MASTER COPY KEEP FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 26, 1998	Final Progress Report

4. TITLE AND SUBTITLE
Lithium Ion Transport Across and Between Phase Boundaries in Heterogeneous Polymer Electrolytes, Based on PVdF

5. FUNDING NUMBERS
DAAG55-97-1-0392

6. AUTHOR(S)
Steven G. Greenbaum

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
Department of Physics/Astronomy
Hunter College of the City University of New York
695 Park Avenue, New York, NY 10021

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park,, NC 27709-2211
jointly with
CE COM
Ft. Monmouth
NJ 07703

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 37793.2-CH

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

19980521 120

13. ABSTRACT *(Maximum 200 words)*

Initial investigations of polymer electrolytes based on PVdF-HFP and $LiPF_6$ dissolved in either EC/PC or EC/DMC mixtures have been carried out via high pressure complex impedance methods and ^7Li NMR. All results indicate that the polymer matrix, while effectively immobilizing the liquid component, does not significantly affect the ion transport mechanism inherent to liquid electrolytes. In the first reported attempt to exploit ^{17}O NMR to study lithium battery electrolytes, we have prepared ^{17}O-enriched Li triflate and several electrolytes containing the isotopically enriched salt dissolved in DEC, DMC, and mixtures of DMC/EC. Line widths were measured as a function of electrolyte solvent and temperature, and suggest that EC inhibits the formation of ion pairs, when added to DMC.

14. SUBJECT TERMS
Polymer Electrolytes, PVdF, ion transport, ^7Li and ^{17}ONMR

15. NUMBER IF PAGES
4

16. PRICE CODE

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

Lithium Ion Transport Across and Between Phase Boundaries in Heterogeneous Polymer Electrolytes Based on PVdF

FINAL PROGRESS REPORT

Steven G. Greenbaum

February 26, 1998

U.S. ARMY COMMUNICATONS AND ELECTRONICS COMMAND,
jointly with U.S. ARMY RESEARCH OFFICE

GRANT #'s
DAAB07-97-1-G019 (CECOM)
and
DAAG55-97-1-0392 (ARO)

Hunter College of CUNY
Department of Physics
695 Park Avenue
New York, NY 10021

Final Progress Report

Lithium Ion Transport Across and Between Phase Boundaries in Heterogeneous Polymer Electrolytes Based on PVdF

Project Co-Funded by U.S. Army CECOM and ARO

1. CECOM RESEARCH AGREEMENT NUMBER: DAAB07-97-1-G019
   ARO RESEARCH AGREEMENT NUMBER:

2. PERIOD COVERED BY REPORT: 2/27/97 - 2/26/98

3. TITLE OF PROJECT: *Lithium Ion Transport Across and Between Phase Boundaries in Heterogeneous Polymer Electrolytes Based on PVdF*

4. NAME OF INSTITUTION: Hunter College of the City University of New York

5. AUTHOR OF REPORT: Steven G. Greenbaum, Professor of Physics

6. MANUSCRIPTS SUBMITTED UNDER CECOM and ARO SPONSORSHIP DURING THIS PERIOD:

   Oxygen-17 Nuclear Magnetic Resonance as a Probe of Ion-Ion Interactions in Lithium Battery Electrolytes, with T.M. Murray, A. Venturelli ans S. Slane, submitted to *Electrochimica Acta*

7. ABSTRACTS SUBMITTED UNDER CECOM and ARO SPONSORSHIP DURING THIS PERIOD:

   High Pressure Electrical Conductivity and NMR Studies on Liquid and Plasticized Polymer Electrolytes, with J. J. Fontanella, M. C. Wintersgill, P. E. Stallworth, and A. S. Gozdz, accepted for presentation at the 8th International Meeting on Lithium Batteries, Scotland, July, 1998.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:
a) Dr. Telitha Murray, postdoctoral associate
b) Ms. Sophia Suarez-Gustave, MA degree candidate (most of her support came from College and other sources).

9. REPORT OF INVENTIONS: None

Technical Description

Specific aims -

A great deal of effort, world-wide, is being spent on the development of gel electrolytes based on poly(vinylidene difluoride) (PVdF). These materials appear to offer the requisite dimensional stability without seriously compromising ionic conductivity. A key requirement of these electrolytes is that they must be homogeneous because, otherwise, long-range ion transport could be impeded at phase boundaries. In previous work published by our group prior to receiving this grant, it was demonstrated that the addition of about 10 wt% nanoscale TiO_2 could have a large effect on suppressing phase boundaries. It is interesting to note that high surface area inorganic oxides such as Al_2O_3 and fumed silica are routinely added to the plasticized polymer prior to injecting the liquid electrolyte, in order to prevent collapse of the film while the plasticizer is removed. Little attention has been given (at least in the published literature) to the effect of the inorganic oxide additives on *electrical* properties. Our efforts are focused on correlating short-range ionic motion, as probed by NMR, with long-range ion transport. A second research activity undertaken was to explore the possible use of oxygen-17 NMR as a alternative (to vibrational spectroscopy) tool to investigate ion-ion interactions in liquid and polymer electrolytes.

Results -

PVdF-electrolytes

In a joint study with long-time collaborators John Fontanella and Phil Stallworth of the U.S. Naval Academy , and also with Tony Gozdz of Bellcore, electrical conductivity and NMR studies have been carried out on liquid electrolytes such as EC:PC and EC:DMC containing $LiPF_6$ and polymer films plasticized using the same liquid electrolytes. The polymer films are (PVdF) copolymerized with hexafluoropropylene (HFP). Complex impedance studies were made at frequencies from 10 Hz to 100 MHz at pressures up to 0.3 GPa (3 kbar) at room temperature. In addition, studies were carried out in vacuum at temperatures down to 5.5K. Significant differences between the EC:PC and EC:DMC liquid electrolytes are found. In addition, the behavior of the plasticized polymer films was compared with the response of the corresponding liquid electrolytes. The variable pressure measurements yield activation volumes for ion transport. The values in the polymer electrolytes are close to those found in the corresponding liquids, indicating that liquid-like conductivity occurs in the PVdF-based electrolyte. By contrast, earlier work by our research group on poly(acrylonitrile) (PAN) - based gels found a difference in activation volumes between the gels and liquid electrolytes, indicating that the polymer matrix interacts strongly with the ions. Lithium-7 NMR relaxation time measurements were utilized to determine ionic motional correlation times in PVdF-electrolytes. Again, these were close to the values obtained for the corresponding liquid electrolytes.

Oxygen-17 NMR

Because the natural abundance of ^{17}O is quite low, isotopic enrichment of electrolyte salts

has potential applications in the investigation of liquid, and eventually, polymer electrolytes. Our investigation was a first attempt to exploit ^{17}O NMR as probe of ion-solvent and ion-ion interactions in lithium battery electrolytes. A novel approach to the synthesis of ^{17}O-enriched lithium triflate (CF_3SO_3Li) was undertaken. The ^{17}O spectra of the enriched salt in a number of solvents, DMC - dimethylcarbonate, DEC - diethylcarbonate and mixtures of DMC and EC - ethylenecarbonate, were then compared. Spectra of solvent oxygens, at natural ^{17}O abundance, were also obtained. Evidence for solvent-separated ion pairs or aggregates was postulated from the C=O and sulfonate ^{17}O NMR line widths, for which the DMC/EC 1:1 electrolyte exhibits the lowest and least temperature-sensitive values. It would be of interest in future investigations to explore the salt concentration dependence of both chemical shift and line width. It would also be of interest to examine electrolytes prepared with Li salts with other oxygen-containing anions that are more soluble than Li triflate.