6758-CH-02

3rd International Symposium on
Polymer Electrolytes

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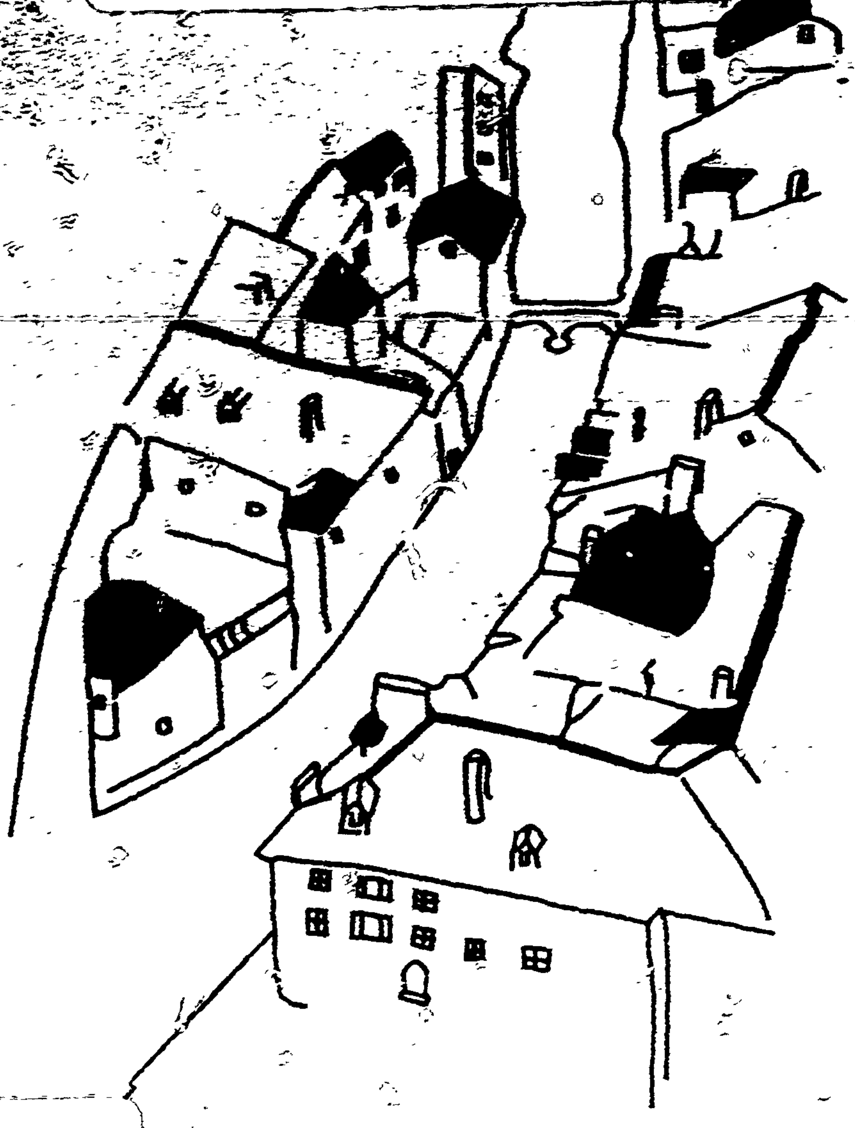

Annecy - France June 17 - 21, 1991

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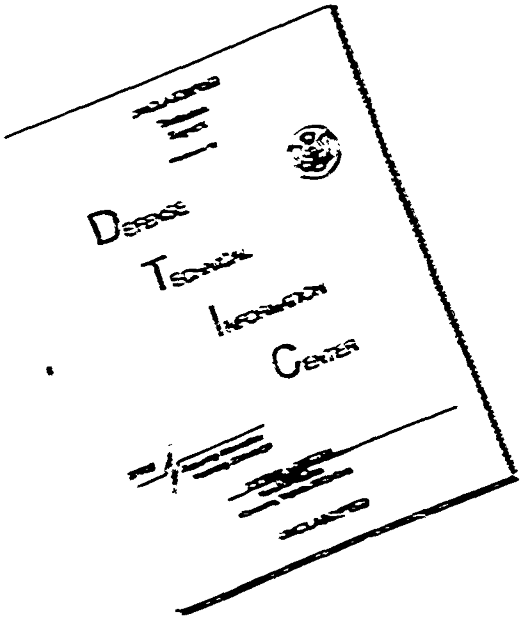

3rd International Symposium on Polymer Electrolytes
ISPE 3 (Annecy, june 17-21 1991)

EXTENDED ABSTRACTS

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Acknowledgments

The conference is been held under the auspices of :

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The organization committee is indebted for financial support from :

Alcatel-Alsthom Recherches, Bolloré Technologies, Bridgestone (Japan), Centre National d'Etudes des Télécommunications, C.N.R.S., Commissariat à l'Energie Atomique, Commission des Communautés Européennes, Compagnie de St.Gobain, Dai-ichi Kogyo Seiyaku (Japan), Direction des Recherches Etudes et Techniques, Electricité de France, ENICHEM (Italy), HITELLA, HydroQuebec (Canada), Imperial Chemical Industries (U.K.), I.N.P.G., Ministère de la Recherche et de la Technologie, Nippon Soda (Japan), SOLEA, U.J.F., U.S. Army -European Research Office (U.S.A.), Yuasa (Japan).

THIRD INTERNATIONAL SYMPOSIUM ON POLYMER ELECTROLYTES

ANNECY (France), June 17th to 21st, 1991

PROGRAMME

Sunday, June 16

16.00 - 19.00 Registration
19.00 Refreshments

Monday, June 17

8.00 - 9.00 Registration

9.00 Opening Ceremony
9.15 Opening Remarks

Session : PROCESSING

Chairpersons : A. GANDINI - J.-Y. SANCHEZ

9.30 G.P. BIERWAGEN
North Dakota State University
Department of Polymers and Coatings, Fargo, ND, USA
FILM COATING TECHNOLOGIES AND ADHESION → page: 1

10.00 I.M. WARD, J.E. MC INTYRE, S.A. DOBROWSKI, S.R. MIRREZAEI, H.V. HUBBARD.
IRC of Polymer Science and Technology, University of LEEDS, UK
IONIC CONDUCTION IN SEQUENTIALLY ORDERED THERMOTROPIC LIQUID-CRYSTALLINE POLYMERS → page: 2

10.15 Z. OGUMI, Y. UCHIMOTO, E. ENDO, Z. TAKEHARA
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, JAPAN.
VAPOR-PHASE PREPARATION OF SOLID POLYMER ELECTROLYTES FOR LITHIUM BATTERIES → page: 4

10.30 Coffee Break

Session : PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATION - THEORY

Chairpersons : **J.-C. LASSEGUES - J.-F. Le NEST**

Chairpersons : **R. ARMSTRONG, D. DEROO**

16.00 Tea Break

Chairpersons : **J.PRZYLUSKI, C.POINSIGNON**

16.30 **P. G. BRUCE, M. T. HARDGRAVE, C. A. VINCENT**
Polymer Electrolytes Group Scotland, Department of Chemistry
University of St. Andrews, Scotland.
DC POLARISATION OF POLYMER ELECTROLYTES → page: 25

16.45 **M. WATANABE, N. OGATA**
Department of Chemistry, Sophia University, Chiyoda-ku, Tokyo, Japan.
ION / ELECTRON MIXED CONDUCTORS BASED ON
POLYMER ELECTROLYTES → page: 28

17.00 **P. G. BRUCE, E. Mc GREGOR, C. A. VINCENT**
Polymer Electrolytes Group Scotland
Department of Chemistry, University of St. Andrews, Scotland
THE PERFECTLY POLARIZED POLYMER ELECTROLYTE /
ELECTRODE INTERFACE → page: 30

17.15 **R.J. LATHAM, R.G. LINFORD, R. PYNENBURG, W.S. SCHLINDWEIN**
Department of Chemistry, Leicester Polytechnic, Leicester, UK.
EXAFS STUDIES OF DIVALENT POLYMER ELECTROLYTES → page: 32

17.30 **S.G. GREENBAUM[1], S. PANERO[2], P. PROSPERI[2], B. SCROSATI[2]**
Weizmann Institute of Science, Hunter College of CUNY, Rehovot, Israel
Dipartimento di Chimica, Università di Roma 'La Sapienza', Roma, Italy
ELECTROCHEMICAL AND 7Li NMR STUDY OF POLY(ETHYLENE GLYCOL)-
BASED POLYMER ELECTROLYTES → page: 34

19.00 **COCKTAIL AND RECEPTION AT CITY HALL**

Tuesday, June 18

Session : NEW POLYMER ELECTROLYTES

Chairpersons : **G. FARRINGTON - Z. OGUMI**

9.00 **J.M.G. COWIE**
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, Scotland
NEW POLYMER ELECTROLYTES → page: 36

9.30 **P. GUEGAN[1], L. LESTEL[1], H. CHERADAME[2], S. BOILEAU[1]**
1 - Collège de France, Paris, France
2 - Laboratoire de Chimie Macromoléculaire et Papetière, St Martin d'Hères, France.
TRANSPORT PROPERTIES OF POLY(ETHYLENE OXYDE)-SILOXANE
NETWORKS CONTAINING LITHIUM PERCHLORATE → page: 37

9.45 **M. ANDREI[1], J.M.G. COWIE[2]**
1 - Eniricerche S. Donato Milanese, Italy - 2- Heriot-Watt University, Edinburgh, Scotland.
POLYMER ELECTROLYTES BASED ON POLY-PHOSPHAZENE WITH
PENDANT 12-CROWN-4 GROUPS AND MONOVALENT SALTS. → page: 39

10.00 L.A. DOMINEY
Covalent Associates Inc., Woburn, MA, USA.
THERMALLY STABLE Li SALTS FOR POLYMER ELECTROLYTES → page: 41

10.15 Z. FLORJANCZYK[1], E. ZYGADLO[1], K. SUCH[2], W. WIECZORECK[2]
1 - Institute of Polymer Technology, Warsaw University of Technology, Warszawa, Poland
2 - Institute of Inorganic Technology, Warsaw University of Technology, Warszawa, Poland
SYNTHESIS AND PHYSICAL-CHEMICAL CHARACTERIZATION OF NEW COPOLYMER ELECTROLYTES. → page: 43

10.30 Coffee Break

Chairpersons : C.A. VINCENT, W. GORECKI

11.00 L. MARCHESE[1], M. ANDREI[1], A. ROGGERO[1], S. PASSERINI[2], P. PROSPERI[3]
1 - Eniricerche S.P.A., S. Donato Milanese, Italy.
2 - Eniricerche S.P.A., Moterotondo, Italy.
3 - Dipartimento di Chimica, Universita "La Sapienza", Roma, Italy.
A NEW CLASS OF POLYMER ELECTROLYTES BASED ON CHAIN-EXTENDED POLYEPOXIDES AND LITHIUM SALTS → page: 45

11.15 K. SUCH[1], Z. FLORJANCZYK[2], J. PRZYLUSKI[1], W. WIECZOREK[1]
1 - Institute of Inorganic Technology, Warsaw University of Technology, Warszawa, Poland
2 - Institute of Polymer technology, Warsaw University of Technology, Warszawa, Poland.
APPLICATION OF ACRYLIC POLYMERS IN BLEND BASED POLYMERIC ELECTROLYTES → page: 47

11.30 X. PENG, H. BA, D. CHEN, F. WANG
Laboratory of Polymer Physics, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, China.
TWO-COMPONENT EPOXY NETWORK-LITHIUM PERCHLORATE POLYMER ELECTROLYTE. → page: 49

11.45 P. ARANDA, J.C. GALVAN, B. CASAL, E. RUIZ-HITZKY
Instituto de Ciencia de Materiales, C.S.I.C., Madrid, Spain
Centro Nacional de Investigaciones Metalürgicas, C.S.I.C., Madrid, Spain
ION-CONDUCTIVITY IN LAYER SILICATES CONTROLLED BY INTERCALATION OF POLYOXYETHYLENE COMPOUNDS → page: 51

12.00 Lunch

14.00 - 18.00 **Poster Session (see list below)**

Wednesday, June 19

Chamonix Tour

Thursday, June 20

Session : NEW POLYMER ELECTROLYTES (continued)

Chairpersons : **J. COWIE - P. ALDEBERT**

9.00 **A. VALLEE, S. BESNER, J. PRUD'HOMME**
Département de Chimie, Université de Montréal, PQ, Canada
COMPARATIVE STUDY OF POLY(ETHYLENE OXIDE) ELECTROLYTES MADE WITH $LiN(CF_3SO_2)_2$, $LiCF_3SO_3$ *AND* $LiCLO_4$. *THERMAL PROPERTIES AND CONDUCTIVITY BEHAVIOUR.* → page: 53

9.30 **F. HUANG, G. XIAO, X. WANG, S.LI**
Department of Polymer Materials, East China University of Chemical Technology, Shangai , China.
IONIC CONDUCTIVITY OF POLYETHER-POLYESTER NETWORKS → page: 55

9.45 **J.F. Le NEST, S. CALLENS, M. ARMAND, A. GANDINI**
Matériaux Polymères, EFPG, INPG, St Martin d'Hères, France.
A NEW POLYMER NETWORK FOR IONIC CONDUCTION → page: 57

10.00 **G. GOULART, J.-Y. SANCHEZ, M. ARMAND**
Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble
ENSEEG, INPG, St. Martin d'Hères , France.
SYNTHESIS AND ELECTROCHEMICAL CHARACTERIZATION OF NEW POLYMER ELECTROLYTES BASED ON DIOXOLANE HOMO AND CO-POLYMERS → page: 59

10.15 **M. POPALL , H. DURAND**
Fraunhofer Institut für Silicatforschung, Würzburg, FRG.
INORGANIC-ORGANIC COPOLYMERS (ORMOCERS) AS SOLID-STATE Li^+ *ELECTRLYTES* → page: 61

10.30 Coffee Break

Chairpersons : **H. OHNO - A. ROGGERO**

11.00 **S. ATCHIA, J.-P. PETIT, J. Y. SANCHEZ, M. ARMAND, D. DEROO**
Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble
ENSEEG, INPG, St. Martin d'Hères , France.
IONIC CONDUCTION IN $(PEO)_x K Cu_y I_{1+y}$ *COMPLEXES* → page: 63

11.15 **E.A. BEKTUROV, A.K. TOLENDINA, T.K. DZHUMADILOV, E.M. SHAIKHUTDINOV**
Institute of Chemical Science , Kazach Polytechnic Institute, Alma-Ata, USSR.
COMPLEXES OF POLY (ETHYLENE GLYCOL) WITH ALKALI-EARTH METAL SALTS → page: 65

11.30 **H. S. CHOE , G.C. FARRINGTON**
Department of Materials Science and Engineering
University of Pennsylvania, Philadelphia, PA,USA.
ELECTROCHEMICAL STUDIES OF POLY (ETHYLENE-GLYCOL) CONTAINING ZINC SALTS. → page: 66

12.00 Lunch

Chairpersons : **J. PRUD'HOMME - M. MASTRAGOSTINO**

14.30 **V. DE ZEA BERMUDEZ, M. ARMAND, C. POINSIGNON,**
L. ABELLO, J.-Y. SANCHEZ
Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble,
INPG, ENSEEG, St. Martin d'Hères, France.
PROTON-VACANCY CONDUCTING POLYMERS BASED ON
POLY(ETHYLENE OXIDE) ANS SULFAMIDE TYPE SALTS → page: 69

14.45 **V.A. SOLOMIN, E.N. LYAKH, V.V. LYAPUNOV, B.A. ZHUBANOV,**
S.V. DRUZ
Institute of Chemical Sciences, the Kazakh Academy of Sciences, Alma-Ata, USSR.
NEW POLYHETEROCYCLES WITH SULPHONIC ACID PENDANT GROUPS AS SOLID
POLYMER ELECTROLYTES → page: 71

15.00 **C. R. MARTIN , E.Z. CAI, N. LIANG, L.S. VAN DYKE**
Departement of chemistry, Colorado State University, Fort Collins, Co , USA
TEMPLATE SYNTHESIS - A METHOD FOR ENHANCING IONIC AND ELECTRONIC
CONDUCTIVITY IN ELECTRONICALLY CONDUCTIVE POLYMERS. → page: 73

15.15 **L. GAUTIER-LUNEAU, C. POINSIGNON, J.-Y. SANCHEZ**
Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble,
INPG, ENSEEG,St. Martin d'Hères , France.
ORGANIC - INORGANIC PROTONIC POLYMER ELECTROLYTES AS
MEMBRANE FOR LOW TEMPERATURE FUEL CELL. → page: 75

15.30 **D. SCHOOLMANN, O. TRINQUET, J-C. LASSEGUES**
Laboratoire de spectroscopie moléculaire et cristalline,
Université de Bordeaux 1, Talence, France.
PROPERTIES AND APPLICATION OF A PROTON CONDUCTING
POLYMER : THE BPEI, xH_3PO_4 *SYSTEM.* → page: 77

15.45 **J-L. PAUL, C. JEGAT, J-C. LASSEGUES**
Laboratoire de spectroscopie moléculaire et cristalline,
Université de Bordeaux 1, Talence , France.
BRANCHED POLY(ETHYLENIMINE)-CF_3SO_3Li *COMPLEXES* → page: 79

16.00 **R.M.V. SILVEIRA, B. MATVIENKO**
Laboratorio Interdisciplinar de Eletroquimica e Ceramica,
Universitade Federal de Sao Carlos, Brazil
ELECTRICAL PUMPING OF HYDROGEN GAS BY MEANS OF A
SOLID ELECTROLYTE MEMBRANE → page: 81

16.15 Tea

16.30 - 18.00 **Poster Session continued**

20.00 **Banquet**

Friday, June 21

Session :APPLICATIONS

Chairpersons : **M. WATANABE - M. DUCLOT**

9.00 **R. NEAT**
UKAEA, AERE Harwell, Applied Electrochemistry, OXON, UK
APPLICATIONS OF POLYMER ELECTROLYTES IN BATTERIES AND SUPERCAPACITORS → page: 83

9.30 **F. CAPUANO, E. CROCE, S. PANERO, B. SCROSATI**
Dipartimento di Chimica, Università di Roma "La Sapienza", Rome, Italy.
IS HIGH CONDUCTIVITY THE MOST CRUCIAL REQUIREMENT FOR A PRACTICAL POLYMER ELECTROLYTE? → page: 84

9.45 **P. BAUDRY, A. MARQUET**
Electricité de France / DER , Clamart, France
APPLICATIONS OF SOLID STATE ELECTROLYTE GENERATORS FOR ELECTRIC UTILITIES → page: 86

10.00 **C. ARBIZZANI[1], M. MASTRAGOSTINO[1], L. MENEGHELLO[1], T. HAMAIDE[2], A. GUYOT[2]**
1 - Dipartemento di chimica "G. Ciamician", Università di Bologna, Italy
2 - Laboratoire des Matériaux Organiques, CNRS, Vernaison, France.
POLY N-OXYALKYLPYRROLE ELECTRODES AND (PEO-SEO)20 LiClO4 POLYMER ELECTROLYTE IN LITHIUM RECHARGEABLE BATTERIES → page: 88

10.15 **X.Q. YANG[1], K.H. XUE[1], H.S. LEE[1], J. Mc BREEN[1], T.A. SKOTHEIM[2], F. LU[2]**
1 - Materials Science Division, Broohaven National Labotary, Upton, NY , U.S.A.
3 - CFFLS, University of Kentucky, Lexington, KY, U.S.A.
X-RAY ABSORPTION STUDIES OF ORGANIC DI-SULFIDE REDOX POLYMERIC CATHODES → page: 90

10.30 Coffee Break

Chairpersons : **B. SCROSATI - L.M. TORELL**

11.00 **K.H. XUE[1], T.A. SKOTHEIM[2], H.S. LEE[1], Y. OKAMOTO[3], J. Mc BREEN[1]**
1 - Materials Science Division, Brookhaven National Laboratory, Upton, NY, U.S.A.
2 - CFFLS, University of Kentucky, Lexington, KY, U.S.A.
3 - Department of Chemistry, Brooklyn Polytechnic University, Brooklyn, U.S.A.
ETHYLENE OXYDE DERIVATIZED POLYPYRROLE. APPLICATION AS COMPOSITE CATHODE MATERIAL IN POLYMER ELECTROLYTE BATTERIES → page: 92

11.15 **T. GUSTAFSSON[1], J.O. THOMAS[1], R. KOKSBANG[2], G.C. FARRINGTON[3]**
1 - Institute of Chemistry, Uppsala University, Sweden.
2 - Innocell Aps., Odense, Denmark.
3 - Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, USA.
THE POLYMER BATTERY AS AN ENVIRONMENT FOR IN SITU X-RAY DIFFRACTION STUDIES OF SOLID-STATE ELECTROCHEMICAL PROCESSES → page: 94

11.30 **H. OHNO, N. YAMAGUCHI, T. SUZUKI**
Department of Biotechnology,
Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan.
SOLID POLYMER ELECTROLYTES AS MATRIX FOR BIOELECTROCHEMISTRY → page: 95

11.45 **B. MARSAN, M. MALSERVISI**
Université du Québec à Montréal, Département de chimie, Montréal, Canada
IONIC CONDUCTIVITY STUDIES OF POLYMER ELECTROLYTES CONTAINING ORGANOSULFUR SPECIES → page: 97

12.00 Lunch

Chairpersons : L. ALCACER - J. THOMAS

14.30 **H. OHNO**
Department of Biotechnology,
Tokyo Universty of Agriculture and Technology
Koganei, Tokyo 184, Japan.
APPLICATIONS OF POLYMER ELECTROLYTES → page: 98

15.00 **C. GUSTAFSSON[1], O. INGANÄS[1], A. M. ANDERSSON[2]**
1 - Laboratory of Applied Physics, IFM, University of Linköping, Sweden.
2 - Physics Department, Chalmers University of Technology Göteborg, Sweden.
CONDUCTIVE POLYMERS AS ELECTRODE MATERIAL IN SOLID STATE ELECTROCHOMIC DEVICES → page: 100

15.15 **M.A.B. GOMES[1], D. GONÇALVES[1], E.C. PEREIRA DE SOUZA[1], B. VALLA[1], M. A. AEGERTER[2], L.O.S. BULHOES[1].**
1 - Laboratorio Interdisciplinar de Electroquimica e Ceramica
Dept. de Quimica - Universidade federal de Sao Carlos - Brasil.
2 - Instituto de Fisica e Quimica de Sao Carlos - Brasil.
SOLID STATE ELECTROCHROMIC DISPLAY BASED ON THE POLYMER ELECTRODE - POLYMER ELECTROLYTE INTERFACE → page:102

15.45 CLOSING REMARKS

POSTER SESSION

A - PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATION - THEORY

1 **W.H. MEYER, R.R. RIETZ, D. SCHAEFER**
Max Planck Institut für Polymerforschung
D-6500 Mainz/FRG
MOLECULAR DYNAMICS IN GLASSY POLYELECTROLYTES A NMR STUDY. → page: 105

2 **H. CAI, G.C. FARRINGTON & R. LINDFORD**
Department of Materials Science and Engineering
University of Pennsylvania, Philadelphia, PA, U.S.A.
STUCTURAL STUDIES OF PEO-BASED NIBR$_2$ ELECTROLYTES → page: 107

3 **B.V.R. CHOWDARI, R. HUQ, G.C. FARRINGTON**
Department of Materials Science and Engineering
University of Pennsylvania,Philadelphia, PA, U.S.A.
STUDIES OF THE MIXED-CATION EFFECT ON A PLASTICIZED POLYMER ELECTROLYTE → page: 109

4 **CHEN. L.Q., H. HONG, H. XUEJIE, X. RONGJIAN**
Institute of Physics, Academia Sinica, Beijing, China
STUDIES ON PAN-BASED LITHIUM SALT COMPLEX → page: 111

5 **G. WILLIAMS, P.E.M. ALLEN, D. MILLER**
Chemical Engineering Dept., University of Adelaide, Australia
EFFECT OF AGEING ON THE CONDUCTIVITY OF POLYMERIION ELECTROLYTES → page: 112

6 **D. BILLAUD[1], S. LEMONT[1], R. YAZAMI[2]**
1 - Labo C.M.A., Université Nancy 1,Vandoeuvre les Nancy, France
2 -Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble,
INPG. ENSEEG, St. Martin d'Hères, France.
ELECTROCHEMICAL LITHIUM AND SODIUM INTERCALATION IN POLYACETYLENE USING POLYETHYLENE OXIDE BASED SOLID STATE CELLS → page: 114

7 **R. SARTORI, L. MORAGA, E. LISSI**
Departamento de Quimica y Bioquimica
Universidad de Chile / Fac. de Medicina Norte, Santiago, Chile
BINDING OF POTASSIUM AND LITHIUM ALKYL XANTHATE TO POLY (ETHYLENE OXIDE) → page: 115

8 **P.N. GUPTA, R.P. SINGH, K.P. SINGH**
Physics Department , Banaras Hindu University, Varanasi, India
ELECTRICAL TRANSPORT IN H_3PO_4 DOPED PVA SYSTEM → page: 118

9 **R. HUQ[1], G.C. FARRINGTON[1], R. KOKSBANG[2], P.E. TONDER[2]**
1 - Department of Materials Science and Engineering,University of Pennsylvania
Philadelphia, PA, U.S.A.
2 - Innocell, Energy Research Laboratory, Odense, Denmark
EFFECT OF PLASTICIZERS ON THE PROPERTIES OF A NEW AMBIENT TEMPERATURE POLYMER ELECTROLYTE → page: 119

B - NEW POLYMER ELECTROLYTES - APPLICATIONS

FILM COATING TECHNOLOGIES AND ADHESION

Gordon.P. BIERWAGEN

North Dakota State University
Department of Polymers and Coatings, Fargo, ND, USA

IONIC CONDUCTION IN SEQUENTIALLY ORDERED THERMOTROPIC LIQUID-CRYSTALLINE POLYMERS

I.M. Ward, J.E. McIntyre, S.A. Dobrowski, S.R. Mirrezaei and H.V.StA. Hubbard

IRC in Polymer Science and Technology
University of Leeds
Leeds, LS2 9JT.

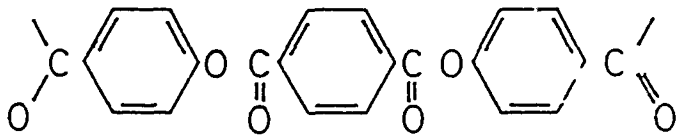
INTRODUCTION

The object of this research programme is to produce thermotropic liquid crystalline polymers, with robust mechanical properties, containing groups which complex with inorganic salts, and to measure the ionic conductivities of the salted polymers.

To this end we require (i) mesogenic (rigid rod) units sufficiently long to confer thermotropic behaviour, (ii) relatively flexible cation-complexing units in sufficient proportion to confer acceptible ionic conductivity. and (iii) physical properties such that the polymer can retain its shape and orientation at the proposed temperature of use.

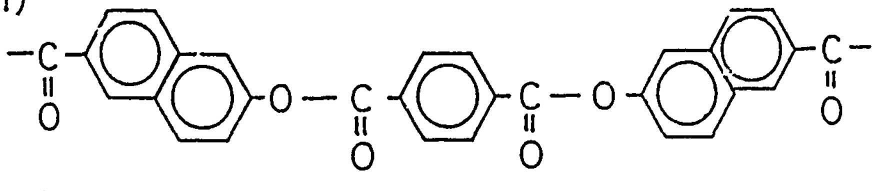
The mesogenic unit was one known to be long enough for mesophase formation in copolymers containing other flexible spacer units, and contained three sets of aromatic rings connected by ester units. Initially it was terephthaloyl bis-1,4-oxybenzoyl (called TCB)

(I)



but at a later stage terephthaloyl-bis-(2,6-oxynaphthoyl) was introduced (called TON).

(II)



In order to avoid randomisation reactions, the mesogenic units were synthesised as the acid chlorides, which were then reacted by a high temperature solution polycondensation with the polyoxyethylene oligomer diols.

POLYMER ELECTROLYTES

Accurately weighed amounts of dry block copolymer and lithium trifluoromethane sulphonate ("triflate") were dissolved in trifluoroacetic acid / chloroform (65/35) and the solutions were cast into 0.1 mm thick films on glass by using a doctor blade and evaporating the solvents first at ambient temperature and finally under reduced pressure at 50° C for at least 48 hrs. The complexes were characterized by thermal analysis, IR, NMR and hot stage polarising microscopy.

Codes

The polymers are coded, for example, TOB-P5EG. The code TOB represents the mesogenic unit (I), and TON mesogenic unit (II). The PEG units are then coded 3, 4, 5, 6 for monodisperse units with these values of DP, and $\overline{6.4}$, $\overline{8.7}$ and $\overline{13.2}$ for the polydisperse units with these mean values of DP. For the latter, the molecular weights of the EO units are respectively 300, 400 and 600.

Bulk ionic conductivities for the salted TOB-PEG polymers (EO:Li $\approx$ 10:1) have been measured. Conductivities are observed to increase with increasing length of the oligoether segment and with temperature. The inflection in each curve corresponds approximately to the main thermal transition observed in the DSC. Conductivities ranging from 10^{-7} S/cm at 20° C to above 10^{-4} at 200° C are obtained which are low in comparison, for example, with PEO with a conductivity of 10^{-4} S/cm at about 70° C.

Bulk ionic conductivities for salted TON-P5EG polymer (EO:Li $\approx$ 10:1) have also been determined. The value of 10^{-7} S/cm at 20° C is similar to that for TOB-P5EG but at 90° C the conductivity of 10^{-5} S/cm is an improvement on the TOB-PEG values.

CONCLUSIONS

Main chain liquid crystalline polymers based on polyester triad mesogenic units together with polyethylene glycol spacers have been successfully synthesized and their properties investigated. The materials are mechanically robust and flexible and exhibit a liquid crystal phase above about 100° C. The polymers are capable of complexing with a suitable lithium salt and reasonable ionic conductivities have been measured.

VAPOR-PHASE PREPARATION OF SOLID POLYMER ELECTROLYTES FOr LITHIUM BATTERIES

Zempachi OGUMI, Yoshiharu UCHIMOTO, Eishi ENDO
and Zen-ichiro TAKEHARA

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Solid polymer electrolytes prepared by the treatment of polyethers with alkali metal salts have received considerable attention owing to their wide application on electrochemistry. Since ionic conductivities of these solid polymer electrolytes are lower than those of typical liquid electrolytes, in order to use solid polymer electrolytes films for practical electrochemical devices it will be necessary to decrease their practical operating resistance. This can be achieved by preparing the polymer in the form of an ultra-thin film.

Plasma polymerization is known to be a useful method for the preparation of pinhole-free ultra-thin polymer films, and, in a series of papers [1,2], we have presented details of the preparation and application of solid polymer electrolytes prepared using this technique. In this report, ultra-thin, uniform, pinhole-free solid polymer electrolyte films of approximately 1 μm thickness were prepared by the complexation of plasma-polymerized dimethyl-2-[(2-ethoxyethoxy)ethoxy]vinylsilane [DEVS] and thermally vapor-deposited lithium iodide or lithium trifluoromethanesulfonate.

The apparatus used to carry out the plasma polymerization and thermal vapor-deposition consisted of a glass reactor equipped with capacitively coupled inner disk electrodes to which an alternating voltage was applied at a frequency of 13.56 MHz. The source temperature of lithium iodide or lithium trifluoromethanesulfonate were kept at 450-500 °C by means of a resistance heater. This reactor was incorporated into a vacuum system consisting of a mechanical booster pump, a rotary pump, and a cold trap. The thin solid polymer electrolyte films were deposited on substrates, which were placed in the after glow region, downstream from the electrodes. Various flow rate of argon gas and

DEVS vapor were introduced into the reactor. The DEVS was kept at 60 °C during the plasma polymerization to enhance its vapor pressure. The pressure was maintained at the desired level by controlling the main valve. Under these conditions, the RF power was turned on, and the plasma polymerization was carried out at various levels of RF power.

FT-IR spectrum of the plasma polymer is similar to that of the DEVS except for the complete absence of the characteristic peak for the olefin group, which appears at 1600 cm^{-1}. The results of the IR spectrum and ^1H NMR measurements indicate that the structure of the plasma polymer is very similar to poly(DEVS). These results indicate that plasma-induced polymerization, which proceeded by a chain propagation mechanism (conventional polymerization mechanism), is dominant. Under high polymerization pressure and low RF power conditions, highly viscous liquid rather than solid films formed on the substrates. In the range of low polymerization pressure (below 0.2 Torr) and high RF power (above 20 W), thin solid films form on the substrates and the surface of the plasma polymer film was planar. Since decreasing the polymerization pressure and increasing the RF power enhance electron temperature and increase electron density, these observations suggest that cross-linking proceeded at low polymerization pressure and high RF power as a result of the attack by highly energetic species in the glow discharge plasma.

SEM observation of the solid polymer electrolyte films indicates that the films are free from pin-holes, and, on the scale of SEM observation, of uniform thickness. Prior to making AC measurements, gold was deposited on both surfaces of the solid polymer electrolyte. The fact that no short circuiting was observed between these sandwiched gold layers shows that the solid polymer electrolyte was free from pinholes. The ionic conductivity of the solid polymer electrolyte was measured by the complex impedance method using gold electrodes. The ionic conductivity of the solid polymer electrolyte was dependent on plasma parameters. Room temperature conductivities greater than 10^{-6} S cm^{-1} (10^2 Ωcm^2 resistance per unit area) were observed.

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PROBING ELECTROLYTE SOLID POLYMERS BY NMR SPECTROSCOPY

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Nuclear magnetic resonance is a powerful tool for studying electrolyte solid polymers. This technique allows two kinds of informations.

- Static informations as of the degree of crystallinity in semicrystalline polymers (1, 2, 3) giving access to the phase diagram.

- Dynamics informations as the lack of any cation and anionic mobility in the crystalline phase (1), the value of the cationic transport number t^+ (3, 4) and the relation between the macroscopic conductivity and the segmental chains motions (6).

The determination of the phase diagram in semicrystalline complexes $[P(EO)(M^+X^-)]_x$ is well described in ref. 1. For this purpose it is necessary to know, for several temperatures, the fractions of protons, ${}^1C$, and of cationic or anionic nuclei, ${}^{\alpha}C$, belonging to the crystalline phase. This is obtained by analysing the shape of the free induction decay signal of the different nuclei, since the signal arising from nuclei in the elastomeric phase decreases much more slowly than that due to nuclei in the crystalline phase. We have deduced the stoechiometry of the crystalline phase from the expression $x_c = x\,{}^{\alpha}C/{}^1C$ (2) where x is the number of cations per monomer unit.

Ten years ago we ignored whether the conductivity is controlled by the crystalline phase or not. We have shown that the ionic conductivity is mainly ensured by the elastomeric phase. In the crystalline phase of the $P(EO)(LiCF_3SO_3)_{0.125}$ (2) complex, no motionnal narrowing of the ^7Li and ^{19}F resonance lines was observed, indicating that neither the cation nor the anion are mobile in this system.

For electrochemists, the knowledge of the cationic transport number is of fundamental importance. The pulsed magnetic field gradient (PMFG) technique allows the determination of the cationic and anionic diffusion coefficient (D^+, D^-) (3, 4). The corresponding transport numbers t^+ and t^- are given by $t^{\pm} = D^+/D^+ + D^-$. This method is compared with more classical techniques (Tubband and potentionmetric methods).

Finally, the correlation between the conductivity and the segmental chains motions is underlined (5). Here we show in P(EO) $(LiClO_4)_{0.125}$ the thermal and frequency dependences of the ^1H and ^7Li spin-lattice relaxation times are similar. The correlation times τ deduced from the maximum of the curves T_1^{-1} vs T^{-1} of both kinds of nuclei (^1H and ^7Li) have been related to the conductivity data. This has proved that the ionic conductivity is governed by the dynamics of the chains.

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NMR Spectroscopy of PEO-based Polymer Electrolytes

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Polymer-based solid electrolytes are more often than not multi-phase systems, including crystalline as well as amorphous components. A proper understanding of the conduction mechanism on a molecular level requires the component phases to be identified and characterized both in terms of structure and dynamics. NMR-spectra are sensitive to the polymer-chain mobility expected in these systems and this mobility is generally quite different in the amorphous and crystalline regions of a polymer material. We have, therefore, measured proton NMR spectra of $Zn(CF_3SO_3)_2.PEO_n$ films as a function temperature and for comparison also proton spectra of a pure PEO film. Examples of such spectra for n=16 are shown in Fig. 1.

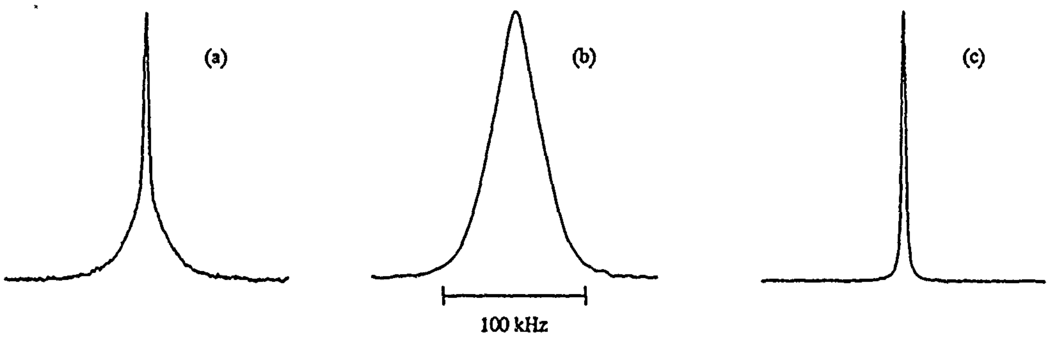

Fig. 1. *Room-temperature proton NMR spectra of (a) a pure PEO film and (b) and (c) of a* $Zn(CF_3SO_3)_2.(PEO)_{16}$ *film. The spectrum in (c) is from a sample that has first been heated to its melting point and has then been cooled to room temperature again, before recording the spectrum.*

The spectrum of the pure polymer film is a superposition of a narrow component and a considerably broader component. The only reasonable sources of the narrow component are regions of high chain mobility, *i.e.* most probably amorphous PEO. In crystalline polymer phases the chain mobility is considerably more limited and, therefore, the spectrum is much broader in such phases. The sample doped with $Zn(CF_3SO_3)_2$ shows a broad spectrum, without the narrow component observed in pure PEO. It is known from X-ray diffraction and from observations in a polarizing microscope that the sample is predominantly amorphous for this composition. Still, the spectrum is very broad and this must be a result of the chain mobility in the system being much slower than in the pure, amorphous PEO. This is not unreasonable, considering the possibility of chain cross-linking by the ions in the system. Heating the sample narrows the spectrum considerably because of the increasing chain mobility. It is interesting to note that the spectrum remains narrow (Fig. 1 (c)) after returning to room temperature. However, keeping the sample overnight at room temperature restores a broad spectrum very closely similar to the one shown in (b).

We have also measured various types of spin-lattice relaxation times for the protons in these systems. One example is shown in Fig. 2, where the temperature dependence of the spin-lattice relaxation rate in the rotating frame, $1/T_{1\rho}$, is shown. This particular relaxation time reflects the rate of relatively slow motions; the maximum at about 320K would correspond to a correlation time of about 10^{-5} s for the motion causing the relaxation. This is consistent with the fact that the spectrum narrows considerably just above room temperature. The abrupt change in slope seen at about 285K is indicative of the presence of at least two major dynamical processes providing a relaxation mechanism for the protons. Two possibilities are chain mobility and mobility of the $CF_3SO_3^-$ ion.

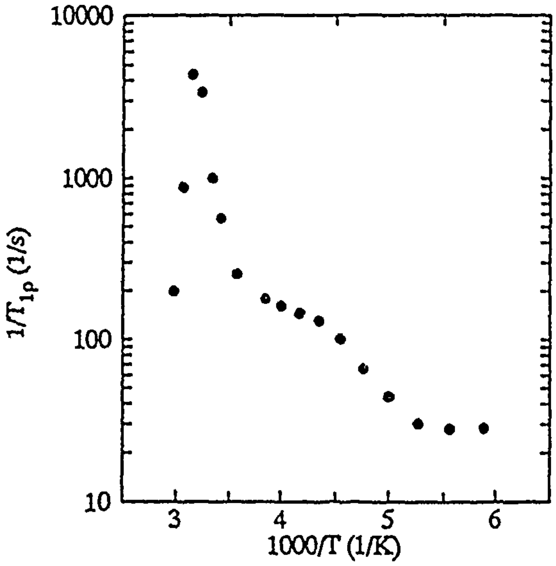

Fig. 2. *The rotating-frame spin-lattice relaxation rate of the protons in a* $Zn(CF_3SO_3)_2$*-*$(PEO)_{16}$ *film.*

Acknowledgements : this work is supported in part by a DARPA grant through a contract monitored by the United States Office of Naval Research, and in part by the Swedish Natural Science Research Council.

"Dielectric and Electric Relaxation in IONENE - Glasses"

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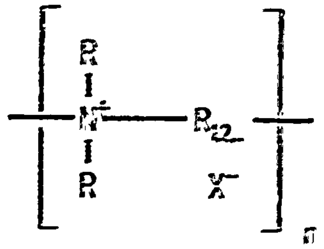
IONENES 1 are polyelectrolytes with N-cations as part of their polymer chain repeat and with low molecular weight anions to balance the coulombic charges 1).

1



$$\left[-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{N^{+}}}}} - R_{12} - \atop X^{-} \right]_n$$

While IONENES with short organic segments and thus high charge density exhibit a high tendency to crystallize 2), their counterparts with large organic components and low charge density form amorphous solids 3). The chemical structure of the polycation chains can be choosen such, that high quality glasses can be obtained. With the introduction of appropriate counterions, high refractive index glasses or materials with NLO - properties can be obtained 4).

The solid state properties of IONENE-glasses have been investigated recently in detail by thermoanalytical, solid state NMR and dielectric techniques. As evidenced by DSC experiments, the glass transition in such glasses can be varied within a wide temperature range, depending on the primary structure of the material; e.g. rigid chain elements give rise for high T_g materials, whereas flexible chain elements make the polyelectrolytes soften already at low temperatures. Both, size and shape of the counterions also influence the softening behaviour of the material: small spherical anions usually give rise for relativly low T_gs as compared to large extended conterions such as dye anions, which lead to high glass transition temperatures. Counterion mixtures in combination with the same polycations show a linear increase of the glass transition temperature with the molar concentration of the large sized anions.

Surprisingly, the specific heat increase at T_g is almost independent from both, structure of the polycations and type of the counterions. Generally the Δc_p values are considerably smaller as compared to well-known thermoplastic polymers. This can be understood if one considers only a minor part of the polyelectrolyte molecules to be involved in the glass transition process.

The molecular dynamics of the IONENES in the glassy state and at the glass transition have been probed by ^{2}H- and ^{19}F- solid state NMR employing solid echo as well as 2 D techniques 5). In the glassy state both, the counterions as well as the chain segments interlinking the N-cations are mobile. The mobility of the individual carbon positions increase at a given temperature with the distance from the N-cations. The cationic centers themselves are frozen into a quasi-lattice in the glassy state and become mobile at the glass transition. Thus, together with the thermoanalytical results it is evident, that the glass transition in this type of polyelectrolytes can be described as the "melting" of a "superlattice" formed by the cationic centers, while the organic components of the molecules are mobile already in the glassy state.

This explains the experimental results obtained with dielectric spectroscopy in the temperature range from 100 to 500 K and in the frequency range from 0.01 to 10000 kHz : At low temperatures, the ionic conductivity is almost independent from temperature, but strongly dependent from frequency. At a critical temperature, the dielectric behaviour changes dramatically with the conductivity becoming strongly thermally activated and more and more independent from frequency with increasing temperature. The critical temperature usually is far below the glass transition and can not be correlated with it. The critical temprature, however, depends on the size and shape of the mobile counterions: in IONENES with small anions T_{crit} is much lower as compared to the same polycations combined with large sized anions. In IONENES with counterion mixtures, T_{crit} increases linearly with the molar concentration of the large sized anions.

The ionic conductivity in IONENES thus can be described as thermally activated hopping of anions in the matrix formed by the rigid cation-"superlattice" and the "melt" of organic segments interlinking the cationic centers. The onset and level of the thermally activated ion transport at T_{crit} depends on the size and shape of the anions to be moved, with increasing size of the counterions the level of the conductivity decreasing and T_{crit} increasing.

This mechanism can be described with a microscopic model proposed by Funke ⁶), who modified the Debye-Hückel-Onsager-Falkenhagen theory of conduction in electrolytes for solid ionic conductors.

Both, experimental results and conductivity model of Funke describe the ionic charge transport in IONENE glasses as being clearly different as compared to the conductivity mechanisms discussed for polymer salt complexes.

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A RAMAN STUDY OF ION-POLYMER AND ION-ION INTERACTIONS IN LOW MOLECULAR WEIGHT POLYETHER - $LiCF_3SO_3$ COMPLEXES

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Phase separation and resulting salting out effects are severe and much debated problems for applications of polymer electrolytes. We have previously demonstrated from Raman observations of poly (propylene glycol) (PPG) salt complexes that the interaction between solvated cations and the oxygens of the polymer chain weakens with increasing temperature in favour of the formation of ion pairs or higher degrees of multiplets. The effect was found to be more pronounced as the molecular weight of the host polymer increased from 7 to 70 repeat units [1]. The phenomenum may be explained in terms of end effects, the PPG macro-molecules are terminated with hydroxyl groups with which the anions can hydrogen bond. Since the number of "OH" groups decreases as the molecular weight increases, then, for a fix O:M ratio (number of monomer per units salt), more anions are freed and become available for ion pairing.

On the other hand it may be argued that the difference in temperature behaviour of the solvation ability of macromolecules of different molecular weight is a free volume dissimilarity effect [2]. This may be phrased in the popular term "like dissolves like". Therefore the larger the difference in size between the macromolecule and the dissolved ions the more readily we expect phase separation to occur as we raise the temperature. It is then interesting to notice that for the extreme case of low molecular weight solvents recent molecular dynamics simulation studies [3] in fact show the opposite behaviour; i.e. the amount of dissolved ions increases and the pair formations break up as temperature increases. If this is also the case for low molecular weight polyethers then we expect the observed weakened temperature dependence for pair formation as molecular weight decreases to ultimately result in a crossover. This may then occur for chain lengths somewhere in the range 1-7 repeat units.

To determine the relative importance of end effects and effects of free volume dissimilarities for the solubility and thereby for the number of charge carriers available for conduction we have investigated salt polymer complexes in which the chain length is varied from 1 to 4 units. Complexes of $LiCF_3SO_3$-polyethers of a O:M concentration of 16:1 were investigated over the broad temperature range of ~200-350 K. (Ethylene oxide)$_n$ was chosen because there is commercially available a range of high quality low molecular weight EO-chains terminated by methyl-groups. Using such endcapped chains the problems of anions coordinated to the ends (as observed in PEO) are circumvented and only cation solvation (through the ether oxygens along the chains) has to be regarded.

The Raman spectrometer uses a double monochromator (SPEX model 1403). Fast recording times (typically 1 s for a spectrum) were possible through the use of CCD-detection. The slits were set to give a resolution better than 2 cm^{-1}. The experimental set up is described elsewhere [1].

To study the ion-ion interaction we chose to investigate the ν_1 symmetric stretching mode of SO^-_3 of the $CF_3SO^-_3$ anion. Fig. 1 show the Raman band profile for the $LiCF_3SO_3$/monomer complex at 300 K. The band comprises a complex of modes representing "free" ions, ion pairs and multiplets. The assignments are based on the following arguments. The low frequency component, which is best fitted with a Lorentzian at 1033,5 cm^{-1}, is attributed to the "free" ions. Schantz studied a dilute (0.1 M) acqeous solution of $NaCF_3SO_3$ in which the ν_1 mode was detected as a one component band at 1033 cm^{-1} [4]. With such a dilute salt concentration in such a high permittivity solvent almost all the ions should be "free" and the single component was thus assigned accordingly. This component is therefore not to be influenced by the change of cation in agreement with the present observation of the low frequency component in Fig. 1. The component at 1043 cm^{-1} is shifted to higher frequencies by 9 cm^{-1} compared to the 5 cm^{-1} shift for the corresponding component in $NaCF_3SO_3$ in PEO [4]. Thus, this component is influenced by the change in cation from Na^+ to Li^+ and is assigned to ion pairs. Contact ion pairs are more probable than solvent separated pairs based on the large frequency shift and the sensitivity to the cation, as discussed by Pereygin and Mikkailow [5]. Finally, the broad component observed at 1053 cm^{-1} we assign to triplets and higher degrees of multiplets.

In Fig. 1 the variation in the relative intensities of the components with temperature is demonstrated. Similar observations were observed independent of the number of repeat units n in the macromolecule in the range n = 1 , 2, 3 and 4. From a three component band profile analysis the corresponding intensities were calculated. Results of the concentration of free ions in the $LiCF_3SO_3$/monomer complex is presented versus temperature in Fig. 2. At low temperatures most of the ions are "free". However a dramatic decrease of the amount of solvated ions are observed as temperature increases. At room temperature most of the ions are associated and only ~15 % are "free". No significant molecular weight dependence was observed for the temperature behaviour.

Several significant observations can be made. The amount of free ions in the present endcapped poly (ethylene oxide) systems is considerable reduced compared to OH-terminated PEO complexes, ~15 % at room temperature compared to 74 % for a $NaCF_3SO_3$-PEO (400) complex of similar salt concentration. Since Li^+ are more easily solvated by the ether oxygen than the lower charge density Na^+ the small amount of free ions in the present $LiCF_3SO_3$ complex can only be explained by the endcapping which reduces anion solvation.

In contrast to predictions from computer simulations of the molecular dynamics of low molecular weight solutions [3] the ion-ion associations increases with temperature for all complexes. No crossover in the temperature behaviour of ion-ion association is observed as the molecular weight is reduced. Thus even in the case of low molecular weight polyethers a lower critical solution temperature is expected for the salt-polyether complex above which salt precipitation may occur.

No significant molecular weight dependence of ion association in the low molecular weight range was observed. Thus the larger difference in the temperature dependence of free ions previously observed for $NaCF_3SO_3$-PEO complexes are due to the solvation of anions by the OH terminated ends of the polymer chains. In the endcapped systems of the present study anion polymer coordinations can be neglected. We note a dramatic temperature dependence similar to the temperature dependence of the cation-polymer interaction of $NaCF_3SO_3$-PPO (4000). This is in contrast to the anion-polymer interaction, i.e. the dominant ion interaction in $NaCF_2SO_3$-PPO (400), which is little affected by temperature. We therefore conclude that the dramatic temperature effect of ion-ion association is governed by the weakening of the cation-ether oxygen interaction as temperature increases rather then by end effects. Thus such dramatic effects are also expected for the high molecular weight complexes used in practical applications of commercial interest.

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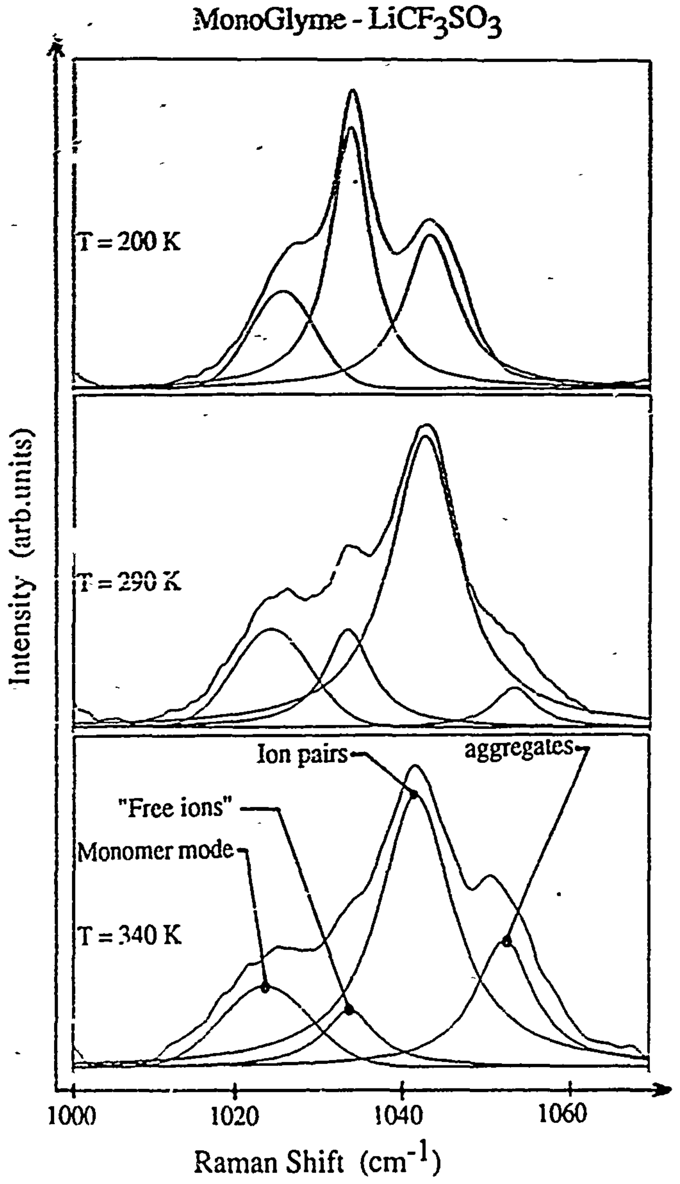
MonoGlyme - LiCF$_3$SO$_3$
T = 200 K
T = 290 K
T = 340 K
Ion pairs
aggregates
"Free ions"
Monomer mode
Intensity (arb.units)
1000
1020
1040
1060
Raman Shift (cm^{-1})

Fig 1

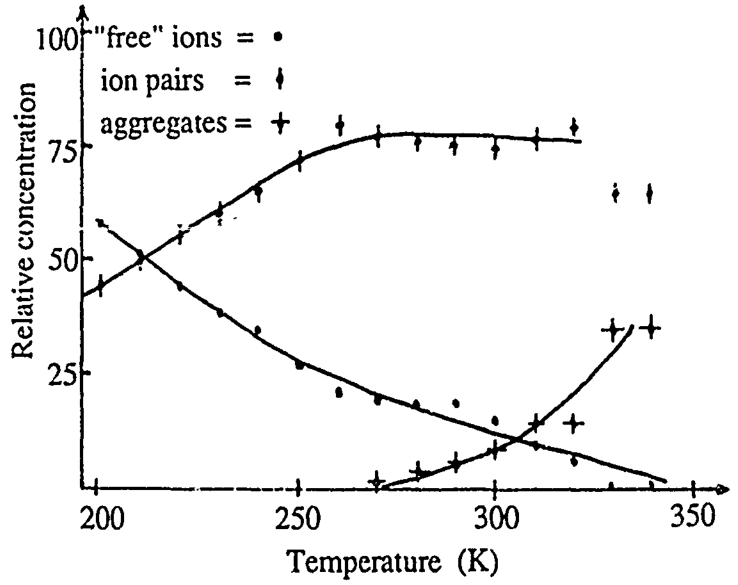
"free" ions = •
ion pairs = ⧫
aggregates = +
100
75
50
25
Relative concentration
200
250
300
350
Temperature (K)

Fig 2

Structure and Static Interactions of Polymer-Salt Complexes

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University of Oklahoma

Complexes of poly(propylene oxide) (PPO) with salts of low lattice energy exhibit high ionic conductivity and have been the subject of widespread scientific interest. In this paper we focus our attention on the nature of the cation-anion interactions in these complexes. We will discuss the results of our Raman and infrared spectroscopic studies of lithium, sodium, and potassium salts of thiocyanate, perchlorate, fluoroborate, and trifluoromethanesulfonate ("triflate") complexes. Although the degree and nature of complexation differ for each anion, two generalizations are possible: (1) a significant degree of ion pairing has been seen in all PPO-salt complexes studied here, and (2) as expected, the ionic association effects are strongest for lithium-containing salt complexes as compared to the corresponding sodium or potassium complexes.

The lithium, sodium and potassium thiocyanate complexes exhibit significant ion pairing at all metal salt concentrations with a strong cation dependence observed in the ν_1 stretching mode. Frequency shift data of the ν_1 and ν_3 stretching modes can be correlated with cation coordination of the nitrogen end of the thiocyanate anion.

Complexes with perchlorate salts exhibit anions in two distinctly different environments as "free" anions and cation-anion pairs. Concentration dependence of the band intensities establishes that the free ions are the predominant species. The absence of unambiguous splittings of the degenerate ν_3 and ν_4 modes even at the highest salt concentrations suggests that the ion pairing is weak.

Only lithium fluoroborate complexes with PPO were examined, due to the limited solubility of the sodium and potassium salts. A high frequency asymmetry in the ν_1 stretching spectral region was attributed to the formation of ion pairs. The degenerate ν_2 and ν_4 internal deformation vibrations of the fluoroborate anion are observed as very broad bands, however the lack of discrete structure in the band envelope precludes any further knowledge of the structure of ion-paired species.

The complexes of alkali metal triflate salts with PPO offer the richest system in which to study ionic association. The Raman spectral data for sodium triflate complexes have been reported by Torell et al [1,2]. In our study we also consider the lithium and potassium triflate complexes and include infrared transmission spectra. The spectral data indicate three different environments for the anion in each complex; we interpret these as two different modes of ion-pairing and a triple ion. One mode of ion pairing occurs at low concentrations in which the cation weakly interacts with the CF_3 end of the triflate ion. A second mode of ion pairing occurs through a strong interaction of the cation with the SO_3 end of the anion. Suggested structures for these associated ion pairs as well as the triple ion will be described. Analysis of temperature-dependent Raman spectral data yields values of the equilibrium constant, enthalpy, Gibb's free energy, and entropy for the process of ionic association.

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Simulation and Modelling of Polymer Electrolytes

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Introduction

It is well known that polymers such as poly(ethylene oxide) (PEO) can solvate a wide variety of inorganic salts to form a special class of ionically conductive materials [1,2]. However, the solvation process and ion conduction mechanisms in these electrolytes are poorly understood at this time. In this work, molecular mechanics and molecular dynamics simulations have been carried out for several PEO/metal salt systems. The results have yielded insight into the ion-ion and ion-polymer interactions in PEO electrolytes. This work demonstrates that molecular simulation can provide important insights into the mechanisms of ion conduction in polymer electrolytes.

Computational Procedure

Molecular simulations are empirical force-field calculations which assume that the total energy of a molecule depends upon its bond lengths and angles as well as non-bonded interactions and tortion angle terms. A comprehensive review of molecular simulation has been given by Brook et al. [3] In this study, POLYGRAF, a molecular simulation package [4] for molecular mechanics and molecular dynamics, was used. Force constants and some geometric constants were selected from the literature [5-6]. The dihedral angle force constants were taken from the Dreiding force field [7], and the parameters of non-bonded interactions (Van der Waals forces) are also from the Dreiding force field except for magnesium and lithium ions. The charge distribution of PEO was calculated using the method of Rappe and Goddard [8].

Results and Discussion

Solvating Ability of Simple Polyethers

In order to accommodate ions in a polymer structure, the spacing between sequential coordinating sites and steric effects are clearly important. It has been found that the solvating ability of simple polyethers is closely related to its -C-O- sequence, the distance between sequential oxygens, as shown in Table 1. PEO, with a monomer unit of -CH_2-CH_2-O-, appears to have the optimum -C-O- sequence. In contrast, poly(methylene oxide) (PMO) and poly(trimethylene oxide) (PTMO) have much lower abilities to dissolve salts and do not readily form polymer electrolytes. Poly(propylene oxide) (PPO), despite the same spacing between ether oxygens as in PEO, also has a much lower solvating power than PEO.

Table 1 Monomer unit and some physical properties of polyethers

Polyether	Monomer unit	Ability to form polymer electrolytes
PMO	-(-CH_2-O-)-	Poor
PEO	-(-CH_2-CH_2-O-)-	Excellent
PTMO	-(-CH_2-CH_2-CH_2-O-)-	Poor
PPO	-(-CH_2-CH(CH_3)-O-)-	Limited

The remarkable differences in solvating power among these polyethers can partially be explained by geometric factors, but it is interesting also to consider the influence of charge distribution along the chains. Our calculations have found a significant difference between the partial charge distribution in pure PMO and PEO. For pure PEO, the calculated partial charges are -0.49 for oxygen, 0.10 for carbon, and 0.07 for hydrogen. The partial charge of the oxygen in PMO is about -0.44, slightly lower than that in PEO. However, the partial charges of the carbon (~0.20) and the hydrogen (~0.12) in PMO are significantly higher than those in PEO. These results suggest that the poor solvating ability of PMO is in part the result of high partial charges in neighboring carbon and hydrogen atoms which effectively reduce the solvating power of the ether oxygens in PMO.

Ion/Ion and Ion/Polymer Interactions

Molecular mechanics and molecular dynamics simulations were performed for a range of PEO/metal salt systems, such as PEO/LiBr, PEO/$MgBr_2$, and PEO/$ZnBr_2$. The results provide considerable information about likely ion/chain and ion/ion complexes formed in these systems.

Acknowledgements
This work was supported by a grant from the Defense Advanced Research Projects Agency through a contract monitored by the Office of Naval Research. Additional support from the NSF-MRL program under grant no. DMR88-19885 is gratefully acknowledged.

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Temperature and pressure effects on ionic association and ion-hesinteractions: a lattice gas model

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The effect of ion-ion and ion -matrix interactions on ionic transport in polymer ionic conductors has been the focus of many studies in the past few years. Ion Matrix interactions play the dominant role both in determining the salt solubility and the density of free ions, and in determining the ionic mobility.

Recent experimental results[1-3] have shown that ion - ion interactions in general and ionic association in particular are strongly affected by the polymer matrix environment. These results show what appear to be unique effects of the polymer environment on ionic association: Ion pair formation in salt PPO systems increase with temperature above the glass transition[3], and salt precipitation at higher temperature is also observed.[1,2] These. observations stand in contrast to previous intuitive expectations that salt in polymer hosts behave as weak electrolytes with ionic dissociation increasing with temperature.

It should be pointed out that decreasing salt solubility and increasing ionic association at increasing temperature are observed also in simpler solvents, including water; $ZnSO_4$/water at room temperature being a notable example. Ionic dissociation is affected by ion-ion, ion-solvent and solvent-solvent interactions and the free energy balance which determine the dissociation-association equilibrium is controlled by both energetic and entropic effects. In a polymer host matrix we expect two general factors to be most important. These are (a). the free volume change which accompanies the ionic solvation and (b). the higher restrictions on polymer chain movements caused by transient crosslinks via the ions. These phenomena are well known to affect the host glass transition temperature as well as the ion mobility, and are expected to affect also the ion solvation thermodynamics. The lattice gas model described below focus on the role of these factors in the ionic dissociation and solvation process.

Denote the reaction coordinate of the dissociation reaction $AM \longrightarrow A^- + M^+$ by ξ (so that if n is the total number of salt molecules, ξn are dissociated). At equilibrium $\xi=\xi_{eq}$, and the equilibrium constant is $K=\xi_{eq}^2 n/(1-\xi_{eq})$. From thermodynamics we have *at equilibrium*

$$\left[\frac{\partial\xi}{\partial T}\right]_P = \frac{1}{G''}\left[\frac{\partial S}{\partial\xi}\right]_{P,T} = \frac{1}{TG''}\left[\frac{\partial H}{\partial\xi}\right]_{P,T}$$

$$\left[\frac{\partial\xi}{\partial T}\right]_V = \frac{1}{A''}\left[\frac{\partial S}{\partial\xi}\right]_{V,T} = \frac{1}{TA''}\left[\frac{\partial E}{\partial\xi}\right]_{V,T}$$

where T,P,V,S,E and H are the temperature, pressure, volume entropy and energy of the system and where $G''=(\partial^2G/\partial\xi^2)_{P,T}$ and $A''=(\partial^2A/\partial\xi^2)_{V,T}$ are derivatives of the Gibbs and Helmholtz free energies respectively at equilibrium. These are just expressions of the Le Chatelier's principle. Since G'' and A'' are positive, we see that the dependence of ξ on T (increasing or decreasing dissociation at higher T) is determined by the signs of $\partial H/\partial\xi$ or $\partial E/\partial\xi$ for constant pressure or volume experiments respectively.

In the simplest lattice gas model the solvent is represented by non overlapping particles moving on a lattice, an ion is represented by an impurity particle which interacts with (e.g.) nearest neighbor lattice particles. An ion pair occupies two lattice sites and in our model was assumed not to interact with the solvent. Free volume in the system is represented by empty lattice sites. Different sizes of solvent molecules may be represented by particles which occupy several sites. The model reveals the roles played by the entropy, enthalpy and free volume in the ionic association/dissociation equilibrium, as well as the qualitative difference expected between constant volume and constant pressure experiments.

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Ionic Conductivity Mechanism of Network Polymer Containing Lithium Perchlorate

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SUMMARY

Amorphous network polyelectrolytes were derived from poly(propylene oxide) and tris(4-isocyanatophenyl) thiophosphate [1] complexed with lithium perchlorate. The complex impedance diagrams of the higher cross-link density samples were found to be a superposition of two semicircles having different time constants, on the other hand, the diagrams of the lower cross-link density samples were a semicircle. Dynamic mechanical thermal spectra show two relaxation peaks in the higher cross-link density samples and $T_{1\rho}$ as a function of temperature obtained by ^{7}Li-NMR study has a well-defined minimum. These results indicate the correlation between the ionic mobility and the molecular motions of the system.

RESULTS AND DISCUSSION

The existance of different time constants in the complex impedance diagram is seen in Figure 1 and network prepared from 1000,3000,4000 MW PPO are designated as N1000, N3000, N4000, respectively. The loci of the diagram did not depend on the temperature, but slightly changed with increasing the salt concentration.

Dynamic mechanical spectra of N1000 and N3000 samples obtained at 1Hz are shown in Figure 2. In N3000 sample with no salt, the tanδ peak at -42 degC is associated with the segmental Tg of the pure network, and the temperature of this transition increases with increasing salt concentration, and this indicates the complexed nature of the chains [2]. On the other hand, the N1000 samples with added salts show two peaks in the primary transition region and this feature is consistant with those observed in the ionic conductivity measurements.

High resolution solid state ^{7}Li-NMR study was carried out for the N1000 and N3000 complexes. T1ρ has a well-defined minimum at 50 degC for N3000 and at 70 degC for N1000, respectively. This temperature difference corresponds to that of the Tg of the samples, and this result indicates the interaction of lithium perchlorate with network chains.

Acknowledgement

The authors thank Dr. M.Watanabe and Professor N.Ogata (Sophia University) for the ionic conductivity measurements and discussion, Dr. L.C.Dickinson (University of Massachusetts) for the NMR study.

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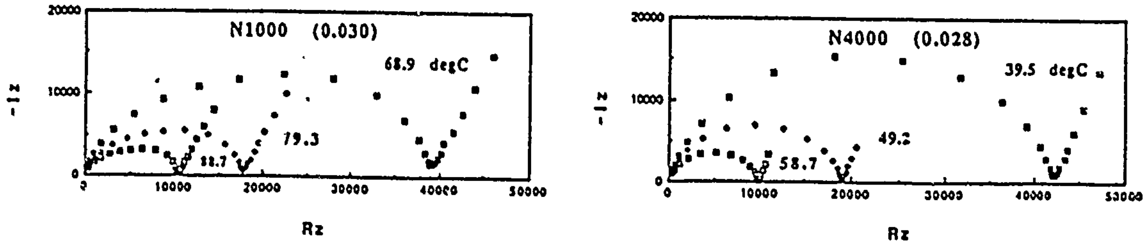

Fig. 1 Complex impedance diagrams of N1000 and N4000 polyelectrolytes.

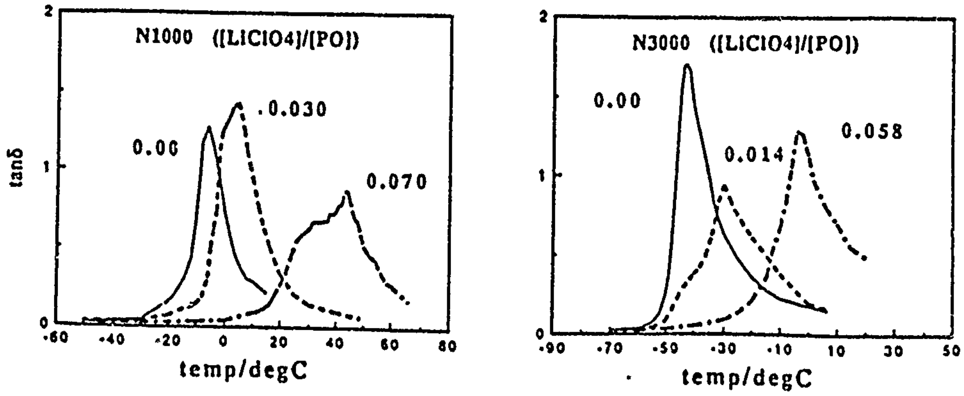

Fig. 2 Dynamic mechanical tanδ of N1000 and N3000 polyelectrolytes obtained at 1 Hz.

Control of Ion Conduction in Solid Polymer Electrolyte by Photoirradiation

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INTRODUCTION

Solid polymer electrolytes have stimulated extensive interest in the preparation of novel matrix polymer for higher ion conduction as well as in the possible applications as electrolyte in solid state electrochemical devices such as battery and ECD[1]. It will open up a wide scope of applications if ion conductivity in solid polymer electrolytes can be controlled by external stimuli such as light, heat or chemical treatment. We have already prepared the unique solid polymer electrolyte with controllable ion conductivity by photoirradiation[2]. In this solid polymer electrolyte, the matrix polymer contains anthryl groups which are well-known to show reversible dimerization behavior by photoirradiation. The ion conductivity change in the solid polymer electrolyte was revealed to be arisen from the photodimerization between anthryl groups covalently onto the polymer chain. Namely, this photodimerization provides cross-linking between polymer chains, and makes the segmental motion decrease. However, this system showed the conductivity of only $3\mathrm{x}10^{-7}$ S/cm at 25°C under dark. The present study is therefore undertaken to decrease Tg and to increase the conductivity and photochemical reaction rate in this system.

EXPERIMENTAL

Poly[(ω-anthryl)oligo(oxyethylene) methacrylate-co-(ω-methoxy) oligooxyethylene methacrylate)] [P(MEO-MEAn)] was prepared as the matrix for the photofunctional solid polymer electrolyte. The polymer obtained was hybridized with $LiClO_4$, and their ion conductive behavior was analyzed with photo-chemical reaction of anthryl groups.

RESULTS AND DISCUSSION

The hybrid composed of P(MEO-MEAn) ([An]=14 mol%) and $LiClO_4$ (3 mol%) showed the conductivity of $6.8\mathrm{x}10^{-6}$ S/cm at 25°C under dark. Temperature dependence of the conductivity in the hybrids was estimated to be curved, suggesting that the ion conductive behavior obeyed WLF type behavior. The conductivity of P(MEO-MEAn)([An]= 14 mol%)/ $LiClO_4$ hybrid films gradually decreased with photoirradiation (500 W, Xe lamp through the UVD-35 filter) as shown in Fig. 1. Absorption peak for anthryl group in polymer matrix also decreased with photoirradiation as shown in Fig. 2. This suggests that the conductivity decrease is probably arisen from photo-dimerization of anthryl groups bound on polymer. This is also supported by the rise of the glass transition temperature (Tg) of the hybrid film after photoirradiation.

The hybrid containing $LiClO_4$ at 3 mol% showed larger conductivity decrease than that containing 7 or 10 mol% as shown in Fig. 1. The same tendency was observed in the decrease of absorbance corresponding to anthryl groups in the hybrid containing $LiClO_4$ at each content. These results suggest that the photochemical reaction and conductivity change proceed more effectively in the hybrid with low Tg than that with high Tg. Time dependence of Tg for the hybrid films after photoirradiation was also analyzed. Tg of the film gradually increased by photoirradiation, and the hybrid containing $LiClO_4$ at 3 mol% showed larger Tg increase than that containing 7 mol%. These results suggest that the increase of Tg by photoirradiation deeply correlates to the photochemical reaction of anthryl groups such as photodimerization. As the results, photodimerization and conductivity decrease were revealed to be deeply affected by the Tg of matrix. Salt content dependence of photochemical reaction rate will be also analyzed.

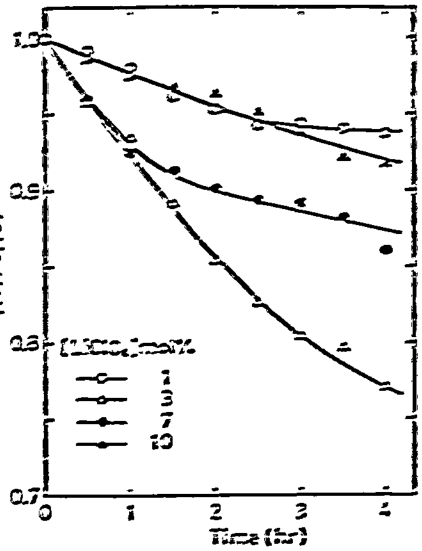

Fig. 1 Time dependence of the conductivity for the hybrid films under photoirradiation. [An]=14 mol%.

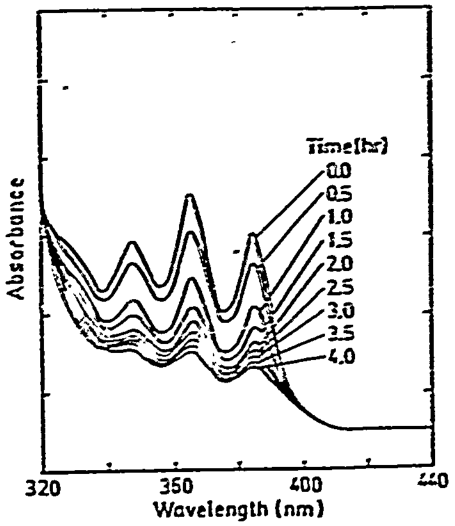

Fig. 2 Change in UV-Vis spectra with time for the hybrid film by photoirradiation. $[LiClO_4]$=7 mol%.

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Dc Polaristion of Polymer Electrolytes

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Measuring the bulk conductivity of a polymer electrolyte yields only limited information. Greater insight into ion transport in such systems may be obtained by polarising the electrolyte with a dc potential under conditions where transport of one of the constituents of the salt is suppressed. For example if a polymer electrolyte which dissociates fully into M^+ cations and X^- anions is placed between electrodes reversible to M^+ i.e.

$$M(s) \mid M^+X^- : polymer\ (s) \mid M(s)$$

and a dc potential applied, a steady state develops where the net transport of the X^- ions is zero and the steady state current is carried by the M^+ ions only.

Previously we have developed equations describing the dependence of the steady state current on the applied potential difference for such an ideal electrolyte (1,2). However polymer electrolytes are not ideal systems since interactions between the ions of the salt are always likely to be significant. First, it is important to consider the possibility that associated groups of ions, such as ion-pairs, are mobile in a polymer electrolyte and may contribute to the transport of components of the electrolyte wherever concentration gradients exist. Second, even in the absence of ion-association, polymer electrolytes at only moderate concentrations are far from ideal and it is therefore necessary to take into account thermodynamic enhancement and the coupling between ionic fluxes. We therefore recently extended the treatment of dc polarisation to take account of ion-ion interactions and have again developed general equations for the potential and current in the steady state. For a *fully dissociated* but *non-ideal* polymer electrolyte containing M^+ and X^- ions, the transport equations of irreversible thermodynamics yield the following expressions for the steady state potential ΔV, and current, I_s^+, for the cell noted above, assuming reversible electrode behaviour:

$$\Delta V = (1 + G)\,(d \ln a_{\pm} / d \ln c)\,\frac{RT}{F} \ln (c_a/c_c)$$

$$-I_s^+ = (1 + G)\,(d \ln a^{\pm} / d \ln c)\,FD_+ (c_a - c_c)$$

where G depends on the coupling of the fluxes and is related to the cross coefficient in the irreversible thermodynamic equations, $(d \ln a_{\pm} / d \ln c)$ is the thermodynamic enhancement factor, D_+ is the cation diffusion coefficient and c_a and c_c are the cation concentrations at the anode and cathode respectively.

In order to relate ΔV and I_s^+ it is necessary to eliminate the concentration terms, and this is possible only for small *ion* concentration differences between the anode and cathode. Under these circumstances c_a/c_c approaches unity and the $(\ln c_a/c_c)$ term may then be linearised, permitting elimination of the c_a and c_c between the two expressions. For dilute electrolytes G and (d ln $a_{\pm}$ / d ln c) both tend to unity and it may be shown that ΔV remains linearly related to I_s^+ effectively up to a maximum of about 20mV. At high ion concentrations both G and (d ln $a_{\pm}$ / d ln c) exceed unity and the predicted linearity limit correspondingly increases above the 20 mV value.

We have previously presented preliminary experimental data on dc polarisation measurements, but have now extended these measurements to a much wider concentration range. For each salt concentration, the cell was polarised at a constant dc voltage until a steady state curent was reached. The applied voltage was corrected for electrode losses as described previously (3). The experiment was then repeated at a series of increasing applied voltages, with the steady state current being recorded in each case. A plot was then constructed of steady state current against (corrected) applied voltage and the limit of linearity obtained. In Figure 1 we present data for the cell

Li(s) I $LiClO_4$: poly(ethylene oxide) I Li(s)

Dividing the plot into low and high concentration regions and considering first the dilute region, it is evident that the limit of linearity far exceeds 20 mV despite the fact that at these low concentrations the electrolyte is likely to approach ideal behaviour. This result can be rationalised by including the concept of ion pairing. In the presence of Li^+, ClO_4^- and $(LiClO_4)^o$, the *migration* of ClO_4^- ions in the steady state in one direction is balanced by the *diffusion* of both ClO_4^- ions *and* $(LiClO_4)^o$ ion pairs (each of which carries the ClO_4^- constituent) in the opposite direction. This permits large potentials to be appied without necessarily inducing a large *ion* concentration gradient and hence permitting linearisation of the logarithmic term.

Turning to the high concentrations, both the predicted and observed linearity limits rise above 20 mV. However we have estimated both the G and (d ln $a_{\pm}$ / d ln c) terms from published data (4,5) and predict a virtually unchanged linearity limit of 20mV at a composition of 15 ether oxygens per Li^+ ion (1.63 mol dm^{-3}) which is significantly smaller than the observed limit of 120 mV, suggesting that the electrolyte is not fully dissociated at these high concentrations. At higher values of concentration, the theoretical linearity limit rises steeply: at 8:1 the limit may be estimated to be 40 mV.

It is also interesting to report the limiting ratio for the steady state current to the initial current, i.e. the ratio for ΔV → O. In the case of an electrolyte where there is no mobility of uncharged ion pairs, this ratio can be shown to be equal to the transference number. Since the results described above suggest that the electrolyte may indeed contain mobile ion pairs, we now choose to call this ratio the "limiting current fraction", F_+. Values of F_+ for $LiClO_4$ and $LiCF_3SO_3$ salts in PEO at 120°C are given in Table 1.

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Figure 1

Linearity limits for current-voltage behaviour of

Li | $LiClO_4$: PEO | Li cells

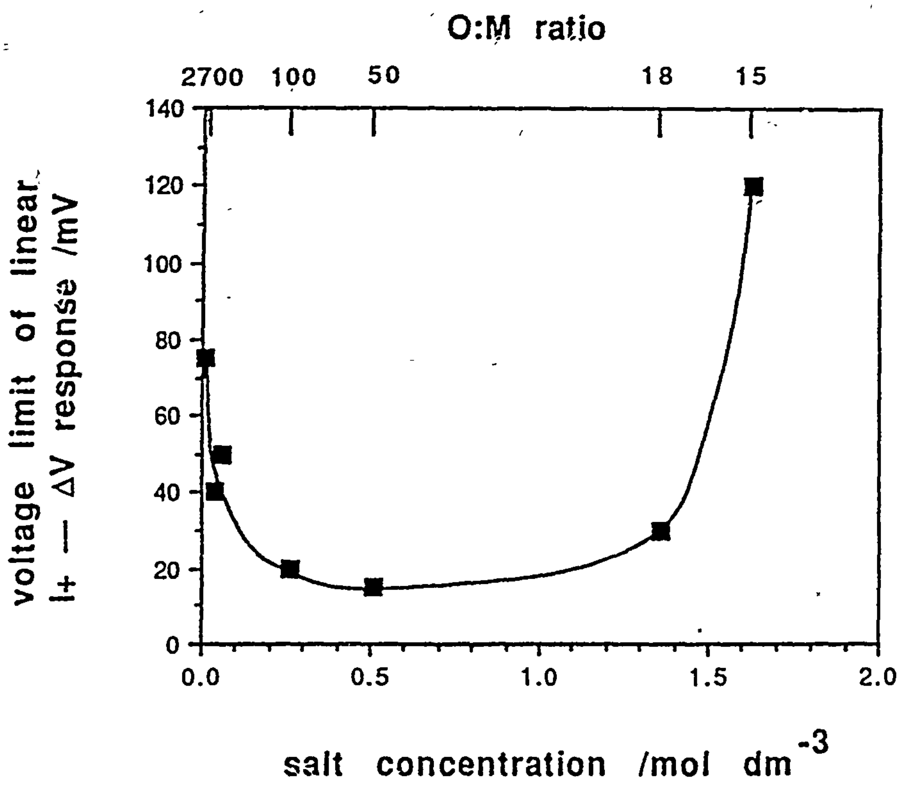

Table 1

Limiting current fractions for PEO_xLiClO_4 and $PEO_xLiCF_3SO_3$ at 120°C.

$LiClO_4$ O:M ratio	F_+	$LiCF_3SO_3$ O:M ratio	F_+
2500	0.55	100	0.60
750	0.47	50	0.52
500	0.43	36	0.49
100	0.34	18	0.44
50	0.29		
18	0.23		
15	0.22		
12	0.21		

Ion/Electron Mixed Conductors based on Polymer Electrolytes

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1. Introduction

Combined use of polymer electrolytes and ultramicroelectrodes has made it possible to conduct quantitative electrochemical measurements (solid state voltammetry) of redox active molecules dissolved in or attached to polymer electrolytes. Electrochemical reactions of the redox molecules in the bulk polymeric phase occur via the diffusion of the redox molecules to electrodes, but electron self exchange reaction or electron hopping between redox centers sometimes plays an important role for the charge transport. Electroactive polymers having the latter charge transport process is called "ion/electron mixed conductor" or "redox conductor".

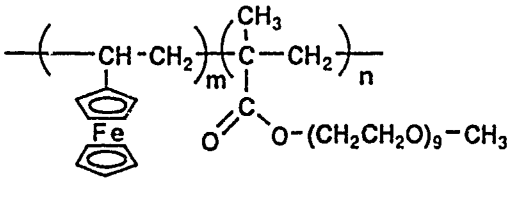
In this study, it is shown that solid state redox conduction in polymer electrolytes is observed in two systems: one is polymer electrolyte in which redox molecule, having high electron self exchange rate constant, is dissolved at a high concentration. LiTCNQ is selected as a molecular solute and is dissolved in network poly(ethylene oxide)(PEO) electrolytes containing LiClO$_4$, and the electron hopping rate between TCNQ$^{-/0}$ couple is studied as a function of concentrations of LiTCNQ and LiClO$_4$, and temperature. The other system is copolymer(P(Fc/MEO$_9$)) consisting of redox active monomer, vinylferrocene (Fc), and ion conductive monomer, methoxy-nona(ethylene oxide)methacrylate (MEO$_9$), in which LiClO$_4$ is dissolved. It is demonstrated that reversible and diffusion-controlled electrochemical reaction occurs via the electron hopping in the copolymers where the redox active sites are fixed to the polymer backbone by covalent bond.

2. Experimental

Electrochemical measurements (solid state voltammetry) were made by using a three electrode microcell and a highly sensitive potentiostat in a Faraday cage. The three electrode microcell consists of tips of three electrodes; Pt microelectrode (10 or 25 μm dia.), and Pt counter and Ag reference electrodes, exposing in an insulating plane.

Network polymer electrolytes were prepared directly onto the microcell surface by crosslinking reaction of PEO triol (mol.wt.=3000) with toluene-2,4-diisocyanate in the presence of LiClO$_4$ and LiTCNQ, for the solid state voltammetry.

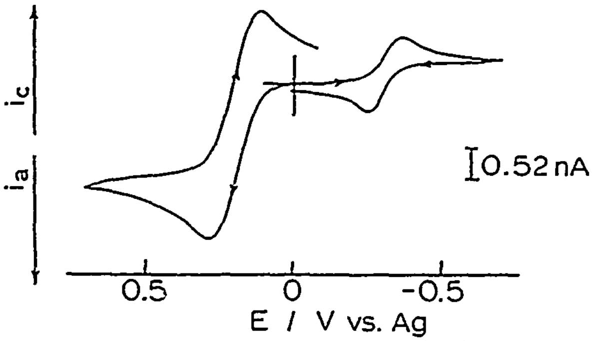
P(Fc/MEO$_9$)s, having several compositions, were prepared by radical copolymerization of Fc and MEO$_9$. The solutions of the copolymers obtained, containing LiClO$_4$, were cast on the surface of the microcells, followed by evaporation of the solvent, for the measurements.



VFc-MEO$_9$ Copolymer

3. Results and Discussion

Figure 1 shows solid state cyclic voltammetry of LiTCNQ in network PEO electrolyte. Two reversible waves, corresponding to TCNQ$^{-/0}$ and TCNQ$^{-/2-}$ reactions, are observed. Although the molecule diffusing in the polymeric phase, toward oxidizing and reducing microdisk electrodes, is the same TCNQ^{-} species, the oxidation wave, the TCNQ$^{-/0}$ couple, gives a much larger current than does the reduction wave, the TCNQ$^{-/2-}$ couple. Since the electron self exchange rate constant for the TCNQ$^{-/0}$ couple is very large (> 10^9 M^{-1}s^{-1} in acetonitrile) and



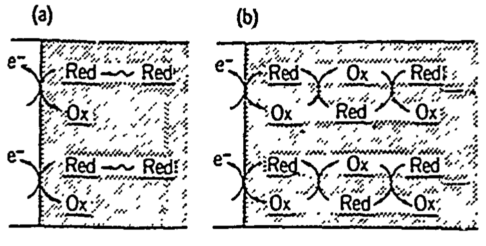


Fig. 1 Solid state cyclic voltammetry(20 mV/s) at 25 μm dia. disk electrode for LiTCNQ(200 mM) dissolved in network PEO/$LiClO_4$ electrolyte(Li/O = 0.02) at 32.5 °C.

Fig. 2 Charge transport mechanisms for redox reaction.

that for the $TCNQ^{-/2-}$ couple is much smaller, the difference in the voltammetric current has been explained by the contribution of the electron self exchange reaction to the $TCNQ^{-/0}$ reaction. In other words, transport of $TCNQ^-$ to the electrode for the $TCNQ^{-/0}$ reaction is brought about by both diffusion (Figure 2 (a)) and electron hopping (Figure 2 (b)), while that for the $TCNQ^{-/2-}$ is brought about by only diffusion. This coupling of physical diffusion and electron self exchange reaction in the diffusion layer has been interpreted by Ruff:

$$D_{app} = D_{phys} + (1/6)k_{ex}\delta^2C$$

where D_{app} is experimental diffusivity, D_{phys} is physical diffusivity, δ is intersite distance at electron transfer, k_{ex} is the electron self exchange rate constant, and C is the solute concentration. Figure 3 shows the diffusion rates for the $TCNQ^{-/0}$ wave, taken as D_{app}, and the $TCNQ^{-/2-}$ wave, taken as D_{phys}, and their differences(electron diffusivity) as a function of LiTCNQ concentration. It should be noted that the electron diffusivity linearly increases up to 0.1 M and surpasses the physical diffusivity at 0.05 M.

Reversible redox reaction in the bulk polymeric phase is also observed for Fc sites in P(Fc/MEO_9). Judging from the facts that Fc sites are covalently fixed to the polymer backbone and can not largely diffuse and that the amount of electrochemically reacted Fc sites during the reaction is far larger than the possible amount of Fc sites on the electrode surface, it is concluded that the redox reaction in P(Fc/MEO_9) is brought about by the electron hopping mechanism (Figure 2(b)). Electron diffusivity at 40 °C in the copolymer is estimated at ca. 10^{-10} cm^2s^{-1}.

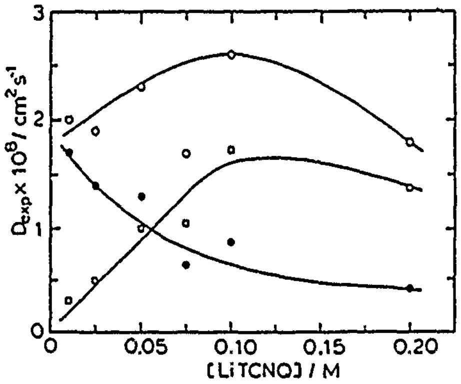


Fig. 3 Diffusion coefficients as a function of [LiTCNQ] in network PEO/$LiClO_4$ (Li/O = 0.02) at 42 °C: ○ , D_{app} ($TCNQ^{-/0}$ couple); ● , D_{phys} ($TCNQ^{-/2-}$ couple); □, D_{app} - D_{phys} (electron diffusivity).

The Perfectly Polarised Polymer Electrolyte / Electrode Interface

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Despite extensive investigation of the bulk properties of solid polymer electrolytes, the interface between such electrolytes and metal electrodes has received relatively little attention(1,2). The behaviour of this interface is however of critical importance to the performance of electrochemical devices such as batteries or smart windows which are based on polymer electrolytes. It is therefore important to develop a fundamental understanding of the nature of the polymer electrolyte / electrode interface, and this should commence with a study of the interface under polarising conditions. Such studies parallel the classical studies of the double layer structure in liquid electrolytes which were an important foundation for modern solution electrochemistry(3). The classical solution studies were carried out using dropping mercury electrodes because of the clean, reproducible and smooth nature of the liquid metal surface. For similar reasons we have conducted our studies of the double layer using a mercury electrode.

A new 3-electrode cell has been constructed. It consists of a lithium foil counter electrode mounted on top of a polymer electrolyte film some 100μm thick. A 3mm diameter Li wire reference electrode contacts the opposite surface of the polymer film and is located close to a channel along which Hg may pass. Measurements may be made at the polymer electrolyte/Hg interface with the mercury flowing across the electrolyte although in our preliminary studies the velocity of Hg flow did not appear to influence the double layer capacitance. Therefore the measurements reported here were obtained by flowing the mercury across the polymer surface for a few minutes then arresting the flow during data collection. Measurements were carried out on polymer electrolytes based on a methoxy linked poly(ethylene oxide) host which is entirely amorphous; $LiClO_4$ was chosen as the salt. After purification and drying of the polymer and salt both were mixed with acetonitrile and the electrolyte cast as a film by slow evaporation of the solvent. Compositions spanning the range from 10,000:1 to 10:1 have been prepared and investigated, where the ratios refer to the number of ether oxygens per Li^+ ion.

The interface was investigated by ac impedance measurements using a Schlumberger Solartron 1255 frequency response analyser and 1286 potentiostat, the combined system being under the control of a Zenith microcomputer. The ac impedance plot for a polymer electrolyte of composition 1,000:1 is shown in Fig. 1. The semicircle corresponds to the bulk ac response and the low frequency spike to the blocking interface. For each electrolyte composition the ac impedance was collected over a range of dc potentials and the differential capacitance of the interface extracted. The results for a 1,000:1 electrolyte are presented in Fig. 2. Evidently over the potential range from 2.5 to 1.6 the interface behaves as a simple potential independent capacitance. At large positive potentials the capacitance rises due to the onset of electrode oxidation which manifests itself as the formation of Hg adatom. There appears to be a small shoulder in the differential capacitance curve at around 2.70V and further work is in progress to confirm this.

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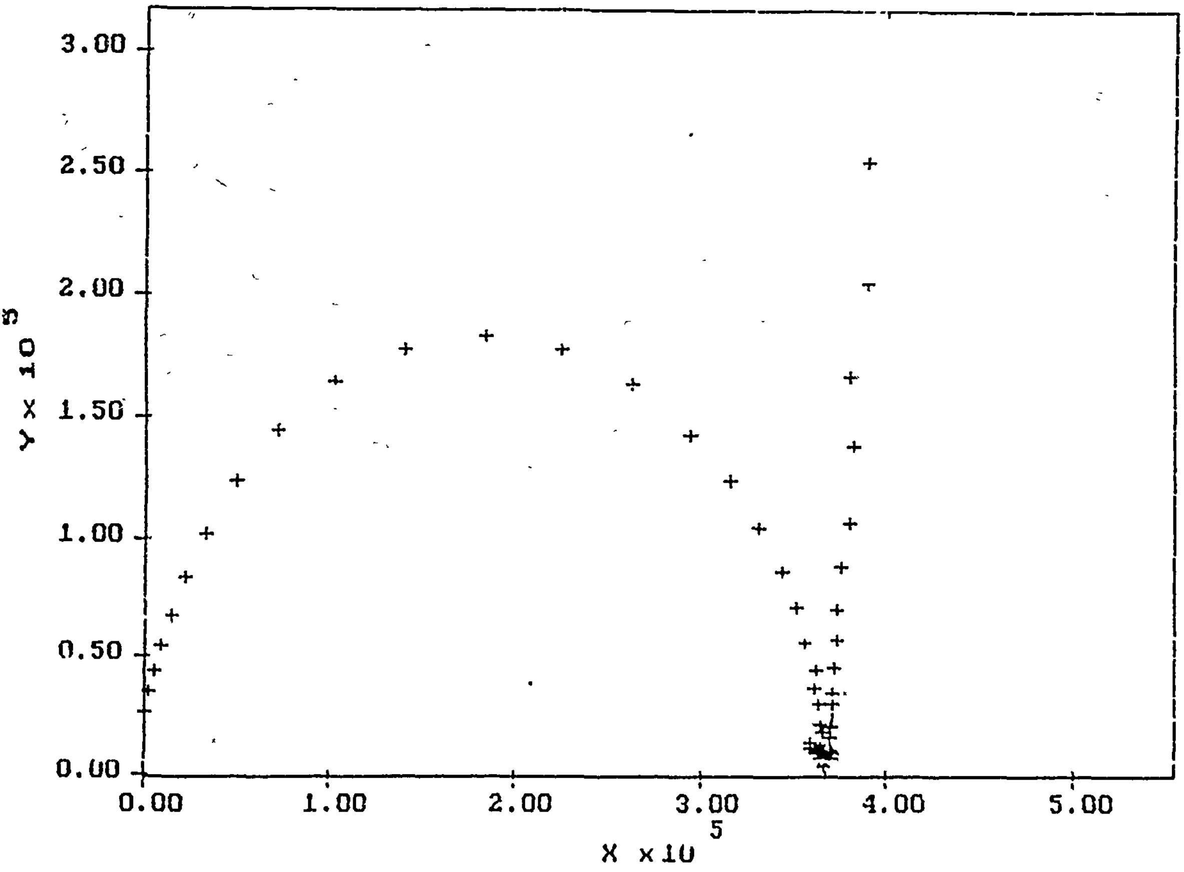

Fig. 1. Ac impedance plot for polymer electrolyte/mercury interface at V_{DC} = +2.40V vs lithium.

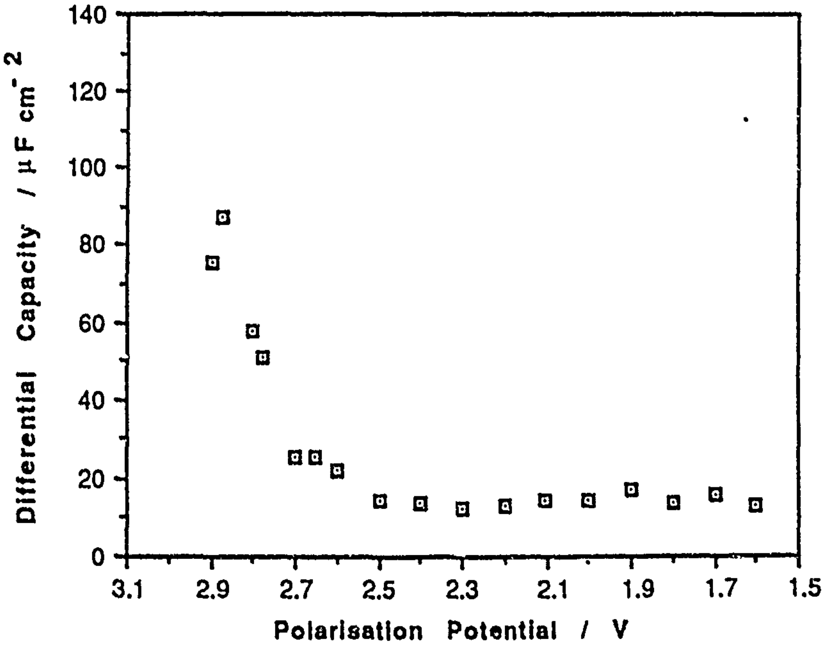

Fig.2. Differential Capacity of the Polymer Electrolyte / Hg interface Potentials are measured with respect to a lithium reference electrode.

EXAFS STUDIES OF DIVALENT POLYMER ELECTROLYTES

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EXAFS studies on polymer electrolyte systems have provided a unique means of addressing local structure-conductivity relationships in these technologically important materials. It has been possible to obtain data suitable for meaningful interpretation for the average local environment of cations within systems of the type $PEO_n:MX_2$ (4 n 100; X = Cl, Br, I, ClO_4, CF_3SO_3; M = Ca, Ni, Zn). Preliminary results for anion environment, especially for Br and I have been encouraging. A full analysis of the data has been impeded by technical factors concerned with the monochromator system on Station 7.1 at the SRS, Daresbury Laboratory. In particular there are over-large angle increments (steps) encountered in the Br energy range. With the iodine L-III edge energy range, glitches were encountered on the Station 8.1 bent crystal monochromator system in our earlier studies. Future work, using other beam stations at the SERC Daresbury Laboratories, will address the local anion environment which is of great scientific interest. It is also technologically important as most divalent materials have a significant anion contribution to the ionic conductivity.

Interest at Leicester has recently been focused on two distinct ways in which conductivity can be potentially enhanced by structural modification. The first is by the comparatively conventional route of the use of plasticisers; EXAFS results will be reported for the electrolyte $PEO_8:ZnCl_2$/70% ethylene carbonate.

The second structural modification that we have explored is the incorporation of two inorganic salts, rather than one, in the polymer matrix. Our thinking here is concerned with the fact that polymer electrolytes involve a subtle balance of factors:-

1. The solvation energetics of the salt-polymer system must be sufficiently favourable to overcome lattice energy considerations so that the salt remains dissolved in the immobile solvent;

2. conversely the polymer-salt interactions cannot be so strong that the

ions are immobile.

Cations vary considerably in the strength of their interaction with PEO. For some, the interaction is too weak to maintain dissolution over the whole of the useful temperature range; this is a noted problem of Rb systems. For others, the interaction is so strong that the cations are immobile; calcium systems are beset with this disadvantage.

We have therefore been studying systems in which more strongly co-ordinating ions are incorporated in order to provide an ionically-cross-linked matrix conducive to conduction, but that a further ionic species, which co-ordinates weakly, is the predominant charge carrier. We call this the 'pit-prop' mechanism. EXAFS results were reported at the MRS meeting at Boston in November 1990 for systems of this type, including $PEO_{15}:ZnI_2/MgX_2$ (X= ClO_4 and CF_3SO_3) and $PEO_{15}:CaI_2/ZnI_2$. It was concluded that Zn played the carrier role whereas Mg and Ca were the 'structure-formers'. EXAFS results will be reported here for the systems $PEO_{12}:ZnX_2/CoX_2$ (X = Br or I) in which the cation roles are lessly obviously distinct.

We have also carried out studies of the effect on the cation environment of having two, potentially competing, anion species present in order to address the timely question of ion pairing in polymer electrolyte systems.

At the MRS meeting, we also reported results for the system $PEO_{15}:CaI_2/CaBr_2$ in which the cation co-ordination to the backbone had earlier been shown to be very strong. Here we report on the somewhat different system $PEO_{12}:ZnI_2/ZnBr_2$ which involves a cation for which transport appears to be facile.

Electrochemical and ^{7}Li NMR Study of Poly(ethylene glycol)-Based Polymer Electrolytes

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We have investigated a series of complexes formed between Li salts and low molecular weight (~400) poly (ethylene glycol) (PEG) by complex impedance, cyclic voltammetry, differential scanning calorimetry (DSC), and ^{7}Li NMR techniques. Figure 1 displays the salt concentration dependence of the ionic conductivity (measured with stainless steel blocking electrodes) of PEG:$LiClO_4$ at several temperatures. The broad conductivity maxima observed between 5 and 7 mol% $LiClO_4$ are understood simply in terms of the balance between the number of ions available for transport and elevation of the glass transition temperature (T_g) resulting from ion coordination by the polyether chains, an effect which has been reported for a wide variety of polyether complexes. Conductivity measurements performed with Li electrodes indicate the formation of a passivating layer at the electrode-electrolyte interface. Cyclic voltammetry analysis of Li deposition and stripping on stainless steel indicates nevertheless that these reactions are highly reversible and efficient. The effect of passivation on long term cyclability is currently under investigation.

The effect of addition of inert fillers, in the present case the ceramic powder $LiAlO_2$ (up to 40 wt%, and particle size ~5 um), on ionic conductivity of $PEG_{25}LiClO_4$ was found to be relatively minor as indicated in Fig. 2. The addition of 25 wt% $LiAlO_2$ to PEG_{25} $LiClO_4$ is sufficient to yield a paste-like consistency of the original moderately viscous liquid complex, although DSC results shown in Fig. 3 indicate that the filler has only a small effect on T_g (raised by about 5K) and on the shape of the melting endotherm centered at about 13°C. DSC results for PEG_9LiClO_4 (not shown) indicate that this particular composition is amorphous, as evidenced by the presence of a strong glass transition occurring some 12K higher than in $PEG_{25}LiClO_4$ and the absence of a melting endotherm.

Finally preliminary ^{7}Li NMR measurements of PEG:Li salt complexes reveal substantial motional narrowing associated with both the glass transition and the melting endotherm. The effects of both ^{1}H and ^{19}F decoupling on ^{7}Li linewidth in PEG:$LiBF_4$ will be employed to assess the degree of cation-polymer and cation-anion association.

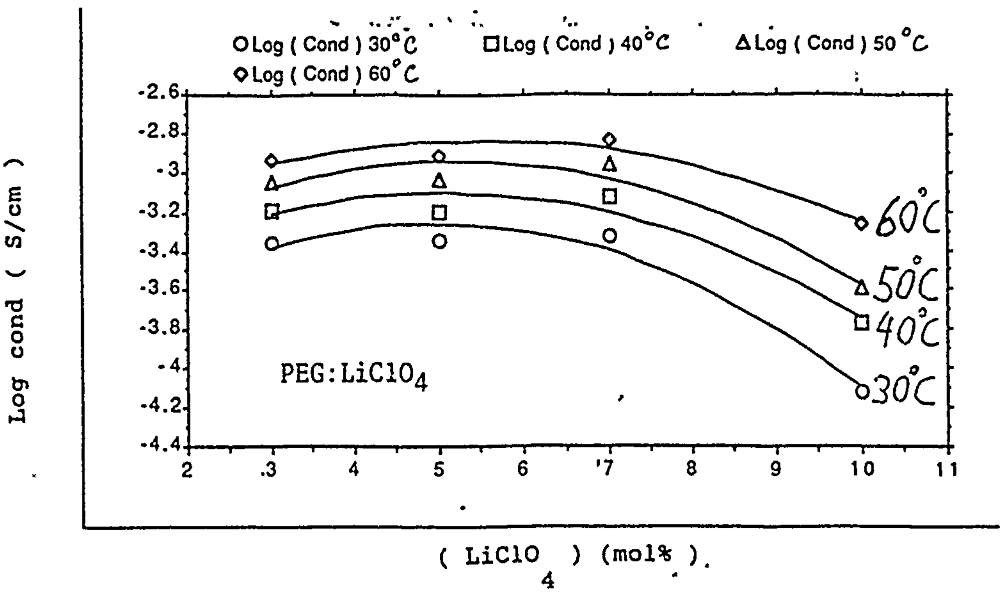

FIG 1

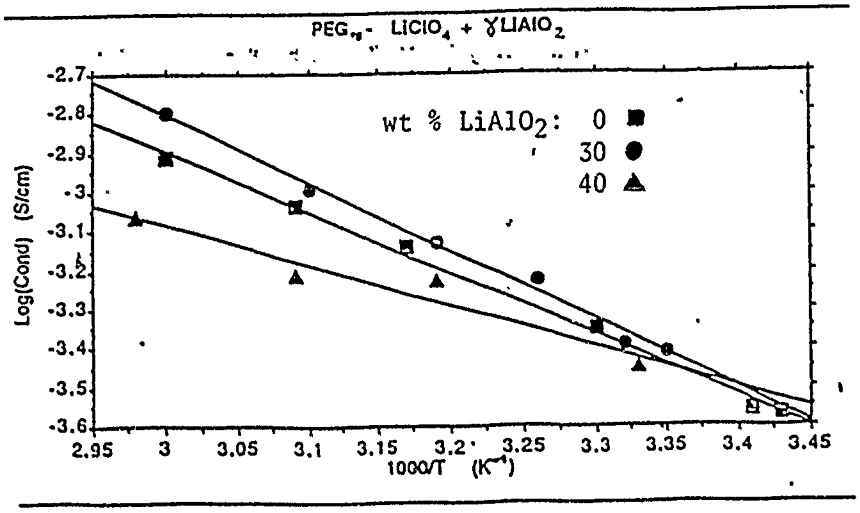

FIG 2

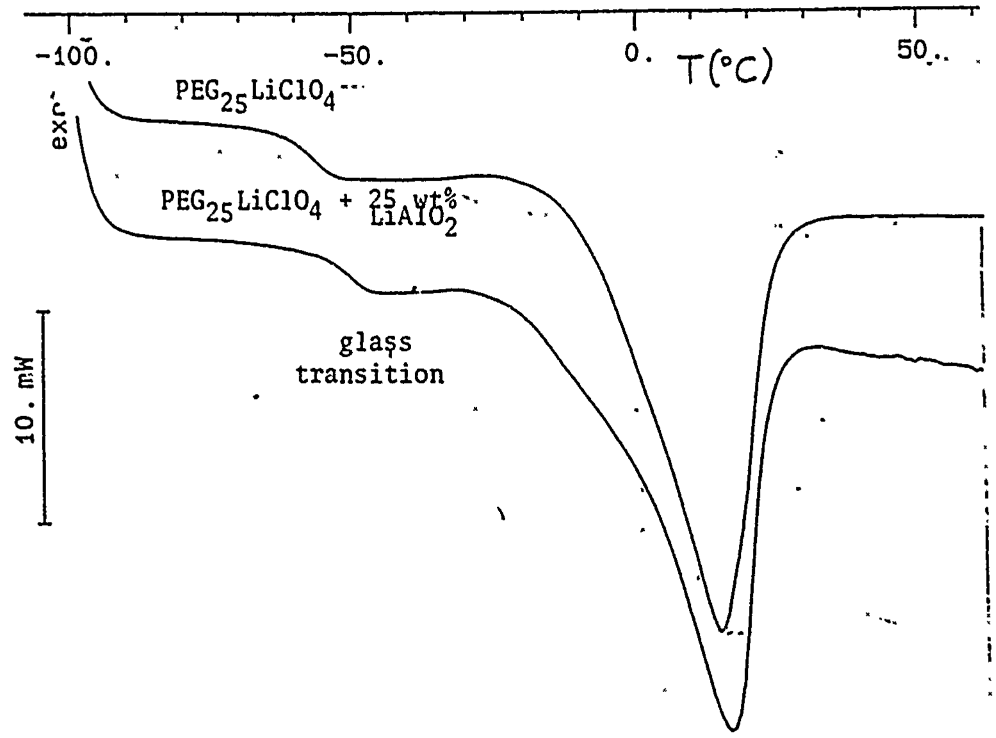

FIG 3

NEW POLYMER ELECTROLYTES

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TRANSPORT PROPERTIES OF POLY(ETHYLENE OXIDE)-SILOXANE NETWORKS CONTAINING LITHIUM PERCHLORATE

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Complexes of poly(ethylene oxide), PEO, with inorganic alkali ion salts have been extensively studied in view of their potential interest as electrolytes in solid-state batteries. In order to increase the conductivity, structures with more segmental chain motion enhancing ion transport through polymer matrices, and less crystallinity than in linear PEO of high molecular weight have been sought after. Well defined PEO networks were prepared which have low T_g values and the following features for the crosslinks : the smallest possible size and a significantly low degree of interaction towards the PEO segments. This was achieved by performing hydrosilylation of α,ω -diallyl PEO of different lengths ($\overline{M}_n$=600, 1000, 2000) with 2,4,6,8-tetramethylcyclotetrasiloxane, D_4H, because the silyl hydride addition to allyl group, in the presence of Pt catalysts, is known to give a Si-C linkage which has a higher hydrolytic stability than the Si-O-C linkage.

The influence of several factors on network formation was checked by looking at the amount of extracted products which were analyzed by ^1H and ^{29}Si NMR. Side reactions were studied on models and the results are as follows : Pt_o catalysts are more efficient and lead to less side reactions than H_2PtCl_6. The lowest yield of extracted product was observed for a ratio $[SiH]/[C=C] \simeq 1.2$. An optimal value of V_c [volume of reagents (PEO + D_4H)/total volume (reagents + solvents)] of 0.75 was found to avoid either a non homogeneous system or cracking

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of the membrane at the curing temperature (60°C). Network formation is very sensitive to traces of water which react with SiH groups leading to H_2 evolution and hydrogenation of allyl functions. Isomerization of allyl groups was also observed in some cases. All these side reactions prevent complete crosslinking. By optimizing different parameters and especially by working under very dry conditions, it was possible to prepare well defined networks with very low amounts of extracted products ($< 5\%$ in all cases).

These membranes were filled with $LiClO_4$, and their conductivity was measured as a function of temperature, salt concentration and length of the PEO segments. Their glass transition temperature, T_g, was also determined, allowing a study of their behaviour at constant reduced temperature, i.e. at constant $T-T_g$. Use of cyclosiloxane crosslinks leads to T_g values lower than of the corresponding networks with urethane crosslinks. This can be explained by the fact that siloxane crosslinks are more flexible and less polar than urethane crosslinks which was confirmed by ^{13}C NMR relaxation time measurements made on similar PEO networks with different crosslinks. Moreover, these filled membranes show a very interesting behaviour since the conductivity increases as the square root of the salt concentration, at constant $T-T_g$, rather than at the first power as observed in the case of PEO networks with urethane crosslinks. The lithium salt behaves like a weak electrolyte, which shows that the crosslinks have a tremendous influence on the charge carrier generation.

Polymer electrolytes based on poly-phosphazene with pendant 12-crown-4 groups and monovalent salts.

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Extended abstract

A poly-phosphazene with pendant 12-crown-4 units has been prepared; the ring is spaced from the chain by 6 methylene units. The polymer has been obtained, starting from bis(trifluoroethoxy)-poly-phosphazene, by substitution of trifluoroethoxy groups with the spaced crown-ether.

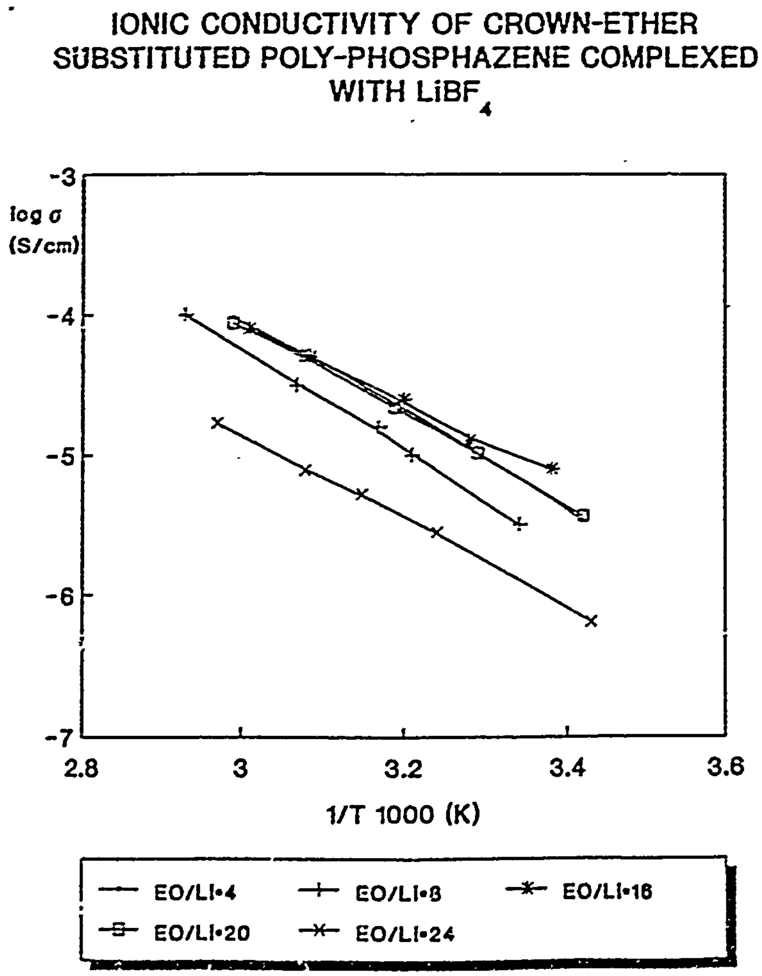
The insertion of flexible spacing units between the ether rings and the main polymer chain decreases the Tg of the crown-ether substituted poly-phosphazene, acting as a plasticizing agent. As a consequence the presence of a methylene oxide spacer should increase the ionic conductivity in the polymer-salt system.

The 12-crown-4 ether should be a more effective binding agent for the Li^+ than the Na^+ and K^+, hence it is expected that a larger number of charge carriers will be present in the system complexed with lithium salts, while in the system complexed with Na and K salts there is probably a large number of non conductive ion pairs.

To verify this hypothesis the ionic conductivity of the polymer with $LiBF_4$, $NaBF_4$ and KBF_4 has been measured as a function of temperature, changing the ratio EO/M^+ between 24/1 and 4/1; the concentrations are expressed as the ratio of the (ethylene oxide) units in the ring per amount of cation (M^+).

The system complexed with $LiBF_4$ exhibited a reasonably good conductivity levels of 10^{-5}–10^{-4} S/cm, for temperature between 290 K and 330K (see Fig.1).

Some lithium transference number measurements have been performed as well.


IONIC CONDUCTIVITY OF CROWN-ETHER SUBSTITUTED POLY-PHOSPHAZENE COMPLEXED WITH $LiBF_4$

-Fig.1-

THERMALLY STABLE LI SALTS FOR POLYMER ELECTROLYTES

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Polymer electrolyte batteries are being developed based on several different general types of electrolytes. Among the electrolytes which appear promising are:

- crosslinked pure amorphous polymers
- plasticized pure polymers
- gels

Although the conduction mechanism for the Li ion in these various systems is not yet satifactorily understood, the role of the Li counterion is thought to impact on the ionic conductivity by a number of mechanisms. These effects include ion-pair and triple-ion equilibria, plasticizing, and film formation at reactive electrodes.

As the room temperature conductivity of polymer electrolytes is still lower than desired for many applications, prototype cells are frequently evaluated at elevated temperature. Many of the Li salts which perform satisfactorily at ambient temperature lack the thermal stability required for elevated temperature operation. This problem is being addressed by the development of novel, thermally stable, highly conductive, organic anion-based Li salts.

We will present results on the electrochemical and physical characterization of some recently prepared, potentially useful thermally stable Li salts, including Li tris-(trifluoromethylsulfonyl)methide [$LiC(SO_2CF_3)_3$] and Li bis-(trifluoromethylsulfonyl)imide [$LiN(SO_2CF_3)_2$]. Results will include cyclic voltammetry studies in liquid solvents, and conductivity and electrochemical impedance spectroscopy studies in polymer matrices including bis-(methoxyethoxyethoxy)phosphazene (MEEP) and polyethyleneoxide (PEO).

"Synthesis and physical-chemical characterization of new copolymer electrolytes"

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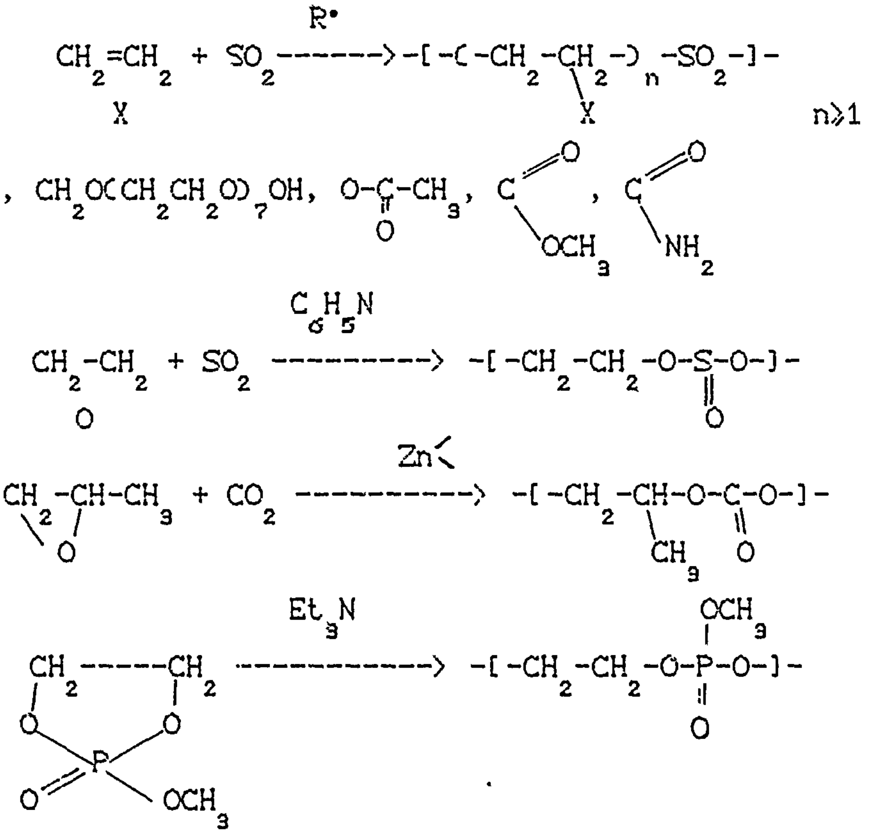
A new group of highly conductive polymeric electrolytes based on aliphatic polysulfones, polycarbonates, polysulphides and on polyphosphates was tested. The way of synthesis of these polar polymeric systems is shown by the following reactions:



$$CH_2{=}\underset{X}{CH_2} + SO_2 \xrightarrow{R\bullet} -[-(-CH_2-\underset{X}{CH_2}-)_n-SO_2-]- \qquad n \gg 1$$

$$X = CH_2OH,\ CH_2O(CH_2CH_2O)_7OH,\ O-\underset{O}{\overset{}{C}}-CH_3,\ C(=O)OCH_3,\ C(=O)NH_2$$

$$\underset{O}{CH_2-CH_2} + SO_2 \xrightarrow{C_6H_5N} -[-CH_2-CH_2-O-\underset{\overset{\|}{O}}{S}-O-]-$$

$$\underset{O}{CH_2-CH}-CH_3 + CO_2 \xrightarrow{Zn<} -[-CH_2-\underset{CH_3}{CH}-O-\underset{\overset{\|}{O}}{C}-O-]-$$

$$\underset{O\quad\ O}{CH_2-CH_2}\,\underset{O=P-OCH_3}{} \xrightarrow{Et_3N} -[-CH_2-CH_2-O-\underset{\overset{\|}{O}}{\overset{OCH_3}{\overset{|}{P}}}-O-]-$$

Polymer electrolytes were prepared by casting technique using acetonitrile as a solvent and $LiClO_4$ as a dopant. However, some of them did not form well defined foils and were obtained rather in a form of powders or pastes. Ionic conductivity of the systems studied was measured by Impedance Spectoscopy The highest values of conductivity measured for several studied electrolytes are presented in Table 1.

As can be seen some of the studied electrolytes exhibit conductivities higher than analogues materials based on poly (ethylene oxide)-PEO. Conductivity of electrolytes containing random SO_2-acrylamide copolymer (29%-mol of SO_2 monomeric units) exceeded 10^{-5}S/cm at room temperature.

In order to improve processibility of the studied systems copolymer electrolytes were mixed with high molecular weight poly (ethylene oxide)-PEO. Thin film flexible foils thermally stable up to 100°C were formed. The applied procedure improved also their room temperature ionic conductivity. (see table 2).

The highest value of ambient temperature conductivity was measured for the electrolytes based on blends conataining sulphur dioxide copolymers with ethylene oxide and acrylamide. This observation evidenced the role of cooperative interaction of polymer groups with metal cation on conductivity of the studied systems. This effect will be wider discussed in a full length paper.

Table 1.

Values of conductivity for copolymer electrolytes doped with $LiClO_4$ (10% mol in respect to copolymer molecular units)

Kind of copolymer	σ_{rt} S/cm	T K	σ_T S/cm
EO-SO_2 (R)	4.9×10^{-6}	343	1.3×10^{-4}
EO-SO_2 (A)	2.4×10^{-6}	374	1.3×10^{-4}
PAA-SO_2 (A)	5.9×10^{-9}	374	4.6×10^{-7}
PVA-SO_2 (A)	3.8×10^{-7}	353	5.3×10^{-6}
PPC (A)	$>10^{-12}$	-	-
PAAM-SO_2 (R)	1.1×10^{-5}	368	3.15×10^{-4}

Symbols are as follows:
EO-ethylene oxide, PAA-poly (allil alcohol), PVA-poly (vinyl alcohol), PPC-poly (propylene carbonate), PAAM-poly (acrylamide), (R)-random copolymer, (A)-alternating copolymer σ_{rt}-room temperature ionic conductivity, T-the highest temperature at wich conductivity σ_T was measured

Table 2.

Values of conductivity for polymeric electrolytes based on blends of poly (ethylene oxide) with various polar copolymers.

Kind of copolymer component	X % wt	σ_{rt} S/cm	T K	σ_T S/cm
EO-SO_2 (R)	30	1.4×10^{-5}	353	2.9×10^{-3}
EO-SO_2 (A)	30	4.8×10^{-5}	370	4.0×10^{-3}
PAA-SO_2 (A)	20	1.1×10^{-5}	369	3.3×10^{-3}
PVA-SO_2 (A)	50	2.4×10^{-6}	376	4.1×10^{-5}
PPC (A)	40	3.8×10^{-6}	372	4.3×10^{-4}
PAAM-SO_2 (R)	40	3.2×10^{-5}	372	3.2×10^{-3}

All samples included in the table were doped with 10% mol of $LiClO_4$ in respect to sum of ethylene oxide and copolymer molecular units. X- concentration of copolymer in blend. Other symbols have the same meanining as in the Table 1.

ACKNOWLEDGEMENT

This work was partially supported by Polish Ministery of Education according to 500/164/136/0 research programme

A NEW CLASS OF POLYMER ELECTROLYTES BASED ON CHAIN-EXTENDED POLYEPOXIDES AND LITHIUM SALTS

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It is well known that polyethylene oxide (PEO) complexes with lithium salts generally exhibit a poor conductivity at room temperature because of their semicrystalline nature.

Ion transport is only significant in the amorphous region in which the segmental motions of polymer chains help the ions to diffuse through the matrix(1).

The synthesis of comb-shaped polymers with oligoethylene oxide units in the side chain, showing the same complexing properties of PEO, has been considered a promising approach to obtain fully amorphous polymers with low Tg and enhanched ionic conductivity at room temperature(2).

Therefore, after the promising results obtained with polyvinylethers(3), we synthesized chain-extended comb-shaped polyepoxides having regular pendant group with a variable number (n) of ethyleneoxide (EO) units.

The chain extended polyethers were obtained by anionic copolymerisation of epoxides, containing n ethylenoxide units, with different amount of diethylenglycol diepoxide.

The length of the pendant group was changed in the range $2<n<8$, while the amount of diepoxide was varied between 2 and 10 % in moles.

Complexes of these polyepoxides with lithium salts have been prepared as polymer electrolyte membranes and their ionic conductivity at different temperature and O/Li ratios have been measured.

The influence of side chain length on conductivity, expecially at room temperature, confirms the trend observed previously for polyvinylethers, infact log σ values increase with the length of the side chain, but when n>6 the conductivity tends to decrease again.

Thermal behaviour of polymers and complexes have been investigated by DSC; most of the polyepoxides are amorphous, but in some cases (n>6) besides Tg a melting peak has been detected. Tm values are relatively low (n=8, Tm=6 °C) and indicate a tendency of the pendant chain to give ordered structures, that could be one of the reason of the reduced mobility of the ion in the corresponding electrolytic membranes.

Finally the comparison between room temperature conductivity and Tg of polyvinylether/$LiClO_4$ and polyepoxide/$LiClO_4$ complexes, at different ratio O/Li, shows a significant improvement in conductivity with the polyepoxide structure in spite of the negligible differences in the Tg of the complexes.

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"Application of acrylic polymers in blend based polymeric electrolytes"

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From our previous studies of poly (ethylene oxide)-PEO - poly (methyl methacrylate)-PMMA blends it is evident that such systems can be succesfully applied as immobilized polymer solvents in highly conductive polymeric electrolytes [1-3]. Since various acrylic polymers exhibit much lower glass transition temperatures than their methacrylate analogues one can expect that PEO-polyacrylate blends should be more flexible than methacrylate containing systems providing better conditions for fast ionic transport.

In order to prove this hyphothesis polymer electrolytes based on blends of PEO with various acrylic polymers (poly (acrylic acid)-PAA, poly (metyl acrylate)-PMA, poly (butyl acrylate)-PBA, poly (acryl amide)-PAAM) were tested. Polymer blends were obtained by mixing homopolymers as well as by thermal polymerization of an acrylic monomer in the presence of high molecular weight PEO. Composition of the blend varied from 10 to 50% by weight of the added acrylic component. Polymer electrolytes were prepared by the casting technique applying acetonitrile or acetonitrile-dichloromethane mixture as solvents and $LiClO_4$ as an inorganic dopant. Ionic conductivity of blend based electrolytes was calculated from Impedance Spectroscopy experiments. The best results obtained for each of the studied systems are summarized in Table 1.

The presented results show that conductivity depends on a kind of added acrylic component and on its concentration. In our opinion differences result from formation of hydrogen bonds in the studied systems which may lower ionic conductivity by immobilization of ions or stiffening polymer hosts. However, there are also systems (like PEO-PAAM) in which presence of hydrogen bonds do not imped ionic transport. Generally electrolytes prepared by mixing homopolymers and a salt exhibit conductivities higher than their methacrylate analogues. Blends prepared by thermal polymerization of acrylic monomer in the presence of PEO are thermaly stable only up to 40-50°C which is probably due to a degradation occuring during polymerization . Lowering temperature of the reaction causes formation of a blend structure unfavourable for charge carrier transport.

The highest values of conductivity were measured for electrolytes based on PEO-PAAM blends prepared by thermal polymeryzation of acryl amide in the presence of PEO. It should be stressed that results obtained for analogues systems prepared by mixing homopolymers are only slightly lower. High values of ionic conductivity (10^{-5}-10^{-4} S/cm at room temperature and 10^{-3}-10^{-2}S/cm at 100°C) seem to be due to cooperative interactions between polar amide and ether groups with lithium cation. Similar observations were previously made by Wan et al. [4]. Up to our knowledge this is one of the highest values of ionic conductivity measured until know for polymer solid electrolytes which are not quasi-liquid systems.

Table 1.
Values of conductivity for polymeric electrolytes based on blends of poly (ethylene oxide) with various acrylic polymers.

Kind of acrylic component	X % wt	σ_{rt} S/cm	T K	σ_T S/cm
PMA	20	1.1×10^{-5}	373	4.3×10^{-3}
PMA (*)	30	8.4×10^{-6}	308	1.8×10^{-5}
PBA (*)	20	8.2×10^{-6}	328	8.7×10^{-5}
PAA	10	1.8×10^{-5}	371	1.7×10^{-3}
PAAM	20	5.7×10^{-5}	375	9.0×10^{-3}
PAAM (*)	40	3.4×10^{-4}	371	5.0×10^{-3}

All samples included in the table were doped with 10% mol of $LiClO_4$ in respect to ethylene oxide molecular units.

(*) - blends prepared by thermal polymerization of acrylic monomer in the presence of PEO. The symbols are as follows:
X- concentration of acrylic polymer in blend, σ_{rt}-room temperature ionic conductivity, T-the highest temperature at wich conductivity σ_T was measured

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ACKNOWLEDGEMENT

This work was partially supported by Polish Ministery of Education according to 500/164/136/0 research programme

TWO-COMPONENT EPOXY NETWORK-LiClO$_4$ POLYMER ELECTROLYTE

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ABSTRACT

In an effort to raise the room temperature ionic conductivity and to improve the mechanical properties of the polyethylene oxide-based polymeric electrolyte, a non-crystalline two-component epoxy network-LiClO$_4$ system was prepared through synthesizing two precursors, diglycidyl ether of polyethylene glycol (DGEPEG) and triglycidyl ether of glycerol (TGEG), and then curing the precursors in the presence of LiClO$_4$, which, in addition to supplying ionic carriers, played here an important role as a curing catalyst. The system was mechanically strong and its room temperature conductivity reached up to ca 10^{-5} S/cm[1-3]. A number of techniques such as ^{13}C NMR, IR, DSC, DDV and conductivity measurement were used to characterize the chemical structure of the precursors and to investigate the correlation between the viscoelasticity and ionic conductivity.

On examining in detail the ^{13}C NMR spectra of the DGEPEG, the assignment of the four main characteristic signals was as follows. 44 ppm was assigned to the secondary and 50 to the tertiary carbon of the epoxy groups, 72 to the carbon connecting the -(CH$_2$CH$_2$-O-)-segment with the terminal epoxy groups, and 70 to the carbon in the PEG segment respectively.

Besides, the IR spectra of DGEPEG's show the characteristic bands for epoxy groups, e.g., 1250 cm^{-1} band for symmetric stretching and 910 cm^{-1} band, which is specific to the aliphatic epoxy for antisymmetric stretching of the epoxy groups.

As evidenced by the DSC traces, all the cured films were completely amorphous at room temperature irrespective of whether the main ingredient of the film, DGEPEG is crystallizable or not, indicating that the ability of regular alignment of the chain segment is seriously inhibited by crosslinks. The inhibition action on segmental motion arising from crosslinks is also manifest in the relationship between the length of the PEG segment in DGEPEG and T_g of the cured films, i.e. the longer the segment, the lower the T_g.

From the correlation between viscoelasticity and ionic conductivity of the cured specimen, it was found that in the iso-free-volume plot of the logarithmic shift factor and reduced conductivity against reduced temperature, $(T - T_g)$, the originally separated shift factor curves in the Arrhenius plot now became superposed on the same curved line, whereas the reduced conductivity curves were still separated each other and raised with increasing salt content of the specimen. Interestingly, the curve for the specimen containing the lowest salt content showed a shape as if it were an extrapolation of the shift factor curve. The findings indicate that the segmental motion is the basis of the transport of the coordinated metal ions and that the iso-free-volume plot[4] is a valuable approach to clarify the dissociation condition of the incorporated $LiClO_4$ salt and to discriminate the increment of ionic conductivity due to carrier generation from that due to segment motion.

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ION-CONDUCTIVITY IN LAYER SILICATES CONTROLLED BY INTERCALATION OF POLYOXY ETHYLENE COMPOUNDS

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Polyoxyethylene compounds as crown ethers and poly (ethylene oxide) materials are able to form stable complexes with alkaline and alkaline-earth ions, even when these cations are located in the interlayer region of 2:1 phyllosilicates (1-2). Taking into account the variable strength established between interlayer cations and the guest complexing ligand, the objective of this work consists in the study of the modifications on the inner ionic conductivity of a natural silicate (montmorillonite) depending on the nature of the intercalated oxyethylene compounds.

Intercalation compounds in homoionic samples of Na^+-montmorillonite (Wyoming) are obtained by treatment of the silicate samples, both as powders or as oriented films of aggregated particles, with methanolic solutions of crown ethers (12-crown-4, 15-crown-5, 18-crown-6 and dibenzo-24-crown-8) and acetonitrile solutions of PEO (molecular mass: 10^5). The resulting organo-inorganic materials are characterized by elemental analysis, IR spectroscopy, X-ray diffraction, thermal analysis and ^{23}Na high resolution solid state NMR.

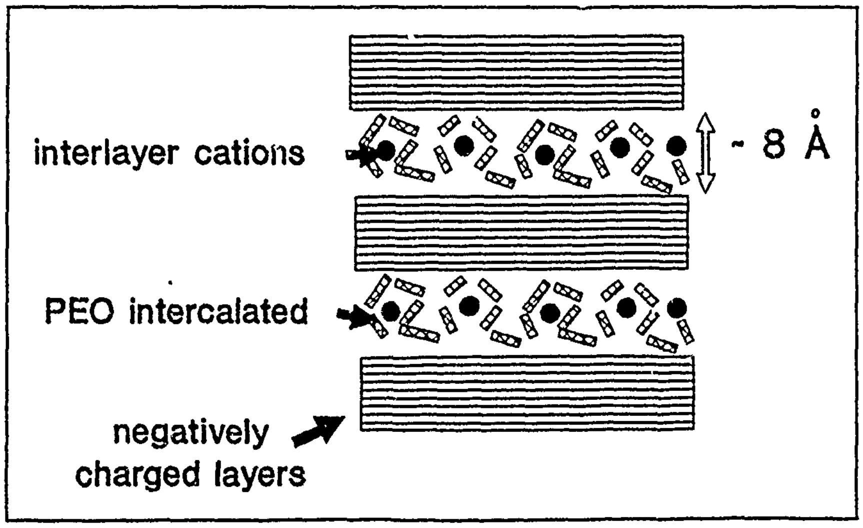

FIG.1. Schematic representation of PEO intercalated complexes in a charged layer silicate.

The electrical conductivity was measured in the 298-700 K temperature range with a Solartron equipement (FRA), under dry nitrogen flow. Circular or rectangular section pellets, pressed at 700 MPa, were used for perpendicular or parallel AC measurements to the (a,b) plane of the silicate, respectively.

The Na^+-montmorillonite exhibits low ion conductivity especially after loss of water molecules belonging the hydration sphere associated to the interlayer cations, in the natural samples. This conductivity is about 10^3 times higher in the parallel direction to the plane defined by the layers than in the perpendicular direction. The anisotropic conductivity is also maintained in the intercalated compounds.

All intercalated materials show higher ionic conductivities compared to the parent silicate, increasing with the temperature until a maximum value around 570 K. At this value, which depends on the nature of the oxyethylene intercalated compound, the conductivity strongly decreases simoultaneously to the progressive decomposition of the intercalated organic material, reaching eventually the characteristic conductivity of the starting Na^+-montmorillonite.

The conductivity of these materials depends on the interactions between cation and the oxyethylene compound. In this way, when the oxygen cavities of the macrocyclic polyethers fit very well the sodium ions, as it is the case of 15-crown-5 and 18-crown-6 compounds and also the 12-crown-4 (which forms a 2:1 stoichiometry complex), the conductivity observed is close to 10^{-6} Scm^{-1} in the parallel direction to the layers. On the contrary, largest cavities (dibenzo-24-crown-8) or in the case of the PEO complexes, weaker interactions or particular conformation can be invoked to explain the significant enhancement of the founded conductivity.

Typical values of ionic conductivity in PEO/Na^+-montmorillonite complexes measured at 570 K in the parallel direction to the plane (a,b) of the silicate, are in the 5×10^{-5} Scm^{-1} order. It is noteworthy that in these materials the contribution of the anions to the conductivity can be considered negligible, because the negatively charged silicate layers constitute the anionic entities (infinite anionic radii), and consequently the transport number for these systems must be assumed to be $t^+ = 1$, in view of the inmobility of the anions. This situation is quite different to PEO-salt complexes where an organic macromolecule acts as a solvent of the salt and dissociates partially, making it possible for the system to operate as a mixed cationic/anionic ion-conductor. In the present intercalated materials exclusively cationic conductivity takes place.

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COMPARATIVE STUDY OF POLY(ETHYLENE OXIDE) ELECTROLYTES MADE WITH $LiN(SO_2CF_3)_2$, $LiCF_3SO_3$ and $LiClO_4$. THERMAL PROPERTIES AND CONDUCTIVITY BEHAVIOR.

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In a recent paper by Armand et al.[1], a new lithium salt, $LiN(SO_2CF_3)_2$, was reported to yield poly(ethylene oxide) (PEO) amorphous electrolytes having conductivity magnitude ca. 5×10^{-5} Ω^{-1} cm^{-1} at 25 °C. This nitrogen-based $(CF_3SO_2)_2N^-$ anion was expected to undergo weaker interactions with alkali cations than the anions currently used in aprotic electrolytes, such as $CF_3SO_3^-$ and ClO_4^-. Another advantage of this bulky and flexible anion over $CF_3SO_3^-$ and ClO_4^- was expected to be lower glass transition temperatures (T_g) of its amorphous mixtures with polyethers.

In the present work, a comparison is made of the phase diagrams of these three systems (Figures 1). Also compared are their T_g-composition relationships (Figure 2), and conductivity isotherms (at 50 and 100 °C) of $LiN(SO_2CF_3)_2$ and $LiClO_4$ over the range EO/Li= 4-64 (Figure 3). All the data were obtained with a low molecular weight PEO sample (M_n = 3.9×10^3, M_w/M_n = 1.02) having a degree of crystallinity of 96%. The conductivity measurements were carried out on completely amorphous (melted or supercooled) electrolytes only. No conductivity measurements were made on $LiCF_3SO_3$ electrolytes because 3/1 crystalline compound readily forms over these ranges of temperatures and compositions.

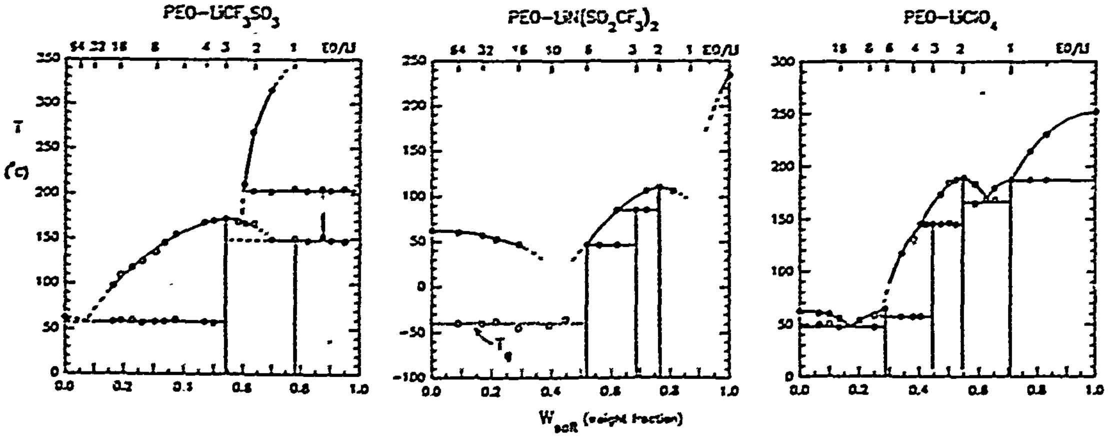

Figure 1. Phase diagrams of the PEO-$LiCF_3SO_3$, PEO-$LiN(SO_2CF_3)_2$, and PEO-$LiCLO_4$ systems. Constructed by DSC measurements made on as-cast mixtures allowed to crystallize for many months at 20 °C.

Phase diagram of the PEO-$LiN(SO_2CF_3)_2$ system exhibits a crystallinity gap over the range EO/Li = 6-16. Another feature of this system, is the presence of an amorphous phase of composition EO/Li = 10 (T_g = -40 °C) for all mixtures with EO/Li > 10. Like the PEO-$LiClO_4$ system, 6/1, 3/1 and 2/1 crystalline compounds form in the PEO-$LiN(SO_2CF_3)_2$ system. However, the 6/1 compound with $LiN(SO_2CF_3)_2$ does not crystallize in mixtures having EO/Li ratios greater than 6. This feature reveals the difficulty for the build up of long sequences of 6/1 complex in the presence of an excess of polymer.

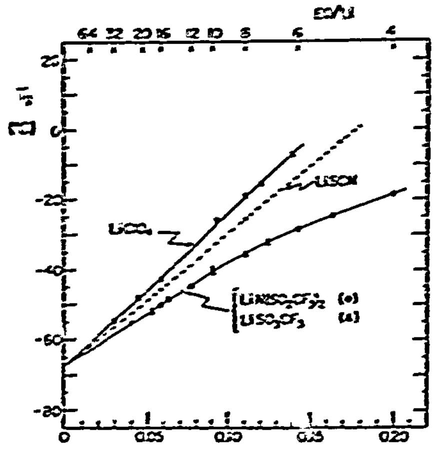

Figure 2. T_g-composition relationships for melt-quenched mixtures.

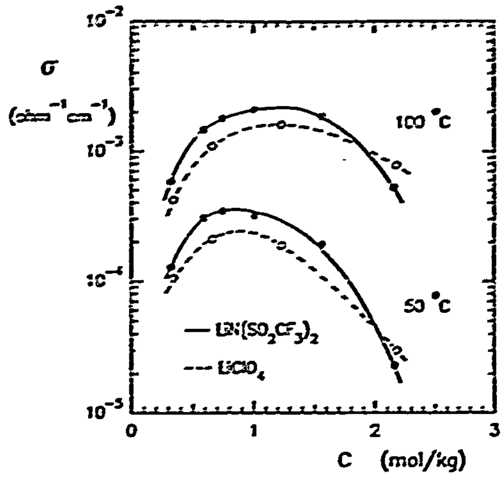

Figure 3. Conductivity isotherms of $LiN(SO_2CF_3)_2$ and $LiClO_4$.

The T_g elevation produced by $LiN(SO_2CF_3)_2$ is considerably less than that produced by $LiClO_4$. On the other hand, for EO/Li > 6, it is about the same as that produced by $LiCF_3SO_3$. This limit corresponds to the greatest salt content for which it has been possible to obtain melt-quenched amorphous mixtures with $LiCF_3SO_3$. Above this range, the T_g-composition curve of $LiN(SO_2CF_3)_2$ exhibits a downward curvature. This behavior confirms that the bulky anion of this salt acts as a plasticizer.

On a mol/kg basis, conductivity of $LiN(SO_2CF_3)_2$ at 50 and 100 °C is greater by a factor of ca. 1.5 than that of $LiClO_4$. A remarkable advantage of $LiN(SO_2CF_3)_2$ over $LiClO_4$, however, is that its mixture with PEO in a EO/Li ratio of 10 (1.4 mol/kg) is noncrystallizable. This particular electrolyte, as well as the amorphous phase in the semicrystalline mixtures with EO/Li > 10, exhibits a conductivity magnitude ca. $4 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 25 °C.

This work was supported by the Research Institute of Hydro-Québec.

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IONIC CONDUCTIVITY OF POLYETHER-POLYESTER NETWORKS

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I. INTRODUCTION

The high ionic conductivity of alkali metal salt complexed with poly(ethylene oxide) has stimulated the wide research of polymer solid electrolytes. Many investigations, including the exploration of materials, the ion transport behavior and mechanism, etc., have been made in the world [1-4]. This paper focuses on the conductivity of a new polymeric material for a solid electrolytes and some interesting results are present.

II. EXPERIMENTAL

Polyethylene glycol capped with maleic anhydride(PEG-c-MA) was synthesized by the condensation reaction of polyethylene glycol and maleic anhydride. The solid polymer materials were prepared by crosslinking PEG-c-MA and methyl acrylate(MA) using benzoyl peroxide as an initiator. The salt $LiClO_4$ was diffused into the crosslinked networks in methanol solution to form complexes. Infrared analysis was conducted with 5DX FT-IR analyzer. The conductance of a material was measured with TR-10T dielectric loss measuring set or CD7A capacitance-conductance measuring instrument. The measuring frequency was 1 KHz.

III. RESULTS AND DISCUSSION

Infrared spectra of PEG-c-MA before and after the crosslinkage show that the crosslinking reaction between PEG-c-MA and MA takes place. In the spectrum, the peaks related with the double bond disappear after the reaction. The swell of the polymer in some solvents also indicates the formation of crosslinked networks.

The conductivity of networks formed by PEG-c-MA with different molecular weight and MA and their complexes with $LiClO_4$ displays that the conductivity increases with the rise in the size of the network. This means that the increase of the size would favour ion transport in the network.

The content of MA in the crosslinked polymers affects the conduction of ions. As the content of MA goes up, the conductivity of the complex drops. This probably relates with the worse conductivity of the polyester complexes[5-6].

Ionic conductivity of the complexes changes with the concentration of $LiClO_4$. It first ascends and then goes down with the increase of $LiClO_4$ concentration. The maximum conductivity is present and the concentration 16%wt(ca.). This is explained by the number of ions and the electrostatic force of charges.

Temperature dependence of conductivity for these complexes is shown in Fig.1. Obviously, the conductive behavior of the electrolytes with lower concentration of $LiClO_4$ can not be described by Arrhenius equation. However, it could properly be explained by WLF equation based on free volume theory.

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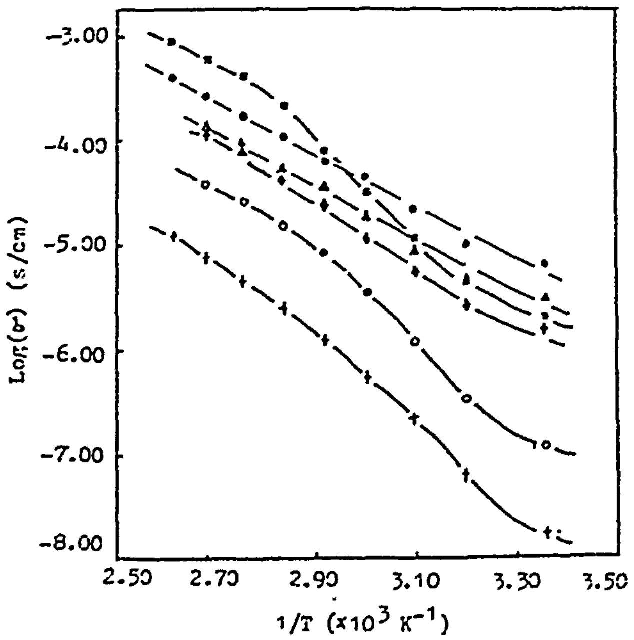

Fig.1 Temperature dependence of the conductivity for the complexes of polyether-polyester network(PEG 400; 30%wt MA) and $LiClO_4$. The concentration of $LiClO_4$(%wt): (†) 1; (∘) 5; (♦) 10; (▪) 12; (•) 15; (▲) 20.

A NEW POLYMER NETWORK FOR IONIC CONDUCTION

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Polyethylene oxide (PEO) has become the exemplary reference structure for ionic conduction. Indeed, if one minimizes crystallization, the high solvating power of the sequence of monomer units coupled with the low glass-transition temperature associated with these chains provides the best-known polymeric medium for ionic dissociation and transport. In previous studies by both groups many features related to the behaviour of this macromolecule used as host for various ions were inspected and interpreted (1,2). The elaboration of cross-linked structures through specific chemical reactions was found to provide a means to thwart crystallization and to preserve the material from creep (2). The most thoroughly studied networks were those arising from the reaction of polyfunctional isocyanates with polyether glycols triols and polyols (others included those formed by the condensation of specific hydrosiloxanes with allylic-type PEO and more elaborate structures bearing anions attached to the polymer chains). All the PEO-urethane networks were characterized by the presence of urethane moieties at the cross-link sites. In other words, the physical point of chain branching coincided with the chemical "anomaly" (urethane group) introduced by the cross-linking reaction. It was felt that the stiffening effect of the urethane functions and their role as barriers to ionic mobility (3) could be attenuated if (i) PEO oligomers bearing directly NCO end-groups could be prepared and (ii) their reaction with OH groups took place away from a branching point.

The synthetic route which opened the way to such structures was based on the transformation of commercial PEO diamines into the corresponding diisocyanates by reaction with bis(trichloromethyl)carbonate and the subsequent condensation of these bifunctional oligomers with commercial PEO triols. The networks resulting from this synthesis had glycerine-ether cross-links joined by PEO chains about 40 units long with a urethane moiety in the middle of each one.

Membranes of these materials were prepared and loaded with variable amounts of lithium perchlorate and lithium bis(trifluoromethanesulfone)imide. The characterization of the various membranes included DSC measurements, viscoelastic properties and ionic conductivity.

The glass-transition temperature of the saltless network was -56°C. Compared with the Tg of PEO-based networks in which the urethane groups were *at* the cross-links, the new structure is associated with a higher overall flexibility. Thus, the fact of having moved the urethane moieties away from the branching points induces a gain in free volume.

The addition of increasing amounts of lithium perchlorate in the network is accompanied by a progressive stiffening as reflected by a growing Tg. More specifically, 1/Tg was found to decrease linearly with the salt concentration. This behaviour is entirely similar to that observed previously with polyether-based networks and is attributed to the establishment of interactions (physico-chemical cross-linking) between ionic species arising from the salt and ether linkager in the PEO chains.

The degree of crystallinity of these networks was very low. This is not surprising given the limited length of the PEO chains aggravated by the presence of a structural irregularity (the urethane group) along each one of them.

The dynamic mechanical properties of the networks, with and without lithium perchlorate, were consistent with the structure proposed, ie an amorphous network essentially characterized by a high-modulus glassy region below Tg and a rubbery domain above Tg. One specific feature was however noticeable, viz the fact that above about 40°C the value of the storage modulus E' was the same for networks without salt and with concentrations of lithium perchlorate higher than 2 M. This clearly suggests that whereas at low temperature, ie below about 40°C, the ionic cross-links play a very important role (see Tg variation with salt concentration), they become negligible when the temperature is raised. The present observation comes as further evidence in favour of a change in the main state of ionic aggregation of lithium perchlorate, which goes from quadrupole to ion pairs as the temperature is raised beyond 40°C(3).

The ionic conductivity of membranes containing various concentrations of lithium perchlorate was studied as a function of temperature. The Arrhenius-type plots always showed a distinct curvature suggesting that the mechanism of ionic transport is not a classical activated phenomenon. A WLF treatment of the data yielded a satisfactory correlation with C1 and C2 values similar to those calculated from the dynamic mechanical master curve. Thus, once again, all indications point to free volume (segmental motions) as the dominant factor affecting ionic conduction.

Logarithmic plots of the ionic conductivity vs the salt concentration at constant free-volume fraction were linear up to fairly high $LiClO_4$ contents, with unit slope. Since the temperatute region covered by these plots was systematically *above* 40°C, it seems logical to attribute this slope to the predominance of ionic species in the form of dipoles (ion pairs), as pointed out above and elsewhere (3).

A comparison of the conductivities of the present systems with those of equivalent $LiClO_4$-containing PEO networks prepared by the direct reaction of PEO glycols with triisocyanates (2) shows that the change in the network architecture conceived in this work brings about a fourfold increase in ionic mobility. The origin of this improvement is not entirely clear at the moment: one possible explanation could be the additional degree of disorder introduced by the presence of urethane groups in the middle of the PEO chains.

The replacement of lithium perchlorate by lithium bis(trifluoromethanesulfone)imide was accompanied by an increase in ionic conductivity, namely by a factor of 2 to 3. This is attributed to the plasticizing role that the anion of this novel salt can play inside the network. The same explanation is given to the fact that the effect of this salt's concentration on Tg was very modest compared with that of lithium perchlorate. In other words, the ionic cross-linking was almost entirely conterbalanced by the plasticizing effect of the $N(CF_3SO_2)_2$ anion.

Given the original features of this new approach to PEO-based networks, the investigation is being pursued in order to extend its scope and arrive at a deeper understanding of its peculiarities.

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"Synthesis and Electrochemical Characterization of New Polymer Electrolytes Based on Dioxolane Homo and Co-Polymers."

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We have recently selected (1) a polyacetal -poly(oxymethyleneoxyethylene), whose trivial name is polydioxolane (PDXL), as host polymer for lithium salts. The PDXL samples were prepared by cationic ring-opening polymerization of 1,3 dioxolane (DXL). We carried out the polymerizations in order to obtain sizable batches of polymer with narrow MW distribution and good enough mechanical properties. According to the GPC measurements (1), the PDXL average molecular weight were respectively $\overline{M}_w = 4.2.10^4$, $\overline{M}_n = 3.10^4$ and therefore I =1.4. The Arrhenius plots of conductivity versus T^{-1} for PDXL/LiTFSI and PDXL/LiClO4 for different ratio n = O/Li are reported in fig.1. In contrast with the conductivity improvements observed (2) when $Li(CF_3SO_2)_2N$ is used in place of $LiClO_4$ in PEO complexes, no significant enhancement were observed with PDXL. Nevertheless, as expected, the former salt decreases the crystallinity as shown on DSC traces (fig.2). The complex PDXL/LiTFSI n = 10 appears completely amorphous meanwhile PDXL /LiClO4 n = 10 is very crystalline. In a further difference with PEO electrolytes, the presence of a crystalline phase does not decrease dramatically the conductivity in PDXL complexes with these two salts.

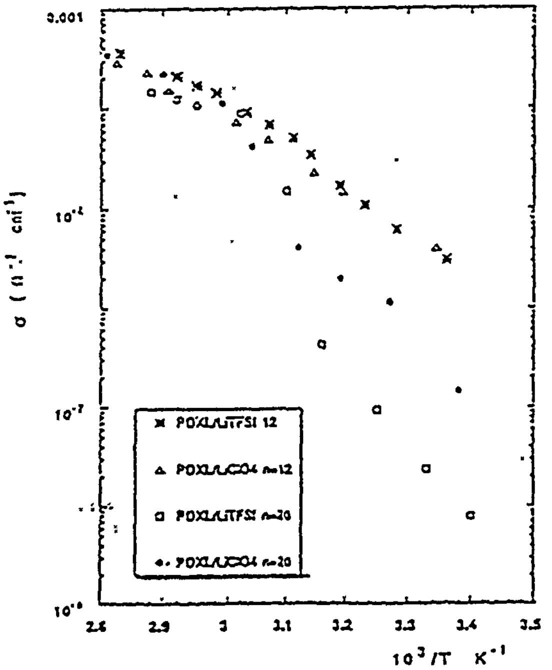


Figure1. Arrhenius plot of the total conductivity for PDXL versus T^{-1} for the salts: $LiN(CF_3SO_2)_2$ (LiTFSI), and $LiClO_4$.

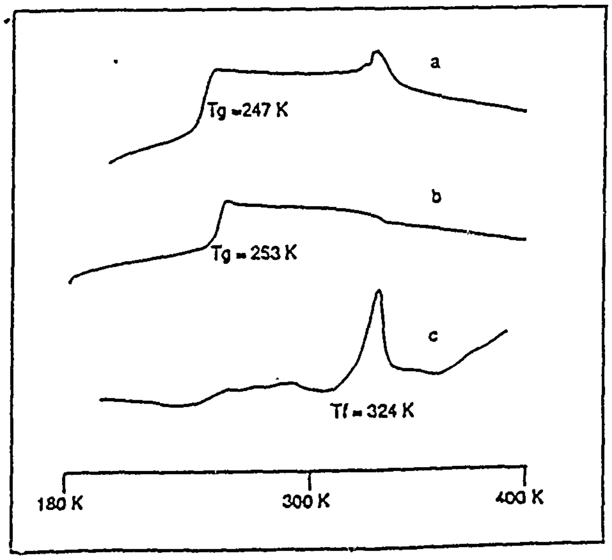
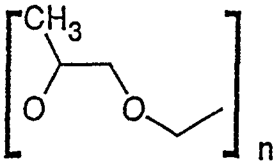


Figure 2. DSC traces recorded at 20 °C/mn
for a) PDXL/LiTFSI n = 12;
b) PDXL/LiTFSI n = 10 and
c) PDXL/$LiClO_4$ n = 10.

In order to obtain an amorphous polymer, we have prepared poly(methyl-dioxolane) PMDXL starting from 4-methyl-1,3-dioxolane (MDXL) whose repeat unit contains a propylene oxide sequence.



The polymerization carried out at -30°C in CH_2Cl_2, using $C_6H_5CO^+SbF_6^-$ as initiator, during 20 hours, affords the polymer as a viscous liquid at room temperature. The average molecular weight calculated by GPC (in polystyrene equivalent) are respectively $\overline{M}_w = 10800$, $\overline{M}_n = 6000$ (I=1.8). The DSC traces of PDXL and PMDXL fig.3, show that the latter is completely amorphous with a Tg = 213 K.

The Arrhenius plot, for two compositions, of PMDXL/LiTFSI are reported in fig.4. The best conductivities are obtained for a ratio O/Li =10 with a value of $3.10^{-6}\ \Omega^{-1}cm^{-1}$ at 25°C. The conductivity tends to level off as the temperature increases, probably due to salt precipitation, considering the weaker solvation properties of this polymer as compared with poly(propylene oxide).

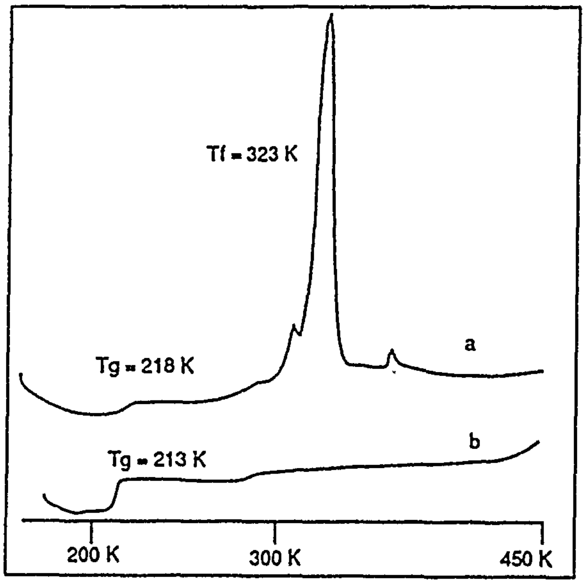


Figure 3. DSC traces recorded at 10 °C/mn for a) PDXL and b) PmDXL.

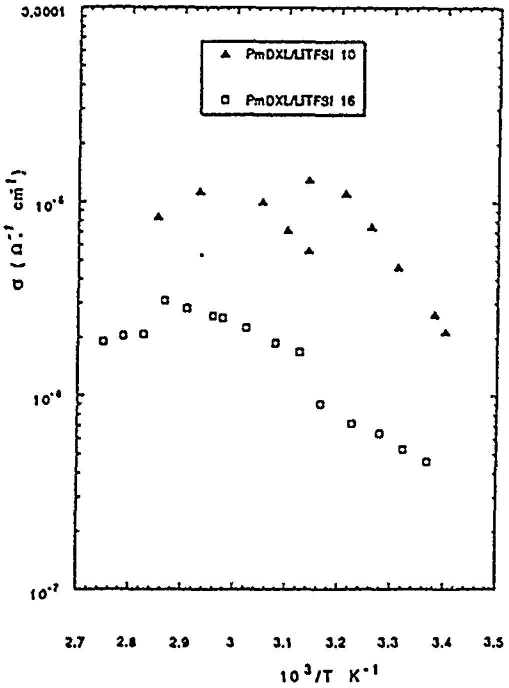


Figure 4. Arrhenius plot of total conductivity for PmDXL versus T^{-1} for the salt LiTFSI.

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Inorganic-organic copolymers (ORMOCERs) as solid state Li^+ electrolytes

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Introduction

Polymeric electrolytes based on polyethylene oxide (PEO) doped with lithium salts are interesting solid state electrolytes(1). Intensive investigations are in progress (2). The main drawback of polymeric matrices like PEO for ion conduction is their partial crystallization at ambient temperatures which causes a drastic decrease in conductivity. Based on investigations of D. Ravaine and al.(3) and the knowledge on protonic conductors synthesized by sol-gel processing (4), inorganic-organic copolymers(5) are modified by incorporation of PEO chains to get an amorphous solvating host material for ions, the properties of which can be adjusted to particular applications or application technology.

Results

Synthesis

The inorganic-organic copolymers in question are synthesized by the sol-gel process. In a first step 3-(methacryloxypropyl)trimethoxysilane (M) and 3-(glycidoxypropyl)trimethoxysilane (G) are hydrolysed with appropriate amounts of water and cocondensed. Then, ethylene glycol diglycidyl ether (E) is added and polymerized to form $(\text{-OCH}_2\text{CH}_2\text{-})_n$ chains which are attached to the inorganic oxidic backbone by copolymerization between the epoxy groups of G and E. 1-methylimidazole is used as efficient catalyst for hydrolysis, condensation and copolymerization of the epoxy groups. Due to the presence of ion solvating $(\text{-OCH}_2\text{CH}_2\text{-})_n$ units lithium salts like $LiClO_4$ can easily be introduced for the preparation of an electrolyte. The material can be applied in the bulk or as a coating material. Final curing is achieved either by thermal treatment and/or by methacrylate (M) polymerization initiated by UV irradiation.

Physico-chemical characterizations

The obtained Li^+ containing as well as the $LiClO_4$ free materials are transparent, yellowish solids. X-rays diffraction analysis of the crushed material shows no crystalline domains. DTA, TG and mass spectroscopy measurements were simultaneously carried out in static air and in flowing argon (heating rate 10 K/min). DTA measurements show no endothermic events, indicating that the material is amorphous as already found by X-ray analysis. According to TG curves (fig. 1) the copolymers are stable until 200°C in air and under argon. As detected by mass spectroscopy, the successive weight loss at higher temperatures is related to the liberation of CO_2 and H_2O (decomposition of the organic chains), and additionally of oxygen and chlorine (reaction of $LiClO_4$) for the doped materials. As expected, under inert atmosphere (argon) the materials decompose slower than in oxidizing atmosphere (air). The faster decomposition (fig. 1) of these copolymers in presence of $LiClO_4$ is related to the strong oxidizing character of the salt.

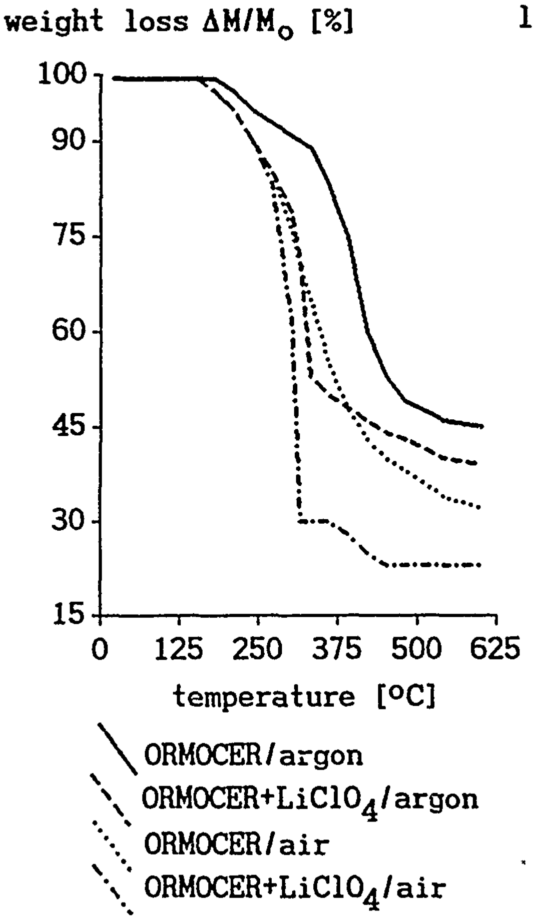

Fig. 1: TG curves in air and under argon

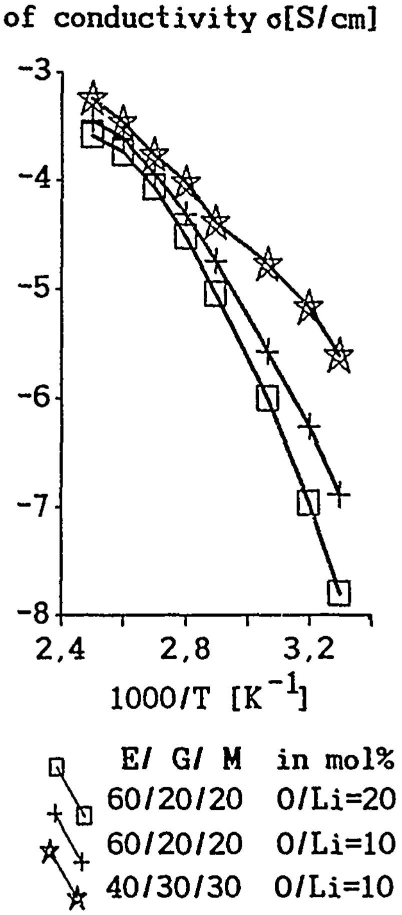

Fig. 2: Conductivity vs. reciprocal temp.

Ionic conductivity

Fig. 2 shows the ionic conductivity vs. the reciprocal temperature for various compositions investigated by the impedance spectroscopy methode with blocking electrodes. The conductivity depends on the lithium perchlorate concentration (i. e. O/Li ratio) and on the ratio between the solvating polymerized PEO precursor and the condensed organosilanes constituting the inorganic oxidic network. First results give conductivities $\sigma = 10^{-6}$ S/cm (not optimized) at room temperature and $\sigma = 5 \cdot 10^{-4}$ S/cm (not optimized) at 125°C.

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IONIC CONDUCTION IN $(PEO)_n\ KCu_xI_{1+x}$ COMPLEXES

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It has been confirmed that, for solid polymer electrolytes, as for liquids, the anionic transference numbers are higher than those of cations. The transference number of lithium in the complex PEO-$LiClO_4$ is around 0.25-0.30 (1,2). That of Hg^{2+} in PEO-$Hg(ClO_4)_2$ is of the same order(3). These results suggest that the anionic transference numbers are always greater than 0.5. The transport process requires the easy formation and breaking of the ion-polymer bonds, and thus weakly solvated cations are those expected to be the most mobile in polymer electrolytes. The mobility of a cation M^{z+} in a PEO medium depends upon the rate of exchange of ligands around this ion. For $z > 1$ and/or for the transition elements, this rate is relatively slow and hence cationic transference numbers are quite low in these complexes. Therefore it seems difficult to perform electrochemical reactions whenever the cation M^{z+} has to reach the electrode, for example metal deposition.

We are introducing a new family of solid polymer electrolytes where M^{z+} is coordinated with an anionic ligand, forming a complex carrying at least one negative charge The resulting complex formula is $(MZ_{z+p})^{p-}$, where Z^- represents the anionic ligand. The high mobility of the anionic species in solvating polymer electrolytes ensures a faster transport : this type of transport is called "*Vehicular Mechanism*".

The complex we have worked on is based on PEO and two iodide salts : $(PEO)_nKCu_xI_{1+x}$ where x represents the Cu/K ratio and n the number of PEO units per K^+ cation. The K^+ cation has been chosen in order to ensure the best conductivity whatever anion present. The ratio O/K=n was chosen in such a way that this value is nearest to the eutectic composition since only amorphous phase exists at this composition (It is generally agreed that it is the amorphous phase which is responsible for ionic conduction (4). The most favourable value for ushas been found to be n=9 giving the complex of general formula : $PEO_9KCu_xI_{1+x}$. We assume that according to the Vehicular Mechanism the mobility of copper is only due to the mobility of CuI_2^- ion.

Conductivity measurements : they were performed using impedance spectroscopy under dynamic vacuum from room temperature to 80°C. For this study, three values of x = Cu/K have been chosen for the complex $PEO_9KCu_xI_{1+x}$ .The figure shows the temperature dependance of the total ionic conductivity of the complex $PEO_9KCu_{0,1}I_{1,1}$ (corresponding to x = 0.1) whose conductivity at room temperature is the highest ($\sigma = 10^{-7}\Omega^{-1}cm^{-1}$). The curve is typical of an amorphous sample and can be described by Vogel-Tamman-Fulcher (VTF) equation, on the basis of a free-volume model of conductivity.

Transference number measurements : different techniques have up to now been used to measure the transference numbers t^+ and t^-. For polymer electrolytes, the classical Hittorf-Tubandt technique is of limited use due to the viscoelasticity of these materials especially when they are not crosslinked. We have used here a potentiometric technique in which the electrolyte suffers no current perturbation. Our aim is to determine the transference number of copper in the complex $PEO_9KCu_xI_{1+x}$. We have used the concentration cell method which has been developed for polymer electrolytes by Bouridah (5).

Our concentration cell is schematized as:

$$\text{Electrode 1} \;/\; \underset{x_1=0.1}{PEO_9KCu_xI_{1+x}} \;/\; \underset{x_2=0.3}{PEO_9KCu_xI_{1+x}} \;/\; \text{Electrode 2}$$

where x_1 and x_1 are related to the electrolyte concentration of 1 and 2 respectively, C_1 being different to C_2.

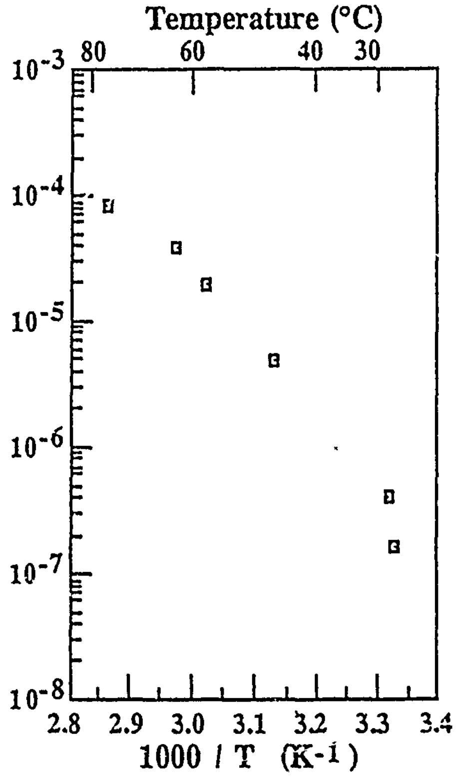
The mobile ions are: K^+, I^- and CuI_2^- (The Cu^+ concentration is negligible since the equilibrium $CuI+I^- \Leftrightarrow CuI_2^-$ is shifted to the right) and the hypothesis are :

i) the ionic movement is exclusively due to the concentration gradient both electrolytes,

ii) the activities are approximated to concentrations (This is fully justified for CuI very diluted media,

iii) the K^+ ion does not appear in the balance since its activity is exactly the same in each partition and the I^- concentration is nearly constant in both partitions (.9 and .7). Consequently, the cell voltage is only a function of the transference number of CuI_2^- and can be expressed as: $E = (RT(1+ t^-)\log(x_1/x_2))/F$.

The measured voltage is 39mV and consequently the transference number for CuI_2^- (approximated to the total Cu) is 0.4.



To conclude, it seems that in electrolytes containing CuI_2^- complexes where the transport of copper is achieved through a Vehicular Mechanism, the conductivities are of the same order than with the simple salts (for example $PEO_nCu(TFSI)_2$ (6)). However the transference number for copper in the electrolytes described above is definitely higher. This could lead us to expect a higher rate of metal deposition.

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COMPLEXES OF POLY (ETHYLENE GLYCOL) WITH ALKALI-EARTH METAL SALTS

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Interaction of poly(ethylene glycol) (PEG) with alkali-earth metal salts ($MgCl_2$, $Mg(ClO_4)_2$, $SrBr_2$) was studied by different physico-chemical methods in solution and solid state. Formation of amorphous molecular complexes for systems PEG-salts was shown. Composition of complexes of systems PEG-metal was determined in methanol solution. Polyelectrolyte effect is observed for poly(ethylenglycole) in presence of cations in solutions. The binding constant for systems polymer-salt was determined.

Electrochemical Studies of Poly(ethyleneglycol) Containing Zinc Salts

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Introduction

Many investigations have been carried out to elucidate the mechanism of ion conduction and the nature of ion-ion and ion-polymer interactions, and to improve room-temperature conductivity of poly(ethylene oxide)-based solid polymer electrolytes. Relatively little is known about the nature of electrochemical reactions in polymer electrolytes. The focus of this work has been to use electrochemical techniques such as cyclic voltammetry and chronopotentiometry to explore the fundamental characteristics and the factors that influence the electrochemistry of the Zn/Zn(II) couple and the diffusion rate of Zn(II) in low molecular weight polymer solvents. Liquid polymer electrolytes have been studied because, unlike polymer electrolytes based on most high molecular weight polymer solvents, they are fully amorphous at room temperature.

In this work, poly(ethyleneglycol) (PEG) containing zinc salts was used as the model system. The chemical structure of PEG is $HO\text{-}(CH_2\text{-}CH_2\text{-}0)_n\text{-}H$ with an average molecular weight of 400. Since PEG has the same bulk structure as poly(ethylene oxide), the behavior of ions in such a system can be correlated with that in the amorphous regions of high molecular weight PEO. The liquid polymer electrolytes are easy to prepare. The salt is added directly to PEG without a secondary solvent. Electrochemical studies on liquid polymer electrolytes are also relatively easy since contact problems between the electrodes and electrolytes are minimized, any physical changes in the system are easily detected, and the re-equilibration of the electrolytes between experiments is more easily achieved than in solid polymer electrolytes.

An electrochemical cell was prepared in which a platinum microelectrode (10 µm in diameter) was used as the working electrode, platinum gauze as the counter electrode and silver wire as the reference electrode. The special advantages of microelectrodes for studying polymeric systems have already been discussed by a number of investigators (3-5) A major advantage of microelectrodes is that the currents measured are very small making them useful for resistive media such as polymer electrolytes.

Results

Various concentrations of zinc triflate in PEG were studied. Lithium triflate was used in an attempt to introduce a supporting electrolyte. As Figure 1 shows, the presence of 0.4M LiTriflate significantly increases the conductivity of a 0.02M ZnTriflate solution. However, it is not yet entirely clear that the LiTriflate is acting as a traditional supporting electrolyte, that is, increasing the conductivity without interfering with the nature of the dissolved Zn(II) species in the solvent, but preliminary evidence suggest it might be. Cyclic voltammetry experiments on these two systems found the peak current for the electrolyte with 0.02M ZnTriflate + 0.4M LiTriflate to be much lower than for that containing only ZnTriflate (Figure 2). The implication is that the cyclic voltammogram without supporting electrolyte is influenced by migration.

There appear to be three reduction/oxidation processes (see Figure 2) involving Zn(II) that occur under these conditions. Reduction/oxidation peak A is due to the redox reaction of a fixed amount of zinc which does not increase with an increase in the deposition time. Peak C appears to result from the deposition of bulk zinc, limited by diffusion. The nature of peak B is not yet clear.

Acknowledgements
This work was supported by a grant from the Defense Advanced Research Projects Agency through a contract monitored by the Office of Naval Research. Additional support from the NSF-MRL program under grant no. DMR88-19885 is gratefully acknowledged.

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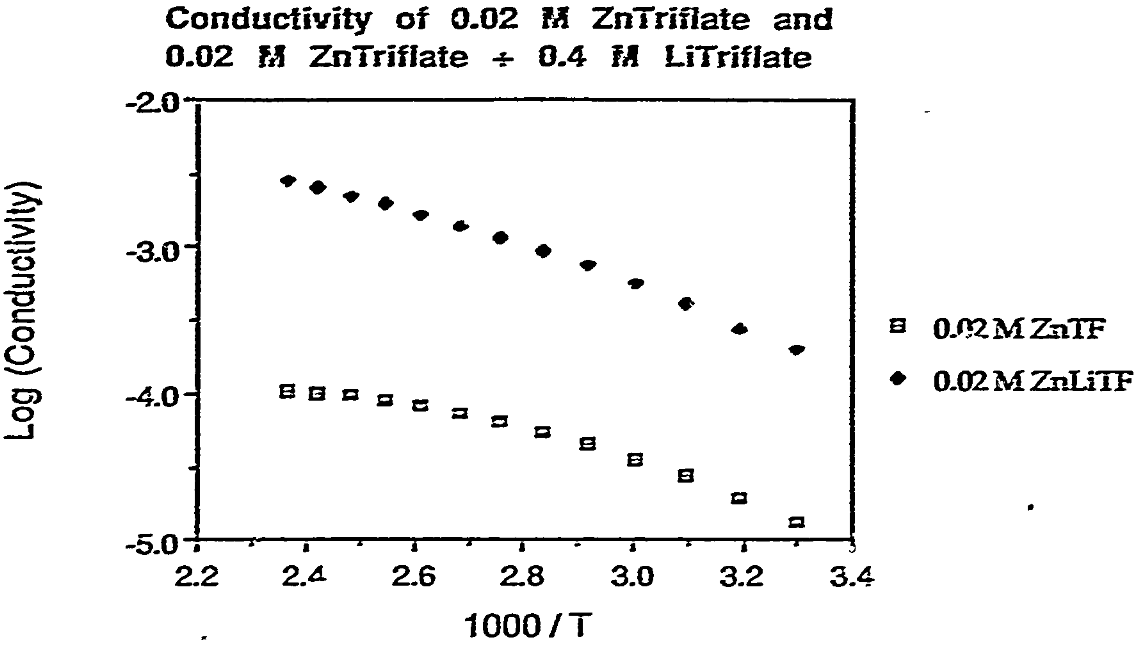

Figure 1

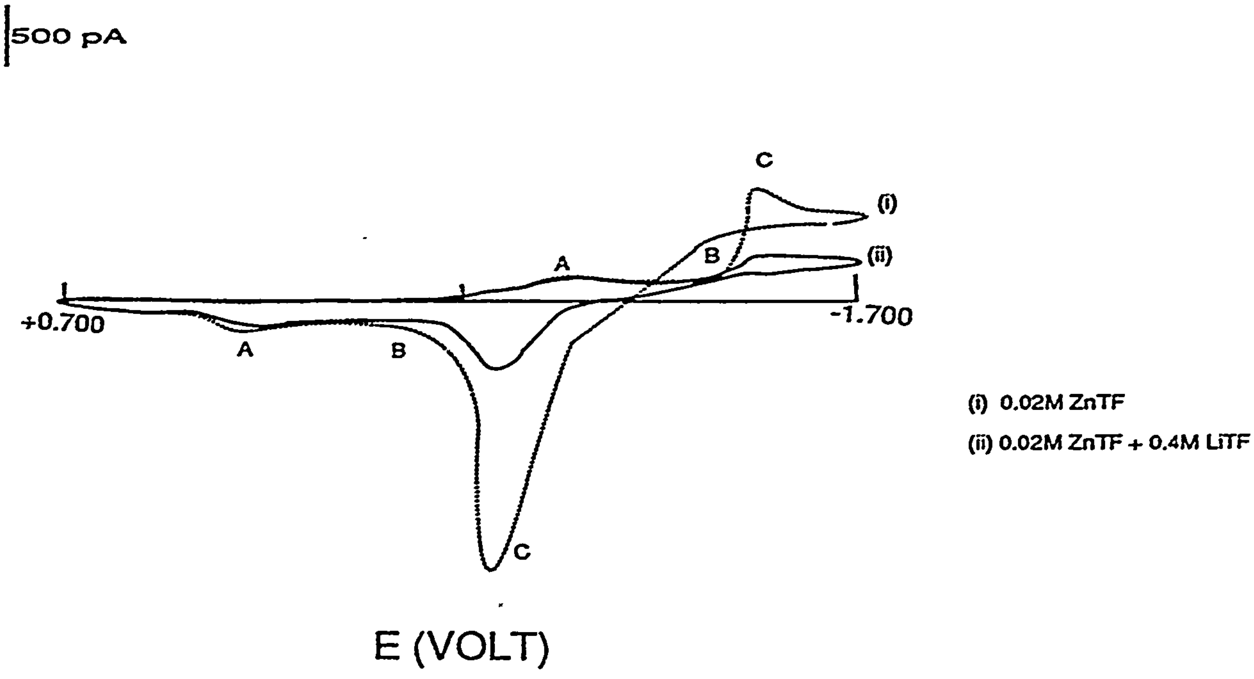

FIGURE 2

PROTON-VACANCY CONDUCTING POLYMERS BASED ON POLYETHYLENE OXIDE AND SULFAMIDE-TYPE SALTS

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Solid Protonic Conductors have been the subject of important developments in the last few years. This interest is justified considering the broad field of potential applications. Their use can be foreseen in classical electrochemical generators or for the preparation of hydrogen. However one of their most immediate domain of application is electrochromism. In host-guest chemistry, including polymer complexes, the proton represents a special case, due to its ubiquity in nature and to its unique chemical behaviour. H^+ differs markedly from other cations in size, making it highly polarizing, leading ultimately to covalent bonds. The large mobility of the proton should lead to an improvement in the conductivity values at room temperature.

Recent studies have focused on anhydrous protonic conducting polymers. A new concept has been put into evidence by mixing strong acids, such as H_2SO_4 or H_3PO_4, with polymers bearing basic sites. Several acid protonic conductors were thus synthesized (1-6). However, neutral to basic proton conducting polymers are expected to be more promising systems, namely in the presence of insertion materials such as oxides and hydroxides whose stability domain ranges from $pK_a=4$ to $pK_a=12$. The family of sulfamide salts constitutes then an ideal case, as the ($-SO_2NH_2$) group exhibits pK_a's of about 10.

The coordination of $NH_2SO_2NH_2$ (sulfamide) and $CH_3SO_2NH_2$ (methanesulfonamide) to linear high molecular weight polyethylene oxide, PEO, results in the formation of complexes which tend to crystallize to some extent. This complexation takes place by hydrogen bonding and is made possible by the considerable flexibility of the PEO backbone allowing the chains to adopt favourable conformations. Conventionally, stoichiometry is given by the ratio n=O/M of monomer units (CH_2-CH_2-O) per cation M and therefore the notation $P(EO)_nMX$, where X stands for the anion. In our case, n will represent the ratio of monomer units per sulfamide molecule (O/S). Better understanding of both systems implies the establishment of phase diagrams. It was found that while the $P(EO)_nNH_2SO_2NH_2$ system presents three eutectics and three intermediate crystalline compounds (Figure 1), six eutectics and six intermediate crystalline compounds are observed for $P(EO)_nCH_3SO_2NH_2$.

In light of vibrational studies reported previously (7,8), the $P(EO)_nNH_2SO_2NH_2$ system is being analysed by Infrared and Raman spectroscopies.

The electrical behaviour of the eutectic compositions of both systems was studied by complex impedance. An ionic transport mechanism based on salt self-protonation and natural production of proton vacancies is suggested. Complexes containing sulfamide appear to be far better conductors. This probably lies in the fact that the methyl group does not participate in the conduction mechanism, consequently reducing the number of charge carriers bound to contribute to it.

This proton-vacancy type conduction is enhanced by the addition of a strong base whose function is to create proton holes without altering the mechanism whatsoever. By doping, conductivity values show a remarkable increase. At room temperature, values of about $10^{-5}\Omega^{-1}$ cm^{-1} are observed for the doped materials (Figure 2). Doping degree will be indicated by the ratio of added base molecules per extracted protons, N/H.

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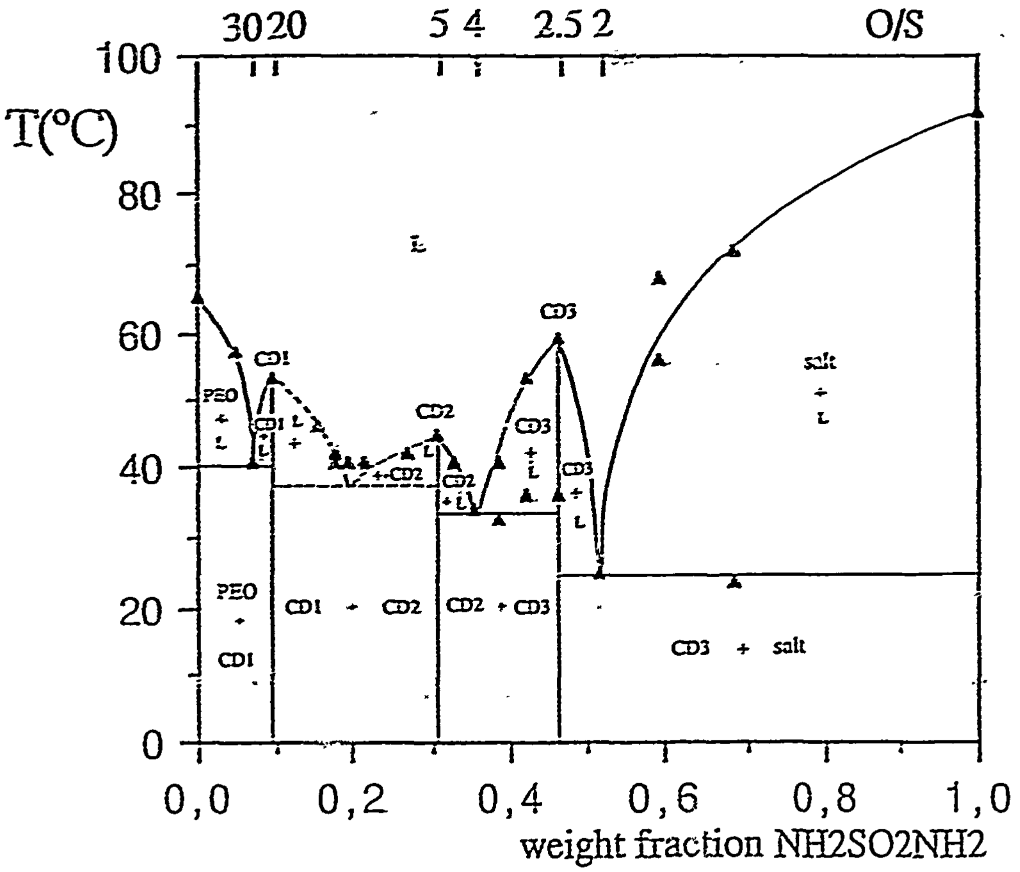

Figure 1 - Phase Diagram for the system $PEO_nNH_2SO_2NH_2$

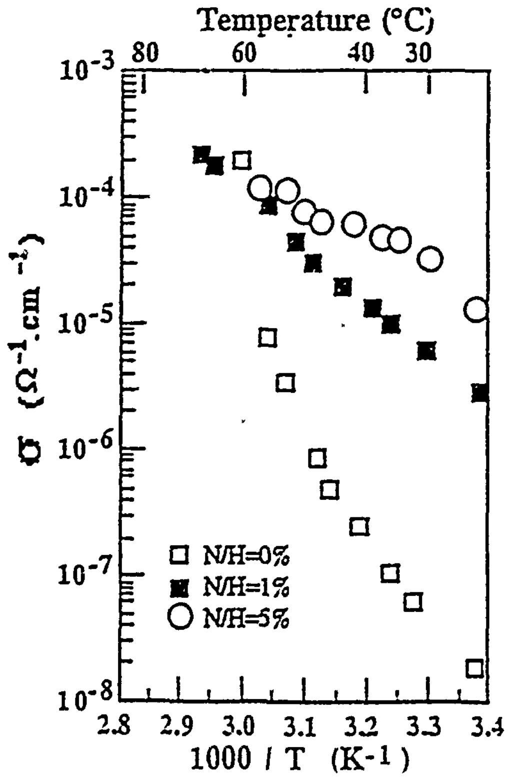

Figure 2 - Arrhenius conductivity plots for the complex $PEO_4NH_2SO_2NH_2$ submitted to different doping degrees

NEW POLYHETEROCYCLES WITH SULPHONIC ACID PENDANT GROUPS AS SOLID POLYMER ELECTROLYTES

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Polyheterocycles on the basis of monomers with sulphonic acid pendant groups show a great promise to be a new class of filmy solid polymer electrolytes with high thermo-,radiation and hydrolytical stability.The original one-stage method of synthesis of high-molecular-weight soluble film-forming polyimide sulphonic acids on the basis of I,4,5,8-naphthalene- and tricyclodecene tetracarboxylic dianhydrides and 4,4'-diaminosulphonic acids was worked out.In dependence on conditions of synthesis it is possible to obtain polymers in the form of lacquers or bulk.Novel high-molecular-weight polynaphthalene- and polytricyclodeceneimide sulphonic acids have been synthesized.Polymers are soluble in dimethylformamide(DMF),dimethylacetamide,non-soluble in water.Thermostable filmy solid polymer electrolytes on the basis of them were obtained.Protonic conductivity was studied in electrochemical single cell working by "hydrogen pump" priciple.The polyimide sulphonic acids membranes were squeezed with two porous disk Ti-Pt-loaded electrodes.The cell contained gas feed inlets and outlets,channels for gas flow behind the porous gas diffusion electrodes.Humidification of hydrogen was carried out by its passing through glass vessels,containing water.Cell potential/current density measurements were made both galvanostatically and potentiostatically with a programmable power supply.The values of conductivity of membranes under conditions of limited feed of hydrogen and different time of experiments were calculated from cell potential/current density plots(Tab.I.).Proton exchange membranes from polynaphthalene- and polytricyclodeceneimide sulphonic acids possess a proton conductivity 0,3-0,5 $Ohm^{-I}sm$, withstand a long-time polarization in the absence of hydrogen, demonstrate a good hydrolytical stability.Physico-mechanical properties of films on the basis of polynaphthaleneimide sulphonic acids were estimated. Films were obtained from DMF solutions. Breaking strength of membranes with thikness about 40μ was 80-90 MPa, elongation at break-20-25%(25°C).

TABLE I
Protonic conductivity of solid polymer electrolytes on the basis of polynaphthaleneimide sulphonic acids(25°C)

Conductivity of non-wermed up membrane, $Ohm^{-1}sm$		Conductivity of warmed up to 400°C membrane, $Ohm^{-1}sm$	
Time of experiment, h		Time of experiment, h	
I	40	I	40
0,3	0,4	0,3	0,4

Study of thermooxidative stability of films gave the possibility to determine that membranes on the basis of polynaphthaleneimide sulphonic acids are stable to rupture stress at high temperature(Tab.2).

TABLE 2
Tensile strength of membranes on the basis of polynaphthaleneimide sulphonic acids at different temperatures

Load, MPa	Temperature of tensile failure, °C
2	560
I0	450
33	405
50	260

Polynaphthaleneimide sulphonic acids not softened up to temperature of the beginning of destruction. These polymers are promising to be a solid polymer electrolytes capable to exploitation in the temperature range 200-400°C.

TEMPLATE SYNTHESIS - A METHOD FOR ENHANCING IONIC AND ELECTRONIC CONDUCTIVITY IN ELECTRONICALLY CONDUCTIVE POLYMERS.

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Introduction. Electronically conductive polymers are interesting chemical systems because they act as both ion and electron conductors. Their ability to act as facile ionic conductors is critical in such proposed applications as polymer batteries and electrochromic devices. Their ability to act as facile electronic conductors is critical if these materials are to replace metallic conductors. We have been investigating the ionic and electronic conductivities of electronically conductive polymer fibrils prepared via a method we call "template synthesis" (1-4). We have used this method to prepare conductive polymer fibrils with diameters as small as 100 A. We will discuss, in this presentation, the template method and the ionic and electronic conductivities of template-synthesized heterocyclic polymers.

Experimental. The template method entails synthesis of an electronically conductive polymer within the pores of a microporous membrane. The membranes used have cylindrical pores with equivalent diameters. These membranes are commercially available filters; e.g. Nuclepore and Anopore filters. We call this the "template method" because the pores in the membrane act as templates for the nascent polymer. Because the pores are cylindrical, conductive polymer fibrils are obtained.

Template synthesis can be accomplished either chemically or electrochemically. We have chemically synthesized fibrils composed of various heterocyclic polymers (1,2) and of polyacetylene (3). Template synthesis can also be accomplished electrochemically (4). In this case the template membrane is attached to the surface of an electrode and this assembly is immersed into a solution of an electropolymerizable heterocyclic monomer. Hollow tubules (2) of electronically conductive polymers can also be obtained via the template method.

Results. An electron micrograph of typical polypyrrole (PPy) fibrils is shown in Figure 1. These fibrils are 2000 A in diameter and are connected at their bases to a common Au electrode. Ion transport to this fibrillar "film" was investigated electrochemically. The PPy was first oxidized by equilibrating the film at a potential of 0.15 V vs. SCE. The contacting electrolyte was 0.2 M Et_4NBF_4 in CH_3CN. The potential of the Au electrode was then stepped to -0.65 V vs. SCE where PPy reduction occurs at the diffusion-controlled rate. Figure 2 shows charge-time transients for the fibrillar film and for a conventional PPy film containing an equivalent mass of polymer. Ion-transport is more facile in the fibrillar film.

Electronic conductivity in electronically conductive polymer fibrils was measured using a two point conductivity method (1). A plot of fibril conductivity vs. fibrils diameter is shown in Figure 3. As can be seen in Figure 3, conductivity increases sharply for small-diameter fibrils. This enhanced conductivity has both molecular and supermolecular origins. The highest conductivity we have obtained to date is 6600 S cm^{-1} for 300 A-diameter poly(3-methylthiophene) fibrils synthesized at -26° C.

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Figure 1. Scanning electron micrograph of PPy fibrils.

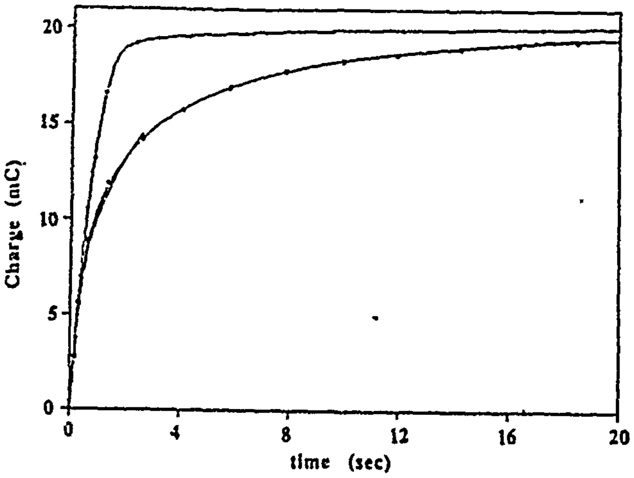

Figure 2. Charge-time transients for reduction of fibrillar (upper) and conventional (lower) PPY films.

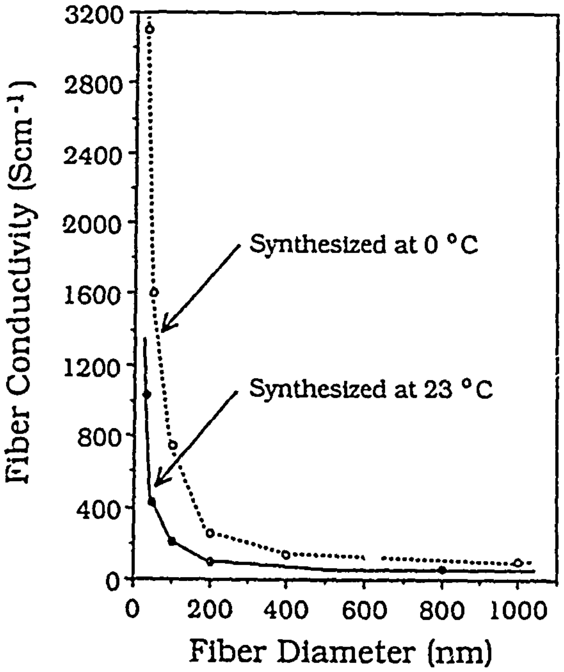

Figure 3. Plot of conductivity vs. diameter for 300 A-diameter PPY fibrils.

ORGANIC-INORGANIC PROTONIC POLYMER ELECTROLYTES AS MEMBRANE FOR LOW-TEMPERATURE FUEL CELL

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Direct methanol fuel cells are highly desirable for transportation applications. Methanol can be produced from coal or natural gas; it has a high volumetric energy density and allows easy refueling.

A solid state direct methanol fuel cell with an operational temperature ca 100°C looks promising in terms of electrode current density (1), electrolyte stability and conductivity (2). This temperature allows gaseous fuel to be used in a pressurized system.

In order to be used in methanol fuel cell, the membrane polymer electrolyte must be crosslinked, to avoid chemical degradation and methanol diffusion across it.

The electrolyte membrane must exhibit the following performance:

- resistance:	1-3 Ohm.cm^2
- conductivity:	10^{-2} S.cm^{-1}
- thickness:	100-300µm

Recent studies in our laboratory, have been focused on ORMOLYTES (ORganically MOdified silicates electroLYTES) as organic-inorganic protonic polymer electrolyteswell adapted forshaping into thin films and membranes.

The membrane should be chemically stable and provide the maximum possible concentration of ionophoretic groups, which implies crosslinking to preserve insolubility and mechanical properties.

This polymer is prepared by the sol-gel method by polycondensation of a mixture of silicon alkoxides whose functions are to crosslinke, plasticize and reinforce the polymeric network.

While mechanical and thermal stability is provided by the inorganic backbone(Si-O-Si), the organic chains induce the flexibility of polymers and bear the ionic groups.

The benzylsilane ($Si-CH_2-\Phi$) linkage was chosen as the best compromise between thermal stability and resistance to acid cleavage. The sulfonation of benzyl groups induces protonic conductivity of 5.10^{-3}S.cm^{-1} at room temperature and in humid atmosphere.

The presentation will concern synthesis, characterization and properties of such polymer system.

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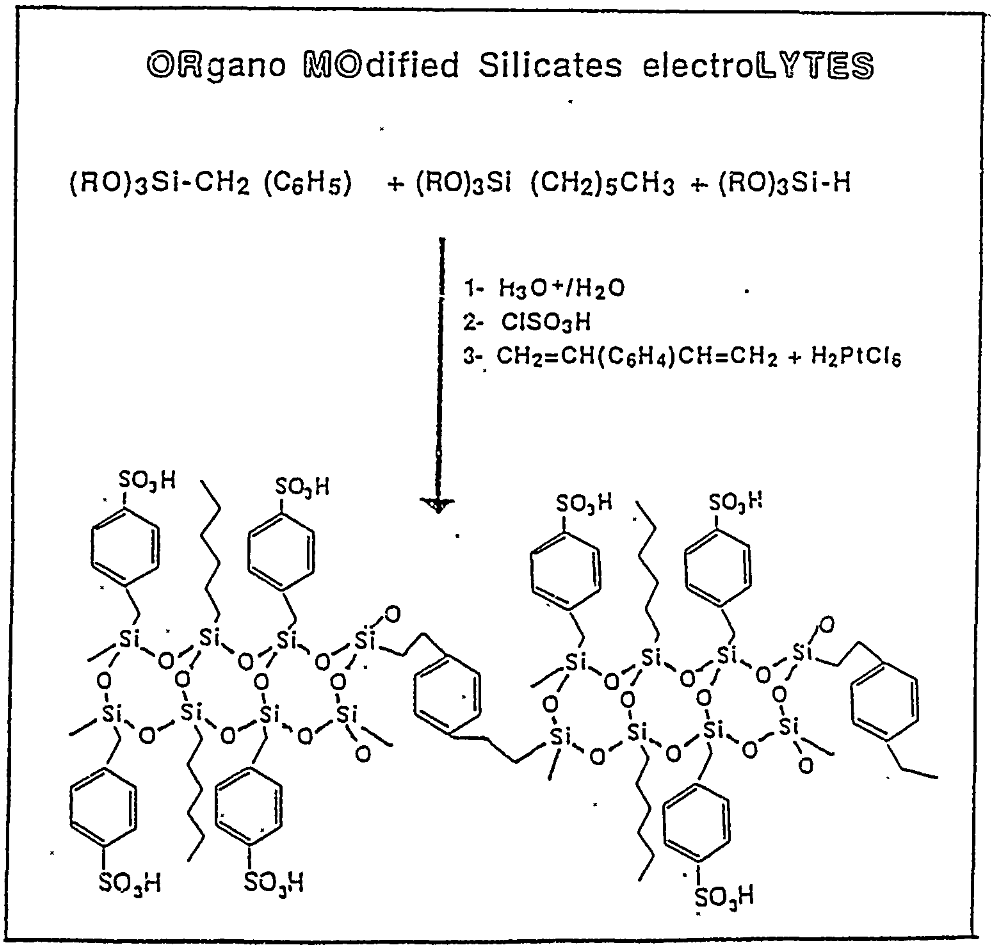
Concept:

The reactions for direct electrochemical oxidation of methanol in a solid state fuel cell without reforming are the following:

Anode reaction : $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$
Cell reaction: $CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2H_2O$

Synthesis :



ORgano MOdified Silicates electroLYTES

$(RO)_3Si\text{-}CH_2\,(C_6H_5) + (RO)_3Si\,(CH_2)_5CH_3 + (RO)_3Si\text{-}H$

1- H_3O^+/H_2O
2- $ClSO_3H$
3- $CH_2{=}CH(C_6H_4)CH{=}CH_2 + H_2PtCl_6$

PROPERTIES AND APPLICATION OF A PROTON CONDUCTING POLYMER: THE BPEI, x H3PO4 SYSTEM.

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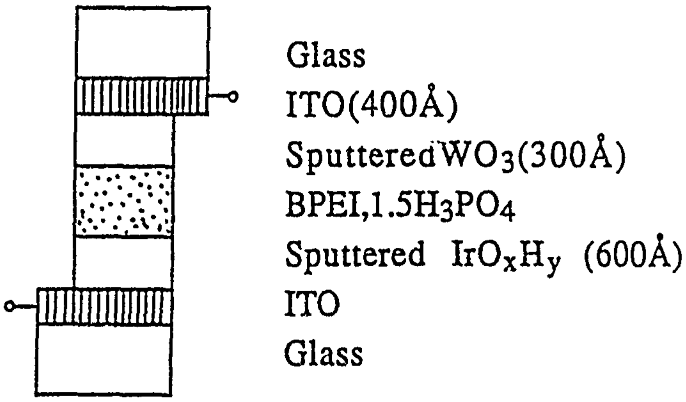
In the new family of proton conductors constituted by mixtures of a strong acid with a basic polymer (1), we have focussed our attention on the BPEI, x H_3PO_4 system with $1< x <2$ moles of acid per polymer repeat unit. BPEI is the commercial Branched Poly(Ethyleneimine) in which only up to about 70 % of the basic amine sites can be protonated by strong acids (2). Thus the studied systems correspond to solvated or plastified polycations in excess acid.

In the acid concentration range $1< x <2$ the conductivity is nearly constant and about 4×10^{-4} Scm^{-1} at 300 K and 10^{-2} Scm^{-1} at 373K. The $\log(\sigma T) = f(1/T)$ plots exhibit a marked curvature with a limitting slope Ea of 0.7 eV at 300K and 0.5 eV at 373K.
In order to define the best conditions for preparation and handling of thin films for applications, we have studied the hygroscopicity of these materials . An aqueous solution layer left in normal atmospheric conditions loses spontaneously excess water down to a limiting value of about 10%. Drying is then achieved by heating at 70°C under vacuum during 4 or 5 hours. Conversely, when the dry film is exposed to a controlled water vapour pressure, the water uptake reaches the same limiting value of about 10% after a few hours. This evolution is followed by Infrared spectroscopy which allows the kind of interactions of the water molecules to be characterized.

The electrochemical stability was determined for a BPEI, 1.5 H_3PO_4 anhydrous system by cyclic voltametry study in a three electrode system (Pt working electrode, stainless steel counter electrode and hydrogen saturated Pd as reference electrode). The obtained voltammograms between -0.5V and 1.5V show that this system is electrochemically stable in a voltage range of about $\Delta E = 1.2V$. Besides the reduction of protons to molecular hydrogen and the reoxydation of hydrogen another reversible electrochemical reaction is happening with cathodical reduction at nearly 800 mV and anodical reoxidation at 200 mV.

An application of the BPEI,1.5 H_3PO_4 electrolyte has been developped in a smart window electrochromic prototype of following structure:



and a surface of about 10x10 cm^2.
Transmittance and reflectance measurements have been performed in the visible / near infrared spectral range on the bleached and coloured system for applied voltages between -0.5 V and 1.5 V.
At λ = 622.8 nm the reflectance is nearly independent of the coloration state and of about 12 %. whereas the transmission decreases from 50 % (bleached system) down to 5.6 % (coloration under 1.4V). The optical efficiency measured on a series of samples is 70 + 15 cm^2/C.
More than 10^5 bleaching / coloration cycles have been performed at room temperature without any degradation of the above performances.

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BRANCHED POLY(ETHYLENE IMINE)-CF_3SO_3Li COMPLEXES

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The conduction properties of polymer electrolytes involving different types of Poly(EthyleneImines), PEI, and NaI (1) or $NaSO_3CF_3$ (2) have already been investigated. We present here a comparative study of complexes between the commercial Branched polymer BPEI and lithium salts.

The conductivity has been measured as a function of salt concentration (N/Li = 30 to 4) and temperature (373 to 273K). As in the case of the sodium salt (2), the best conduction occurs at low salt concentration ($\sigma^{298K} \approx 10^{-6}$ $S.cm^{-1}$ for N/Li ≈ 20) and the temperature dependence exhibits a non-Arrhenius behavior (*Fig.1*).

A fit with the Vogel-Tamman-Fulcher (VTF) equation gives the parameters reported in *Table I*. It can be seen that the thermodynamic glass transition temperature T_0 follows nicely the variation of the T_g values measured by DSC.

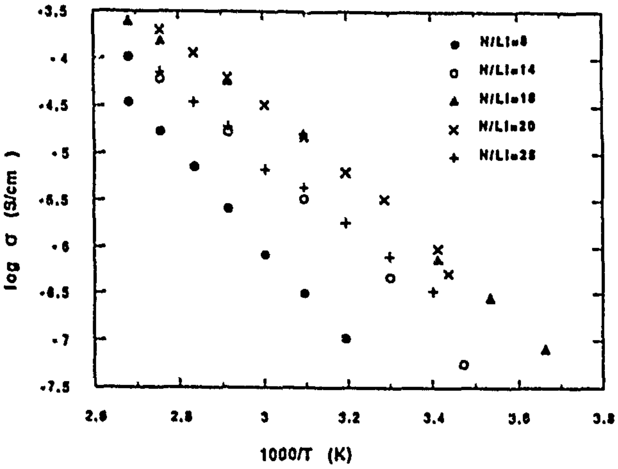

Fig. 1 : Temperature dependence of the conductivity for various salt concentration in BPEI-$LiSO_3CF_3$.

N/Li	A($S.cm^{-1}.K^{1/2}$)	E (eV)	T0 (K)	Tg (K)	Tg/T0
8	70,6	0,166	206,3	268,2	1,3
14	26,4	0,149	189,9	246,9	1,3
16	18,7	0,132	189,4	246,2	1,3
18	13,8	0,130	183,2	238,2	1,3
25	13,5	0,141	182,2	236,9	1,3

Table I : Parameters of the VTF equation and glass-transition temperature T_g of various BPEI-$LiSO_3CF_3$ complexes.

Infrared spectroscopy has been used to characterize the polymer-salt interactions. Transmission spectra have been recorded from a thin film of the material spread on a silicon window the temperature of which can be regulated between 80 and 400 K under vacuum. This allows complete in situ removal of solvent and water.

The most sensitive vibrations of the $-CH_2-NH_2$ or $-CH_2-NH-$ BPEI segments are the νNH_2, νCH_2 and νCN stretching modes in the 3400-3100, 3000-2800 and 1200-1000 cm^{-1} regions respectively. When salt is progressively added to the polymer, the first two families of vibrations are shifted to higher wavenumbers and the third one to lower wavenumbers. This can be interpreted as resulting by a change from the original N-H....N hydrogen bond network of the pure polymer to Li^+...N-H....X^- interactions in which the nitrogen atom is submitted to two opposite effects: decrease of electron density for the Li^+ solvation and increase of electron density for the anion X^- solvation by hydrogen bonding. The first effect is stronger than the second and the latter is of variable strength according to the anion basicity as shown by frequency differences between $LiSO_3CF_3$ and LiSCN.

The lithium solvation is directly observed in the far-infrared spectra under the form of a broad absorption centered at about 480 cm^{-1} which corresponds to the Li^+ vibration in the cage of solvating nitrogen atoms. Substitution of Li by Na shifts this absorption to 180 cm^{-1}, as expected from the reduced mass ratio. For salt concentrations higher than about N/Li ≈ 10 a new absorption appears at 450 cm^{-1} with Li. It can be assigned to ion pairs and ionic aggregates. Simultaneously, some internal modes of the triflate anion are broadened.

In conclusion, the complexes of BPEI with lithium salts are relatively poor conductors but they present good chemical and thermal stabilities and can easily be processed as thin films for applications as electrolyte. Furthermore, the usual technique of plasticization by a solvent such as PEG can be applied to improve the conductivity by one or two orders of magnitude.

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Electrical pumping of hydrogen gas by means of a solid electrolyte membrane

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Two gas compartments containing hydrogen are separated by a polymeric electrolyte membrane. Each face of the membrane is covered by a thin layer of a porous metal, as for example electroless silver deposits. These have external electrical contacts. A manometer, consisting of a U-tube containing water, is connected to the compartments so as to indicate the difference of pressure. When a potential difference is estabilished between the two faces of the membrane and a fixed current is allowed to flow through the membrane the pressure in the compartment next to the cathode grows to a limiting value.

Our membrane consisted of an ionic polymer made of sulphonated poly-perfluor-ethylene, which is sold by DuPont under the brand name NAFION. It was 0.15mm thick and had the form of a disk 15 mm in diameter. The gas compartments plus the manometer dead space had a volume of about 1 ml each. A membrane when kept in air showed a resistance of about 2 kilo-Ohms across it when measured with an electronic multimeter.

We have performed extensive measurements of pressure difference versus time for various currents. In preparation to a typical measurement a membrane with silvered faces was hydrated by keeping it under water for some 30 minutes at room temperature. Then it was clamped into its cell which established the two gas compartments, one on each side of the membrane, and provided the connections to the manometer. We then flushed both compartments during an additional half hour or so, using hydrogen from a cylinder.

When the current i was established and kept for about an hour the pressure difference increased to its limiting value as shown in the table for a typical run where the current was 165 mA. The relationship between pressure difference and time t is also described by this empirical equation:

$$p = A\ i\ \exp(-s/it)\ (1 - \exp(-bt))$$

where the constants A, s and b have the following values: $A=17.746$ cm H_2O, $s=47.048$ Coulomb cm^{-2}, $b=1.411$ $milliseconds^{-1}$.

We acknowledge support by CNPq and FAPESP, two brazilian financing agencies. We thank Dr. R. Giesbrecht of DuPont, Brazil, for graciously supplying us with Nafion samples.

Table. Pressure difference, in cm water, as a function of time.

T(sec)	P(cm H_2O)	T(sec)	P(cm H_2O)	T(sec)	P(cm H_2O)
0	0.0	600	0.9	1200	2.0
60	0.1	660	1.0	1260	2.0
120	0.1	720	1.1	1320	2.1
180	0.2	780	1.3	1380	2.1
240	0.2	840	1.4	1440	2.1
300	0.2	900	1.6	1500	2.1
360	0.4	960	1.7	1560	2.1
420	0.6	1020	1.8	1620	2.1
480	0.7	1080	1.9	1680	2.1
540	0.8	1140	1.9	1740	2.1

APPLICATIONS OF POLYMER ELECTROLYTES IN BATTERIES AND SUPERCAPACITORS

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IS HIGH CONDUCTIVITY THE MOST CRUCIAL REQUIREMENT FOR A PRACTICAL POLYMER ELECTROLYTE?

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Following the discovery of Wright(1) in 1975 and the first characterization of Armand (2) in 1978, the interest in polymer electrolytes and in their application for advanced-design, high-energy lithium batteries, has been progressively increased. In fact, thin-film, polymer electrolyte lithium cells have already reached an advanced state of development and prototypes are currently under production in various industrial and academic laboratories.

However, in this first stage, the research on polymer electrolytes has been mainly focused on the transport characteristics with the major objective of developing new materials having high conductivity at ambient and sub-ambient temperature. Indeed, in this respect the results have been very encouraging and in a few years substantial progress has been achieved with the characterization of various classes of polymer electrolytes(3-6).

However, a high conductivity, while in principle important for assuring a low internal resistance to the polymer electrolyte battery, is in practice not sufficient to guarantee acceptable operational behavior to the battery itself, especially in terms of cyclability and power. The crucial parameter in this respect is the stability towards the electrode materials. Even the most conductive electrolyte is of no practical use if not compatible with the electrodes.

This is a very well known fact in liquid-electrolyte lithium batteries where passivation phenomena, especially at the lithium side, have greatly restricted the types of electrolyte media which can be successfully used for the development of systems of practical interest.

While extensive investigation has been carried out on the characteristics of the electrodic interfaces in liquid electrolyte batteries, very few studies of this type have been so far carried out in polymer electrolyte batteries. On the other hand, there are preliminary but convincing results, obtained in our laboratory(7-10) as well as in others(11,12), that lithium passivation phenomena - which are phenomenologically similar to those commonly experienced in liquid electrolytes- also take place in polymer electrolyte cells. Impedance studies of Li/PEO-LiX interfaces have shown that the metal electrode passivates with the growth on its surface of a non-conductive layer. However, the nature and the mechanism of the passivation phenomena are still unclear: one can only postulate that they appear to depend, by a non-predictable manner, on the type of electrolyte involved, the temperature of operation and the residual impurities.

On the other hand, it is clear that these passivation phenomena affect considerably the cycling life of the polymer electrolyte cells. Therefore, particular attention has to be devoted to the study and the improvement of the interfacial properties and in this work we report some considerations and results obtained in this direction.

ACKNOWLEDGEMENTS.

This work has been carried out with the support of ENEA, the Italian Government Agency for Nuclear and Alternative Energy Sources.

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APPLICATIONS OF SOLID STATE ELECTROLYTE GENERATORS FOR ELECTRIC UTILITIES

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Energy storage is a very desirable interface between production and consumption of electricity. Among the different kinds of energy storage systems, electrochemical generators remain the best solution for low scale distributed storage and autonomous systems.

So far, electric utilities are interested in the development of advanced secondary batteries. Applications may concern the network management as well as electric vehicle (EV) which could substitute progressively combustion engines during the next decades, especially in urban environment. The amplitude of this latter development will mainly depend on the batteries available on the market at that time.

Solid polymer electrolyte generators (batteries and supercapacitors), using an all solid state thin film technology, appear to be one of the most suitable systems for high requirements applications. We will evaluate the possible impact for electric utilities of the specific advantages of these systems related to the applications concerned.

ELECTRIC VEHICLE

An example of possible energy and weight caracteristics of an EV using a lithium polymer battery is shown on table 1.

total weight of the vehicle	1000 kg
average energy consumption	0.1 Wh/km.kg
battery weight	300 kg
specific energy	150 Wh/kg
specific power	100 W/kg
theoretical autonomy	**450 km**

Table 1

The autonomy provided by lead-acid or NiCd batteries with the same ratio of battery weight/total EV weight would be in the range 100-150 km. In this case, the battery must be recharged daily. With lithium polymer batteries, one can think of a weekly recharge for urban utilisation.

The impact of EV development and of the kind of recharge on electricity consumption has to be investigated. As an illustration, typical electricity consumption in France for a winter week is shown on Fig.1. The fluctuations between, in one hand night and day, and on the other hand, week day and week-end, must be underlined.

The power call for one million EV recharging at a 5 kW rate would be 5 GW. Thus, a favorable repartition of EV recharge periods could be a non negligeable factor to improve the network management.

NETWORK MANAGEMENT APPLICATIONS

Electric utilities have needs of improved batteries for signalisation, communications, standby power, substation powering, high quality voltage grids.

For these applications, polymer generators are interesting for control and safety considerations:

- no maintenance
- very low self discharge
- no effluents
- possible control of the discharge state and residual life

FUTURE EXPECTATIONS

The first objective is to succeed in scaling-up the batteries so that prototypes in the 1 kWh range could be cycled. Problems of conectics and thermal management have to be carefully investigated.

Supercapacitors which are supposed to undergo less technological problems than lithium secondary batteries should be considered actively. Their principal interest lies on cyclability and instantaneous available power.

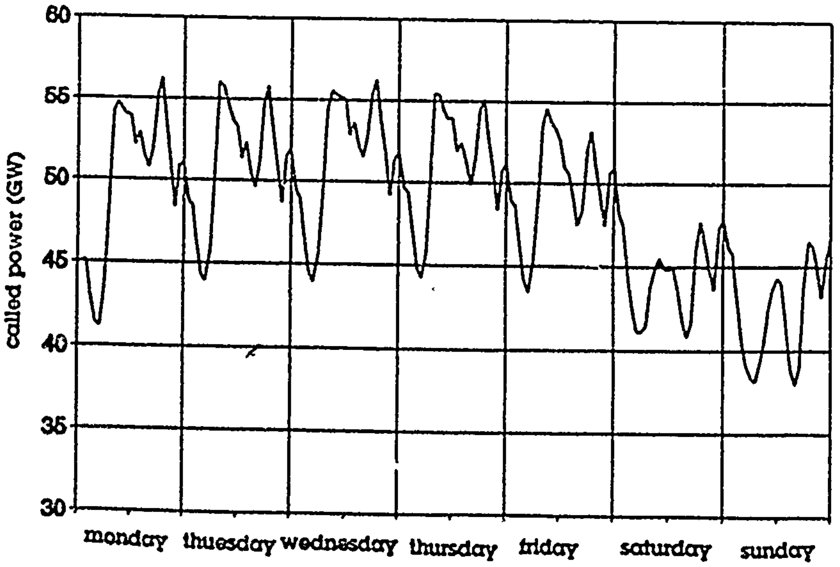

Figure 1. Weekly modulation of electricity consumption in France in December 1989

POLY N-OXYALKYLPYRROLE ELECTRODES AND (PEO-SEO)$_{20}$LiClO$_4$ POLYMER ELECTROLYTE IN LITHIUM RECHARGEABLE BATTERIES.

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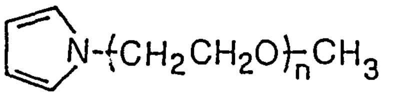
Polymer electrolytes as well as heterocyclic polymer electrodes can easily be prepared in the form of thin films, an attractive feature in advancing the development of new types of flexible plastic-like Li batteries.

It is, however, well known that the kinetics of charge-discharge processes of these polymer electrodes are controlled by the ionic movement into the polymer matrix. This is an intrinsic limitation of these electrode materials, especially in the solid state-battery configuration. The cyclability performance of polypyrrole (pPy) electrodes is very different in liquid and solid-state configurations [1], although the difference is not so marked with polybithiophene electrodes [2].

In order to improve the performance of pyrrole-based polymer electrodes in solid-state batteries with PEO-based polymer electrolytes we electrosynthesized new "tailor made" substituted polypyrroles with polyether groups [3,4,5]:



n=1,2,3

Because of their known cation coordinating properties the ether groups were expected to enhance the ionic movement into the polymer electrodes. In addition the compatibility of ether groups of these polymers with PEO-based electrolytes was expected to improve the electrode-electrolyte interface.

Electrosynthesis conditions and electrochemical characterization of three substituted polymers, polyN-(3-oxabutyl)pyrrole (pNOPy), polyN-(3,6-dioxaheptyl)pyrrole (pNDPy) and polyN-(3,6,9-trioxadecyl)pyrrole (pNTPy) will be reported and discussed; data for pPy electrode will be also shown for comparison.

Solid-state lithium batteries with thin films of pNDPy and pNTPy and with (PEO-SEO)$_{20}$LiClO$_4$ polymer electrolyte (designed for room temperature applications [6]) were tested at 25°C and 36°C by repeated charge-discharge galvanostatic cycles in the potential range from 2.2 to 4.2 V at different current densities. At 25°C the shelf-life of these solid-state batteries was also tested.

Cyclability and stability data of these batteries as well as shelf-life data will be reported and discussed.

Figure 1 shows the capacity data evaluated by recovered charge during discharge at 26 µA cm^{-2} and figure 2 shows discharge curves at different current densities at 25°C working temperature.

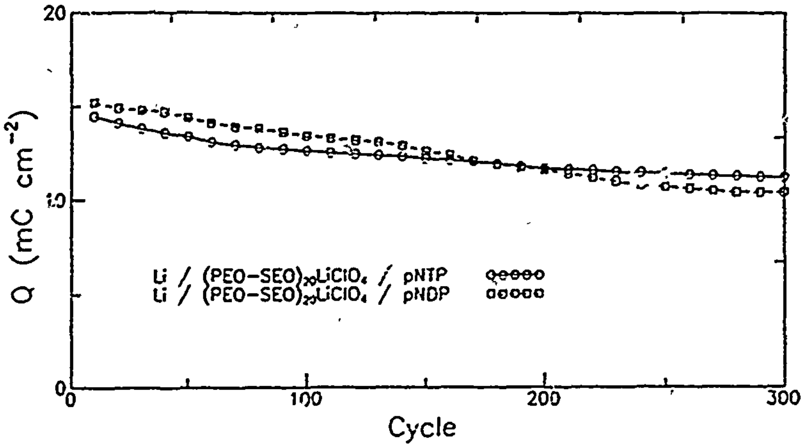


Figure 1. Capacity values of Li/$(PEO-SEO)_{20}LiClO_4$/pNDPy and and Li/$(PEO-SEO)_{20}LiClO_4$/pNTPy batteries ($1.2 \cdot 10^{-6}$ mol monomer unit cm^{-2}) at different number of galvanostatic cycle at 26 µA cm^{-2} at 25°C.

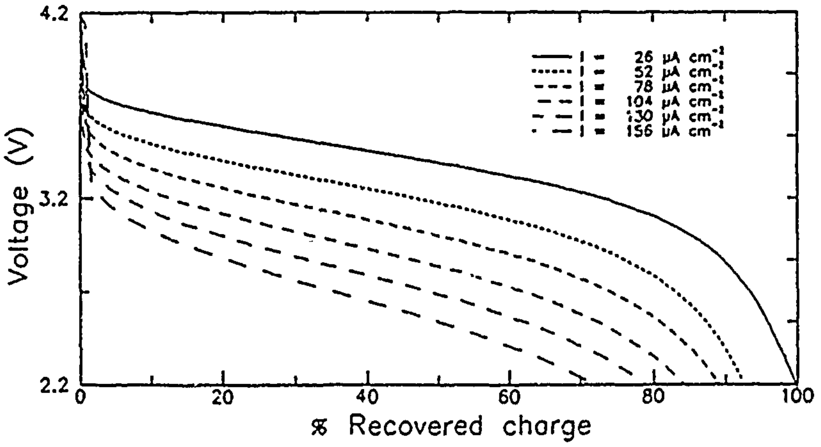


Figure 2. Discharge curves of Li/$(PEO-SEO)_{20}LiClO_4$/pNTPy battery ($1.2.10^{-6}$ mol monomer unit cm^{-2}) at different current densities: 26, 52,78,104,130,156 µA cm^{-2} at 25°C; 10 mC cm^{-2} of charge.

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X-ray Absorption Studies of Organo-disulfide Redox Polymer Electrodes.

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INTRODUCTION

Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy provides a powerful tool to study the interatomic bonding and coordination geometry with high element selectivity. We report here our preliminary results of NEXAFS studies of organo-disulfide polymers above sulfur *k*-edge in both charged and discharged states. This provides spectroscopic evidence for the depolymerization and polymerization mechanism of energy storage in organo-disulfide cathode materials.

EXPERIMENTAL

Three systems were studied: (1) 2,5-Dimercapto-1,3,4-thiadiazole, its lithium and potassium salts and polymer; (2) Trithiocyanuric acid, its lithium and potassium salts and polymer; (3) poly(vinylmercaptan), and its lithium and potassium salts. 2,5-Dimercapto-1,3,4-thiadiazole and trithiocyanuric acid were purchased from Aldrich Chemical Co. and were recrystallized from a mixed solvent of THF and hexane. The synthesis of poly(vinylmercaptan) has been reported in the literature[1]. The NEXAFS measurements were made at beam-line X19A at the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. As the incident x-ray photon is scanned through the sulfur *k*-edge, the ejected photoelectrons sequentially probe the empty electronic levels of the compound, resulting in fine structure of the near edge absorption spectrum depending on bonding, valence, and coordination geometry of the sulfur atom in the compound being studied. Unlike in NEXAFS spectra for low Z atoms such as carbon and oxygen, where the individual spectral features can be assigned to particular transitions[2], the interpretation of NEXAFS spectra for sulfur is more complicated. In order to relate the spectral changes to the microscopic structural changes for the disulfide polymers during electrochemical reactions, we have studied the spectra of several selected reference systems. For each of the disulfide polymers, the NEXAFS spectra of the corresponding monomeric lithium and potassium salts were taken as references for S-Li and S-K bonding.

The composite cathodes were made by mixing the disulfide polymers with $LiBF_4$ salt, copolymer of poly(ethylene oxide) and polysiloxane, and ultra fine carbon black. The cathodes were immersed in $LiBF_4$/acetonitrile electrolyte. The anodes were made of lithium foil. After the cells were assembled, the fully charged voltages were about 3 volts. The discharged state was obtained when the voltage was dropped to 0.25 volts after 2 hours discharging. After discharge, the cathode was removed from the cell and then rinsed and dried before the NEXAFS measurements. The recharged state was obtained by passing current through the cell until 3 volts was reached.

The NEXAFS spectra of poly(trithiocyanuric acid) and related compounds are plotted in figure 1. The spectrum of poly(trithiocyanuric acid), lithium trithiocyanurate, and potassium trithiocyanurate are marked as curve a, b, and c respectively. The spectrum of poly(trithiocyanuric acid) in discharged and recharged states are marked as curve d and e. In comparison with the spectrum of poly(trithiocyanuric acid) in curve a, the spectra for the alkali-metal salts(curve b and c) showed of new features labeled as 1, 4, and 6. Feature 3, the characteristic peak of poly(trithiocyanuric acid) spectrum is disappeared. All of these new features are more pronounced in curve c when lithium has been replaced by potassium. We refer these new features as characteristic peaks of sulfur-alkali metal bonding. Peak 1 is the π^* transition related to S=C bon as a result of the S^-Li^+ bonding. The narrowing of feature 2 is caused by the symmetry breaking of the electric field surrounding the sulfur atom when the C-S-S bond was replaced by $C\text{-}S^+Li^-$. This symmetry breaking removes the degeneracy of the final 3*p* states of sulfur and narrows the white line labeled as feature 2. The other new peaks such as 4 and 6 results from multi-scattering effects due to the changing of the first shell scatterer from sulfur to alkali metal. All of the new features related to S^+Li^- bonding are apparent in curve d after the poly(trithiocynauric acid) cathode has been discharged. At the same time, the intensity of peak 2 is decreased and the peak width is narrowed. This gives us strong evidence that the electrochemical reduction is indeed taking place through the depolymerization in which the S-S bonds were broken and replaced by S^-Li^+ bonds. The electrochemical reversibility of this reaction could be seen in curve e, which was taken after recharging the battery. In curve e, all the features related to S^-Li^+ bonding are weakened while the feature 2 related to S-S bonding grows stronger and is broadened compared to curve d. This is a clear indication of the forming of S-S bonds by electrochemical polymerization. The other two systems showed similar effects and will be discussed in a separate paper. Our NEXAFS study provides a clear spectroscopic evidence that the charge-discharge process in lithium-disulfide polymer batteries is realized by the electrochemical polymerization and depolymerization through the S-S bond formation and breaking.

ACKNOWLEDGEMENT

This work was partially supported by the U. S. Department of Energy Division of Materials Science of the Office of Basic Energy Sciences, Under Contract No. DE-AC02-76CH00016.

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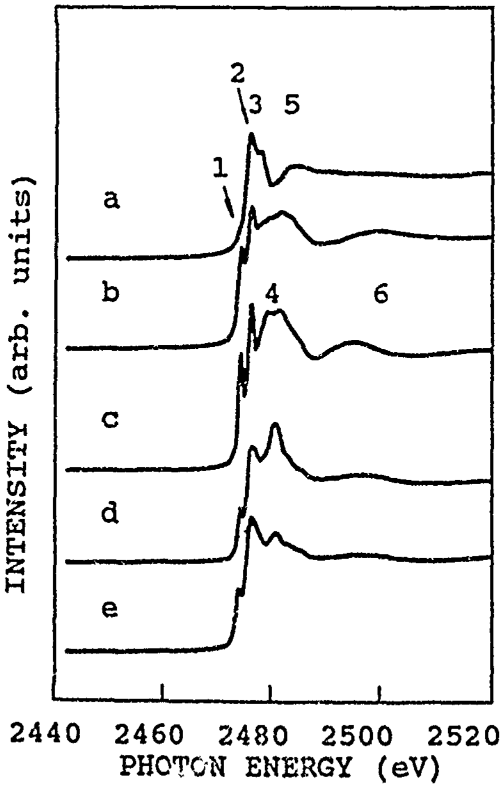

Figure 1
NEXAFS spectra of
(a) poly(trithiocyanuric acid)
(b) lithium trithiocyanurate
(c) potassium trithiocyanurate
(d) poly(trithiocyanuric acid) discharged
(e) poly(trithiocyanuric acid) recharged

Ethylene Oxide Derivatized Polypyrrole. Application as Cathode Material in Polymer Electrolyte Batteries.

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INTRODUCTION

The necessity to have both electronic and ionic conductivity in the insertion cathode material normally requires the fabrication of composite structures of polymer electrolyte, insertion compound and carbon black. A homogeneous distribution of the components is required for efficient and reversible electrochemical reactions.

We have developed a new class of polymeric cathode materials which incorporates both the electronic and ionic conducting functions in a one component system. This allows for ease of fabrication of homogeneously mixed thin film cathodes.

RESULTS AND DISCUSSION

With ion conducting moieties grafted onto a conducting polymer backbone, a combined electronic and ionic conducting material can be fabricated which provides complete, homogeneous mixing of the two functions without phase segration. This may provide cathode materials with a higher rate and improved reversibility compared with materials produced by physical mixing of separate components. With this in mind we have synthesized the poly(pyrrole-ethylene oxide) polymers shown in figure 1.

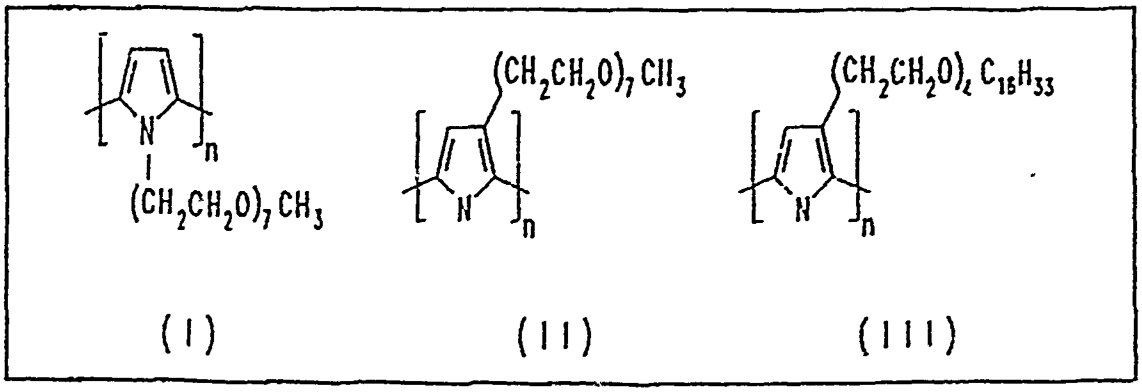

Figure 1. Poly(pyrrole-ethylene oxide) polymers.

The polymers were electropolymerized at constant potential of 1.4 V (vs SCE) for polymer I and 1.2 V for polymers II and III, in acetonitrile solutions containing 0.02 M concentrations of the monomer and $LiCF_3SO_3$ salt. The electronic conductivity as measured by a four point probe were 0.1 S/cm for I, 100 S/cm for II, and 3.5 S/cm for III. Unsubstituted polypyrrole made under the same conditions had a conductivity of 120 S/cm. The large differences in conductivity most likely comes from steric effects.

Figure 2 shows the cyclic voltammograms (first scan only) of unsubstituted polypyrrole and polymers I, II and III. As can be seen from the figure, the oxidation and reduction of the substituted polypyrroles is similar to that of unsubstituted polypyrrole.

A remarkable property of the ethylene oxide substituted polypyrroles is their solubility in a number of organic solvents and water. This opens the possibility for continuous thin film processing of the polymer as a cathode material.

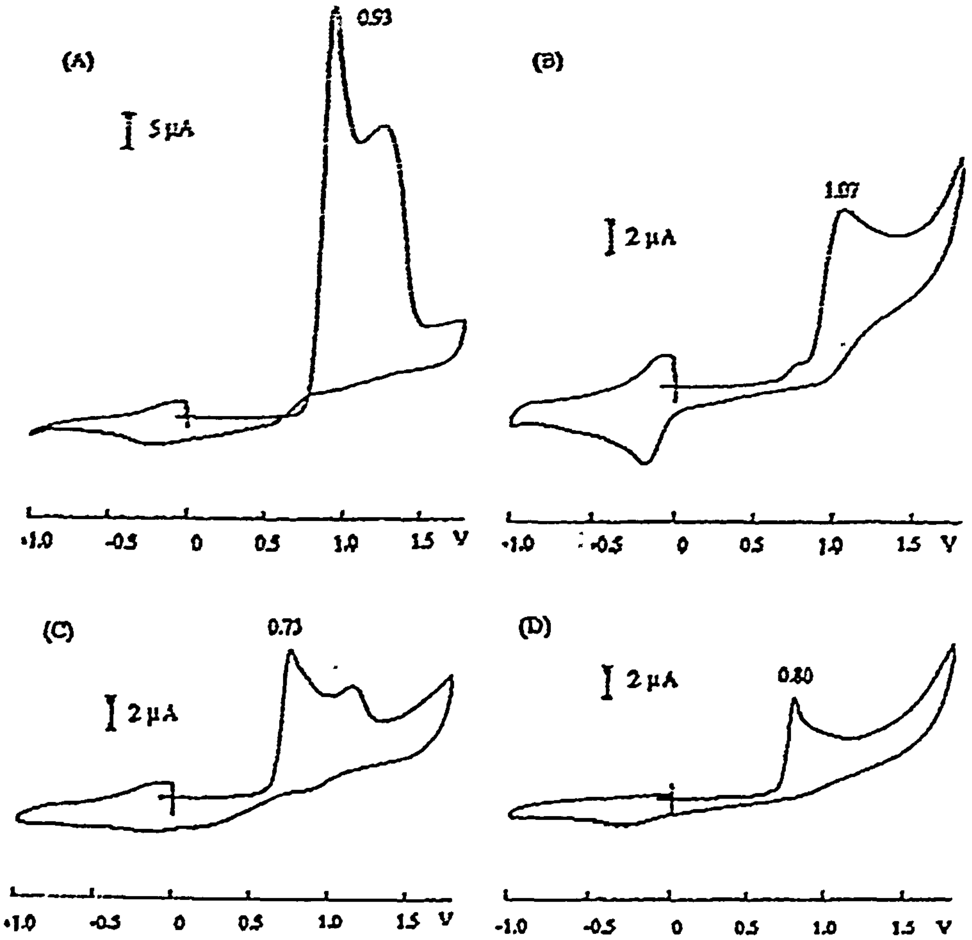

Figure 2. Cyclic voltammograms of unsubstituted polypyrrole (A) and polymers I (B), II (C) and III (D).

ACKNOWLEDGEMENT

This work was partially supported by the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Sciences, under contract No. DE-AC02-76CH00016 and contract No. DE-FG01-90ER81050.

The polymer battery as an environment for *in situ* X-ray diffraction studies of solid-state electrochemical processes

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Much of the current excitement surrounding the remarkable ionic conduction properties of certain polymer-salt electrolytes stems from the impressive advances made in recent years in thin-film polymer-battery technology; see, for example, [1]. Efforts to optimize the design of this battery on the part of the Innocell company of Odense, Denmark have led to the use of an *in situ* fast X-ray diffraction technique particularly suitable for following electrochemical processes occurring in the V_6O_{13} cathode, whereby a sequence of diffractograms is able to identify structural changes as the cell discharges.

During the course of this work,it has become apparent, however, that the form of the battery presents an almost ideal diffraction environment within which to study solid-state electrochemical processes in a more general context under conditions not readily attainable by any other method. Indeed, what better technique for studying the structural properties of a potential battery material than X-ray diffraction from a functioning battery under charge / discharge conditions !

While illustrating the use of this approach for the <Li | polymer-electrolyte| V_6O_{13} > thin-film battery in particular, we shall also endeavour to suggest ways in which this technique could be exploited in a wider perspective.

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Acknowledgements : this work is supported in part by a DARPA grant through a contract monitored by the United States Office of Naval Research, and in part by the Swedish Natural Science Research Council.

Solid Polymer Electrolytes as Matrix for Bioelectrochemistry

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Introduction

There are so many redox active materials analyzed or applied in the category of inorganic, organic and even biological fields. As the redox reactions require the migration of counter ions to compensate the charge changes, these redox reactions have been analyzed only in polar solvents containing supporting salts. However, quire recently, the development of solid polymer electrolytes allured us into the solid state electrochemistry. Even in solid polymers, redox reaction should be carried out because migration of counter ions were assured. We have been analyzing the electrochemical redox behaviors of lanthanide ions [1], alkyl viologens [2], porphyrins [3], phthalocyanines, and even proteins [3] such as cytochrome-C, myoglobin and hemoglobin in polyethylene oxide (PEO) oligomers containing some supporting salts.

Experimental:

Hemoglobin (Hb) and Myoglobin (Mb) were chemically modified with activated PEO, and purified by column chromatography [3]. For example, PEO(3500x5)-Hb , i.e., Hb containing 5 chains of PEOs with molecular weight of 3500, could be dissolved in PEO_{200} without denaturation.

Electrochemical redox reaction of these hybrid proteins in PEO oligomer was analyzed by visible spectral changes under the given potential using thin-layer cell composed of ITO-electrode (working electrode). Pt and Ag wires were also used as counter and reference electrodes, respectively. The optical light path length was 150 micron.

Results and Discussion

Intact Hb and Mb were denaturated by mixing them with PEO oligomers. On the other hand, the PEO-modified Hb and Mb (PEO-Hb and PEO-Mb) could be dissolved into PEO oligomers without denaturation. When PEO-Hb was dissolved in PEO_{200} containing 0.5 M KCl, the complete reduction of the PEO-Hb was observed by applying potential (< -0.5 V vs. Ag). It took about 2 hr to reduce the PEO-Hb in the electrochemical thin-layer cell. The reaction was analyzed to be the first-ordered reaction. Visible spectral change clearly shows a few isosbestic points during reduction (Fig. 1). These strongly suggest that the PEO-Hb was directly reduced at the surface of the ITO electrode. The redox reaction was reversible but acceleration was observed after the initial stage of repeated redox reactions. This suggests local concentration of PEO-Hb near the ITO-electrode.

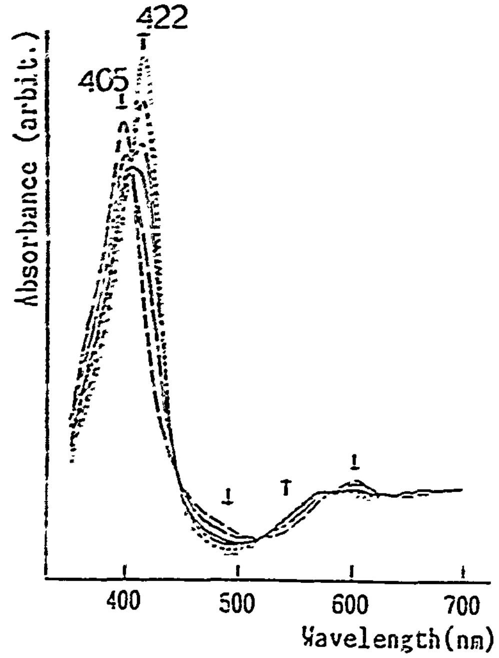

Fig. 1 Spectral changes for PEO-Hb in PEO_{200} at -1.0 V (vs. Ag).

Acknowledgments:

This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

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Ionic conductivity studies of polymer electrolytes containing organosulfur species

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The electrolyte composed of a PEO-based polymer complexed with an alkali metal thio/disulfide organic redox couple in used in an all solid-state electrochemical photovoltaic cell in this laboratory. We investigated the redox couple T^-/T_2 (T_3^-), where T^- stands for mercaptomethyltetrazole ion and T_2 for its dimere. Ionic conductivity studies of the electrolytes modified PEO - MT/T_2 (M = Li, Na, K) were carried out over the temperature range 25°C - 100°C, using ac impedance spectroscopy. The polymer electrolytes (~ 40 µm thick) were fixed in the symmetrical cell Pt/modified PEO - MT/T_2/Pt. As expected, the results show that the conductivity measured at the same temperature increases with the atomic weight of the alkali cation (in the order $Li^+ < Na^+ < K^+$). On the other hand, the conductivity increases with the organosulfur concentration in the polymer, due to the greater free carrier concentration. The ionic conduction mechanism is discussed in relation to the nature of the phases present in the electrolyte.

All Applications of Polymer Electrolytes

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Introduction

In these days, many applications based on the unique characteristics of solid polymer electrolytes are remarkably developed, however further advancement requires the progress of ionic conductivity and other characteristics. Especially, efforts are being paid in preparation method, syntheses of new polymers, new salts, and new measurements. In the present paper, latest study, trends and future of some applications of polymer electrolytes will be reviewed.

Trends

Film batteries are collecting a great interest of scientists in several fields. Several polymers for electrodes and electrolyte layer are developed to clear the remained problems. Plasma polymerization was tried to prepare ultra thin film of PEO. New salts and new polymers are being designed for higher degree of dissociation of the incorporated salts. These novel approaches will be essential for the coming advanced film battery.

Other devices are also expected to be developed such as electrochromic display (ECD), fuel cell, sensory system and so on. For example, cation conductor was applied to the ECD, because most electrochromic reactions required migration of only cations. This is known but lower ionic conductivity in the single ionic systems suppressed this kind of application. Thus, single ionic conductors with excellent ionic conductivity have considerable potential to be applied in several fields.

On the other hand, a few scientists started to use the solid polymer electrolytes as solid solvents for chemistry fields. Polymerization of redox active molecules and electrochemical analyses of the redox reactions have been carried out in solid polymers. As the redox reactions require the migration of counter ions to compensate the charge changes, these redox reactions have been observed even in solid polymers only when sufficient ionic conductivity was provided.

Quite recently, the solid polymer electrolytes are also used as solid solvents for biomaterials. For examples proteins and metal complexes are dissolved into polymers or oligomers, and their electrochemical response is being analyzed. This may develop dry electrobiochemistry.

Some other topics in these fields will also be introduced briefly.

Conductive Polymers as Electrode Material in Solid State Electrochromic Devices.

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By combining a processable electronically conductive polymer [poly(3-octylthiophene) (P3OT), polypyrrole (PPy)], a solid polymer electrolyte [$(PEO)_8LiClO_4$] and a metal oxide (V_2O_5), a solid state electrochromic device was constructed. The polymer films were fabricated by spin coating from solution (P3OT) and template polymerization (PPy). The metal oxide was electrochemically doped with Li^+ and the electrodes were mounted in a sandwich structure with a thin film of polymer electrolyte in between (fig.1)

The sample was placed in a spectrophotometer and the electrichemical equipment was connected. As the applied cell potential is changed, the optical absorption of the cell is changed between red and blue (fig.2). The experiment was run at room temperature, which resulted in a switching time of several hours. Owing to the difference in coloumbic capacity between the different materials, the optical changes of the cell are due to optical changes of the polymer only (fig.3). This means that, instead of having to adapt often contradictory optical changes in two electrochromic materials for the desired application, one can use a polymer with a proper optical signature, letting the band gap determine the electrooptical behaviour of the cell.

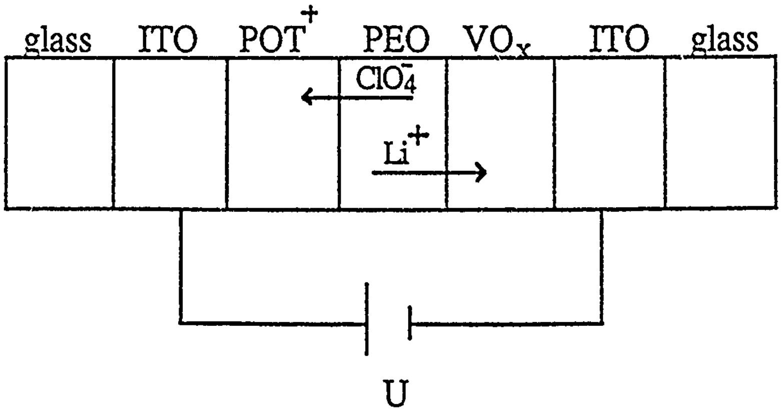

Fig.1: Sample structure.

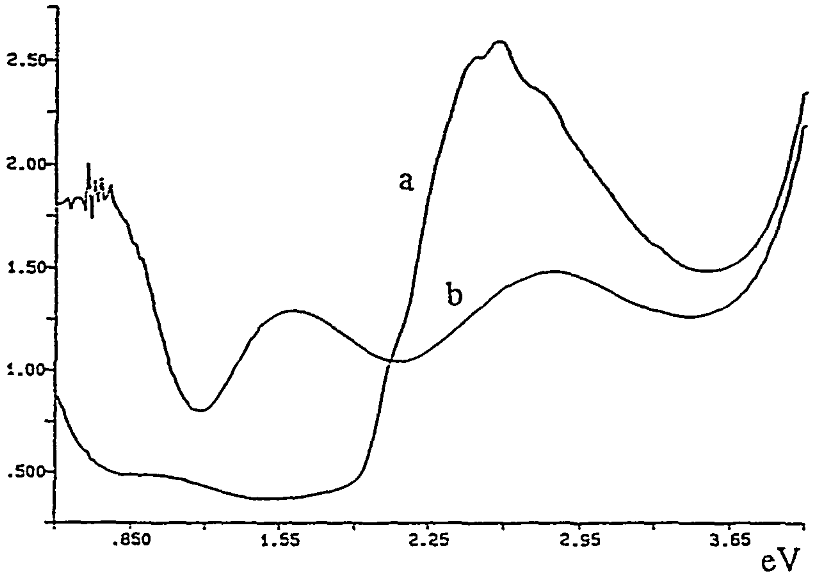

Fig.2: Optical absorption for the P3OT cell at different cell potentials.

a) U=+0.9 V

b) U=+2.0 V

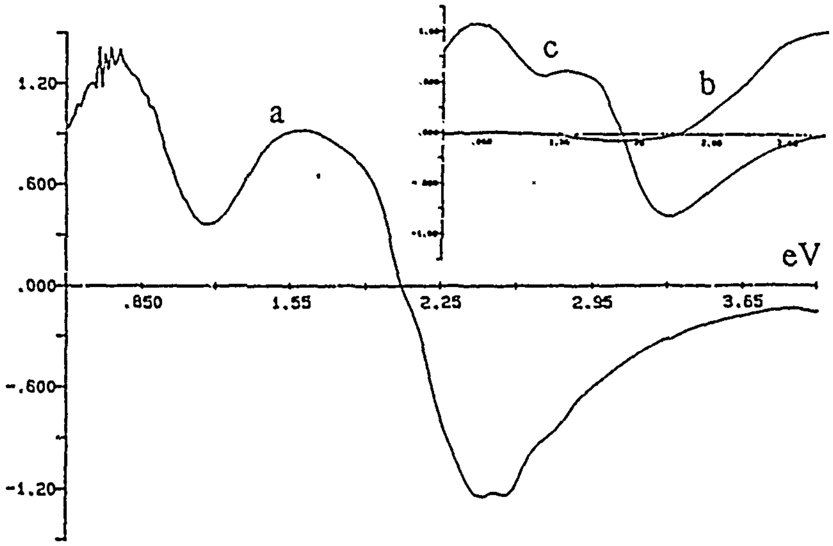

Fig.3: a) Difference in optical absorption for the P3OT cell.

b) Difference in optical absorption between Li^+ doped and undoped VO_x.

c) Difference in optical absorption between oxidized and neutral P3OT.

SOLID STATE ELECTROCHROMIC DISPLAY BASED IN THE POLYMER ELETRODE/POLYMER ELECTROLYTE INTERFACE

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Electropolymerized polyaniline films have received considerable attention in the last years due to their electrical conductivity and wide application in electrochemistry(1-5). The electrochromic properties of polyaniline films have been investigated for applications in display devices.

In this paper we discuss the electrochromic properties of polytoluidine and polyanisidine films and compare the electrochemical and spectroscopic response of these films in aqueous, non-aqueous and polymeric electrolytes. Finally a solid state TiO_2-CeO_2 /polytoluidine cell having a polymeric electrolyte based on polyethylene oxide (PEO) - $LiN(SO_2CF_3)_2$ complex has been assembled and analysed.

Electronic absorption spectra of polytoluidine and polyanisidine - coated ITO were measured in situ at different potentials. In both polymeric electrodes the colour of the films changed from transparent to dark blue in aqueous and non-aqueous electrolytes. As known(6-7) the conductivity of PEO - based polymer electrolytes with $LiN(SO_2CF_3)_2$ is appreciable at room temperature. A reversible response is observed in the cyclic voltammogram of the polytoluidine/(PEO)-Li^+ interface at 25°C, where the charge passed during the anodic cycle is similar to that obtained during the following cathodic cycle. In the impedance plot of TiO_2-CeO_2 /(PEO)-$LiN(SO_2CF_3)_2$/ Polytoluidine cell at lower frequency a 45° line is obtained indicating that the kinetics of the process is controlled by ionic diffusion. (CNPq-FAPESP)

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" Molecular Dynamics in Glassy Polyelectrolytes - a NMR-Study "

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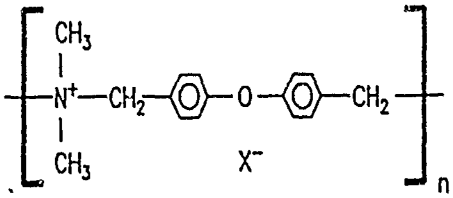
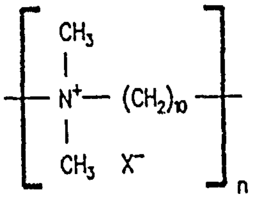
IONENES are polyelectrolytes with quarternary ammonium groups as part of their repeat units and low molecular weight anions X [1]). The stiffness of the polycation chains can be changed from rigid to flexible, e.g.





The solid properties of IONENES cover a broad range of materials varying from single crystalline [2]) to glassy solids [3]). The properties are determined as well by the nature of the polymer chains as by ionic interactions. These depend on the density of ionic centers in bulk materials, e.g. the glass transition can be varied within a wide temperature range depending on their primary structure.

The presence of both ionic centers and polymer chains raises interesting questions with respect to the molecular dynamics in these amorphous materials. In particular, is the glass transition associated with the melting of the ionic structure or is it due to molecular motions of the polymer chain?

The solid state properties of IONENE-glasses have been investigated recently in detail by thermoanalytical, dielectric and solid state NMR techniques, including ^{2}H- and ^{19}F-NMR. The dielectric properties of the IONENES were studied in the frequency range between 0.1 Hz and 10GHz and at temperatures between 100 K and 500 K. At a certain critical frequency, which is shifted to lower values with decreasing temperature, a dispersion of the conductivity begins. At higher frequencies the conductivity obeys a power law which is typical for hopping conduction. At a critical temperature T_{crit} the ion transport becomes strongly thermally activated. This critical temperature usually is far below the glass transition. T_{crit} is not correlated with T_g and depends on the size and shape of the mobile counterions [4]).

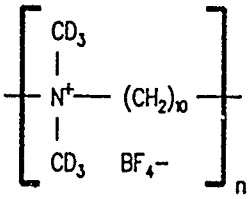
^{2}H NMR of selectively deuterated polymers is well established as a tool for studying the mechanisms of molecular motions over a broad range of rates and moreover, providing information about the motional mechanisms involved. Two-dimensional (2D) exchange NMR is especially suited to probe the ultraslow motions at the glass transition [5]).

Therefore, in order to clarify the motional behaviour around T_g and T_{crit} of the polymer chain, the cation centers, and the counterions, selectively deuterated IONENES with different primary structures were investigated by ^{2}H solid echo spectroscopy and 2D-^{2}H-NMR as well as ^{19}F solid state NMR to probe the motion of the BF_4-anions.

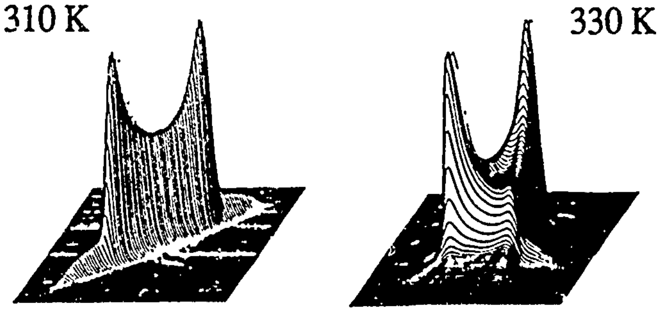
In the glassy state, both the counterions as well as the chain segments interlinking the quarternary ammonium ions are mobile far below T_g. At a given temperature the mobility of the individual carbon positions of aliphatic IONENES increases with the distance from the N-cations. The cationic centers themselves are frozen into a quasi-lattice in the glassy state and become mobile above the glass transition.

As example the 2D-^{2}H-NMR spectra at temperatures below and above T_g of two labelled poly[(dimethylimino)decamethylene tetrafluoroborate] **1a** ⁶⁾ and **1b** are given:

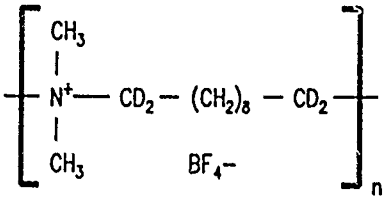
1a



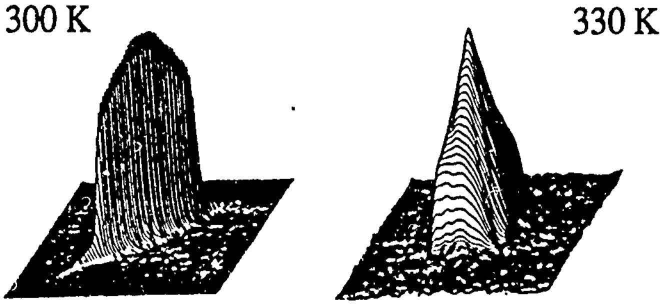
$$\left[-N^{+}(CD_3)_2-(CH_2)_{10}- \quad BF_4^{-} \right]_n$$



1b



$$\left[-N^{+}(CH_3)_2-CD_2-(CH_2)_8-CD_2- \quad BF_4^{-} \right]_n$$



The spectra of the methyl-deuterated glassy IONENE **1a** show that the exchange intensity markedly increases only at temperatures above T_g (323 K). The methylene chains **1b**, however, are already involved in rapid motions at temperatures well below the glass transition. Therefore, the glass transition in this IONENE is attributed to the melting of the ionic packing.

^{19}F solid state NMR of amorphous IONENES with BF_4 anions reveal that the motional behaviour of the counterions is almost unchanged around T_g as shown by the insignificant line narrowing.

These experimental results show that the glass transition of IONENES is clearly different from the softening behaviour of conventional polymers as well as of polymer salt complexes.

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Structure Studies of PEO-Based $NiBr_2$ Electrolytes

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Introduction

The exceptional solvating power of poly(ethylene oxide) (PEO: $[CH_2CH_2O]_x$) for inorganic salts of monovalent, divalent and trivalent cations is well known [1-4]. Many PEO-salt solutions have substantial ionic conductivities. One challenge is to understand why PEO is such a good solvent for strongly bonded ionic salts in spite of its low macroscopic dielectric constant of about 5, an aspect of which involves characterizing the local structures that account for the unusual solvation power of PEO.

Many spectroscopic, thermodynamic and conductivity studies have been undertaken to explore the atomic level structure of polymer electrolytes and its correlation with ion solvation and ion motion. Understanding local structure in PEO-based electrolytes is complicated by the fact that the electrolytes are often multiphase mixture containing crystalline phase and amorphous phases. Electrolytes that contain dissolved Li(I) salts, which are most interesting from a technological viewpoint, are particularly difficult to probe due to the rather uncooperative spectroscopic and scattering characteristics of Li(I) ions. The variety of experimental techniques that can be used to learn about structure issues in PEO and related electrolytes is far more extensive if the electrolytes contain heavier cations.

PEO-based $NiBr_2$ electrolytes formed with high molecular weight PEO (MW $5x10^6$) were studied in this work. Samples were prepared using a two solvent method and then dried under vacuum for 24hrs at 140°C. X-ray powder diffraction and real space analysis were carried out on compositions having the general formula, $NiBr_2(PEO)_n$, where n is the molar ratio of ether oxygens to cations and equalled 100, 32, 16, 8 and 2, to study how the PEO-$NiBr_2$ complex changes structure with increasing $NiBr_2$ salt concentration. Extended X-ray Absorption Fine Structure (EXAFS) and Anomalous X-ray Scattering [5] techniques were used to explore the local structure around Ni(II) and Br(-I) ions in a sample of $NiBr_2(PEO)_8$.

Results

X-ray powder diffraction patterns show that no crystalline PEO-$NiBr_2$ complex phase is formed at values of n>16 (low salt concentrations). Dried samples of this compositions are green in color. At n values of 16 and lower (high salt concentrations), in addition to the Bragg peaks from the pure PEO crystalline phase, Bragg peaks from a PEO-$NiBr_2$ complex phase are detected. Dried samples in this composition range are brown, which suggests that different local structures are formed around Ni(II) at high salt concentrations. At very high $NiBr_2$ salt concentrations, such as n=2, the Bragg peaks from the pure PEO crystalline phase disappear and PEO forms a single crystalline phase with $NiBr_2$. This crystalline PEO-$NiBr_2$ complex has the characteristics of a two dimensional layer structure. Detailed data analysis and the real space analysis technique are underway to understand it more completely.

EXAFS was used to detect the local structure around Ni(II) and Br(-I) ions in $NiBr_2(PEO)_8$ electrolytes. The results show that, at room temperature, Ni(II) is surrounded by about two Br(-I) ions and four ether oxygens at distances of 2.58Å and 2.10Å respectively. However, EXAFS fails to yield information about the local environment of the Br(-I) ions, which suggests that the local Br(-I) structure may be highly disordered. In an attempt to learn more about the local structure around the Br(-I) ions, the anomalous x-ray scattering technique has been used and, in principle, should provide medium range atomic order information. Analysis of these data is underway.

Acknowledgments

This research was supported by University Research Initiative No. N000214-86K-0766 subcontracted through Office of Naval Research. Additional support from the National Science Foundation, MRL program, under Grant No. DMR-8819885, is gratefully acknowledged.

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Studies of Mixed-Cation Effect on a Plasticized-Polymer Electrolyte

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In the search for materials with high ionic conductivity, solid electrolytes based on multiple glass formers have been found to be more conductive than individual compositions. Conductivity enhancement in these systems is believed to be due to what is usually referred as the "mixed-anion effect" or "mixed-former effect" [1,2]. Similarly, the presence of two different cations in a glass is found to produce nonlinear deviations in physical properties such as conductivity, dielectric loss and internal friction [3,4]. The maxima or minima that are usually observed in these data as a function of mole fraction of cations have been referred to as the "mixed-cation effect". If the cations involved in the transport are alkali ions, the same effect is noted as "mixed-alkali effect". Similar effects are found in the beta and beta"- aluminas [5,6] and beta-gallates [7]. The theoretical understanding of these peculiar but common phenomena is limited, and no theory has won universal acceptance.

In view of recent surge in interest in polymer electrolytes and also from the point of view of some similarities between polymer electrolytes and glassy electrolytes, polymer electrolytes could be an obvious choice for the extension of studies of the mixed-cation and mixed-anion effect; in spite of the fact that the conduction mechanisms in these two different kinds of materials are very different. Presumably because of the complexity of the structures and difficulty in obtaining single amorphous phases, the mixed ion effects have not been as well studied in polymers as in glasses.

We have undertaken the study of the effect of different mixed-cations on the conductivity, thermal, and structural characteristics of various plasticized-polymer electrolytes. This paper presents results from thermal and electrical investigations of solution-cast solid polymer films of $[xZnBr_2 + (1-x)LiBr][0.5PEO + 0.5PEGDME]_{16}$ with x ranging from 0.0 to 1.0 and the molecular weight of PEO and poly (ethyleneglycol) dimethylether (PEGDME) being $5x10^6$ and 400 respectively.

Thermogravimetric analysis (TGA) studies carried out on the films of various compositions have shown that they exhibit a complicated mechanism of decomposition. All the films have shown relatively negligible weight loss, ~1% , (perhaps due to dehydration) in the temperature range of 50 to 100°C. Further weight loss due to decomposition was observed at four different temperatures in the range 200 to 450°C with maximum weight loss around 375°C.

Detailed differential scanning calorimetry (DSC) studies carried out in the temperature range -120 to 250°C have shown that all the samples dried at room temperature under dynamic vacuum exhibit glass transitions (T_g), melting points (T_{m1}) due to crystalline PEO, and melting points (T_{m2}) due to crystalline PEO/salt complexes, implying that the polymer electrolytes are inhomogeneous mixtures of amorphous regions, crystalline PEO, and PEO/salt complexes. T_{m2} was found to be absent in samples that were dried at 60°C under dynamic vacuum, showing the existence of an entirely amorphous phase beyond 70°C. The changes observed in T_g, T_{m1} and/ T_{m2} values as a function of composition are correlated with the electrical transport properties.

Acknowledgements
This work was supported by the NSF-MRL program under grant no. DMR88-19885.

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Studies on PAN-based Lithium Salt Complex

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ABSTRACT

An exciting new type of lithium polymer electrolyte,the PAN-based lithium salt complex has been studied.The conductivities from -15°C to 55°C have been measured.Comparing with PEO,the new electrolyte composition appears to have many advantages,such as high ionic conductivity,excellent stability and good mechanical property.The results of IR and NMR investigation will also be presented.

THE EFFECT OF AGEING ON THE CONDUCTIVITY OF POLYMER / ION ELECTROLYTES

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The incorporation of water into the polymer/ion structure seemingly creates an unnecessarily complicated system to model conductivity behaviour but there are several reasons which prompted the study.

Firstly polymers and copolymers of hydroxy ethylmethacrylate (HEMA) form the basis of many commercial contact lense compositions and one of the problems of contact lenses arises from diffusion of inorganic ions such as potassium, sodium and calcium from the tear duct fluid into the gel with increasing deterioration of the function of the lens. Little is known about the mobility of the ions or the effect of polymer/water ratios. Secondly, physical ageing studies on plasticised acrylate polymers have shown that the available free volume can be markedly increased by the addition of a plasticiser and the rapid quenching from above the glass transition temperature. There is promise therefore that rapid quenching may produce higher ionic conductivities.

The system studied was a lightly crosslinked poly(hydroxyethylacrylate)-water-KBr system. The electrical conductivity was measured by the complex impedance method using an automated LCR HP bridge connected to a PC computer. Flat specimens of PHEMA were soaked in various concentrations of KBr solution to equilibrium and the water content varied from 0 - 40 % by drying under vacuum. The KBr concentration was between 3.10^{-4} g/g and $4.5. 10^{-2}$ g/g (g of KBr per g of dry PHEMA). Specimens were loaded into guarded flat plate cells that would allow the temperature to be either held isothermally at T_g-T` or scanned from -100 C to + 120 C. Complex impedances of PHEMA/water/KBr specimens were measured over a range of temperatures spanning the appropriate glass transition.

At room temperature and low concentrations of KBr and water a simple electrical model appeared appropriate but the impedance plots became more complex at high concentrations of salt and water.

Maximum physical ageing effects were produced by rapid quenching. This was achieved by plunging the polymer from above the glass transition (T_g + 20 C) into liquid nitrogen with rapid stirring.

Ageing of the sample was either observed by measurements at an isothermal temperature Tg - T` or by scanning from $T<<T_g$ to Tg + 20 C. Thermomechanical analysis revealed typical dimensional changes due to physical ageing. Similiar measurements using complex impedance methods showed that the technique could also characterise the ageing process. Early results indicated that rapid quenching noticeably altered both the conductivity and the mechanism.

Electrochemical intercalation of alkali metal cations into polyacetylene using solid state cells

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Polyacetylene films were electrochemically doped with alkali metals M(M=Li,Na,K) in solid state cells using polyethylene oxide (POE) as solid polymer electrolyte. The electrochemical chain can be represented by the following chain :
+ stainless steel / $(CH)_x$ // $(POE)_yMX$ // M / stainless steel -
with M = Li, Na, K and X = CF_3SO_3.
Cyclic voltammetry (CV) and chronopotentiometry experiments show that alkali metal intercalation proceeds via successive steps related to the formation of phases which differ in their stoichiometry and their structural characteristics. CV experiments show that the charge-discharge cycles become reproducible after the 10th run, whatever the alkali metal used. The large differences observed between the first and the second cycles using either a cis or a trans isomer can be related to the energy needed for the relaxation of the polymer chains around the intercalated alkali metal columns. This effect is less important during lithium intercalation, because of the small size of lithium cation compared to those of sodium and potassium. The influence of the isomerization is also discussed. The diffusion coefficients of the alkaline ions through the polymer matrix have been measured either by galvanostatic intermittent titration or by potential relaxation method. These intrafibrillar coefficients, in the range 10^{-17} - 10^{-18} cm^2/s, limit the penetration depth of the ions into the polymer which, in case of relatively high potential sweep rate, is the cause of their accumulation at the $(POE)_yMX/(CH)_x$ negative potential of the working polymer electrode compared to that of the reference. Such a concentration of the cations at the interface is the consequence of the differences observed in the Nyquist complex impedance spectra during the evolution from out of equilibrium systems (containing accumulated ions at the interface) to thermodynamically stable ones.

BINDING OF POTASSIUM AND LITHIUM ALKYL XANTHATE TO POLY (ETHYLENE OXIDE).

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INTRODUCTION

The binding of electrolytes to poly (ethylene oxide), (PEO) is a well know phenomenon closely related to cation complexation by crown ethers (1-6). This binding to PEO has been investigated by conductivity measurements (7-9), solvent extraction (10), viscosimetry (11) and ultrafiltration-fluorimetry (12). The most comprehensive studies have been carried out by Ono et al. (7-9), who established that the ion binding is due principalt to cation-PEO interaction. However, studies with a series of potassium salts indicate that the anion also plays an important secondary role.
Although, there are a large publications on alkali cation binding in low dielectric constant solvents (13-15), only a few deal with the complexation of PEO in solvents of high dielectric constant.

In a previous publication we reported the binding of alkali metal cation and a series of different anions, ranging from hydrophilin (e-g fluoride) to those with hydrophobic alkyl chain (e.g. pentonoate), in water solution. In the present work, we have employed U.V. spectrophotometric technique to evaluate the binding a series of potassium n-alkyl xanthate of varying chain lenght to PEO in aqueous and ethanolic solutions. The concentration of the free salt was also evaluated in PEO and diclohexyl-18-crown-6 in ethanol and cycle hexane.
These data point to a participation of the xanthate alkyl chain in the binding interaction.

EXPERIMENTAL

Commercial poly (ethylene oxide) (PEO) of nominal molecular weight $2x10^4$ (Merck) was employed. Potassium alkyl xanthates were prepared by refluxing potassium hydroxide (Merck) during 1 hour with the corresponding alcohol, and after cooling in an ice bath, adding CS_2 (Merck). These product was filtered, washed, with two portions of ethyl ether (Merck), and recrystallized from a mixture of acetone ether. The pure solid was characterized by UV, IR and NMR.
The solution of each salts were prepared in presence of differents concentrations of PEO. The concentration of the salts were measured in Shimadzu 160 UV-visible spectrophotometer at pH 5-6. The viscosities of the potassium or lithium ethyl and hexyl xanthates withouth or with PEO were measured with the Ubbehohde type

capillary viscometer thermostated at 25°C.

RESULTS AND DISCUSSION

The absorbances of the solution of alkyl xanthates in differents concentrations of PEO were measured at X max = 301 nm to get the free concentration of the xanthates in the total solutions. The analytical concentration in the PEO solution, (C PEO), and the free concentration of xanthate, Cx^{-}) simple mass balance provide the concentration of PEO bound salt (C Bound)

$$C\ Bound = C\ PEO - Cx^{-}$$

The corresponding apparent binding constant was calculated from:

$$K_{B}\cdot + \frac{C_{PEO} - Cx^{-}}{[PEO]\ Cx^{-}}$$

Where : [PEO] is the monomolar concentration of polyoxythelene. The values of the binding constants shown that the association with Lithium as very little and significant binding is verified for potassium and also shown that the association increase with the higher of -CH2 groups of the alkyl chain when the PEO concentration is low. This association is not important at high concentration of PEO.

This suggests that the anions remain mainly outside of the polymer coil, much that their interaction with the polymer results in little or no shielding from contact with the solvent.

The former observation suggests that electrostatic interactions are of only seconday importance, while the latter is consistent with enhancement of the binding affinity due to either a binding induced conformation change of the PEO or association between PEO-bound ion pairs at high xanthate/PEO ratios.

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Electrical transport in H_3PO_4 doped PVA system

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To understand charge transfer processes, the current-voltage characteristics of PVA complexed with phosphoric acid in different ratio by weight has been analysed. I-V characteristics which consists of three regions has been explained using electronic and ionic motion (region I), the injection of electrons from cathode side (region II) and space charge limited current (region III). Various electrical parameters such as shallow trap density, density of trapped carriers, free carrier concentration, mobility of free charge carrier, effective carrier mobility etc. Further, from the variation of dc conductivity with temperature, activation energy has been evaluated which varies with the variation of dopant concentration. The measurements support mixed transport processes that is hopping of polarons as well as drift of the carriers.

Effect of Plasticizers on the Properties of New Ambient Temperature Polymer Electrolytes

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Considerable effort has been devoted to synthesizing polymer electrolytes with high ambient temperature conductivities for use in rechargeable Li^+ batteries and electrochromic windows [1-11]. The goal has been a conductivity of 10^{-3} S/cm or greater at room temperature, and it seems very unlikely that it would be achieved with conventional polymer electrolytes such as poly(ethylene oxide) (PEO) and related compounds. Hence most of the recent investigations have dealt with polymer electrolytes which are mixtures of polymers and plasticizers. One of the approach [6,7] has involved encapsulating Li^+-solvates of organic solvent blends, such as ethylene carbonate/propylene carbonate (EC/PC), EC/PC/tetraglyme, etc.) within an polymer-matrix such as polyacrylonitrile which itself contributes relatively little to ionic conductivity. Another approach being pursued is the formation of lithium gel electrolytes [8-11], synthesized either by free-radical polymerization and radiation cross-linking of a macromolecular organic substance like 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) containing $LiCF_3SO_3$ salt [11], or by radiation polymerization of a polyether [8-10] with containing $LiClO_4$, $LiAsF_6$ or $LiCF_3SO_3$. The resulting polymer electrolytes are reported to have conductivities in the range of 10^{-3}S/cm at ambient temperature, but the sub-ambient temperature conductivities of the first two are presently unknown.

Our previous work [8-9] has shown it possible to form a high conductivity polymer electrolyte by the radiation polymerization and cross-linking of a mixture of acrylate oligomer containing plasticizer and dissolved salt. Several new electrolytes prepared in this way have room temperature conductivities of 10^{-3} S/cm and about 10^{-4} S/cm at 0°C. As would be expected, the plasticizer has a large influence on the physical, chemical and electrochemical properties of the electrolyte. For example, changing the plasticizer from propylene carbonate (PC) to poly(ethylene glycol dimethyl ether) (Poly 500) improved the thermal, mechanical and Li cycling properties of the electrolyte, somewhat at the expense of room temperature conductivity.

This paper reports results of a study of the effect of mixed plasticizers on the conductivities and the physical/chemical properties of radiation-polymerized polyethers electrolytes. The plasticizers investigated were mixtures of ethylene carbonate and propylene carbonate containing 1M $LiAsF_6$. The conductivities of all the compositions studied were in the range of 10^{-3} to 10^{-4} S/cm at room temperature. The mixed plasticizer compositions appear to have better thermal, mechanical and Li cycling properties.

Acknowledgements
This work was supported by the Office of Naval Research.

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ELECTROCHEMICAL STUDIES IN SOLID POLYMER ELECTROLYTES WITH ULTRAMICROELECTRODES.

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The ohmic drop (iR) is the limiting factor of any electroanalytical measurement made with a resistive electrolyte. To obtain meaningful results, iR should be eliminated or at least minimized. Compensation of iR by electronic feedback requires sophisticated circuits with a precise knowledge of the resistivity between the working and reference electrodes during measurement. The use of ultramicroelectrodes (UME) leads to a negligible ohmic drop effect even in resistive mediums beause the currents measured are generally quite low (nA or pA for $\sigma = 10^{-5}$ s.cm^{-1}).

The objective of this present work is to demonstrate the possibility of using UME as an electroanalytical device by making voltammetry and chronoamperometry measurements in solid electrolyte. The electrochemical cell is an assembly using a thin film of solid poly(ethylene oxyde) (anionic POE, mol.weight 180 000 g.mole^{-1}, 30–100 µm) complexed with a lithium salt, and heat press-stud on a lithium foil used as reference electrode. The working electrode is a platinum microdisc of 125 µm diameter and it is placed parallel to the lithium electrode surface. Since very low currents are obtained during the mesurement, a two electrode configuration can be used without any noticable perturbation of the reference electrode.

Using the ferrocene ($Fe(C_5H_5)_2$) as a probe, we caracterised the diffusion mode present at a Ø = 25 µm UME in solid POE. Fig. 1. shows the steady-state behavior at low sweep rate (0.3 V.min^{-1}) whitch is characteristic of a spherical diffusion; other verifications were made by chronoamperometry. For a Ø = 125 µm electrode, the diffusion of the electroactive components towards the electrode is a combination of linear and spherical diffusion. The reversible potential ($E_{1/2}$) of the ferrocene/ferricinium$^+$ couple was established at 3.49 V (vs. Li^+/Li^o) with a diffusion coefficient value of 1.10^{-8} cm^2 s^{-1} (POE electrolyte, 0.75M $LiClO_4$, 35°C). With the same electrochemical cell, we observed the Li_xPt and Li_xAl alloys formations at 80°C and 100°C on metals wires.

We also demonstrated the electrochemical stability of POE-LiX complexes by using various type of electrode materials (Ni, Mo, Pt, C). Fig. 2. show the large electrochemical stability range (4.2 V) of $POE_{30}LiN(SO_2CF_3)_2$ at 100°C on a Ø = 125 µm platinum electrode.

Thus the combination of UME and POE based solid polymer electrolyte, now gives us the possibility of making electrochemical studies in stable aprotic medium within a large temperature range (35°C to 140°C).

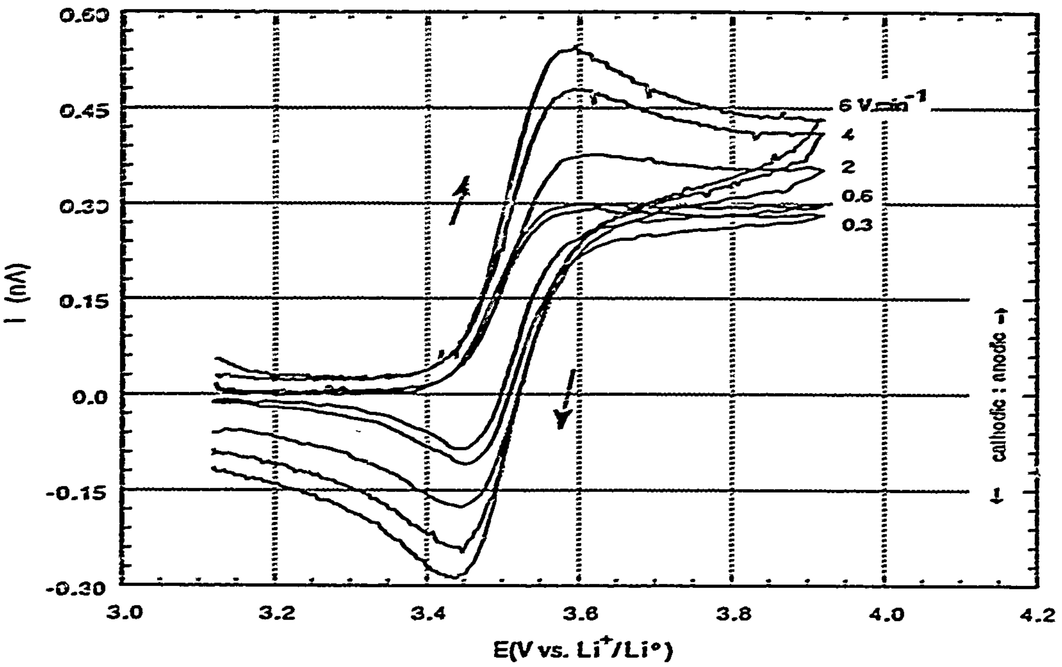

FIGURE 1. Voltammogram of the ferrocene oxydation in $POE_{30}LiClO_4$. Platinum ultramicroelectrode, Ø = 25 µm, T = 35°C, ferrocene = 60 mM.

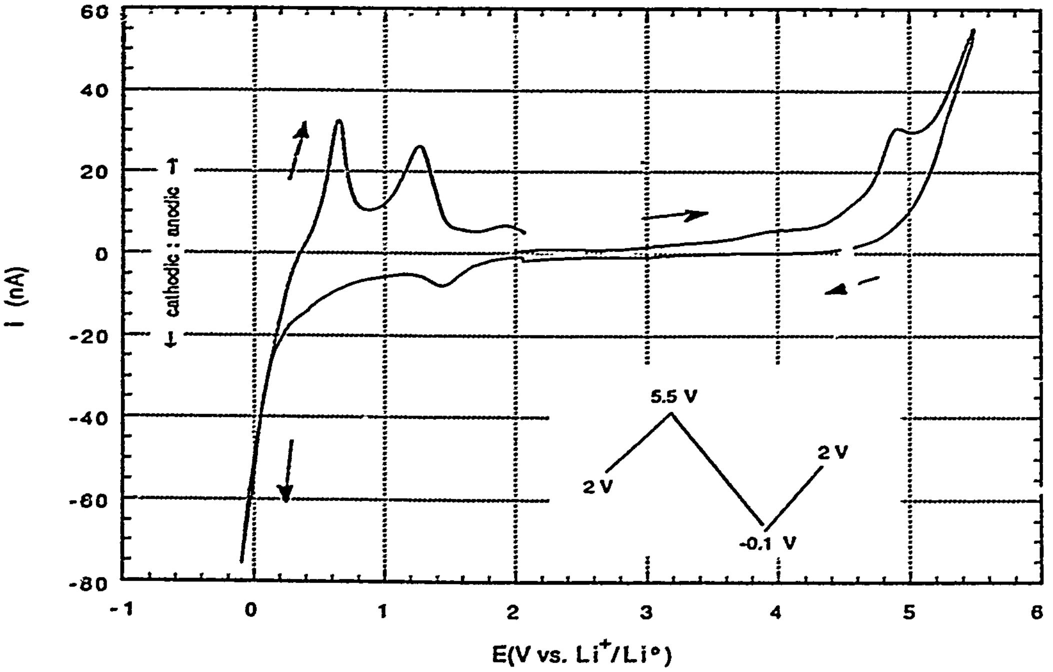

FIGURE 2. Voltammogram of the electrochemical stability range of $POE_{30}LiN(SO_2CF_3)_2$. Platinum microelectrode, Ø = 125 µm, v = 2 V.min⁻¹, T = 100°C.

NMR INVESTIGATION OF P(EO) $(LiClO_4)_x$

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Abstract

We present a NMR investigation of P(EO)($LiClO_4$) for x = 0.125. This includes spin-lattice relaxation times measurements vs temperature both in the laboratory and rotating frames (T_1 and T_{1p}) pf ^1H and ^7Li nuclei. A remarkable feature of our data is the lack of any significant difference between the ^1H and ^7Li relaxation behaviour. It is also suggested that the microscopic motion of the Li^+ ions is closely related to the segmental motion of the chain.

Introduction

The P(EO) $(LiClO_4)_x$ system has been the object of great attention according to its good conductivity (1, 2, 3) and its relatively low melting point of the eutectic (42°C) for x ~ 0.125. Its phase diagram is well know and the cationic transport number t^+ is $0.15 < t^+ < 0.3$ (2, 3). But we have no informations concerning the mecanisms of migration of the cHarge carriers. Here we give some preliminary NMR results giving access to the dynamics of the cation.

Results and discussion

Figures 1 and 2 show the temperature dependence of the ^1H and ^7Li NMR relaxation rates in P(EO)$(LiClO_4)_{0.125}$. In both cases, the data display T_1^{-1} and T_p^{-1} maxima. As shown in figures 1 and 2, there is no significant difference between the ^1H and ^7Li relaxation behaviour. Both exhibit peak rates at the same temperature and show a similar frequency dependence, suggesting that the reorientation of the chemical species arising from the lithium perchlorate is closely related to the segmental motion of the chain.

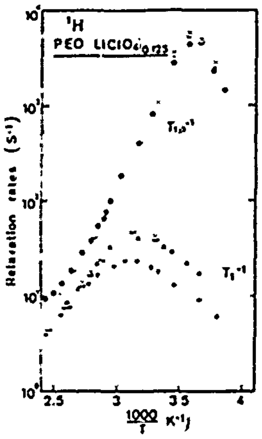

Figure 1. Proton NMR relaxation rates as a function of reciprocal temperature in P(EO)$(LiClO_4)_{0.125}$ at the larmor frequency of 19 MHz (▵, ▴, o) and 34 MHz (+, •). For T_{1r} measurements the rotating field H_1 were equal to 5 Gauss. Data have been collected during a heating (▵) and a cooling (▴) cycle.

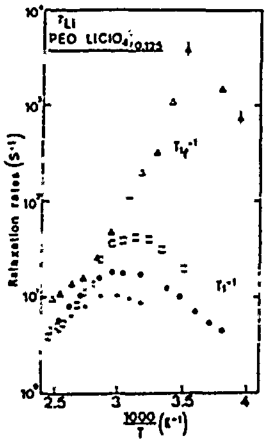

Figure 2. Lithium NMR relaxation rates as a function of reciprocal temperature in P(EO)$LiClO_4$) 0.125 at the Larmor frequency of 8 MHz (▫), 19 MHz (•, o) and 34 MHz (+). For T_{1r} measurements the rotating field H_1 were equal to 5 Gauss. Data have been collected during a heating (o) and a cooling (•) cycle.

In order to determine the effects of the polymer chain motion on the cation diffusion coefficient, we have plotted in figure 2 the lithium correlation time τ deduced from, the T_1^{-1} maxima ($\gamma H_0 \tau = 1$) and the T_p^{-1} maxima ($2\gamma H_1 \tau = 1$) vs the conductivity σ of the system. This figure shows that the τ values scale fairly well with the conductivity data, within the limits of experimental errors, showing that the conductivity is governed by the segmental motion of the chains, as previously observed in alkali metal P(EO) complexes(4, 5, 6).

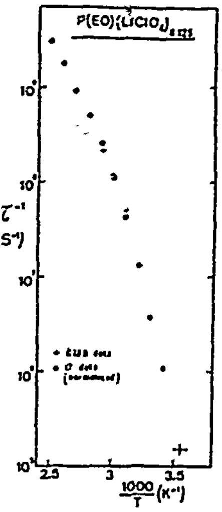

Figure 3.

Temperature dependence of the lithium correlation time τ deduced from the spin-lattice relaxation data (see text) and the conductivity data, in P(EO)(LiClO$_4$)$_{0.125}$.

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The influence of water on the structure and morphology of the system M $(CF_3SO_3)_2$ PEO_n for M = Ni, Zn and Pb.

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It is well known that certain solid polymer electrolytes can have exceptionally high ionic conductivities (1,2). In recent years increasing attention has been focussed on PEO-salt electrolytes involving divalent cation salts. It has been found that these can be highly-selective in their relative anion / cation transport numbers (3). Just as for ion solvation in liquids, PEO dissolves a wide range of salts by coordination of the ether oxygens to the cations.The situation for the anions is generally less well characterized, however.

In this work, FTIR spectroscopy and X-ray "powder" diffraction have been used to study polymer films with compositions M $(CF_3SO_3)_2$ PEO_n for M = Ni, Zn and Pb, and n = 9, 16 and 24 . The $CF_3SO_3^-$ anion (the triflate ion) has been chosen since its internal vibrational modes can be readily observed using FTIR. This provides valuable information about the anion surroundings. Preliminary results indicate that the S - O vibrational modes are highly sensitive to the number of triflate ions which coordinate to the cation. This is, in turn, sensitive to the amount of water present in the system [Fig.1]. For the case of M = Pb we also find a strong dependence on the nominal salt concentration. The C-O-C stretching mode in the polymer chain is also significantly affected by the ether oxygen coordination to the cations (4). In this connection, variable temperature FTIR studies have been made using a heating stage incorporating a microscope attachment [Fig.2].

X-ray diffraction studies show that the only crystalline phase in the films is PEO, but that the degree of crystallinity decreases rapidly during the hydration process. This is confirmed by observations made with the FTIR polarizing microscope attachment, where it is possible to correlate the areas of the O-H stretching bands from water to the degree of spherulite formation in the films.

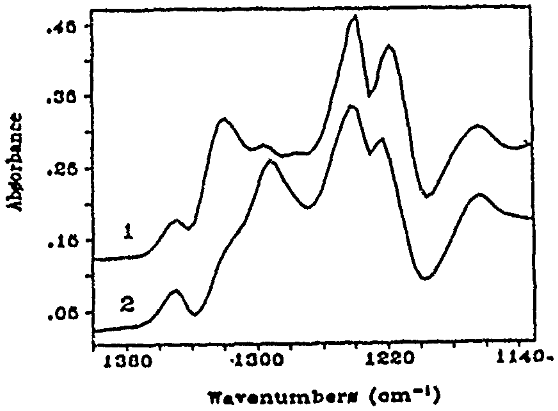

Fig.1 FTIR spectra showing the S - O streching modes for: (1) dry $Zn(CF_3SO_3)_2PEO_9$, (2) hydrated $Zn(CF_3SO_3)_2PEO_9$.

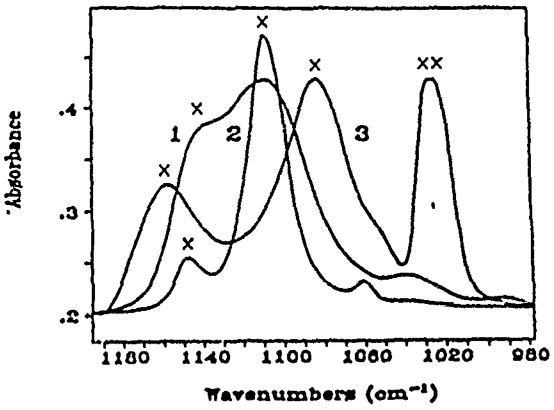

Fig.2 FTIR spectra for: (1) amorphous PEO at 70°C, (2) crystalline PEO at RT, and (3) $Pb(CF_3SO_3)_2PEO_9$.

× : C - O - C stretching modes

××: S - O stretching mode

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Electrical and Electrochemical Properties of Polyacrylonitrile and Polysiloxane Blended Ethylene Oxide Gel Electrolytes

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1. Introduction

Polymeric form of acrylonitrile (PAN) is actively under investigation as a macromolecular support structure to trap and immobilize a plasticizing liquid phase, e.g. a lithium salt dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) solvents and encapsulating it in a host polymer matrix, thus forming gel electrolytes [1,2]. These are easy to prepare, needs no radiation curing for polymerization and resembles the well studied PEO with a different functional group. Polyacrylonitrile based electrolytes with mol% 42 EC - 42 PC - 4 $LiClO_4$ - 12 PAN composition resulted in a gel, that is macroscopically a solid and microscopically a liquid, thus exhibiting high Li^+ ion conductivity at ambient temperature. As a result, the gels exhibit interesting transport and electrochemical properties due to the dual electrolyte behavior.

The mechanical integrity of the free-standing films appear to be dependent on the polymer content and the solvent concentration. The conductivity of the gels depend on the trapped solvent content, heating time and the preparation environment. Thus gel electrolytes with different lithium salts and different ratios of PAN/EC-PC were prepared to determine the highest conducting composition in each case and the variation of conductivity, glass transition temperature as a function of mol% solvent content. An attempt is also made to increase the flexibility and stability of PAN gels by blending ethylene oxide to the acrylonitrile and comparing its properties with pure PAN gels. In addition, polysiloxane gels were also prepared to compare their performance with PAN based gels in a Li/redox polymer cathode environment.

2. Experimental

Gel electrolytes with a general formula EC-PC-LiX-PAN where X = AsF_6, BF_4, CF_3SO_3 and ClO_4 were prepared in an inert atmosphere glove box. Based on the electrolyte composition in mol%, the corresponding weight ratios of analar grade chemicals were calculated, weighed and stored in sample bottles. An aluminum weigh dish is heated to 60 °C on a hot plate situated in the glove box. First, solid EC is transferred into the weigh dish and then liquid PC is added to it. Next, the lithium salt is dissolved in EC-PC mixture contained in the aluminum weigh dish. As the temperature is raised to 120 °C, the polymer powder is added in small quantities, until a colorless and transparent viscous liquid is formed. The viscous liquid is then poured in glass ring moulds kept on a glass plate covered with a teflon sheet and transferred into the ante-chamber. The vacuum pump valve is slowly opened for vacuum suction and by trial and error the optimized time for excess solvent evaporation is determined, thus leaving behind a gel electrolyte.

3. Results

X-ray diffraction studies were performed on the gel electrolytes soon after preparation. The results revealed that the diffractograms (XRD) are featureless and peakfree thus indicating that the gels were amorphous in nature. Figure 1 is an XRD of a PAN-EC-PC-$LiClO_4$ gel electrolyte recorded 12 hours after preparation. After several months of storage, only PAN-EC-PC-$LiCF_3SO_3$ tends to be amorphous and the rest of the gel electrolytes showed the growth of crystallization centers as evident from the XRD of PAN-EC-PC-$LiClO_4$ shown in Figure 2, recorded after six months.

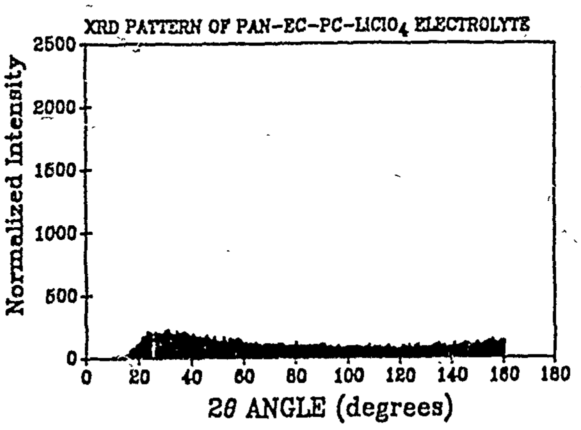

Figure 1

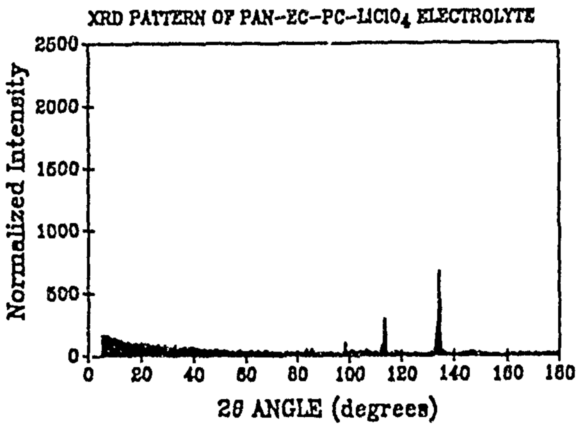

Figure 2

Electrical properties of the gel electrolytes were studied by both ac impedance and dc I-V characteristic techniques over the temperature range of 298 - 393 K. A typical impedance plot of PAN-EC-PC-LiX electrolytes at 25 °C in the frequency range 62 kHz - 10 kHz is shown in Figure 3, which indicates that for a constant mol% composition, PAN-EC-PC-$LiClO_4$ exhibits higher conductivity and the equivalent electrical circuit can be represented by a resistor in series with a capacitor.

Frequency dependent conductivity and the temperature dependent conductivity of the gel electrolytes showed interesting features and will be discussed in the paper.

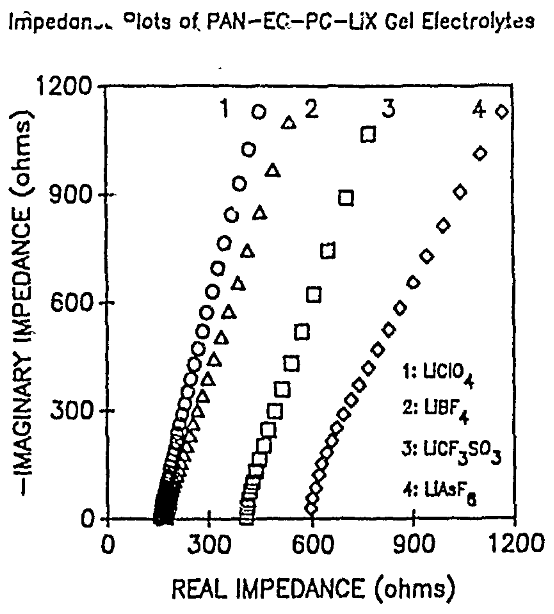

Figure 3

The thermal stability of PAN based gels is in the temperature range -150 to +140 °C. The glass transition temperatures are in the -100 to -50 °C temperature range and endothermic inflections are observed in the temperature range 40 to 140 °C. The electrochemical stability of the gel electrolytes was also determined using linear sweep voltammetry. Lithium plating and stripping efficiencies in the cell configuration Li/Gel/Ni are also determined and the results will be presented in the paper.

Acknowledgements: This work was partially supported by the US Department of Energy, under SBIR Contract No. DE-FG01-90ER81050 and Office of Basic Energy Sciences, under contract No. DE-AC02-76CH00016.

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Solvation of Cobalt Salts by Oligomeric Polyethers

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In solid polymeric electrolytes, ionic conductivity occurs in the amorphous polymer phase containing dissolved inorganic salt.[1] Unfortunately polyethylene oxide (PEO)-based electrolytes generally possess several crystalline phases as well as the conductive amorphous phase. In order to learn more about salt solvation in amorphous polyether systems, this study has focused on several oligomeric model systems. Cameron and Ingram[2] have already pointed out the advantages of studying short chain polyethers: these oligomers should exhibit the same solvation phenomena as their higher molecular weight analogs because the chemistry of the repeat unit is the same; however the oligomers, being liquids, have the advantage of being fully amorphous. In addition, these liquid systems are easier to handle and readily amenable to conventional viscosity and spectroscopic analysis. This study involves the following oligomeric polyethers: polyethylene glycol (PEG) [$HO(CH_2CH_2O)_nH$], mol. wt. 400; polyethylene glycol dimethyl ether (PEGM) [$CH_3O(CH_2CH_2O)_nCH_3$], mol. wt. 400; polytetramethylene glycol (PTMG) [$HO(CH_2CH_2CH_2CH_2O)_nH$], mol. wt. 600; and polypropylene glycol (PPO) [$HO(CH(CH_3)CH_2O)_nH$], various mol. wts. ranging from 400 to 4000.

The spectroscopies are the principal methods for learning about local structure in amorphous systems. Uv-visible spectroscopy has been largely neglected in this field, particularly due to the fact that most researchers are concerned only with alkali metal cations, which are not effectively probed by this technique. For transition metal ions, however, uv-visible spectroscopy can be enormously informative. In this study, divalent cobalt salts dissolved in oligomeric polyethers are investigated.

Preliminary studies have involved $CoBr_2$ because so much is known about this salt's nonaqueous solution chemistry. The work of Katzin[3] indicates that significant cation-anion interaction should occur in nonaqueous solvents of such low dielectric constant as the PEO-type oligomers, and five halogeno complex ions would be expected: ${}^{oct}CoL_6{}^{2+}$, ${}^{oct}CoBrL_5{}^{+}$, ${}^{tet}CoBr_2L_2$, ${}^{tet}CoBr_3L^{-}$, and ${}^{tet}CoBr_4{}^{2-}$, where L=neutral ligand (solvent molecule). The isolated uv-visible spectra of the highly absorbing tetrahedral forms have been identified by Fine[4] for $CoBr_2$ in acetone (Fig. 1).

Our studies have indicated that the behavior of $CoBr_2$-polyether systems is completely consistent with this complexation scheme. For a PEG-$CoBr_2$ system of salt concentration O/M (oxygen/metal) =400, the uv-visible spectrum (Fig. 2) indicates the presence of both the neutral $CoBr_2L_2$ and the charged $CoBr_3L^-$ species (in this case L=ether oxygen from oligomer). If LiBr, a source of excess Br^-, is added while keeping the $CoBr_2$ concentration constant, the formation of higher bromo-complexes should be favored. This is indeed the case. At low Li/Co ratios, more and more of the cobalt becomes involved in the $CoBr_3L^-$ species and at higher concentrations of LiBr (Li/Co = 10 or 50), the doubly charged $CoBr_4^{2-}$ species begins to form (Fig. 2). This behavior is completely analogous to $CoBr_2$-LiBr-acetone systems.[4] Even more importantly, the spectra of the complex ions in the oligomer systems closely matches those identified in acetone. Uv-visible spectroscopy affords quantitative, unambiguous local structure assignments for these systems.

Variation of the oligomeric repeat unit alters the equilibrium of the complex ions. For the PTMG system, analysis indicates that all of the cobalt present in solution can be accounted for by the neutral $CoBr_2L_2$ species. For the PEG and PPO systems, there are varying distributions of species: $CoBr_2L_2$ and $CoBr_3L^-$ can be identified in the spectra, and in these cases a positively charged species such as CoL_6^{2+} or $CoBrL_5^+$ must be present as well (from considerations of stoichiometry), but such octahedral species produce only weak electronic transitions which are completely overshadowed by the highly absorbing tetrahedral species. The concentration of octahedral species can be estimated by subtracting the calculated tetrahedral concentrations from the known overall cobalt concentration.

This study focuses on the complexation/solvation processes in amorphous polyether systems. Preliminary analysis shows that uv-visible spectroscopy is an effective tool for determining the solvated species present in $CoBr_2$-polyether systems quantitatively as a function of salt concentration and can be used to explore the effects of variations in oligomer end group, molecular weight, and repeat unit chemistry. In addition, this study allows the correlation of bulk solution properties, such as ionic conductivity and viscosity, with local structural information.

Acknowledgements

This research was supported by University Research Initiative No. N000214-86K-0766 subcontracted through Office of Naval Research. Additional support from the National Science Foundation, MRL program, under Grant No. DMR-8819885, is gratefully acknowledged.

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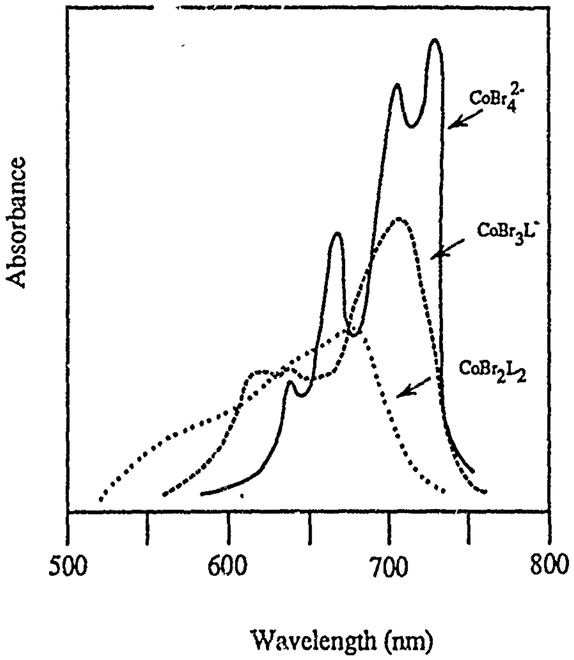

Figure 1. Spectra of Pseudotetrahedral Bromo Complexes of Co(II) in Acetone. (Fine, 1962)

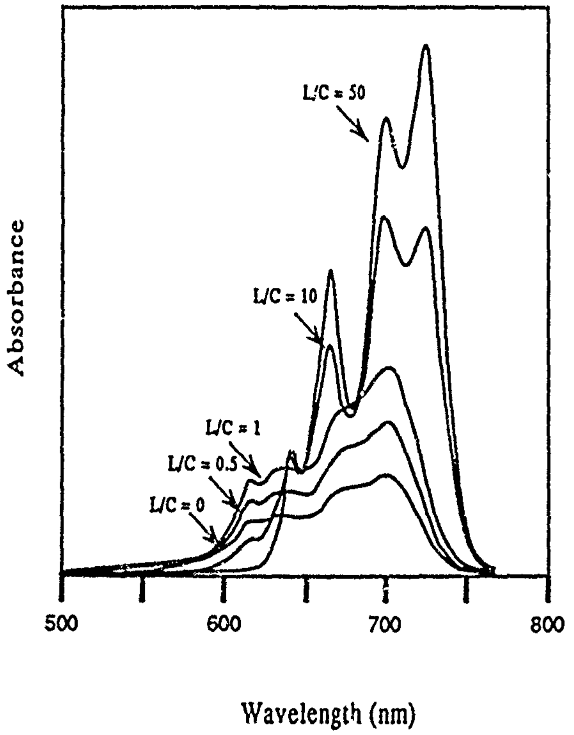

Figure 2. Spectra of $CoBr_2$-LiBr-PEG Systems. O/Co = 400. Li/Co (L/C) ranging from 0 to 50.

ELECTROCHEMICAL STUDY OF LINEAR AND CROSS-LINKED POE BASED POLYMER ELECTROLYTES

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The host polymers, owing both good solvating properties towards lithium salts and a wide electro-chemical window such as poly(oxyethylene) and poly (oxymethylene oxyethylene),exhibit mostly an important cristallinity.Various attempts to decrease it ,using copolymers or adding plasticizers have been reported(1). Recently Armand and coworkers (2) have shown that Lithium bis(trifluoromethane sulphone) imide -LiTFSI- is a very attractive salt .The presence of two electron-withdrawing groups-CF_3SO_2-on the nitrogen atom explain the high dissociation degree of the ionic nitrogen/lithium bond. In addition, the flexibility of the nitrogen covalent bonds favours the melting point decrease and the T_g lowering. On the other hand, LiTFSI has good chemical and thermal stability and therefore, the handling of large amounts is not dangerous.

We present here the results obtained, using high molecular linear POE (Mw= 5.106) and a cross-linked POE . All the samples, prepared in a glove-box under anhydrous argon, have not undergone a preliminary heating before the conductivity measurement.They present a wide amorphous domain and conductivity values are close to 10^{-6}S.cm^{-1} at 25°C and 10^{-5} S.cm^{-1} at 40°C (fig.1). The cyclic voltammogram of POE/LiTFSI (oxyethylene units/Li = 22) plotted in fig.2 shows a wide electrochemical stability domain near to that of CF_3SO_3Li .

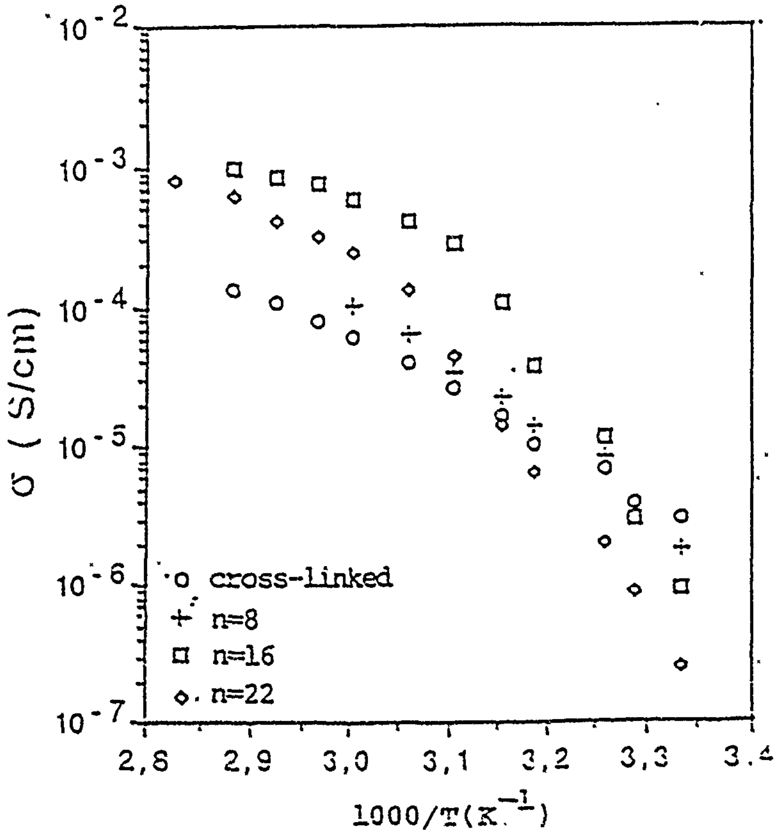

Figure 1 :
Temperature dependency of ionic conductivity of POE_n - LiTFSI complexes and cross linked POE_{20} - LiTFSI

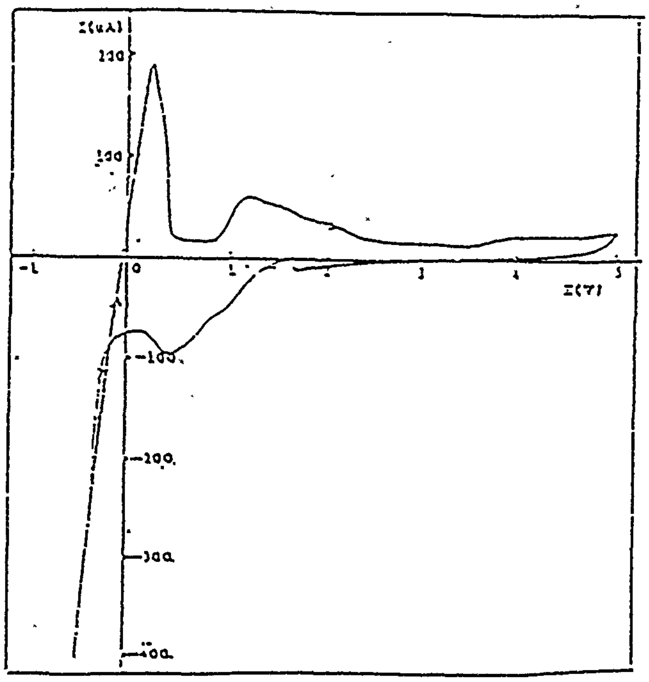

Figure 2 :
Cyclic Voltammogram of
POE_{22} - LiTFSI on stainless steel
at 57°C and v=60mV/S
vs Li/Li^+

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LAMINATED ELECTROCHROMIC DISPLAYS: AN EMERGING TECHNOLOGY.

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The driving force for the development of polymer electrolytes has been so far the prospect of utilization in advanced, high-energy batteries. For this purpose, the main goal was the characterization of materials having high conductivity at ambient and subambient temperature. Indeed, substantial success has been obtained in the latest years and various classes of new materials have been disclosed. In synthesis, there are now available classes of systems based on the combination of modified poly(ethylene oxide) PEO structures and lithium salts and/or the addition of plasticizers to the common PEO-LiX complexes. In addition, new concepts, such as systems formed by trapping in a polymer matrix liquid solutions of lithium salts in aprotic organic solvents or gel electrolytes formed by crosslinking gel precursors in non-aqueous lithium salt media, have been exploited.

However, some of these new generation polymer electrolytes, rather than solids, may be regarded as highly viscous liquids. Such a poor mechanical consistency which is not desirable for battery applications, is instead quite welcome in optical display technology. In fact, viscous polymer electrolytes have adhesive properties which make them as ideal materials for the realization of self-sealing, laminated electrochromic glass windows.

This concept has been experimentally confirmed in our(1-3) and other(3-6) laboratories and in this work we discuss the latest development of this emerging technology and propose some consideration on its possible impact in academic and industrial sectors.

ACKNOLEDGEMENTS.

This work has been carried out with support from the Consiglio Nazionale delle Ricerche, CNR, Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate.

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A zinc trifluoromethane sulphonate polymer electrolyte

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Introduction

Considerable interest has been shown in zinc-ion based polymer electrolytes for a number of theoretical reasons (in particular because of the existence of useful structural data obtained from EXAFS studies) and because of the possibility of practical applications. There is, however, considerable confusion in the literature over the question of the mobility of the zinc. Using various systems and criteria, different authors have characterised zinc as being either "immobile" or "very highly mobile". The reasons for this are not hard to find . As Farrington has pointed out, PEO-based electrolytes containing zinc II are usually complex mixtures of several phases and compositions. Further, the zinc may be present both as the simple cation solvated by the polymer or as a "complex" such as ZnX^+ , ZnX_2 , ZnX_3^- , etc. ; the complexes may or may not be mobile. Further, zinc is known to form highly resistive passivating layers which make the interpretation of dc measurements in cells with zinc anodes difficult. For example, it now seems likely that the deduction of very low zinc mobility in the experiments by Blonsky et al. on $Zn(CF_3SO_3)_2$ in MEEP may have been influenced by neglect of the interfacial resistance.

We have therefore carried out a series of experiments with a view to resolving some of these problems and have chosen to use, in the main, an amorphous high molecular weight methoxy-linked PEO which obviates the complication of crystalline phases. We have also restricted our attention to anhydrous $Zn(CF_3SO_3)_2$ salts since the anion does not form covalent bonds to zinc, and there is therefore likely to be a lower tendancy for ion association than, for example, with the zinc halides. For comparison, we have also undertaken a number of parallel studies using commercial PEO as polymer host.

Experimental

Amorphous methoxy-linked poly(ethylene oxide) of molecular weight approximately 10^5 was prepared using a modification of the synthesis reported by Booth et al. Electrolytes having a concentration range of 10:1 to 100:1 were prepared by conventional casting techniques. Bulk conductivities were obtained using the standard variable frequency analysis method on data from constant volume cells with stainless steel electrodes. Dc studies were carried out using symmetrical two-electrode Zn | polymer electrolyte | Zn cells. Hittorf transference number measurements were made using the cell designed by Hardgrave. All experiments were undertaken in an argon-filled glove box with a water content of less than 1ppm.

Results and discussion

Ac conductivity data are summarised in Figure 1 : in all cases the conductivity follows the empirical relationship $\sigma = \sigma_0 \exp(-B/(T-T_0))$ generally observed for amorphous systems.

The concentration dependence of the conductivity is large, especially at low temperature. The 50:1 samples showed the highest conductivity at all temperatures for the concentrations studied. At high temperatures, the conductivity values are comparable with results reported for other zinc/PEO-based systems, but as expected, the room temperature conductivities in the present studies were considerably higher. Conductivities in this system showed neither history nor time dependence.

Direct current flowing in Zn | polymer electrolyte | Zn cells is generally limited by the interfacial resistance, even when the zinc is freshly scraped in the glove box prior to cell assembly. (In comparison, the well-known passivating film on lithium has a much smaller effect.) We have investigated a number of methods for reducing the interfacial resistance, and have settled on a technique of pretreatment using dc current reversal, as in "electrochemical polishing". Figure 2 shows the reduction in the interfacial impedance following current reversal treatment.

Measurements of initial and steady state currents have been carried out using symmetric cells with pre-treated electrodes for a range of applied voltages. Interpretation of such data is difficult, and is not worth contemplating unless a number of conditions are met - in particular it is essential (i) to measure the resistance of the interfacial component of the cell impedance before and after polarisation and make appropriate corrections to the applied voltage and (ii) to compare the conductivity of the bulk electrolyte before and after polarisation, since if the salt concentration gradient at steady state is too high, the average conductivity may deviate significantly from the conductivity prior to polarisation. For these zinc-based systems we have generally found that the steady state current remains a linear function of the corrected applied voltage up to 50 mV, after which the current rose more slowly. Since the steady state bulk conductivity also began to deviate from the unpolarised value at about this voltage, no great significance can be read into this finding. The linear region is somewhat longer than that anticipated for an ideal, unassociated electrolyte; it is known that low ionic activity coefficients or the presence of mobile ion pairs have the effect of extending the linear range.

The ratio of the steady state to the initial current, i_s/i_o, or better, the corrected ratio, $i_s(\Delta V - i_oR_o)/i_o(\Delta V - i_sR_s)$, where ΔV is the applied voltage and R_o and R_s are the initial and steady state interfacial resistances, is often used to estimate the cationic transference number, T_+, in polymer electrolytes. As we have discussed elsewhere, this ratio can only be accurately identified with T_+ when no mobile ion pairs are present. It may therefore be preferable to use the term "corrected current fraction", F_+, for this ratio. F_+ values were measured for 10:1, 20:1 and 50:1 electrolytes as a function of ΔV at several temperatures. In general, F_+ did not vary with ΔV until the linear $i_s/\Delta V$ range had been exceeded, after which the values of F_+ fell. For experiments in the temperature range 30-35°C all three electrolyte concentrations gave F_+ values of 0.30 ± 0.02, while measurements in the range 63-85°C the F_+ values were 0.2[illegible] ± 0.04. A measurement on a 50:1 sample with a PEO host had $F_+ = 0.28 \pm 0.10$ - the large error bar is due to problems encountered in estimating the interfacial correction.

Hittorf measurements of the zinc transference number, T_+, showed clearly that positively charged zinc species were indeed mobile in PEO-based electrolytes. Analysis of the cathode compartments has not so far proved feasible since we have not yet been able to remove the electrolyte from a zinc or lead electrode without contamination by electrodeposited zinc dendrites. Determination of T_+ has therefore been based on analysis of the anode compartment (and the two central compartments).

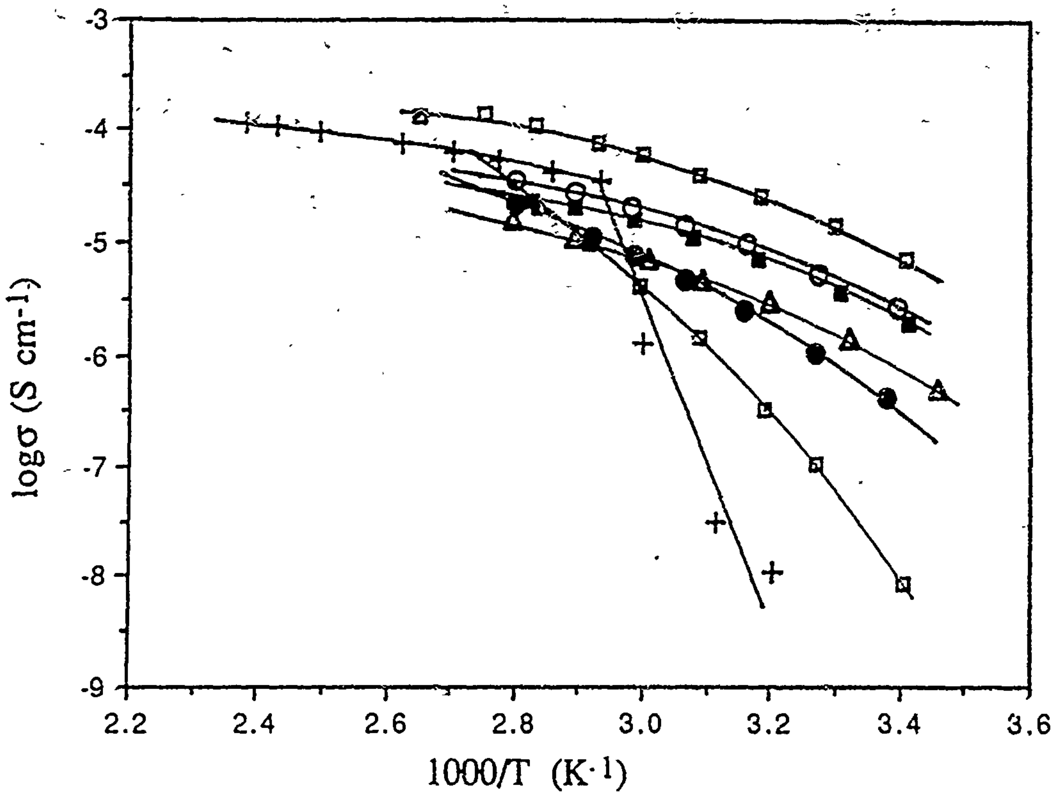

Fig1 Conductivity variation with temperature for amorphous PEO-$Zn(CF_3SO_3)_2$ electrolytes: ▫ EO/Zn=10; ● EO/Zn=20; Δ EO/Zn=30 ◻ EO/Zn=50 ■ EO/Zn=70 O EO/Zn=100 + 50:1 semicrystalline PEO-$Zn(CF_3SO_3)_2$ electrolyte.

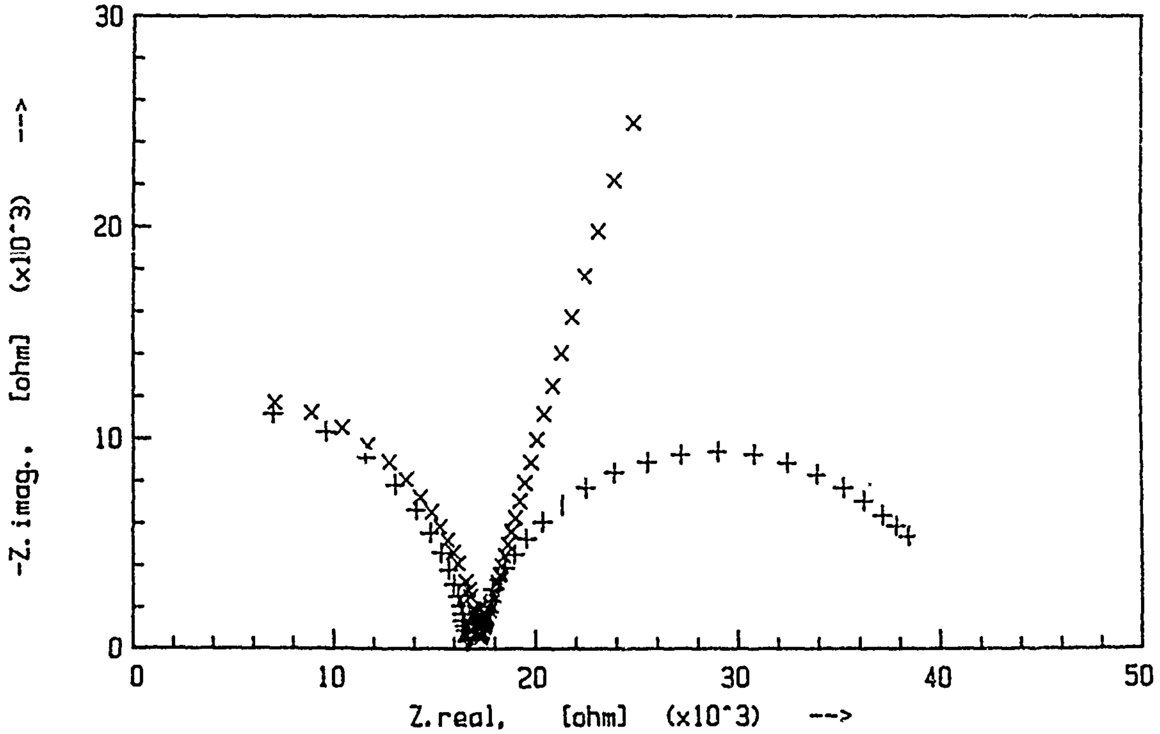

Fig2 AC impedance spectra at 30°C before (x) and after (+) polarisation of ± 0.5V dc potential.

ELECTROCHEMICAL PROPERTIES OF COPPER-BASED POLYMER ELECTROLYTES

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Consistent interest has been lately devoted to complexes formed between poly(ethylene oxide) (PEO) and multivalent metal salts, since these polymer electrolytes offer challenging prospects of investigation, both in terms of definition of bulk transport properties of complicated systems and of interesting practical applications in advanced electrochemical devices, such as flat, thin-film batteries and laminated electrochromic windows.

In our laboratory (1-3) we have started a systematic investigation of polymer electrolytes based on copper salts, mainly of the PEO-Cu$(CF_3SO_3)_2$ type. Preliminary results indicated that the transport properties of these electrolytes are quite intriguing. Although copper ion transport has been demonstrated by Cu plating and stripping processes on inert substrates (2), the exact nature of ion mobility is still unclear. Interfacial reactions of undetermined nature lead to serious experimental difficulties in determining the value of the copper ion transport number by standard electrochemical techniques. Alternative method, such as electron spin resonance (ESR) studies (3), have provided some evidence of ionic motional effects; however, the obtained results do not allow to distinguish between long range Cu^{2+} transport or the motion of copper ions attached to polyether segments.

In this paper we present some recent results obtained by complex impedance, cyclic voltammetry and differential scanning calorimetry on a series of PEO-Cu(CF_3SO_3) complexes prepared using different techniques. The data confirm that these complexes are indeed copper ion conductors, even if the overall transport may be described in terms of mixed ionic-electronic nature.

ACKNOLEDGEMENTS.

This work has been supported by the Commission of the European Community, Contract BREU-0167-C(SMA).

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Structural changes in Vanadium oxide-based cathodes during cycling in a lithium polymer electrolyte cell.

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Introduction

The discovery of polymeric solid electrolytes based on complexes of poly(ethylene oxide) (PEO) and lithium salts (e.g., $LiClO_4$, $LiCF_3SO_3$) by Armand and co-workers [1] has led to the development of high energy density lithium polymer batteries [2-4]. The performance of the battery system utilising a PEO-$LiClO_4$ electrolyte, a lithium anode and a composite cathode incorporating an intercalation compound, such as V_6O_{13}, makes it suitable for electric vehicle traction and general space power applications. Although V_6O_{13} possesses a high theoretical energy density (~ 880 W h kg^{-1}) it exhibits a characteristic capacity decline upon cycling which reduces its practical energy. In order to investigate the reversibility of the lithium insertion reaction an X-ray post test technique has been used to examine the structural changes of V_6O_{13} in composite cathodes taken from cycled cells.

Experimental

Composite cathodes containing V_6O_{13} , carbon, PEO and $LiClO_4$ were prepared by doctor blade casting. Sheets of the electrolyte PEO-$LiClO_4$ ([EO units]/[Li] = 12) were cast from acetonitrile onto silicone release paper. Solid state cells incorporating a lithium foil anode with an active area of 40 cm^2 were constructed in a dry room (T = 20° C, dew point -30 °C) using a combination of heat and pressure. Cells were tested in an oven at 120 °C at the C/10 rate using constant current between the limits 3.25 V and 1.7 V. Cathodes from cycled cells were removed in the dry room before carrying out X-ray diffraction analysis using Cu K_α radiation.

Results and Discussion

The initial discharge curve of a V_6O_{13} cell has a series of characteristic well defined voltage plateaux. However, on cycling these gradually disappear until the discharge curve decreases monotonously with the degree of lithium insertion. The first and twentieth discharge curves for a typical cell are given in Figure 1. X-ray diffraction data on cycled cathodes show a loss of the peaks associated with crystalline V_6O_{13}. This is consistent with a transformation into an amorphous-like material. Results from extended cycling of these cells, does however indicate that any amorphous-like V_6O_{13} is still capable of reversible intercalation with lithium. The effect of depth-of-discharge and extension to other vanadium oxide-based cathodes will be discussed.

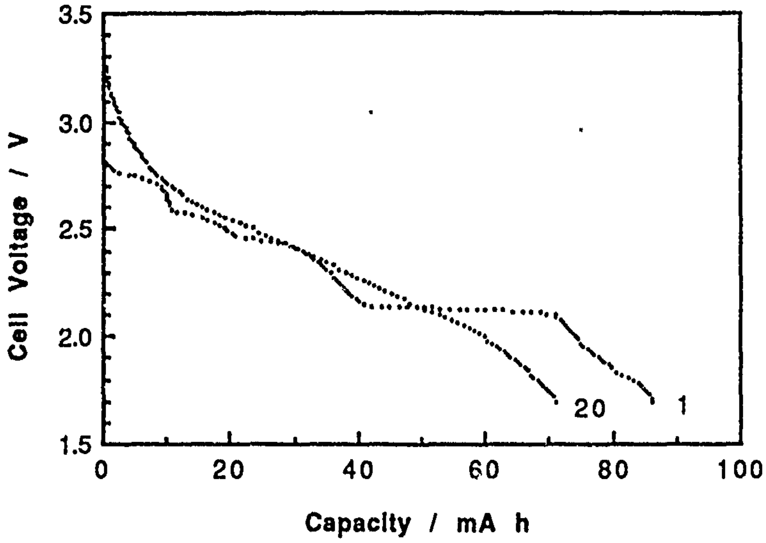

Figure 1. 1st and 20th discharge curves for a typical V_6O_{13} cell.

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ELASTOMERIC IONIC CONDUCTORS FROM POLY(ETHYLENE OXIDE-CO-EPICHLOROHYDRIN)S

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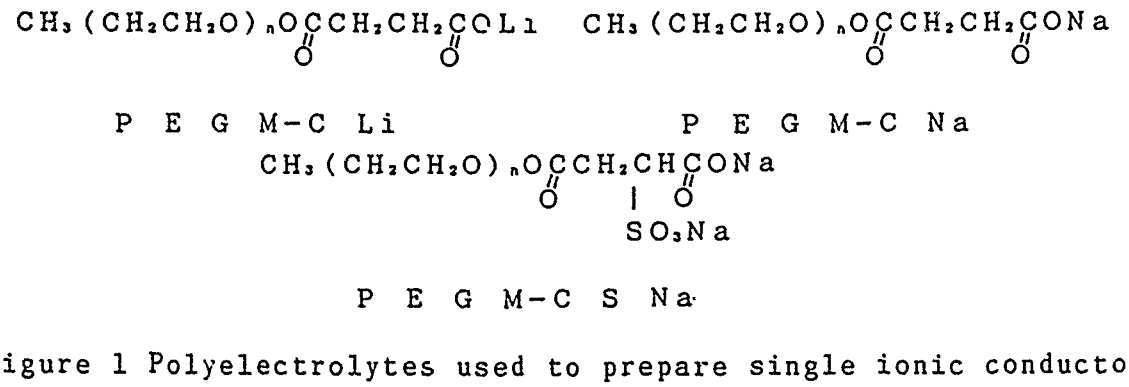
A few kinds of poly(ethylene oxide-co-epichlorohydrin) were used as ion-conducting matrix. Oxyethylene units contents of the copolymers are 0, 24, 48, and 63 mole-%, which are designated as CHR, PEOE-24, PEOE-48, and PEOE-63, respectively. CHR and PEOE-48 were commercially available, and PEOE-24 and PEOE-63 were synthesized.

By doping these polymers with lithium perchlorate, the resulted solid polymer electrolytes showed the conductivities between 10^{-9} and 10^{-6} S/cm (measured by AC impedance method) depending on the oxyethylene units contents. Addition of ologomeric poly(oxyethylene) increased the conductivities. The oligo(oxyethylene) was effective in plastisizing the polymer matrix to mechanically soften it, hence to facilitate the diffusion of ions. In the both types of ionic conductors, the temperature dependency of the conductivities were not the Arrehnius type but the Williams-Landel-Ferry (WLF) type.

The described polymer electrolytes were bi-ionic, i.e., both cation and anion were supposed to migrate in the matrix. In order to obtain a single ionic conductor, a few polyelectrolytes were synthesized, which are shown in Figure 1. PEGM-CSNa carries two Na cations yet is single ionic.



$$CH_3(CH_2CH_2O)_nO\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C}OLi$$

PEGM-CLi

$$CH_3(CH_2CH_2O)_nO\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C}ONa$$

PEGM-CNa

$$CH_3(CH_2CH_2O)_nO\underset{\overset{\|}{O}}{C}CH_2\underset{\overset{|}{SO_3Na}}{CH}\underset{\overset{\|}{O}}{C}ONa$$

PEGM-CSNa

Figure 1 Polyelectrolytes used to prepare single ionic conductors

The copolymers were mixed with these polyelectrolytes to get single ionic conductors. Single or bi-ionic can be determined by the measurement of transport numbers of cations and anions. Figure 2 shows the cell current variation with time for PEOE-63/LiClO4 and PEOE-63/PEGM-CSNa using metallic Na or Li as anode. Decrease of the electric current for PEOE-63/LiClO4 clearly demonstrated that both Li cation and perchlorate anion did migrate in the matrix. The constant current observed on PEOE-63/PEGMCSNa suggests that only Na cation

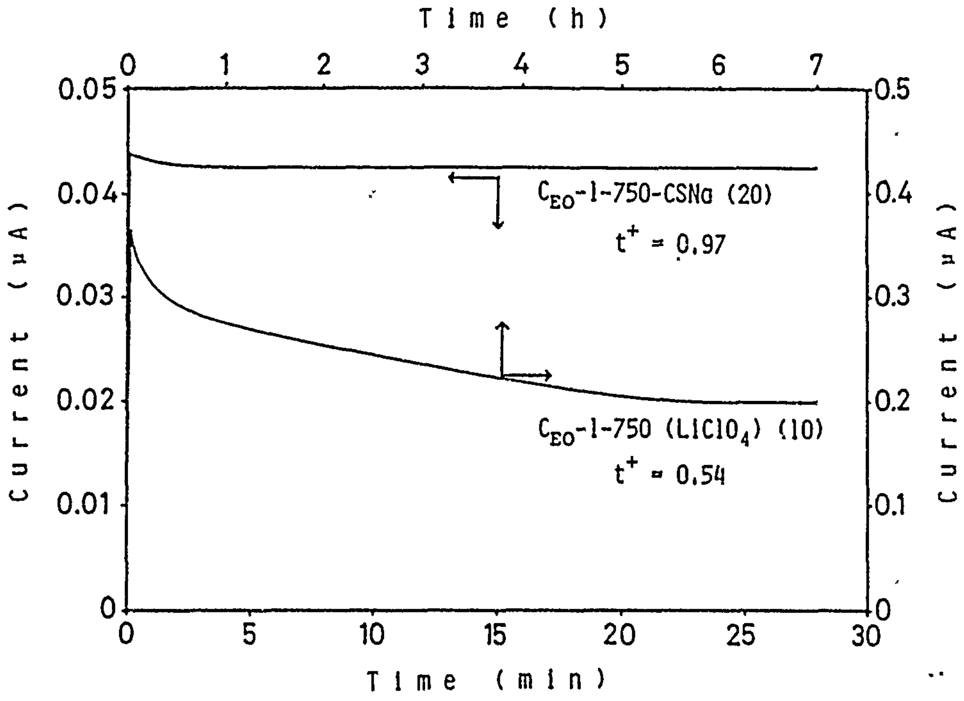


Figure 2 Variation of the cell current with time

diffused. The transport number of cation was calculated by the following equation:

$$t+ = I_\infty / I_0$$

The values are listed in Table 1. The transport numbers for cations were found to be between 0.95 and 0.97, which suggest single ionic nature of these systems. The values were around 0.5 for bi-ionic conductors (the polymers doped with inorganic salts).

Table 1 Transport Numbers for Cations

Sample code	Applied voltage	Cationic transport number
PEOE-63/CSNa	500	0.95
PEOE-63/$NaClO_4$	40	0.42
PEOE-63/CLi	100	0.97
PEOE-63/$LiClO_4$	50	0.55

The temperature dependency of these polymer electrolytes were WLF type or Vogel-Tamman-Fucher (VTF) type or in a few cases gave a straight line in their Arrhenius plots.

Synthesis and Characterization of Novel Comb-type Polymers Having High Ionic Conductivity.

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Introduction:

It has been reported that comb-type polymer electrolytes, having oligo(ethylene oxide) [OEO] as side-chains, improve the OEO's segmental motion and show high ionic conductivity[1-3]. Most studies have been done with poly(methacrylate) and poly(phosphazene) based materials, and especially been focused on the rolls of side-chains. However, those materials seem difficult to control the length and linearity of the backbone polymer. On the other hand, the linear poly(ethylenimine) [PEI] has been reported to be easy to control the polymerization degrees [PD] and possible to graft some polymers[4,5]. Furthermore PEI has moderate polarity to form polymer electrolyte itself[6]. We chose the linear PEI as a backbone to synthesize novel comb-type polymer [PEI(m)-OEO(n)-NCO] (m and n are PD for backbone and side-chain, respectively) by using tolylene 2,4-diisocyanate [T-2,4-D] as addition reagent.

Experimental:

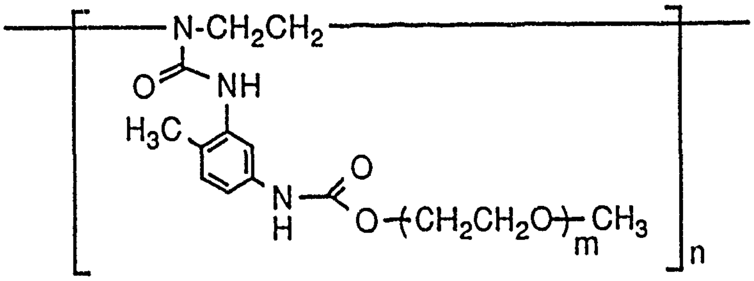

Fig. 1. The structure of PEI(n)-OEO(m)-NCO.

Several types of PEI(m)-OEO(n)-NCO with different length of component polymer chains were synthesized by OEO(n) covalently bound on linear PEI(m) using T-2,4-D as addition reagent. The linear PEI for the backbone was prepared following the procedure of Saegusa et al, i.e. the alkaline hydrolysis of the poly(N-acetylethylenimine)s obtained by the ring-opening polymerization of 2-methyl-2-oxazoline [MeOXZO] initiated by methyl p-toluenesulfonate [MeOTs] in acetonitrile at 80°C[4, 5]. The length of PEI chain was controlled by the initial molar ratio of [MeOXZO]/[MeOTs].

Side-chain was prepared by adding poly(ethylene glycol methyl ether) [Aldrich, average Mw 350 or 550] to T-2,4-D with equivalent molarity at room temperature in DMSO. Subsequently by adding the dried linear PEI to the side-chain reactor with heating at 120°C, PEI-OEO-NCO was obtained. Fraction separation and purification were performed by reprecipitation from DMSO or acetonitrile into diethylether. Degree of substitution [DS] was calculated from the results of elemental analysis.

The polymer electrolyte membranes were prepared according to classical procedure, i.e. after casting from acetonitrile solution of preweighted amounts of the polymer and lithium perchlorate, the solvent was evaporated in vacuum oven at 40°C for a day. Conductivity measurement was carried out by impedance analysis method under inert gas atmosphere.

Results and Discussion:

Effect of PD of component polymers, DS, and salt concentration was analyzed, and the best ionic conductivity of around 1×10^{-4} S/cm was observed for PEI(30)-OEO(13)-NCO at DS = 64%, and [Li]/[EO] = 12.5. It was indicated that decrease of DS to 21% causes increase of T_g and decrease of ionic conductivity to 1×10^{-7} S/cm. Temperature dependence of the ionic conductivity was also analyzed to be described by VTF equation (Fig. 2, 3). It was suggested that ionic conduction mainly depended on OEO's liquid phase, but the high ionic conductivity at relatively high salt concentration owed to the linearity and polarity of PEI-NCO's solid phase. The relation between salt concentration and ionic conductivity will be reported in detail.

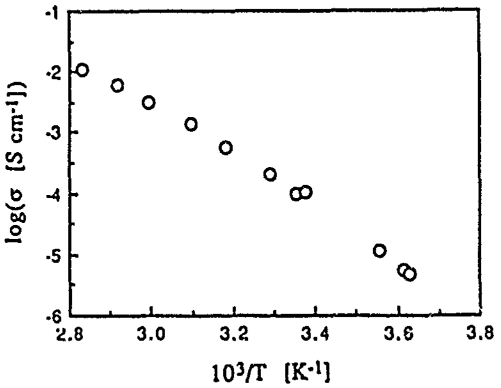

Fig. 2. Arrhenius plot of PEI(30)-OEO(13)-NCO at DS=64%, and [Li]/[EO]=12.5.

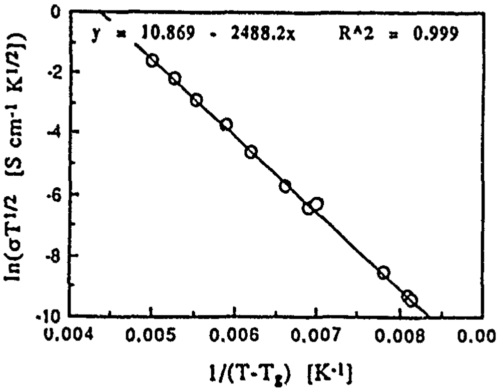

Fig. 3. VTF plot of PEI(30)-OEO(13)-NCO at DS=64%, and [Li]/[EO]=12.5.

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Polyethylene glycol (PEG) Based Polymeric Electrolytes

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Complexes of polyethylene oxide (PEO) and alkali metal salts have been under scrutiny ever since Wright et al published their work in 1973[1]. Armand[2] proposed that the high conductivity of the polyether complexes is associated with enhanced ionic conduction in the amorphous region.It has been observed that highly concentrated polymeric electrolytes are generally highly crystalline near room temperature.The ionic conductivity (σ) value typically in the range 10^{-7} - $10^{-3}\Omega^{-1}$ cm^{-1} at 25°C for PEO-LiX electrolytes.It has also been noticed that the polymeric electrolytes which are less crystalline at room temperature show a higher σ value.[3] Since polyethylene glycol(PEG) is much less crystalline than PEO, it is expected to yeild better results. Moreover, low molecular weight PEGs(mol. wt.300) have been used in the past as plasticizer additives to some metal-polymer complexes.[4] Further, PEG being chemically almost identical to PEO, it was assumed that high molecular weight PEG(mol.wt.:10,000) would have complexing tendencies similar to PEO.This paper reports the phase diagram and the conduction

The phase diagrams have been determined using DTA, XRD and electrical conductivity studies. The dc conductivities of each sample was obtained by analysing the impedance data using standard software packages (IONICS, EQUIVICT). Since the complexes were found to be highly sensitive to moisture, they were handled in a controlled atmosphere glove box and the measurements carried out under vacuum.

The phase diagram of the PEO-LiClO has been determined in the past.[5] The phase diagram of the PEG-$LiClO_4$ system indicates the formation of two intermediate compounds of stoichiometry $(PEG)_8LiClO_4$ and $(PEG)_3LiClO_4$. The complexes formed over the studied composional range are noncrystalline near room temperature. Their conduction characteristics are in accordance with the VTF equation. The effect of Al_2O_3 additive on this system has also been studied. The conductivity values vary in the range 10^{-5} - 10^{-2} Ω^{-1} cm^{-1}.

The phase studies on the PEG-NaSCN system, however, suggest the formation of complexes that are crystalline near room temperature. The conductivity values varied from 10^{-7} - 10^{-3} Ω^{-1} cm^{-1} over a temperature range of 20 - 100 °C.

These results suggest that polyethylene glycol (PEG) based electrolytes are promising materials for battery applications, and hence should be examined in greater detail.

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CONDUCTIVITY MEASUREMENTS OF POE-$LiClO_4$ COMPLEXES IN PRESENCE OF NON-VOLATILE PLASTICIZERS

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Among the polymer electrolytes POE appears as the best host polymer,because of its powerful solvating properties towards salts and its good mechanical strength. Unfortunately the complexes POE/salts are semicrystalline at r.t, exhibiting therefore low conductivities.

Different attempts (1,2) to enhance conductivity of these complexes by addition of plasticizers have been reported .This paper focused mainly on the effect of several non-volatile plasticizers on the conductivity of a complexe PEO/$LiClO_4$ (OE unit/Li=16).

The plasticizers used were the following :

- DOP (dioctyl phtalate) and DBP (dibutylphtalate) which are the most used at the industrial stage
- TBEP(tri butoxy ethyl phtalate) : this plasticizer ,thanks to its phosphate group, is expected to improve conductivity by increasing the dielectric constant of the system and therefore to favour the salt-dissociation.
- NPPGE(nonyl phenol polyglycol ether) has a high molecular weight . We selected two plasticizers Antarox 15 et 20 ®which differ by the number of oxyethylene units.They should be more compatible and so more effective than the other plasticizers.

The mixtures prepared in a common solvent ,CH_3CN, were cast in a glass ring placed on a PTFE surface and dried at 40°C.DSC records, as well as conductivity measurements ,were carried out under Argon .The results are summarized in table 1 and figures 1 to 4.

Table 1: *thermal caracterization of plasticized POE/$LiClO_4$, complexes (O/Li=16)*

Plasticizer %(a)	10%		30%	
	Tg*	mp*	Tg*	mp*
D.O.P	- 44	50	- 44	52
T.B.E.P	- 49	56	- 52	
Antarox N=15	- 43	48	- 45	47
Antarox N=20(b)	- 41	48	- 44	45

(a) : the Tg and mp of non-plasticized POE/$LiClO_4$ are respectively -41°C and 50°C.
* : temperature are expressed in °C.
(b): the Tg and mp of Antarox 20 are respectively -63°C and 13°C.

Plots of $\log \sigma = f(10^3.T^{-1})$ for several plasticizers:

-fig.1 : POE/LiClO$_4$ + 0%, 10% and 30% of DOP
-fig.2 : POE/LiClO$_4$ + 0%, 10% and 30% of TBEP
-fig.3 : POE/LiClO$_4$ + 0%, 10% and 30% of Antarox 15
-fig.4 : POE/LiClO$_4$ + 0%, 10% and 30% of Antarox 20

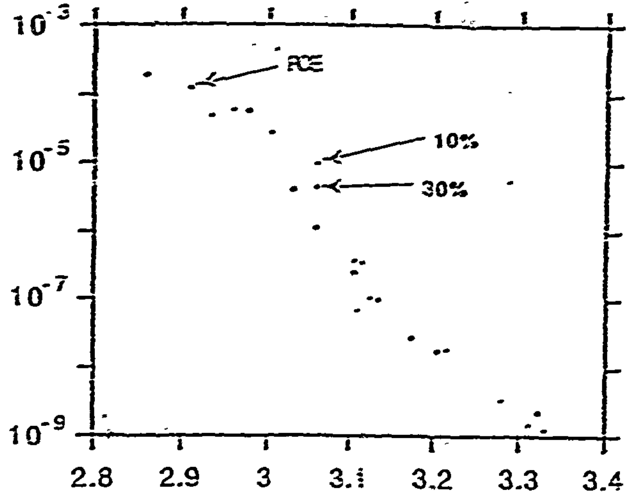

fig.1

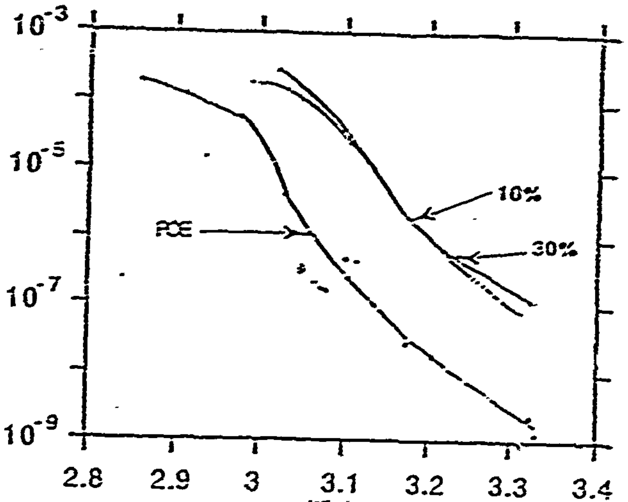

fig.2

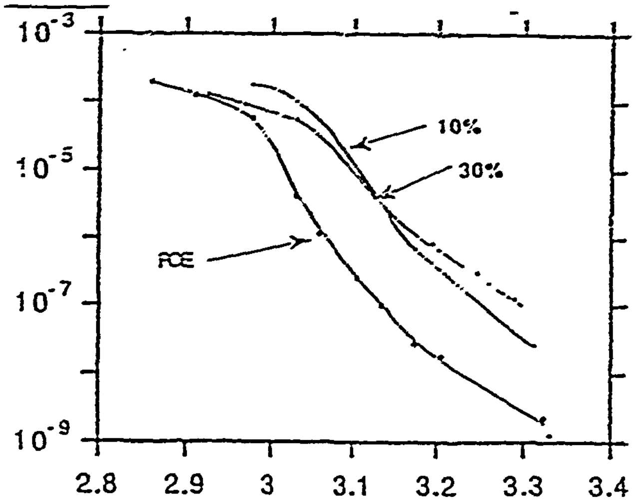

fig.3

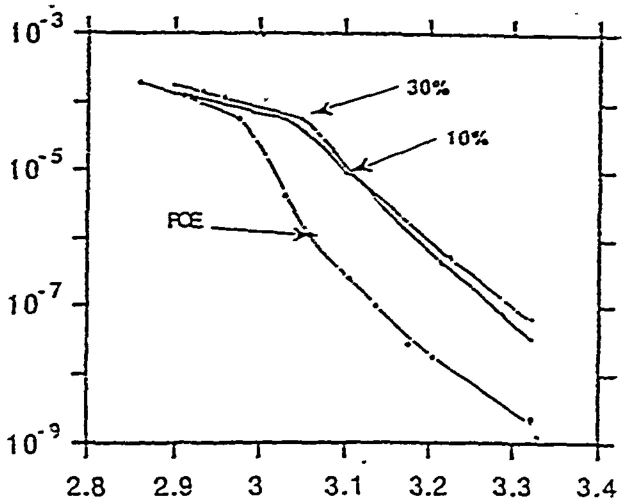

fig.4

DOP is not compatible with the complex and doesn't modify the conductivity. In opposite, the last three plasticizers induce a significant increase of conductivity without compromising the mechanical properties of the polymer electrolyte.

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A New Polymer Electrolyte Based on Polyglycidylether

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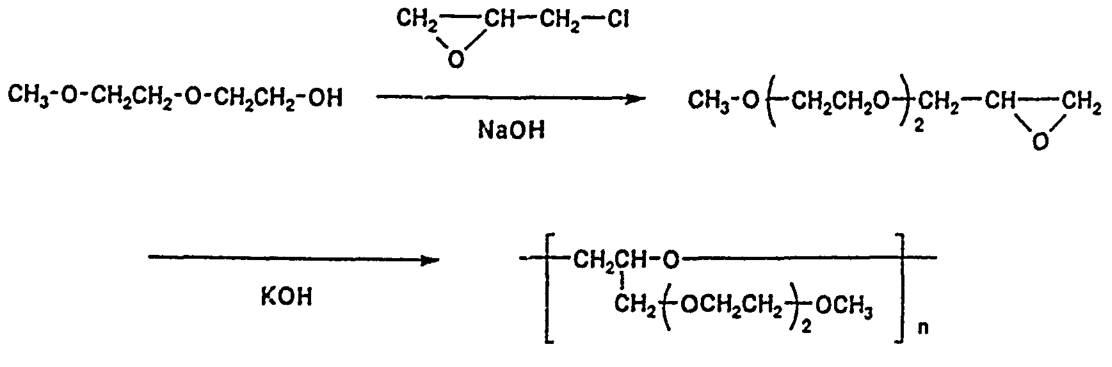
1. Introduction

Ionic motion in polymer electrolytes is coupled, in most cases, with segmental motion of polymer main chain, which is considered to be cooperative motion of several(15-20) repeat units. Consequently, the ionic motion or conductivity is dominated by the main chain motion, having relatively long relaxation time and large temperature dependence (WLF type), though size of conducting ion is rather small.

In order to achieve highly conductive polymer electrolytes, having small temperature dependence of conductivity, we have directed our attention to the possibility of the coupling of ionic motion with side chain motion that is characterized by relatively short relaxation time and its small temperature dependency, compared with those of main chain motion, and have designed a new polymer host; polyglycidylether with short polyether chain, where ionic motion can be coupled with the side chain motion. A typical polymer is poly[2-(2-methoxyethoxy)ethylglycidylether] (PMEEGE). In addition to the above concept, we also take the following points into consideration for the molecular design: (i) As ion-coordinating structure, -OCCO- group is introduced to the polymer in a high density; (ii) Ether structure is introduced not only in the side chain but also in the main chain to keep the main chain flexible; (iii) Electrochemically unstable group is excluded to make the potential window wide; (iv) For mechanical strength and its thermal stability the polymer electrolyte is made network structure. We describe here preparation and ionic conductivity of the new polymer electrolyte.

2. Experimental

PMEEGE was synthesized by anionic polymerization of 2-(2-methoxyethoxy)ethylglycidylether(MEEGE), which was prepared by condensation reaction of epichrolohydrin with 2-(2-methoxyethoxy)ethanol, according to Scheme 1. Side chain length of the polyglycidylether can be easily changed by changing the structure of alcohols for the monomer synthesis. In order to make network polymer electrolytes, MEEGE was polymerized in the presence of glycerol



Scheme 1 Preparation of poly[2-(2-methoxyethoxy)ethylglycidylether].

as a starting substance to result in PMEEGE triol (mol.wt.=5000). This triol was crosslinked by toluene-2,4-diisocyanate(TDI) in the presence of $LiClO_4$ (PMEEGE 1, in Fig. 1). The terminal -OH in PMEEGE triol was converted to acrylate, and resulting PMEEGE triacrylate was crosslinked by UV irradiation(PMEEGE 2, in Fig. 1).

The network polymer electrolytes based on poly(ethylene oxide) triol (mol.wt=3000) or ethylene oxide/propylene oxide random copolymer triol (mol.wt.=3000) and TDI were also prepared for comparison (PEO and P(EO/PO), respectively, in Fig. 1).

3. Results and Discussion

Fig. 1 shows temperature dependence of ionic conductivity for four different network polymer-$LiClO_4$ electrolytes and their polymer structures. PEO shows relatively high ionic conductivity above room temperature. However, rapid decrease in the conductivity occurs below room temperature. This decrease is due to partial crystallization of PEO chain in the electrolyte and is observed when optimization of the room temperature conductivity is achieved by changing the electrolyte concentration. This problem is solved if P(EO/PO) is used instead of PEO. Randomly introduced PO units into PEO sequence prohibit the crystallization of the PEO chain. As a result, low temperature conductivity is much improved.

PMEEGE' s are better ionic conductors than PEO and P(EO/PO) in terms of high conductivity at low temperatures as well as its small temperature dependency. The ionic conductivity of 10^{-5} Scm^{-1} at 20 °C and of 10^{-7} Scm^{-1} even at -20 °C is achieved. The conductivity is also influenced by the structure of crosslinking reagent, and PMEEGE 2, crossliked by acrylate, gives higher conductivity than PMEEGE 1, crossliked by TDI. The correlation between the high conductivity and its small temperature dependency of PMEEGE and the side chain motion will be discussed.

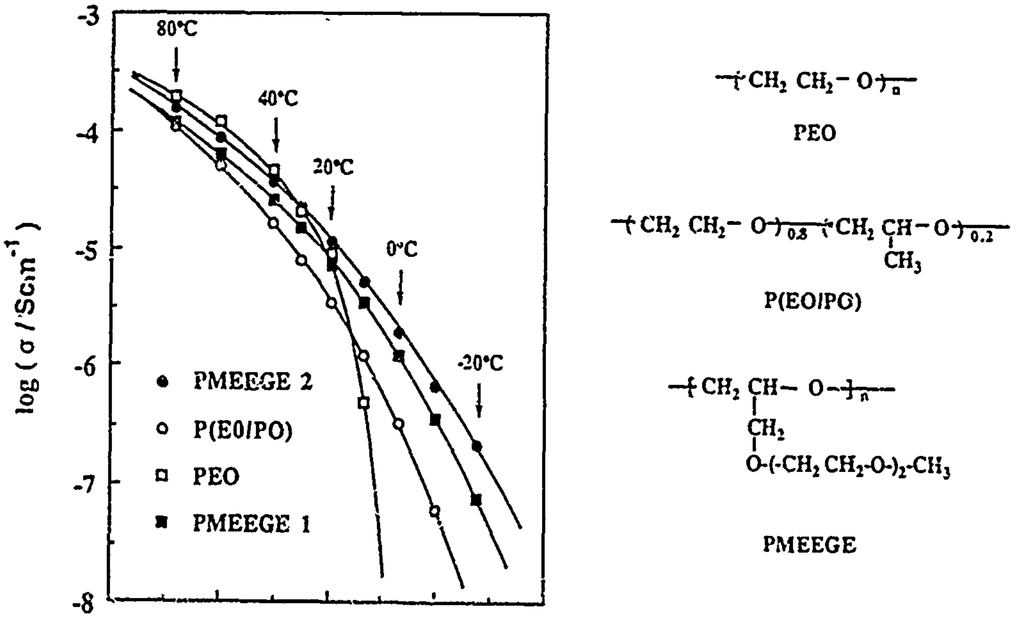


Fig. 1 Temperature dependence of ionic conductivity for network polymer-$LiClO_4$ electrolytes: Li^+/EO unit is 0.015 for PMEEGE 1 and 2, and 0.025 for PEO and P(EO/PO).

CONDUCTIVITY MEASUREMENTS OF LiTFSI TRIBLOCK COPOLYMERS WITH CENTRAL PEO SEQUENCE

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Polymer electrolytes based on polyethylene oxide exhibit good mechanical properties and high ionic conductivity at 80°C. Nevertheless, due to their high cristallinity content, they present poor conductivity at room temperature.

Our study deals with block copolymer A-B-A, prepared by anionic polymerization, starting with a sodium dialcoolate oligo polyethylene glycol, obtained by addition of sodium hydride on the corresponding PEG. Thus the central block must provide good solvating properties versus lithium cation, whereas the lateral sequences will insure the mechanical properties. According to the length chain the PEG block is either completely amorphous or crystalline with a melting point close to room temperature. In this paper we report the conductivities of triblock copolymers with poly (styrene oxide) (PSO) and poly (allyl glycidyl ether) (PAGE) as lateral sequences.

We previously prepared PSO by anionic bulk polymerisation of styrene oxide in a sealed tube at 100°C, using potassium tertiobutoxide as initiator. Complexes LiTFSI/PSO exhibit low conductivities (fig.1), due probably to the high T_g value (313K) of this polymer.The copolymers PSO-PEG-PSO were also prepared in bulk and the number of styrene oxide repeat units added was determined by H^1NMR. These values are in good agreement with both GPC and VPO measurements (table 1). The Arrhenius plots (fig2) of complexes LiTFSI/copolymer are compared with the values of the initial PEG. Although an improvement in mechanical properties is obtained by the addition of POS sequences as expected, the conductivity decreases.

The addition of small amounts of AGE units to the PEG block results in the enhancement of the electrolyte strenght electrolyte. The cross-linking of the copolymer is ensured by the addition of a radical initiator such as peroxide dibenzoyl at 70°C.These copolymeres exhibit very good mechanical properties. For low molecular weight PEO's (1000, 1500, 2000) σ= f(1/T) plots follow the Free Volume Model of conductivity which is typical of amorphous electrolytes. Room temperature conductivities of about 10^{-6} Ω^{-1} cm^{-1} are observed (fig.3).

molecular weight PEG (g/mole) 400	1000	1000	
initiator per cent	9	9	5
repeat units (NMR)	7	11	20
Mn (g/mole) NMR	1240	2320	3400
Mn (g/mole) VPO	1400	2100	3800
Mn (g/mole) GPC	-	2200	2800
Mp (g/mole) GPC	-	2283	2900

Table 1: Molecular weight of copolymers PEG-POS

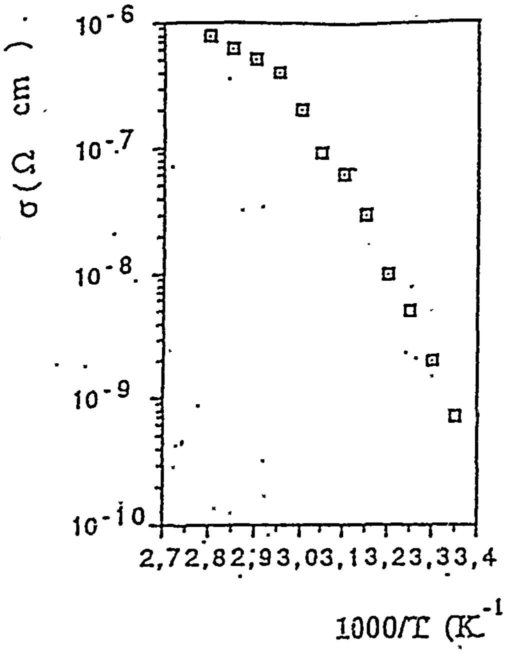

Fig 1 : The temperature dependance of the conductivity of POS O/Li=16

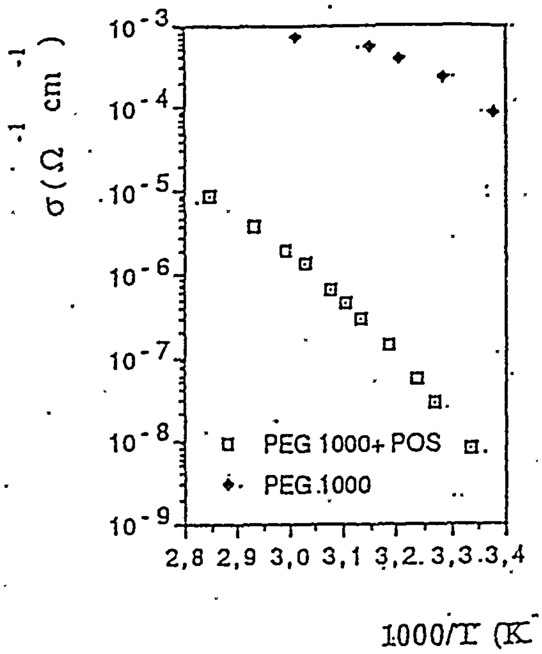

Fig 2: The temperature dependance of the conductivity of PEG1000 and PEG1000-POS O/Li=

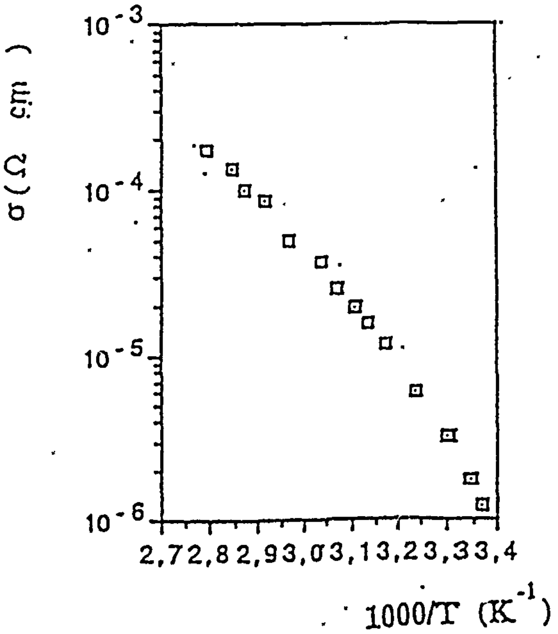

Fig 3 : The temperature dependance of the conductivity of PEG2000 + allyl glycidyl ether (8 units) O/Li=19

"Novel proton polymer ionic conductors"

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Novel proton polymeric electrolytes based on complexes of phosphoric acid with poly (ethylene oxide)-PEO - poly (methyl methacrylate)-PMMA or poly (acrylic acid)-PAA blend systems are described. The studied ionic conductors exhibited conductivities higher than 10^{-3} S/cm at room temperature. The present paper deals with relation between conductivity and phase structure of the studied electrolytes.

Polymer blends were prepared by mixing homopolymers followed by dissolution in acetonitrile or acetonitrile -dichloromethane mixture as well as by thermal polymerization of methyl methacrylate or acrylic acid in a presence of high molecular weight PEO. The latter procedure was followed by dissolution of thermally prepared blend in acetonitrile. After homogenization of an electrolyte solution phosphoric acid was added as a proton donor. Acid concentration varied from 5 to 50%-mol in respect to ethylene oxide molecular units. The weight ratio of PEO to the second blend component varied from 9:1 to 1:1.

The dependence of conductivity on blend composition as well as on concentration of the added proton donor is evidenced by results included in Table 1. It should be stressed that up to 20-30% mol of the added H_3PO_4 electrolytes were obtained in a form of foils. For higher acid concentrations paste or glue like structures were produced. These electrolytes were mechanically unstable under pressure applied during conductivity experiments (particularlyly at temperatures exceeding the melting point of PEO). In order to perform impedance spectroscopy experiments electrolytes were placed onto a porous membrane. Values of conductivity measured for protonic electrolytes are much higher than for their alkali metal analogues and for a few systems exceeded 10^{-3} S/cm at room temperature.

NMR and X-ray investigations showed highly inhomogenous structure of the studied electrolytes. T_1 spin - lattice relaxation time measurements performed on PEO-PMMA-H_3PO_4 systems evidenced presence of three phases of different proton mobilities. The results of the experiments were compared with previous data obtained for pure PEO, PEO-NaI electrolyte and PEO-PMMA undoped blend. The main conclusions which can be assumed on the basis of this comparison are as follows:
-upon temperature dependence of relaxation times T_1 particular phases of PEO-PMMA-H_3PO_4 electrolyte can be ascribed as: crystalline PEO phase , amorphous phase with low proton donor

content (characterized by relaxation times similar to that reported for amorphous PEO phase), amorphous phase of high proton donor content (which is not present in spectra of pristine PEO-PMMA blend)

-the latter phase is characterized by short liquid-like T_1 relaxation times which evidenced possibility of limited difussional motion of protons

-addition of phosphoric acid plasticized blend structure which is evident by higher mobility of protons belonging to both amorphous phases in comparison to pristine PEO-PMMA blend

-concentration of mobile amorphous phases at room temperature exceeded 60%-mol

NMR experiments shows that fast ionic motion is connected with the presence of flexible amorphous phase containing dissolved H_3PO_4. Mobility of protonic carriers in this phase is comparable to that characteristic of liquid systems. Similar or even higher values of conductivity, obtained for PEO-PAA-H_3PO_4 systems, are probably also connected with existence of highly mobile polymer phases. X-ray diffraction technique shows amorphous character of these electrolytes.

Table 2.
Values of conductivity for proton polymeric electrolytes based on blends of PEO with PMMA and PAA

Kind of blend component	X % wt	X_{ac} % mol	σ_{rt} S/cm
PMMA (*)	20	50	3.0×10^{-3}
PAA	20	5	4.4×10^{-4}
PAA	20	10	4.6×10^{-4}
PAA	20	50	3.3×10^{-3}
PAA	10	10	4.6×10^{-5}
PAA	30	10	4.8×10^{-5}
PAA	40	10	2.3×10^{-5}

X - concentration of acrylic or methacrylic component. X_{ac} - concentration of phosphoric acid in respect to ethylene oxide molecular units concentration. σ_{rt} - room temperature conductivity of protonic polymer electrolyte. (*) - blend prepared by thermal polymerization of methyl methacrylate in the presence of high molecular weight PEO.

ACKNOWLEDGEMENT
This work was financially supported by the Headmaster of the Warsaw University of Technology according to 101/6 research programme.

Li/MnO$_2$ Batteries with New Polymer Electrolytes

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Since several years the efforts to make polymer electrolyte batteries were focused on increasing ionic conductivity of the electrolyte. To date some materials of conductivities exceeding 10^{-4} S/cm at ambient temperatures are available [1,2], however the battery performances are worse than expected from the above value. The batteries suffer from high serial resistances appearing at electrode/polymer electrolyte interfaces. The aim of our work was to study the properties of polymer batteries with respect to the problem of interfacial resistances.

The batteries of a Li/(polymer + LiClO$_4$)/MnO$_2$ system were fabricated and their OCV values, short circuit currents and discharge curves were measured. Polymer electrolytes comprised of high m.w. poly(ethylene oxide) blended with poly(methyl acrylate) - PEO/PMMA or with poly[poly(propylene glicole) acrylate] - PEO/PAPG of chemical formula:

$$[-CH_2-(COOCH_2CH_2(-O-CH_3CH-CH_2-)_{14}OH)CH-]_n.$$

Both polymers were complexed with LiClO$_4$. These electrolytes exhibit ionic conductivities around 10^{-4}S/cm at 25°C. Batteries with both electrolytes gave OCV's about 3.5V and practical energy densities above 120 Wh/kg (weight of casing and current collectors not included). The short circuit currents were about 40 mA/cm^2 at 76°C, however for lower temperatures significant differences between the electrolytes were observed. The batteries containing PEO/PMMA gave 90 mA/cm^2 at 25°C and those with PEO/PAPG only 10 mA/cm^2.

In order to find the reasons of the high inner resistance the structures Li/polymer electrolyte/Li and MnO_2/polymer electrolyte/MnO_2 were prepared and their impedance spectra were registered. It was found that the MnO_2/polymer interface did not contribute to the overall resistance. This effect is probably due to the specific morphology of the cathode. The MnO_2 particles are distributed uniformly in the polymer electrolyte matrix thus increasing significantly the real phase boundary area. Most problems were related to the Li/polymer boundary. In the case of PEO/PAPG an additional highly resistive layer is created which was not found for PEO/PMMA. The layers originate probably from a chemical reaction of lithium with the polymer containing -OH groups at the end of the side chains. Despite the high ionic conductivity and good mechanical properties of this electrolyte it cannot be used with lithium at ambient temperatures.

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IONCONDUCTING COMPLEXES OF POLYVINYLPYRIDINES WITH ALKALI METAL SALTS

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Physico-chemical properties and ionic conductivuty of the complexes of polyvinylpyridines with alkali metal salts have been investigated by methods of electroconductivity, viscosity, NMR-spectroscopic and X-ray diffractometric in solution and solid state. It is established that the binding ability of the cations with macromolecules is arranged in order: $Li^+ > Na^+ > K^+ > Cs^+$. Ionic conductivity of the complexes of polymer-salts is placed in region 10^{-3}- $1-^{-7}$Sm.sm^{-1}. Degree of binding of cations (x), macromolecules (Θ) and binding constants (K_n) have been determined.

NEW POLYAMIDE-ETHER ELECTROLYTES

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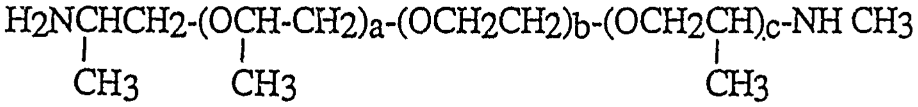
Polyethers exhibiting solvating properties can form ionic conducting complexes with alkali metal salts. Among them, polyethylene oxide (POE) is a good candidate. However PEO-salt complexes generally present a large tendency to crystallize at room temperature and consequently ionic mobility is reduced. In order to overcome this problem, we have synthetised a novel family of polyamides by polycondensation between jeffamine ® and diacid chloride(or triacid chloride) monomers.

The jeffamine products are polyether diamines based on a predominately polyethylene oxide backbone having the following structure:



$$H_2N\underset{CH_3}{CH}CH_2\text{-}(O\underset{CH_3}{CH}\text{-}CH_2)_a\text{-}(OCH_2CH_2)_b\text{-}(OCH_2\underset{CH_3}{CH})_c\text{-}NH\ CH_3$$

These functional oligoethers can also serve as precursors for reactions involving these functions. Two jeffamines of molecular weights equal to 646 and 935.5, respectively, have been used in this work . Polyamides form conducting complexes with bis(trifluoromethanesulphone)imide lithium salt (LiTFSI).

Preliminary data for some of the polymer-salt mixtures reveal conductivities comparable to those reported for alkali complexes of poly(oxyethylene).
Linear polyamides /Li TFSI with O.E units/Li = 8 reach a conductivity of 10^{-6} ohms $^{-1}$ cm^{-1} at room temperature, while the same value is obtained for the corresponding crosslink network at 30 °C.

Figure.1 shows the conductivity data for a series of polyamides-ether.

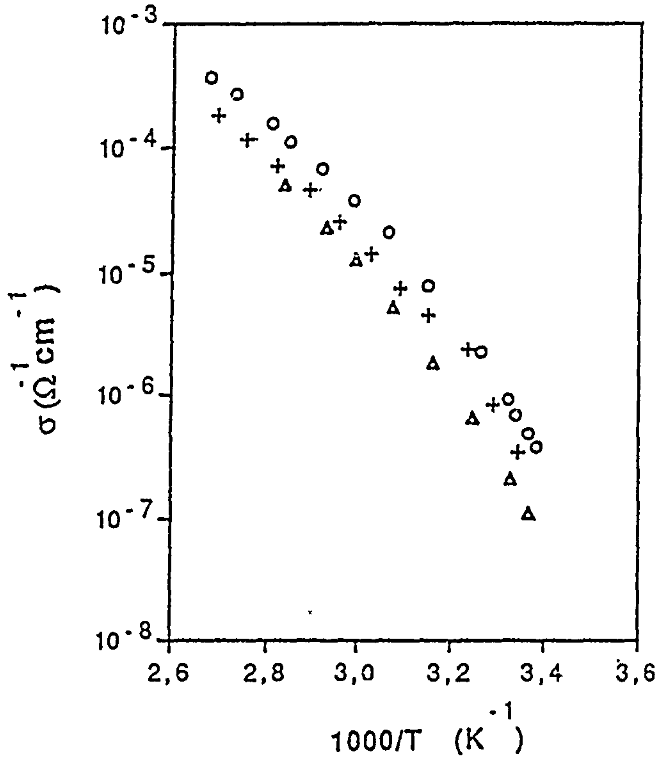


Figure1. Arrhenius plots $\sigma = f(T^{-1})$ for several networks.

- o Poly $C_6H_3(CO)_3$(Jeffamine 935)$_3$ / LiTFSI.
- + Poly $C_6H_3(CO)_2$(Jeffamine 935)$_2$(N-MethylAllylamine) / LiTFSI.
- ▿ Poly $C_6H_3(CO)_2$(Jeffamine 935)$_2$(N-Diallylamine) / LiTFSI.

Step-growth polycondensation has a considerable draw-back, insofar as the molecular weight of polycondensate can not be accurately controlled. So, we are also exploring ways to chemically crosslink the polymers, and to investigate polyamides with a low glass transiton temperature.

SOLID STATE ELECTROCHEMISTRY - ELECTROCHEMICAL MEASUREMENT OF OXYGEN-TRANSPORT IN NAFION MEMBRANES IN THE ABSENCE OF A CONTACTING ELECTROLYTE PHASE

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Introduction. Research in solid polymer electrolyte (SPE) fuel cells is gaining momentum because of the prospects of attaining high energy efficiency and power density power plants for electric vehicles and other applications. The most widely-investigated SPE's for such fuel cells are the perfluorosulfonate ionomers (PFSI's), such as du Pont's Nafion[2] and the Dow PFSI's. PFSI's are attractive materials for SPE fuel cells because these polymers show high O_2 solubilities, high proton activities and conductivities, and excellent chemical stabilities.

We will describe results of investigations of O_2 transport and electrochemical kinetic parameters in Nafion membrane. These measurements were made using a novel solid state electrochemical cell. The unique feature of this cell is that it operates without a contacting electrolyte phase. Thus, this cell mimics the environment extant in the SPE fuel cell. This cell was used to evaluate the solubility and diffusivity of O_2 in Nafion and the kinetics of O_2 reduction at the Pt/Nafion interface.

Experimental. A schematic diagram of the electrochemical cell is shown in Figure 1. This cell consists of a 100 μm-diameter Pt disk working electrode, a perforated Pt foil counter electrode, and a solid state version of a dynamic hydrogen working electrode. These electrodes are either spring-loaded (reference) or are mounted via thumb screws (working and counter). This allows for a known and adjustable pressure to be applied between each electrode and the Nafion membrane. The cell is mounted inside a gas-tight enclosure which is equipped with regulated gas-inlet valves so that the partial pressure of O_2 presented to the Nafion membrane can be precisely controlled. Cyclic voltammetric, potential step, and AC impedance methods were used to obtain the O_2 kinetic, transport and solubility data.

Results. O_2-reduction exchange current densities at various Pt/electrolyte interfaces are shown in Table I. The solid state Pt/Nafion interface investigated here shows the highest exchange current density obtained to date (Table I). This is not too surprising since Nafion is essentially the polymeric equivalent of trifluoromethane sulfonic acid (TFMSA) which is nonadsorbing and thus allows for high O_2 reduction kinetics (Table I).

Diffusion coefficients and solubilities for O_2 in various Nafion membrane environments are shown in Table II. The solubility obtained in this study is the highest to be reported to date. A reasonably high diffusion coefficient is also obtained (Table II). The differences in O_2 solubility and diffusivity seen in Table II are undoubtedly due to differences in water contents in the Nafion membranes used.

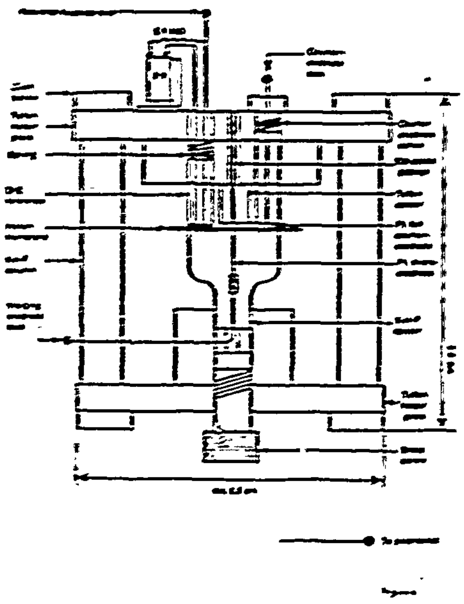

Table I. Exchange current density at various Pt/electrolyte interfaces.

Electrolyte*	Tafel slope, b (mV/decade)	i_0 (A/cm^2)	Ref.
Nafion membrane	-119	7.3×10^{-7}	This work
	-65	2.05×10^{-9}	
9.5 M TFMSA**	-115	1.48×10^{-7}	1
6.0 M TFMSA	-61	1.4×10^{-8}	1
1.1 N TFMSA	-60	9×10^{-11}	2
0.1 N HClO$_4$	-60	5×10^{-11}	3
85% H$_3$PO$_4$	-60	4×10^{-13}	4

*T=298 K, p=1 atm O$_2$ except for **; ** T=308 K.

Table II: Diffusion coefficients and solubilities of oxygen in Nafion under various experimental condition.

Parameter	Nafion solid polymer electrolyte (this work)^a	Nafion immersed in water^b	Nafion in H$_3$PO$_4$
Diffusion coefficient, D cm^2/s	$7.4(\pm 0.3) \times 10^{-7}$	2.4×10^{-7}	2×10^{-6}
Concentration, C mM	25(± 1)	7.2	3.8

a. Temp. = 25°C b. Temp. = 30°C, ref. 5 c. ref. 6

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IONIC CONDUCTION IN PEO-PERFLUOROSULPHONIMIDE DIVALENT SALTS COMPLEXES

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High molecular weight PEO has been the most widely used polymer in all these electrolytes in the last decade because of its good ability to solvate ionic salts. Most of these electrolytes have good mechanical strength and achieve high conductivity at about 80°C. However, they suffer from relatively low conductivity below 65°C because of high crystallinity.

Recently, Armand and al. (1) have shown that the PEO-Lithium Perfluorosulphonimide complex (PEO-LiTFSI) shows no evidence of a crystalline phase above room temperature. The conductivity of this complex is higher ($5.10^{-5}\ \Omega^{-1}.cm^{-1}$ at 25°C) than those involving $LiClO_4$ or $LiCF_3SO_3$. This new salt LiTFSI of formula $Li(CF_3SO_2\text{-}N\text{-}CF_3SO_2)$ acts as a plasticizer. Some recent studies on metal deposition of copper use electrolytes containing the salt of a divalent cation and a monovalent anion like PEO-$Cu(CF_3SO_3)_2$ (2). Among other possibilities of metal deposits, the following salts have been considered $ZnCl_2$ (3), $PbBr_2$ (4), $Pb(ClO_4)_2$ (5). We present some results obtained with complexes involving PEO and perfluorosulphonimide salts of divalent metals: lead, copper and nickel.

Copper : the total ionic conductivity curves of $PEO_{12}Cu(TFSI)_2$ and $PEO_{16}Cu(TFSI)_2$ are typical of amorphous samples and can be described by Vogel-Tamman-Fulcher (VTF) equation, on the basis of a free-volume model of conductivity. as compared to $(POE)_9Cu\ (CF_3SO_3)_2$, the complex $PEOnCu(TFSI)_2$ shows better conductivity (one order magnitude) over the whole range of temperature. DSC traces for $PEO_{12}Cu(TFSI)_2$ show no peaks neither during the first heating no during the second heating. This could confirm the amorphous nature of this compound. This is different from $PEO_9Cu(CF_3SO_3)_2$ complexes (4) in which DSC traces show crystalline to amorphous transition. Crystalline to amorphous transition is also observed with $PEO_n\ Cu(ClO)_4$ complexes (5).

Lead : the Arrhenius plots of the conductivities of the complexes $PEO_nPb(TFSI)_2$ (n = 8, 12) follow again the free-volume model of conductivity which is typical of amorphous samples. Besides DSC traces indicate amorphous behaviour over the temperature range -73°C to 127°C. The complex $PEO_{20}Pb(TFSI)_2$ shows an Arrhenius type of behaviour at low temperatures with a melting temperature around 45°C. This result was consistent with those obtained in DSC the table 1 compares the results obtained with $PEO_{20}Pb(TFSI)_2$ with other lead complexes from the available literature when another anion is involved. It can be noticed that one order of magnitude is gained when the $(TFSI)^-$ anion replaces Br^- for example (4). According to DSC traces, the compositions n = 8,12 in the complexes $PEO_nPb(TFSI)_2$ are entirely amorphous. As in the case of copper complexes, the complexes with ClO_4^- anion or with halides salts exhibit a different behaviour : these complexes are generally crystalline at room temperature (cf table 1).
Curiously the complex $PEO_{20}Pb(TFSI)_2$, crystalline in nature, which has the highest conductivity at room temperature.Though no explanation can be proposed, many systems show a better low temperature conductivity for non-eutectic compositions, especially towards the PEO-rich side.

Nickel : for $PEO_nNi(TFSI)_2$ n=8, a typical curvature which can be modelled with a free-volume equation is obtained, typical of an amorphous electrolyte. The curved plots are reversible on heating and on cooling. A problem arises for n=12 when an Arrhenius behaviour is obtained at low temperatures while DSC traces indicate that the complex is entirely amorphous over the whole temperature range. Electrolytes containing nickel salts have not been widely studied. The only one found in the literature involves $NiBr_2$(6). This complex has a total ionic conductivity of $10^{-6}\Omega^{-1}cm^{-1}$ at 150°C which could indicate that the conductivity at 25°C must be quite low.

REF.	COMPLEX	σ at 25°C ($\Omega^{-1}cm^{-1}$)	Tg (K)	MELTING TEMPERATURE (K)
(3)	$(PEO)_6Cu(CLO_4)_2$	10^{-6}	270	310
(4)	$(PEO)Cu(CF_3SO_3)_2$	$\approx 10^{-7}$	303	308 for O/Cu = 9
		(since 10^{-6} at 40°C)		293 for O/Cu = 6
	$(PEO)_{16}Cu(TFSI)_2$	5 10^{-6}		amorphous for
	$(PEO)_{12}Cu(TFSI)_2$	2 10^{-6}	261	T > room temperature
(5)	$(PEO)_{20}Pb(CLO_4)_2$	$\approx 10^{-10}$		
(4)	$(PEO)_8 PbBr_2$	1.1 10^{-9}		
(4)	$(PEO)_{16} PbCl_2$	4.6 10^{-10}		
(4)	$(PEO)_{12} PbI_2$	5.5 10^{-11}		
	$(PEO)_{20}Pb(TFSI)_2$	1.8 10^{-8}	238	318
	$(PEO)_{12}Pb(TFSI)_2$		258	amorphous
	$(PEO)_8Pb(TFSI)_2$	9.5 10^{-9}		amorphous
	$(PEO)_8Ni(TFSI)_2$	3 10^{-8}		amorphous
	$(PEO)_{12}Ni(TFSI)_2$	1.02 10^{-8}	258	amorphous
	$(POE)_{16}Ni(TFSI)_2$		246	crystalline
	$(PEO)_{20}Ni(TFSI)_2$		238	crystalline

Table I - Comparison between the conduction properties of some divalent complexes.

In conclusion, encouraging results have been obtained with the TFSI anion as the conductivity measurements are definitely higher than those involving the same cations with other anions. In addition to that, these complexes are generally entirely amorphous for compostions n ≤ 12 above room temperature. The plasticizing effect of TFSI ion is again noticed here.

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ELECTRICAL AND THERMAL PROPERTIES OF GAMMA IRRADIATED PEO BASED POLYMER ELECTROLYTES.

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In recent years, crosslinked polymers based on poly(ethylene oxide), PEO, doped with lithium salts, have been prepared with several chemical and radiochemical methods (1-3). In particular, crosslinks have been introduced into the macromolecular chains of PEO by exposing aqueous solutions of the polymer to an appropriate dose of gamma radiations (2, 3).

In this paper we report the preparation and the electrical, thermal and mechanical characterization of some films of PEO doped with lithium perchlorate, obtained after irradiation with a total dose of 1.0 Mrad in aqueous solution.

The effects of the irradiation of the polymer have been evaluated by means of a.c. measurements from -150 to 150 °C in the frequency range 1 Hz - 100 kHz. The ionic conductivity and the dielectric constant of the irradiated materials have been compared with those observed on the unirradiated ones: in particular, at room temperature, the ionic conductivity is significantly higher in the irradiated samples.

Thermomechanical data and thermooptical observations have also shown that the irradiated polymers display better mechanical properties and are less crystalline than the usual PEO based films.

Further developments of the present work will include tests of some promising compositions in solid state electrochemical devices.

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THE DETERMINATION OF THE MOBILITIES OF IONS IN PLASTICIZED PVC

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Plasticized PVC membranes are extensively used in potentiometric ion sensors. A typical membrane will consist of 33% (by weight) of PVC and 66% of a plasticizer. The membrane will have dissolved in it an ionophore (eg valinomycin) and a salt (eg $KBPh_4$). Generally the salt is present at a low concentration, perhaps 1mM and the ionophore is present at a much higher concentration. The membrane is contacted on both sides by aqueous solutions, one of which contains the ion being measured (eg K^+) at a well defined concentration whilst the other contains the ion at an unknown concentration. The EMF across the membrane is used to determine the difference of ion concentrations between the aqueous phases.

At the University of Newcastle we have set out to determine the concentrations and mobilities of ions in such membranes. We have used 3 different methods in order to separate the mobilties of cations and anions. These are:

1. The preparation of membranes containing the salt $AsPh_4BPh_4$.
Because of the equal size of these ions it can be safely assumed that they have identical mobilities. However the fact that most membranes have low dielectric constants means that it is necessary to determine the conductivity of membranes with at least 4 different concentrations of $AsPh_4BPh_4$ and then use the Ostwald Dilution Law to determine the numbers of ion pairs and free ions [1]. Whilst this method can cope with the presence of large numbers of ion pairs it is not clear how to use it when there are triple ions present.

2.The measurement of "liquid junction" potentials across membranes. This method depends on finding a salt which is soluble both in the aqueous phase and in the membrane. The only salt which we have found to be suitable is $NaBPh_4$. A membrane free of dissolved substances is sandwiched between two aqueous solutions of $NaBPh_4$ at different concentrations. A concentration gradient of $NaBPh_4$ is thus established across the membrane. In the absence of ion pairs in the membrane the measurement of the potential between the aqueous solutions gives the transport numbers in a straightforward manner. The presence of ion pairs can be tested for by making meeasurements at different concentration ratios [2].

3.The measurement of the response of membranes to small potentiostatic impulses. This method has benn widely used by Bruce and Vincent. We have found it useful in cases where there are very small concentrations of ion pairs, such as membranes containing Ca^{2+}, the ionophore ETH129 and BPh_4^- .

1."Properties of PVC based membranes used in ion selective electrodes"
R D Armstrong and G Horvai Electrochim Acta 35 (1990) 1

2."Transport numbers in PVC based membranes from diffusion potential measurements"
R D Armstrong W G Proud and L Starforth J Electroanal Chem 273 (1989) 209

PREPARATION CONDITIONS AND PROPERTIES OF PEO-$Cu(ClO_4)_2$ ELECTROLYTES.

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As previoulsy recognized, the properties of the polyelectrolytes are very sensitive to the preparation conditions, namely, the water content and thermal history.

In this communication, we report some results of the studies on the PEO-$Cu(ClO_4)_2$ system.

Samples have been prepared by the ususal casting method, using acetonitrile as a common solvent and mixtures of acetonitrile/methanol (1:1).

Some samples have been prepared using the components as "received" (namely, using $Cu(ClO_4)_2.6H_2O$), and dried under dynamic vacuum for several days at room temperature. Others have been prepared after drying of the components.

Conductivity, DSC and EPR studies have been used in the characterization of the samples.

One of the most interesting results is that the conductivity appears to increase with the dryness of the samples.

POLYMER ELECTROLYTES BASED ON POLY(ETHYLENE OXIDE) AND ZINC SALTS

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$(PEO)_nZnX_2$ films, in the range n=4-40 were prepared by casting acetonitrile solutions containing the appropriate ammounts of PEO (MW=$5x10^6$, Aldrich) into glass formers on Teflon sheets. Residual solvent was removed in vacuum for 48 hours and the films were then put in a dry box where they were kept for approximately 4 weeks until use. All subsequent handling was performed in dry atmosphere.

Differential scanning calorimetry, polarization microscopy observation, complex impedance spectroscopy and electrochemical studies have been carried out on the electrolytes prepared as described. Detailed studies have being performed in the $(PEO)n-ZnX_2$ electrolytes, in the range of concentrations n=4-40. From our analysis, defined complexes appear to exist and at least one eutectic is always present. The ionic conductivities are of the order of 10^{-7} $S.cm^{-1}$ at room temperature for some compositions.

A paramagnetic Cu^{2+} ion was used as an EPR probe to obtain information about the coordination of the metal ion to the polymer. EPR spectra were obtained for samples of $(PEO)n-ZnX_2$ containing 1% of $CuCl_2$. The g values and hyperfine constants are typical of Cu^{2+} ions coordinated to O in a distorted octahedral configuration (three different g values are observed instead of the usual $g_\perp$ and $g_\parallel$ values expected for nondeformed octahedra.

POLYMER ELECTROLYTES BASED ON POLY(ETHYLENE OXIDE) AND RARE EARTH SALTS

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A series of PEO-Rare Earth electrolytes has been prepared and some preliminary characterization has been done. Several compositions of the following systems have been prepared with PEO of MW=$5x10^6$: PEO-$PrCl_3$, PEO-Nd Cl_3, PEO-$EuBr_3$.

Anhydrous rare earth salts (bromides and chlorides) have been used as starting reagents and the usual solvent casting technique (from ethanol/acetonitrile mixtures) was used to prepare the electrolytes. All subsequent handling was performed in dry conditions.

We carried out preliminary photoluminescence spectroscopy experiments on PEO based electrolytes containing Europium. Emission and excitation spectra were obtained for two different compositions, $(PEO)_{16}$:$EuBr_3$ and $(PEO)_{32}$:$EuBr_3$, in the range 3500-7400 A. The temperatures varied between 13 K and room temperature. Both samples show qualitatively similar spectra, typical of Eu(III) ions, although relative intensities are quite different. The main peaks in the emission spectra (which are in large number) appear at 6140-6170 A which may possibly be assigned to the $^5D_0 \rightarrow {}^7F_2$ transition and 5929-5930 A ($^5D_0 \rightarrow {}^7F_1$). Although the intensities of the peaks are sensitive to temperature, the general shape of the responses are not altered either by the temperature or the excitation wavelength. Excitation sectra show several bands, the main ones being at 4647 A ($^7F_0 \rightarrow {}^5D_2$), 3953 A ($^7F_0 \rightarrow {}^5L_6$) and 5255 A ($^7F_0 \rightarrow {}^5D_1$). Once more, intensities are dependent upon temperature and relative intensities are different for the two samples. In general terms, results compare well with published data[1].

Time resolved analysis of the photoluminescent peaks have also been performed. Fitting of the experimental curves indicate two distinct life-times, the slowest one being of the order of 1 ms.

The richness, in very well defined peaks (bands) of the spectra shows that luminescence studies may provide usefull information about the coordination and neighbourhood of the rare-earth ions inside polymer electrolytes. Spectroscopic investigation of the role of Eu(III) and other lanthanides in those materials is being pursued.

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[1] R. Huq and G. C. Farrington, Second International Symposium on Polymer Electrolytes, B. Scrosati, (editor); Elsevier Applied Science, (1990), p. 273

Molecular Dynamics Simulations for Conductivity and Structure in Model Polymer Electrolytes

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While free-volume, configurational entropy and dynamic percolation models provide useful and convincing pictures for ion mobilities in polymer electrolyte materials, they do not allow full understanding of the conductivity, because interionic interactions are ignored. The importance of such interactions has been underscored in a series of recent experimental studies in which ion clustering, pair formation "salting out," and changes in solubility have been correlated with temperature - and stoichiometry - dependent changes in conductivity. To understand such interionic interaction behavior, we discuss results of molecular dynamics (MD) simulations on models for ionic solutions.

The MD studies have been analyzed to reveal both qualitative and quantitative measures of interionic association. In particular, we discuss both structural and transport results, as experimentally - relevant parameters (temperature, dielectric constant of host, concentrations, pressure) vary. The phenomenon of increased clustering with increasing temperature is observed with high host dipole moment. We see no direct evidence for triple ions as an important species; rather, large clusters are found, with fluctuating nearly-free ions that can undergo large local displacements.

The clustering can be analyzed in thermodynamic terms, centering on changes in entropy, energy and free energy as pairs separate. The transport process is more complicated, since (as has been suggested experimentally) quasifree ions, on long timescales, do not really exist in these concentrated electrolyte materials. Mechanistic details, and reasonable conceptual bases for structure and transport, will be presented.

AUTHOR INDEX

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