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COMPLETED PROJECT SUMMARY Approved for public release; distribution unlimited.

TITLE: CHEMISTRY AND ELECTROCHEMISTRY IN LEWIS ACID AND SUPERACID IONIC LIQUIDS

PRINCIPAL INVESTIGATOR: Dr. Robert A. Osteryoung
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Raleigh, NC 27695-8204

INCLUSIVE DATES: 1 July 1992 - 31 December 1993

GRANT NO: F49620-92-J-0326

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SENIOR RESEARCH PERSONNEL:

Dr. Leonid Goldenberg
Dr. Ian Quarmby
Dr. John O'Dea

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JUNIOR RESEARCH PERSONNEL:

Captain Robert Mantz*

*Not paid on grant funds

PUBLICATIONS:

Jinsong Tang, Kunio Shimizu and Robert A. Osteryoung, "Electrochemical Studies of Tris-(acetylacetonato)ruthenium(III) Complex in Ambient Temperature Chloroaluminate Molten Salts", Inorg. Chem., 31, 3980-3985 (1992).

S. Song, J. Tang, M. Kajitani, K. Shimizu, and Robert A. Osteryoung, "Electrode Processes of (η^5 -Cyclopentadienyl)-(1,2-Substituted 1,2 Ethylenedithiolato)Cobalt(III) Complexes in an Ambient Temperature Molten Salt", J.. Chem., 455, 211-217 (1993).

Richard Carlin, Paul Trulove and Robert A. Osteryoung, "Electrochemical and Spectroscopic Study of Anthracene in a Mixed Lewis-Brønsted Acid Ambient Temperature Molten Salt System", Electrochim. Acta, 37, 2615-2628 (1992).

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Michael Carter and Robert A. Osteryoung, "Interaction of 9,10-Anthraquinone with Tetrachloroaluminate and Proton in Basic Aluminum Chloride:1-Ethyl-3-Methylimidazolium Chloride Room Temperature Molten Salts", J. Electrochem. Soc., 139, 1795-1802 (1992).

Paul C. Trulove and Robert A. Osteryoung, "Proton Speciation in Ambient Temperature Chloroaluminate Ionic Liquids", Inorg. Chem., 31, 3980-3985 (1992).

Paul C. Trulove, Dinesh K. Sukumaran, and Robert A. Osteryoung, "NMR Studies of the Proton Equilibrium in Basic Ambient-Temperature Chloroaluminate Ionic Liquids", Inorg. Chem., 32, 4396 (1993).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of this work was to perform chemical and electrochemical studies in an ambient temperature ionic liquid or molten salt composed of mixtures of aluminum chloride and 1-ethyl-3-methylimidazolium chloride. Work carried out was in the major areas of: a) studies of polymer modified electrodes in the molten salts; b) general electrochemistry and fast pulse voltammetry; c) chemistry and electrochemistry in superacid systems.

In the electroactive polymer area, benzene was polymerized to poly (p-phenylene) and its electrochemistry examined in the molten salts. ClSi(Phenyl)_3 was polymerized and the electrochemistry and XPS spectroscopy of the films were examined.

The electrochemistry of tris-(acetylacetonato)ruthenium(III) and of two derivatives of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-ethylenedithiolato})\text{cobalt(III)}$ complexes with substituents, cyano (CN) and 4-pyridyl (${}^4\text{Py}$) at the ethylenedithiolato moiety, were studied at a glassy carbon electrodes in the melts. The electrochemistry was rather complexed, and some considerations of mechanisms of solution chemistry and electrochemistry was given.

The electrode kinetics of the ferrocenium/ferrocene couple were measured throughout the basic range of composition of the ambient temperature chloroaluminate ionic liquids. Large changes in viscosity occur as the melt is made more basic, and this results in a significant decrease in the heterogeneous electron transfer rate constant.

The electrochemistry, NMR and uv-vis spectroscopy of anthracene in the melts was investigated. In acidic melts, electrochemical oxidation of anthracene produces a cation radical which exhibits stability similar to that found in "superdry" dichloromethane. Electrochemical and spectroscopic measurements in the acidic melts show that anthracene protonates to form anthracenium cation.

The electrochemical behavior of 9,10-anthraquinone was studied in the melts, in pure ImCl , and in ImHCl_2 . A number of conclusions on aspects of the mechanism of the electrode reaction were made.

Finally, proton speciation in the melts was examined by ^2H -NMR and FT-IR spectroscopies and the equilibrium between hydrogen chloride and hydrogen dichloride ion in the basic melts was examined by ^2H and ^1H NMR spectroscopies.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) <p style="text-align: center;">Studies in an ambient temperature chloroaluminate molten salt composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride were carried out. A variety of topics were investigated. Work on poly(p-phenylene) and silane based electroactive polymers was carried out. The electrochemistry of several Ru and Co complexes was examined, as was the kinetics of the ferrocene-ferrocenium couple as a function of melt viscosity. The electrochemistry of anthracene and 9,10 anthraquinone was examined under conditions where protonation of these species was important. Finally, proton speciation and proton equilibrium were examined by NMR and FT-IR spectroscopies.</p>				
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This is a Final Report on AFOSR Grant No. F49620-92-J-0326,
Chemistry and Electrochemistry in Lewis Acid and Superacid Ionic Liquids.

The research carried out under this grant involved studies of the chemistry and electrochemistry of ambient temperature chloroaluminate ionic liquids. The ionic liquids consist of mixtures of an organic chloride, 1-methyl-3-ethylimidazolium chloride, with aluminum chloride. A Bronsted acid was added in some instances and the resultant chemistry of solutes examined.

This activity was funded under a grant which started on 1 July 1992, following the Principal Investigators move to North Carolina State University from the State University of New York at Buffalo. The Contract terminated on December 31, 1993. Funding levels were \$74,304 for a six-month period (FY 1992), and \$149,540 (FY 1993).

This Final Report discusses topics as submitted in our proposal in this area. In the interest of brevity, abstracts or summaries of work published will be used. All publications under this, and prior, AFOSR support are listed in Appendix A, as are listings of formal meeting presentations under the current grant.

The principal investigator left the State University of New York at Buffalo to become a Research Professor at North Carolina State University in July, 1992. The work reported below represents work carried out at North Carolina State University and work carried out at the State University of New York at Buffalo which was incomplete at the time of our previous Final Report, but which has been completed, and published, during the period of the present Contract..

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SUMMARY OF WORK, 1 JULY 1992 - 31 DECEMBER, 1993

INTRODUCTORY COMMENTS

Although the Principal Investigator moved to North Carolina State in July, 1992, laboratory space was not available until February, 1993. Brand new laboratories were constructed, and took longer to complete than had been anticipated. Two post-doctoral fellows were hired a bit in advance of this time, and one graduate student, Captain Robert Mantz, joined our research group in August, 1993. Prior to his starting Graduate School here, Captain Mantz and Captain Paul Trulove, a former graduate student now at Seiler Laboratory in Colorado Springs, spent some time here and were instrumental in helping get one of our large dryboxes operational; in addition, they carried out a substantial amount of research work, to be described below.

I. COMPLETED WORK

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

This continued work on electroactive polymers in the ambient temperature molten salt system.

1. Polymerization of Benzene

A manuscript "Benzene Polymerization in 1-Ethyl-3-Methylimidazolium Chloride- AlCl_3 Ionic Liquid" is in press in Synthetic Metals. See Ref. 121 in Appendix A.

ABSTRACT

Poly(p-phenylene) films have been prepared by the electropolymerization of benzene in an ambient temperature molten salt, or ionic liquid, consisting of 1-ethyl-3-methylimidazolium chloride-aluminum chloride. Polymerization was carried out in melts of varying acidity and in neutral buffered melts. The films were then examined in the 1-ethyl-3-methylimidazolium chloride-aluminum chloride melts of varying acidity. The polymerization and electrochemical behavior of the films are independent of melt acidity; the films show reasonably facile electrochemical behavior.

2. Silane-Based Electroactive Polymer

A manuscript, "A Silane-Based Electroactive Film Prepared in Imidazolium Chloroaluminate Molten Salt" was prepared and is in press in the Journal of the Electrochemical Society (See. Ref. 122 in Appendix A). The experimental work

was carried out at the State University of New York at Buffalo, but was only recently rewritten for submission for publication.

ABSTRACT

Electrochemical oxidation of ClSiPh_3 (Ph=phenyl) in the room-temperature molten salt, $\text{AlCl}_3\text{:EMICl}$ (EMICl = 1-ethyl-3-methylimidazolium chloride) results in the formation of an adherent electroactive film on the surface of solid electrodes. The film is reversibly oxidized and reduced in the molten salt is conducting when in the oxidized state. Based on XPS analysis, the film consists of both a silane and an imidazole component, and the charge storage properties of the film are localized on the heterocyclic rings. This electroactive film compares favorably to other conducting polymers currently being investigated as positive electrodes in room-temperature molten salt batteries.

B. General Electrochemistry/Fast Pulse Voltammetry

1. Study of Tris(acetylacetonato)ruthenium (III)

A manuscript, "Electrochemical Studies of Tris-(acetylacetonato)ruthenium(III) Complex in Ambient Temperature Chloroaluminate Molten Salts", was published in *Inorganic Chemistry* (see Reference 123 in Appendix A). This work was also carried out at the State University of New York, but was published during the tenure of this grant.

ABSTRACT

The electrochemical behavior of tris(acetylacetonato)ruthenium(III), $\text{Ru}(\text{acac})_3$, in a room temperature molten salt composed of a mixture of aluminum trichloride and 1-ethyl-3-methylimidazolium chloride is studied as a function of melt composition. $\text{Ru}(\text{acac})_3$ decomposes in acidic melts, but is stable in neutral and basic melts, dissolving readily to give intense red solutions. The complex undergoes a Nernstian one-electron reduction process at a glassy-carbon electrode independent of the basic melt composition. The reduced $\text{Ru}(\text{acac})_3^-$ complex, depending on the melt basicity, can react with AlCl_4^- on the voltammetric time scale probably to form the adduct $[\text{Ru}(\text{acac})_2(\text{acacAlCl}_3)]^-$, which gives a one-electron oxidation step at a more positive potential than that of $\text{Ru}(\text{acac})_3^-$. When a small amount of $\text{Ru}(\text{acac})_3$ is reduced by bulk electrolysis in the basic melt and allowed to stand for 1 day at room temperature, all remaining $\text{Ru}(\text{acac})_3$ is transformed into the colorless hexachlororuthenium(III) anion, RuCl_6^{3-} . This reaction is initiated by the attack and an Ru-O bond in $\text{Ru}(\text{acac})_3^-$ by AlCl_4^- , followed by the breakage of the Ru-O bond. In addition, the intermediate, $\text{Ru}(\text{acac})_{3-n}\text{Cl}_{2n}^{(n+1)-}$, generated by the rupture of an Ru-O bond, acts as a redox catalyst for the ligand replacement of $\text{Ru}(\text{acac})_3^-$ to form RuCl_6^{3-} .

2. Electrochemistry of Cobalt Complexes

A manuscript, "Electrode Processes of (η^5 -Cyclopentadienyl)-(1,2-Substituted 1,2 Ethylenedithiolato)Cobalt(III) Complexes in an Ambient Temperature Molten Salt", has been published in the Journal of Organometallic chemistry (See Reference 124 in Appendix A).

ABSTRACT

The electrochemistry of two derivatives of (η^5 -cyclopentadienyl)(1,2 ethylenedithiolato)cobalt(III) complexes with substituents, cyano (CN) and 4-pyridyl (4 Py) at the ethylenedithiolato moiety, was studied at a glassy carbon electrode in an ambient temperature ionic liquid composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (AlCl₃-ImCl). The reduction of Co^{III} to Co^{II} in the two complexes was a diffusion controlled reversible process in basic and neutral melts. The half-wave potentials for both complexes were slightly dependent on melt composition. Because the ethylenedithiolate ligands also participated in the electrochemical reaction, the CN-substituted complex showed an irreversible anodic peak, while the 4 Py substituted complex not only gave a quasi-reversible anodic peak but also displayed another irreversible cathodic peak at very negative potentials. The oxidation of the metallocene ring is believed responsible for the anodic peaks of both complexes. The diffusion coefficients of the complexes in basic and neutral melts were estimated from the Cottrell equation. The Stokes radius estimated for the CN-substituted complex was 0.26 nm in the 0.8:1.0 melt and 0.29 nm in the 1.0:1.0 melt. The slightly larger radius in the 0.6:1.0 melt (0.38 nm) was interpreted in terms of the solvation of the complex in the more basic melt.

3. Kinetics of Ferrocene as a Function of Melt Viscosity

A manuscript, "Dependence of Electron Transfer Kinetics of the Ferrocene/Ferrocenium Couple on the Viscosity in Ambient Temperature Chloroaluminate Ionic Liquids", is in press as an invited paper in a special issue of Inorganic Chimica Acta devoted to electron transfer reactions (see Reference 125 in Appendix A below).

ABSTRACT

The heterogeneous electron transfer kinetics of the ferrocenium/ferrocene couple have been measured throughout the basic range of composition of the ambient temperature chloroaluminate ionic liquid composed of 1-ethyl-3-methylimidazolium chloride (ImCl) and aluminum chloride. Normal and reverse pulse voltammeteries with pulse times as short as 5 μ s were employed. After

subtraction of the background currents, the experimental voltammograms were directly compared with those calculated from the COOL algorithm using a model for reversible and quasi-reversible electron transfer reactions. The standard rate constants, uncorrected for double layer effects, were found to decrease from $0.45 \pm 0.35 \text{ cm s}^{-1}$ at 0.95:1 to $0.27 \pm 0.004 \text{ cm s}^{-1}$ at 0.45:1 mole ratio of aluminum chloride to ImCl. Possible factors contributing to the observed dependence are discussed. The most likely reason for the retardation of the electron transfer rate is the slow relaxation of the increasingly associated basic ionic liquid.

C. Chemistry and Electrochemistry in Superacid Systems

1. Electrochemistry of Anthracene

A manuscript, "Electrochemical and Spectroscopic Study of Anthracene in a Mixed Lewis-Brønsted Acid Ambient Temperature Molten Salt System", was published in *Electrochimica Acta* (see Reference 126 in Appendix A.). The work was carried out at the State University of New York prior to leaving, but was published during the period of this grant.

ABSTRACT

The electrochemistry, NMR and uv-vis spectroscopy of anthracene in ambient temperature molten salts composed of a mixture of AlCl_3 :1-ethyl-3-methylimidazolium chloride (ImCl) have been investigated. In acidic mixtures of AlCl_3 :ImCl, where the molar ratio is greater than 1, electrochemical oxidation of anthracene produces a cation radical which exhibits stability similar to that found in "superdry" dichloromethane. Electrochemical and spectroscopic measurements in the acidic melts show that anthracene protonates to form anthracenium cation. The anthracenium ion cannot be oxidized within the melt electrochemical window, but is reduced to yield H_2 and free anthracene. In basic mixtures of AlCl_3 :ImCl, where the molar ratio is less than 1, no anthracene electrochemistry is observed. However, NMR and uv-vis spectra in the basic melts show anthracene to be unprotonated.

2. Electrochemistry of 9,10 Anthraquinone

A manuscript, "Interaction of 9,10-Anthraquinone with Tetrachloroaluminate and Proton in Basic Aluminum Chloride:1-Ethyl-3-Methylimidazolium Chloride Room Temperature Molten Salts", was published in the *Journal of the Electrochemical Society* (see Reference 127 in Appendix A below). This work was also carried out at the State University of New York, but was written and published during the duration of this grant.

ABSTRACT

The electrochemical behavior of 9,10-anthraquinone (AQ) in a basic room temperature molten salt composed of a mixture of AlCl_3 and 1-ethyl-3-methylimidazolium chloride (ImCl) is described. In the absence of a proton source, AQ is reduced via a quasireversible two-electron transfer to $\text{AQ}(\text{AlCl}_3)_2^{2-}$. The homogeneous chemical steps coupled to the electron transfers are displacement of Cl^- from AlCl_4^- to form $\text{AQ}(\text{AlCl}_3)_2^{2-}$. Addition of a proton source, imidazolium hydrogen dichloride (ImHCl_2) causes the coupled chemical reactions to shift from solvent leveling of reduced AQ by AlCl_4^- to more facile protonation steps. Visible spectroscopy of AQ in 0.8:1 melt and neat ImHCl_2 show that AQ is present as the neutral, unprotonated quinone in its oxidized form. The two-electron, two-proton reduction product 9,10-dihydroxyanthracene (AQH_2) is formed under these conditions but is unstable in the AlCl_3 :ImCl melt. It is converted to $\text{AQ}(\text{AlCl}_3)_2^{2-}$ which is the reoxidizable form regardless of whether protons are present in the melt. AQH_2 is stable on the voltammetric time scale in neat ImHCl_2 . Under these conditions, the hydroquinone is formed exclusively and the electrochemistry tends toward that on the classical $2e, 2\text{H}^+$ case found in aqueous systems. Experiments in molten ImCl, at 90°C , show that the quinone anion radical and dianion are stable only under conditions where no Lewis acid is available for adduct formation.

3. Proton Speciation

A manuscript, "Proton Speciation in Ambient-Temperature Chloroaluminate Ionic Liquids" has been published in *Inorganic Chemistry* (see Reference 128 in Appendix A.) This work was also carried out at the State University of New York but was published during the duration of the present grant.

ABSTRACT

Proton speciation in ambient temperature chloroaluminate ionic liquids composed of 1-ethyl-3-methylimidazolium chloride (ImCl) and aluminum chloride has been examined by ^2H -NMR and FT-IR spectroscopies. In oxide free basic melts (excess ImCl), two proton-containing species, HCl and HCl_2^- , exist which are in an equilibrium that strongly favors the formation of the dichloride ion. In oxide free acidic melts (excess AlCl_3) HCl is the only proton-containing species. There is a single aluminum hydroxychloride species in acidic melts containing oxides, and there is at least one aluminum hydroxychloride species in basic melts containing oxides.

D. Miscellaneous

1. NMR Study of Proton Equilibrium

A manuscript, "NMR Studies of the Proton Equilibrium in Basic Ambient-Temperature Chloroaluminate Ionic Liquids" has been published in Inorganic Chemistry (see Reference 129 in Appendix A below). This work was also performed at the State University of New York, but was written and published during the duration of this grant.

ABSTRACT

In basic mixtures of the molten salt composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride, proton, in the absence of oxides, is partitioned between hydrogen chloride and hydrogen dichloride ion. The equilibrium between these two species has been examined by ^2H and ^1H NMR spectroscopies. The magnitude of the hydrogen chloride/dichloride equilibrium constant demonstrates that the equilibrium strongly favors the formation of the hydrogen dichloride ion. The ratio of ^2H and ^1H equilibrium constants at 90°C gave an equilibrium isotope effect of 0.67 ± 0.26 , which indicates that deuterium accumulates in the hydrogen chloride molecule. An equilibrium isotope effect of 0.712 was calculated from hydrogen chloride and hydrogen dichloride vibrational frequencies. Analysis of the temperature dependence of the hydrogen chloride/dichloride equilibrium constant gave values for the enthalpy of the reaction, ΔH_{RXN} , and the entropy of the reaction, ΔS_{RXN} of $-9.8 \pm 0.8 \text{ kJ mol}^{-1}$ and $4.8 \pm 2.5 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Comparison of the ΔH_{RXN} for the hydrogen chloride/dichloride equilibrium in the melts with values obtained for other solvents suggests that the melt interacts more strongly with chloride ion than with hydrogen dichloride ion.

II. Work in Press and in Progress

There is considerable work in progress or being written up. We have found that the neutral buffered melts possess a latent acidity, in that the addition of a weak base to these melts generates an AlCl_3 adduct; the source of the AlCl_3 is the AlCl_4^- ion, normally considered a very weak acid. However, the neutral buffered melt contain sodium ions, and the precipitation of NaCl(s) provides an additional driving force for the reaction. A poster on this was presented at the Gordon Research Conference on Molten Salts and Metals in Augusts, 1993, and a Communication to the Journal of the American Chemical Society is in preparation. Work to quantitate this study is also in progress.

A considerable amount of work, in collaboration with Seiler Laboratory personnel, involving the study of the Cu(II)/Cu(I) couple in the ambient temperature molten salt, is in progress. This has been done in our laboratory using ultramicroelectrodes, and very fast pulse voltammetry. Portions of this work are being written up for publication.

Work on the electrochemistry of tetrathiafulvalene in the ambient temperature molten salt has been completed, and is being written up for publication.

Further efforts aimed at understanding more about the proton acidity in the acidic melts, where they function as superacids, are in progress.

III. Interaction with Air Force Laboratories and Personnel

Numerous interactions with personnel from the Frank J. Seiler Research laboratory were made during the period of this grant; as described previously, visits from Captain Paul Trulove and Captain Robert Mantz were instrumental in aiding us in getting our laboratory operational. In addition, the fast pulse voltammetry was carried out here by Captain Trulove and additional work was done here by Captain Robert Mantz, who entered graduate school here in the Fall of 1993.

IV. Other Activities

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

V. Personnel

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

Senior Research Personnel:

Dr. Leonid Goldenberg
Dr. Ian Quarmby
Dr. John O'Dea

Junior Research Personnel:

Captain Robert Mantz*

Secretarial Personnel:

Ms. Susan Sherry
Ms. Konnie McCauley

* Not paid on grant 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).
9. H. Lloyd Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroaluminate Solvents", *Advances in Molten Salt Chemistry*, Vol. 3, Edited by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Publishing (1975).

10. R. J. Gale and R. A. Osteryoung, "Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvent", *Inorg. Chem.*, 14, 1232 (1975).
11. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, "An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt", *J. Am. Chem. Soc.*, 97, 3264 (1975).
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) .

20. Helena Li Chum, T. Rabockai, J. Phillips and R. A. Osteryoung, "Ligand-Oxidation in Iron Diimine Complexes. III. Electrochemical Oxidation of tris-(glyoxalbis(methylimine))Iron(II)", *Inorg. Chem.*, 16, 1812 (1977).
21. Helena Li Chum, D. Koran and R. A. Osteryoung, "The Electrochemical Behavior of Metal Carbonyls in a Mixture of a Room Temperature Molten Salt and Benzene", *J. Organometallic Chem.*, 140, 349 (1977).
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) .
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121. Leonid Goldenberg and Robert A. Osteryoung, "Benzene Polymerization in 1-Ethyl-3-Methylimidazolium Chloride- AlCl_3 Ionic Liquid", Syn. Met., in press.
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Appendix B:

Presentations at Meetings Related to Grant Activities
AFOSR Grant No. F49620-92-J-0326; 1 July, 1992 - 31
December, 1993.

Invited Presentations

272. Robert A. Osteryoung, "Prof. H. A. Laitinen - A Long-ago Student's View", Division of Analytical Chemistry Memorial Symposium Honoring Herbert A. Laitinen, American Chemical Society, Fall Meeting, Washington, D.C., August, 1992.
273. Robert A. Osteryoung, "Superacid Chemistry in Low Temperature Chloroaluminate Ionic Liquids", Gordon Research Conference on Molten Salts and Metals, Wolfeboro, NH, August, 1993.
274. Robert A. Osteryoung, "Electrochemistry in Ambient Temperature Chloroaluminate Ionic Liquids: An Overview for the Uninitiated!", Symposium on Electrochemistry in Unconventional Media and in Media Under Extreme Conditions, The Electrochemical Society, Fall Meeting, New Orleans, October, 1993.
275. Michael Carter and Robert A. Osteryoung, "Redox Chemistry of Tetrathiafulvalene in Ambient Temperature Molten Salts", Symposium on Electrochemistry in Nonaqueous Media, The Electrochemical Society, Fall Meeting, New Orleans, October, 1993.
276. Paul C. Trulove, R. T. Carlin, Robert A. Mantz, John J. O'Dea and Robert A. Osteryoung, "Electrode Kinetics of Cu(I)-Ethylene Complex in Acidic Ambient-Temperature Chloroaluminate Molten Salts", Symposium on Electrochemistry in Nonaqueous Media, The Electrochemical Society, Fall Meeting, New Orleans, October, 1993.

Contributed Presentations

77. Ian C. Quarmby and R. A. Osteryoung, "Acetylferrocene - A Probe of Chemical Speciation in NaCl Buffered Neutral Melts", poster, Gordon Research Conference on Molten Salts and Metals, Wolfeboro, NH, August, 1993.