AD-A191 412 FAST ION CONDUCTING GLASSES(U) PURDUE UNIV LAFAYETTE IN 1/1
DEPT OF CHEMISTRY C A ANGELL OCT 87 N00014-84-K-0289

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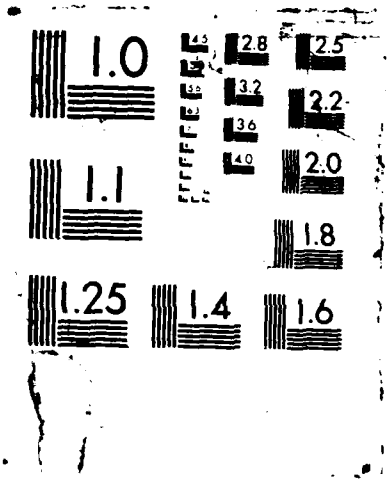
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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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END OF YEAR REPORT

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1 Oct 1986 through 30 Sept 1987

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"Fast Ion Conducting Glasses"

C.A. Angell

Purdue University
Department of Chemistry
West Lafayette, IN 47907

PART I.

(a) Papers submitted to journals (and not yet published):

1. "High Conductivity in PEO · PPG Block Polymer + Salt Solutions," R. Xue and C.A. Angell, Solid State Ionics (in press).
2. "Ion-Matrix Coupling in Polymer Electrolytes from Relaxation Time Studies," L.M. Torell and C.A. Angell, Polymer J. (Proc. 1st International Conference on Polymer Electrolytes) (1987) (in press).
3. "Contrasting Conductance/Viscosity Relations in Glassy and Polymer 'Solid' Electrolytes," M. McLin and C.A. Angell, J. Phys. Chem. (in press for Letters Section).
4. "Strong and Weak Electrolytes in Polyether Solutions Under Pressure," R. Xue and C.A. Angell, J. Phys. Chem. (submitted).

(b) Papers Published in Refereed Journals

1. "Far Infrared and Dielectric Relaxation Spectra in Supercooled Water and Water + Propylene Glycol Solutions," L. Boehm, D.L. Smith and C.A. Angell, J. Mol. Liquids, (invited for R.H. Cole Honor Issue), *36*, 153 (1987).

(c) Books Submitted: none

(d) Books Published: none

(e) Technical Reports Published and Papers Published in Non-Refereed Journals: none

(f) Patents Filed: none

(g) Patents Granted: none

(h) Invited Presentations at Topical or Scientific/Technical Conferences:

1. "Insights Into Ion-Matrix and Ion-Ion Couplings in Polymer-Salt Electrolytes from Relaxation Spectroscopy," Presented to participants of the International Symposium on Polymer Electrolytes, University of St. Andrews, Scotland, June 17, 1987 (invited lecture).
2. "Ion-Matrix and Ion-Ion Couplings in Rival Amorphous Solid Electrolyte Systems," Invited for American Physical Society Solid Electrolytes Symposium, March meeting at New Orleans, 1988

(i) Contributed Presentation at Topical or Scientific/Technical Conferences: none

(j) Honors/Awards/Prizes

1. Purdue University Science Faculty Research Award (1987) (McCoy Award).

(k) Number of Graduates Receiving Full or Partial Support on ONR Contract

1 (Mike McLin)

1 visiting research student (Zhou Jinfeng)

(l) Number of Post-Doctoral Fellows Receiving Full or Partial Support on ONR Contract

1 (at present John Kieffer - early in year, Rongjian Xue)

PART II.

(a) Principal Investigator: C. Austen Angell

(b) Cognizant ONR Scientific Officer: Robert Nowak

(c) Current telephone number: (317) 494-5256

(d) The focus of this research has been on fast ion conduction in amorphous materials. Early work concentrated on silver and copper ion containing systems. Since then the program has broadened to include the study of the kinetic processes which determine whether or not an amorphous solid is formed during the cooling of an ionic liquid. Another new development has been the introduction of the pressure variable. Initially this was intended to determine whether conductivity of glasses could be increased by compaction under pressure. However, this work branched into a study of the effect of pressure on elastomer ion systems (ion-polymer solutions) to check a possibility we raised in a plenary lecture in 1983, viz., that ion pair dissociation (which was suspected of limiting the conductivity of these systems) could be enhanced and conductivity thereby be increased. In the last year we have returned to and completed the study of pressure effects on conductivity in inorganic glasses and have also extended the polymer salt studies.

(e) Significant results during last year:

(1) (Mike McLin) A comparison study to the viscosity-conductance comparison for the liquid state of superionic glasses reported at this time last year has been made for the case of the rival solid electrolyte type, a polymer salt mixture (PPG-$NaCF_3SO_3$) using solvents of two different molecular weights. Since the viscosity of the pure polymer solvents depends on the molecular weight, the same comparison of conductivity and shear response times made for the molten superionics cannot be made. However a comparison of the rival systems can be made by separating out the temperature dependences of the electrical and shear responses. The polymer salt systems show the same temperature dependence, in stark contrast to the molten superionic, in which the energy barrier for the electrical response is always small. Using a reduced temperature scale based on a scaling by the glass transition T_g, we have shown how the rival polymer-salt and superionic glass systems differ in opposite ways from a reference aqueous solution. The comparison permits separation of mobility from carrier concentration effects in the polymer salt systems and points the way to improving polymer-salt performance (paper submitted to J. Phys. Chem.)

(2) (Zhou Jinfeng) To check on earlier reports that the ionic conductivity of AgI-Ag oxysalt glasses increase in conductivity on compression, we have carried out conductivity measurements of good precision on AgI-$AgPO_3$ glasses in the pressure range 1-1500 bar and at temperatures both above and below T_g. Well below T_g, the conductivity decreases with a slope of $d\ln\sigma/dP$, close to that expected from the ionic volume. Close to T_g and above it, the slope is much smaller, apparently due to the higher compressibility of the liquid state which brings more ions into the conductance path to compensate for decreases in ion mobility. To separate these effects a cyclic path in pressure and temperature has been followed. Results indicate that the two effects are comparable in magnitude.

(3) (John Kieffer) To get a better idea of the conductance mechanism, ion dynamics computer simulation programs formerly used in the study of alkali silicate systems have been developed to produce graphical output which can be projected in 3-dimensional images using simultaneous projection of red and blue images on a color screen. The feasibility of this projection has been demonstrated during a loan period of a Silicon Graphics Iris computer. This project gives exciting results and will be pursued in the remainder of this grant period.

(f) Plans for the coming year.

Our contract is due to expire in 3/88. Therefore there are no plans under this contract. It is hoped to pursue a new line of study in infrared transmitting halide glasses in the future.

(g) Graduate students receiving support under this grant.

(i) Initially, Hemlata Senapati (glasses)
(ii) Presently, Mike McLin (Polymers)

Visiting student: Zhou Jinfeng

Post-doctoral fellows receiving support:

(i) Initially, Xue Rongjian
(ii) Presently, John Kieffer

(h) Technical reports submitted to ONR during the past year

1. "High Ionic Conductivity in PEO.PPG Block Polymer + Salt Solutions," Rongjian Xue and C.A. Angell.
2. "Far Infrared and Dielectric Relaxation Spectra in Supercooled Water and Water + Propylene Glycol Solutions," L. Boehm, D.L. Smith and C.A. Angell.
3. "Crystallization and Vitrification in Cryoprotected Aqueous Systems," C.A. Angell and H. Senapati.
4. "Ion-Matrix Coupling in Polymer Electrolytes from Relaxation Time Studies," L.M. Torell and C.A. Angell.
5. "Contrasting Conductance/Viscosity Relations in Liquid States of Vitreous and Polymer "Solid" Electrolytes," M. McLin and C.A. Angell.

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