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13. ABSTRACT (Maximum 200 words) <p>Studies of ambient temperature chloroaluminate ionic liquids composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride were carried out. The major activity involved studies in alkali halide buffered neutral melts. We have observed that these buffered melts exhibit a "latent acidity". Weak Lewis bases, B:, which are uncomplexed by AlCl₃ in an unbuffered neutral melt, form AlCl₃ adducts in a buffered melt. This occurs because the equilibrium $B: + AlCl_4^- + Na^+ = B:AlCl_3 + NaCl(s)$ is driven to the right by the precipitation of NaCl(s). The extent to which the reaction takes place depends quantitatively on the [Na+]. ROESY NMR was carried out to obtain information of local structure in basic chloroaluminate ionic liquids. The ROESY spectra clearly showed cross-peaks due to intramolecular and intermolecular NOE transfers between various protons on the ring system. This confirmed hydrogen bonding between chloride and various ring hydrogen giving rise to structure in the basic melts. Battery related studies involving the use of an additive in the neutral buffered melts to passivate and minimize corrosion of Na and Li surfaces were carried out. SOCl₂ was found to be superior to HCl as a passivating agent.</p>				
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This is a Final Report on Contract F49620-94-1-0056, "Chemical Studies in Lewis Acid and Superacid Systems".

This activity was funded for a one year period for \$157, 378 (FY 94) starting January 1, 1994. The AFOSR program under which this grant was funded was terminated as a renewal proposal was being prepared. Rather than operating at the full funded level, requests for a one year no cost-extension , followed by a six-month no cost extension, were made and granted. Thus, the period of the grant was from January 1, 1994 through June 30, 1996.

A major reason for extending the period of the grant, and bringing the research project to an orderly conclusion, was that an Air Force officer, Capt. Robert Mantz, was in our laboratory working on his Ph.D. Captain Mantz entered graduate school here in August, 1993. It was felt very desirable to have at least one post-doc, or other personnel, in the laboratory at the same time that Capt. Mantz was working on his thesis.

SUMMARY OF WORK, 1 January, 1994 - 30 June, 1996

INTRODUCTORY COMMENTS

As described above, this work was initially funded for a one year period, but, as a result of changes in funding, was extended to the 2.5 year period covered by this report at a considerably lower level of effort than originally envisioned. As has been the case in past reports, completed work will be presented as abstracts from materials published. Topics are listed below, generally, as items which appeared in the proposal for this Contract.

I. COMPLETED WORK

A. Studies of Polymer Modified Electrodes in Ambient Temperature Molten Salts

A limited amount of work in this area was performed during the period of this report. Two manuscripts, listed as "in press" in the Final Report for AFOSR Grant No. F49620-92-J-0326, have been published. (Appendix A, Ref. 127, 129.) A "Proceedings" manuscript on this work has also been published. (Appendix A, Ref. 134).

B. General Electrochemistry/ Fast Pulse Voltammetry

One manuscript listed as in press in the Final Report for AFOSR Grant No. F49620-92-J-0326, has been published. (Appendix A, Ref. 128).

A manuscript, "Electron Transfer Kinetics for Weakly-Bonded, Labile Metal-Ligand Complexes", has been submitted, and will be published in, the Journal of the Chemical Society: Faraday Transactions, in a special volume on electrochemistry dedicated to Prof. Roger Parsons. Portions of this work were carried out at North Carolina State University and at the then existing Seiler Research Laboratory. (Appendix A, Ref. 138).

Abstract

The electron transfer kinetics for the weakly-bonded, labile Cu(I)-L (L = CO and ethylene) complexes were investigated with square wave voltammetry (SWV) in the ionic liquid solvent AlCl₃-EMIC (EMIC = 1-ethyl-3-methyl-1*H*-imidazolium chloride). The oxidation of Cu(I)-L to Cu(II) and free ligand proceeds through an asymmetric quasi-reversible electron transfer mechanism in which the heterogeneous rate constant (k_a^0) is decreased relative to the rate constant for uncomplexed Cu(I), and the anodic transfer coefficients (β) is much less than 0.5. The Cu(I)-L bond energies were determined using potentiometric methods

and found to be $9.4(\pm 0.8)$ and $11.1(\pm 0.1)$ kcal mol⁻¹ for the CO and ethylene complexes, respectively.

C. Chemistry and Electrochemistry in Superacid Systems

Work on the concept of "latent acidity" in the ambient temperature chloroaluminate buffered neutral melts was continued. A quantitative study of this concept was undertaken, completed, and published in *Analytical Chemistry* (Appendix A, Ref. 131). A "Proceedings" paper on this work has also been published. (Appendix A, Ref. 132).

Abstract

Chloroaluminate ambient temperature ionic liquids consisting of AlCl₃ and 1-ethyl-3-methylimidazolium chloride can be both neutralized and buffered by the addition of an alkali halide to an acidic melt, one containing excess AlCl₃. Such melts possess an electrochemical window of ~4.4 V. The ionic composition of a NaCl-buffered neutral melt is modified such that $[Im^+] + [Na^+] = [AlCl_4^-]$. We have observed that these buffered melts exhibit a latent acidity. Weak Lewis bases, B:, which are uncomplexed by AlCl₃ in an unbuffered neutral melt, form AlCl₃ adducts in a buffered melt. This occurs because the equilibrium $B: + AlCl_4^- + Na^+ = B:AlCl_3 + NaCl(s)$ is driven to the right by the precipitation of NaCl(s); in the absence of Na⁺, this reaction does not take place. The reaction was observed for the weak bases acetylferrocene, dimethylaniline, and pyrrole with use of electrochemical and spectroscopic techniques and is limited by the amount of Na⁺ present in solution in the initially buffered neutral melt.

Although not specifically in this task area, work on NMR studies of these molten salt systems was continued. ROESY NMR of basic ambient temperature chloroaluminate melts was examined to obtain interaction pertaining to the structural interactions in the system. This work was published in *Inorganic Chemistry* (Appendix A, Ref. 132). A "Proceedings" paper on this work was also published. (Appendix A., Ref. 133).

Abstract

ROESY NMR was carried out to obtain information of local structure in basic chloroaluminate ionic liquids consisting of mixtures of AlCl₃ and 1-ethyl-3-methylimidazolium chloride. The ROESY spectra clearly showed cross-peaks due to intramolecular and intermolecular NOE transfers between various protons on the ring system. This confirms hydrogen bonding between chloride and various ring hydrogen giving rise to structure in the basic melts.

D. Material Synthesis

We had felt it possible to synthesize crystals based on oxidation of tetrathiafulvalene. This is reported in a manuscript, "Heterogeneous and Homogeneous Electron Transfer Reactions of Tetrathiafulvalene in Ambient Temperature Chloroaluminate Molten Salts", which was published in the Journal of the Electrochemical Society. (Appendix A, Ref. 130).

Abstract

The electrochemistry of tetrathiafulvalene (TTF) in an ambient temperature chloroaluminate molten salt composed of 1-ethyl-3-methylimidazolium chloride mixed with AlCl_3 has been examined. In both basic and acidic melts, TTF is oxidized in two consecutive one-electron steps to TTF^+ and then to TTF^{2+} . In basic melts, neutral TTF is stable and its oxidations are well behaved on the voltammetric time scale. TTF^{2+} is adsorbed at a glassy carbon working electrode in basic melts. constant current electrolysis of TTF to TTF^+ at a Pt electrode in basic melt produces purple crystals which appear to be electronically conductive. In acidic melts, HCl, present as an impurity, oxidizes TTF to TTF^+ . Diffusion coefficient measurements by pulse voltammetry suggest that TTF forms a slowly diffusing AlCl_3 adduct in acidic melts.

E. Battery Related Studies

Towards the end of this Contract period, work was carried out related to battery activities then underway at the Frank J. Seiler Research Laboratory, and in collaboration with personnel there. The first work on this involved an effort to passivate sodium or lithium anodes in buffered melts, and has been published in J. Electrochem. Soc. (Appendix A, Ref. 133).

Abstract

Lithium and sodium deposition-stripping studies were performed in room temperature buffered neutral chloroaluminate melts containing low concentrations of thionyl chloride (SOCl_2). The SOCl_2 solute promotes high cycling efficiencies of the alkali metals in these electrolytes. Staircase cyclic voltammetry and chronopotentiometry show cycling efficiencies of approximately 90% for both lithium and sodium. High cycling efficiencies are maintained following extended exposure of the melt to the dry box atmosphere and after time delays at open circuit. The performance of the SOCl_2 promoted systems is substantially improved over previous studies in room temperature melts containing hydrogen chloride as the promoting solute.

A second piece of work followed up on this and attempted to optically examine the lithium and sodium surfaces in the same system. This work is in press in J. Electrochem. Soc. (Appendix A, Ref. 134).

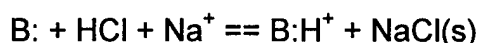
Abstract

Previous work performed in both sodium and lithium buffered chloroaluminate molten salts have shown that the addition of small amounts of SOCl_2 promotes the reversible stripping behavior of lithium and sodium metal with cycling efficiencies between 80-90%. In this work we have performed a series of optical studies in conjunction with electrochemical experiments at varying SOCl_2 concentrations in both lithium and sodium chloride buffered melts. On investigation, the lithium deposit is dendritic in nature and does not form a uniform film on the tungsten electrode. After discharging at moderate current densities, disconnected lithium metal is observed at the electrode surface. In contrast, the sodium deposits as a uniform flat film on the tungsten electrode with little or no dendritic growth. The sodium electrodeposits undergo complete stripping from the tungsten electrode without dendritic or disconnected sodium metal left on the electrode surface.

II. Work in Progress/Incomplete

A. Latent and Superacidity Studies

We are attempting to determine if the acidity of the proton, which, in the acidic melt behaves as a superacid, is enhanced in the neutral buffered melt by a reaction:



We are using a number of arenes to investigate this phenomenon, both electrochemically and spectroscopically. Initial findings show that there is, in fact, an increased proton activity in a neutral buffered melt compared to a neutral unbuffered, or basic, melt. We have found that HCl is a weaker Brønsted acid in a NaCl-neutral buffered melt, originally 55% mole % AlCl_3 prior to buffering, than in the 55% mole % AlCl_3 -ImCl melt itself. However, in a LiCl-neutral buffered melt, originally 55% mole % AlCl_3 prior to buffering, HCl appears to be a stronger Brønsted acid than in the 55% mole % AlCl_3 -ImCl melt itself. We have shown that the latent acidity, as it affects the proton acidity in the melt, is a function of both the concentration and type of alkali metal ion employed to buffer the system. This work is carried out by investigating the extent to which 9,10-dimethylantracene and hexamethylbenzene is protonated. The Brønsted acidity of HCl within either of these systems can be altered by varying the partial pressure of gaseous HCl over the melt. For example, in a neutral-NaCl buffered

melt, originally 55 mole% AlCl_3 , the percent of protonation of 9,10-dimethylantracene changes monotonically from zero, at 0 partial pressure of HCl, to 80% protonated at 800 mm of HCl above the melt. This reaction is being studied quantitatively, and a solubility study of HCl as a function of partial pressure of HCl over the buffered neutral melts is being carried out. This should permit us to estimate a Hammett acidity function for these melts. Two oral presentations of this work have been made at a meetings. (Appendix B, Ref. 11 and 17). A "Proceedings" paper of the preliminary findings has been submitted. (Appendix A, Ref. 140).

B. Buffered Melts

We have suspected, and have confirmed, albeit with difficulty, that oxide is capable of forming a neutral buffered melt having the same electrochemical window as the alkali metal neutral buffered melts. The difference here, though, is that the buffers involved, oxide and Al-O-Cl entities, are all soluble. Work on this is in progress. A talk on this work was presented at a local ACS meeting. (Appendix B, Ref. 18)

C. NMR Studies

Work on Gutmann Donor-Acceptor numbers, using triethyl phosphine oxide as a probe molecule, is being carried out in buffered neutral melts. It has been found that there are differences in the acceptor numbers if different alkali halides are used for buffering and if the concentration of alkali metal present in the buffered neutral melt is varied. A talk on this has been presented. (Appendix B, Ref. 10 and 16). A manuscript on this is in preparation. A "Proceedings" paper on preliminary aspects of this work has been submitted. (Appendix A, Ref. 139).

III. Interaction with Air Force Laboratories Personnel

Although numerous interactions with Air Force personnel had been frequent, the closing of the Seiler Laboratories at the Air Force Academy has limited such interaction.

IV. Other Activities

Talks presented at various meetings during the Contract period are given in Appendix B below.

V. Personnel

Personnel associated with the activity for any extended time during the contract period are listed below.

Senior Research Personnel

Dr. Ian Quarmby
Dr. Jack Summers
Dr. Leonid Goldenberg
Dr. Joan Fuller

Junior Research Personnel

Ms. Dawn King*
Capt. Robert Mantz**

* Will receive M.S. degree in July, 1996.

** Not paid on Contract funds

APPENDIX A

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

AFOSR-71-1955: 1 Jan. 1971 - 28 Feb. 1975

1. Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters", *Electrochimica Acta*, 16, 525 (1971).
2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry", Vol. II, "Application of Computers to Chemical Instrumentation", Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
3. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Solvent Equilibria in $\text{AlCl}_3\text{-NaCl}$ Melts", *J. Electrochem. Soc.*, 120(2), 223 (1973).
4. H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrode Reactions in Fused AlCl_3 Containing Solvents", *J. Electroanal. Chem.*, 38, 476 (1972).
5. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in $\text{AlCl}_3\text{-NaCl}$ Melts", *J. Electroanal. Chem.*, 121, 212 (1974).
6. H. Lloyd Jones and R. A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl_3 :II.", *J. Electroanal. Chem.*, 49, 281 (1974).
7. R. J. Gale and R. A. Osteryoung, "Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten NaCl-AlCl_3 Solvents", *J. Electrochem. Soc.*, 121, 983 (1974).
8. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate", *J. Org. Chem.*, 39, 2416 (1974).
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12. D.E. Bartak and R. A. Osteryoung, "The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate", *J. Electrochem. Soc.*, 122, 600 (1975).
13. J. Phillips, R. J. Gale, R. G. Wier and R. A. Osteryoung, "Glassy Carbon Rotating Ring-Disc Electrodes for Molten Salt Studies", *Anal. Chem.*, 48, 1266 (1976).
14. D. E. Bartak and R. A. Osteryoung, "The Redox Behavior of Tetrachloro-p-Benzoquinone-Tetrachlorohydroquinone Systems in Molten Aluminum Chloride-Sodium Chloride Solvents", *J. Electroanal. Chem.*, 74, 69 (1976).

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

15. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylations in a Room Temperature Molten Salt Media", *J. Am. Chem. Soc.*, 98, 5377 (1976) .
16. K. A. Paulsen and R. A. Osteryoung, "Electrochemical Studies on Sulfur and Sulfides in AlCl_3 -NaCl Melts", *J. Am. Chem. Soc.* ,98, 6866 (1976) .
17. R. A. Osteryoung, "Chemistry and Electrochemistry in Aluminum Chloride Molten Salt Systems", *Proceedings of the Symposium on Molten Salts*, edited by J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, pp. 240-253, The Electrochemical Society, Pennington, NJ (1976) .

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

18. J. Phillips and R. A. Osteryoung, "Molybdenum Chemistry in NaCl-AlCl_3 Melts at 175°C ", *J. Electrochem. Soc.*, 124, 1405 (1977).
19. J. Robinson, B. Gilbert and R. A. Osteryoung, "The Acid-Base Chemistry of Oxide and Chalcogenides in Sodium Tetrachloroaluminate Melts at 175°C ", *Inorg. Chem.*, 16, 3040 (1977) .

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22. Helena Li Chum, D. Koran and R. A. Osteryoung, "Photochemistry of Iron(II)Diimine Complexes in a Room Temperature Molten Salt", *J. Am. Chem. Soc.*, **100**, 310 (1978) .
23. J. Robinson and R. A. Osteryoung, "Electrochemical Studies of Selenium and Selenium Compounds in Molten Sodium Tetrachloroaluminate Melts", *J. Electrochem. Soc.*, **125**, 1454 (1978) .
24. B. Gilbert and R. A. Osteryoung, "Electrochemical Studies on Nickel Electrodes in Molten Sodium Tetrachloroaluminates", *J. Am. Chem. Soc.*, **100**, 2725 (1978).
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28. J. Robinson and R. A. Osteryoung, "The Electrochemical and Spectroscopic Behavior of Some Aromatic Hydrocarbons in the Room Temperature Molten Salt System $AlCl_3$:n-Butylpyridinium Chloride", *J. Am. Chem. Soc.*, **101**, 321 (1978) .
29. J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung, 1H and ^{13}C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide-Alkyl Pyridinium Halide Molten Salts and Their Benzene Solutions", *J. Am. Chem. Soc.*, **101**, 3776 (1979).

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

31. J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Aluminum in the Low Temperature Molten Salt System n-Butyl Pyridinium Chloride; Aluminum Chloride and Mixtures of this Molten Salt with Benzene", *J. Electrochem. Soc.*, 127, 122 (1980).
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AFOSR-81-0007: 1 October, 1980 - 31 August, 1984

38. B. J. Welch and R. A. Osteryoung, "Electrochemical Studies in Low Temperature Molten Salt Systems Containing Aluminum Chlorides", *J. Electroanal. Chem.*, 118, 455-466 (1981).
39. Z. StoJek, H. Linga and R. A. Osteryoung, "A Titration Procedure for the Determination of Oxide in Basic n-Butylpyridinium Chloride: Aluminum Chloride Melts", *J. Electroanal. Chem.*, 119, 365-70 (1981).

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48. G. T. Cheek and R. A. Osteryoung, "Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System", *Inorg. Chem.*, 21, 3581 (1982).
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*Work related to pulse methodology development but not supported by A.F.O.S.R.

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140. Dawn King and Robert A. Osteryoung "Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts", Proceedings of Tenth International Symposium on Molten Salts, The Electrochemical Society, submitted, May, 1996.

Appendix B:

Presentations at Meetings Related to Activities on Contract
F49620-94-1-0056, ; 1 January, 1994 - 30 June, 1996

Invited Presentations

1. Robert A. Osteryoung, "Ambient Temperature Ionic Liquids: **Real** Nonaqueous Solvents", Kolthoff Memorial Symposium, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, March, 1994.
2. Ian C. Quarmby, Robert Mantz and Robert A. Osteryoung, "Latent Acidity in Buffered Chloroaluminate Ionic Liquids", Ninth International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Francisco, May, 1994.
3. Robert A. Mantz, Robert A. Osteryoung, Paul C. Trulove, Richard T. Carlin, and Hanna Sierzputowska-Gracz "ROESY NMR of Basic Ambient Temperature Chloroaluminate Ionic Liquids", Ninth International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Francisco, May, 1994.
4. Richard T. Carlin and Robert A. Osteryoung, "A Silane-Imidazole Electroactive Film for Battery Cathodes", Ninth International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Francisco, May, 1994.
5. John J. O'Dea, Robert Mantz, M. Khaled and R. A. Osteryoung, "Very Fast Square Wave Voltammetry at Microelectrodes", American Chemical Society, Division of Analytical Chemistry Electrochemistry Award Symposium Honoring Fred C. Anson, Fall Meeting, Washington, August, 1994.
6. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry, and Witchcraft!", Departmental Colloquium, University of Iowa, Iowa City, Sept. 2, 1994.
7. Robert A. Osteryoung, "Brownsted and Lewis Acidity in Ambient Temperature Chloroaluminate Molten Salts", Symposium on Organic Reactions in Highly Acidic Media, Southeast/Southwest Regional ACS Meeting, Memphis, Nov. 29-December 1, 1995.
8. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: An Overview", Pittsburgh Analytical Chemistry Award Symposium Honoring Johannes Coetzee, Pittsburgh Conference, Chicago, IL, March 3-8, 1996.
9. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: An Overview for the Uninitiated", Seminar, Department of Chemistry, University of North Carolina, April 8, 1996.

10. Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, and Robert A. Osteryoung, "Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient-Temperature Chloroaluminate Liquids," Tenth International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, Los Angeles, May, 1996.
11. Dawn King and Robert A. Osteryoung, "Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts", Tenth International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, Los Angeles, May, 1996.

Contributed Presentations

12. Richard T. Carlin, Paul C. Trulove, Robert Mantz and R. A. Osteryoung, "Concurrent Electron Transfer and Bond Dissociation in Weak and Strong Metal Complexes", poster, Gordon Research Conference on Electrochemistry, Ventura, CA, January, 1994.
13. R. A. Mantz, P. C. Trulove, R. T. Carlin and R. A. Osteryoung, "ROESY NMR of Basic Room-Temperature Molten Salts", North Carolina ACS Section Meeting, Durham, NC, April, 1994.
14. P. C. Trulove, R. T. Carlin, R. A. Mantz, J. J. O'Dea, and R. A. Osteryoung, "Application of Square Wave Voltammetry to Asymmetric Electron Transfer in Cu(I)-Ligand Systems", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March, 1995.
15. L. M. Goldenberg, John J. O'Dea and Robert A. Osteryoung, "Pulse Voltammetry of Polyaniline Films on Microelectrodes", International Workshop on Electrochemistry of Electroactive Polymer Films, Moscow, Russia, April 8-12, 1995 (poster).
16. Robert Mantz, Robert A. Osteryoung, Paul C. Trulove, Richard Carlin and T. Sweem, "Gutmann Acceptor Number of LiCl, NaCl, and KCl Neutral Buffered Chloroaluminate Room Temperature Molten Salts", North Carolina ACS Section Meeting, Chapel Hill, NC, April, 1995.
17. Dawn King, Robert Mantz, and Robert A. Osteryoung, "Bronsted Acidity in Chloroaluminate Molten Salts", North Carolina ACS Section Meeting, Raleigh, NC, April, 1996.
18. Robert Mantz, Jack Summers, and Robert A. Osteryoung, "The Behavior of Oxide in Chloroaluminate Molten Salts", North Carolina ACS Section Meeting, Raleigh, NC, April, 1996.