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END-OF-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENT REPORT

for

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Contract N00014-88-K-0482, Mod/Amend: P00001

R&T Code 413d017

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AD-A223 566

Applications of Scanning Tunneling Microscopy to Electrochemistry

Nathan S. Lewis
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Department of Chemistry
Pasadena, California 91125

May 29, 1990

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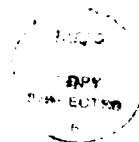
CERTIFICATION OF TECHNICAL DATA CONFORMITY

The Contractor, Nathan S. Lewis hereby certifies that, to the best of his knowledge and belief, the technical data delivered herewith under Contract No. N00014-88-K-0482, Mod/Amend P00001/R&T Code 413d017 is complete, accurate, and complies with all requirements of the contract.

Date May 29, 1990

Name and Title of Certifying Official Nathan S. Lewis, Associate Professor of Chemistry.

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OFFICE OF NAVAL RESEARCH

CHEMISTRY DIVISION

RENEWAL PROPOSAL

Date Submitted: May 29, 1990

Date Received:

TITLE: Applications of Scanning Tunneling Microscopy to Electrochemistry

PRINCIPAL INVESTIGATOR: Nathan S. Lewis

Address: Department of Chemistry, California Institute of
Technology, Pasadena, California 91125

Telephone: (818) 356-6335

BITNET/ARPANET Address:

Circle PI sex/minority status: ☒ M ☐ F Black Asian Hispanic
Native American

CONTRACTS & GRANTS OFFICIAL: Earl J. Freise

Address: Mail Code: 213-6, California Institute of Technology,
1201 E. California Boulevard, Pasadena, California 91125

Telephone: (818) 356-6357

Requested Funds: FY91 \$75,000 FY92 FY93
TOTAL

Instrument Funds: FY91 FY92 FY93
TOTAL

CONTRACT #: N00014-88-K-0482

R&T PROJECT CODE:

End date of current contract: September 30, 1991

Responsible Chemistry Division Scientific Officer: Robert Nowak

Title of Last Technical Progress Report: Electrochemistry Using Nanometer-
Sized Electrodes

Authors: Reginald M. Penner, Michael J. Heben, Teresa L. Longin, and Nathan S. Lewis

ENCLOSURE(2)

Part I:

a. *Papers submitted to refereed journals:*

R.M. Penner, M.J. Heben, T.L. Longin, N.S. Lewis, Electrochemistry at Nanometer-Sized Electrodes, submitted to *Science*.

N.S. Lewis, Mechanistic Studies of Light-Induced Charge Separation at Semiconductor/Liquid Interfaces, *Accts. Chem. Res.*, in press.

b. *Papers published in refereed journals:*

R.M. Penner, M.J. Heben, N.S. Lewis, Preparation and Electrochemical Characterization of Conical and Hemispherical Ultramicroelectrodes, *Anal. Chem.*, 1989, 61, 1630.

M.J. Heben, A. Kumar, C. Zheng, N.S. Lewis, Efficient Photovoltaic Devices From InP Semiconductor/Liquid Junctions, *Nature (London)*, 1989, 340, 621.

N.S. Lewis, et.al., Searches for Low-Temperature Nuclear Fusion of Deuterium in Palladium, *Nature (London)*, 1989, 340, 525.

G.M. Miskelly, M.J. Heben, A. Kumar, R.M. Penner, M.J. Sailor, N.S. Lewis, Analysis of the Published Calorimetric Evidence for Electrochemical Fusion of Deuterium in Palladium, *Science*, 1989, 246, 793.

c. *No books were submitted for publication.*

d. *No books were published.*

e. *No technical reports were published in non-refereed journals.*

f. *No patents have been filed.*

g. *No patents have been granted.*

h. *Invited presentations:*

Gordon Research Conference on Inorganic Chemistry, July 31-August 1, 1989. N.S. Lewis: Chemical Investigations of Semiconductor/Liquid Interfaces. Other Support: DOE, NSF.

American Chemical Society National Meeting, September 11-15, 1989, Miami Beach, FL. N.S. Lewis: Photochemistry of Semiconductor/Liquid Interfaces. Other Support: DOE.

NSF-EPRI Workshop on Anomalous Effects in Deuterated Metals, Oct. 16-18, 1989, Washington, D.C. N.S. Lewis: Overview of Relevant Electrochemistry to Cold Fusion. Other Support: DOE.

Gordon Research Conference on Electrochemistry, January 15-19, Ventura, CA. N.S. Lewis: Chemistry and Physics of the Semiconductor/Liquid Interface. Other Support: DOE, NSF.

Gordon Research Conference on Chemistry of Electronic Materials, February 26-March 2, 1990, Ventura, CA. N.S. Lewis: Chemistry and Physics of the Semiconductor/Liquid Interface. Other Support: DOE, NSF.

i. *Contributed presentations:*

American Chemical Society National Meeting, April, 1990, Boston, MA. E.J. Ginsburg, M.J. Sailor, C.B. Gorman, N.S. Lewis, R.H. Grubbs: Electrochemical Properties of Films of Poly (Me₃Si-COT): A Soluble Polyacetylene Derivative.

j. *Honors and Awards:* Dreyfus Teacher/Scholar, NSF Presidential Young Investigator

k. Three graduate students received support on the ONR grant: Teresa Longin, Russ Pyllki, and Michael Heben. (No Asian or minorities).

l. Two postdoctoral fellows received partial support on the ONR grant: Reginald Penner and Rik Blumenthal.

m. *Other funding:*

NSF: Chemical Control of Recombination at Semiconductor Interfaces: 4/1/90 to 3/31/91: \$75,000.

DOE: Picosecond Dynamic Studies of Electron Transfer Rates at III-V Semiconductor/Liquid Interfaces: 8/1/90 to 7/31/91: \$138,000.

Gas Research Institute: Electrochemical Activation of Carbon Dioxide: 11/1/89 to 10/31/90: \$100,000.

Petroleum Research Fund: Cyclic Voltammetry of Semiconductor Electrodes: 1/1/89 to 8/31/90: \$20,000.

Part II.

- a. Principal Investigator: Nathan S. Lewis
- b. Telephone Number: 818-356-6335
- c. ONR Scientific Officer: Robert J. Nowak
- d. Description of Project:

The focus of research in the last year has been STM (Scanning Tunneling Microscopy) studies of electrode/solution interfaces. STM, and its derivatives (e.g. AFM, Atomic Force Microscopy) are the only surface analytic methods capable of yielding real-space, atomic resolution, electronic and structural maps of immersed electrode surfaces. To achieve this goal, in the previous contract period we have developed STM tip preparation methodologies that enable atomic resolution imaging of electrode surfaces in solutions containing high (0.1 M) concentrations of electron donor and acceptor species. These techniques have significantly extended the applicability of STM to electrochemical investigations. Recent STM investigations of electrochemical systems have focused on elucidating the structure of adsorbate monolayers and of single strands of conducting polymers. Recently we have also used these ultra small STM tips to perform measurements of very rapid heterogeneous electron transfer rate constants at electrodes as small as 1 nm in radius.

- e. Significant Results During 1989/90:

In the previous contract period (1988/89) we discovered that techniques suitable for the preparation of insulated STM tips could be modified to yield ultramicroelectrodes (UMEs) with conical and hemispherical geometries. We have now discovered that slight modifications in the glass coating procedure of the Pt wires can yield microelectrodes with electrochemical radii as small as 10 Å. These ultra-small electrodes (nanodes) are two orders of magnitude smaller than any previous reported microelectrode. They have obvious advantages in terms of speed and current density, and will have uses in a variety of areas. We have exploited these nanodes to determine heterogeneous electron transfer rate constants in a variety of redox systems for which no prior rate data existed. These nanodes enable measurement of extremely rapid rate constants, and therefore allow correlation of heterogeneous rate constants with those predicted from self exchange measurements by Marcus theory.

We have continued our investigations of STM imaging of conducting polymers. Sub-monolayer amounts of a soluble electronically conductive polymer have been dispersed on highly ordered pyrolytic graphite (HOPG) surfaces and have been imaged with the STM in air and in aqueous solutions. The polymer, poly[trimethylsilane cyclooctatetraene] (poly[TMSCOT]), is the first soluble polyacetylene, and was developed recently at Caltech by Robert Grubbs and coworkers. Films were prepared by casting benzene solutions of the polymer onto the graphite, and the films were subsequently doped with gaseous I₂. STM images of these surfaces reveal elongated, high tunneling current features which possess a width of ≈ 10 Å, which is approximately that expected for single chains of this polymer. Significantly, no evidence of the TMS substituents is present in these images. Since orbitals of the TMS moieties are not involved in the linear conduction of electrons through the conjugated polymer chain, one possible interpretation of this result is that only the electronically conductive backbone of the polymer is seen by the STM. The STM images obtained for this system are the first atomic resolution images of an electronically conductive polymer. They also yield great insight into the mechanism of imaging nonconductive adsorbates using tunneling currents. We are currently improving the imaging procedures and are attempting to make modifications to

the polymer chain in order to understand the chemical features that result in the observed image.

f. Summary of future plans:

Work in the upcoming contract period will involve the logical extension of the research described above. Our specific expectations are as follows:

With respect to electrochemical investigations involving ultramicroelectrodes, other uses of these 10 Å radius electrodes will be explored. They should enable small scale metal deposition and other electrochemical processes on dimensions that are not available with previous large (micron scale) electrodes. STM imaging capabilities will also be enhanced, as the faradaic current rejection offered by these electrodes makes them far superior to other tip/sample combinations in use at present.

STM investigations of conducting polymer films will be extended to include soluble polyacetylenes with substituents other than TMS such as phenyl and alkyl. Unlike TMS substituted PA, aromatic substituents, which form part of the conjugated π system of the polymer, are expected to possess significant "electronic conductivity", and may be visible as high tunneling current features in STM images. Systematic STM examination of a number of substituted PAs should contribute to our understanding of the mechanisms underlying STM imaging of adsorbed organic species.

We are also continuing attempts to obtain dynamic images of phase transitions in electrochemical systems using STM. Our objective is to investigate the Pt/I system in situ, and to investigate the well-defined Pt/I/Ag surface phases prepared by underpotential deposition (UPD) of Ag onto the iodine covered Pt surface. These would be the first dynamic investigations of adsorbate rearrangements in an electrochemical cell, and will then be extended into elucidating the mechanism of the phase transitions in several electrochemical systems.

g. Co-workers currently on project:

Teresa L. Longin, a graduate student, is currently working on the project.

Reginald M. Penner, a postdoctoral fellow, is currently working on the project.

Rik Blumenthal, a postdoctoral fellow, is currently working on the project.

Russ Pylki, a graduate student, is currently working on the project.

Part III:

Enclosed are three viewgraphs: an introductory viewgraph, a viewgraph of electrochemistry at nanometer-sized electrodes, and concluding viewgraph. Also included is a 35 mm slide of an STM image of a conducting polymer. We are making this into a high quality viewgraph and will forward this to your attention within the next few days. The explanatory text is for the slide and viewgraph is as follows:

Nanometer-sized microelectrodes have been fabricated in our laboratory. They will enable unprecedented measurements of rapid rate constants, of ultra-small scale lithography and etching, of in-vivo biological detection, and of in situ scanning tunneling microscopy. Goals of the entire project are summarized in the first viewgraph.

The second viewgraph displays voltammetry at various sized microelectrodes. The smallest electrodes, with radii about 10 Å, show kinetic voltammograms even for redox systems such as ferrocene. The measurements of these fast rate constants illustrated here is one initial application of these nanometer-sized electrodes.

The third viewgraph shows an STM image of a feature on a graphite surface that has been coated with a dilute solution of a soluble, conducting polymer (polyacetylene with one $(\text{CH}_3)_3\text{Si}$ side group attached to every eighth carbon, on average). The feature is of the correct dimension for a single strand of polymer, and is not observed on a bare graphite surface. Note that the $(\text{CH}_3)_3\text{Si}$ side groups are not visible on the polymer, even though, on average, 1-2 groups should appear in this 200Å by 200Å image window. Modifications to the polymer chain are currently being made in order to determine which atoms can be imaged and which are invisible to the STM. In collaboration with the Grubbs group, STM imaging is also being developed as a tool for polymer characterization.

Future work and conclusions are included on the fourth viewgraph.

Applications of STM to Electrochemistry

N.S. Lewis

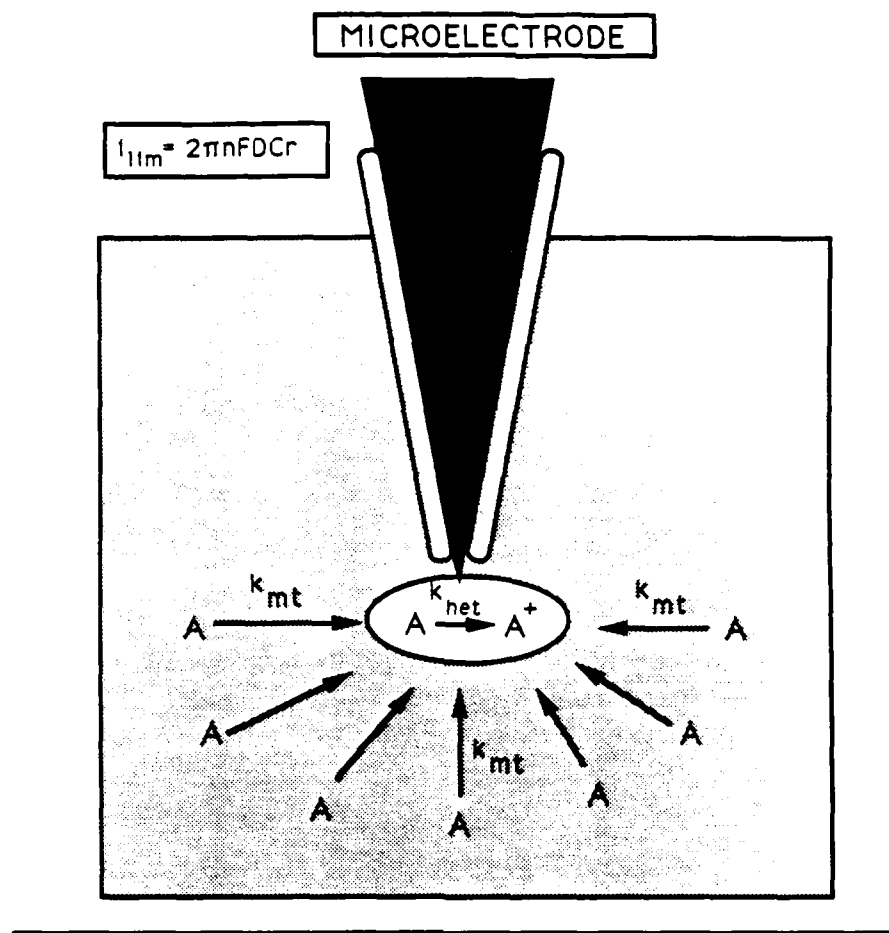
Caltech

GOALS:

- In situ images of electrode/electrolyte interfaces
- Dynamic studies of surface rearrangements
- Molecular/polymer imaging

ACCOMPLISHMENTS:

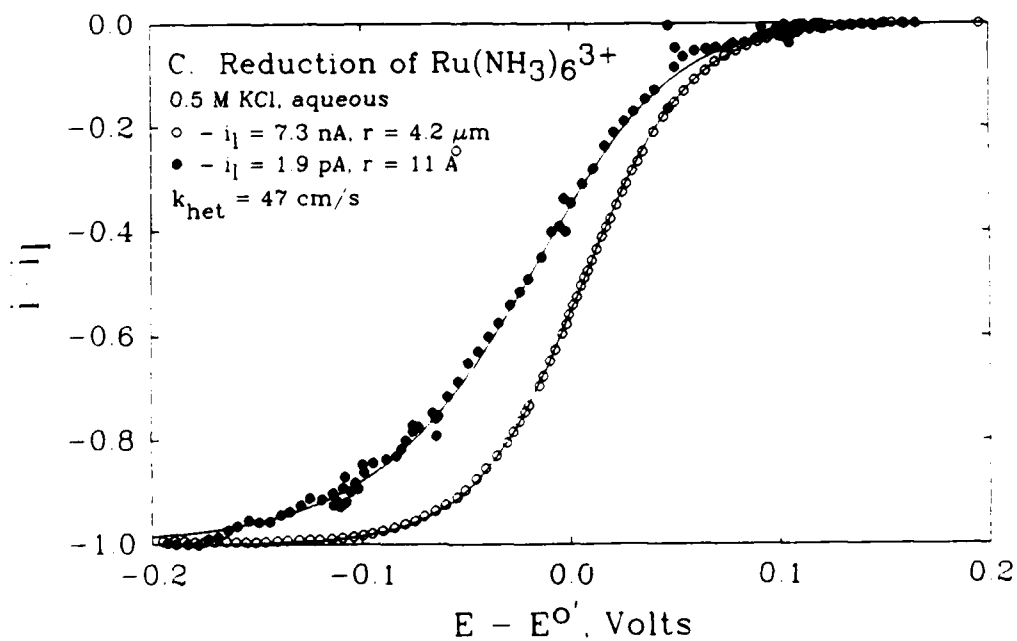
- Imaged graphite in contact with aqueous and other conducting electrolytes
- Made STM tips as small as 10 Å in radius to enable the above imaging
- Used these nanometer-scale electrodes for electrochemistry
- Imaged single strands of conducting polymers



$$k_{mt} \sim 1/r$$

$$\frac{1}{k} = \frac{1}{k_{mt}} + \frac{1}{k_{het}}$$

for $r = 10 \text{ \AA}$: $k_{mt} = 100 \text{ cm/sec}$



Future Directions

- Make modifications to polymer chains to investigate mechanism of STM imaging
- Investigate other uses of nanometer-scale electrodes
- Take advantage of dynamic STM capability to image surface rearrangements in real time