

AD-A283 965



①

ARMY RESEARCH LABORATORY



Conductivity of Polyacrylonitrile Based Lithium Polymer Electrolytes

Steve Slane and Eric Shapow

ARL-TR-361

August 1994

DTIC
ELECTE
SEP. 01 1994
S B D

copy

94-28354



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

94 8 31 159

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government endorsement or approval of commercial products or services referenced herein.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE August 1994	3. REPORT TYPE AND DATES COVERED Technical Report: Mar to Aug 93	
4. TITLE AND SUBTITLE CONDUCTIVITY OF POLYACRYLONITRILE BASED LITHIUM POLYMER ELECTROLYTES			5. FUNDING NUMBERS PE: 612705 PR: 52MP02P	
6. AUTHOR(S) Steve Slane and Eric Shapow				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Electronics and Power Sources Directorate (EPSD) ATTN: AMSRL-EP-PB Fort Monmouth, NJ 07703-5601			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-361	
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) Preparation of solid state polymer lithium electrolytes based on polyacrylonitrile (PAN) have achieved room temperature conductivities equal to that of liquid organic electrolytes. Polymer films of ethylene carbonate, propylene carbonate, PAN, and lithium salts have yielded conductivities as high as 0.004 S/cm at 25 deg C. These high conductivities make the use of polymer electrolytes a viable possibility in advanced batteries. Reported here are film preparation technique, conductivities from -70 to 70 deg C, and Vogel-Tammann-Fulcher (VTF) relationships.				
14. SUBJECT TERMS Polymer electrolyte; polyacrylonitrile; lithium electrolyte; rechargeable batteries; ionic conductivities			15. NUMBER OF PAGES 18	
			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	

CONTENTS

	PAGE
INTRODUCTION	1
EXPERIMENTAL	1
RESULTS AND DISCUSSION	2
CONCLUSIONS.	10
REFERENCES	10

FIGURES

FIGURE 1. Arrhenius plot of electrolyte conductivities.	3
FIGURE 2. Arrhenius plot of electrolyte conductivities.	5
FIGURE 3. Arrhenius plot of electrolyte conductivities.	6
FIGURE 4. Arrhenius plot of electrolyte conductivities.	8
FIGURE 5. VTF Plot.	9

TABLES

TABLE 1. Electrolyte Conductivities at 25°C	4
TABLE 2. VTF Equation Values.	7

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTRODUCTION

The use of solid polymer electrolytes (SPE) in rechargeable lithium batteries is currently being widely investigated. Polymer electrolytes can be prepared into very thin films possessing large surface area yielding high power densities. An energy advantage of a solid flexible electrolyte is its ability to enable the design of more volume efficient battery configurations. In an electrochemical cell, especially in a reversible cell, a flexible electrolyte can accommodate the volume changes that occur with charge/discharge cycles. Polymer electrolytes can increase cell safety by preventing ignition by acting as a shut down separator, if thermal runaway should occur within a cell. A thin Li^+ ion conducting polymer film acts as both the electrolyte and a separator between the lithium anode and a lithium insertion compound as the cathode. The use of high energy cathode films of reversible compounds such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , V_2O_5 , or V_6O_{13} with thin lithium foil anodes and the structural flexibility of polymer electrolytes make the lithium polymer battery a promising candidate for advanced battery systems for electric vehicles (EV) or consumer/military electronics applications.

One of the first polymer electrolyte chemistries consisted of poly(ethylene oxide) PEO-LiX complexes (1,2) which need to operate at around 100°C . New multiphase systems involve adding plasticizing solvents to PEO-LiX or trapping liquid electrolyte solutions in a polymer matrix to form a "gel" electrolyte. The latter more "liquid like" chemistries can operate at room temperature and therefore are of interest for further research. One of the basic fundamental problems in the development of solid state ionic materials based on polymers is the conductivities of these materials. Recently, room temperature conductivities as high as $10^{-3} \text{ S cm}^{-1}$ have been reported for polyacrylonitrile (PAN) based lithium salt complexes (3). It is ionic conductivity measurements on this chemistry that is the focus of this report.

EXPERIMENTAL

The preparation of the solid gel electrolytes involved the immobilization of LiClO_4 , LiAsF_6 , or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in ethylene carbonate (EC) and propylene carbonate (PC) mixtures with PAN. The LiAsF_6 (Lithco "Lectro-salt") and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3M) were dried under vacuum at 60°C for 24 h.; LiClO_4 (Alfa reagent grade) was recrystallized in distilled water, then dried under vacuum at 150°C for 24 h. PC (Burdicke and Jackson) was dried with type 4A molecular

sieves for 48 h then distilled under vacuum. EC (Fluka AG) was fractionated under vacuum. Dimethyl carbonate (DMC) (Burdick and Jackson) was fractionated in an argon atmosphere. Karl Fisher titration for EC, PC, and DMC indicated water contents of <24 ppm. Poly(acrylonitrile) (Polyscience Inc.) with an average molecular weight of 150,000 was dried under vacuum at 60°C for 48 h.

The liquid electrolyte EC:PC:LiX was prepared in a vial with a stirring bar. PAN powder was then added and the mixture stirred to ensure wetting of the PAN. The mixture was heated slowly in an oil bath to 100°C, avoiding overheating and decomposing the PAN. The mixture turned to a clear highly viscous gel and was cast between glass plates, with 0.25 mm spacers, and allowed to cool. The resulting polymer electrolyte was an elastomeric mechanically stable film. Two general film compositions were prepared with mole percentages of 40EC:34.75PC:21PAN:4.25LiX (17.6:1 EC+PC:LiX) and 38EC:33PC:21PAN:8LiX (8.8:1 EC+PC:LiX). Variations to these compositions include the use of DMC with EC/PC mixtures, the addition of ground molecular sieves to form a composite film, and a film with a lower concentration of PAN (12%).

Electrolyte conductivities were determined from ac impedance measurements using an EG&G PAR model 388 impedance system with a frequency range of 5 Hz to 1000 kHz. The test cell was made of ceramic with an electrode configuration of SS/SPE/SS. A thermocouple was in close proximity to the SPE in the cell. The cell assembly was inserted into a wide-mouthed glass reaction vessel packed with molecular sieves, and nitrogen bubbled through. The temperature testing (70°C to -70°C) was performed in a Tenney environmental chamber. All chemical storage, film casting, and cell assembly was performed in a Vacuum Atmospheres argon-filled dry box.

RESULTS AND DISCUSSION

For polymer electrolytes to be of practical use, Li-ion mobility must be high enough to enable useful rate capabilities in lithium batteries. As a general comparison of two types of polymer electrolyte chemistries, Figure 1 shows an Arrhenius plot of the ionic conductivities of PEO-LiClO₄ film, a PAN:EC:PC:LiClO₄ film, and a EC:PC:LiClO₄ liquid electrolyte. The PAN-based electrolyte film demonstrates conductivities approaching that of the liquid and a significant increase in ion mobility over the PEO electrolyte. It is this result, first demonstrated by Abraham and Alamgir for this chemistry (3), that makes a mechanically stable free-standing film a possible battery

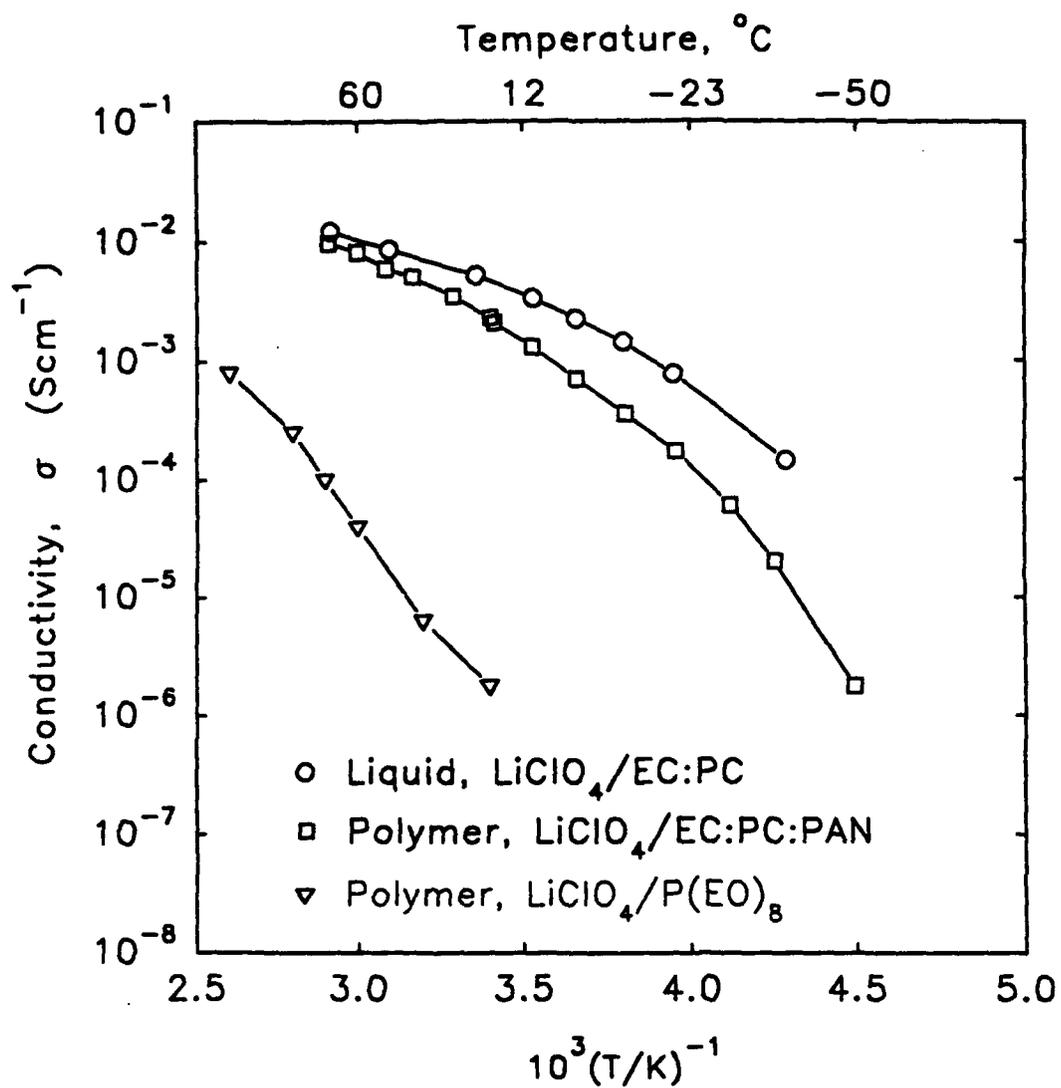


Figure 1. Arrhenius plot of electrolyte conductivities.

electrolyte. The difference in conductivity of the PAN-based electrolyte and the liquid at decreasing temperatures is due to the lower viscosity of the polymer.

Having established that PAN-based films can be prepared and can produce ionic conductivities close to liquid organic electrolytes, further studies of Li-ion mobility in these types of electrolytes were performed. Table 1 lists the polymer electrolyte molar compositions, solvent:LiX ratio, and conductivities at 25°C of the films studied.

TABLE 1. Electrolyte Conductivities at 25°C

ELECTROLYTE	Solvent:LiX	CONDUCTIVITY (S cm ⁻¹)
45EC:45PC:LiClO ₄ (liquid)	9:1	5.2 x 10 ⁻³
38EC:33PC:21PAN:8LiClO ₄	8.8:1	2.9 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiClO ₄	17.6:1	4.5 x 10 ⁻⁴
56.5:EC:23PC:16PAN:4.25LiN(CF ₃ SO ₂) ₂	17.6:1	2.0 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiAsF ₆	17.6:1	3.7 x 10 ⁻³
40EC:34.75PC:21PAN:4.25LiAsF ₆ :5wt%3Å	17.6:1	1.6 X 10 ⁻³
33EC:28PC:13.5DMC:20PAN:5.5LiAsF ₆	13.5:1	9.9 x 10 ⁻⁴
44.3EC:39PC:12PAN:p4.7LiAsF ₆	17.6:1	2.8 x 10 ⁻³
38EC:33PC:21PAN:8LiAsF ₆	8.8:1	1.0 x 10 ⁻³

In Figure 2, the conductivities of three LiX salt complexes, LiAsF₆, LiClO₄, and LiN(CF₃SO₂)₂ with EC:PC: PAN, are shown. As in liquid organic electrolytes, the LiAsF₆ electrolyte gives the highest conductivity. The imide, LiN(CF₃SO₂)₂, known as a high temperature stabilizing salt, demonstrated poor conductivity at low temperatures. This is believed to be due to precipitation of the imide salt from the EC:PC mixture resulting in loss of lithium ions for charge transfer.

The arrhenius plots in Figure 3 show the conductivities of three chemical variations with the LiAsF₆ electrolyte. Changing the solvent to LiAsF₆ ratio from 17.6:1 to 8.8:1 (i.e., doubling the amount of salt while holding the PAN concentration at 21 mole percent) lowers the conductivity over the whole temperature range. This again is a viscosity effect on the ionic mobility. The addition of DMC, which in liquids makes the electrolyte more stable with the lithium metal anode, lowers the conductivity. This is expected since LiAsF₆/DMC electrolyte has a lower conductivity than

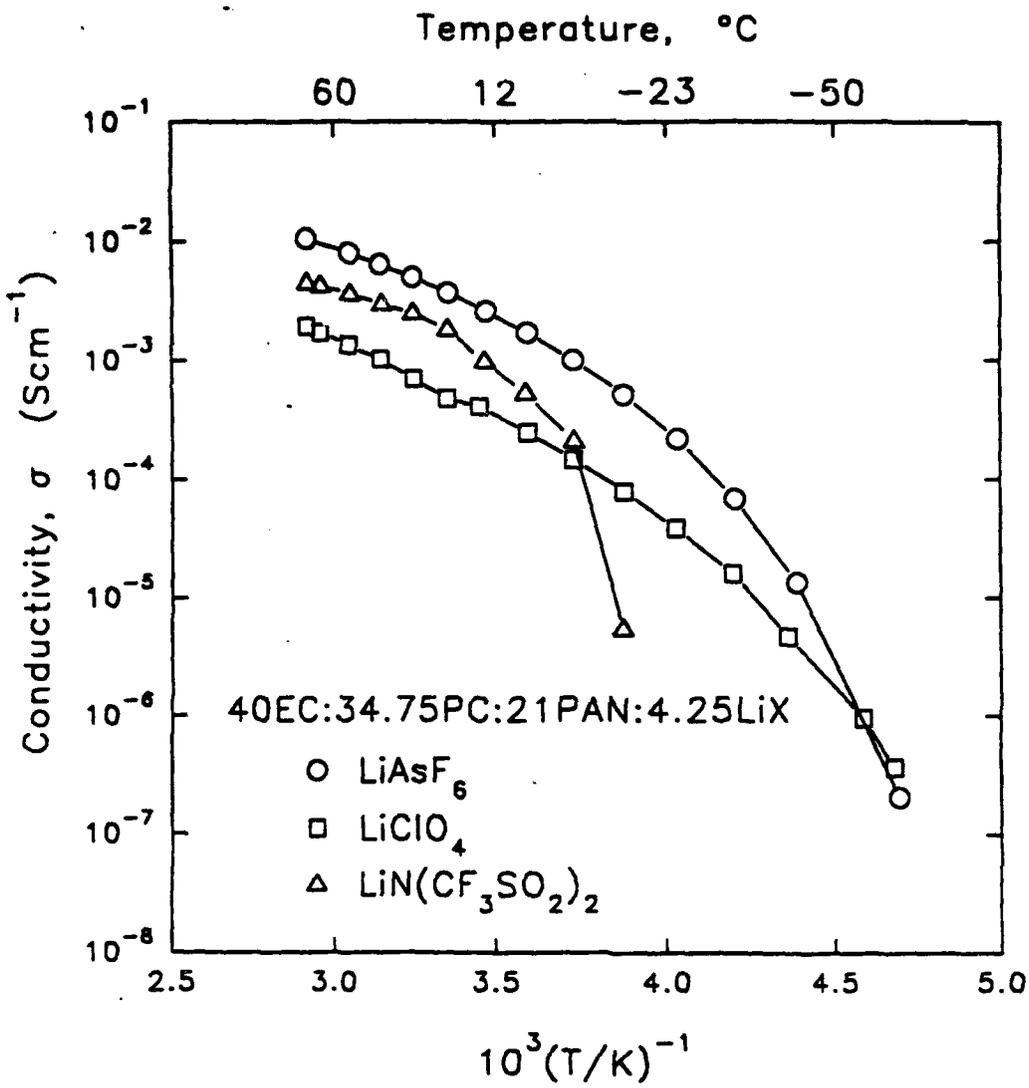
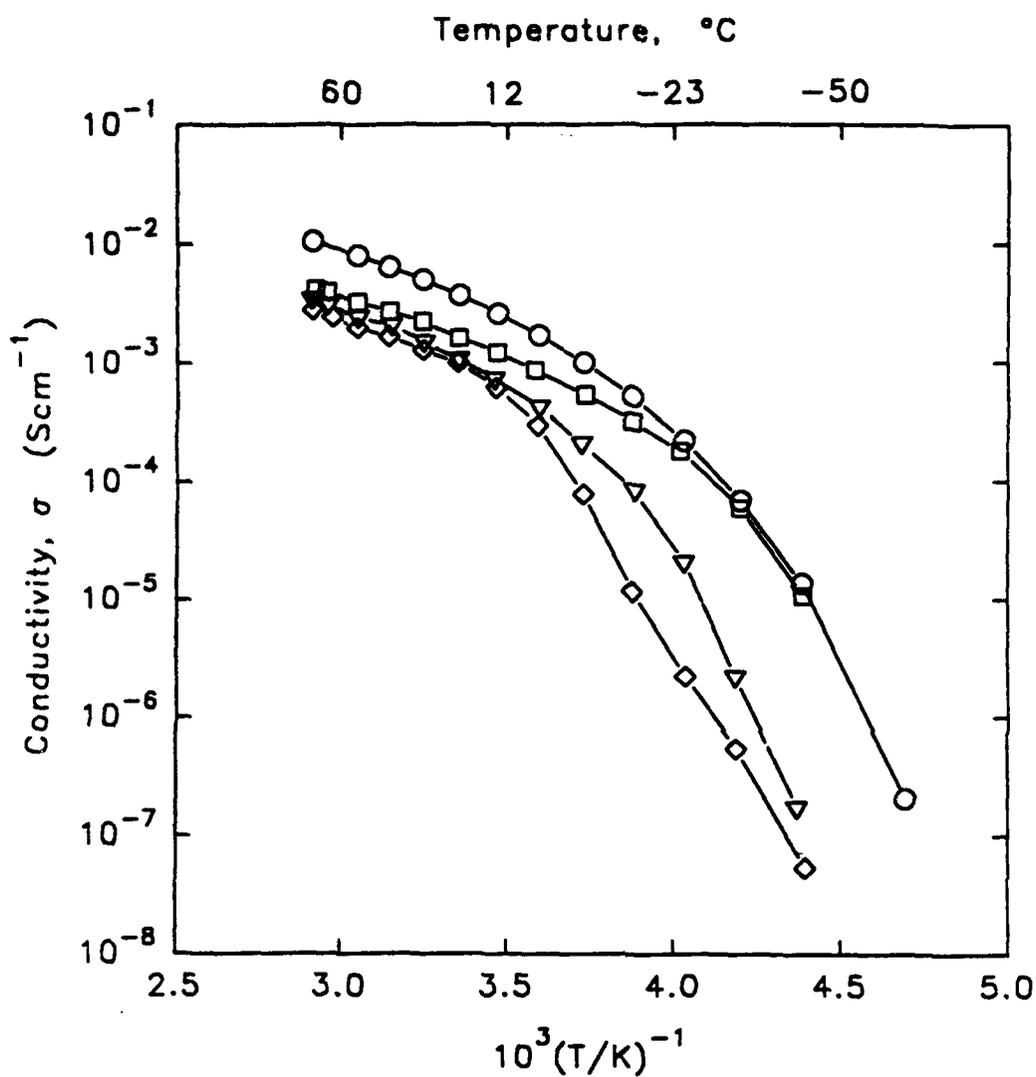


Figure 2. Arrhenius plot of electrolyte conductivities.



- EC:PC:PAN:LiAsF₆ (17.6:1)
- EC:PC:PAN:LiAsF₆ (17.6:1) w/5wt% 3A sieves
- ▽ EC:PC:PAN:LiAsF₆ (8.8:1)
- ◇ EC:PC:DMC:PAN:LiAsF₆ (17.6:1)

Figure 3. Arrhenius plot of electrolyte conductivities.

LiAsF₆/EC:PC in liquids due to its much lower dielectric constant (ϵ : EC=39.6, PC=64.9, DMC=3.1). A film with a 12% concentration of PAN was prepared. Its conductivity (seen in Figure 4) at lower temperatures was greater than films prepared with 21% PAN. This is expected since the film with less PAN is more liquid like. The electrolyte was "wetter," but still had the physical integrity of a solid film.

All the arrhenius plots for the gel electrolytes exhibit significant curvature, which is characteristic of Vogel-Tammann-Fulcher (VTF) behavior (1). The VTF relationship is an application of free-volume distribution to conductivity in polymer dynamics and is expressed by the equation

$$\sigma = AT^{-1/2}\exp[-E_a/(T-T_0)] \quad (1)$$

where A is a prefactor related to the transport coefficient, T₀ is the idealized temperature corresponding to zero configurational entropy, and E_a is the activation energy for charge transport within the gel electrolytes. Table 2 gives these calculated values for some of the electrolytes studied.

TABLE 2. VTF Equation Values

ELECTROLYTE	A	T ₀ (°C)	E _a (eV)
EC:PC:LiClO ₄ (Liquid)	2.68	176	0.036
EC:PC: PAN:LiClO ₄ (17.6:1)	5.38	130	0.093
EC:PC: PAN:LiAsF ₆ (17.6:1)	4.12	176	0.043
EC:PC: PAN:LiAsF ₆ (8.8:1)	5.10	162	0.066

Figure 5 shows the straight line VTF plots from which the activation energies were determined. These calculations were performed over a temperature range of -20°C to 70°C. As shown, the higher the ionic conductivity the lower the activation energy. This is expected since E_a is calculated from the conductivity. What Figure 5 does show is that the activation energy of the electrolytes does not change over the temperature range. This may indicate the solid gel is homogenous.

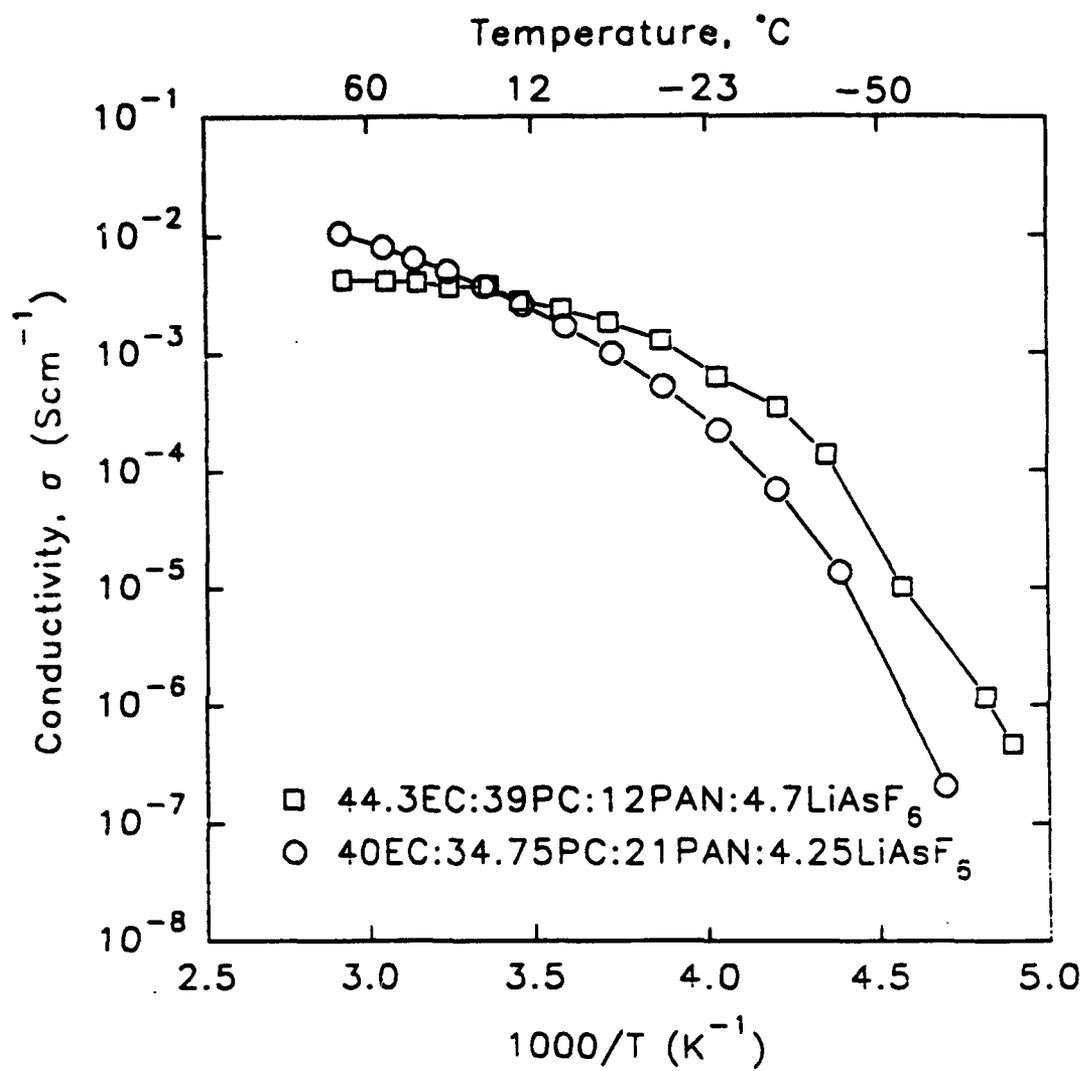


Figure 4. Arrhenius plot of electrolyte conductivities.

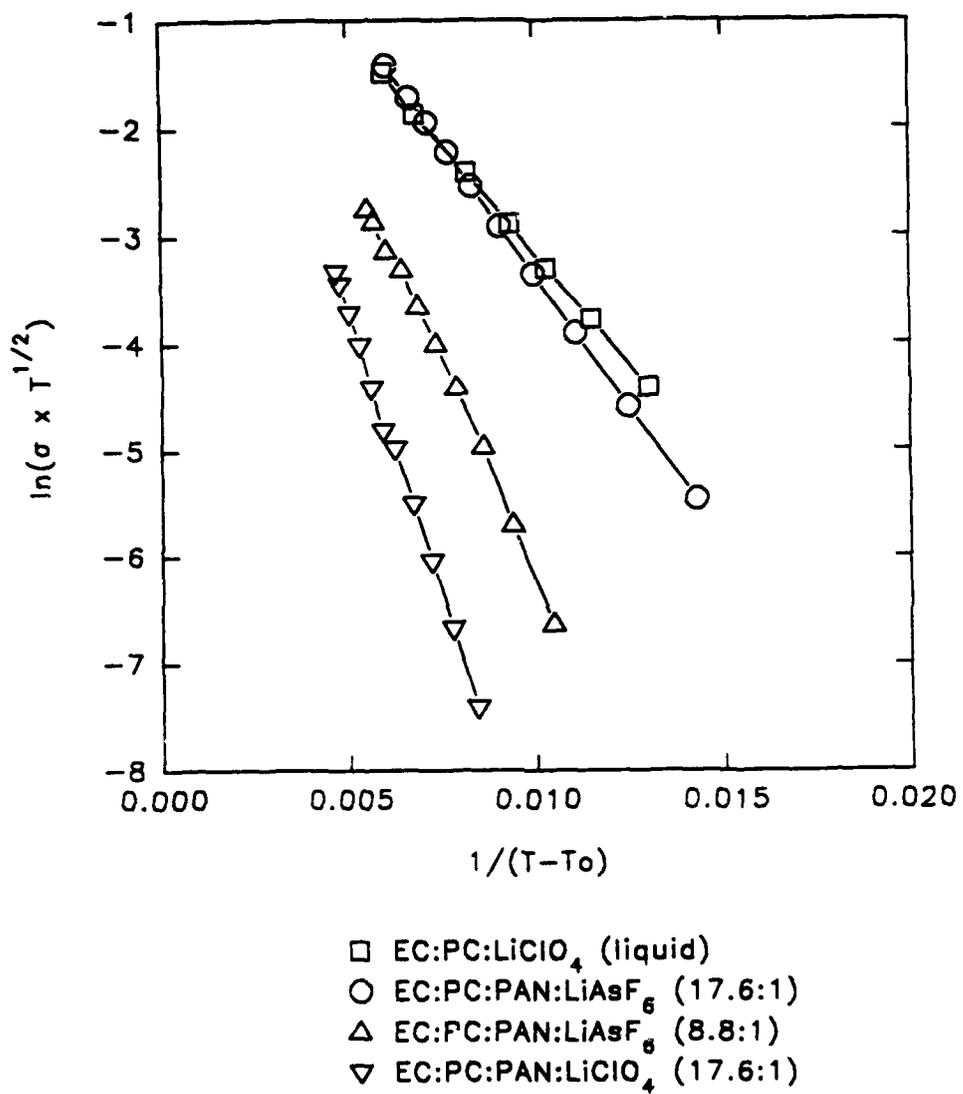


Figure 5. VTF Plot.

CONCLUSIONS

It can be concluded from this study that solid gel polymers based on PAN and LiX salt complexes possess adequate ionic conductivities to be used in lithium rechargeable batteries. The next logical step in the development of these electrolytes is to study their lithium stability and interfacial properties and their use in actual anode/electrolyte/cathode configurations.

REFERENCES

1. F.M. Gray, "Solid Polymer Electrolytes," VCH Publishers Inc., New York, 1991.
2. J.R. MacCallum and C.A. Vincent, eds. "Polymer Electrolyte Reviews," Vol. 2, Elsevier Applied Science, London, 1988.
3. K.M. Abraham and M. Alamgir, J. Electrochem. Soc., 106, 1657 (1990).

ARMY RESEARCH LABORATORY
ELECTRONICS AND POWER SOURCES DIRECTORATE
CONTRACT OR IN-HOUSE TECHNICAL REPORT
MANDATORY DISTRIBUTION LIST

Page 1 of 4

Defense Technical Information Center*
ATTN: DTIC-OCC
Cameron Station (Bldg 5)
Alexandria, VA 22304-6145
(*Note: Two copies will be sent from
STINFO office, Fort Monmouth, NJ)

Commander, CECOM
R&D Technical Library
Fort Monmouth, NJ 07703-5703
(1) AMSEL-IM-BM-I-L-R (Tech Library)
(3) AMSEL-IM-BM-I-L-R (STINFO ofc)

Director
US Army Material Systems Analysis Actv
ATTN: DRXSY-MP
(1) Aberdeen Proving Ground, MD 21005

Commander, AMC
ATTN: AMCDE-SC
5001 Eisenhower Ave.
(1) Alexandria, VA 22333-0001

Director
Army Research Laboratory
ATTN: AMSRL-D (John W. Lyons)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1145

Director
Army Research Laboratory
ATTN: AMSRL-DD (COL William J. Miller)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1145

Director
Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1145
(1) AMSRL-OP-CI-AD (Tech Pubs)
(1) AMSRL-OP-CI-AD (Records Mgt)
(1) AMSRL-OP-CI-AD (Tech Library)

Directorate Executive
Army Research Laboratory
Electronics and Power Sources Directorate
Fort Monmouth, NJ 07703-5601
(1) AMSRL-EP
(1) AMSRL-EP-T (M. Howard)
(1) AMSRL-OP-RM-FM
(22) Originating Office

Advisory Group on Electron Devices
ATTN: Documents
2011 Crystal Drive, Suite 307
(2) Arlington, VA 22202

ARMY RESEARCH LABORATORY
ELECTRONICS AND POWER SOURCES DIRECTORATE
SUPPLEMENTAL DISTRIBUTION LIST
(ELECTIVE)

Page 2 of 4

- (1) Deputy for Science & Technology
Office, Asst Sec Army (R&D)
Washington, DC 20310
- (1) Cdr, Marine Corps Liaison Office
ATTN: AMSEL-LN-MC
Fort Monmouth, NJ 07703-5033
- (1) HQDA (DAMA-ARZ-D/
Dr. F.D. Verderame)
Washington, DC 20310
- (1) Director
Naval Research Laboratory
ATTN: Code 2627
Washington, DC 20375-5000
- (1) Cdr, PM JTFUSION
ATTN: JTF
1500 Planning Research Drive
McLean, VA 22102
- (1) Rome Air Development Center
ATTN: Documents Library (TILD)
Griffis AFB, NY 13441
- (1) Dir, ARL Battlefield
Environment Directorate
ATTN: AMSRL-BE
White Sands Missile Range
NM 88002-5501
- (1) Dir, ARL Sensors, Signatures,
Signal & Information Processing
Directorate (S3I)
ATTN: AMSRL-SS
2800 Powder Mill Road
Adelphi, MD 20783-1145
- (1) Dir, CECOM Night Vision/
Electronic Sensors Directorate
ATTN: AMSEL-RD-NV-D
Fort Belvoir, VA 22060-5677
- (1) Dir, CECOM Intelligence and
Electronic Warfare Directorate
ATTN: AMSEL-RD-IEW-D
Vint Hill Farms Station
Warrenton, VA 22186-5100

ELECTRONICS AND POWER SOURCES DIRECTORATE
SUPPLEMENTAL CONTRACT DISTRIBUTION LIST
(ELECTIVE)

Page 3 of 4

Dow Chemical Company
M.E. Pruitt Research Center
Midland, MI 48674
ATTN: Mr. Don Dix

Michigan Molecular Institute
1910 West St., Andrews Road
Midland, MI 48640
ATTN: Dr. Robert Hotchkiss

Westinghouse Electric Corp.
R&D Center
1310 Beulah Road
Pittsburgh, PA 15235
ATTN: Dr. L. Mandlkorn

3M Company
3M Center
St. Paul, MN 55144-1000
ATTN: Dr. Dave Redmond

Sprague
Film Capacitor Group
Longwood, FL 32750
ATTN: Dr. Mark Carter

3M Company
3M Center
St. Paul, MN 55144-1000
ATTN: Dr. E.F. Hampl

Aerovox, Inc.
740 Belleville Ave.
New Bedford, MA 02745
ATTN: Tim Egan

General Electric
Capacitor and Power Division
381 Upper Broadway
Fort Edward, NY 12828
ATTN: Don Nicols-MESS

ABB Power T&D Company
300 North Curry Pike
Bloomington, IN 47402
ATTN: George S. Papadopolous

E.I. DuPont
P.O. Box 2700
Richmond, VA 23261
ATTN: Dr. Thomas K. Bednarz

E.I. DuPont, Electronics Dept
BMP21-2126
P.O. Box 80021
Wilmington, DE 19880-0021
ATTN: Dr. Roger O. Uhler

Celanese Hoechst
86 Morris Avenue
Summit, NJ 07901
ATTN: Bill Timmons

Eni Chem Americas, Inc.
2000 Princeton Park Corp Ctr
Monmouth Junction, NJ 08852
ATTN: Dr. Alex Jen

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91109
ATTN: Dr. S.P.S. Yen

Sandia National Laboratories
Passive Components Division 2552
P.O. Box 5800
Albuquerque, NM 87185
ATTN: Dr. James O. Harris

General Electric
Capacitor Division
381 Upper Broadway
Fort Edward, NY 12828
ATTN: Larry Bock

3M Company
Federal Systems Research &
Development
Building 224-2S-25
St. Paul, MN 55144
ATTN: Ed Westlund

Maxwell Laboratories, Inc.
888 Balboa Avenue
San Diego, CA 92123-1506
ATTN: Joel B. Ennis

Defense Nuclear Agency
6801 Telegraph Road
Alexandria, VA 22310
ATTN: John Farber

Commander
U.S. Army AMCCOM, ARDEC
ATTN: SMCAR-FSP-E/E.J. Zimpo
Bldg 1530
Picatinny Arsenal, NJ 07801

Allied-Signal, Inc.
P.O. Box 1987R
Morristown, NJ 07960
ATTN: Dr. Cheng-Jiu Wu

Exfluor Research Company
P.O. Box 7807
Austin, TX 78713
ATTN: Dr. H. Kawa

Defense Nuclear Agency
6801 Telegraph Road
Alexandria, VA 22310
ATTN: Janet Meiserhelder

GE Corporate Research & Development
K1-2S86, P.O. Box 8
Schenectady, NY 12301
ATTN: Dr. Clive Reed