

AD-A198 974

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

4

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 021	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Basic Studies of Polymer Electrolytes Suitable for Advanced Electrochemical Devices		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT 06/01/80 - 04/30/88
7. AUTHOR(s) D. F. Shriver and D. H. Whitmore		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Northwestern University Department of Chemistry and Materials Research Center		8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0532
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-746
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 24, 1988
		13. NUMBER OF PAGES 5
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Approved for public release and sale. Distribution unlimited.		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) polymers, electrolytes, polymer-salt complexes, polyelectrolytes, solid state ionics.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) New polymer electrolytes were prepared and studied by complex impedance spectroscopy, pulsed field gradient, and MAS NMR. A new class of polymeric mixed ionic-electronic conductors was also prepared and studied.		

DTIC
SELECTE
SEP 01 1988

D

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-80-C-0532

Technical Report No. 21

Basic Studies of Polymer Electrolytes Suitable for
Advanced Electrochemical Devices

by

Duward F. Shriver and D. H. Whitmore

(312) 491-5655

Northwestern University

Department of Chemistry

Evanston, IL 60208

August, 1988

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

* This document has been approved for public release and sale: its distribution is unlimited.



88 9 1 014

Research Accomplishments

As we have described in previous end-of-year reports, we have made advances in several areas of polymer electrolytes, only the highlights are listed here.

- (i) Experiments on the polyethylene oxide NaBF_4 complex doped with varying amounts of NaBH_4 strongly indicate that the cations are not transported down helical tunnels as originally proposed.
- (ii) A new class of polyphosphazene comb polymers was synthesized (eg. $[\text{NP}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3)_2]_n$) and the salt complexes were well characterized. For many years these polymer salt complexes displayed the highest ionic conductivity of any solvent-free polymer electrolyte.
- (iii) Pulsed field gradient NMR studies of polymer electrolytes were performed to determine diffusion coefficients for Li^+ (^7Li NMR) and SO_3CF_3^- (^{19}F NMR). These represent some of the most precise and extensive data on diffusion coefficients in polymer electrolytes, and they provide insight into ion pairing in these materials.
- (iv) A new class of mixed ionic-electronic conductors was synthesized and investigated. These consist of a polar polymer complexed with NaI_x . When $x = 1$, the material is a simple ionic conductor. As x increases, electronic conductivity is observed and eventually at large values of x electronic conductivity dominates. In the intermediate range, both ionic conductivity and electronic conductivity increase with increasing x . We hope to continue studies of this correlation between ionic and electronic conductivity, and the mechanism for electronic conductivity.

- (v) We prepared the first solvent-free polyelectrolytes with good ionic conductivity. Initially these were plasticized materials but more recently, phosphazene comb polymers have been synthesized and studied. The latter include new anion conductors that have higher conductivities than any previously reported.

Listing of Technical Reports and Journal Articles

<u>Report No.</u>	<u>Title and Authors</u>
001	"Transference Number Measurements for the Polymer Electrolyte Poly(ethylene oxide)•Na SCN", R. Dupon, D. H. Whitmore and D. F. Shriver, J. Electrochem. Soc., <u>128</u> , 715 (1981).
002	"Structure and Ion Transport in Polymer Salt Complexes", D. F. Shriver, B. L. Papke, M. A. Ratner, R. Dupon, T. Wong and M. Brodwin, Solid State Ionics, <u>5</u> , 83-88 (1981).
003	"Ion Pairing in Polyether Solid Electrolytes and its Influence on Ion Transport", B. L. Papke, R. Dupon, M. A. Ratner and D. F. Shriver, Solid State Ionics, <u>5</u> , 685-88 (1981).
004	"Mechanism of Ionic Conduction in Alkali Metal-Polymer Complexes", D. F. Shriver Matthew Stainer, and R. Dupon, Journal of Power Sources, <u>2</u> , 383-88 (1983).
005	"The Influence of Ion Pairing on Cation Transport in the Polymer Electrolytes formed by Poly(ethylene oxide) with Sodium Tetrafluoroborate and Sodium Tetrahydroborate", R. Dupon, B. L. Papke, M. A. Ratner, D. H. Whitmore and D. F. Shriver, J. Am. Chem. Soc., <u>104</u> , 6247 (1982).
006	"Ion Transport in the Polymer Electrolytes formed between Poly(ethylene succinate) and Lithium Tetrafluoroborate", R. Dupon, B. L. Papke, M. A. Ratner and D. F. Shriver, J. Electrochem. Soc., <u>131</u> , 3, (1984).
007	"Stoichiometry of Formation and Conductivity Response of Amorphous and Crystalline Complexes formed between Poly(ethylene oxide) and Ammonium Salts", M. Stainer, L. C. Hardy, D. H. Whitmore and D. F. Shriver, J. Electrochem. Soc., <u>131</u> , 4 (1984).
008	"Chloride Ion Conductivity in a Plasticized Quaternary Ammonium Polymer", L. C. Hardy and D. F. Shriver, Macromolecules, <u>17</u> , 975 (1984).

- 009 "Polyphosphazene Solid Electrolytes", P. M. Blonsky, P. Austin, H. R. Allcock and D. F. Shriver, J. Am. Chem. Soc., 106, 6854 (1984).
- 010 "Preparation and Electrical Response of Solid Polymer Electrolytes with Only One Mobile Species", L. Charles Hardy and D. F. Shriver, J. Am. Chem. Soc., 107, 3823 (1985).
- 011 "Polyphosphazenes with Etheric Side Groups: Prospective Biomedical and Solid Electrolyte Polymers", H. R. Allcock, P. E. Austin, T. X. Neenan, J. T. Sisko, P. M. Blonsky and D. F. Shriver, Macromolecules, 19, 1508 (1986).
- 012 "Complex Formation and Ionic Conductivity of Polyphosphazene Solid Electrolytes", P. M. Blonsky, D. F. Shriver, P. Austin and H. R. Allcock, Solid State Ionics, 18 & 19, 258-64 (1986).
- 013 "Increased Dimensional Stability in Ionically Conducting Polyphosphazenes Systems", D. F. Shriver and J. S. Tonge, J. Electrochem. Soc., 134, 269 (1987).
- 014 "Ionic Conductivity in Branched Polyethylenimine-Sodium Trifluoromethanesulfonate Complexes. Comparisons to Analogous Complexes made with Linear Polyethylenimine", C. S. Harris, M. A. Ratner and D. F. Shriver, Macromolecules, 20, 1778 (1987).
- 015 "Synthesis, NMR Characterization and Electrical Properties of Siloxane-Based Polymer Electrolytes", R. Spindler and D. F. Shriver, Macromolecules, 21, 648 (1988).
- 016 "Effect of Sidechain Length and Crosslinking on Ionic Conductivity", J. S. Tonge, P. L. Blonsky, D. F. Shriver, H. R. Allcock, P. A. Austin, T. X. Neenan and J. T. Sisko, submitted to Electrochem. Society.
- 017 "Ion Transport in Solvent-Free Polymers", D. F. Shriver and M. A. Ratner, Chem. Rev., 88, 109 (1988).
- 018 "Solvent Free Polymer Electrolytes", J. S. Tonge and D. F. Shriver, Polymers in Electronics, in press.
- 019 "Polymeric Electrolytes", P. M. Blonsky, S. Clancy, L. C. Hardy, C. S. Harris, R. Spindler, J. S. Tonge and D. F. Shriver, ChemTech, Vol. 17, No. 22, 758 (1987).
- 020 "A New Class of Cation Conductors: Polyphosphazene Sulfonates", S. Ganapathiappan and D. F. Shriver, Macromolecules, 21, 2299 (1988).

Names of Research Participants

Ryan Dupon
Sankar Bhattacharja
L. C. Hardy
P. M. Blonsky
S. Clancy
S. Ganapathiappan
Hans Conrad Zur Loye
Caroline Harris

D. H. Whitmore
D. F. Shriver
M. A. Ratner
M. Stainer
J. S. Tonge
Ann Crespi
Ralph Spindler