

AD-A125 964

CHEMICAL MODIFICATION OF CARBON ELECTRODES(U) NORTH
CAROLINA UNIV AT CHAPEL HILL DEPT OF CHEMISTRY
R W MURRAY 31 JAN 83 TR-21 N00014-76-C-0817

1/1

UNCLASSIFIED

F/G 7/4

NL

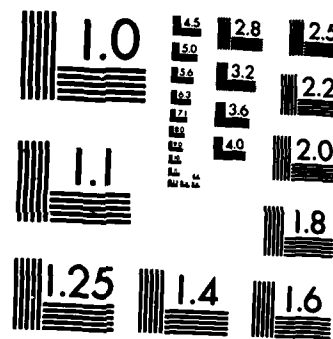


END

TURNED

IN

OFFICE



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A 125964

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0817

Task No. NR 359-623

FINAL TECHNICAL REPORT

CHEMICAL MODIFICATION OF CARBON ELECTRODES

Royce W. Murray, Principal Investigator

Department of Chemistry

University of North Carolina

Chapel Hill, North Carolina

SELECTED
MAR 22 1983
A

January 31, 1983

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

DTIC FILE COPY

83 03 22 080

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|-------------------------------------|--|
| 1. REPORT NUMBER FINAL (#TWENTY-ONE) | 2. GOVT ACCESSION NO. AD-A125964 | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) CHEMICAL MODIFICATION OF CARBON ELECTRODES | | 5. TYPE OF REPORT & PERIOD COVERED FINAL TECHNICAL REPORT |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s) Royce W. Murray, Principal Investigator | | 8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0817 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217 | | 12. REPORT DATE January 31, 1983 |
| | | 13. NUMBER OF PAGES |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 15. SECURITY CLASS. (of this report) Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 15. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 19. SUPPLEMENTARY NOTES | | |
| 23. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon electrode, chemically modified electrode, surface chemistry, carbon, vinylferrocene, ruthenium, radiofrequency plasma, titanium dioxide, semiconductor electrode, organosilane, tetraphenylporphyrin, electrocatalysis, X-ray photoelectron spectroscopy, plasma polymerization, diffusion, | | |
| 25. ABSTRACT (Continue on reverse side if necessary and identify by block number) This project had as its objectives the development of chemical and physical pathways to immobilize interesting chemicals on the surfaces of carbon electrodes, to develop surface analytical methods for the characterization and validation of surface immobilization procedures, to study the chemical and electrochemical behavior of the immobilized substances, and to exploit their chemical and electrochemical properties for electrocatalysis in various forms. ↙ | | |

BLOCK 13, KEY WORDS, continued:

multimolecular layer, monomolecular layer, electron transfer, modified electrode, porphyrin, fluorescence, reflectance spectroscopy, spectroelectrochemistry, cobalt, rotated disk electrode, chronoamperometry, kinetics, bromoalkyls, polymers, diodes, cyclic voltammetry, bilayer electrode, rectifier, electrochemical theory, redox polymer, polymer film, viologen, electrochemical theory, plasma polymer, iridium, ascorbic acid, membrane, diffusion, permeation, polymer film, electropolymerization.

FINAL TECHNICAL REPORT
CHEMICAL MODIFICATION OF CARBON ELECTRODES
PROJECT NR 359-623

Royce W. Murray, Principal Investigator

Department of Chemistry

University of North Carolina

Chapel Hill, North Carolina

This project had as its objectives the development of chemical and physical pathways to immobilize interesting chemicals on the surfaces of carbon electrodes, to develop surface analytical methods for the characterization and validation of surface immobilization procedures, to study the chemical and electrochemical behavior of the immobilized substances, and to exploit their chemical and electrochemical properties for electrocatalysis in various forms. The project began on the theme of covalent bond attachments to carbon surfaces by a variety of strategies to achieve monomolecular layer quantities of attached species. Immobilizations were extended to multimolecular layers of immobilized redox sites when we discovered good electrochemical properties for radiofrequency plasma polymerized vinylferrocene. And finally the project expanded into the first examples of spatially structured electrode surfaces when the rectifying properties of multiple (bilayer) films of redox polymers were demonstrated after having been predicted in an ONR proposal 2 1/2 years before materials were available to make an example. Thus, three discernable thrusts were made, and much was accomplished in each.

To more specifically cite accomplishments under this project, in particular those which opened new ground in the chemically modified electrode area:

** The necessary procedures and chemistry for attachment of monolayers of amine-substituted reagents to surface oxides of vitreous carbon via amide bonds were developed.

** Chemistry for attachment of reactive organosilane reagents was invented enabling immobilization of interesting molecules with the organosilane as a bridge, in submonolayer to multimolecular layer amounts.

** Amino porphyrins and ferrocenes were attached via both chemistries and their electrochemical reactions demonstrated.

** Extensive surface structural information on quantity, existence of two surface bonds per molecule, average orientation, axial ligation equilibria and kinetics, and stability of immobilized aminoporphyrins was obtained by combinations of cyclic voltammetry, differential pulse voltammetry, fluorescence and reflectance spectroscopies, and X-ray photoelectron spectroscopy experiments.

** Electrocatalytic activity of several metallated forms of the immobilized aminoporphyrins was demonstrated toward dioxygen reduction and alkyl halides, and for the latter, the electrocatalysis kinetics were evaluated as a function of surface quantity from monolayer to multilayer amounts of catalyst.

** Radiofrequency polymerization of vinylferrocene and of vinylpyridine was shown to yield adherant films on carbon surfaces and thereby redox polymer films containing ferrocene and pentachloroiridate respectively were found to exhibit attractive

electrochemical properties.

** An XPS molecular spacer experiment on carbon showed that about 50% of the carboxylic surface oxide functions were separated by the length of an ethylenediamine molecule or less

** It was found that oxide-free carbon surfaces generated by abrasion in absence of air and in the presence of certain vinylsubstituted molecules would stably bind such molecules.

** The first example of a spatially structured coating of redox polymers, the bilayer electrode, was devised by sequentially coating polymeric films of two different electropolymerizable ruthenium complexes on the electrode.

** The bilayer electrode was shown to exhibit the predicted charge rectification at the polymer film/film boundary, in directions predicted from the redox levels of the polymer films, for a series of different bilayers of polymer films.

** A preliminary theory for the rate of switching a bilayer electrode from one state to another was devised; the theory provided an example of control of electron transfer rate between two contacting (polymer) surfaces.

Complete List of Technical Reports

The research results have been reported in a series of publications a listing of which follows in order of the Technical Report each comprised:

J. C. Lennox and R. W. Murray, Chemically Modified Electrodes. VI. Binding and Reversible Electrochemistry of Tetra(Aminophenyl)Porphyrin on Glassy Carbon, J. Electroanal. Chem. 78 (1977) 395. Technical Report #1.

B. Firth, L. L. Miller, M. Mitani, T. Rogers, J. C. Lennox and R. W. Murray, Anodic and Cathodic Reactions on a Chemically Modified Edge Surface of Graphite, J. Am. Chem. Soc. 98, 8271 (1976). Technical Report #2.

J. C. Lennox and R. W. Murray, Chemically Modified Electrodes. X. ESCA and AC Voltammetry of Glassy Carbon-Bound Tetra(Aminophenyl)Porphyrins, J. Am. Chem. Soc. 100 (1978) 3710. Technical Report #3.

P. R. Moses, L. M. Wier, J. C. Lennox, H. O. Finklea, J. R. Lenhard and R. W. Murray, Chemically Modified Electrodes. IX. ESCA Studies of Alkylaminesilanes Bound to Metal Oxide Electrodes, Anal. Chem. 50 (1978) 576. Technical Report #4.

J. R. Lenhard, R. Rocklin, H. Abruna, K. Willman, K. Kuo, R. Nowak and Royce W. Murray, Chemically Modified Electrodes. XI. Predictability of Formal Potentials of Covalently Immobilized Charge Transfer Reagents, J. Am. Chem. Soc. 100 (1978) 5213. Technical Report #5.

R. Nowak, F. A. Schultz, M. Umana, H. Abruna and Royce W. Murray, Chemically Modified Electrodes. XIV. Attachment of Reagents to Oxide-Free Glassy Carbon Surfaces. Electroactive RF Polymer Films on Carbon and Platinum Electrodes, J. Electroanal. Chem. 94 (1978) 219. Technical Report #6.

H. O. Finklea and Royce W. Murray, Chemically Modified Electrodes. XII. Effects of Silanization on TiO_2 Electrodes, J. Phys. Chem. 83 (1979) 353. Technical Report #7.

A. B. Fischer, M. S. Wrighton, M. Umana and Royce W. Murray, An X-Ray Photoelectron

Spectroscopic Study of Multilayers of an Electroactive Ferrocene Derivative Attached to Platinum and Gold Electrodes, J. Am. Chem. Soc. 101 (1979) 3442. Technical Report #8.

Roy D. Rocklin and Royce W. Murray, Chemically Modified Carbon Electrodes. XVII. Metallation of Immobilized Tetra(aminophenyl)porphyrin with Manganese, Iron, Nickel, Copper, and Zinc, and Electrochemistry of Diprotonated Tetraphenylporphyrin, J. Electroanal. Chem. 100 (1979) 271. Technical Report #9.

R. J. Nowak, F. A. Schultz, M. Umana, R. Lam, and R. W. Murray, Chemically Modified Electrodes. XX. Radiofrequency Plasma Polymerization of Vinylferrocene on Glassy Carbon and Platinum Electrodes, Anal. Chem. 52 (1980) 315. Technical Report #10.

M. Umana, D. R. Rolison, R. Nowak, P. Daum and R. W. Murray, X-ray Photoelectron Spectroscopy of Metal, Metal Oxide, and Carbon Electrode Surfaces Chemically Modified With Ferrocene and Ferricenium, Surface Science 101 (1980) 295. Technical Report #11.

R. W. Murray, Chemically Modified Electrodes, Accts. Chem. Res. 13 (1980) 135. Technical Report #12.

C. P. Jester, R. D. Rocklin and R. W. Murray, Electron Transfer and Axial Coordination Reactions of Cobalt Tetra(aminophenyl)porphyrins Covalently Bonded to Carbon Electrodes, J. Electrochem. Soc. 127 (1980) 1979. Technical Report #13.

K. W. Willman, R. D. Rocklin, R. Nowak, K. Kuo, F. A. Schultz and R. W. Murray, Electronic and Photoelectron Spectral Studies of Electroactive Species Attached to Silanized C and Pt Electrodes, J. Am. Chem. Soc. 102 (1980) 7629. Technical Report #14.

R. D. Rocklin and R. W. Murray, Kinetics of Electrocatalysis of Dibromoalkyl Reduction Using Electrodes With Covalently Immobilized Metallotetraphenylporphyrins, J. Phys. Chem. 85 (1981) 2104. Technical Report #15.

H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer and R. W. Murray, Rectifying Interfaces Using Two-Layer Films of Electrochemically Polymerized Vinylpyridine and Vinylbipyridine Complexes of Ruthenium and Iron, J. Am. Chem. Soc. 103 (1981) 1. Technical Report #16.

P. Denisevich, K. W. Willman and R. W. Murray, Unidirectional Current Flow and Charge State Trapping at Redox Polymer Interfaces on Bilayer Electrodes: Principles, Experimental Demonstration, and Theory, J. Am. Chem. Soc. 103 (1981) 4727. Technical Report #17.

R. W. Murray, Chemically Modified Electrodes for Electrocatalysis, Phil. Trans. R. Soc. London 302 (1981) 253. Technical Report #18.

J. Facci and R. W. Murray, Binding of Pentachloroiridite to Plasma Polymerized Vinylpyridine Films and Electrocatalytic Oxidation of Ascorbic Acid, Anal. Chem. 54 (1982) 772. Technical Report #19.

T. Ikeda, R. Schmehl, P. Denisevich, K. Willman and R. W. Murray, Permeation of Electroactive Solutes Through Ultrathin Polymeric Films on Electrode Surfaces, J. Am. Chem. Soc. 104 (1982) 2683. Technical Report #20.

In press is:

R. W. Murray, Chemically Modified Electrodes, Chapter 3 in Electroanalytical Chemistry, Vol. 13, A. J. Bard, Ed., M. Dekker, NY, publication in 1983.

The research collaborators on this project, with current locations, were:

Graduate Students, degree granted, current address:

Roy D. Rocklin, Ph.D. 1980, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Hector D. Abruna, Ph.D. 1980, Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931

Kenneth W. Willman, Ph.D. 1981, Proctor and Gamble Company, 6060 Center Hill Road, Cincinnati, Ohio 45224

John Stephen Facci, Ph.D. 1982, Xerox Corporation, Joseph C. Wilson Center for Technology, W-114, Webster, NY 14582

Colleen Parks Jester, M.A. 1979, 607 Donnelly, Columbia, Missouri 65201

Post-Doctoral Associates:

Dr. Mirtha Umana, Research Triangle Institute, Research Triangle Park, NC 27709

Dr. John Lennox, Burroughs-Wellcome Company, Greenville, NC 27834

Dr. Robert Nowak, Naval Research Laboratory, Washington, DC 20375

Dr. Harry O. Finklea, Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, VA 24060

Dr. Peter Denisevich, Chevron Research Laboratories, P. O. Box 1627, Richmond, CA 94802

Visiting Professors

Professor Franklin A. Schultz, visiting from Florida Atlantic University, current address Charles F. Kettering Research Laboratory, 150 East South College Street, Yellow Springs, Ohio 45387

Professor Peter Daum, visiting from Northern Illinois University, current address Brookhaven National Laboratory, Upton, Long Island, NY 11973

Professor Seichi Nakahama, visiting from Tokyo Institute of Technology, Tokyo Kogyo Daigaku, O-Okayama, Meguro-ku, Tokyo 152, Japan.

Collaborative Faculty at Other Institutions

**Professor Larry L. Miller, Department of Chemistry, University of Minnesota, 139
Smith Hall, 207 Pleasant Street SE, Minneapolis, MN 55455**

**Professor Mark Wrighton, Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, MA 02139**

Undergraduate Assistants, University of North Carolina

Kenneth Shelton

Richard Lam



A

4-8
DTI