AD-A094 039 NORTHWESTERN UNIV EVANSTON IL F/G 11/9
TRANSFERENCE NUMBER MEASUREMENTS FOR THE POLYMER ELECTROLYTE PO--ETC(U)
JAN 81 R DUPON, D H WHITMORE, D F SHRIVER N00014-80-C-0532
UNCLASSIFIED NL

END
DATE FILMED
2-81
DTIC

LEVEL II

12

AD A094039

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
001		

4. TITLE (and Subtitle)
Transference Number Measurements for the Polymer Electrolyte Poly(ethylene oxide)·Na SCN

5. TYPE OF REPORT & PERIOD COVERED
Interim Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
R. Dupon, D.H. Whitmore, and D.F. Shriver

8. CONTRACT OR GRANT NUMBER(s)
N00014-80-C-0532

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Departments of Chemistry and Materials Science, and Materials Research Center, Northwestern Univ. Evanston, IL 60201

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 359-746

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Arlington, VA22217

12. REPORT DATE
January 1981

13. NUMBER OF PAGES
10

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
This document has been approved for public release and sale. Its distribution is unlimited.

DTIC
ELECTE
JAN 26 1981
E

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
Accepted for publication in J. Electrochemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Solid Electrolyte
Polymer Electrolyte
Poly(ethylene oxide)
Polymer-salt Complexes
Electrical Conductivity

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Emf measurements have been determined in a Na/Hg amalgam concentration cell containing the solid electrolyte poly(ethylene oxide)·NaSCN. These results in conjunction with measurements made with blocking electrodes of the frequency dependent conductivity, demonstrate that the main charge carrier is $Na^{(+)}$.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DDC FILE COPY

Transference Number Measurements for the Polymer Electrolyte Poly(ethylene oxide)·NaSCN

R. Dupon, D. H. Whitmore, and D. F. Shriver
Departments of Chemistry and Materials Sciences, and
Materials Research Center, Northwestern University
Evanston, Illinois 60201

Current interest in the development of high energy density batteries has focused considerable attention on solid electrolytes. The leading solid electrolytes in developmental batteries are hard ceramic materials, which usually are employed at elevated temperatures with liquid electrodes. A more compliant solid electrolyte, such as a polymer electrolyte, should enable contact to be maintained at the electrode-electrolyte interfaces in an all solid state battery and lower operating temperatures might be facilitated. Potential application of ion-containing polymers as battery electrolytes, and electrical measurements on salt complexes with poly(ethylene oxide) and with poly(propylene oxide) have been presented by Armand (1,2), and structural studies of poly(ethylene oxide) salt complexes have been reported from our laboratory (3). The original synthesis and characterization of these materials was reported by Wright (4,5) and extended by James (6).

A fundamental parameter in the characterization of any solid electrolytes is the fraction of the total current which is carried by the mobile ion, i.e. the transference number. Prior to the present work, a rigorous determination of the transference number for poly(ethylene oxide) based electrolytes was not available. The present study is based on the measurement of emf between ion reversible amalgam electrodes which are separated by the solid electrolyte in a concentration cell (7,8).

Key words: Solid electrolyte, polymer electrolyte, transference number, poly(ethylene oxide).

EXPERIMENTAL

Poly(ethylene oxide) with an average molecular weight 600,000 was obtained from Aldrich. The polymer was purified by ion-exchange of an aqueous solution and the solvent was subsequently removed under high vacuum. Reagent grade NaSCN (B & A) was recrystallized from methanol and dried under high vacuum. Reagent grade methanol (MCB) was dried by distillation from iodine-activated magnesium under a nitrogen atmosphere.

A PEO·NaSCN complex, 4.5:1 mole ratio of polymer repeat unit to salt, was prepared from stoichiometric quantities of the polymer and salt in anhydrous methanol. Following complete dissolution of the two solids, the methanol was removed under vacuum. All manipulations were carried out using standard inert atmosphere techniques (9). The identity of the PEO·NaSCN complex was confirmed by infrared spectroscopy and differential scanning calorimetry, and in previous research the material prepared by this same procedure has been characterized by optical microscopy and x-ray diffraction, which demonstrate the absence of free NaSCN.

Amalgams were prepared with triple distilled mercury and reagent grade sodium (MCB). Molten sodium was filtered through fritted glass to remove sodium oxide. The concentration of the stock amalgam, solution No. 1, Table I, was determined gravimetrically and checked by the gasometric method based on the amount of hydrogen evolved from the reaction of the sodium amalgam with hydrochloric acid. Concentrations of the remaining solutions were determined gravimetrically by successive dilution of the stock amalgam.

The sample and amalgams were placed in a cell which permitted exclusion of the atmosphere, Fig. 1. A pressed pellet of the PEO·NaSCN complex, 4.5:1, was fitted into an o-ring which was then clamped between the side arms. All loading of the polymer complex was carried out in a nitrogen

filled dry box. One side arm was filled with the stock amalgam solution while the other was successively filled with the dilutions of the stock. Introduction of amalgam solutions was done with a gas-tight syringe under a flush of dry nitrogen.

The potentials of the cell were measured using a Keithley 177 multimeter together with an electrometer containing an RCA CA3140 E MOS/FET operational amplifier designed to increase the input impedance of the measuring device to 10^{12} ohms. All measurements were made at room temperature, 23.5 ± 0.2 °C, which was monitored using an iron-constantan thermocouple and millivolt meter. The cell and connecting leads were placed in an aluminum box designed to shield the system from extraneous radiation. Reversing the cell polarity produced insignificant changes in the magnitude of the observed potentials. The emf was read after the potential had maintained a stable (± 0.3 mV) value over a period of one hour. Typical stabilizaton times were of the order of one to two hours. The measured results are given in Table I. As a check on these measurements, emf values were determined on a different batch of the polymer electrolyte using different amalgam preparations. Agreement between the data sets was good.

A value of the cell impedance was obtained by loading standard resistors in parallel with the cell and observing the change in emf. The observed room temperature cell impedance of 3.9×10^6 Ω was well within the capability of the measuring device and yielded a D.C. conductivity of 6.3×10^{-8} $(\Omega\ cm)^{-1}$, which is in general agreement with the A.C. value shown by Armand (2).

The emf of the concentration cell Hg-Na(x_1) | PEO·NaSCN | Hg-Na(x_2) is expressed by (8):

$$E_{obs} = (1 - t_e)E_{id} = (1 - t_e)\frac{RT}{nF}\ln\frac{a_1}{a_2} = (1 - t_e)\frac{RT}{nF}\ln\frac{\gamma_1 x_1}{\gamma_2 x_2}$$

The activity coefficients for dilute amalgams (present case) may be calculated from the relationship (10):

$$\text{Log } \gamma = Qx$$

where

$$Q = 18.720 - 8.00 \times 10^{-3}\ T$$

From this, E_{id} may be calculated:

$$E_{id} = \frac{RT}{F}2.303\ \log\frac{x_1}{x_2} + \frac{RT}{F}2.303\ Q(x_1 - x_2)$$

A plot of E_{obs} vs. E_{id} for each x_2 (x_1 being fixed as the stock amalgam, solution No. 1) yields a straight line (Fig. 2) of slope $(1-t_e)$.

DISCUSSION

For a purely ionic conductor the value of $(1 - t_e)$ should be unity. Least squares treatment of E_{obs} vs. E_{id} produced a line of slope 1.005 ± 0.005, Fig. 2. This result establishes that the electronic contribution to the total electrical conductivity of PEO·NaSCN is negligible and that the ionic component is responsible for the conduction. Since sodium-reversible electrodes were employed and since the conductivity is close to the published ac data, the sodium ion is implicated as the major charge carrier in the PEO·NaSCN complex.

Definition of variables:

E_{obs} = the measured emf

t_e = electronic transference number

E_{id} = ideal emf, value of E_{obs} when $t_e = 0$

R = universal gas constant

T = absolute temperature

n = number of electrons transferred

F = Faraday constant

a_1, a_2 = activities of sodium in the amalgams

γ_1, γ_2 = activity coefficients of sodium in the amalgams

x_1, x_2 = mole fractions of sodium in the amalgams

ACKNOWLEDGMENT

We wish to thank Mr. J. R. Anderson for discussions and help with the instrumentation. This research was supported in part by the Office of Naval Research.

REFERENCES

1. M. Armand, J. M. Chabagno, and M. J. Duclot, Abstract 6.5, Extended Abstracts, Second International Conference on Solid Electrolytes, St. Andrews, Scotland, Sept. 20-22, 1978.
2. M. Armand, J. M. Chabagno, and M. J. Duclot, in "Fast Ion Transport in Solids," P. Vashishta, J. N. Mundy, and G. K. Shenoy, Editors, p. 131, North-Holland, Amsterdam (1979).
3. B. L. Papke, M. A. Ratner, and D. F. Shriver, J. Phys. Chem. Solids, in press.
4. D. E. Fenton, J. M. Parker, and P. V. Wright, Polymer, 14, 589 (1973).
5. P. V. Wright, Br. Polym. J., 7, 319 (1975).
6. D. B. James, R. S. Stein, and W. J. Macknight, Bull. Am. Phys. Soc., 24, 479 (1979).
7. L. Hsueh and D. N. Bennion, This Journal, 118, 1128 (1971).
8. R. Galli, F. A. Tropeano, P. Bazzarin, and U. Mirarchi, in "Fast Ion Transport in Solids," W. van Gool, Editor, p. 573, North-Holland, Amsterdam (1973).
9. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York (1969).
10. T. Mussini, A. Maina, and A. Pagella, J. Chem. Thermodyn. 3, 281 (1971).

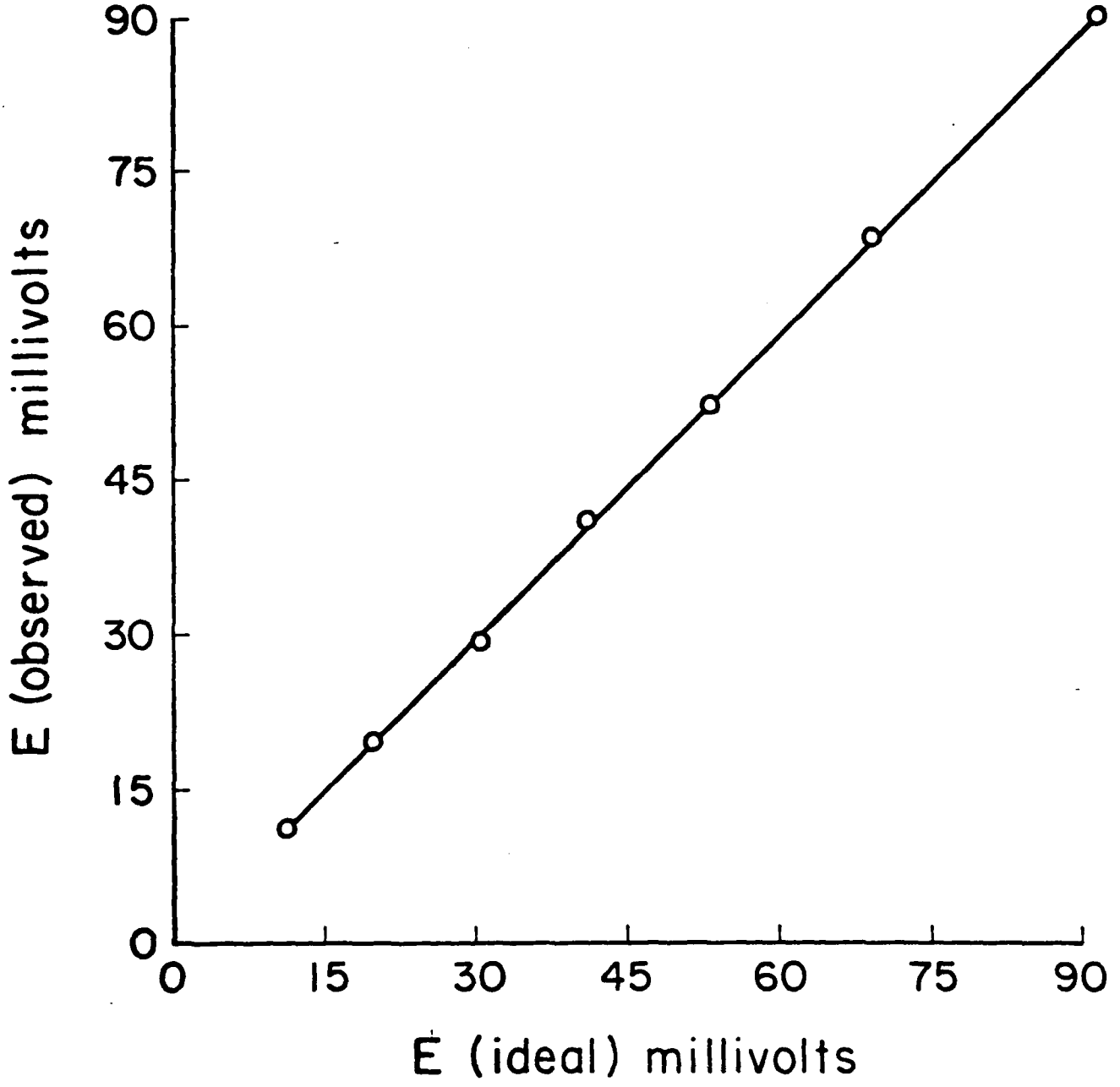
Table I. Ideal and observed emf's of concentration cell at room temperature.

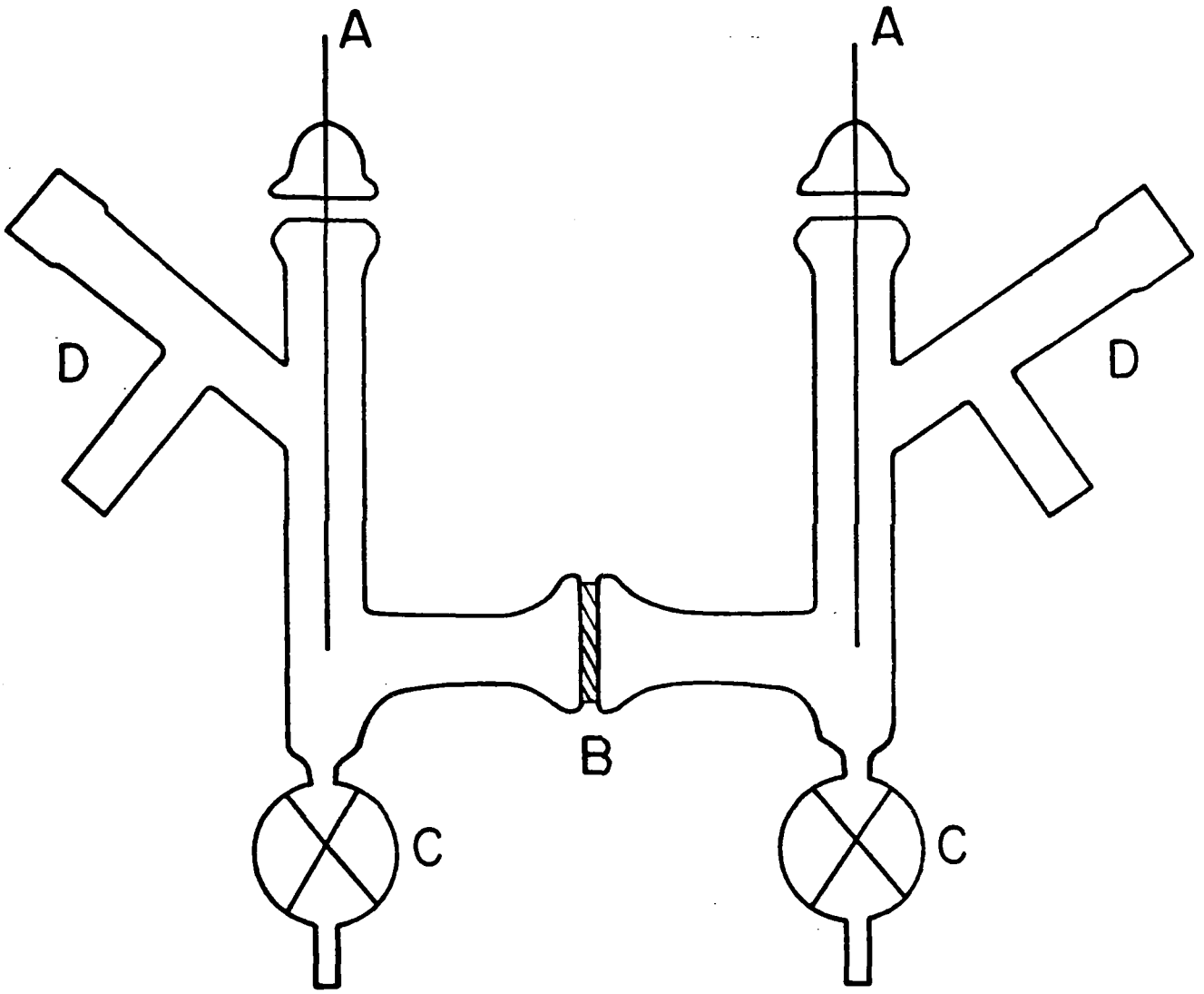
Solution No.	x_{Na}	E_{id} (mV)	E_{obs} (mV)
1	0.04103	-	-
2	0.03426	11.13	10.98
3	0.02944	19.64	19.47
4	0.02406	29.99	29.11
5	0.01928	40.25	40.89
6	0.01440	52.36	52.10
7	0.009477	67.84	68.34
8	0.004753	90.00	89.83

FIGURE LEGENDS

Figure 1. Cell for transference number measurements. A, nickel electrode; B, polymer electrolyte; C, stopcock; D, teflon in glass valves for N_2 inlet.

Figure 2. Observed vs. ideal emf values for a Na/Hg concentration cell with NaSCN·PEO polymer electrolyte.


90
75
60
45
30
15
0
E (observed) millivolts
0
15
30
45
60
75
90
E (ideal) millivolts


A
A
D
D
B
C
C

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	No. Copies
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1
Dr. P. J. Hendra Department of Chemistry University of Southhampton Southhampton SO9 5NH United Kingdom	1
Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	No. Copies
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	No. Copies
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1
Dr. Alan Bewick Department of Chemistry The University Southampton, S09 5NH England	1
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1
Dr. John Kincaid Department of the Navy Stategic Systems Project Office Room 901 Washington, DC 20376	1
M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1


DATE
ILME