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CATALYSTS FOR THE ELECTROCHEMICAL
GENERATION OF OXYGEN

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I. SUMMARY

The development of more effective electrocatalysts for the generation of O_2 as well as other electrochemical processes of importance to NASA requires further insight into the surface properties controlling the catalysis including both surface morphology and electronic properties. The present research involves the study of single crystal surfaces of platinum and gold and transition metal oxides of the spinel type. The single crystal studies involve the use of low energy electron diffraction (LEED) and Auger electron spectroscopy as complementary tools to the electrochemical measurements. A special transfer system and a special thin-layer electrochemical cell have been designed to facilitate the transfer between the ultrahigh vacuum environment of the electron surface physics equipment and the electrochemical environment with a minimal possibility of changes in the surface structure.

During the six-months reporting period, the modifications in the transfer system described in earlier reports have been completed and used successfully. These modifications now permit the return of the

single crystal surfaces to the LEED-Augur system following the electrochemical measurements with the thin-layer cell, using completely volatilizable electrolytes such as aqueous hydrofluoric acid. The system now also has provisions for rinsing off non-volatilizable electrolytes in instances where completely volatilizable electrolytes cannot be used.

This system has been used for the first time to examine the underpotential electrodeposition of lead on the three low index surfaces (100,110,111) of gold and the structure of the lead submonolayers formed on these surfaces.^a The peaks in the voltammetry curve are strongly dependent on the particular low index plane. The LEED studies indicate pronounced restructuring. The (100) surface exhibits a highly irreversible gross restructuring, evident in the voltammetry curve as well as LEED. These results will prove very helpful in interpreting the electrocatalytic properties of such UPD systems.

Research has also been initiated on the high index surfaces of single crystal platinum including the stepped surfaces found by Somorjai (1) to have high activity for solid-gas phase reactions. Particular emphasis will be placed in hydrogen electrosorption and stability.

Research is also in progress on the Co_3O_4 and NiCo_2O_4 spinels, including their preparation on titanium substrates and also in the form of high surface area powders using the freeze-dry technique; and their characterization with X-ray diffraction, ESCA and linear sweep voltammetry. These oxides are expected to have high electrocatalytic

^a The research on underpotential electrodeposition of foreign metals on various substrates is also supported with funds provided by the Office of Naval Research as part of a study of the structural properties of electrode surfaces. The development of the LEED-Augur-thin layer electrochemical cell has been assisted also with funds from ONR.

activity for O_2 generation. Mechanistic and kinetic studies are planned.

II. PRIMARY OBJECTIVES

To find new, more effective catalysts for the electrolytic evolution of oxygen and to understand the mechanism and kinetics for the electrocatalysis in relation to the surface electronic and lattice properties of the catalyst.

III. SPECIFIC OBJECTIVES FOR THIS REPORTING PERIOD

1. Further upgrading of the thin-layer cell-LEED-Auger system.
2. Studies of the electrosorption underpotential deposition of Pb onto the Au(111), (100) and (110) single crystal surfaces with the thin-layer cell-LEED-Auger system.
3. Synthesis of spinels for oxygen evolution studies.

IV. SUMMARY OF RESEARCH DURING THE PAST SIX MONTHS

A. LEED-Auger-Thin-layer cell Electrochemical Studies: Equipment Modifications

In the last report plans for several modifications to the experimental apparatus were mentioned. Detailed drawings of these modifications are presented here.

In Figure 1 is shown the new solution delivery system. All parts which come in contact with the HF electrolyte are now made of Teflon. The system provides for in-situ monitoring of the counter-reference electrode by use of an auxiliary working electrode. Repeated rinsing of the electrode with fresh electrolyte or water is also provided.

Figure 2 is an updated drawing of the electrochemical half of the vacuum chamber. Shown in the drawing are the new sample carousel which provides for the mounting of six samples in the vacuum chamber at one time and the Knudsen cell which will be used to deposit monolayer

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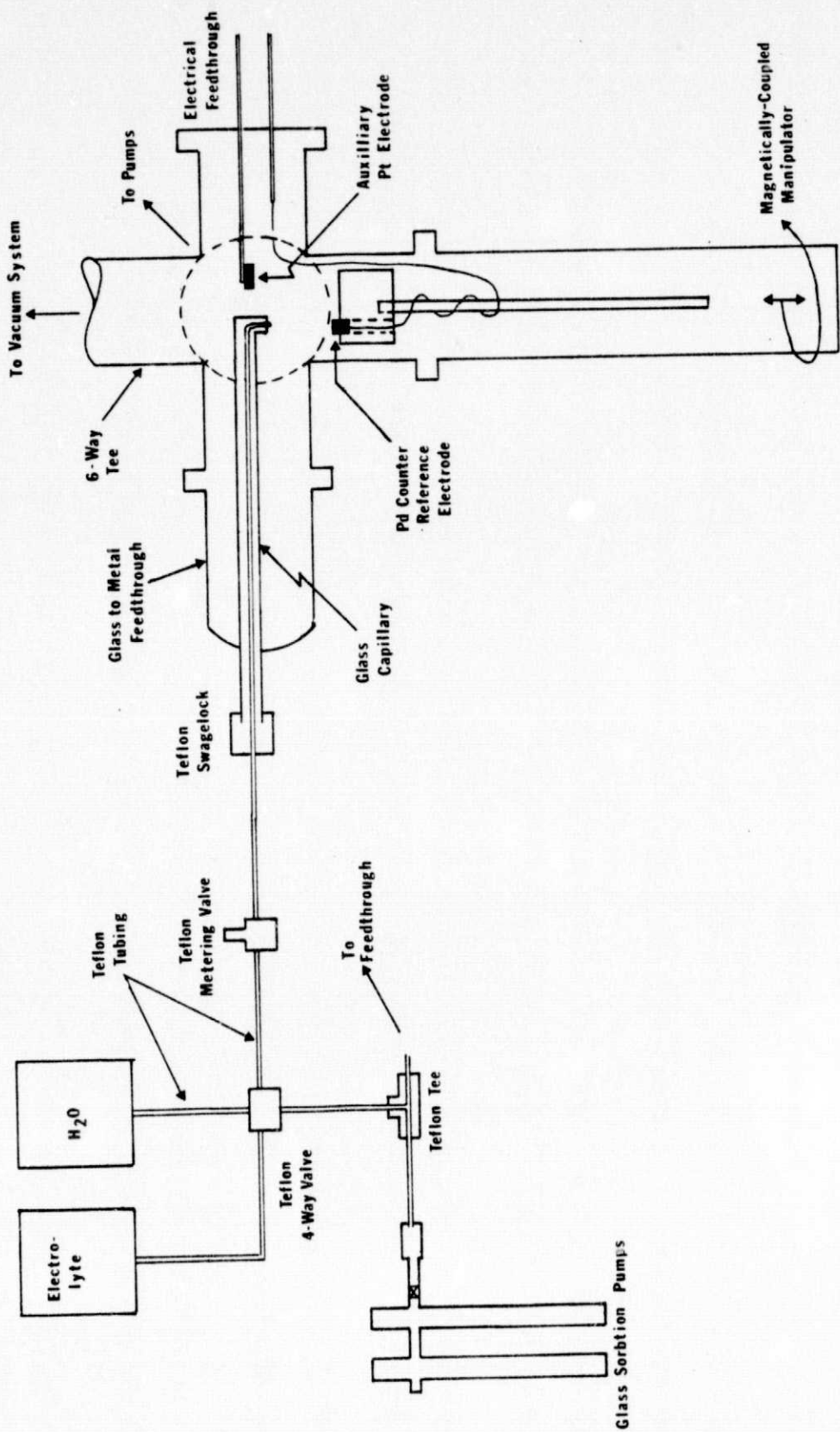


Fig. 1 Electrochemical Portion of the LEED-Auger - Thin-Layer
Cell System

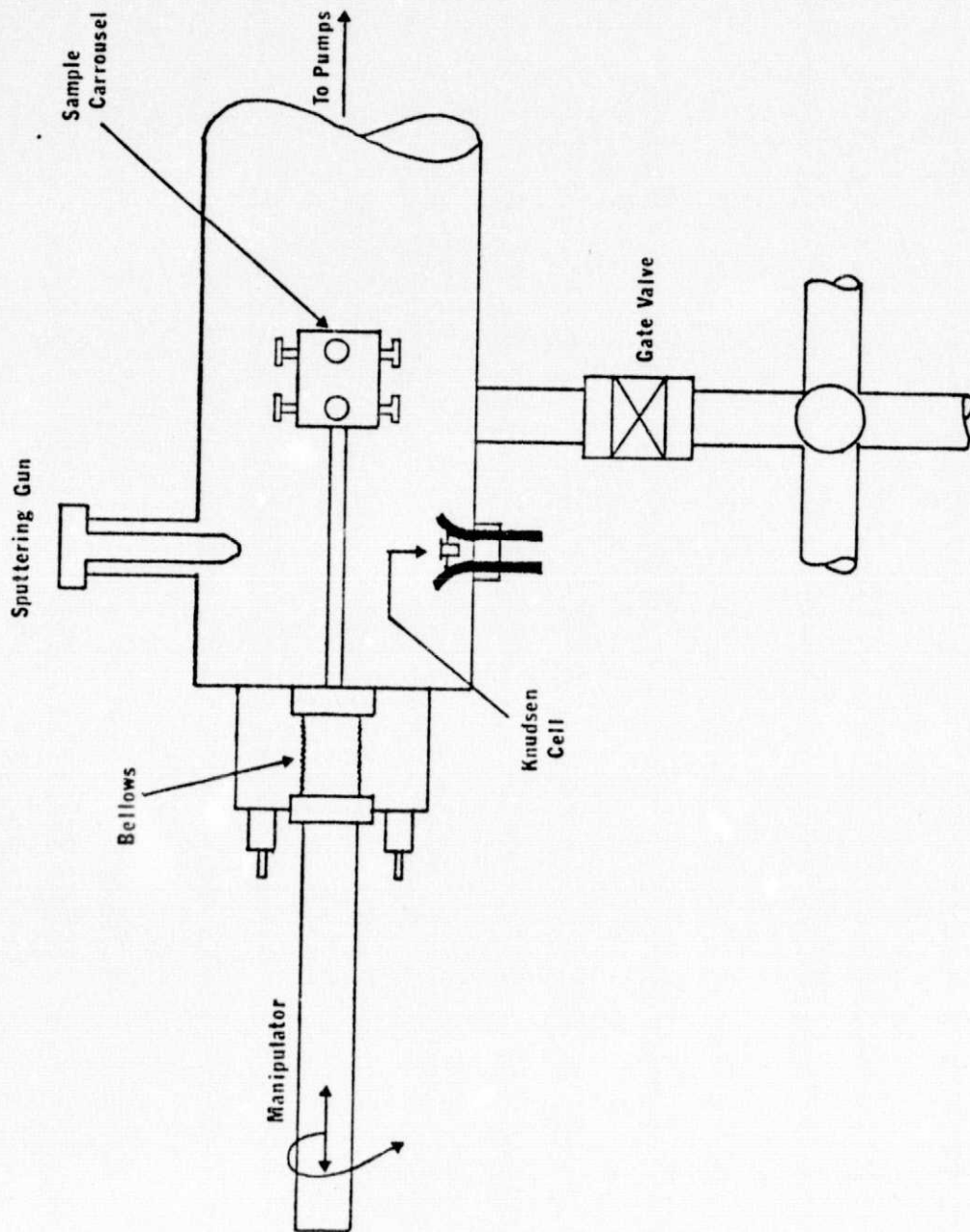


Fig. 2 Further Details of the Electrochemical Portion of the LEED-Auger Thin-Layer Cell System

and sub-monolayer quantities of foreign metals onto the working electrode surface.

Figure 3 is a detailed drawing of the new heater in the LEED-Auger half of the vacuum system. The samples can now be heated radiatively to temperatures in excess of 1300°C. The sample holder itself acts as a shield to prevent contamination from any tungsten which may evaporate from the filament. Large filaments (0.5 mm in diameter) are used which add an order-of-magnitude lifetime over the old heater.

The quality of the Auger spectra obtained has also been greatly improved by a relatively simple modification. Upon addition of the new heater it was discovered that the spectra lacked resolution. Some detective work revealed that the heater assembly placed the sample too close to the Auger optics and was no longer at the geometric center of the electron optics. This was alleviated by addition of a one-inch spacer between the optics and the LEED-Auger part of the vacuum chamber. A typical Auger spectra obtained after this adjustment is presented in Figure 4. It displays the normal derivative-type peaks expected from a retarding field type analyzer. This spectrum is also an improvement over those previously presented in these reports as the old heater assembly had the same effect but to a lesser degree than the new, larger heater.

Underpotential Deposition of Pb on Au Single Crystals

One of the more exciting developments in electrocatalysis is the use of mono- and submonolayers of foreign metals on noble metal substrates. Such layers can either be vapor deposited or electrodeposited. The latter is usually the preferable procedure. Mono- and submonolayers of metals such as Pb, Ag, Cu and Pt can be electrosorbed on gold at potentials quite anodic to the reversible potential of the bulk metal. Such under-

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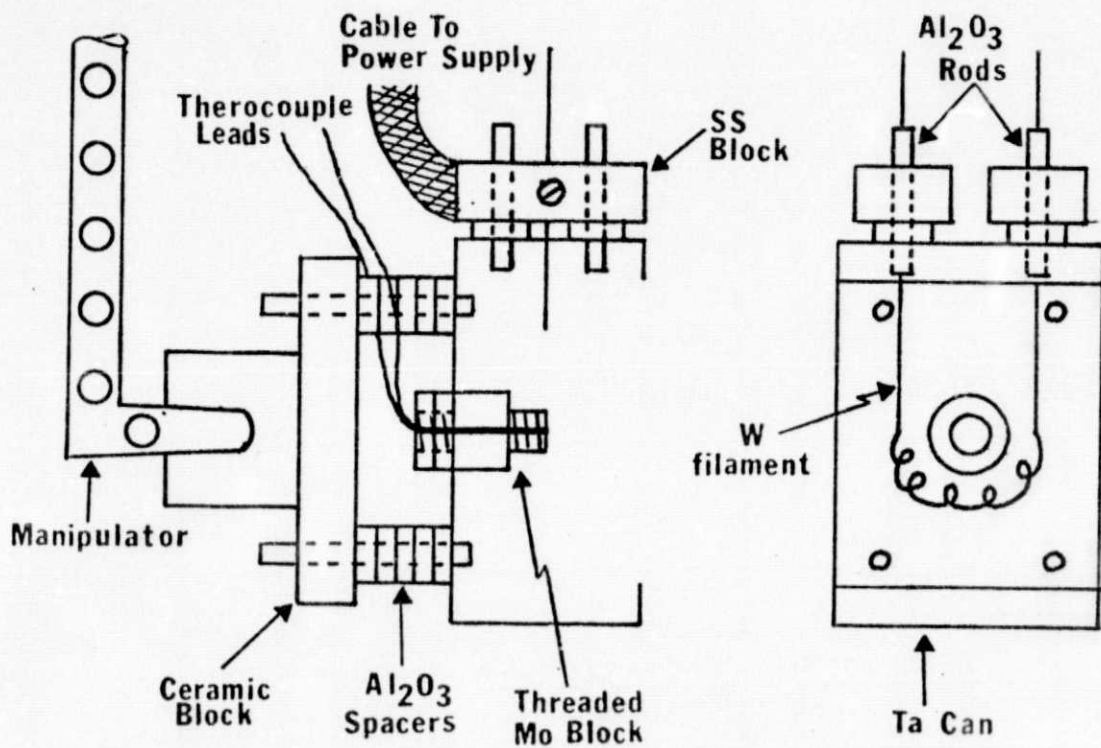
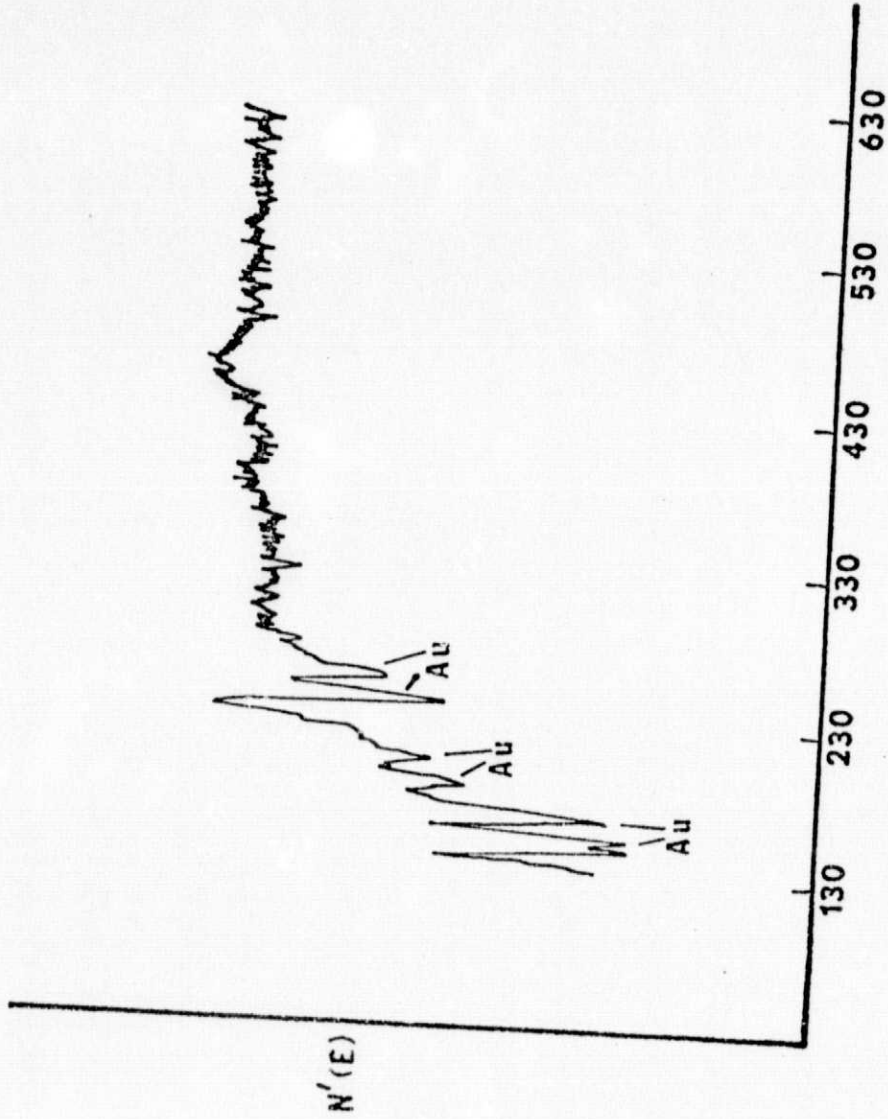


Fig. 3 Heater System for High Temperature Annealing of Single Crystals in the LEED-Auger Portion of the Vacuum System.



Energy (eV)

Fig. 4 Auger Spectrum of a Clean Au(111) Single Crystal. Beam Energy: 1800 eV. Beam Current: 13 μ A. Modulation Voltage: 10 V p-p.

potential deposited (UPD) layers are therefore considerably more noble than the bulk metal. These layers offer particularly interesting possibilities for hydrogen electrocatalysis and, in a few instances, also oxygen electrocatalysis. The first system chosen for study with the LEED-Auger electrochemical system is the UPD of Pb onto Au single crystals. Some very interesting preliminary results of this study are reported below.

A typical Auger spectra for a clean Au surface is presented in Figure 4. The surface was cleaned by repeated cycles of Ar-ion sputtering followed by a high-temperature anneal for 30 minutes. Major contaminants found were carbon, oxygen and calcium. Five or six sputtering-annealing cycles were required to achieve this freedom from impurities and a well defined LEED pattern. LEED patterns for the clean Au(111) surface are shown in Figure 5. Figure 5a shows the typical (1x1) hexagonal diffraction pattern expected from the (111) plane of a face-centered cubic crystal. Some of the spots appear to split to a small extent. Figure 5b shows the same surface after far more extensive annealing (5 to 6 hours) at 650°C in the final cycle. Several of the spots are definitely split with each now being surrounded by several satellite spots. This reconstruction has been reported previously in the literature (2) and by private communication (3) and is attributed to a 5% contraction in the lattice parameter (2).

LEED patterns for the clean Au(100) and (110) surfaces are found in Figure 6. The (5x20) pattern for Au(100) and the (1x2) pattern for the Au(110) surface are those expected from clean, reconstructed surfaces (4).

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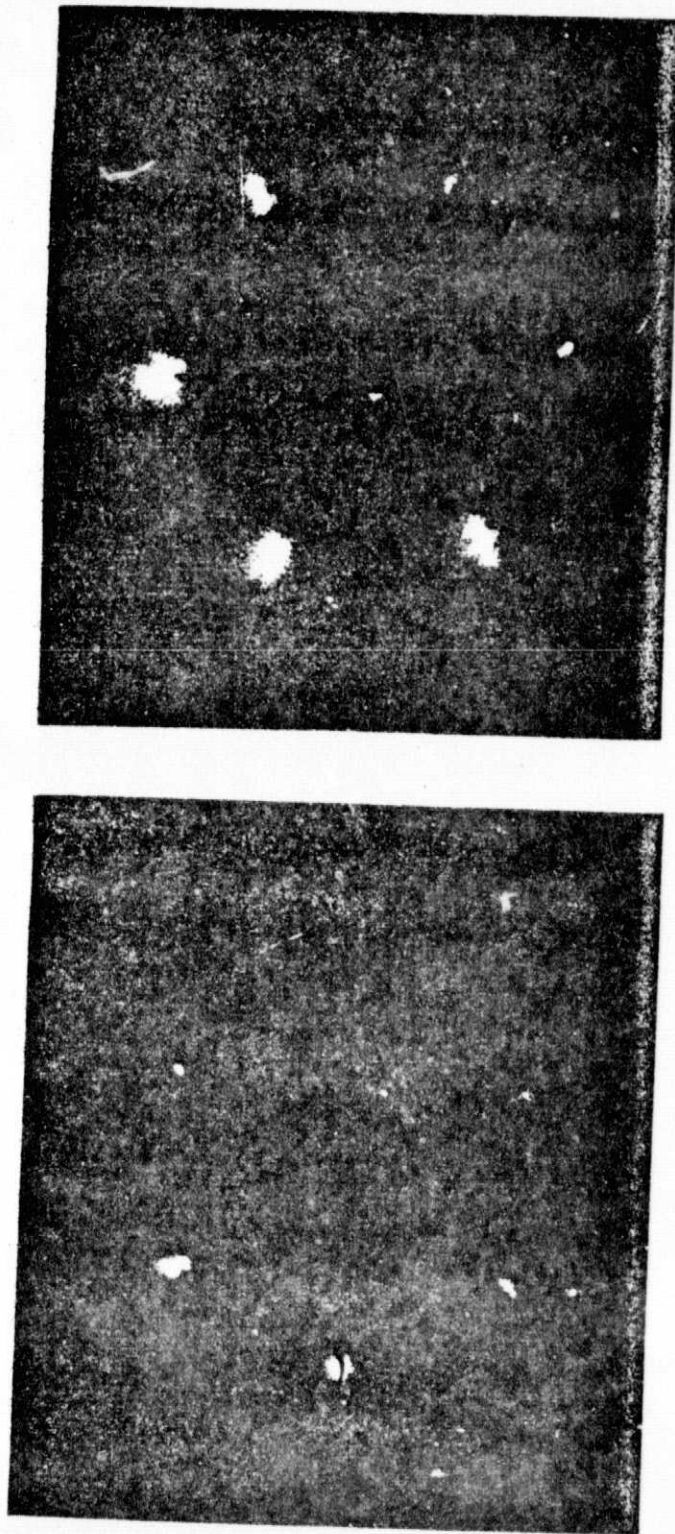


Fig. 5 LEED Patterns for the Clean Au(111) Single Crystal. Beam Energy: 45 eV.
a) 30 min. anneal after final sputtering, b) after several hours of annealing.

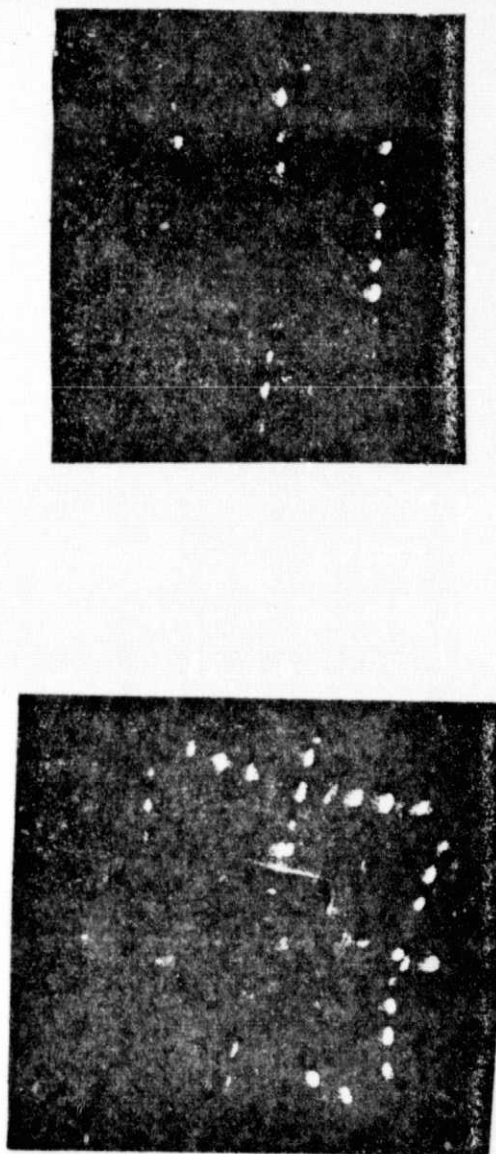


Fig. 6 a) Clean Au(100) - (5x20) and b) Au(110) - (1x2)
LEED Patterns. Beam Voltage: 50 eV. for (100)
and 80 eV. for (110).

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Transfer of the crystals to the thin-layer cell produced the Pb underpotential voltammetry curves shown in Figure 7. All curves are the first sweep utilizing Pb as the counter-reference electrode and 0.1M HF as the electrolyte. For the sweeps on Au(100) and Au(110), the electrolyte also contained 10^{-3} M $\text{Pb}(\text{NO}_3)_2$. In early phases of this work, lead was not initially added to the electrolyte but rather the experiment relied on lead dissolution from the counter Pb electrode to provide the Pb^{2+} in solution. This procedure was abandoned because of the lack of adequate control of the amount of Pb^{2+} introduced into solution and uncertainty as to the potential of the lead counter-reference electrode. The voltammetry curves for the Au(111) surface have not yet been rerun with Pb^{2+} added instead but such will be done in the near future. In the case of Au(111) the first three sweeps are shown. The anodic peak which rises in height with each sweep indicates removal of bulk Pb which is electrodeposited during the last portion of the cathodic sweep. In future work the cathodic sweeps will be terminated at less cathodic values to avoid bulk deposition for such deposition can lead to or accelerate alloy formation and gross restructuring of the surface (see for example Beckmann et al. (5)).

These curves are to be compared with those obtained in an ex-situ thin-layer cell for polycrystalline Au (see Figure 8). The curve for the polycrystalline surface resembles those for the (111) and (110) surfaces although there are some differences especially in peak potentials and current density maxima. On the other hand, the curve shown for the (100) surface is quite strikingly different than that for the polycrystalline sample. New structure has developed which has not been previously observed in ex-situ experiments. Before this structure is

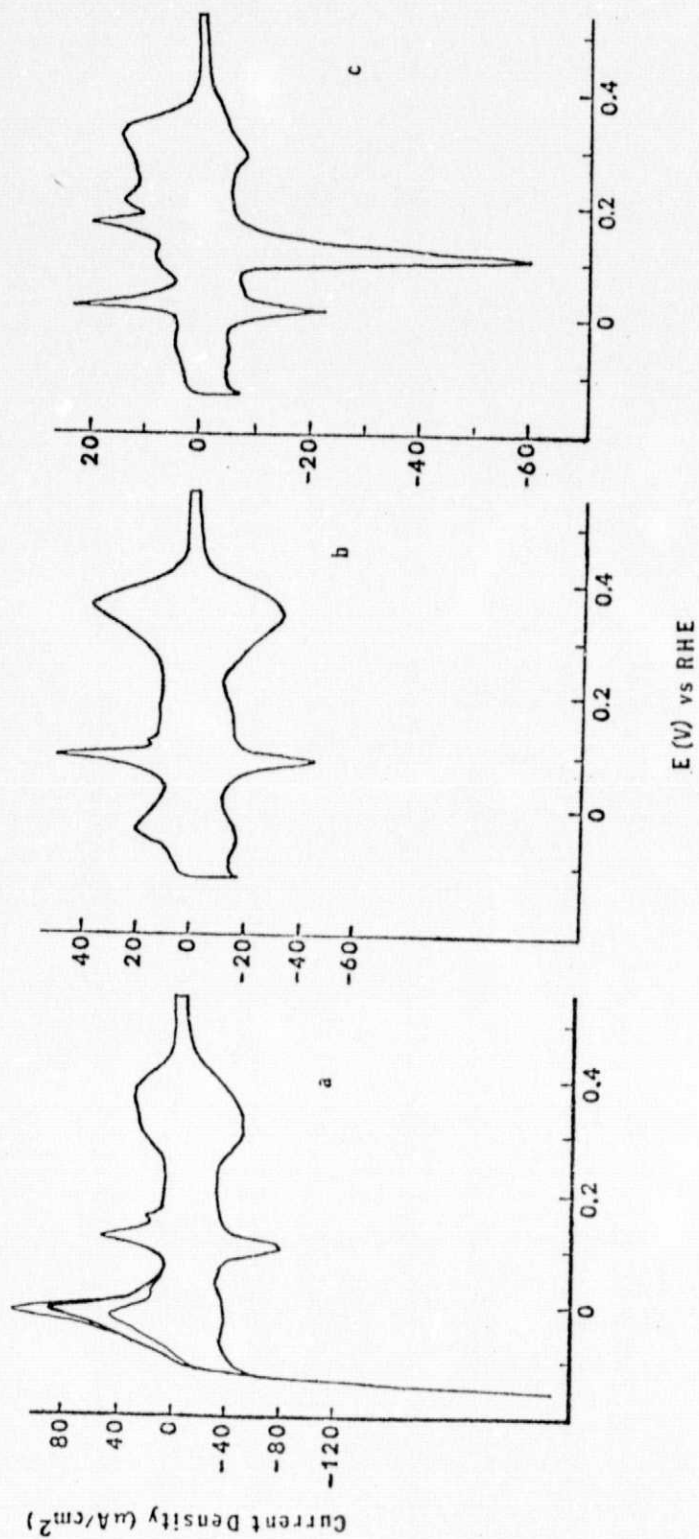


Fig. 7 Voltammetry Curves for the UPD of Pb on a) Au(111) - (1x2) and c) Au(110) - (1x2) only). Sweep Rate: 50 mV/sec.

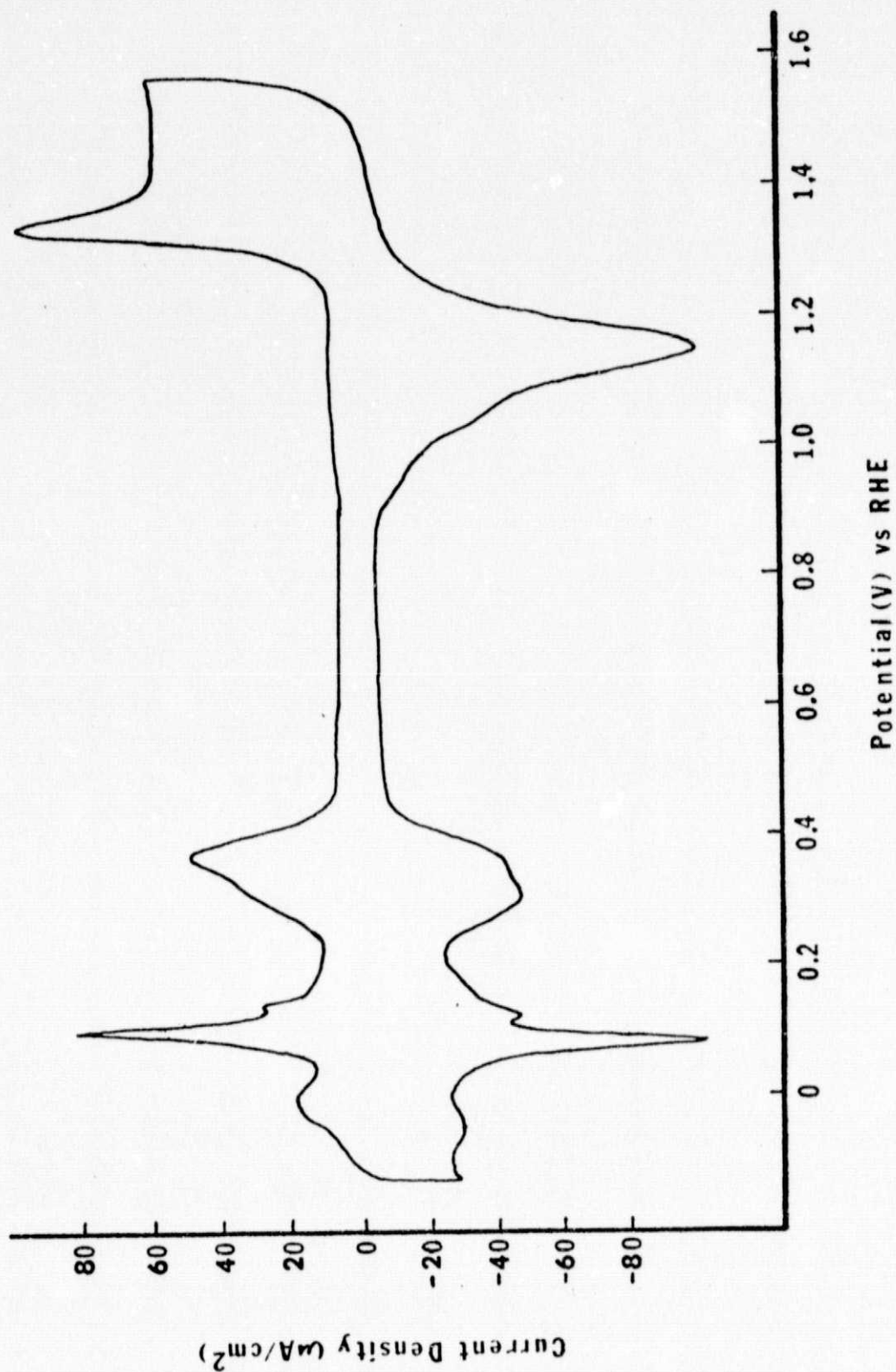


Fig. 8 VOLTAMMOGRAM FOR THE UPD OF Pb ON POLYCRYSTALLINE Au IN 0.1M HF OBTAINED BY THIN-LAYER TECHNIQUE IN AN EXTERNAL CELL.

discussed in any detail, several comments should be made on what processes are believed to cause the structure found in the voltammetry curve for polycrystalline Au.

In earlier work in this laboratory (6) the UPD of Pb onto Au has been explained in terms of two processes. The first is the adsorption of Pb accompanied by only partial discharge. This process appears to occur over a wide range of potentials, commencing with the first cathodic voltammetry peak at $\sim 0.3V$ vs. RHE. The second proposed process involves a phase transition attended by a change in the state of charge in the adsorbed layer since it is characterized by a quite sharp peak at approximately 50 mV vs. RHE in the curve and considerable charge transfer. Experimental evidence including optical studies supports the view that this proposed phase transition involves the formation of metal-like islands or patches of Pb of monolayer dimensions in which the valence bands of Pb merge with the band structure of the gold. Such a peak is characteristic not only of the Pb/Au system but also has been observed in the underpotential deposition of other metals on Au (7) and for Pb and Tl deposited on Ag (8).

The voltammetry curve for Pb on clean Au(100) contains the same general features discussed above for polycrystalline Au with the exception of the pronounced cathodic peak. The broad adsorption region commencing at 0.3V and the sharp spike at 10 mV are similar to those found on polycrystalline Au except that there is a 40 mV difference in the peak potential of the sharp spike. The most interesting feature of the sweep on Au(100) occurs at approximately 0.11V where a very

large spike, not previously reported in the literature, is observed. When the voltage scale is expanded, some sub-structure in this peak also becomes visible. The anodic counterpart of this peak is shifted anodic 70 mV and contains considerably less charge indicating that the process responsible for these peaks occurs quite irreversibly.

A tentative explanation involves a process by which further adsorption of Pb induces a surface structure change in the Au. There is no question that the structure of the Au(100) surface changes because of the following experimental work. After the voltammetry studies were completed, the electrodes were pulled apart at a potential just before bulk Pb deposition occurred and transferred back to the LEED-Auger chamber without any other treatment than evaporation of the electrolyte to dryness. The number of coulombs of charge of Pb obtained from integration of the voltammetry curves is $180\mu\text{c}/\text{cm}^2$. If the lead is essentially in the 0 valency state, this corresponds to ~ 0.5 Pb per surface Au atom assuming the surface to be Au(100). LEED showed that the surface structure had changed from that responsible for a (5x20) diffraction pattern to that for a (1x1) pattern.

The Auger signal for Au was reduced by $\sim 20\%$ by the lead layer and a strong lead signal was obtained. Unfortunately the sensitivity factors at mono- and submonolayer levels are not known for lead and, even if they were available for another Auger apparatus they would not necessarily apply to the present system. Auger results in the present study also indicated that fluorine, nitrogen (of nitrate) and oxygen were absent from the electrode surface. The lack of F and N is somewhat surprising since the $\text{Pb}(\text{NO}_3)_2$ was present at 10^{-3}M . If a layer of volatilized

PbF_2 or $\text{Pb}(\text{NO}_3)_2$ were remaining on the surface at the coverage commensurate with 10^{-3}M solution in a $\sim 10^{-3}$ cm electrolyte gap, it certainly would have been detectable. The most likely explanation is that during evaporation the electrolytic solution forms relatively few droplets on the surface rather than remaining as a continuous film. If the residual left from these droplets is widely spaced, then the electron beam may impinge on the surface between the residue from the droplets. This marks the first time that meaningful results were obtained with LEED after the electrochemical experiment due to the absence of both water and electrolyte absorption.

Further experimental work is in progress to examine the LEED patterns following the UPD of lead as a function of the crystal structure and potential. An effort will be made to see if the UPD layer after anodic stripping results in residual changes in the gold single crystal surface, similar to those reported by Beckmann et al. (5) for Cu UPD on Au. The probability is high that such is the situation. An effort will be made to establish whether surface alloy formation and gross restructuring occur under the same conditions.

In summary the voltammetry curves for Pb adsorption on clean Au(111) and (110) surfaces are similar to that found for Pb adsorption on polycrystalline Au in an external thin-layer cell. The curve for Au(100), however, contains remarkably different structure than that for polycrystalline Au. Part of this new structure has been tentatively assigned to a gold surface reconstruction.

Some kinetic studies have also been made on the UPD of Pb on polycrystalline Au in the outside thin-layer cell. Plots of peak potential

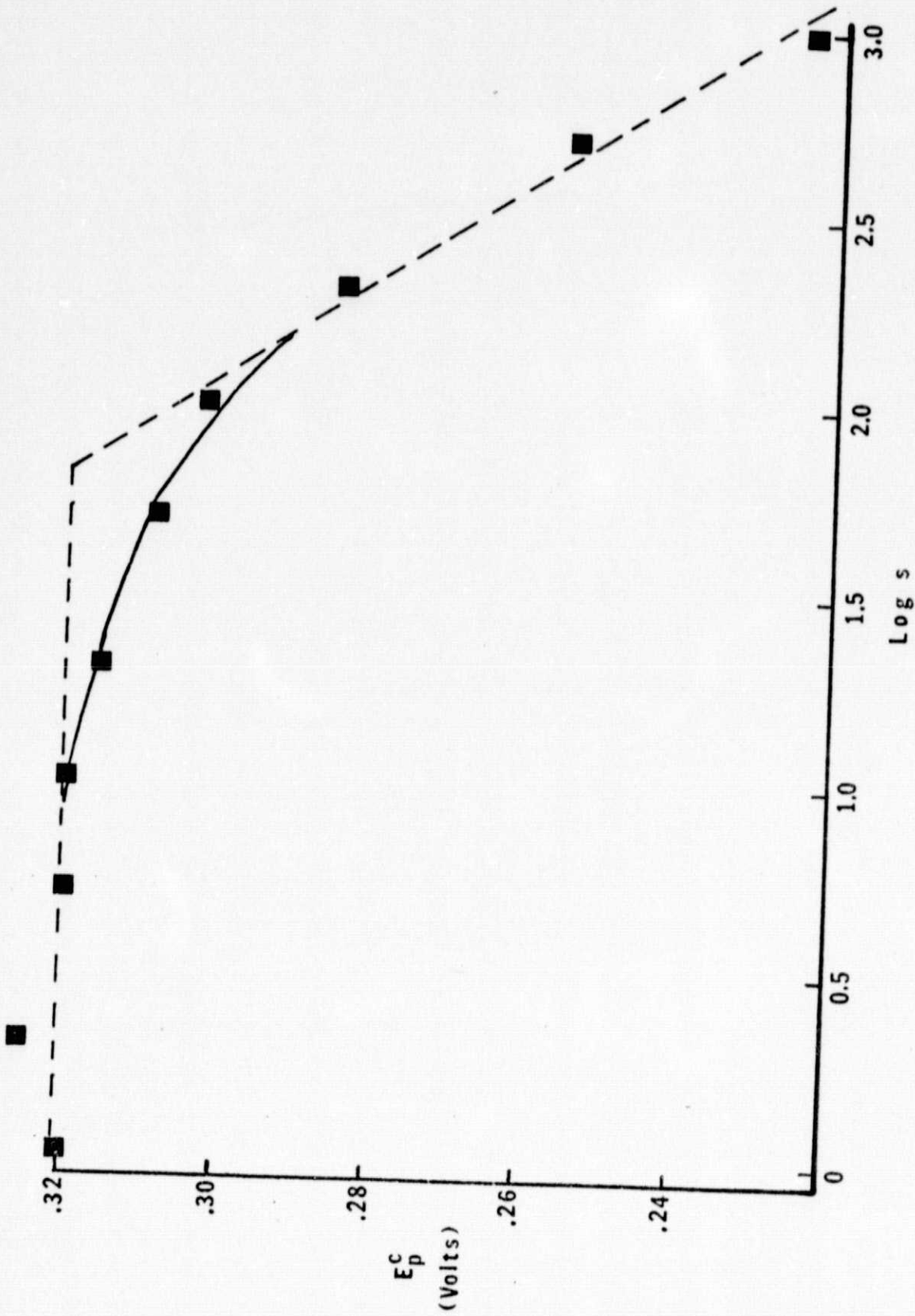


Fig. 9 Plot of Peak Potential vs. Logarithm of the Sweep Rate for the Cathodic Peak at 0.3V Shown in Figure 8. S in mV/sec.

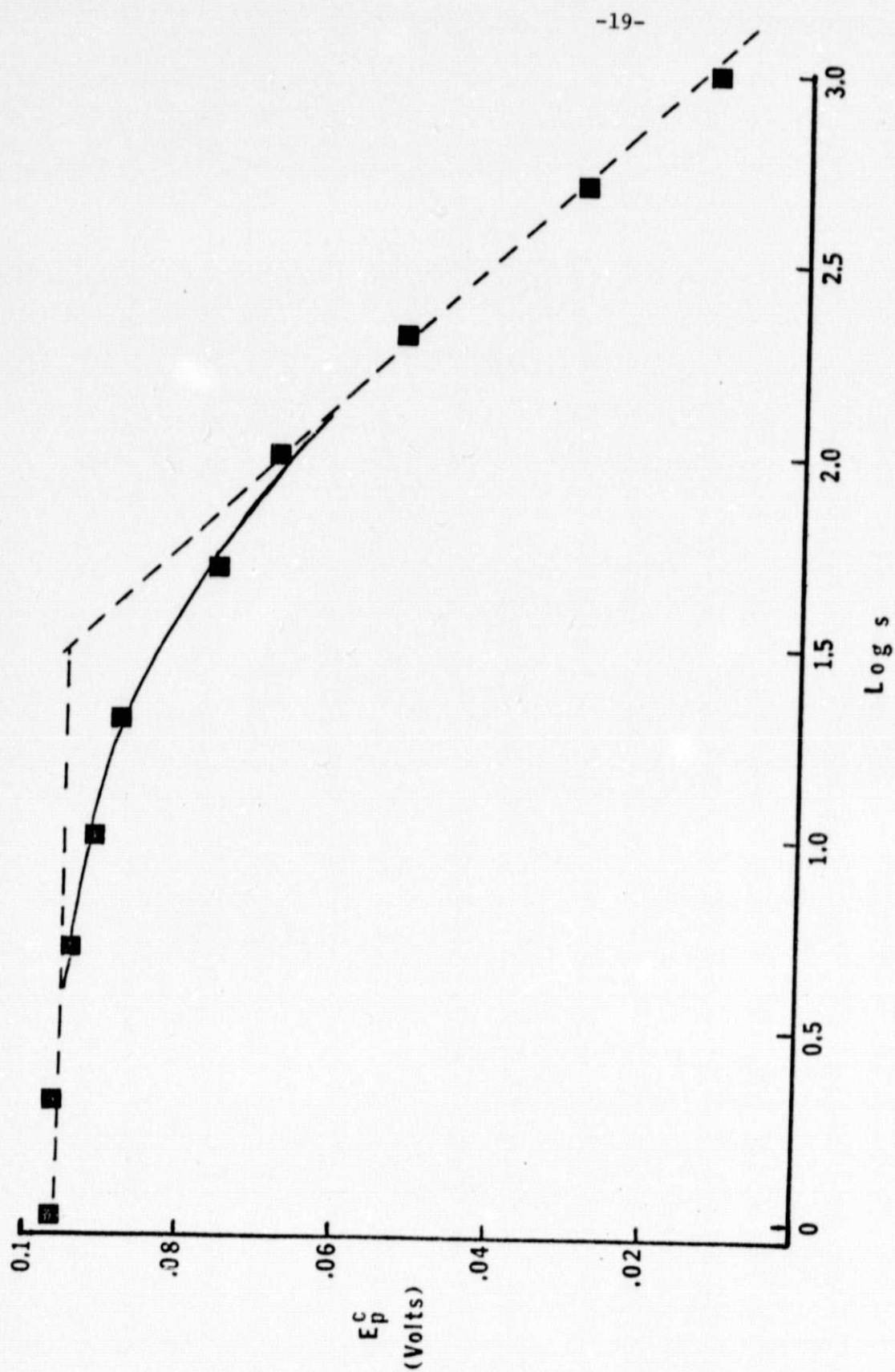


Fig. 10 Plot of Peak Potential vs. Logarithm of the Sweep Rate for the Sharp Cathodic Spike at 70mV Shown in Figure 8. S in mV/sec.

versus log of the sweep rate for the sharp spike and the first adsorption peak in the cathodic (deposition) sweep are shown in Figures 9 and 10. According to Gileadi and Srinivasan (9) the slope of the linear portion of this plot for a irreversible adsorption step should be the Tafel slope. Using these Tafel slopes and assuming β , the transfer coefficient, is equal to 0.5, the charge transferred per Pb ion that is adsorbed (n) is calculated to be 1.4 electrons for the first, large adsorption peak and $\sqrt{2}$ electrons for the sharp spike. The assumption that $\beta = 1/2$ is open to question and hence the values of the apparent charge transferred are provisional. Nonetheless, if the rate controlling step for the first adsorption peak is simply the ion adsorption step with the simultaneous removal of a single water molecule, then perhaps the value of 1.4 does have some significance in view of the earlier discussed mechanism proposed that this peak corresponds to partial charge transfer to form an adion of intermediate charge (6). The sharp peak, corresponding to the proposed phase change, probably has kinetics too complex for the apparent charge value to have direct significance. It is somewhat surprising that the apparent exchange currents for both peaks are relatively close in value (within a factor of $\sqrt{2}$ of each other). Further analysis of this data in terms of various mechanisms is planned.

C. Electrochemical Properties of Single Crystal Pt.

Hydrogen electrosorption measurements have been carried out earlier on the low index surfaces of Pt: 100, 110 and 111, but the electrode surfaces were not subsequently examined with LEED. Such measurements are planned for the next few coming months not only on the low index

surfaces but also on higher index surfaces such as have been reported by Somorjai to have unusual catalytic activity for various solid-gas interface reactions. The Pt (1x1)-6(1x1) step surface has been prepared for these studies.

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V. PROJECTED WORK

- a) Conclusion of work on UPD of Pb on Au.
- b) Study of hydrogen adsorption and oxide formation on various single crystals of Pt and Au using HF as the electrolyte.
- c) Examination of restructuring of Pt and Au, particularly in the anodic film formation potential region.
- d) Studies of O₂ electrogeneration on transition metal oxides of the spinel layer.

In regard to item d, various oxides of the spinel structure have been prepared by the electrochemical group at CWRU as part of the study of O₂ reduction catalysts. Some of the oxide systems should also be quite good catalysts for the O₂ electrogeneration reaction.

We plan to examine their electrocatalytic properties for O_2 generation as part of the present project. At this point two spinels Co_3O_4 and $NiCo_2O_4$ have been synthesized by two different methods: 1) the freeze-dry method and 2) thermal decomposition of thin layers of $Ni(NO_3)_2$ and $Co(NO_3)_2$ on titanium substrates. These salts are applied to the titanium surface by evaporating solutions of these salts to dimers. These oxides have been examined with both x-ray diffraction and ESCA to confirm their spinel structure. These materials are now being examined electrochemically by cyclic voltammetry. The preliminary electrochemical measurements already indicate that the surface valency states change with potential and that excursions too far cathodic can produce irreversible changes which modify the subsequent O_2 catalytic activity.

VI. PROJECT PERSONNEL

	<u>Percent of full time</u>
Patric Hagans, Graduate Student	(100)
Boris Cahan, Adjunct Associate Professor	(10)
Ernest Yeager, Professor of Chemistry, Project Director	(5)