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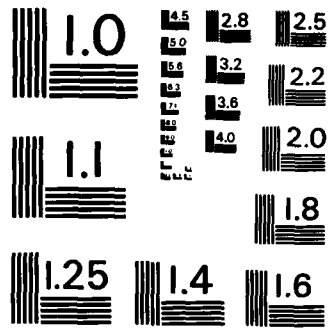
ELECTROCHEMISTRY AT VERY SMALL ELECTRODES(U) STATE UNIV 1/1
OF NEW YORK AT BUFFALO DEPT OF CHEMISTRY
R A OSTERYOUNG ET AL. SEP 85 N00014-79-C-0682

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work was carried out in three areas; correlation of spectroscopy with the results of electrochemical experiments in ionic liquids (molten salts); studies of cathodic stripping voltammetry, primarily at silver electrodes; studies of the behavior of "micro-electrodes" - electrodes with micron dimensions. Results are summarized, primarily with reference to TEchnical Reports and journal publication.		

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INTRODUCTION

This is a Final Report on Contract N00014-79-C-0862. This contract has a peculiar history. It originated in 1979, under the title "Studies in Cathodic Stripping Voltammetry and Spectroscopic Correlations to Non-Aqueous Electrochemistry", with Robert A. Osteryoung as Principal Investigator. In July, 1980, Prof. Janet Osteryoung was added as a co-principal investigator when her previously funded ONR contract was essentially merged into this present contract. Also, at that time funds were requested, and granted, together with University Matching Funds, for the purchase of a Fourier transform infra-red spectrometer. In July, 1981, a two year proposal entitled "Electrochemistry at Very Small Electrodes", with both Robert A. Osteryoung and Janet G. Osteryoung as co-principal investigators was submitted and funded under this contract. At about that time, however, it was decided to move the starting date of the newly funded activity to October 1, 1983, and interim funding, for the period July 1, 1981 through September 30, 1981, was awarded. In 1983, it was decided to again split off the work carried on by Prof. Janet Osteryoung, and a renewal proposal by Prof. Robert Osteryoung, then entitled "Studies in Electroanalytical Chemistry" was submitted. This was funded for a one year period; a no cost extension was approved, bringing the termination date of the present contract to March 31, 1985.



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SUMMARY OF RESEARCH RESULTS

During the period of this contract, 22 Technical Reports were distributed and 22 publications resulted. The work could be divided into three categories.

The first category involved studies in inorganic solvents, primarily ambient temperature ionic liquids (molten salts), which consisted of mixtures of organic chlorides with aluminum chloride. Efforts were made to correlate spectroscopic, both infrared and visible-UV, and electrochemical behavior in these ambient temperature ionic liquids. This work is reported in Technical Reports No's. 1, 2, 9, 18, 20 and 21 and the like numbered publications. As a result of the finding that a so-called "neutral" melt possessed a very large electrochemical window, we were able to effect the electrochemical polymerization of pyrrole, and study other polymer coated electrodes, in these liquids. This work is reported in Technical Reports 14, 15 and 16 and the like numbered publications.

The second category involved studies of cathodic stripping voltammetry of various materials, primarily at silver electrodes. Work carried out involved both analytical and mechanistic studies, and is reported in Technical Reports 3, 4, 5, 6, 8, 11, 13, and 17 and the like numbered publications. In addition, the observation that silver electrodes catalyzed the reduction of thyroxines was utilized for an analytical determination reported in Technical Report 19 and publication 19. The behavior of the thermodynamics of $n\text{-TiO}_2$ in fluoride media was also described in Technical Report 10 and publication 10.

In the third category, studies of microelectrodes - electrodes of dimensions several microns - were carried out and are reported on in Technical Reports 7, 12 and 15, and the like numbered publications.

TECHNICAL REPORTS

1. "Infrared Spectral Investigations of Ambient Molten Aluminum Chloride:1-Butylpyridinium Chloride Systems", R.J. Gale and R.A. Osteryoung, October, 1979.
2. "Electrochemical and Spectroscopic Studies of 9,10-Anthraquinone in a Room-Temperature Molten Salt", G.T. Cheek and R.A. Osteryoung, July, 1980.
3. "Determination of Sulfide by Cathodic Stripping Voltammetry at a Rotating Disc Electrode", K. Shimizu and R.A. Osteryoung, February, 1981.
4. "Electrochemical Behavior of Sulfide at the Silver Rotating Disc Electrode: I. Polarization Behavior of Silver Sulfide Films", K. Shimizu, K. Aoki and R.A. Osteryoung, May, 1981.
5. "Electrochemical Behavior of Sulfide at the Silver Rotating Disc Electrode:II. Mechanism of Sulfide Film Formation", K. Aoki, K. Shimizu and R.A. Osteryoung, May, 1981.
6. "Determination of Diffusion Coefficients of Anions at a Rotating Silver Disc Electrode", K. Shimizu and R.A. Osteryoung, September, 1981.
7. "Chronoamperometric Transients at the Stationary Disk Electrode", T. Hapel and J. G. Osteryoung, November, 1981.
8. "Interaction of Methylated Adenine Derivatives with the Mercury Electrode", E. Palacek, J. Osteryoung and R.A. Osteryoung, April, 1982.
9. "An Electrochemical and Infrared Study of Chloranil in n-Butylpyridinium Chloride:Aluminum Chloride Ionic Liquid", G.Cheek and R.A. Osteryoung, June, 1982.
10. "Thermodynamics and Photoelectrochemical Behavior of the n-TiO₂ Electrode in Fluoride Containing Solutions", T. Hapel, M. Hapel and R.A. Osteryoung, September, 1982.
11. "Cathodic Stripping Analysis Complicated by Adsorption Processes; Determination of 2-Thiouracil at a Rotating Silver Disk Electrode", M. Hapel and R.A. Osteryoung, January, 1983.
12. "Correction to "Chronoamperometric Transients at the Stationary Disk Microelectrode", T. Hapel, W. Plot and J. G. Osteryoung, January, 1983.
13. "Electrochemical Behavior of 2-Thiouracil on Silver Electrodes", M. Hapel and R.A. Osteryoung, June, 1983.

14. "Polymer Coated Electrodes in Ambient Temperature Molten Salts", P. G. Pickup and R.A. Osteryoung, August, 1983.
15. "Arrays of Very Small Electrodes Based on Reticulated Vitreous Carbon", N. Sleszynski, J. G. Osteryoung and M. Carter, October, 1983.
- 15'. "Increased Electrochemical Window in Ambient Temperature Molten Salts", M. Lipsztajn and R.A. Osteryoung, January, 1984.
16. "Electrochemical Polymerization of Pyrrole and Electro-Chemistry of Polypyrrole Films in Ambient Temperature Molten Salts", P.G. Pickup and R.A. Osteryoung, January, 1984.
17. "Cathodic Stripping Voltammetry of Thioamides on a Rotating Silver Disk Electrode", M. Iwamoto and R.A. Osteryoung, January, 1984.
18. "Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II)/Fe(III) and Ru(II)/Ru(III) in the Aluminium Chloride:N-(1-Butyl)pyridinium Chloride Molten Salt", by S. Sahami and R.A. Osteryoung, January, 1984.
19. "Reduction of Thyroxine and Related Compounds on Silver", by M. Iwamoto, A. Webber and R.A. Osteryoung, April, 1984.
20. "Spectrophotometric Studies of Iodine Complexes in an Aluminium Chloride-Butylpyridinium Chloride Ionic Liquid", Z. Karpinski and R.A. Osteryoung, July, 1984.
21. "An Infrared Study of Ambient Temperature Chloroaluminates as a Function of Melt Acidity", by S. Tait and R.A. Osteryoung, July, 1984.

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1. "Infrared Spectral Investigations of Ambient Molten Aluminum Chloride:1-Butylpyridinium Chloride Systems", R.J. Gale and R.A. Osteryoung, *Inorg. Chem.* 19, 2240 (1980).
2. "Electrochemical and Spectroscopic Studies of 9,10-Anthraquinone in a Room-Temperature Molten Salt", G.T. Cheek and R.A. Osteryoung, *J. Electrochem. Soc.*, 129, 2488 (1982).
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6. "Determination of Diffusion Coefficients of Anions at a Rotating Silver Disc Electrode", K.Shimizu and R.A. Osteryoung, *Anal. Chem.*, 53, 2350 (1981).
7. "Chronoamperometric Transients at the Stationary Disk Microelectrode", T. Hapel and J. G. Osteryoung, *J. Phys. Chem.*, 86, 1406 (1982).
8. "Interaction of Methylated Adenine Derivatives with the Mercury Electrode", E. Palacek, J. Osteryoung and R.A. Osteryoung, *Anal. Chem.*, 54, 1389 (1982).
9. "An Electrochemical and Infrared Study of Chloranil in n-Butylpyridinium Chloride:Aluminum Chloride Ionic Liquid", G.Cheek and R.A. Osteryoung, *J. Electrochem. Soc.*, 129, 2379 (1982).
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13. "Electrochemical Behavior of 2-Thiouracil on Silver Electrodes", M. Hapel and R.A. Osteryoung, *J. Electroanal. Chem.*, 150, 217 (1984).
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15. "Arrays of Very Small Electrodes Based on Reticulated Vitreous Carbon", N. Sleszynski, M. Carter and J. G. Osteryoung, *Anal. Chem.*, 56, 116 (1984).
- 15'. "Increased Electrochemical Window in Ambient Temperature Molten Salts", M. Lipsztajn and R.A. Osteryoung, *J. Electrochem. Soc.*, 130, 1968 (1983).
16. "Electrochemical Polymerization of Pyrrole and Electrochemistry of Polypyrrole Films in Ambient Temperature Molten Salts", P.G. Pickup and R.A. Osteryoung, *J. Am. Chem. Soc.*, 106, 2294 (1984).
17. "Cathodic Stripping Voltammetry of Thioamides on a Rotating Silver Disk Electrode", M. Iwamoto and R.A. Osteryoung, *J. Electroanal. Chem.*, 169, 181 (1984).
18. "Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II)/Fe(III) and Ru(II)/Ru(III) in the Aluminum Chloride:N-(1-Butyl)pyridinium Chloride Molten Salt", by S. Sahami and R.A. Osteryoung, *Inorg. Chem.*, 23, 2511 (1984).
19. "Reduction of Thyroxine and Related Compounds on Silver", by M. Iwamoto, A. Webber and R.A. Osteryoung, *Anal. Chem.*, 56, 1202 (1984).
20. "Spectrophotometric Studies of Iodine Complexes in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid", Z. Karpinski and R.A. Osteryoung, *Inorg. Chem.*, 23, 4561 (1984).
21. "An Infrared Study of Ambient Temperature Chloroaluminates as a Function of Melt Acidity", by S. Tait and R.A. Osteryoung, *Inorg. Chem.* 23, 4352 (1984).

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Note: The last four individuals listed have worked on aspects of our present ONR Contract which, in part, continues work carried out under this Contract.

* Only portion of salary paid on ONR Contract or involved only short period of time.

** Graduate students.

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