DEVELOPMENT OF A LITHIUM SECONDARY BATTERY SEPARATOR[*]

J. A. Moore and Roice Willie
Rensselaer Polytechnic Institute

ABSTRACT

A non-porous membrane based on the polymerization of 2,3-dihydrofuran followed by crosslinking in situ has been prepared. The material is compatible with rechargeable Li battery components and, when swollen with an appropriate solvent such as tetrahydrofuran, exhibits separator resistance and Li^+ transport equivalent to Celgard.

INTRODUCTION

Efforts to develop light-weight batteries have lead to the production of ambient temperature, lithium metal-chalcogenide secondary cells (Li, TiS_2) containing ionic conductors (lithium hexafluoroarsenate) in aprotic, inert solvents such as tetrahydrofuran (THF).[1] The development of these batteries will be aided by improvements in separator technology which should significantly enhance cell performance and cycle life. Among the problems which exist with microporous separator materials (such as Celgard) is the formation of Li dendrites which penetrate through the pores of the separator from the anode to the cathode and ultimately short circuit the cell. Thus, a non-porous membrane which selectively transports solvated Li^+ cations from one electrode to the other may well outperform a microporous separator in terms of enhancing cell life during charge and discharge.

Among the requirements for such separators are that the material be insoluble in, but wettable by the solvent-electrolyte solution, that it be unreactive with metallic lithium and the cathode and that it be capable of ion transport. Because a large mass of data indicates that tetrahydrofuran and its derivatives are stable under normal battery conditions and fulfill all of the above criteria, it is reasonable to believe that incorporation of tetrahydrofuran units into a polymer chain will yield a material which will be an effective separator. Such a polymer would be completely compatible with the electrolyte solvent systems in use and could be made insoluble by appropriate crosslinking reactions. Extensive literature documents the activity of ether groups in general, and THF rings, in particular.

It has been reported that vinyl ethers such as 2,3-dihydrofuran can be polymerized to high molecular weight, processable materials.[3a,b] Such materials could fulfill the requirements for a useful separator and therefore we have undertaken a reinvestigation of this, and related systems.

P23
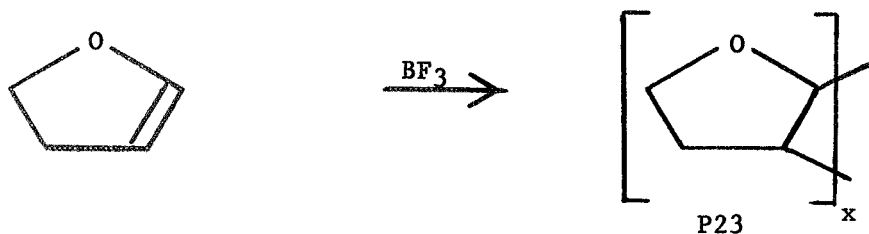
This work describes the preparation and preliminary study of poly(2,3-tetrahydrofurandiyl) (P23) separator. This material was subjected to a series of compatibility experiments with rechargeable Li battery components as well as other physicochemical measurements. The results were compared to those from a Celgard 2400 standard.

EXPERIMENTAL

GENERAL

Electrochemical and transport properties were measured by Covalent Associates, Inc., Woburn, MA. All electrochemical experiments were conducted at 28°C. Compatibility tests were conducted in an oven thermostatted at 70±2°C. Atomic absorption (AA) analyses were accomplished with a Perkin Elmer Model 403 spectrometer. Optical microscopy was conducted with an American Optical binocular zoon instrument to 40X. Scanning electron microscopy (SEM) was run by Photometrics, Inc., Woburn, MA. The P23 Separator, shipped under N_2 in sealed vials, was opened in an Ar filled glovebox and not exposed to air unless otherwise indicated. Infrared spectra were recorded on a Perkin Elmer Model 237 spectrometer, ultraviolet spectra were recorded on a Perkin Elmer Model 552 spectrometer and ^{13}C and ^1H nuclear magnetic reonance spectra were obtained with a 200 MHz Varian Model 200XL spectrometer.

MEMBRANE PREPARATION

The polymerization of 2,3-dihydrofuran in bulk and in solution has been effected using $BF_3 \cdot Et_2O$ as initiator. Typically, a solution of $BF_3 \cdot Et_2O$ in CH_2Cl_2 was added to the monomer in bulk and in CH_2Cl_2 solution at -78°C. Anhydrous conditions and a N_2 atmosphere were maintained. At the completion of the reaction the initiator was deactivated with $MeOH/CH_2Cl_2$ solution, and the white, ropey polymer was precipitated into methanol.

Membranes were prepared by dissolving the reprecipitated polymer [reduced viscosity = 0.77dL/g] in chlorobenzene at a concentration of about 30% and adding 1% triphenyl phosphite and 5% benzoyl peroxide. Films were cast on a Teflon block with a draw knife to the nominal dimensions and, after drying for 9 hr at room temperature under N_2, then heated in an oven under vacuum at 78°C for 12 hr. After cooling under vacuum, the films were peeled from the casting surface, solvent extracted to remove byproducts, cut to size and stored under N_2.

COMPATIBILITY TESTS

Measurements of physical dimensions were made on two 1.0 cm x 2 mil P23 pieces cut from the membrane as received and after a 2 hr soak in tetrahydro-furan [(THF) Burdick and Jackson] and 2-methyltetrahydrofuran [(2-MeTHF) Aldrich] distilled from CaH_2 under Ar. Additional 1 cm x 4 cm x 2 mil P23 samples and 1 cm x 4 cm x 1 mil Celgard 2400 samples were cut for the compatibility tests. Weight changes of P23 were assessed after 7 days storage at 70°C in both 2-MeTHF and 1.4M $LiAsF_6$ (U.S. Steel Agrichemicals)/2-MeTHF.

All compatibility tests were conducted in duplicate in Teflon-taped screw cap vials. The components comprised Li foil (Lithcoa, 10 mil), TiS_2 (Cerac, battery grade), as well as 2-MeTHF and 1.4M $LiAsF_6$/2-MeTHF prepared at dry ice temperature followed by pre-electrolysis between 2 Li electrodes.

The following quantities of materials were used:

Li foil: 1 cm x 4 cm

TiS_2: 1.0 g

Celgard 2400 or P23: 1 cm x 4 cm

Solvent or electrolyte: 5.0 ml

A series of 20 vials was prepared and numbered as follows:

Vial Number	Contents
1	solvent, P23
2	electrolyte, P23
3	electrolyte, P23, Li
4	electrolyte, P23, Li, TiS_2
5	solvent, Celgard
6	electrolyte, Celgard
7	electrolyte, Celgard, Li
8	electrolyte, Celgard, Li, TiS_2
9	electrolyte
10	electrolyte, Li
11	duplicate of 1

```
12                 duplicate of 2
13                 duplicate of 3
14                 duplicate of 4
15                 duplicate of 5
16                 duplicate of 6
17                 duplicate of 7
18                 duplicate of 8
19                 duplicate of 9
20                 duplicate of 10
```

CYCLIC VOLTAMMETRY AND INFRARED ANALYSIS

Cyclic voltammetry (CV) was conducted directly in Vials 2, 3, and 6 after the 7 day storage period. A 3 mm dia. polished vitreous C working electrode along with Li counter and reference electrodes were inserted into the vial inside the glovebox. Voltammograms were generated by a BAS CV-1B instrument and recorded on an HP 7015B XY recorder. Infrared spectroscopy was conducted in sealed matched and polished KCl cells (Wilmad) with a 0.1 mm path length.

RESISTIVITY MEASUREMENTS

A two-compartment polypropylene cell (designed by Covalent Associates) was used for all resistance measurements. The membrane was supported by Viton "O"-rings which sealed the cell and fixed the area exposed to the electrolyte at 6.0 cm^2. Resistivity data was taken with a GenRad Model 1650A impedance bridge.

LI ION TRANSPORT STUDY

The flux of Li^+ through the P23 membrane was conducted in the same cell used for resistivity measurements. One compartment contained 2.0M $LiClO_4$/THF while the other contained 2.0M $NaClO_4$/THF. Because the P23 material swelled to a much greater degree in THF than in 2-MeTHF (vide infra), THF was the solvent of choice. The cell was filled and allowed to equilibrate. Subsequently, 1.0 ml aliquots were removed from the $NaClO_4$/THF compartment and analyzed for Li^+ content with AA spectroscopy. This experiment was then repeated with Celgard 2400 separator material.

RESULTS AND DISCUSSION

COMPATIBILITY TESTS

The sealed tubes were opened inside the glovebox and the 2 mil and 5 mil P23 membranes were measured for uniformity of thickness. The normal 2 mil membrane ranged from 1.5 to 2.5 ml in thickness, while the 5 mil membrane

ranged from 2.0 to 3.0 mil in thickness. Both samples were flexible and cellophane-like in mechanical behavior. The P23 samples could be folded and unfolded many times without structural damage.

Under the 40X microscope, neither bubbles nor cracks were evident in either the 2 mil or the 5 mil sample. Two pieces of P23 were deliberately exposed to air for 3 days. Microscopic examination revealed no visible structural changes nor was any embrittlement detected.

All of the 70°C compatibility tests employed 2 mil P23. All visual observations were identical for their corresponding duplicates. No loss of solvent volume was detected over the 7 day storage period.

After 20 hr of storage at 70°C, a yellowing of the P23 membrane in vials containing $LiAsF_6$ was observed. The yellowing was enhanced in vials containing $LiAsF_6$ and Li foil.

In Vial 1 containing only 2-MeTHF, the P23 sample was clear and colorless. but in the presence of $LiAsF_6$ (Vial 2), P23 turned uniformly yellow. Vial 13 revealed an amber color permeating the membrane with the edges being the most intensely colored. It is important to note that the electrolyte solutions in Vials 2 and 13 were clear and colorless. Only the membrane was affected. Similarly, the Celgard 2400 samples in Vials, 5, 6, and 7 were unchanged as were the blanks (Vial 19 and 20).

Experience with this membrane suggests that the yellowing may be caused by oxidation of the polymer by residual O_2, and that this oxidation is exacerbated by the presence of halide. Over the following 6 days no further changes were noted with the exception of a slight yellowing of the electrolyte in contact with P23.

At the end of the 7 day storage tests the samples were removed from the vials and examined. As the samples dried they shriveled to a form which makes microscopic examination or dimensional measurements difficult. P23 from vial 12 seemed to be markedly yellow when compared to P23 from vial 11. The Celgard 2400 standard was unchaged after storage for 7 days at 70°C. When rinsed with methanol to remove small particles of TiS_2, the P23 membrane from Vials 4 and 14 was as yellow in color as the P23 from Vials 3 and 13. Even after solvent evaporation in the glovebox, the membranes retained their plasticity —similar to commercial Saran Wrap rather than cellophane. None of the P23 samples manifested any sign of brittleness.

Infrared scans on 2-MeTHF from Vial 11 and 1.4M $LiAsF_6$/2-MeTHF from Vial 12 were obtained and compared to electrolyte from Vial 16 which contained Celgard 2400. All spectra were identical. The spectrum of electrolyte from Vial 12 compared to the spectrum of electrolyte from Vial 16 showed no extraneous absorbances. Thus the spectral evidence indicates that P23 is not dissolving in the solvent or solvent-electrolyte solutions. Attempts by reweighing the test samples to determine if dissolution was occuring were inconclusive.

To probe further the possibility of P23 degradation, cyclic voltammetry scans were made on electrolyte from Vial 6 (Celgard 2400), Vial 2 (P23), and Vial 3 (P23 + Li). With the exception of a slight increase in cathodic current from electrolyte in Vial 3, no large quantities of electroactive materials are present between 0.8 and 4.4 V vs. Li. A slightly enhanced current from Vial 3 may well be caused by small amounts of electrolyte-Li reaction products.

RESISTIVITY MEASUREMENTS

A 2 mil sample of P23 was placed in the resistivity cell after which the cell was filled with 1.4M $LiAsF_6$/2-MeTHF electrolyte. After 5 min, the total cell resistance was 41,000 ohms; after 30 min, 2150 ohms; after 1.5 hr, 520 ohms; after 3 hr, 204 ohms; after 5 hr, 170 ohms. The total cell resistance stabilized at this last value. In the absence of the P23 separator, the cell manifested a resistance of 165 ohms. Thus, the separator resistance multipled by the 6 cm^2 geometric area gave a value of 30 ohm cm^2.

When Celgard 2400 was substituted for P23, the cell resistance was found to be below the sensitivity of the impedance bridge after just 5 minutes. Thus, the P23 separator resistance is at least 30 times greater than that of Celgard in 2-MeTHF.

To ascertain whether the P23 might swell more readily in THF rather than in 2-MeTHF and thereby become less resistive, the resistance of a P23 separator in 1.4M $LiAsF_6$/THF was measured. After 5 min, the total cell resistance was essentially equivalent to the cell resistance without P23 as in the case for Celgard 2400. This result clearly demonstrates that P23 is a good Li^+ transporter when it can be made to swell by an appropriate solvent.

LI ION TRANSPORT STUDY

Based on the results with THF, it was decided to conduct this experiment with 2.0 M $LiClO_4$/THF and 2.0 M $NaClO_4$/THF electrolytes. Over a 3.6 hr period the average rate was found to be 2.2 x 10^{-1} mmole Li^+/h/cm^2. Under exactly the same conditions, Celgard 2400 was also found to give a rate of 2.2 x 10^{-1} mmole Li^+/hr/cm^2. This result corroborates the resistivity data acquired in $LiAsF_6$/THF for P23 and Celgard 2400. It should be noted that because of the propensity of P23 to swell in THF (vide infra), the geometric area and actual swollen area may differ by up to 100%. However, this uncertainty should not prevent P23 from being used as an effective battery separator.

MISCELLANEOUS TESTS

P23 Wetability and Swelling Measurements. It was found that methanol, 2-MeTHF, and THF readily wet P23 while H_2O does not. In 2-MeTHF (7 days), P23 went from 2-3 mil to 3-3.5 mil in thickness. In THF (5 min) P23 went from 2-3 mil to 3-4 mil in thickness. These numbers are grossly approximate because of the difficulty of measuring thickness accurately on a gelatinous material.

Dimensional changes for P23 in THF and 2-MeTHF were roughly assessed in their respective vials because removing the membranes from the solvent resulted in rapid shrinkage. Thus, P23 in 2-MeTHF increased in length and width by about 13% after 2 hr at 28°C. But in THF, P23 appeared to undergo a 90% increase in length and width within 5 min of contact with THF at 28°C. No further changes were noted with time.

Heat Sealing. A sample of P23 was heat sealed to itself satisfactorily with a jaw impulse heater at a setting of 5. P23 requires more heat than Celgard 2400, but this fact presents no problem in suitably bagging battery electrodes with P23.

SEM Study of P23 Structure. All attempts at obtaining SEM images of the THF-swollen membrane failed because of the shriveling phenomenon as the solvent evaporated. The dry membrane surface (shiny side) is remarkably smooth and featureless at 11,000X. To obtain a cross section free of distortion from a cutting implement, a sample of 2 mil P23 was fractured at liquid N_2 temperature. The cross section is amorphous and pinhole-free at 4,440X.

CONCLUSIONS

P23 is pliable, insoluble in 2-MeTHF and in THF, and manifests adequate conductivity in THF-electrolyte systems. Further work and extended compatibility studies in THF-based electrolytes would be fruitful. Indeed, the latest EIC electrolyte (50:50 THF:2-MeTHF plus 2-methylfuran) is an obvious choice. Finally, P23 must be tested as a separator in rechargeable Li cells to ascertain its resistance to dendrite penetration and long term chemical and electrochemical stability. The very promising results obtained from these initial efforts bode well that continued study of novel polymers containing heterocyclic rings may lead to separator systems which are superior to those currently in use.

REFERENCES

1. "Status of the DOE Battery and Electrochemical Technology Program", Mitre Corp., report #MTR-8026, September, 1979.

2a. C. J. Pedersen and H. K. Frensdorff, Angew. Chem. Int. Ed. Engl. 11, 16 (1972).

2b. J. J. Christensen, D. J. Eatough and R. M. Izatt, Chem. Rev. 74, 351 (1974).

2c. W. J. Schultz, M. C. Etter, A. V. Pocius and S. Smith, J. Am. Chem. Soc. 102, 7981 (1980).

2c. W. J. Schultz, M. C. Etter, A. V. Pocius and S. Smith, J. Am. Chem. Soc. 102, 7981 (1980).

3a. D. A. Barr and J. B. Rose, J. Chem. Soc. 1954, 3766.

3b. G. J. Schmitt and C. Schuerch, J. Polym. Sci. 49, 287 (1961).

TOTAL CELL RESISTANCE

Membrane

	THF					2MTHF				
	5 min.	30	90	180	300	5 min.	30	90	180	300
P23	∿0	—	—	—	—	41,000Ω	2150	520	204	170
Celgard 2400	∿0	—	—	—	—	∿0	—	—	—	—

Electrolyte = 1.4M LiAsF$_6$

Li$^+$ TRANSPORT

2.0 M LiClO$_4$/THF//2.0 M NaClO$_4$/THF

Membrane	Average Rate (MMole Li$^+$/hr/Cm^2)
P23	2.2 x 10^{-1}
Celgard 2400	2.2 x 10^{-1}