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Materials & Molecular Research Division

ELECTRODE SURFACE CHEMISTRY
FY 1980 ANNUAL REPORT

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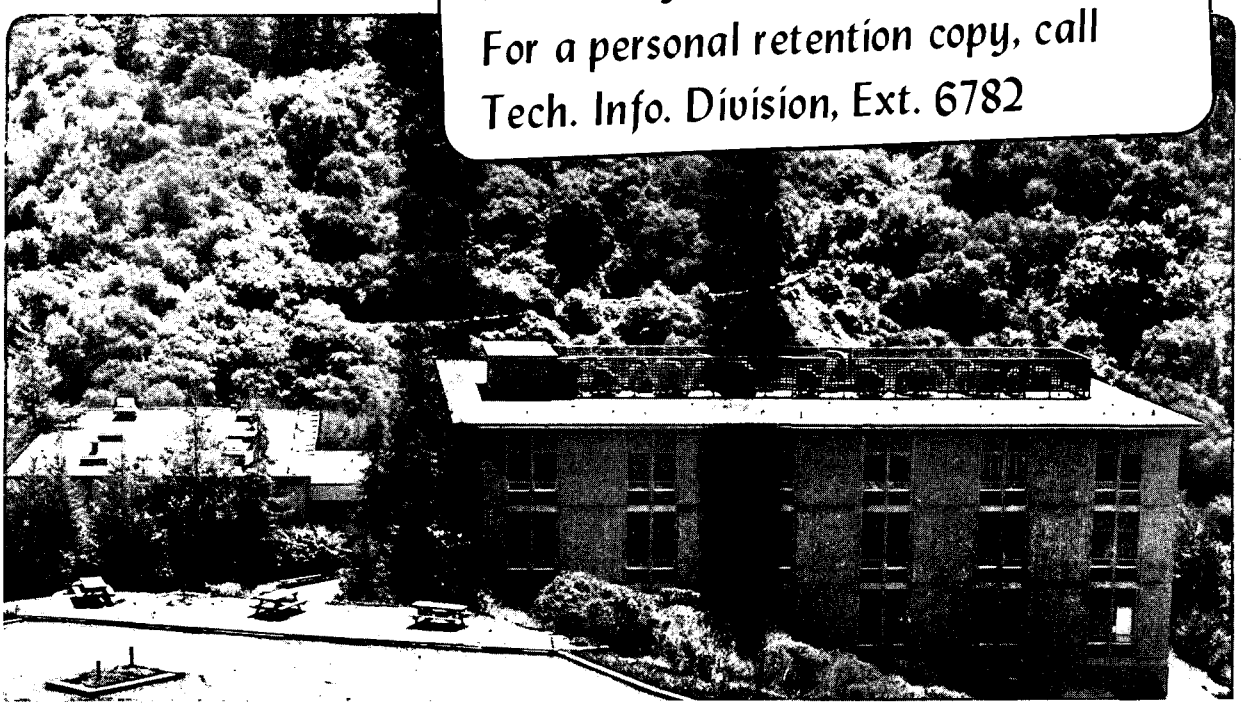

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ELECTRODE SURFACE CHEMISTRY

FY 1980 ANNUAL REPORT

September 30, 1980

Prepared for NASA Lewis Research Center
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I. INTRODUCTION

A. Program Objectives

Commercialization of phosphoric acid fuel cell technology requires a capital cost reduction and an extension of power section life compared to currently available technology. Significant capital cost reduction can be achieved if an oxygen reduction catalyst can be developed which is both catalytically more active and thermodynamically more stable than Pt supported on graphitized carbon black.

Previous studies at LBL have shown that very small (20 Å) Pt clusters are oxidized (to PtO) more rapidly than macroscopic (>50 Å) clusters causing a decline in oxygen reduction kinetics with crystallite size due to too strong an interaction with oxygen on the small clusters. These results suggest modification of the adsorptive properties of Pt by the substitution of ligands to the Pt coordination sphere, e.g., by alloying, could result in enhanced Pt catalysis.

The objective of the present research is to develop the physical and chemical understanding of oxygen-platinum-alloy ligand interaction necessary for the rational selection of alloying components. Fundamental studies of the alloy-electrolyte interface using modern surface science techniques should provide the means to optimize the alloy ligand or to redirect the search for more active materials along the most rational paths. Alloying may have significant beneficial effects on electrode performance above and beyond effects on the oxygen reduction kinetics, e.g. reduced Pt dissolution and surface area loss.

B. Scope of Work

The experimental approach, which is unique to this laboratory, combines the study of the interaction of the oxygen molecule with bimetallic surfaces in vacuum and in aqueous solution in a single apparatus. This apparatus combines

classical electrochemical methods together with the analytical methods of surface science: low energy electron diffraction (LEED), Auger electron spectroscopy (AES), photoemission spectroscopy (XPS and UPS), and thermal desorption mass spectroscopy (TDS).

Task I. Studies of Modified Pt Surfaces in Acidic Solutions

A series of Pt surfaces modified both structurally and compositionally shall be prepared. Structural modifications will be accomplished using Pt single crystals of different crystallographic orientations and by using inert ion bombardment to produce amorphous (highly disordered) surfaces. Pt surfaces will be modified compositionally by alloying with selected ligands. Ligand modification will be accomplished by such techniques as thin film evaporation, electrodeposition and ion implantation. The choice of alloy ligands shall be guided by the FY'79 EPRI-funded study at LBL on bimetallic clusters for oxygen electroreduction. Tantalium, vanadium and zirconium are indicated to be the likely choices.

The structure, composition and nature of the Pt-ligand chemical bond will be determined before and after contact with electrolyte using LEED, AES, XPS and UPS. Fundamental electrochemical measurements to be made are: rate of Pt oxide formation; rate of Pt oxide reduction; rate of oxygen electroreduction. The role of the alloy ligand in modifying these selected properties of the surface shall be elucidated.

Task II. Studies of Oxygen Adsorption on Modified Pt Surfaces

Using the same modified surfaces as studied in Task 1, the nature of the interaction between the oxygen molecule and the modified surfaces shall be observed using LEED, AES, XPS-UPS and TDS. The effect of structure and ligand modification will be related to: the structure of chemisorbed oxygen; the rate of oxygen chemisorption; the rate of Pt oxide formation; the structure and chemistry of the oxidized surface.

Task III. New Modified Pt Electrocatalysts

The information obtained in Tasks I and II, together with other basic knowledge, shall be used to deduce new Pt catalyst formulations. These new electrocatalysts shall be synthesized and evaluated as oxygen reduction catalysts using the standard procedures developed here for the EPRI programs.

Task IV. New Acid Electrolytes for Fuel Cells

This Task will be a follow-up to a program initiated under EPRI funding to explore newly synthesized phosphonic, sulfonic and carboxylic acids. Of particular interest is the use of non-Pt catalysts (e.g., Pd based) since some non-Pt metals have shown better stability in fluorosulphonic acids than in phosphoric acid. The basic electrochemical properties of Pt and Pd electrocatalysts in tetrafluoroethanedisulphonic and perfluorosuccinic acids will be determined.

II. TECHNICAL PROGRESS SUMMARY

This was a new program for LBL in 1979. Because of the complexity of the experimental apparatus, the construction was divided into two independent modules which could be assembled, tested, and used separately in the first generation of experiments.

The first module has the low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) for surface characterization in vacuum along with the state-of-the-art capability (ion bombardment, thermal annealing, etc.) for preparing clean well-ordered surfaces in vacuum. (See Fig. 1). Electrochemical analysis and surface reactions are accomplished using a differentially pumped microcell mounted on a high vacuum feedthrough. (See Fig. 2). The surface to be studied is transferred into the microcell by remote manipulation.

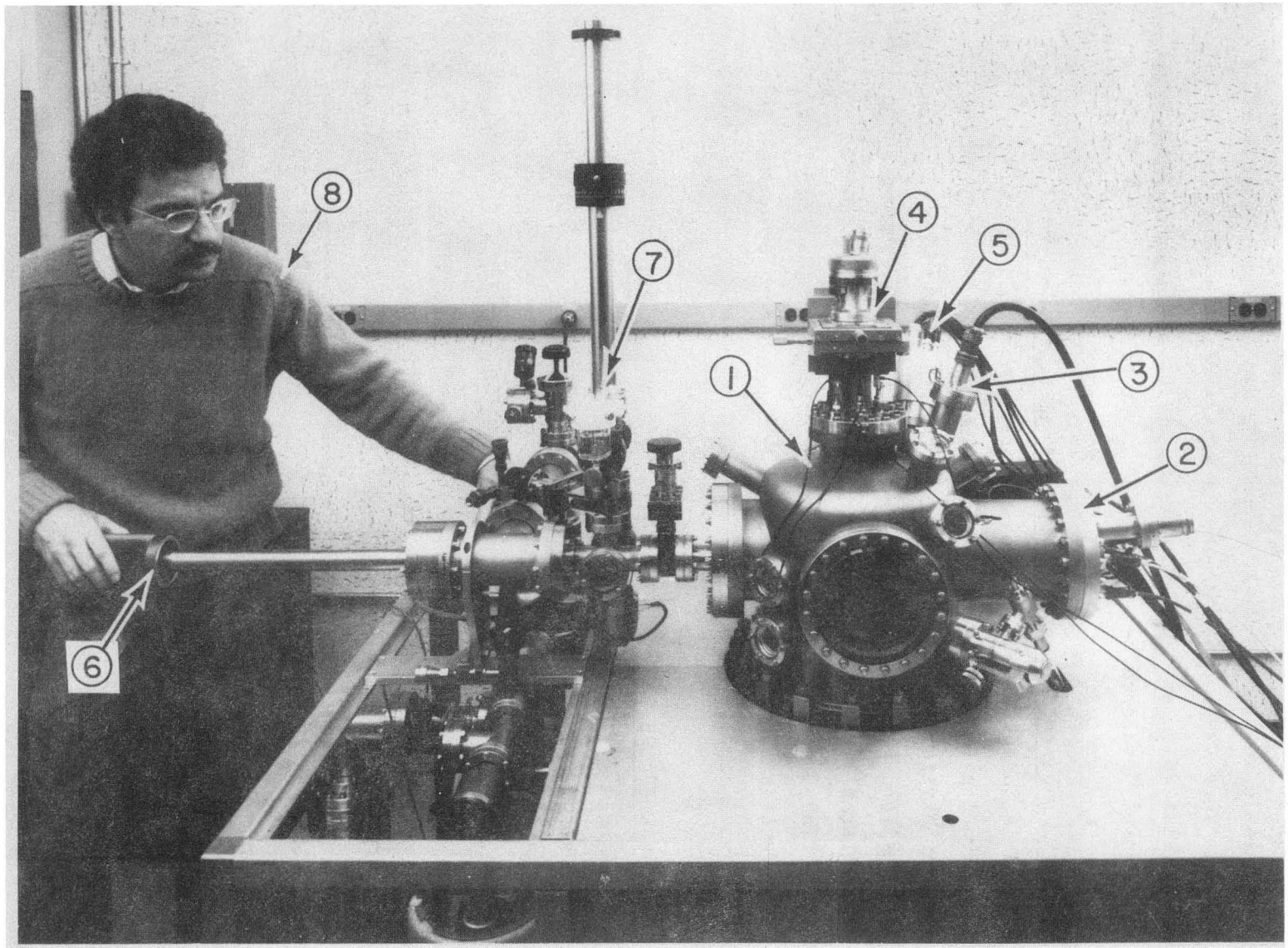

Fig. 1. A LEED/AES-Electrochemical Analysis Module showing (1) LEED optics, (2) AES cylindrical mirror analyzer, (3) Auger excitation electron gun, (4) sample manipulator, (5) ion gun, (6) sample transfer rod, (7) electrochemical cell feedthru, and (8) author.

(XBB 790-16210A)

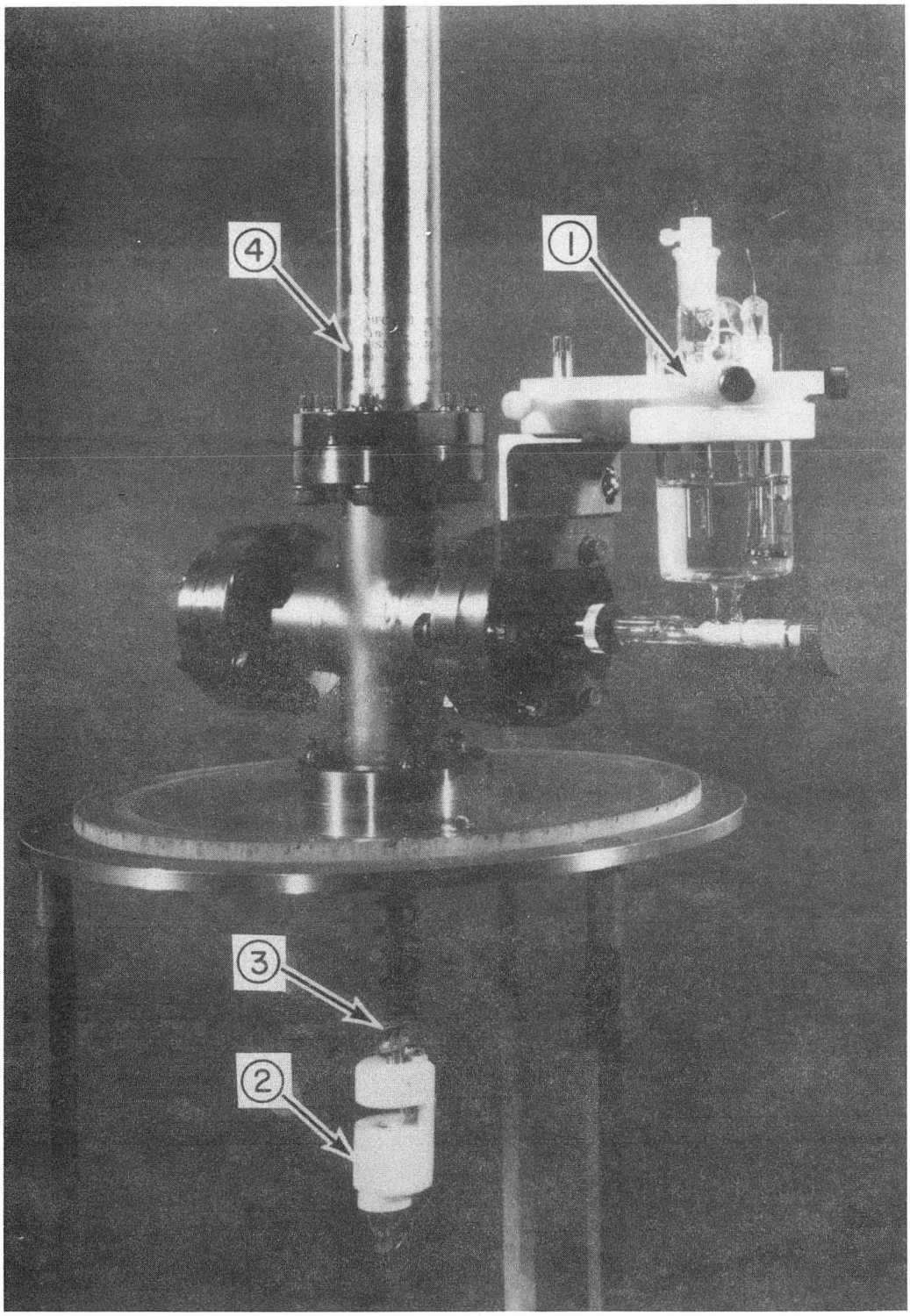

Fig. 2. A detail of the electrochemical cell feedthru showing (1) electrolyte reservoir, (2) Teflon minicell with α-PdH reference electrode, and gold ring counter electrode, (3) electrical leads and electrolyte transport tubing, and (4) magnetically coupled linear motion feedthru. (XBB 790-16212A)

Construction of the first module was completed in late FY'79 and the first experiments were conducted in the system in the first quarter of FY'80. The first experiments were related to the Task I program.

Because of funding limitations (and thus manpower limitations) the Task I experiments on the first module were terminated in order to construct the second module. As the first experiments with the second module fall under the Task II program, we describe the progress made in the construction and assembly in the Task II narrative below.

Task I. Progress

In FY'79 work began on the electrosorption of hydrogen and hydroxyl groups on Pt single crystals and was completed in FY'80. A final manuscript of the work was written and accepted for publication in Surface Science. A copy of the manuscript is provided as an Appendix to this report. No further work was conducted on Task I.

Task II. Progress

The past year has been devoted to the actual construction of the second module of the experimental apparatus. This fabrication work is nearly complete, and it is hoped that the oxygen adsorption experiments can be put into operation soon. The following is a brief description of the apparatus pictured in Figures 3-5.

Figure 3 shows the vaccum chamber and accompanying surface analysis hardware. At the rear is the sample manipulator, with X, Y, and Z motion, polar rotation capability, and a sample "flip" activator. Clockwise from this is the ultraviolet photon source, a helium discharge lamp producing 21.2 eV and 40.8 eV photons. Two stages of differential pumping separate the discharge region from the ultrahigh vacuum, with a bakeable valve for isolation when not using the lamp. Clockwise from the UV source is an ion gun to be used for sputter cleaning the sample

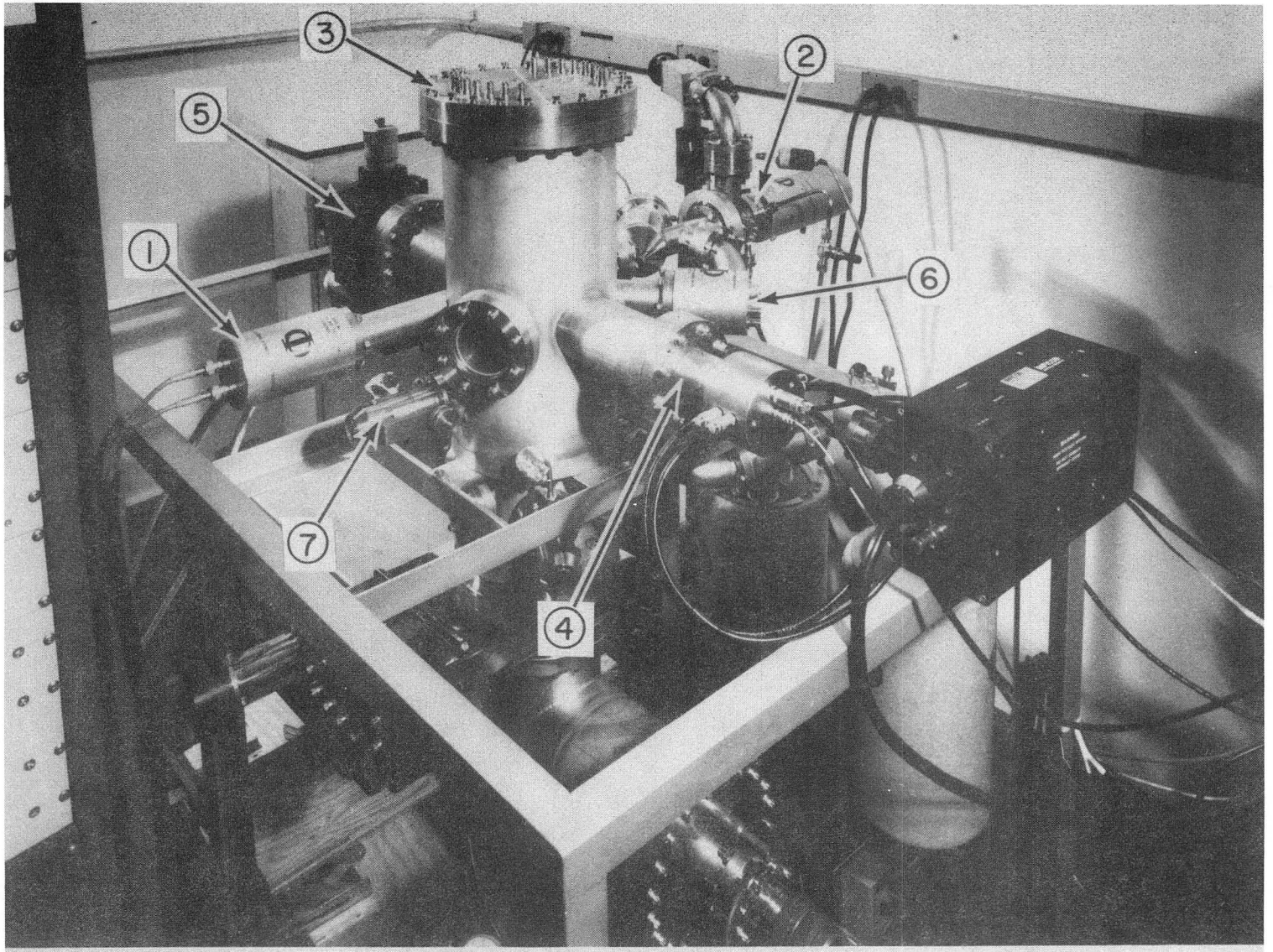

Fig. 3. A photoemission spectroscopy module showing: (1) x-ray source, (2) VUV source, (3) electron energy analyzer, (4) quadrupole mass spectrometer, (5) sample manipulator, (6) ion gun, and (7) leak valves. (XBB 809-10696)

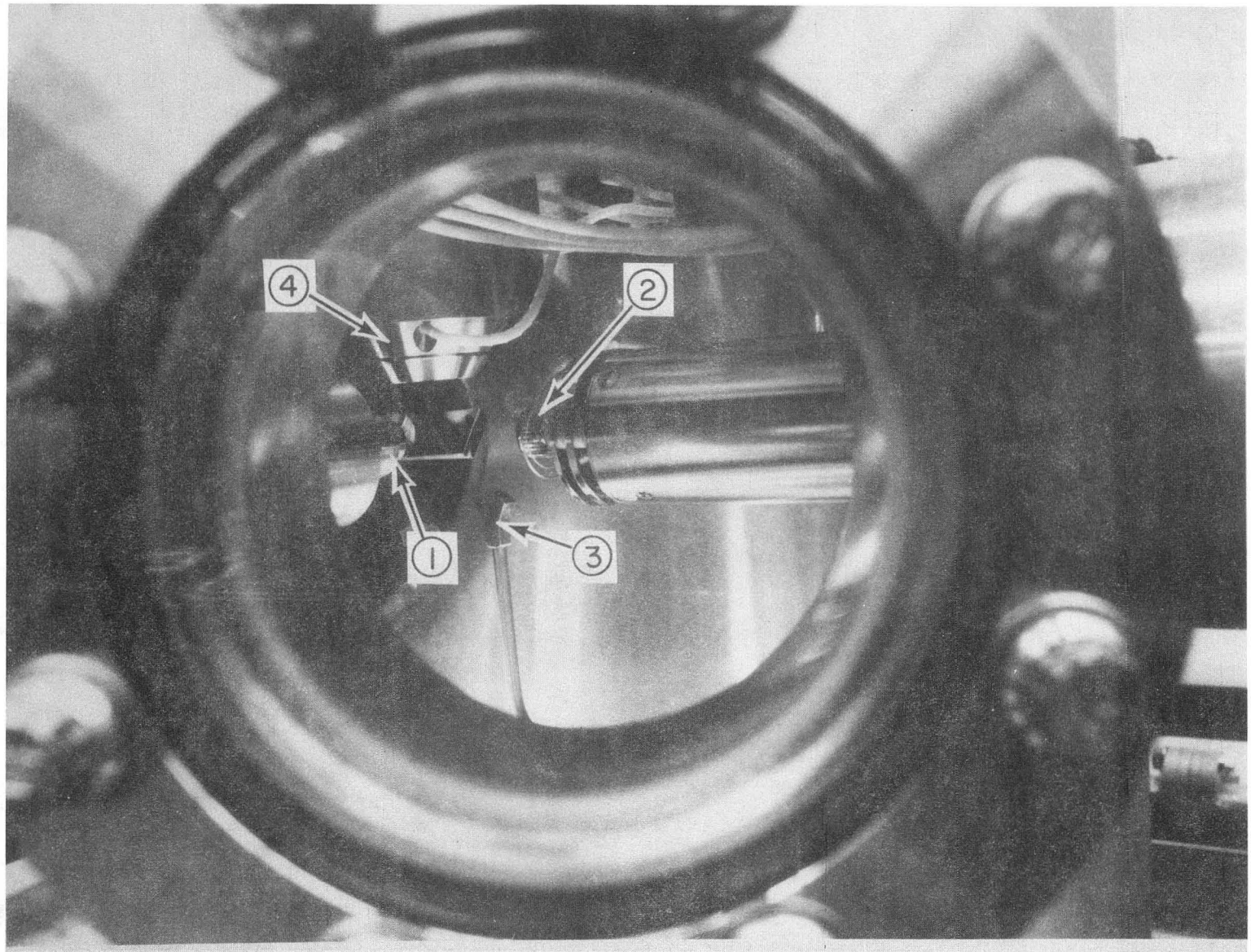

Fig. 4. A detail of the photoemission chamber showing (1) x-ray anode, (2) mass spectrometer ionizer, (3) oxygen beam source, and (4) electron spectrometer retarding lens. (XBB 809-10694A)

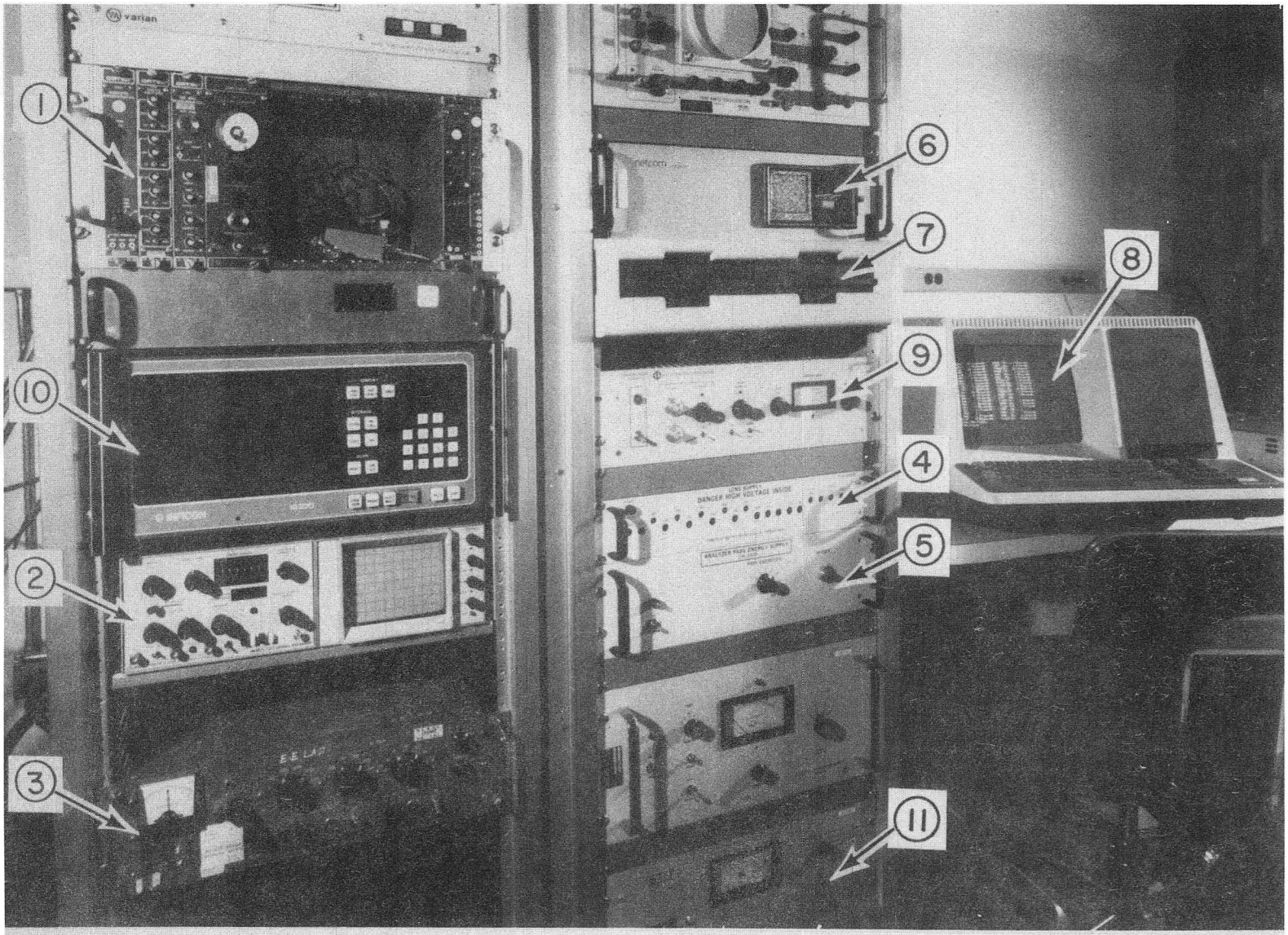

Fig. 5. The electronic instrumentation panels showing (1) pulse counting electronics, (2) signal averager, (3) electron multiplier power supply, (4) analyzer retarding lens supply, (5) analyzer pass energy supply, (6) LSI-11 main frame, (7) dual floppy disc drive, (8) VT-55 terminal, (9) ion gun control unit, (10) mass spectrometer control unit, and (11) pump control.

(XBB 809-10698A)

surface. Opposite to the same manipulator is the quadrupole mass spectrometer. This will be used to perform thermal desorption (TDS) experiments, providing information supplementary to the photoelectron spectroscopy work. The x-ray source (far left) employs an aluminum anode and produces $K\alpha$ x-ray photons of 148.6 eV. Below this equipment are two precision leak valves for dosing the sample surface with oxygen and for ion sputtering gas introduction. Suspended from the top flange is the electron energy analyzer and detector. The energy analyzer is a hemispherical sector having two focusing Einzel lenses and a retarding stage at the input. At the output is the detector, consisting of a channel plate electron multiplier and a resistive strip. The design of the spectrometer is such that it will be easily converted to multi-channel (position sensitive detection) operation, increasing the counting rate by a factor of greater than 20.

The photograph in Figure 4 was taken through the viewport and shows the inside of the sample chamber. For testing purposes, a gold foil mounted on a temporary holder is being used. Facing the surface is the output of the x-ray source. Opposite the sample holder (on the right of the photo) is the head of the quadrupole mass spectrometer. Above the surface is the input lens of the electron spectrometer. Below the surface is the sample dosing tube, with an additional outlet to the mass spectrometer for calibration purposes. The ion gun and ultraviolet source are unseen behind the quadrupole head.

Figure 5 shows the electronics used to run the experiment. At the top left, below the partially shown ionization gauge controller, is a rack of pulse counting instrumentation in a NIM configuration. Below it is an interfacing box for the computer's connections to the rest of the apparatus. Underneath this is the microprocessor-equipped control unit for the mass spectrometer. The signal averager is used with the pulse counting electronics to extract the photo-emission line from the background. At the

lower left is the channel plate bias voltage supply. On the upper right, below the partially shown oscilloscope, is the central processor, memory, and peripheral boards of the LSI-11 computer system. Immediately below it is the "floppy disk" memory storage, and at the far right is the keyboard and video terminal. Underneath the floppy disk unit is the controller for the ion gun. That is followed by two of the power supplies designed to provide proper voltages to the components of the electron spectrometer. Control units for the titanium sublimation pump and the ion pump are on the bottom right of the rack. Not shown, due to maintenance, are the programmable high-voltage supply discharge lamp.

After the experiment is fully operational, we will commence a study of oxygen chemisorption on clean single-crystal plantinum surfaces. Of particular interest is the "epitaxial oxide" structure seen under certain conditions. This has not been well characterized, and we hope to use the surface sensitive photoelectrons collected at glancing take-off to gain information about the depth profile of the oxide structure.

Task III. Progress

No work done.

Task IV. Progress

New Task for FY'81.

III. CURRENT PROBLEMS

A. Technical Problems

No technical problems were encountered in the assembly of the first analytical module and we expect rapid future progress in Task I as soon as the problems in Task II are overcome. The assembly of the second module, described in the Task II narrative, has produced some unexpected problems in the power

supplies for the electron spectrometer. These power supplies were designed and built at LBL, as was the electron spectrometer. The power supplies have not worked since delivery from the electronics shop. We believe the problem has been isolated, but we have lost about two months time. Provided no problems occur with the electron spectrometer, we expect to complete the assembly and testing of this module in November, and start Task II experiments in December.

B. Schedule Problems

The program at present contains more Tasks than can reasonably be conducted with the current level of funding, which has been substantially below that requested in Field Task Proposals. Since the program was only initiated in April of 1979, some problems in getting the whole program funded are understandable. With the present (FY'80) funding level, we can work on only one Task area at a time and a start-stop program schedule. We do not feel the best results can be obtained in this manner, and if underfunding continues through FY'81 and into FY'82, the program will be revamped to make optimum use of the personnel and the apparatus.

IV. WORK PLANNED

No commitment has yet been made for FY'81 support which awaits receipt of FY'81 guidelines from DOE and overall FY'81 planning. Two Work Plans are given, one for the present budget, one for the proposal budget.

WORK PLAN

Present Budget ($50K)

	FY'81					FY'82				
	FTE	Oct-Dec	Jan-Mar	Apr-June	July-Sept	FTE	Oct-Dec	Jan-Mar	Apr-June	July-Sept
Task I	0.5	Δ	———	———	Δ	0.5	Δ	———	———	Δ
Task II	0.5	Δ	———	———	Δ					
Task III		No Work				0.5	Δ	———	———	Δ
Task IV		No Work					No Work			

WORK PLAN

Proposed Budget ($175K)

	FY'81					FY'82				
	FTE	Oct-Dec	Jan-Mar	Apr-June	July-Sept	FTE	Oct-Dec	Jan-Mar	Apr-June	July-Sept
Task I	1.0	Δ	———	———	Δ	1.0	Δ	———	———	Δ
Task II	1.0	Δ	———	———	Δ	1.0	Δ	———	Δ	
Task III						0.5		Δ	———	Δ
Task IV	1.0			Δ ———	Δ	1.0	Δ	———	———	Δ

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