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CONSTRUCTION OF A SURFACE ELECTROCHEMISTRY INSTRUMENT
(U) CALIFORNIA UNIV SANTA BARBARA DEPT OF CHEMISTRY
A T HUBBARD MAY 86 AFOSR-TR-87-0043 AFOSR-85-0168

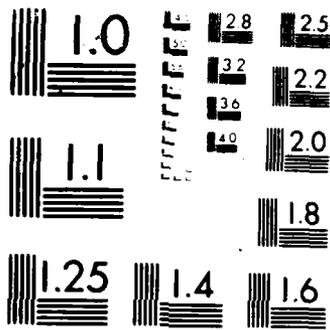
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MICROCOPY RESOLUTION TEST CHART

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A surface electrochemistry instrument was constructed, tested and put into service. The instrument consisted of an ultra high vacuum work chamber, and electrochemistry antechamber, a titanium sublimation pumping chamber and an ion-pumping plenum. Analytical methods attached were LEEDS, Auger spectroscopy, EELS and an electron gun. The purpose of the apparatus is to study the details of electrochemical processes at electrode surfaces by state-of-the-art surface spectroscopic methods.

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Final Report: Construction of a Surface Electrochemistry Instrument
AFOSR 85-0160.

Construction of the Surface Electrochemistry Instrument described in the proposal is proceeding normally and is nearing completion at the time of this writing (May, 1986).

Components and parts with which to construct the Instrument were requisitioned in March and April, 1985. Additional components were requisitioned in July, 1985 with funds provided by the University of California. The final component was received on May 2, 1986.

The amount of this award was \$100,000. Matching funds amounting to \$82,000 were provided by the University of California. The budget total was \$182,000. The amount originally requested was \$309,074. A generous discount of 25% on all components obtained from Perkin-Elmer Corporation and from Physical Electronics Industries made up part of this difference. The University of Indiana Foundation supplied the vibrational spectroscopy components at 50% of the cost originally budgeted (based upon prices quoted by Nicolet, Inc., a typical supplier of such equipment) which made up most of the remainder.

Vacuum enclosures were built to my design by Huntington Mechanical Laboratories of Mountain View, California. These are: the work chamber; the electrochemistry antechamber; the titanium-sublimation-pumping chamber; and the ion-pumping plenum. Devices for ion-bombardment-cleaning of the electrode, electrochemical characterization of the electrode and manipulation of the electrode, and the interconnecting manifolds were constructed to my design in the UCSB Chemistry Mechanical Shop.

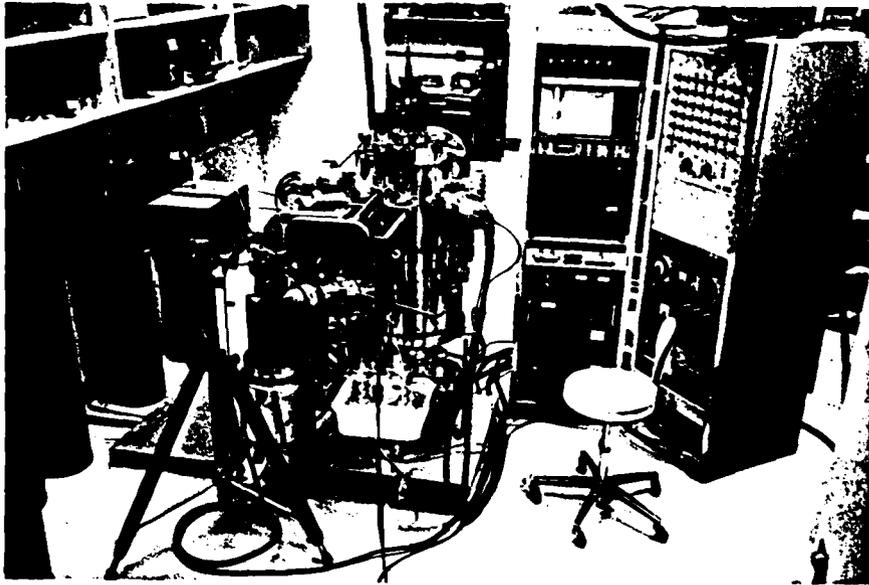
A LEED optics and control unit were purchased from Physical Electronics

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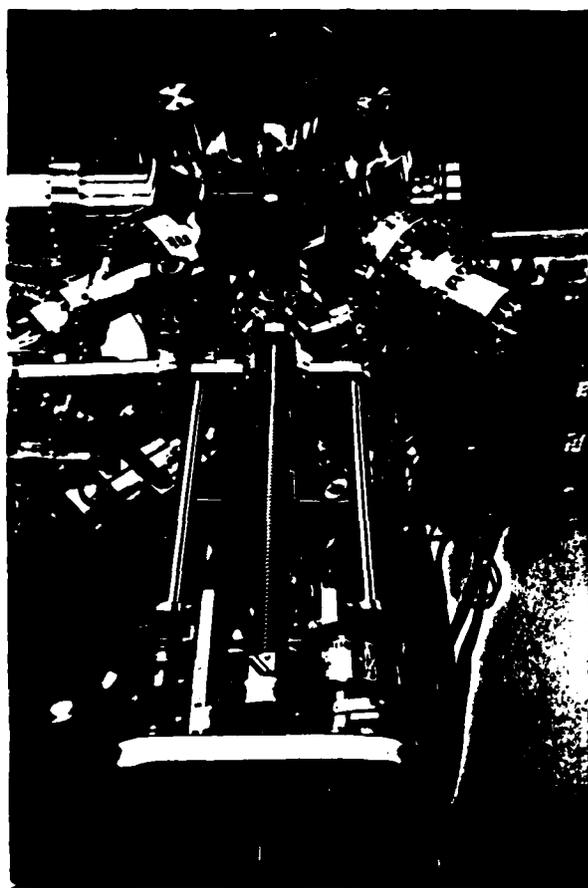
Industries. An Auger spectroscopy cylindrical mirror, electron gun and control units were obtained from Physical Electronics Industries also. A 240 L/S ionization pump and a vibration-isolated cryogenic pump were purchased from Perkin-Elmer Corporation. An electron energy loss spectrometer (EELS) having double-pass monochromator and analyzer for surface vibrational spectroscopy of adsorbed atomic, ionic, and molecular layers was constructed for us by Professor L.L. Kesmodel of the Physics Department, University of Indiana, and purchased through the Indiana Foundation.

As a result of this DoD instrumentation program our AFOSR project now has the use of a state-of-the-art surface electrochemistry apparatus which is designed specifically for use in the projects supported by AFOSR. Capabilities of this instrument include: (i) fast cycling between ultra-clean ambient pressure inert gas or reactive gas atmospheres and ultra-high vacuum; (ii) a full complement of electrochemical and electroanalytical procedures for quantitation of surface composition, charging and reactivity; (iii) high resolution electron energy loss spectroscopy (HREELS) for surface molecular functional group identification and surface chemical bonding investigations; (iv) Auger electron spectroscopy for elemental analysis of the surface; (v) ion-bombardment for preparation of ultra-clean metal surfaces as a reference point of each investigation; (vi) low-energy electron diffraction (LEED) for surface atomic structure identification; (vii) molecular leak vapor dosing of the surface for surface chemistry studies; (viii) and thermal desorption mass spectroscopy for exploration of the temperature instability of surface layers on metals, metal oxides, and semiconductors. Pictures of the completed instrument are shown in the next few pages.

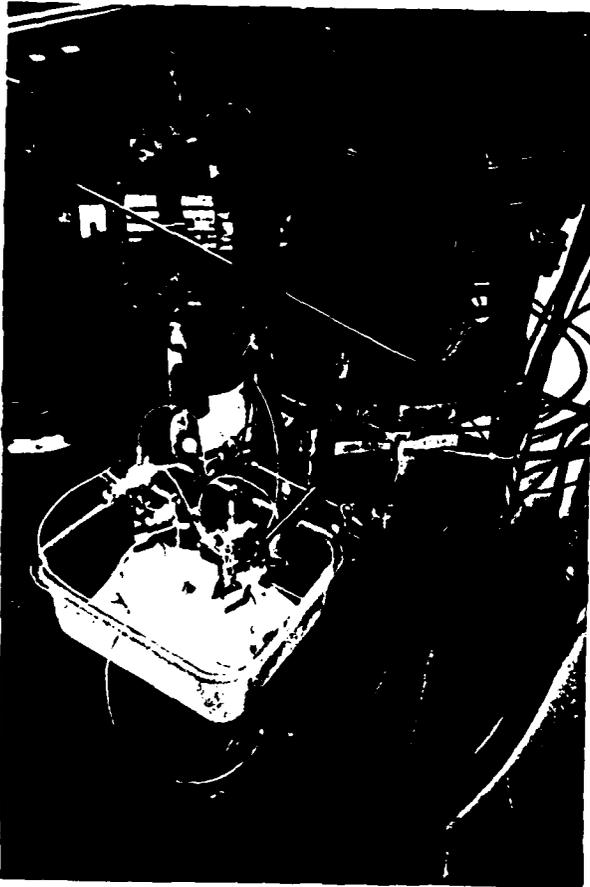
DoD SURFACE ELECTROCHEMISTRY INSTRUMENT



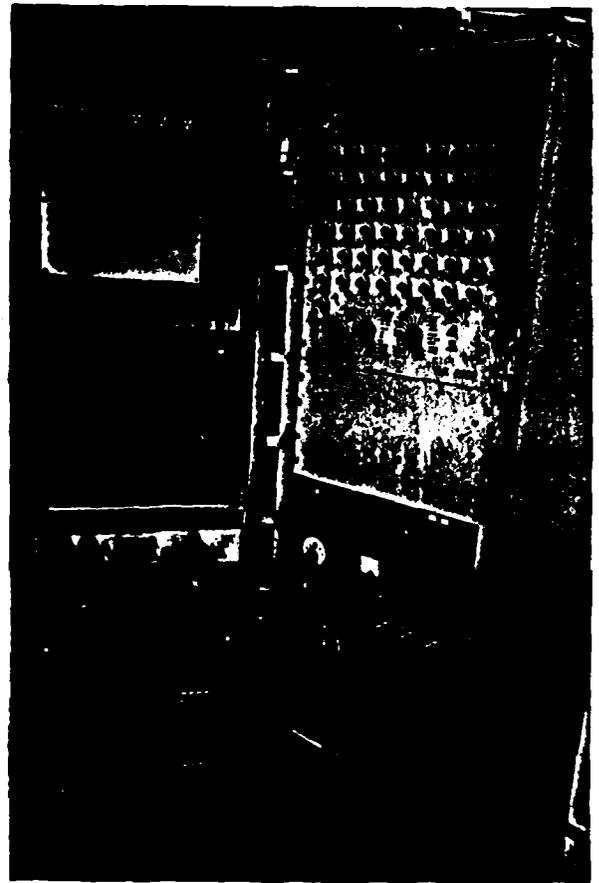
Overview of the instrument, showing the vacuum chambers and electron optics, electronic control units (computer not shown), electrochemistry apparatus, inert-atmosphere manifolds, and sample manipulators.



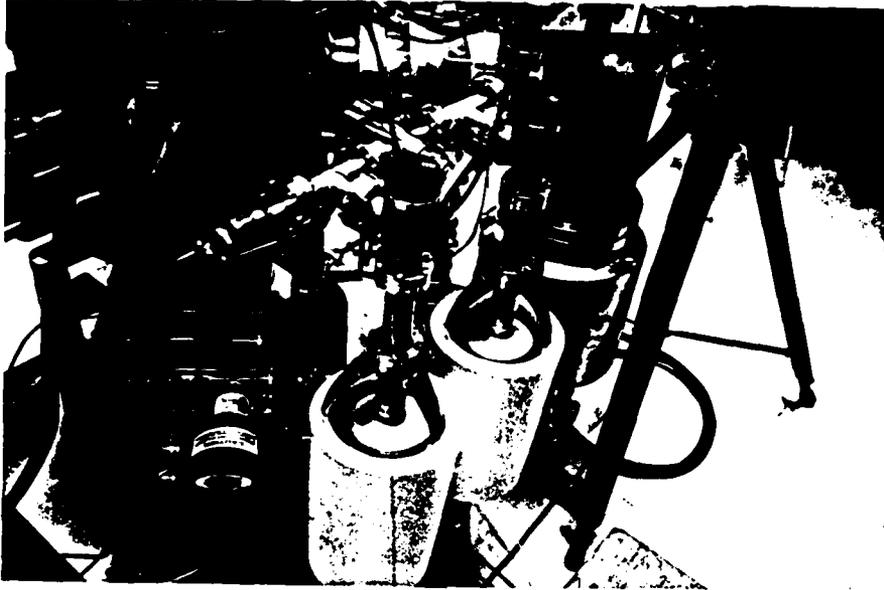
Vacuum chamber and electrochemistry port. Crystal manipulator is in the foreground. Clock wise from left: quadrupole mas spectrometer, LEED optics, electron energy-loss spectrometer, viewport, and Auger electron spectrometer.



Electrochemistry apparatus



Electronic control units



Vacuum Pumping System.

Foreground: Zeolite molecular sieve
sorption pumps.

Bottom left: triode ionization pumps.

Top left: Titanium sublimation pump (getter).

Right center: closed cycle helium cryopump

This new Surface Electrochemistry Instrument is the vital center of the author's AFOSR project (85-0192) "Electrochemistry of Molecules Attached to Metal Surfaces," to investigate the (a) structure and (b) orientation, (c) composition and (d) reactivity of molecules at metal surfaces. Atoms, ions, and molecules attached to metal surfaces are largely responsible for the practical behavior of metals in contact with chemical compounds, combustion products, natural waters and the atmosphere. Our previous work supported by AFOSR has led to major breakthroughs in each of these areas (a-d) as described in 52 scientific articles acknowledging AFOSR support during the past five years (43,46,48-66,69-73, 76-80,82,84,86-94,96-100,102,104,105,108). This research is also opening up new research areas of interest to the DoD.

Recent advances and current areas of progress include the following:

- (i) Determination of the spatial orientations of molecules attached to electrode surfaces by chemical bonding (43,46,48-50,52,58-65,69,72).
- (ii) Identification of the modes of chemical bonding responsible for attachment to the surface (42,46,48,52,61).
- (iii) Correlation of the adsorbed states with the molecular structure of the adsorbate (43,46,48,52,61).
- (iv) Observation of electrochemical reactivity as a direct function of the orientation and mode of bonding of the adsorbate (49,50,52,60,62,64,73).
- (v) Comparison of the reactivity of adsorbed and unadsorbed states of the same compound (46,48).
- (vi) Definition of the influence of temperature on adsorbate orientation and reactivity (58,60).

- (vii) Exploration of the influence of anions on adsorbate orientation (43,62,65,69).
- (viii) Systematic determination of the influence of interfacial electric potential on adsorbate orientation (62,64).
- (ix) Correction of a series of major conceptual and experimental errors in the literature of electrosorption (62,64,79,84).
- (x) Determination of the structures of electrodeposited layers, namely of Ag onto Pt(111) (54), Cu onto Pt(111) (55), Ag onto Pt(100)(56), Ag onto a stepped surface, Pt(s)(6(111)x(111)) (67), Sn onto Pt(111) (102), and Pb onto Pt(111) (104). This was the first time for determination of the structures of electrodeposited metal monolayers.
- (xi) Demonstration of the stability of the van der Waals surface (001) of MoSe_2 , in a class of compounds widely used as photocell materials and high temperature lubricants.
- (xii) Exploration of the influence of adsorbed layers on the reflection of infrared radiation by metals (71,72,78,90).
- (xiii) Discovery for the first time that ions form an ordered layer at well-defined metal surfaces (76).
- (xiv) Demonstration that surface roughness disrupts molecular packing at metal surfaces, thus altering stability of the layer and catalytic activity of the metal surface (79).
- (xx) Exploration of competitive adsorption and order-disorder phenomena of aromatic mixtures at Pt surfaces (80,82,96,97).
- (xvi) Studies of competitive cation retention by metals in aqueous salt

solutions (at well-defined metal surfaces for the first time) (86).

(xvii) Studies of the influence of adsorbed monolayers on the electrochemical conduction of metals in electrolytic solution (87,88).

(xviii) Quantitative measurements of the pH-dependence of cation-retention at metal surfaces (89,92).

(xix) Exploration of the influence of non-aqueous solvents on chemisorption and adsorbate molecular orientation at metallic (Pt) surfaces (91,93,105).

(xx) Determination of the structure and composition of Pt(111) surfaces following immersion into aqueous ionic solutions as a function both of electrode potential and of pH (98).

(xxi) studies of the kinetics of adsorption at a metal (Pt) to form an oriented molecular layer, the principal layer in understanding the practical behavior of metal surfaces (99,108).

(xxii) Two invited reviews of this research have been published recently (77,100).

A remarkable series of new experiments are currently in progress as a result of DoD funding for construction of the new instrument (AFOSR-85-0160) and support for its use (AFOSR-85-0192):

(a) Studies of the reactivity of oriented adsorbed ionic and molecular intermediates in non-aqueous media, conditions which could lead to improved performance of high energy batteries and other electrolytic devices.

(b) Studies of the mode of surface attachment of transition metal compounds

for improved understanding of metal surface corrosion and passivation.

(c) Electrolysis products starting from chemisorbed intermediates are being directly determined (106).

(d) Adsorption of aromatic compounds at non-Pt surfaces is being studied to bring existing knowledge to bear upon typical structure and electronic materials.

(e) Infrared and HREELS spectra are being obtained for adsorbed molecular layers at metal surfaces in order to form a body of reliable information by which to understand the nature of surface ionic and molecular species, and the manner in which such species are attached/bonded to metals.

(f) The nature of adsorption of non-water polar solvents at metal surfaces is being explored by use of the Surface Electrochemistry Instrument multi-technique approach.

(g) Adsorption of ions at metal surfaces is being investigated, pursuing the clues uncovered in previous AFOSR-supported research (76,-6,89,92,98).

(h) The influence of surface pretreatment on the structure and stability of adherence of metal electrodeposits is being investigated using techniques described in Refs. 52-58, 67, and 101-104.

(i) Adsorption profiles of organic molecules are being determined by Auger spectroscopy so as to generalize the methodology for determining the strength of binding of chemical compounds to metal surfaces.

(j) Auger intensity ratios are being measured for adsorbed layers to probe adsorbate stoichiometry and molecular orientation.

(k) LEED examination of chemisorbed layers continues to reveal structural

characteristics of adsorption processes which are valuable clues as to the nature of adsorption.

(l) Electrodeposition of metals into adsorbed organic layers is being studied with emphasis on non-aqueous batteries and electrodeposition brightening agents.

(m) Correlations between the long-range order of adsorbed layers and their chemical reactivity are being sought by LEED and electrochemical techniques.

(n) The influence of terrace size on adsorption and reactivity at step-terrace electrode surfaces is being explored. The characteristics of kink-terrace surfaces will be explored later by similar methods.

(o) Well-defined alloy single-crystal surfaces (81, 83, 85, 109) are being investigated as electrodes in search of behavior unique to the alloys and distinct from that of the pure constituent elements. Potentially useful surface properties of alloy single-crystal planes are also being sought.

This project has certainly entered a very significant and productive stage.

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