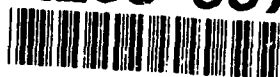


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CONTRACT N00014-93-WR-24016

R&T Code 4133038

Technical Report No. 2

Synthesis and properties of a cation-conducting,
high temperature polymer electrolyte

by

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Prepared for Publication

in the journal

Solid State Ionics

United States Naval Academy
Department of Physics
Annapolis, MD

April 16, 1993

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 16 April 1993	3. REPORT TYPE AND DATES COVERED Interim Technical 3/92 - 4/93	
4. TITLE AND SUBTITLE Synthesis and properties of a cation-conducting, high temperature polymer electrolyte		5. FUNDING NUMBERS N00014-93-WR-24016 R&T Code 4133038	
6. AUTHOR(S) Y. Okamoto, Z. S. Xu, M. G. McLin J. J. Fontanella, Y. S. Pak, S. G. Greenbaum		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 2	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Physics Department U. S. Naval Academy Annapolis, MD 21402-5026		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217		11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS High temperature polymer electrolyte, sulfonated polyaromide lithium conductor, sodium conductor			15. NUMBER OF PAGES 16
17. SECURITY CLASSIFICATION OF REPORT Unclassified			16. PRICE CODE
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

Synthesis and Properties
of a Cation-Conducting, High Temperature
Polymer Electrolyte

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Abstract

A new class of polymer electrolyte, high temperature polymer electrolytes, as an electrolyte in high discharge rate batteries is proposed. As an initial effort in the development of these materials, sodium and lithium salts of sulfonated poly(p-phenyleneterephthalamide) have been prepared. DSC and electrical conductivity studies have been performed on these films. The conductivity exhibits Arrhenius behavior over the temperature range in which they are thermally stable (180-240°C) with the material containing sodium being more conductive than those containing lithium. Although the electrical performance of these materials is inadequate from a practical standpoint, it is suggested that with additional development these materials could function as electrolytes for high discharge rate batteries.

Introduction

Polymer electrolytes have been the focus of much attention since the pioneering work of Wright (1) and the later suggestion of Armand (2) that they could be used as an electrolyte in high energy-density secondary batteries. The primary goal of much of the research to date has been to produce a polymer electrolyte suitable for an ambient-temperature secondary cell. Typically, these materials consist of a polyether-based host in which alkali salts are dissolved. It is well established by reliable transference number measurements (3-4) that the conductivity of these electrolytes is dominated by anionic conductivity which is not advantageous for battery applications. Thus, some investigators have immobilized the anion by covalently bonding it to the sidechain of a linear polymer host (5-11) or incorporating it into a polymer network (12-13), but the ambient cationic conductivity of these materials remains low probably due to a high degree of ion pairing between the cation and the immobilized anion. The addition of ether-based cation-complexing agents such as low molecular weight ethylene oxide oligomers (14), crown ethers (15), or cryptands (15) have been effective to varying degrees at reducing the ion-pairing and concomitantly increasing the cationic conductivity.

In the present work a novel class of polymer electrolyte, those designed to operate at high temperature, is described. It is suggested that these materials have potential as an alternative electrolyte for high discharge rate secondary cells. Molten salts are the electrolyte usually associated with these applications due to their

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high conductivity, wide electrochemical window, and low electrode overpotential. However, molten salt electrolytes also have significant drawbacks such as their corrosiveness (16). A high temperature polymer electrolyte would also be expected to offer a wide electrochemical window and low electrode overpotential while offering a significant improvement in chemical stability over molten salts. It is believed that a high temperature polymer electrolyte need not be as conductive as a molten salt to be a suitable electrolyte for a high discharge rate cell since it could be used in a thin-film cell configuration. In addition, a cell using a polymer electrolyte (as is the case for any solid electrolyte) would not require a separator as is the case for a molten salt cell. This weight savings along with the ability to stack many thin film cells in a polymer electrolyte battery helps offset the energy density advantage of molten salt cells which is primarily due to the high conductivity electrolyte.

In order to withstand the harsh environment of a high temperature cell, a new type of polymer host is necessary since typical polyether hosts do not have the necessary thermal stability. Ionic conductivity has been reported in high-performance polyimides doped with low levels of lithium or lead salts (17). It is noteworthy that the motivation of that study was an attempt to better understand the undesirable ionic conductivity at ambient temperatures attributable to impurity ions since polyimides are often used in electronic packaging.

Poly(p-phenylene terephthalamide) (PPTA) was developed by DuPont under the tradename Kevlar (18). It is a rigid rodlike polymer with high tensile strength, stiffness, crystallinity, and

thermal stability. This aromatic polyamide is very difficult to process due to its insolubility in organic solvents.

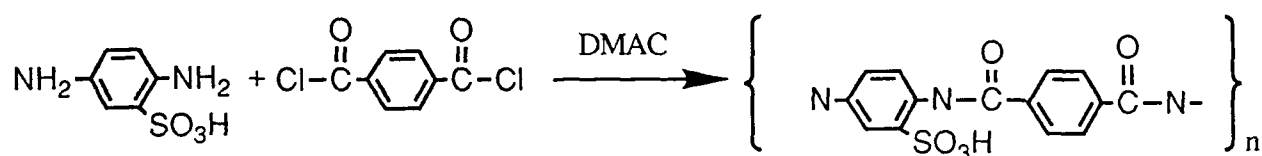
Recently, water-soluble aramides have been prepared by polymerization of sulfonated aromatic diamines with terephthaloyl chloride (19-21). These polymers were then neutralized with lithium or sodium bases and cast into films. Although ion pairing has been the significant limitation of the electrical performance of previously investigated sulfonated polyelectrolytes (6,9,11), it was anticipated that an increased thermal dissociation would help offset this complication since the use of low molecular weight cation complexing agents in these materials is impractical due to their volatility. In addition, the most effective of these cation-complexing agents, cryptands, has been shown to increase the electrode resistance at the the cathode (15) which would be detrimental to battery performance in high discharge rate applications.

Experimental

Polymer Synthesis

Sulfonated poly(*p*-phenyleneterephthalamide), PPTS, was prepared by the condensation polymerization of terephthaloyl chloride and 2,5-diamino phenylene sulfonic acid in dimethylacetamide (DMAC) using a slight excess (~5%) of the diamino monomer. The product obtained was precipitated into water. The polymer was then thoroughly washed with acetone. Amino end groups were detected in the product by IR spectroscopy. The sulfonic acid groups were neutralized with excess Li_2CO_3 and Na_2CO_3 to obtain the Li and Na salt polyelectrolytes. Terephthaloyl

chloride obtained from Aldrich Chemical Co. was purified by sublimation. 2,5-Diaminophenylene sulfonic acid also obtained from Aldrich Chemical Co. was recrystallized from water solution and dried at 120° C.



Scheme 1. Preparation of PPTS

MW Determination

PPTS of two different molecular weights have been prepared. The molecular weight was determined in a dimethylacetamide solution by light scattering (22). The MW of PPTS(I) was found to be 13.000 with an intrinsic viscosity of 1.39 dl/g (in 97% H₂SO₄), whereas PPTS(II) was 5.400 with an intrinsic viscosity of 0.76 dl/g.

Thermal Analysis

Thermal analysis was performed using a Thermal Analyst Model 2100 Differential Scanning Calorimeter. All salt samples were placed in non-hermetically sealed aluminum pans and scanned at 10°C/min under N₂ gas.

Complex Impedance Measurements

All complex impedance measurements were performed at 17 audio frequencies from 10-100,000 Hz under vacuum in a extensively modified Dupont Differential Thermal Analysis Module. Temperature control of the finished cell up to $350^{\circ}\text{C} \pm .1^{\circ}\text{C}$ was accomplished using a Lakeshore Cryotronics Model DRC 82C Temperature Controller under computer control. Automated complex impedance measurements were performed using a Model CGA-82 Impedance Bridge.

The measurements were performed on dried films with gold blocking electrodes sputtered onto them. DC conductivities were calculated from the results of complex impedance analysis using geometrical factors which were calculated from the thickness of the dried films before electrode deposition and the surface area of the blocking electrodes. To insure that the character of the films had not been changed, the conductivities of the films were checked for irreversible changes after the conductivity had been measured at a new maximum temperature over 200°C .

Results

The results of complex impedance analysis are shown in Figure 1. All films exhibited Arrhenius behavior over temperature ranges in which the films are thermally stable. The activation enthalpy for the PPTS(II)-Na film is 3.08 kcal/mole. The lithium salt films, PPTS(I)-Li and PPTS(II)-Li, differed only in molecular weight, but exhibited almost the same conductivity. In addition, the conductivity activation enthalpy was found to be the same for both lithium films,

3.82 kcal/mole, over the temperature range in which the films were stable. At temperatures above approximately 280°C for PPTS(I)-Li and PPTS(II)-Na, the conductivity of the films decrease below what is expected from an extrapolation of the Arrhenius behavior observed at lower temperatures. An identical effect is observed above about 240°C for PPTS(II)-Li. In addition to the irreversible decrease in conductivity, the films blackened after being heated above the aforementioned transition temperatures.

The DSC trace for PPTS(II)-Na, which is representative of the other samples, is shown in Figure 2. The trace is essentially featureless except for a slight exothermic rise corresponding to the temperature regime in which the samples blackened and exhibited an irreversible decrease in their conductivity. It is concluded that the films are thermally decomposing at these temperatures.

Discussion and Conclusions

Judging from the results for the lithium salt films, the conductivity of these Kevlar-like films over the temperature range 180-240°C does not appear to depend on the molecular weight from MW= 5.400-13.000. However, MW does appear to have a profound effect on the thermal stability of the lithium films, with the film of lower MW being much less stable.

The sodium salt film is more conductive than the lithium salt films which is not surprising since sodium salts have smaller dissociation energies than their respective lithium salts. The determination of the relative roles of ionic mobility and dissociation with respect to temperature will require a direct spectroscopic probe

of ion dissociation of both the cation (23) and anion (24). However, the Arrhenius behavior implies that the role of the polymer in the conductivity mechanism of these particular materials differs from that of "conventional" polymer electrolytes and is probably more analogous to the role of the host in "more traditional" fast-ion conductors.

As was described in the experimental section, each repeat unit is sulfonated which would make this a relatively concentrated polymer electrolyte. While it is possible that the electrical performance of these materials could benefit from reducing the salt concentration, we believe a more efficacious strategy to improving the electrical performance of high temperature polymer electrolytes would be to strive for thermally stable, completely amorphous materials which would be expected to have a conductivity mechanism typical of polymer electrolytes. Although the electrical performance of these particular films is inadequate from a practical standpoint, it is suggested that with additional development, this class of ion-containing polymer might serve as an alternative electrolyte for high discharge rate, high temperature secondary batteries.

Acknowledgements

This work was supported in part by the Office of Naval Research. M.G. McLin gratefully acknowledges support by the Office of Naval Technology Postdoctoral Fellowship Program.

References:

1. Wright, P.V. *Br. Polym. J.* 1976, 7, 319.
2. Anderson, M.B.; Chabagno, J.M.; Duclot, M.J. In *Fast-Ion Transport Solids*; Vashishta, P., Mundy, J.N., Shenoy, G., Eds.; North-Holland: Amsterdam, 1979, p. 131.
3. Cameron, G.G.; Ingram, M.D.; and Harvie, J.L. *Farad. Disc. Chem. Soc.* 1989, 88, 5.
4. Bruce, P.G.; Hardgrave, M.T.; and Vincent, C.A. *Solid State Ionics*, in press.
5. Hardy, L.C. and Shriver, D.F. *J. Am. Chem. Soc.* 1988, 220, 3823.
6. Bannister, D.J.; Davies, G.R.; Ward, I.M.; and McIntyre, J.E. *Polymer* 1984, 25, 1291.
7. Liu, H.; Okamoto, Y.; Skotheim, T.; Pak, Y.S.; Greenbaum, S.G.; and Adamic, K.J. *Mat. Res. Soc. Symp.* 1989, 135, 337.
8. Liu, H.; Yeh, T.F.; Lee, H.S.; Skotheim, T.; and Okamoto, Y. *J. Polym. Sci., Part A* 1992, 30, 879.

9. Ganapathiappan, S.; Kaimin, C.; and Shriver, D.F. *J. Am. Chem. Soc.* **1989**, 111, 4091.
10. Kobayashi, N.; Uchiyama, M.; and Tsuchida, E. *Solid State Ionics* **1985**, 17, 307.
11. Zhou, G.; Khan, I.M.; and Smid, J. *Polym. Comm.* **1989**, 30, 52.
12. Dean, K.E.; Ratner, M.A.; and Shriver, D.F. *Chem. Mat.* **1991**, 3, 418.
13. LeNest, J.F.; Gandini, A.; Cheradame, H.; and Cohen-Addad, J.P. *Polym. Comm.* **1987**, 28, 302.
14. Takeoka, S.; Horiuchi, K.; Yamagata, S.; and Tsuchida, E. *Macromolecules* **1991**, 24, 2003.
15. Chen, K.; Ganapathiappan, S.; and Shriver, D.F. *Chem. Mat.* **1989**, 1, 483.
16. Marassi, R.; Zamponi, S.; and Berrettoni, M. In *Molten Salt Chemistry* Mamantov, G. and Marassi, R., Eds.; Reidel, 1987, p. 491.
17. Khor, E. and Taylor, L.T. *Macromolecules* **1982**, 15, 379.

18. Salamone, J.C.; Krauser, S.F.; Richard, R.E.; Clough, S.B.; Waterson, A.C.; Vandenberg, F.J.; Dineley, W.R.; and Filer, L.J. *Polym. Mater. Sci. Eng.* 1987, 57, 144.
19. Vanderberg, F.J.; Dineley, W.R.; Filer, L.J.; Patel, S.R.; and Barth, H.G. *Polym. Mater. Sci. Eng.* 1987, 57, 139.
20. Salamone, J.C.; Krauser, S.F.; Richard, R.E.; Clough, S.B.; Waterson, A.C.; Vandenberg, F.J.; Dineley, W.R.; and Filer, L.J. *Polym. Mater. Sci. Eng.* 1987, 57, 144.
21. Salamone, J.C.; Clough, S.B.; Bennett, S.L.; and Waterson, A.C. *Polym. Prepr.* 1988, 29, 273.
22. Chu, Evan Polytechnic University, to be published.
23. Greenbaum, S.G.; Pak, Y.S.; Wintersgill, M.C.; and Fontanella, J.J. *Solid State Ionics*, 1988, 31, 241.
24. Kakihana, M.; Schantz, S.; and Torell, L.M. *J. Chem. Phys.* 1990, 92, 6271.

Figure Captions

Figure 1. Arrhenius plot of the DC conductivity as determined by complex impedance for the lithium and sodium salts of sulfonated poly(p-phenyleneterephthlamide).

Figure 2. DSC trace for PPTS(II)-Na.

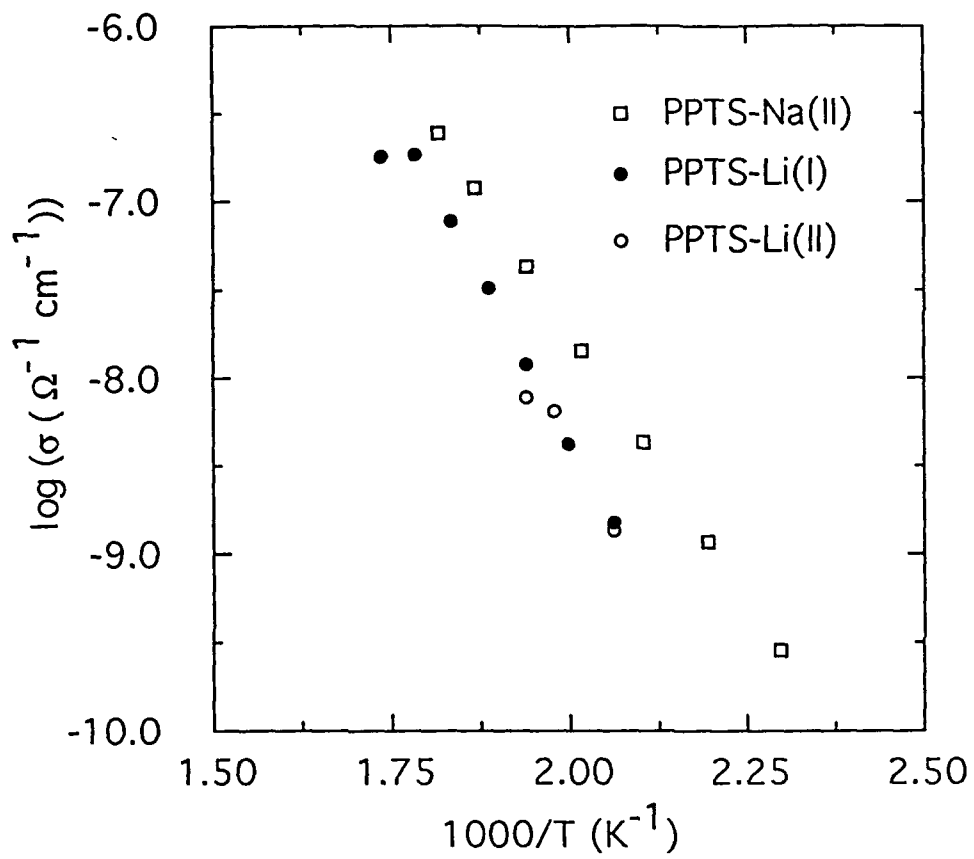


Figure 1

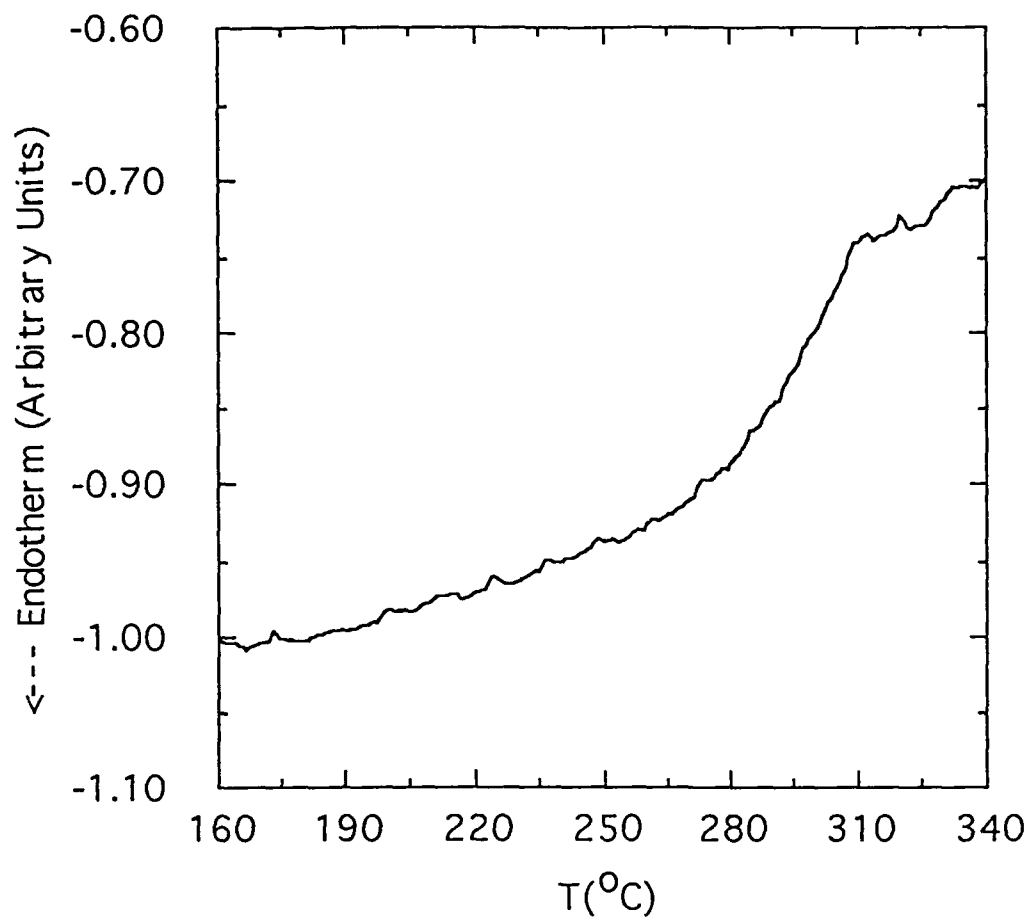


Figure 2