**Abstract**

Electrochemistry in ambient temperature ionic liquids was performed. A portion of the work was carried out in haloaluminate melts, mainly 1-ethyl-3-ethyl imidazolium chloride - aluminum chloride. This was to complete work initiated under prior grants and involved studies of buffering of these systems. The bulk of the work involved electrochemical studies in non-haloaluminate ionic liquids, mainly 1-butyl-3-methylimidazolium hexafluorophosphate. Alkali metal reduction potentials were measured, an apparent anomaly with a rotating disc electrode was found and explained, and turn-on potentials and conductivities of polypyrrole films in the non-haloaluminate ionic liquids were measured.

**Subject Terms**

Ionic liquids; rotating disc voltammetry; conducting polymers.
Final Report on Grant No.F49620-00-1-0061  
Studies in Buffered Chloroaluminate Ionic Liquids

This activity was funded from December 1, 1999 through January 31, 2004 for $308,423. In addition, a supplement of $30,545 was added from August 1, 2002 through January 31, 2004. This was added as a separate grant with the same title.

The Principal Investigator has been funded continuously since 1971, by AFOSR. He has been fortunate to have had incredibly capable Program Managers – Denton Elliott, John Wilkes, Hugh De Long, and Paul Trulove – who have allowed him to perform this work. He's also been fortunate to have had superb students and post-docs over the years, without whom none of the work carried out would have been done. Two of his graduate students were Air Force officers sent to do Ph.D. work in the molten salt area. Appendix A lists publications, which acknowledge AFOSR support since support was initiated in 1971. During the period of support, the PI has received several awards, which are listed in Appendix C. All are in part the result of the AFOSR support.

For the past several months, most of the effort has been devoted to winding down all laboratory work and cleaning up a laboratory that has had over 30 years of AFOSR support to amass chemicals and equipment. With the PI's retirement, the laboratory goes to other researchers.
SUMMARY OF WORK, 1 December, 1999 – 31 January, 2004

Completed Work

I. Work Carried Out Under Previous Grant

Several manuscripts listed as “in press” or as “submitted” in the Final Report on Contract F49620-96-1-0097, “Studies of Latent Acidity and Neutral Buffered Chloroaluminate Ionic Liquids,” have been published. These include:


II. Work Completed under Present Grant

Most of the work carried out under this present contract has been published, or is in press. Titles and Abstracts of the work follow.

A. Haloaluminate Ionic Liquids


Abstract: The buffering of 1-ethyl-3-methyl imidazolium chloride (EMIC) – aluminum trichloride (AlCl₃) room-temperature ionic liquids (melts) using alkali metal bromides and iodides was studied. The bromide or iodide salts buffer the melts, but the bromide or iodide ions do not replace the chloride ions in the melts. Unlike melts buffered with alkali metal chlorides, it is relatively easy to deposit the alkali metals, and thus it may be possible to use these buffered melts in power sources. In melts buffered with a mixture of lithium chloride and iodide, it is possible to both deposit and strip lithium metal. As has been seen with melts buffered with alkali metal chlorides, the buffered melts appear to be more acidic than would be expected from the low concentration of the acidic Al₂Cl₇⁻ ion.

**Abstract:** Pulsed-field-gradient spin-echo NMR has been used to determine the diffusion coefficients of the cation species in a series of chloroaluminate room-temperature molten salts as well as that of 1,2-dimethyl-3-propylimidazolium tetrafluoroborate and a molten salt polymer gel. Based on the diffusion coefficients, the activation energy for diffusion of the melt cations has been calculated. In addition, the hydrodynamic radius of the melt cation has been determined using the Stokes-Einstein relation.

**B. Studies in Non-Haloaluminate Ionic Liquids**


**Abstract:** Formal potentials and diffusion coefficients of the alkali metal couples of lithium, sodium and potassium hexafluorophosphate salts dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate were determined using a hanging mercury drop electrode as the working electrode. Chronoamperometry was used to determine the diffusion coefficients, which ranged from $1.4 \times 10^{-8}$ to $4.5 \times 10^{-8}$ cm$^2$/s for the Na and K cations, respectively. Formal reduction potentials of $-2.96 \pm 0.006$ V and $-3.35 \pm 0.003$ V vs. the ferrocene/ferrocnium couple were obtained for sodium and potassium using normal pulse voltammetry. The presence of adsorption maxima in the lithium normal pulse voltammograms necessitated the use of chronopotentiometry to determine a lithium formal potential of $-2.45 \pm 0.025$ V.


**Abstract:** An apparent anomaly is described in which maxima on rotating disk voltammograms for ferrocene oxidation in an ionic liquid were found. The ionic liquid, 1-butyl-3-methyl imidazolium hexafluorophosphate, bmimPF$_6$, is a neoteric solvent of current interest. The maxima are shown to be due to the very high viscosity of the solvent, 3.26 poise, which yields an unusually high Schmidt number of $3.5 \times 10^3$, compared to a value of about $10^3$ for aqueous solutions. It is estimated that over 100 revolutions of the disk are needed to achieve the Levich
limiting current following application of a voltage step to the disk. The current transient resulting from application of a voltage step to the rotating disk is found to be in agreement with previously developed theory, even for these highly viscous systems. Analysis of the transient permits a determination of the Schmidt numbers without measurement of the viscosity and density of the solvent, or diffusion coefficient of the reacting species.


**Abstract:** Polypyrrole (ppy) and poly(N-methylpyrrrole) (pmpy) films were prepared galvanostatically at the ring of a rotating ring-disk electrode from the corresponding monomers dissolved in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$). Rotating ring-disk voltammetry was used to determine switching potentials and conductivity of the films while immersed in bmimPF$_6$. Switching potentials of 0.63 ± 0.04 V and 1.07 ± 0.03 V vs. the cobaltocenium/cobaltocene couple, [CoCp$_2$]$^{+}$, were determined for the ppy and pmpy films, respectively, from negative potential scan voltammograms. Positive potential scan voltammetry was used to obtain the potential dependent conductivity of the films as the films switched from their insulating (at potentials more negative than switching potential) to quasi-metallic state. Two different computational models (non-linear vs. linear conductance gradients) and two different redox probes ([CoCp$_2$]$^{+}$ and decamethylferrocenium/decamethylferrocene) were used in the calculation of film conductivity. The conductivity of the ppy films was found to increase by an order of magnitude for every 72 ± 8 mV change in the applied potential. At potentials less than the switching potential, the conductivity of the pmpy films increased ten-fold for every 110 ± 15 mV change in the applied potential. At potentials greater than the switching potential, the pmpy films required a 200 mV change to induce the same degree of change in film conductivity.

**III. Personnel**

**Senior Research Personnel**

Dr. Deborah Boxall  
Dr. John O'Dea  
Dr. Peter Koranaios
APPENDIX A

Publications--Grant Related Activity - since AFOSR support initiated.


AFOSR 75-2776; 1 March 1975 - 31 May 1976


AFOSR 766-2978; 1 April 1976 - 30 June, 1979


AFOSR F49620-79-C-0142: 1 June 1979 - 30 Sept. 1980


32. J. Robinson and R. A. Osteryoung, "An Investigation into the Electrochemical Oxidation of Some Aromatic Amines in the Room Temperature Molten Salt


AFOSR-81-0007; 1 October, 1980 - 31 August, 1984


*Work related to pulse methodology development but not supported by A.F.O.S.R.


AFOSR-87-0088; 1 December, 1986 - 30 November, 1989


*98. R. Carlin and R. A. Osteryoung, "Aluminum Anodization in Basic Ambient

AFOSR 90-0099; 1 December, 1989 - 30 June, 1992


* Work relevant to this grant but supported in part by SDIO/IST, managed by ONR.


* Work relevant to this grant but supported in part by NSF


118 Michael T. Carter and Robert A. Osteryoung, "Electrochemistry of 9,10-Anthraquinone in the Presence of Proton and Tetrachloroaluminate in Ambient Temperature Molten Salts," Proceedings of Eighth International Symposium on Molten Salts, R. J. Gale, George Blomgren, and H. Kojima,


Transactions, Special Issue on Electrochemistry Honoring Roger Parsons, 92, 3969-3973 (1996).


AFOSR Contract F49620-00-1-0061, December 1, 1999 through January 31, 2004


APPENDIX B

Presentations at Meetings Related to Activities on Grant No.F49620-00-1-0061
Studies in Buffered Chloroaluminate Ionic Liquids
December 1, 1999 through January 31, 2004

Invited Presentations


Contributed Presentations

APPENDIX C

Honors and Awards to PI during period of AFOSR support.

- Distinguished Service Award, Colorado State University, 1975.
- American Chemical Society Colorado Section Award, 1978.
- Elected Fellow, American Association for the Advancement of Science, 1980.
- Winner of C. N. Reilley Award in Electroanalytical Chemistry, 1987
- Awarded Schoellkopf Medal, Western New York Section, American Chemical Society 1990
- Elected as Fellow, The Electrochemical Society, 1990-
- Recipient of the American Chemical Society, Division of Analytical Chemistry, Award in Electrochemistry 1991.
- Recipient of the Physical Electrochemistry Division of the Electrochemical Society Max Bredig Award in Molten Salt Chemistry, 1991
- Outstanding Alumnus of the Year Award, College of Arts and Sciences, Ohio University, 1992