(LiCF_3SO_3)$; □ $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1(DEP)_5$.
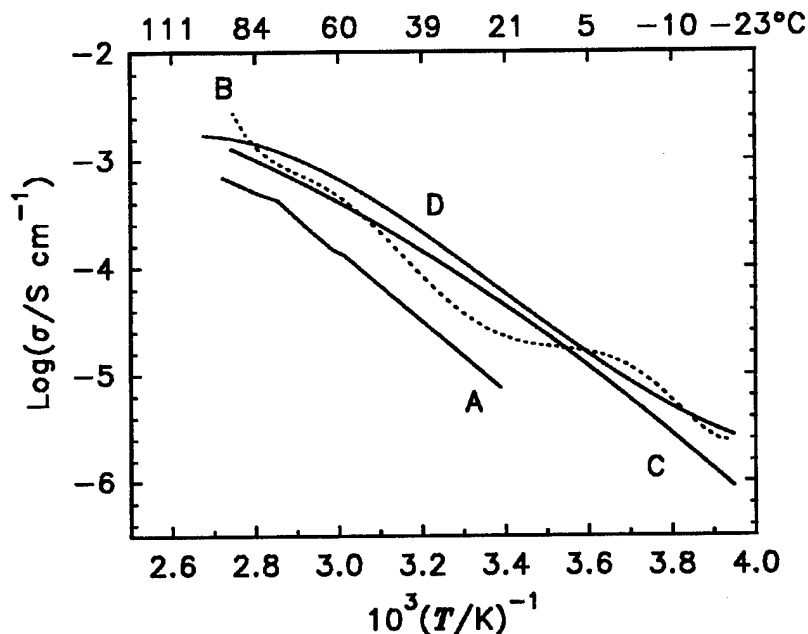
Figure 14. Conductivity vs temperature for $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1$, A, and films containing $(DMGP)_1$, B; $(DMP)_5$, C; and $(DEP)_5$, D.

PEO containing lithium triflate and $(DMGP)_5$ was covered in the "Plasticizing Solvents" section, where $x(DMGP) = 5$ was found to exceed the solubility limit of DMGP, causing an oily film. At a lower concentration of $x(DMGP) = 1$, a "dry" film that also contained the imide salt was prepared, $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1(DMGP)_1$. The conductivity of this film (Figure 14) was approximately equal to films containing $(DEP)_5$ at temperatures between -20 to 0°C, while above 0°C, conductivity was lower until about 84°C, where they converged.

Dibutyl sebacate (DBS) was used in conjunction with $LiN(CF_3SO_2)_2$ to prepare a dry, flexible electrolyte of $(PEO)_{20}(LiN[CF_3SO_2]_2)_1(DBS)_1$. Conductivity (Figure 15) was about equivalent to electrolyte containing $(PEO)_{40}(LiCF_3SO_3)_1(LiN[CF_3SO_2]_2)_1(DMP)_1$ as described above. At a higher concentration of $(DBS)_5$, the film was so "wet" and oily that it was not usable.

Tris(2-ethylhexyl) trimellitate (TEHT) was also combined with the imide salt to prepare $(PEO)_{20}(LiN[CF_3SO_2]_2)_1(TEHT)_1$. Solubility of TEHT in PEO is poor, since, although a very flexible film formed, it was extremely "oily". Conductivity of this film was measured, realizing that the true concentration of TEHT was much less than one. Conductivity was comparable to film containing DBS (Figure 15). Another film was prepared with half the concentration of TEHT, $(PEO)_{20}(LiN[CF_3SO_2]_2)_1(TEHT)_{0.5}$. At this lower concentration, the film was dry and slightly tacky. Compared to $(PEO)_8(LiN(CF_3SO_2)_2)_1$, this film has comparable conductivity up to 50°C. Above 50°C,

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conductivity is a little better in the film with TEHT (Figure 16).
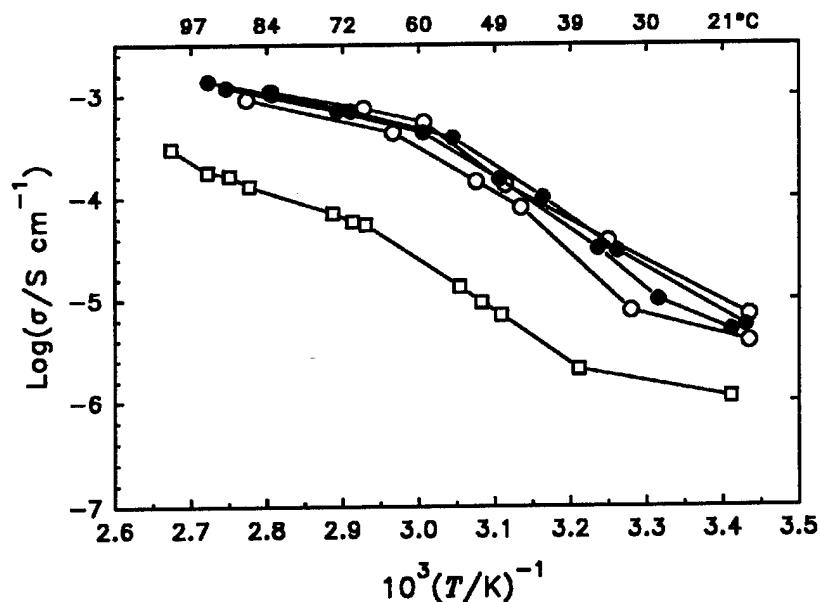
Figure 15. Conductivity as a function of temperature for thermally cycled $(PEO)_{20}(LiN[CF_3SO_2]_2)_1$ □; $(PEO)_{20}(LiN[CF_3SO_2]_2)_1$ with $(DBS)_1$ ○, first (lower) and second (upper) thermal cycles; $(PEO)_{20}(LiN[CF_3SO_2]_2)_1$ with $(TEHT)_1$ ●, first and second thermal cycles.

Figure 16. Conductivity vs temperature for $(PEO)_x(LiN[CF_3SO_2]_2)_1$ film with and without $(TEHT)_{0.5}$ plasticizer.

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One combination that was not tested due to lack of material was the combination of the imide salt with 6,6-dibenzyl-14-crown-4 (coordinating agent). We would expect that use of these materials in a 1:1 ratio to each other could provide conductivity which is superior to all other films tested.

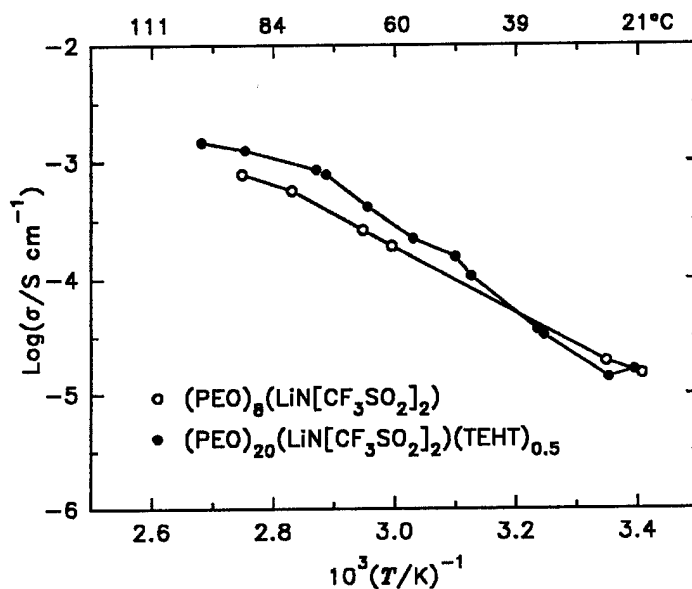**Electrochemical Stability.** In addition to raising conductivity, the most desirable plasticizing agents are those that show electrochemical stability over the widest range of potentials. The range of stability and reversibility of redox reactions were determined via cyclic voltammetric studies. It was not possible to produce useful cyclic voltammograms with PEO films due to their high resistance, so solution studies of plasticizers were conducted. Because metallic lithium is not stable with acetonitrile (the preferred solvent), PC was used as the solvent. Also, PC is stable above 4 V. Besides the plasticizer of interest, $LiCF_3SO_3$ was added to make the solution more conductive.

Electrochemical stability between 4.2 V and 2 V (vs Li) is critical because some of the metal oxide cathode materials (e.g., $LiCoO_2$) must be charged up to 4.2 V, and 2.0 V is the usual cell cutoff for military battery applications. Repetitive cycling was performed within these limits (and sometimes beyond) in addition to single sweeps below 2 V. Sweeping below 2 V was to determine the extent of plasticizer reduction and to observe for reversible reactions; this being important to know for overdischarge conditions.

Figure 17 shows 5mV s^{-1} sweeps for 0.25M $LiCF_3SO_3$-PC "baseline" electrolyte without any plasticizer added. The counter electrode and reference electrodes were lithium, and the working electrode was either glassy carbon or pure aluminum (both polished to a mirror finish). Using the glassy carbon working electrode, this baseline electrolyte was stable to nearly 0.5 V before any appreciable reduction ($Li^+ \rightarrow Li^\circ$) occurred. No oxidation was observed up to 4 V. With the aluminum working electrode, the electrolyte was stable to 4V, and reduction of Li^+ did not occur until 0.05V. Aluminum forms an alloy with lithium simultaneous with deposition of lithium metal. On the reverse (anodic) sweep, current continued to increase to a peak of 0.68 mA cm^{-2} at 0.05V. This suggests that the Al-Li alloy is more electrocatalytic and accepts Li^+ at a faster rate. The crossover to anodic currents occurs at 0.34V, with deposited lithium oxidizing before the alloy. The peak current (0.57 mA cm^{-2}) for de-lithiation occurs at 0.63V.

Sweeping to 1 V and using a more sensitive scale for current density, we observed small currents between 4.2 to 1 V (Figure 18) with a maximum oxidation current less than 20 μA cm^{-2} at 4.2 V. A reduction current begins at about 2.5 V, becoming 11 μA cm^{-2} at a potential of 2.0 V, and reaching a maximum of 60 μA cm^{-2} at 1.0 V. A solution twice as concentrated (0.5 M $LiCF_3SO_3$) showed about the same oxidation current but approximately twice the reduction current (as expected). Repetitive cycling between 4.3 and 1.8 V showed no change in the oxidation peak after 50 cycles (Figure 19). The reduction peak which developed at 2.5 V and below diminished by about 6 μA cm^{-2} from a peak current density of 28 μA cm^{-2}.

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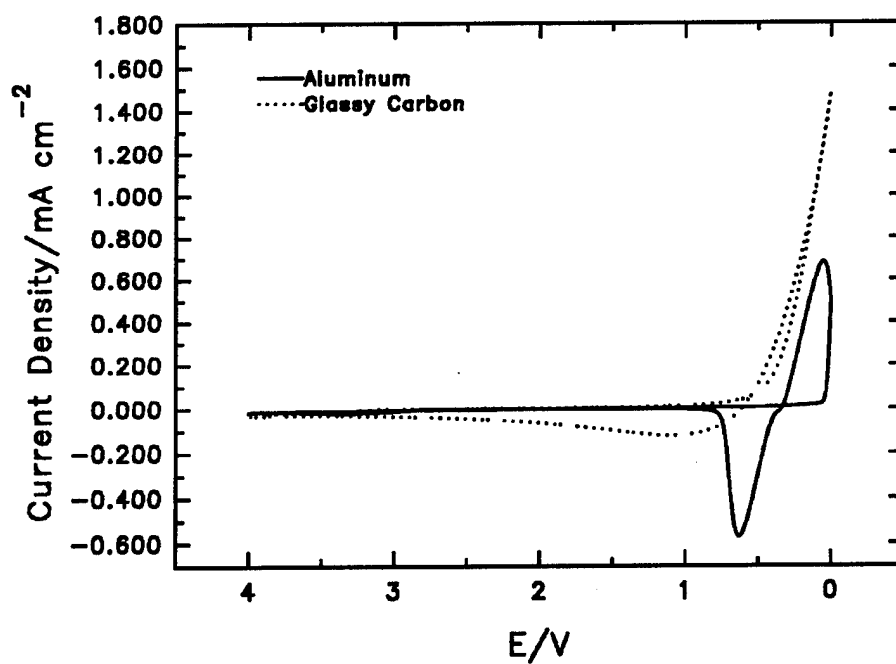
Figure 17. Cyclic voltammogram of 0.25 M LiCF₃SO₃ in propylene carbonate. Lithium counter electrode, glassy carbon or aluminum working electrodes, vs Li reference.
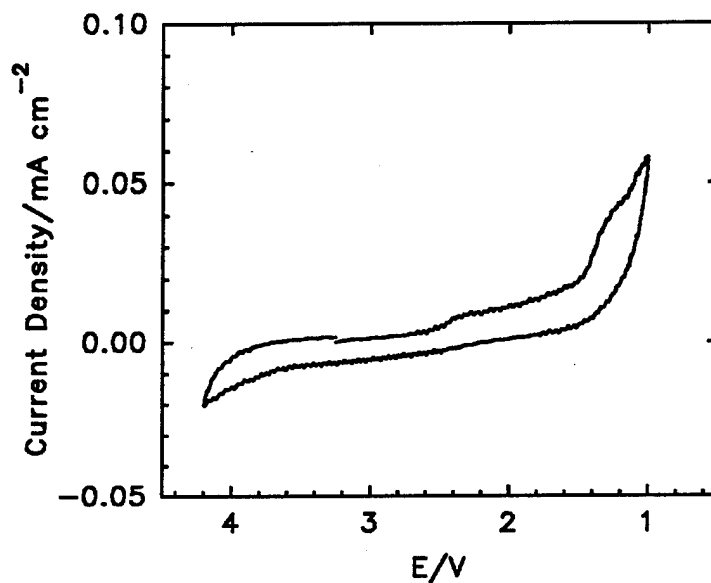
Figure 18. Glassy carbon vs lithium (5mV s⁻¹) from 3.25 OCV to 1.0 V to 4.2 V to 3.25 V in 0.25 M LiCF₃SO₃-PC.
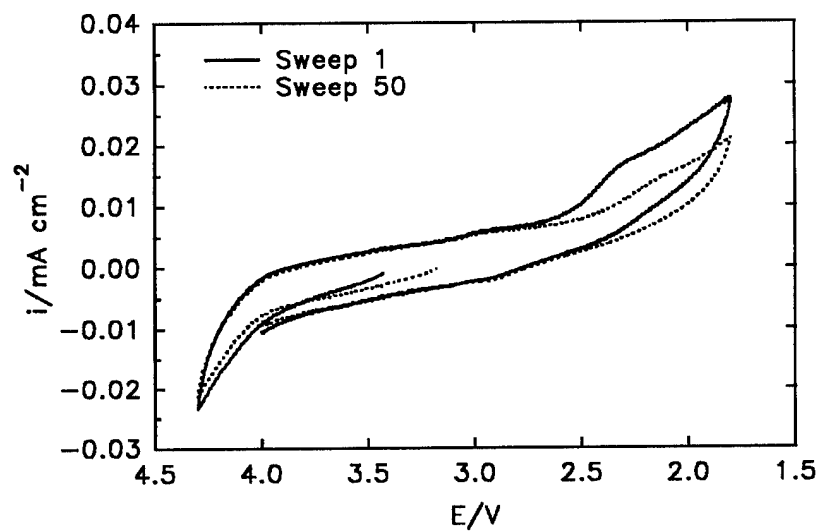
Figure 19. First and fiftieth sweeps of glassy carbon in 0.5M LiCF$_3$SO$_3$-PC (5mV s^{-1}) from OCV to 4.3 V to 1.8 V (middle 48 cycles at 100 mV s^{-1}).
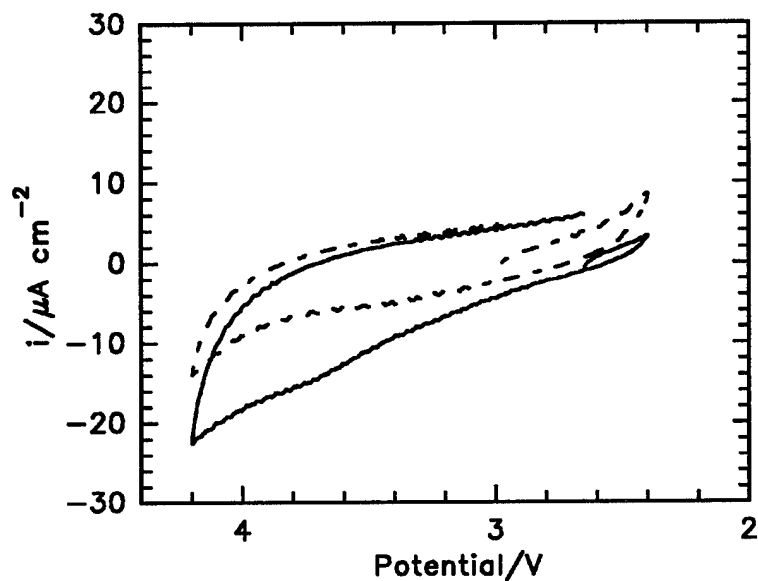
Figure 20. Cyclic voltammogram (5 mV s^{-1}) of glassy carbon in 0.25 M LiCF$_3$SO$_3$-PC containing PEO. First (solid) and fiftieth (dash) sweeps (middle 48 sweeps at 100 mV s^{-1}).

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PEO was added to this "baseline" electrolyte to determine the stability of this polymer within the voltage range of interest. The reversible intercalation/alloying seen at about 0 V with aluminum in the "baseline" electrolyte was also seen when a low concentration of 0.073 M PEO was added. However, in a solution saturated with PEO (somewhere below 0.25 M) the reversible behavior was not seen. A large reduction occurred but oxidation did not occur on the return sweep. Perhaps PEO is being reduced simultaneously with intercalation/alloying of lithium and fouling the electrode so as to make it irreversible. In the voltage range relevant for cycling a $Li/LiCoO_2$ cell, 4.2 V to 2.4 V, there was no significant current (<25 μA cm^{-2}) over 50 cycles (Figure 20), indicating that PEO should be electrochemically stable during cycling.

Voltammetric sweeps (5 mV s^{-1}) between 4.3 and 1.0 V of baseline electrolyte containing either 0.25M DEP or 0.25M DMP are shown in Figure 21. Large reduction currents occur with both plasticizers beginning just below 1.5 V. By comparison, the baseline electrolyte exhibits almost no reduction current. None of the electrolytes show significant oxidation up through 4.3 V.

In electrolyte containing 0.25M DEP, after 20 cycles between 4.2 and 2.0 V at 20 mV s^{-1} and 50 cycles between 4.3 V and 1.8 V, a couple of small peaks were observed, but there was no change in the voltammogram, indicating a high degree of electrolyte stability. In electrolyte containing 0.25M DMP, 100 cycles between 4.3 and 2.0 V at 100 mV s^{-1} showed a 5 μA cm^{-2} increase in the small reduction current (30 μA cm^{-2}) and a 30 μA cm^{-2} decrease in peak oxidation current (from 60 μA cm^{-2}). In a second case,
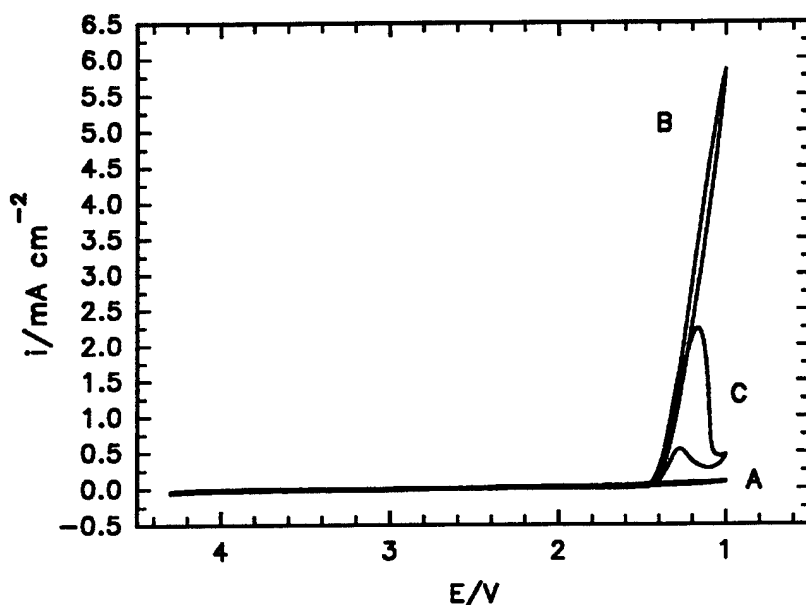
Figure 21. Glassy carbon vs lithium in 0.5 M $LiCF_3SO_3$-PC (A), with 0.25 M DEP (B), with 0.25 M DMP (C) at 5 mV s^{-1} cycled from OCV to between 1.0 V and 4.3 V.

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50 cycles at 10 mV s^{-1} between 4.0 and 2.0 V showed no change in either reduction or oxidation currents, which both peaked at 4 μA cm^{-2}.

A cell containing 0.25 M DMGP in the electrolyte immediately began to turn yellow, suggesting a chemical reaction with lithium. DMGP begins to be reduced cathodic to 1.5V, and shows no anodic peak up to 4.3V (Figure 22). A second sweep a few minutes later (not shown) exhibited an increased peak current. A few hours later, the solution color was a darker yellow/orange. The cathodic peak grew very large, indicating a relationship between the amount of material produced by the chemical reaction and this reduction peak. The i_{peak}, which in the "fresh" cell was about 0.35 mA cm^{-2}, grew to just over 2.1 mA cm^{-2}, a 6-fold increase. Despite the reaction that was occurring, the cell was cycled 100 times at 100 mV s^{-1} between 4.2 V and 2.0 V. In this limited potential range, currents were very low (<0.1 mA cm^{-2}) initially, and changed very little after 100 cycles. Oxidation current at its peak decreased by 20 μA cm^{-2} while reduction current increased by 20 μA cm^{-2}. This is insignificant considering that the high sweep rate will produce larger currents than are seen at the 5 mV s^{-1} rate.
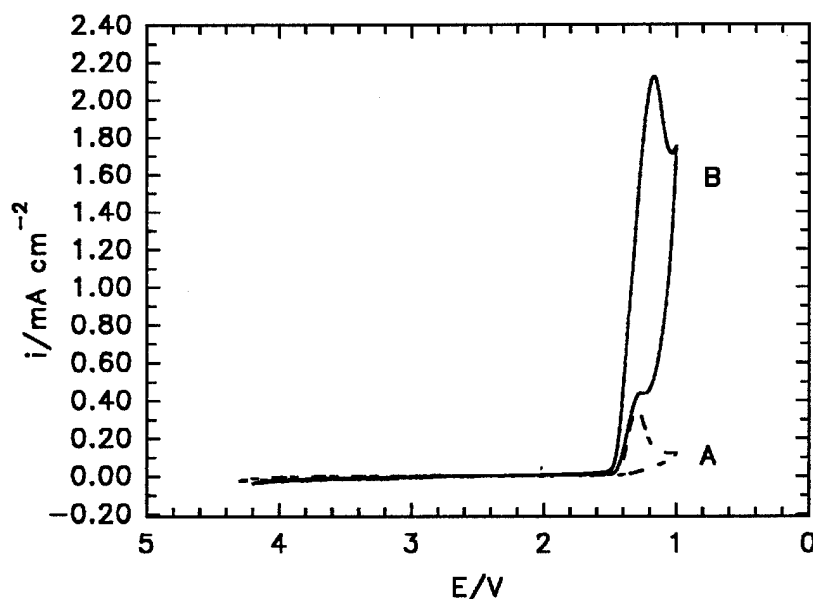
Figure 22. Glassy carbon vs lithium in 0.36 M LiCF$_3$SO$_3$-PC containing 0.25 M DMGP at 5mV s^{-1} between 1.0 V and 4.3 V. Initial sweep (A) and after a few hours (B).

Figure 23 shows 5 mV s^{-1} sweeps of electrolyte containing 0.25M DMIP. Reduction begins at 1.5V and reaches i_{peak} (about 1.3 mA cm^{-2}) at 1.1V. After 101 cycles (100 mV s^{-1}) the scan was unchanged. Sweeping to 0V, very little current (0.1 mA cm^{-2}) was produced at 0V (in contrast to 1.5 mA cm^{-2} shown in Figure 17), indicating little deposition of lithium. This indicates that the reduction products formed at 1.1V were inhibiting to deposition of metallic lithium but did not interfere with electrode kinetics

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Figure 23. Sweep 1 and 101 for glassy carbon vs lithium in 0.25 M LiCF$_3$SO$_3$-PC with 0.25 M DMIP at 5 mV s^{-1} between 4.2 V and 1.0 V. Other sweeps at 100 mV^{-1}.

Figure 24. Glassy carbon vs lithium at 5 mV s^{-1} in 0.25 M LiCF$_3$SO$_3$-propylene carbonate/acetonitrile (3:1 v/v) containing <.03 M TEHT.

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for the reduction of electrolyte.

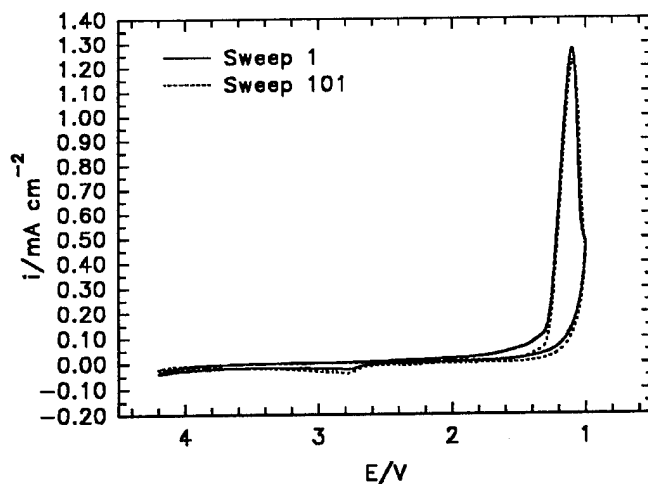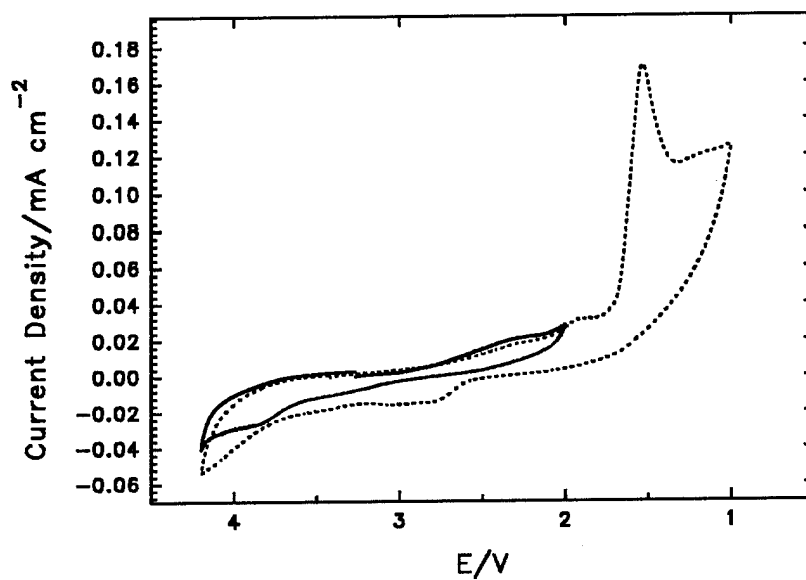TEHT was not very soluble in PC showing a clear TEHT/PC liquid separation even after vigorous stirring and standing for several days. TEHT was dissolved in acetonitrile and added to $LiCF_3SO_3$-PC to prepare a solution containing 0.03 M TEHT. Because TEHT is immiscible in PC, the actual concentration was less, although some TEHT did go into solution as it was easily detected with cyclic voltammetry (Figure 24). Between 4.2V and 2.0V very small currents (<40 μA cm^{-2}) were observed. When taken to 1.0V, large reduction peaks occurred at 1.55V and 1.0V.

The two sebacate plasticizers (not shown) showed properties similar to the other plasticizers we have described. A solution containing 0.25M DBS showed low currents, with no significant reduction occurring until potentials cathodic to 1.5V. This observation also applies to electrolyte containing DOS.

In all cases, significant reduction of electrolyte (containing plasticizer) occurs beginning at 1.5V and is not reversible. Since manportable military batteries are discharged to a 2.0 V cutoff, this provides a 0.5 V margin of overdischarge protection. However, a further discharge below 1.5 V or operation into reversal will irreversibly degrade the electrolyte.

Chemical Stability with Metallic Lithium. To get some idea of the chemical stability of the plasticizing solvents with metallic lithium, metal coupons of lithium were sealed in vials containing the pure solvents and then observed over a period of months.

Uncontaminated lithium metal has a shiny silver appearance. A few hours after contact with DOS the lithium took on a slight gray tarnish. There was no change over the next several days. After 12 and 16 months, the solution remained clear, while most of the surface of the lithium was black, with some areas of silver-gray. No pitting or reduction in size of the lithium was seen. Because the DOS did not degrade and the lithium corrosion was limited, it is likely that corrosion was due to either: 1) growth of a protective film covering the lithium, or 2) the reaction of water or other impurities in the DOS with lithium, which ceased after all the impurities were reacted.

In DMP, the lithium looked pristine after 3 days. After 10 days a slight gray tarnish had developed on the lithium while the DMP remained clear. No change occurred after 4 weeks. After 10 months, the DMP remained clear with some of the lithium discolored silver-gray while the rest had a black tarnish. Again, it seems corrosion was due to either a self-limiting oxidation reaction or a reaction with impurities.

Lithium was noted to react in DMGP-PC during the cyclic voltammetric studies, where an immediate discoloration of the electrolyte was noticed. Lithium appeared unaffected in neat DMGP but the liquid deteriorated and turned dark brown.

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In DEP, lithium stayed pristine during the first 24 hours, but after two weeks the solution began to discolor. The majority of the lithium remained shiny, but one edge was pitted/corroded. Eventually, the entire metal coupon completely dissolved, leaving a brown liquid.

If plasticizers are to be used in lithium batteries, stability with metallic lithium is necessary. However, instability toward lithium can be circumvented by replacing the metallic lithium electrode with a Li^+ ion intercalating material. Although this will reduce gravimetric engergy density, chemical reactions that would occur with metallic lithium can be avoided.

Conclusions

The ionic conductivity of a PEO-based solid polymer electrolyte has been improved through the use of plasticizers. We studied plasticizers whose chemical structures included ester linkages, believing that the multiple oxygen sites would provide coordination sites for the Li^+ ions. Some plasticizers (e.g., DOS) simply reduced crystallinity of the PEO. The amorphous structure shows increased conductivity only below the melting temperature of PEO ($\approx 66°C$), and is similar to a thermally cycled film without plasticizer. Other plasticizers reduced crystallinity and also increased conductivity. The ability to increase conductivity was evident above the T_m of PEO, where plasticized films had higher conductivity than completely amorphous films without plasticizer. The best improvement in conductivity was seen with a combination of $LiN(CF_3SO_2)_2$, a plasticizing salt, and one of three plasticizing solvents: DEP, DMP, and DMGP. DEP was slightly better than the other two, but DMGP was effective at one fifth the concentration of DEP.

In films without plasticizers, a coordinating compound, 6,6-dibenzyl-14-crown-4, was found to significantly increase conductivity. If combined with plasticizers, this combination might provide higher conductivity than any of the other formulations tested.

Electrochemically, all of the plasticizers (in general) proved to be relatively stable between 4.3 V and 1.5 V versus lithium. Reduction of plasticizers began at 1.5 V and was irreversible. This wide range of stability is a promising result for use of these compounds in a rechargeable lithium battery. For example, one of the highest lithium couples, $Li/LiCoO_2$, operates between about 4.2 V and 2.5 V, well within the stability limits of these plasticizers.

However, some plasticizers that were tested for chemical stability with lithium metal were found to react with lithium or were of questionable stability. This may not be a serious problem since the lithium metal anode can be replaced with a lithium intercalating material such as Li_xC_6. This would also reduce the tendency to form dendrites. This "lithium-ion" technology represents the ultimate in safety, being the most attractive alternative for use in the consumer market.

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At present, ambient temperature conductivity of solid polymer electrolytes is still low compared to liquid electrolytes, preventing operation at high rates. If cells can be operated at 60°C where electrolyte conductivity is very good, a solid state rechargeable lithium battery with a more practical rate capability would result. Identifying even better plasticizers is necessary if a practical ambient temperature (or low temperature) battery with a PEO-based solid polymer electrolyte is to be a commercial success.

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White Sands Missile Range
(1) NM 88002-5501

Dir, ARL Sensors, Signatures,
Signal & Information Processing
Directorate (S3I)
ATTN: AMSRL-SS
2800 Powder Mill Road
(1) Adelphi, MD 20783-1145

Dir, CECOM Night Vision/
Electronic Sensors Directorate
ATTN: AMSEL-RD-NV-D
(1) Fort Belvoir, VA 22060-5677

Dir, CECOM Intelligence and
Electronic Warfare Directorate
ATTN: AMSEL-RD-IEW-D
Vint Hill Farms Station
(1) Warrenton, VA 22186-5100

Cdr, Marine Corps Liaison Office
ATTN: AMSEL-LN-MC
(1) Fort Monmouth, NJ 07703-5033

Naval Surface Weapons Center
Code R-23
ATTN: Patricia Smith
(1) Silver Spring, MD 20903-5000

DARPA/TTO
ATTN: Dr. Peter Kemmey
1400 Wilson Blvd
(1) Arlington, VA 22209

US Army Armament Research,
Development & Engineering Ctr
ATTN: SMCAR-FSE
(1) Dr. A. Graf
(1) Dr. K.C. Pan
(1) Ms. Laura Krzastek
(1) Ms. Pam Stevens
Picatinny Arsenal, NJ 07806-5000

US Army Armament Research,
Development & Engineering Ctr
ATTN: SMCAR-FSC
(1) Mr. G. Ferdinand
(1) Ms. H. Naber-Libby
Picatinny Arsenal, NJ 07806-5000

US Army Armament Research,
Development & Engineering Ctr
ATTN: SMCAR-TD
(1) Dr. T. Davidson
Picatinny Arsenal, NJ 07806-5000

US Army Armament Research,
Development & Engineering Ctr
ATTN: SMCAR-CCL-FA
(1) Mr. H. Moore
Picatinny Arsenal, NJ 07806-5000

US Army Armament Research,
Development & Engineering Ctr
ATTN: SMCAR-AEE-B
(1) Dr. D. Downs
Picatinny Arsenal, NJ 07806-5000

US Army Ballistic Research Lab
ATTN: SLCBR-IB-B
(1) Mr. W. Oberle
(1) Dr. K. White
Aberdeen Proving Ground, MD
21005-0566

US Army Ballistic Research Lab
ATTN: SLCBR-TB-EP
(1) Mr. A. Zielinski
Aberdeen Proving Ground, MD
21005-0566

Dr. John Transue
1901 North Beauregard St
Suite 380
(1) Alexandria, VA 22311

Westinghouse
Naval Systems Division
ATTN: Mr. Steven Specht
476 Center Street
(1) Chardon, OH 44024

University of Texas at Austin
ATTN: Mr. John H. Gully
10100 Burnet Road
EME, Bldg 133
(1) Austin, TX 70758-4497

University of Texas at Austin
Institute for Advanced Technology
ATTN: Dr. Harry D. Fair, Jr.
10100 Burnet Road
(1) Austin, TX 70758-4497

FMC Corporation
Advanced Systems Center
ATTN: Mr. Michael Seale
4800 E. River Road
(1) Minneapolis, MN 55459-0043

General Dynamics Land Systems Div
ATTN: Dr. Bruce VanDeusen
P.O. Box 2074
(1) Warren, MI 48090-2074

State University of NY at Buffalo
Electrical and Computer Engrg Dept
ATTN: Dr. Walter J. Sarjeant
Bonner Hall, Room 312
(1) Buffalo, NY 14260