Surface Forces Microbalance and Microelectrode
Measurements of Interfacial Molecular Structure and
Electron-Transfer Rates

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Note: Professor H. S. White moved his research laboratories on April 1, 1993 from the University of Minnesota to the University of Utah. The work summarized below was performed at both institutes.

Brief Summaries of Major Accomplishments.
(Detail descriptions are provided in published articles listed at the end of the report.)

**Fundamental Investigations of Microelectrodes.**

- The voltammetric response of microelectrodes (dimensions between 10 and 1000 Å) have been simulated using Poisson's equation coupled with the Nernst-Planck transport relationships. The results demonstrate that a significant error in the values of standard heterogeneous rates result from using conventional electroanalytical treatments that assume electroneutrality. The results were used to reanalyze data previously published by other research groups.

- High electronic conductivity (~1 Amp/cm²) in concentrated organic solutions was discovered and characterized by microelectrode techniques. A mechanism of this unusual conduction based on homogenous self-exchange reactions was developed.

**Scanning Tunneling Microscopy and Spectroscopy.**

- Atomically smooth adlayers of halogen atoms (F, Cl, Br, and I) have been synthesized on Ag(111) surfaces. The adlayer structures have been determined using scanning tunneling microscopy. Resonant tunneling through individual adatoms has been observed in tunneling spectroscopy.

- Tip-induced surface reconstruction on Au(111) surfaces and dislocation motion on ordered pyrolitic graphite were discovered.

**Conducting Polymer Fiber Processing.**

- A new hydrodynamic-electrochemical process for synthesizing electrically conductive polymer (polypyrrole, polythiophene) fibers was developed. Composite Kevlar/polypyrrole fibers have also been synthesized which exhibit excellent mechanical and adhesion properties. A patent for the electrochemical process and the conductive fibers was issued in 1995.
Theoretical Description of The Interfacial Structure and Voltammetric Response of Molecular Films

- A new theory has been developed that allows voltammetric data of adsorbed monolayers to be quantitatively analyzed for effects of the interfacial potential distribution on electron-transfer rates. The theory is in excellent agreement with experimental data and replaces previous heuristic models. The theory is now widely accepted and employed by electrochemists investigating redox-active self-assembled monolayers.

Breakdown of Oxide Films on Titanium Electrodes.

- Scanning electrochemical microscopy has been used to identify, a priori, precursor sites for oxide breakdown and pitting corrosion on Ti foils. A direct correlation between electron-transfer rates and oxide breakdown has been established.

Personnel who participated in research.

Graduate students

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Refereed Publications (regularly submitted as Agency Technical Reports)

Fundamental Investigations of Microelectrodes.


Molecular Simulations.


Scanning Tunneling Microscopy and Spectroscopy.


**Conducting Polymer Fiber Processing.**


**Theoretical Description of The Interfacial Structure and Voltammetric Response of Molecular Films**


**Breakdown of Oxide Films on Titanium Electrodes.**


Miscellaneous Publications.
