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13. ABSTRACT (Maximum 200 words)

In the Phase-I study, TechDrive synthesized several phenol monomers. Two of these monomers, one of which is new, were converted to phenolic polymers by enzymatic means, using horseradish peroxidase and hydrogen peroxide. The monomers and polymers were fully characterized using thin layer chromatography, FT-IR and NMR spectroscopy, gel permeation chromatography and light scattering analyses. Solid polymeric electrolytes (SPEs) were formulated using the processable polyphenols. Ionic conductivity measurements of one of the SPEs based on a substituted polyphenol showed promising levels of ionic conductivity. Addition of a plasticizer dramatically improved the room temperature conductivity of the SPE film. Laboratory cells, fabricated using the SPEs, gave very promising results.

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Solid Polymer Electrolytes Derived from Polyphenols

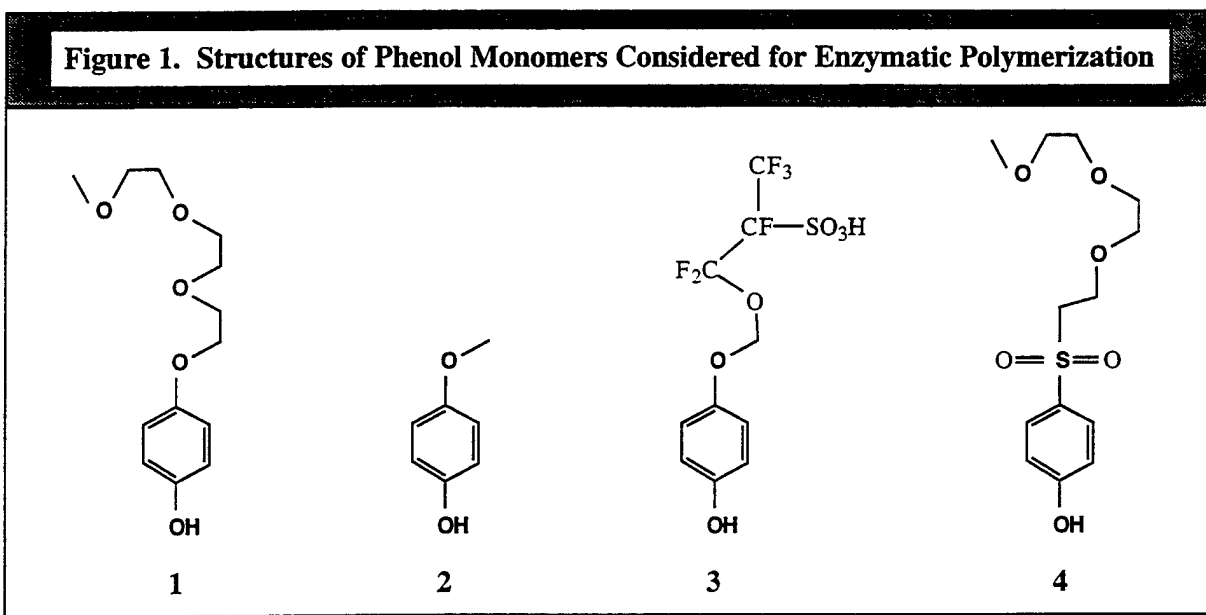
Robert Filler
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TechDrive, Inc.

Phase-I Final Report

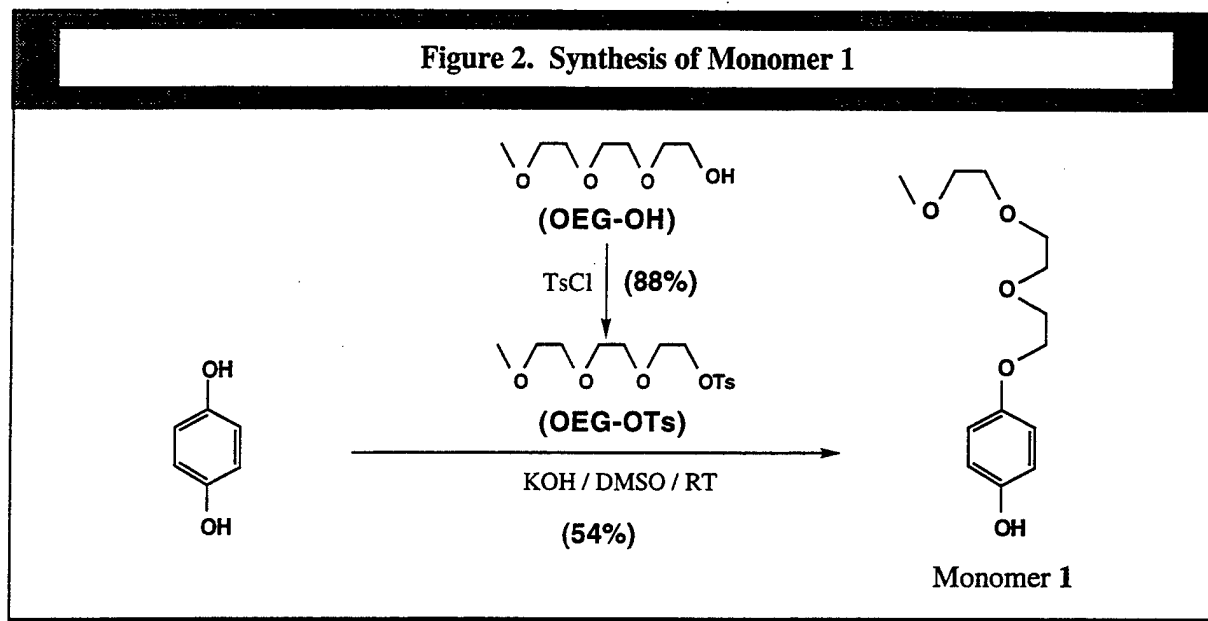
The Phase-I research was focused on the following six primary objectives: (i) Synthesis of Phenol Monomers. (ii) Synthesis of Polyphenols. (iii) Lithiation of Polyphenols. (iv) Characterization of Phenol Monomers and Polyphenols. (v) Characterization of SPEs. (vi) Evaluation of SPEs in Laboratory Cells. This section provides a summary of the results relevant to the Phase-II proposal.

Synthesis of Phenol Monomers

We have attempted to synthesize a number of phenol monomers suitable for the enzymatic polymerization reaction (Figure 1). Among these, only monomers 1 and 2 were pursued from the standpoint of synthetic flexibility and commercial applications.



The reaction conditions for the synthesis of monomer 1 was established after a thorough study of various reaction parameters such as concentration, temperature, time, work-up and purification procedure. The optimized conditions allowed us to prepare monomer 1 in larger quantities (Figure 2). The procedure is given below:



Synthesis of Monomer 1: In a 500 ml single-neck round bottomed flask fitted with a mechanical stirrer, hydroquinone (30.88 g), OEG-OTs¹ (88.96 g) and KOH (46.97 g) were added to 200 ml of DMSO and stirred overnight at room temperature (water bath). The mixture was transferred to a separatory funnel using 50 ml of water. The solution was first extracted 3x with diethyl ether (100, 50 and 50 ml) to remove both unreacted tosylate and disubstituted derivative. The solution was then acidified with 50 ml of conc. HCl, extracted 3x with chloroform (100, 50 and 50 ml), the organic layer washed twice with 100 ml water, dried over MgSO₄, and concentrated in vacuo. The product, which contained traces of sludge, was further purified by filtering through a 1 cm alumina column with ethyl acetate: methanol (95:5) as eluent. Yield: 38.5 g (54%, straw colored liquid).

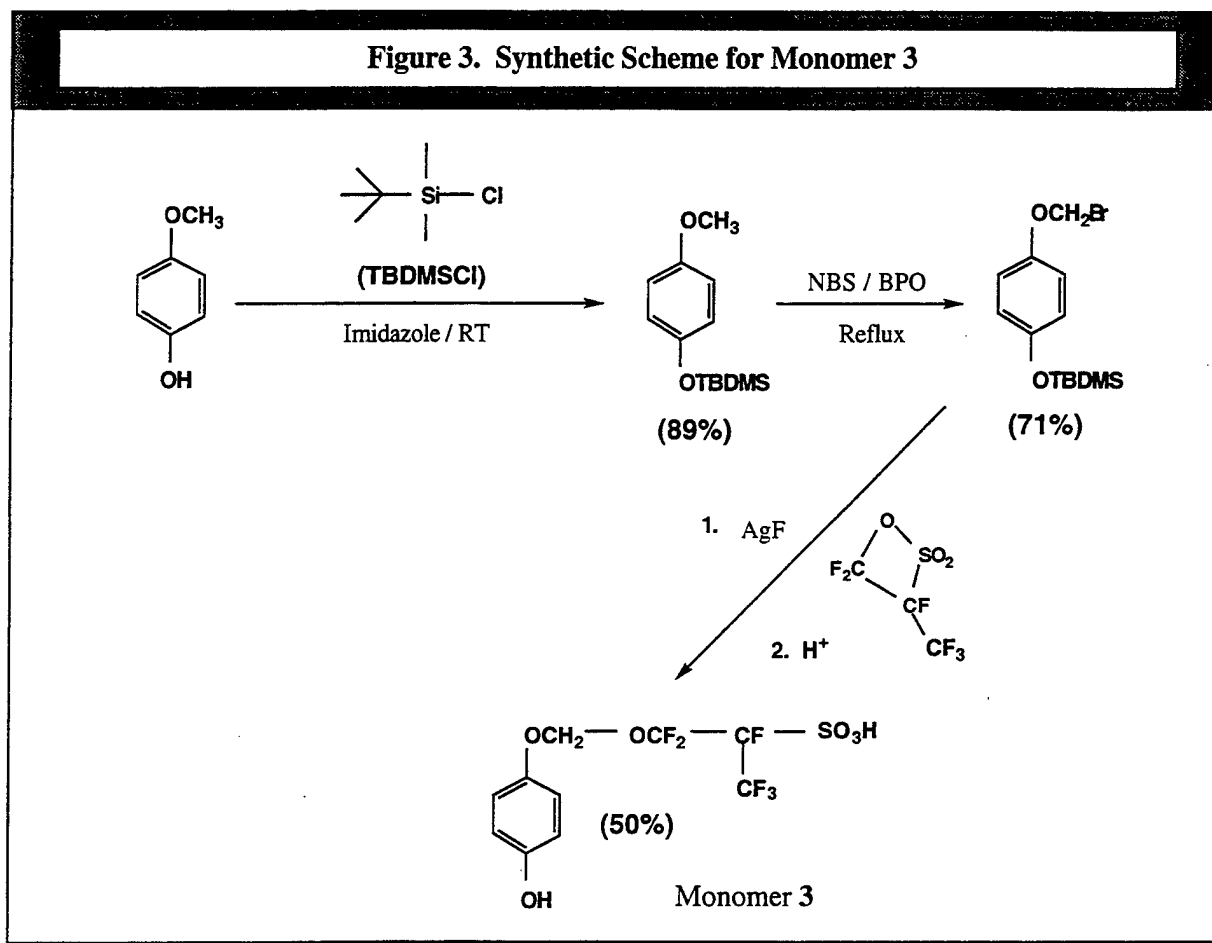
This method is very short and eliminates extensive chromatographic separations. The above procedure was also performed by using OEG-Br in place of OEG-OTs. The yield was about the same. Since OEG-OTs is easy to prepare in larger quantities from the corresponding alcohol, OEG-OH, we prefer the use of OEG-OTs. We are also quite confident that the yield can be further improved by scaling up the reaction and/or varying the proportion of the solvent.

We have also attempted a systematic study using longer polyether chains such as OEG-OH ($M_w \sim 550$). Both the tosylation and bromination reactions of OEG₅₅₀-OH were conducted under a variety of conditions. Unfortunately, OEG₅₅₀-OH was found to be very unreactive towards

TsCl or PBr_3 . The yields were less than 10% after each attempted reaction. We did not pursue this approach further, considering the cost effectiveness of the process.

Monomer 2 is commercially available and inexpensive (Aldrich). We chose this compound in order to compare the properties of electrolytes derived from these monomers and to gauge the attributes of using an oligomeric ether group (OEG) such as in monomer 1.

Monomer 3, which contains a fluorinated sulfonic acid group, was prepared successfully in moderate yields as shown in Figure 3, but the corresponding polymer, obtained by enzymatic polymerization, was not processable (insoluble in common organic solvents).



The synthesis of monomer 4, which bears a sulfone group attached to the phenyl ring was not completed because of great difficulty in reducing the aryl nitro group to the substituted aniline (Figure 4). After several attempts and extensive chromatographic separations, we isolated the aniline derivative (which was unstable in the presence of air), in poor yields (<10%). From a practical point of view, the investigation on this monomer was also abandoned.

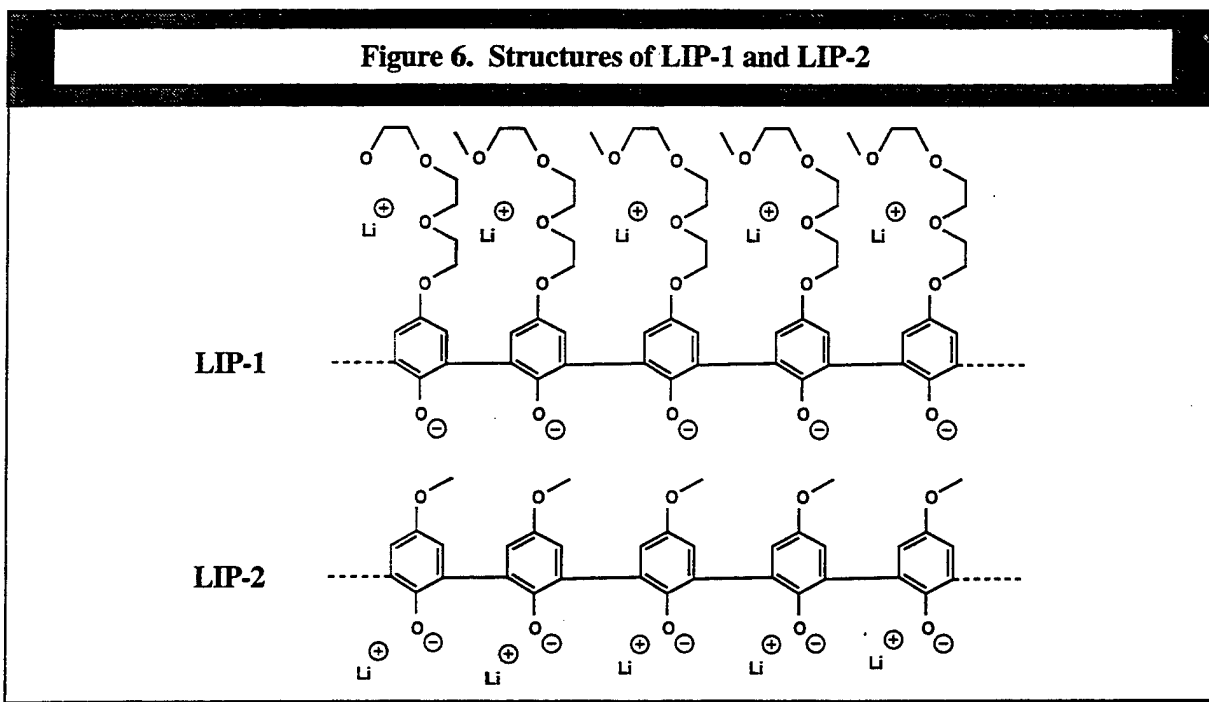
Our thorough study indicates that the following set of conditions is most suitable for polymer 1.

Synthesis of Polymer 1: In a 250 ml single-neck round bottomed flask fitted with a mechanical stirrer, 8.31 g of monomer 1 dissolved in 25 ml of dioxane was added to an ice-cold (5°C) solution of 24 mg of HRP-II in 55 ml of HEPES buffer. A total of 5 ml of 30% hydrogen peroxide solution was then added in 5 parts (1 ml each time, 10 min interval). The stirred solution was then allowed to come to room temperature and stirring continued overnight. Dioxane was removed under reduced pressure in a rotovap. Highly viscous polymer, which separated from the aqueous layer adhered on the wall of the flask. The top aqueous layer was decanted off, and the contents of the flask were washed with water (3x), and isopentane (2x), and the residue dried at 50°C under high vacuum. Yield: 7.1 g (86%, deep red waxy solid).

Polymer 2 was prepared following the aforementioned procedure in 90% yield as a light brown solid.

Lithiation of Polyphenols

Lithiation of polyphenols was performed by dissolving the polymer (4 g) in 20 ml of dioxane followed by addition of LiOH (1 eq. with respect to the repeat unit) in 10 ml of water. The solution was stirred for 1/2 h, and evaporated to dryness in a rotovap. Final drying was performed at high vacuum at 60°C. The lithiated polymer electrolytes (**LIP-1** and **LIP-2**) were obtained as dry dark red powders (Figure 6).

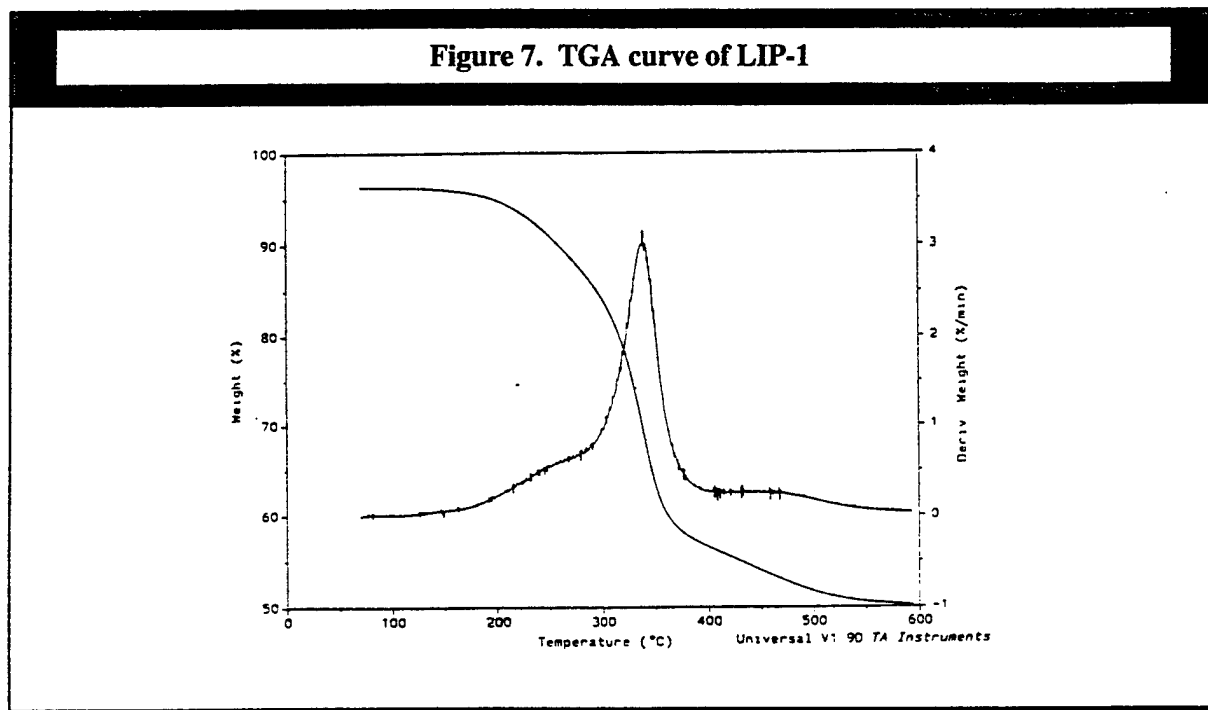


Characterization of Phenol Monomers and Polyphenols

The structural characterization of both the monomers and polymers and their intermediates were performed by elemental analysis, FTIR and NMR.

The molecular weights of Polymer 1 were determined by both gel permeation chromatography and laser light scattering techniques. The former method afforded a relative M_w value near 3,700 (with a polydispersity index of 1.6) while the latter provided an absolute M_w value near 10,000 (with radius of gyration 13.8 ± 8.5 nm). This value compares well with the highest known molecular weights for polyphenols reported from an extensive study performed by the Army-Natick research group.²⁻⁷

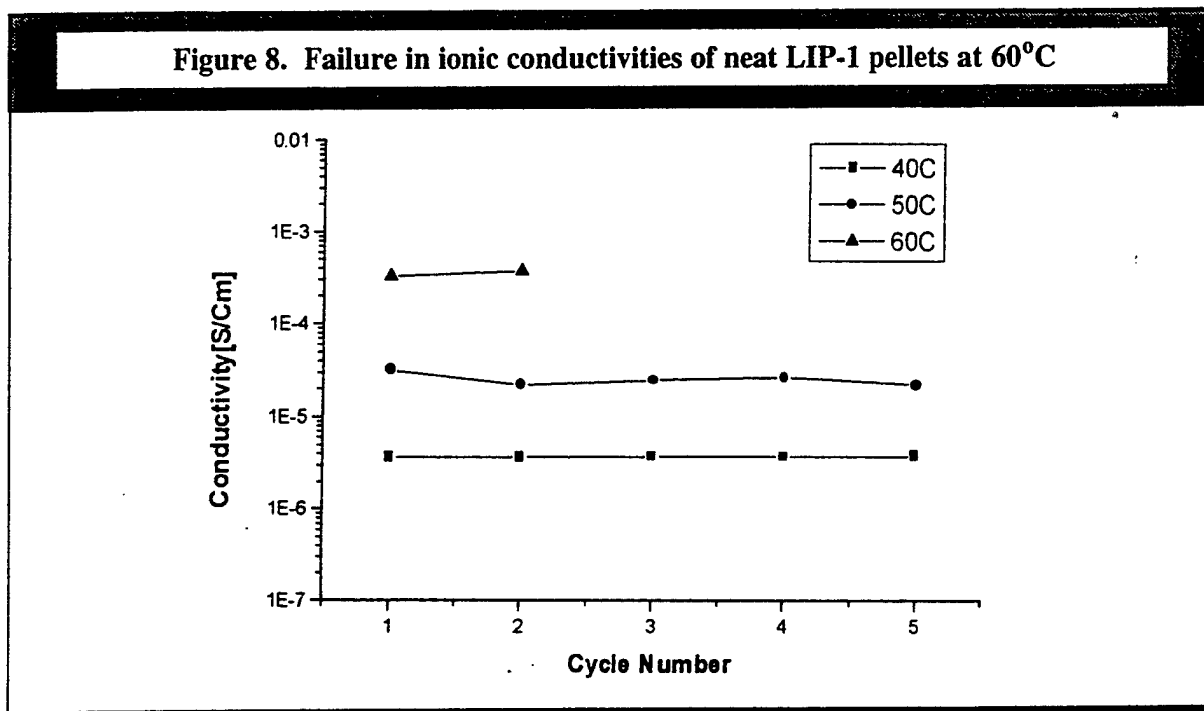
The thermal analysis of **LIP-1** was found to be satisfactory (indicates stability above 200°C, which is adequate for battery applications) (Figure 7).



Characterization of SPEs

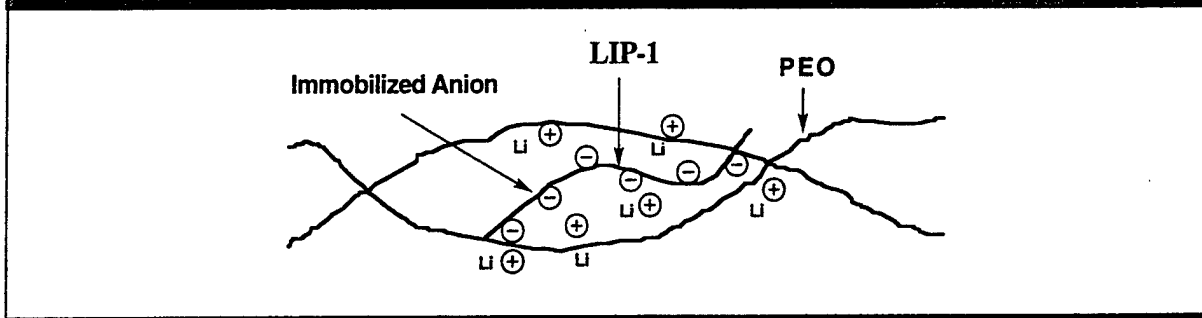
Ionic conductivity measurements of **LIP-1** pellets were performed at 30°C (room temperature), 40°C and 50°C (Figure 8). The values obtained were promising and were similar to the numbers observed for most acclaimed solid polymer electrolytes (SPEs) (in the absence of liquid plasticizers) reported thus far.⁸⁻¹⁰ We reasoned that the higher conductivity is due to the presence of short flexible polyether chains which created a conduction region. Unfortunately, we could not perform measurements at temperatures higher than 60°C due to melting of **LIP-1** near 60°C.

The lower melting point is due to lower molecular weights of the polymer together with the presence of pendant flexible ether chains. In this context, we would like to emphasize that it would be impossible to design a practical SPE based solely on **LIP-1**. The room temperature conductivity of **LIP-2** was found to be very low ($\sim 10^{-8}$ S/cm). Consequently, no further investigation was conducted.



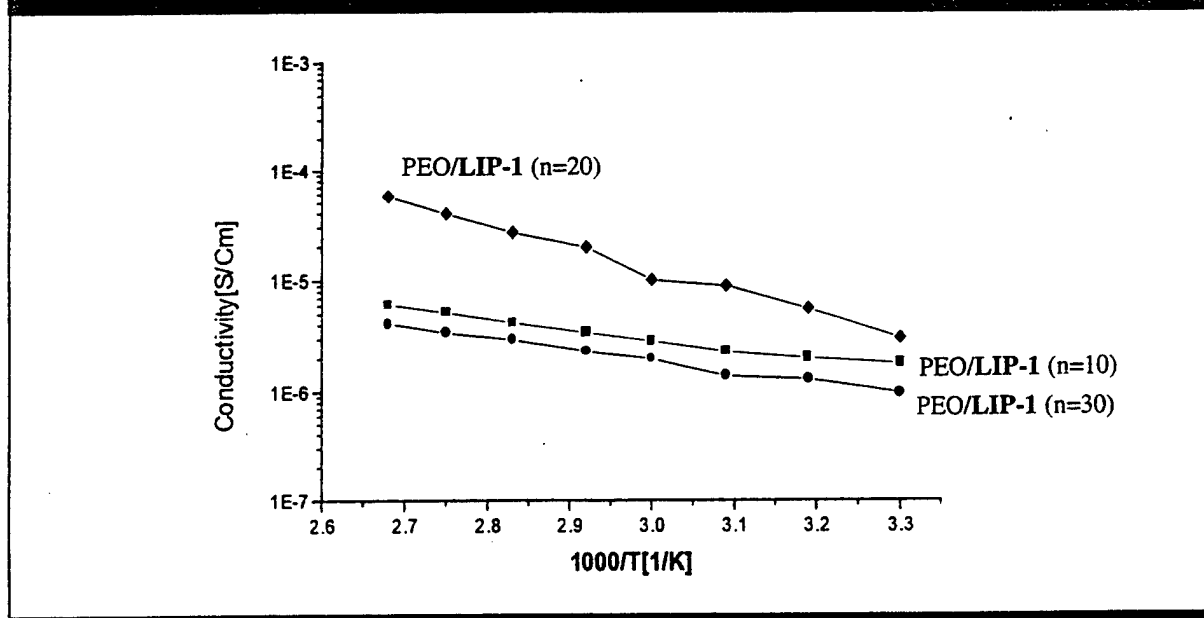
In view of these observations, we initiated a thorough study of the use of **LIP-1** as a novel stable lithium ion source in a PEO based SPE (Figure 9). This design has many advantages and has proved to be very promising. First, the necessary mechanical properties and conductivity are available, and the SPE system has been shown to be stable in a laboratory cell. Also, bi-ion based SPEs [such as lithium bis (trifluorosulfonyl)imide (**LIM**)] have the problem of cell polarization when the cell is charged.¹¹⁻¹⁴ The mobile anions and cations migrate towards the oppositely charged electrode. When the polarization is reversed and the cell is discharged the polarized electrolyte will be less conductive than an unpolarized electrolyte. A lithium ion source that contains immobile anions will solve this problem. Fortunately, this opened up a new avenue for obtaining highly conducting SPEs using enzymatic polymers.

Figure 9. Schematic of PEO Film Containing LIP-1

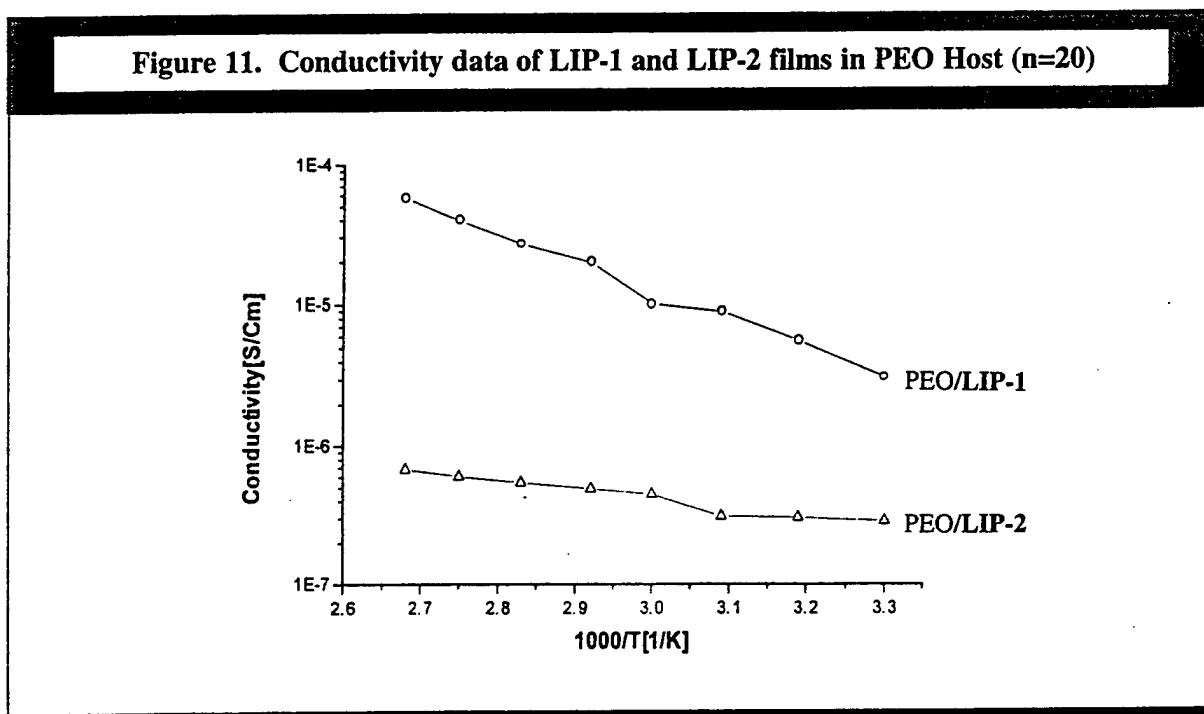


We prepared three samples (electrolyte films) containing one repeat unit of LIP-1 vs. 10, 20 and 30 repeat units of PEO. The films were produced by casting an acetonitrile solution of PEO and LIP-1 on polished teflon plates. The solvent was allowed to evaporate slowly in a glove box (moisture content <1 ppm). The process takes about 7 days to obtain void-free samples. The films were further dried at 60°C under high vacuum overnight. The results are promising and are shown in Figure 10. The best results were obtained for $n = 20$. This type of behavior is common for PEO-based electrolytes with low molecular weight electrolytes such as LIM.¹⁵ The decrease in conductivity at higher loading is due to the crystallization of the PEO matrix in the presence of lithium ions.

Figure 10. Ionic conductivities of LIP-1 blended PEO films at various temperatures



In the past six months, our extensive studies on various phenol monomers suitable for enzymatic polymerization indicate that polymer 1 is the best when considering both cost and performance. For instance, polymer 2, which was prepared from an inexpensive commercially available starting material, p-methoxyphenol, exhibits very poor conducting properties compared to that of polymer 1 in both neat pellets (as mentioned earlier) and in films containing a PEO host (Figure 11). We believe that without softening groups such as OEG, it would be impossible for any polymer matrix to exhibit acceptable levels of ionic conductivity. The softening oligoether segments are necessary to give the lithium cation a flexible channel in which to migrate. Therefore, other proposed monomers and polymers not containing the OEG segment would be expected to exhibit very low levels of conductivity.

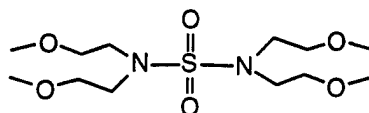


Evaluation of SPEs in Laboratory Cells

For a successful laboratory cell operation, it is very important that we have an SPE with room temperature ionic conductivities between 10^{-2} - 10^{-4} S/cm.⁸⁻¹⁵ The room temperature conductivity of LIP-1 in PEO host was measured near 10^{-5} S/cm, which is comparable to the room temperature data of 3M unplasticized PEO-LIM commercial product. The 3M product is currently used for applications with operating temperatures over 50°C, such as a Pentium[®] microprocessor in personal computers. In view of this result, we performed preliminary studies with a new class of plasticizers (prepared by TechDrive) such as SAP-1 (Figure 12). These

plasticizers, which should exhibit high permittivity (ϵ), are not only expected to improve chain mobility (by reducing T_g of the electrolyte film) but also enhance salt dissociation.

Figure 12. Representative Example of TechDrive's New Line of Plasticizers



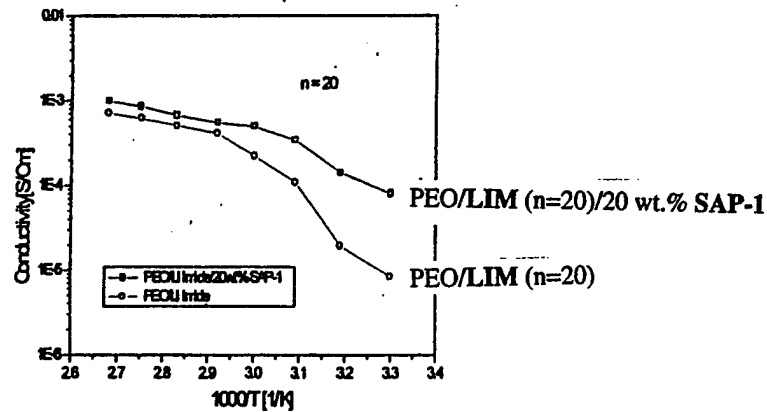
SAP-1

As a part of this initiative, we have also developed a solid state film processing technique with or without plasticizers. This melt processing technique takes only a few minutes to prepare SPE films compared to the 7 days required in the solution cast technique. Moreover, the solution cast technique cannot be applied when liquid plasticizer is used, due to loss of plasticizer during vacuum drying.

Solid State Film Processing Technique: Ingredients for the film are weighed and mixed as thoroughly as possible by trituration. The triturated mass is homogenized by melt mixing. Most frequently, films are formed near the softening point under pressure and these films are folded and re-folded and new films formed until the film is visually homogeneous. A heated platen press is preheated to a temperature just above the softening point (135°C) of the mixture. A frame from steel or brass shim stock is prepared. This frame can be of any shape, but a "picture frame" or outline of the shape to be used for testing is the most practical. A sandwich is constructed by first laying down a piece of teflon-coated glass fiber large enough to cover the platen and the shim stock frame placed on it. A quantity of the test mixture which has been calculated to fill the cavity in the frame is placed in the cavity. Another piece of teflon-treated glass is placed on top to complete the sandwich. The sandwich is slid into the press and pressure applied up to 20,000 psi. Pressure is released after 20 to 30 seconds and the sandwich is removed to a cool flat surface to cool. The film is carefully removed from the frame and stored in a glove box.

Our preliminary data indicate an excellent result with the new plasticizer. The use of 20 wt.% of **SAP-1** improved the room temperature conductivity of SPE film (prepared by the melt processing technique) by over an order of magnitude larger than that of unplasticized film (Figure 13). We are confident that the optimization of plasticizer type and loading will further enhance the room temperature ionic conductivity.

Figure 13. Dramatic increase in conductivity with TechDrive's novel plasticizer^a



^aFilms prepared by melt processing technique

The performance of plasticized PEO/LIP-1 films has been tested in a laboratory cell. The procedure for fabricating a laboratory cell is outlined in the Phase-I proposal. The cell operated smoothly at ambient temperature with an output open circuit voltage (OCV) of about 3 V. Figure 14a is a demonstration of the open circuit stability of the full cell over a period of 600 minutes. At temperatures above 70° C, there is a small drop in the open circuit voltage (Figure 14b). These preliminary results indicate that the membranes developed are stable separators as well as ion conductors.

Figure 14. Lab cell test results of Plasticized PEO-LIP-1 films

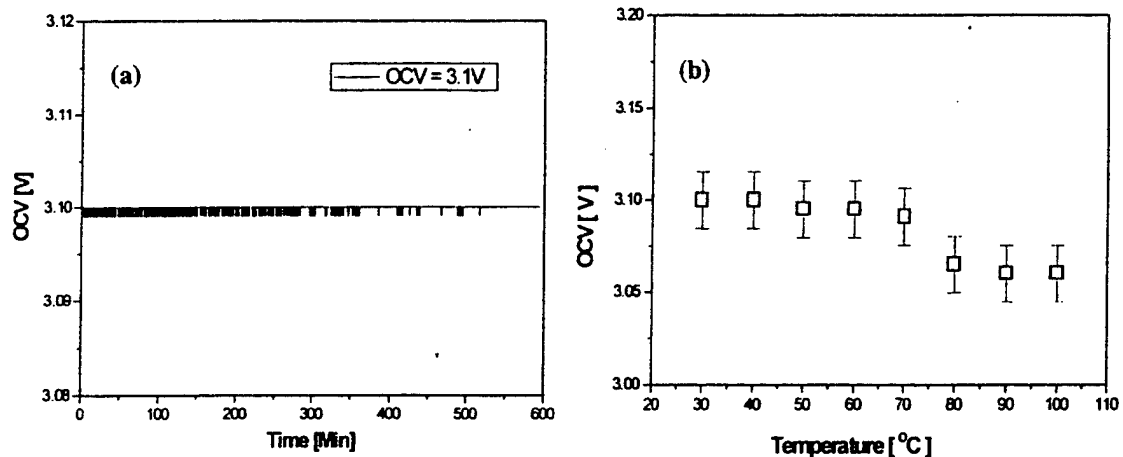
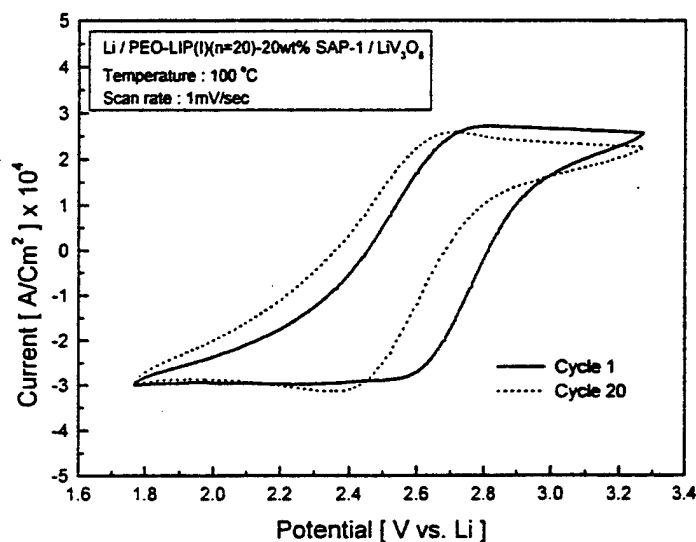


Figure 15 shows the steady state cyclic voltammetry of the Li/PEO-LIP-1 battery cell. The construction of the cell was described in the Phase-I proposal. The LiV_3O_8 cathode was used as the working electrode and the counter and reference electrode leads of the PAR 273A potentiostat were short-circuited to the lithium anode. The cell setup uses the anode as the reference electrode. The cell is currently being modified to include a lithium reference electrode in the cell. The battery was cycled under extreme conditions from overcharge to deep discharge. The twentieth cycle was initiated 16 hrs after start of cycling. The extent of fading is evident from the shift of the cathodic wave to more negative potentials from cycle 1 to cycle 20. While these batteries require further optimization, it is clear that the test cell is fully functioning and capable of monitoring the progress of the electrolyte development program at IIT.

Figure 15. Slow scan CV of Li/Plasticized PEO-LIP-1/ LiV_3O_8 battery



Concluding Remarks on Phase-I Effort

As a result of these observations, we believe that Polymer 1 warrants a thorough Phase-II investigation on how to improve monomer yields, polymer molecular weights and room temperature conductivities. Clearly, the oligoether chains present in the LIP-1 provide better compatibility with PEO and the addition of plasticizer causes dominant effects on ionic conductivities of SPEs.

If this research is successful, it would lead to a new class of materials that conduct ions through a solid matrix as quickly as liquid electrolytes, which would have a wide-ranging impact and benefit. Solid phases that are highly conductive to ions will drive technologies in areas outside of the energy sector. The biochemical and analytical chemistry sectors require ion conducting membranes for the development of new artificial muscles and sensors. Also, the mechanism of conduction of ions in solid phases needs further investigation and these materials would be prime candidates for these studies. Besides these technical benefits, there would also be economic and social benefits. If successful, this research could lead to large scale production of composite electrolytes, thus generating good paying employment and providing the basis for an entire line of products based on this technology. This would be enough of a foundation from which this small company could generate real growth for years to come.

This research would also have direct benefits to the nation as a whole in the defense sector. Flexible rechargeable solid lithium batteries (RSLBs), made possible with solid, flexible electrolytes, could be used as energy sources from which a soldier's equipment could be operated. The RSLBs could be easily fabricated into the form of a "belt-battery" which is lightweight, durable, would generate a high energy density, and be fully rechargeable. Of course, this type of military application could easily be converted for civilian use. Lightweight, solid batteries could safely drive cameras, phones, laptop computers, and many other field-specific devices and instruments. Clearly, it is of great interest that SPEs with high conductivity be commercialized since nearly every person would enjoy the wide ranging benefits of a RSLB.

The process resulting from this Army-funded research would be the development, licensing, production, and sale of SPEs for the RSLB. If this research is successful, the likelihood of commercializing and selling these materials is quite high. There is great current demand for these materials and is not limited to the United States. Real products could be sold internationally, which is desirable, in a highly competitive, global market. The market for high density, plastic and rechargeable batteries is very large and rapid growth should be expected in the next ten years. This country needs to have businesses produce marketable products for this technology as soon as possible.

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