THE EFFECTS OF ANIONS ON HYDROGEN ELECTROSORPTION ON PLATINUM SINGLE-CRYSTAL ELECTRODES *

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ABSTRACT

Hydrogen adsorption on the low index planes of single crystal Pt has been investigated using a technique which involves annealing in a H_2 flame and transfer through the air into the electrolyte. The results are compared with those obtained with a special vacuum transfer system. The effects of adsorbed anions such as NO_3^- and Cl^- are very pronounced. This paper discusses several of the factors controlling hydrogen adsorption on Pt and particularly anion effects.

INTRODUCTION

The purpose of this paper is to present the results for anion effects on platinum single-crystal surfaces prepared with a modification of the Clavilier method. These results will be compared with results on surfaces prepared in ultrahigh vacuum.

The electrochemical properties of solid metal electrodes are strongly dependent on the exposed crystal planes. Several groups have attempted to devise techniques which permit the study of single-crystal electrode surfaces under conditions of low surface contamination and high morphological integrity. In the case of Pt single crystals, these techniques involve either ultrahigh vacuum (UHV) preparation and characterization [1–4], or preparation ex vacuo, such as Clavilier's flame quenching technique [5].

The authors' group [4,6] has employed the UHV approach and developed a system for preparation and characterization of single-crystal electrode surfaces free of impurities using low-energy electron diffraction (LEED), Auger electron spec-

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troscopy (AES) and X-ray photoelectron spectroscopy (XPS). These surfaces are transferred into an electrochemical environment using techniques designed to minimize the possibility of restructuring and contamination of the surfaces during the transfer. Following electrochemical characterization, the electrode surface is then returned to the ultrahigh vacuum environment for re-examination with LEED, XPS and AES.

Recently, in many laboratories, platinum monocrystalline beads have been prepared essentially by the method developed by Clavilier and co-workers. This involves the heating of properly cut and polished Pt beads in an open flame followed by fast quenching in water or electrolyte. Clavillier's flame–quenching technique is also thought to provide high quality surfaces, although this method has not yet generally benefitted from the surface characterization spectroscopies of the UHV.

In spite of careful efforts by each group to maintain surface cleanliness and structure, controversy still persists on the electrochemical properties of Pt single crystals due to some lack of reproducibility of results from group to group. This paper reports a set of the experimental measurements which may resolve some of this long standing controversy and provide detailed evidence that the main sources of the differences were varying levels of NO_3^- and Cl^- impurities.

The flame technique involved in the present work is similar to the method used by Clavillier, but lends itself to the preparation of relatively large crystals. Clavillier's flame–quenching technique is not compatible with the preparation of large crystals because of the large stresses induced in a large crystal when it is cooled rapidly. The flame-annealed crystals in this work were cooled slowly in H_2 gas at room temperature. Since this method can be applied to large pre-grown crystals, kinetic and mechanistic studies can be performed on well-defined Pt single-crystal surfaces without the experimental difficulty intrinsic to UHV methods.

EXPERIMENTAL

Flame technique

Cylindrical Pt single crystals were purchased from Metal Crystals Ltd. (6.35 mm diameter × 6.35 mm long) and were guaranteed 5N pure. The orientation of each low index surface was found to be within 0.5° by Laue backscattering. A platinum wire (0.5 mm diameter × 100 mm long) was spot-welded to the back of each crystal. The surfaces of the single-crystal sample were then polished to a mirror finish using standard metallurgical techniques with the final polishing step involving 0.05 μm alumina. The polished single-crystal electrodes were etched in hot aqua regia for ca. 50 s to remove the damaged surface layer and possible contaminants. It has been found, however, that this final etching could be omitted with no effect on the subsequent electrochemical results. After rinsing the single crystal rigorously with water, the spot-welded platinum wire was inserted into an 8 cm length of 3 mm Al_2O_3 tubing, which in turn fit into a Teflon cap compatible with the working electrode receptacle of an electrochemical cell (see Fig. 1).
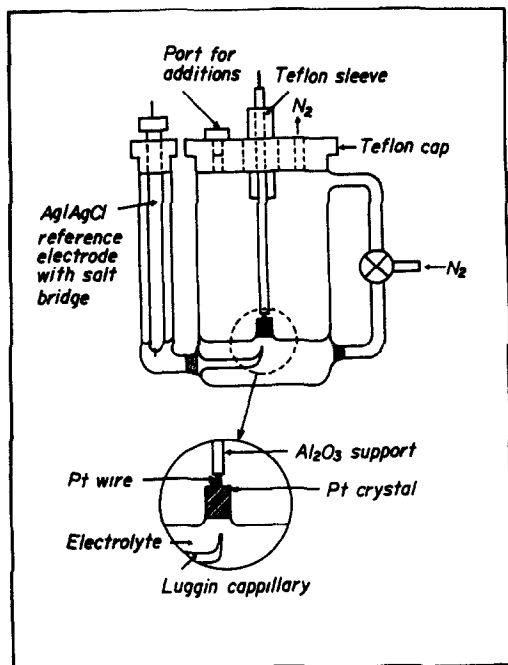
Fig. 1. Illustration of the electrochemical cell. For clarity, the counter Pt screen is not shown.

A typical experiment using a single-crystal electrode began with annealing for 12 min in a hydrogen + air flame. Annealing for a longer time or annealing in an open hydrogen + oxygen flame produced the same results. The temperature of the annealed crystals, $1000\,^{\circ}C \pm 50\,^{\circ}C$, was monitored with an optical pyrometer. Immediately after removal from the flame, the crystal was transferred in less than 5 s into a closed quartz tube purged with flowing hydrogen. After cooling for 80 s, the electrode was removed while still warm (ca. 70–90°) and a drop of ultra-pure water was placed on the crystal face with a pipet. The thin film of water protected the surface from air contamination and helped to prevent any organic impurities concentrated on the surface of the electrolyte from coming in direct contact with the crystal surface during immersion.

The crystal was placed face down into the electrochemical cell under potential control (0.25 V vs. Ag/AgCl) and a meniscus formed between the electrode and the electrolyte in the way shown in the insert of Fig. 1. All the voltammetric curves reported in the paper correspond essentially to the steady-state curves (e.g. after 10 sweeps). The first sweeps were made in the negative direction and showed anomalous behaviour in all cases.

The electrolyte solutions were prepared using concentrated HF, $HClO_4$, HNO_3 and HCl (all Baker Ultrex) and ultrapure water purified by one of two methods. In one set of measurement, water distilled after reverse osmosis was used. In the other,
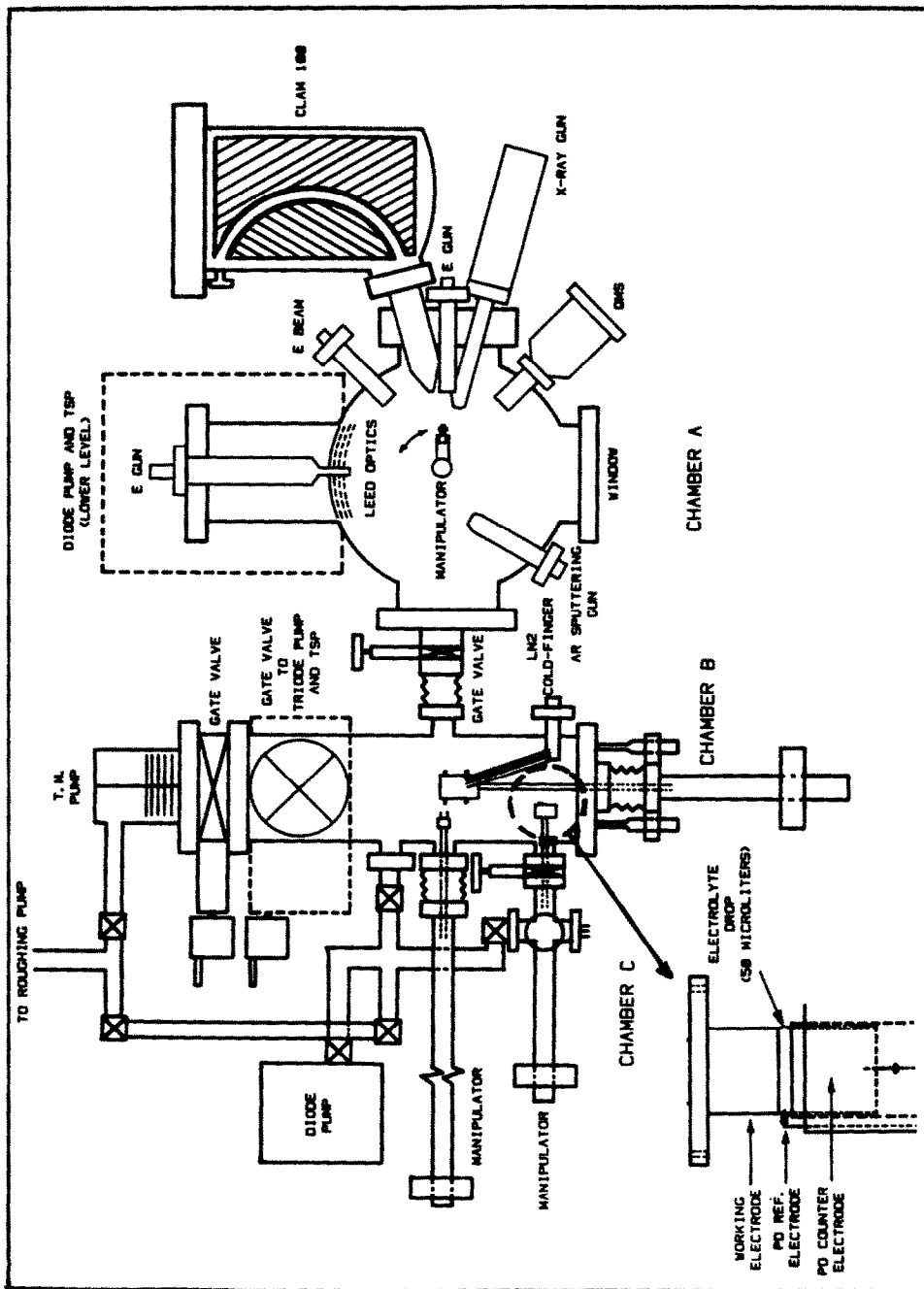
Fig. 2. Schematic diagram of the LEED–XPS–AES electrochemical system. Insert: illustration of the electrochemical cell inside the vacuum system.

this water was pyrolyzed prior to use. The electrochemical results with water purified by these two methods were the same. Hydrofluoric and perchloric acids were used as the electrolytes, since neither F^- or ClO_4^- are strongly adsorbed on platinum. Any shift in the potential at which hydrogen adsorption and desorption occur in these electrolytes is due, in part, to the difference in pH in 0.1 M solutions of these acids. Calculations place the pH at 2.3 for the 0.1 M HF and 1.0 for the 0.1 M solutions of the other electrolytes.

The glass cell used for the electrochemical measurements (Fig. 1) consisted of a main compartment and separate compartments for counter (Pt screen) and reference electrodes. The reference was an Ag/AgCl electrode submerged in 4 M KCl saturated with AgCl inside a jacket containing 1 M KNO_3. A bridge containing the same electrolyte as used in the cell was placed between the reference electrode and the cell, reducing any contamination of the electrolyte by NO_3^-. All electrode potentials for results obtained by the flame technique are referred to this Ag/AgCl reference electrode. The voltammetry measurements with the UHV–electrochemical system were made against an α-Pd/H reference electrode. The potentials have been converted to the Ag/AgCl reference, with the pH of the electrolyte solution taken into account.

All experiments were performed in nitrogen-saturated solutions. A stream of nitrogen flowing over the surface of the solution minimized oxygen contamination during measurements (see Fig. 1). The cell was cleaned with a mixture of 1 : 1 concentrated HNO_3 and H_2SO_4, followed by submergence in distilled water for 24 h and steam treatment for 3 h. Removal of all residual nitrate or sulfate was very important as will be shown in the results and discussion section.

UHV technique

The Pt single crystals used in the UHV experiments were purchased from the same source as the previously mentioned crystals and were of the same size. A detailed account of the crystal polishing procedure is given elsewhere [7]. The crystals were polished by Dr. Heppler of Lawrence Berkeley Laboratory, and determined to be oriented within 0.5° for the Pt (100) and Pt (111) surfaces and 1° for the Pt (110) surface as judged by Laue backscattering. The UHV system is shown in Fig. 2.

The initial cleanup of the crystals in the UHV required ca. 10 treatments with O_2 of 5 min each (3×10^{-8} Torr O_2, 600°C), until the surfaces were determined to be free of carbon by AES. They were then Ar-ion sputtered and annealed at 900°C. After the initial cleanup, the crystals did not require further O_2 treatments and subsequently were always cleaned by Ar-ion sputtering. LEED patterns of the clean, annealed surfaces were characteristic of well-ordered surfaces 100 (5 × 20), 110 (2 × 1) and 111. Within the sensitivity limits of AES and XPS (ca. 1% of a monolayer), there were no detectable surface impurities before transfer to the electrochemical chamber.

RESULTS AND DISCUSSION

The voltammetry curves for flame-annealed Pt single crystals in 0.1 M HF are shown in Fig. 3. The Pt (100) and (110) surfaces differ both in peak potentials and profile in the region corresponding to hydrogen adsorption–desorption. The positive sweeps of the voltammograms show two closely spaced peaks on both surfaces, at -0.02 V for Pt (100) and -0.05 V for Pt (110). The smaller of these anodic peaks on each of these surfaces and the asymmetry between positive and negative sweeps were believed to be caused by chloride contamination levels of at least 5×10^{-7} M, as will be discussed later. The negative and positive sweeps for Pt (111) are remarkably symmetrical. It is interesting to note that the voltammetry curves obtained for Pt (111) in 0.1 M HF do not seem to be affected to any significant extent by addition of Cl^- up to a concentration of 1×10^{-4} M.

In the double-layer region, the cyclic voltammograms obtained for Pt (100) and Pt (111) show anomalous peaks in the positive or negative sweep (see arrow in Fig. 3) which are probably the result of impurities.

The voltammetry curve for Pt (111) is very different from that of the other two low-index surfaces. According to some authors [8], the "butterfly" peaks at ca. -0.5 V are caused by the adsorption–desorption of a strongly bound form of hydrogen, corresponding to 1/3 of a monolayer. Wagner and Ross [2], however, suggest that the butterfly peaks correspond to the formation of surface OH species.

In prior publications [2] including some from this laboratory [4] the voltammetry curves of UHV-prepared Pt single crystals in aqueous HF differ significantly from those shown in Fig. 3. The results in Fig. 3, however, are very similar to those obtained in recent measurements (see Fig. 4) carried out on Pt single crystals prepared in the UHV and examined with the UHV electrochemical system de-
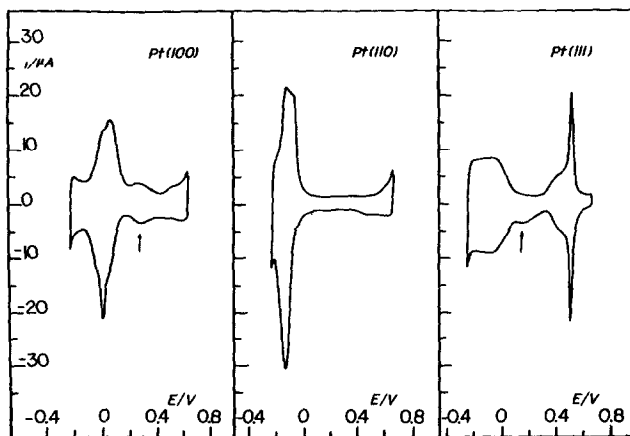

Fig. 3. Cyclic voltammetry for flame-annealed Pt single crystals in 0.1 M HF. Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.
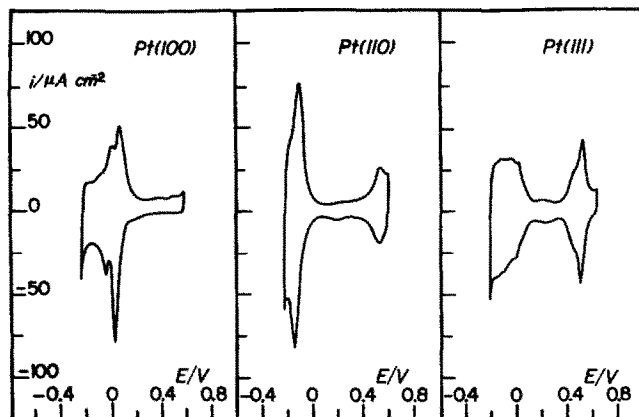
Fig. 4. Cyclic voltammetry for UHV-prepared Pt single crystals in 0.1 M HF. Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.

scribed earlier. The most noticeable difference is the absence of an additional small cathodic peak in the hydrogen electrosorption region on Pt (100) prepared by the flame technique. Further, the voltammogram of the UHV-prepared Pt (111) surface shows an excess of negative charge in the hydrogen adsorption region and the butterfly peak is smaller in magnitude. The differences in these voltammetry curves for flame- and UHV-prepared surfaces is believed to be due primarily to differences in the impurity levels. Specifically, the levels of NO$_3^-$ were believed to be higher and those of Cl$^-$ smaller in the measurements with the UHV-prepared surfaces.

In spite of using the same UHV apparatus and a similar procedure for the preparation and characterization of Pt single crystals, the new UHV results (shown in Fig. 4) exhibit a marked difference from the earlier results [4] for all three surfaces. The most outstanding difference is that the cathodic spike in the positive sweep in Fig. 5 is absent in the corresponding curves in Figs. 3 and 4. A possibility pointed out by other workers [8] is that this spike may be due to an electrolyte impurity such as nitrate. In fact, it has been shown in a number of electrochemical systems, including Ag single crystals [9], Au [10] and Pt (100) [11,12], that relatively low concentrations of nitrate can produce anomalous features such as a cathodic spike in the positive sweep attributable to nitrate reduction.

This evidence prompted the examination of the voltammetry of flame-treated Pt (100) in solutions containing nitrate. The effects of various concentrations of HNO$_3$ in HF on the cyclic voltammetry curves of Pt (100) are shown in Fig. 6. Beginning with a concentration greater than 10^{-6} M, the anomalous cathodic spike appears after partial hydrogen desorption during the positive sweep, if the lower limit of the negative sweep is more negative than 0.3 V. Increasing the NO$_3^-$ concentration has a substantial effect on the position and relative sharpness of the cathodic spike (see Fig. 6). These results indicate clearly that the NO$_3^-$ concentration also influences the shape and position of the irreversible anodic peak at 0.45 V and the cathodic peak
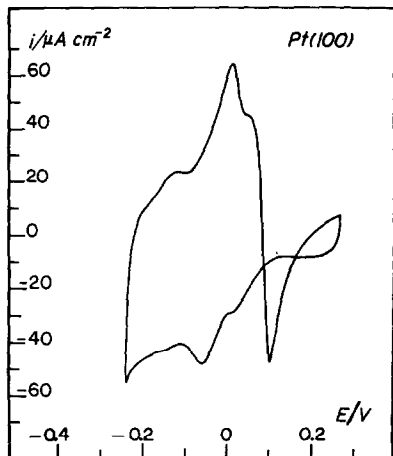
Fig. 5. Cyclic voltammogram for UHV-prepared Pt (100) single crystals in 0.1 M HF [4].

at 0.15 V. The cyclic voltammograms show that the size of these peaks correlates with the charge of the anomalous cathodic spike, indicating some N-containing species as the origin of all three features. We do not have direct experimental evidence supporting the exact nature of the specific reactants and products involved in these three anomalous peaks. Mechanistic studies are continuing and will be reported in a future publication.

In the earlier work with the UHV technique in our group, the Teflon electrolyte delivery system and the Pd counter electrode were cleaned with nitric acid. In more
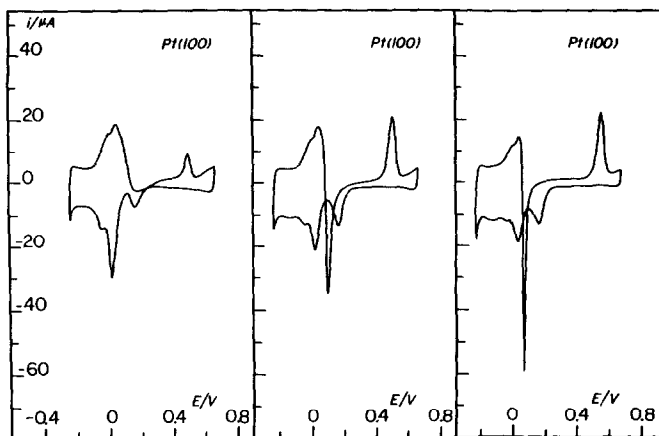

Fig. 6. Cyclic voltammetry for flame-annealed Pt (100) crystals in 0.1 M HF and 5×10^{-6} M (left): 1×10^{-4} M (center) and 1×10^{-2} M HNO_3 (right); electrode area: 0.283 cm^2.

recent work, the contamination from residual HNO_3 has been far less. It is our contention that in future work, cleaning procedures involving nitric acid should be avoided.

The effect of the surface orientation of flame-annealed Pt single crystals on H adsorption–desorption behavior in 0.1 M $HCLO_4$ is shown in Figs. 7–9. Except for the Pt (100) surface, the curves for the HF and $HClO_4$ solutions resemble each other. In contrast to the relatively symmetrical voltammetric curves for hydrogen adsorption–desorption on Pt (100) in $HClO_4$, those in HF exhibit asymmetry. Since ClO_4^- and F^- are not thought to adsorb significantly on any of the three surfaces, differences existing in the voltammetry curves for Pt (100) in these two solutions are probably due to residual impurities in the HF.

The shape and height of the peaks in the hydrogen region on Pt (100) suggest that the 0.1 M HF was contaminated with a species capable of adsorbing strongly on this surface. According to the manufacturer's specifications, the 0.1 M HF solution contained 10^{-7} M Cl^-. Since Cl^- is known to adsorb strongly on Pt [13], it is
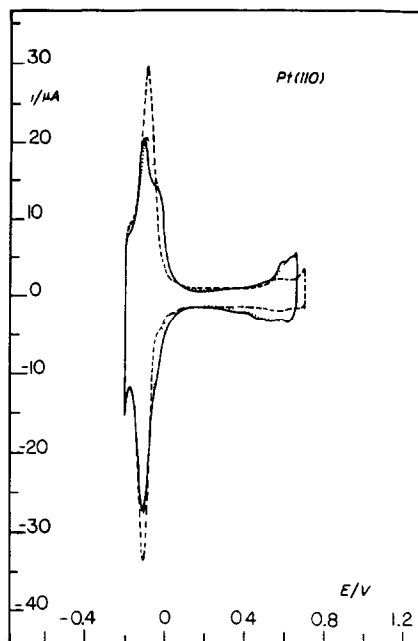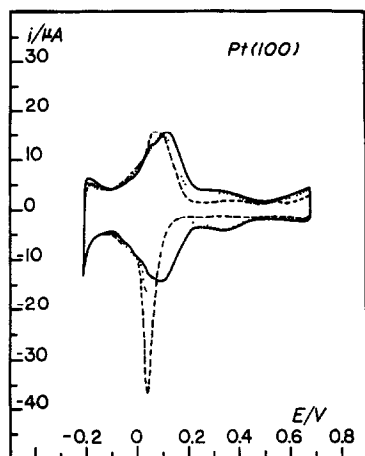

Fig. 7. Cyclic voltammetry for flame-annealed Pt (100) in 0.1 M $HClO_4$ (———); 0.1 M $HClO_4 + 5 \times 10^{-7}$ M HClO ($\cdots\cdots$) and 0.1 M $HClO_4 + 5 \times 10^{-6}$ M HCl (— — —). Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.

Fig. 8. Cyclic voltammetry for flame annealed Pt (110) in 0.1 M $HClO_4$ (———); 0.1 M $HClO_4 + 1 \times 10^{-5}$ M HCl ($\cdots\cdots$) and 0.1 M $HClO_4 + 1 \times 10^{-4}$ M HCl (— — —) Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.
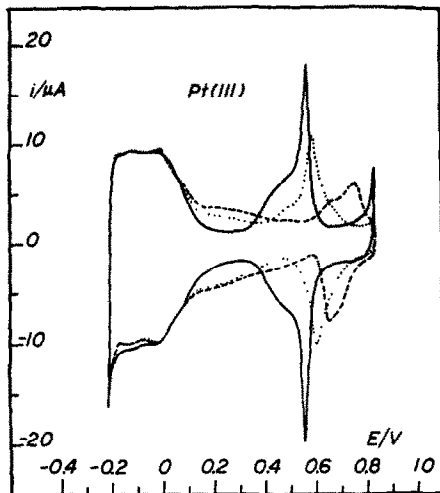
Fig. 9. Cyclic voltammetry for flame-annealed Pt (111) in 0.1 M HClO$_4$ (———); 0.1 M HClO$_4$ + 1 × 10^{-5} M HCl (·····) and 0.1 M HClO$_4$ + 1 × 10^{-4} M HCl (— — —). Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.

possible that even this relatively small amount of Cl$^-$ impurity might account for the unusual voltammetry of Pt (100) in dilute HF.

These deductions are supported by experiments on flame-annealed Pt (100) in dilute HClO$_4$ with a small amount of HCl added intentionally to the solution (see Fig. 7). The addition of HCl has a substantial effect on the peak positions and their relative heights during the H adsorption and desorption processes. In the presence of ca. 5×10^{-6} M Cl$^-$, the symmetrical voltammetric curve for Pt (100) 0.1 M HClO$_4$ is changed to an asymmetrical curve. The structure of the hydrogen adsorption–desorption region as well as the double-layer region becomes almost identical to the voltammogram for Pt (100) in "clean" HF (see Fig. 3). The sharp peak in the hydrogen region observed in the negative sweep is probably caused by the simultaneous rapid desorption of Cl$^-$ and the adsorption of H. After desorption, Cl$^-$ diffuses away from the surface, then re-adsorbs slowly under diffusion control simultaneously with H desorption during the positive sweep. This will cause asymmetry between the positive and negative sweeps in the H adsorption–desorption region.

Figure 8 shows the voltammetric curves obtained from a Pt (110) surface in 0.1 M HClO$_4$ by itself, as well as with successively higher amounts of HCl. The cyclic voltammetric curves for a Pt (110) surface in 0.1 M HClO$_4$ show one principal hydrogen adsorption peak; a shoulder at -0.05 V appears during the positive sweep. The different shape of the anodic and cathodic portions of the hydrogen adsorption–desorption and a small charge inbalance are probably due to the Cl$^-$ adsorption–desorption behavior alluded to above. The addition of HCl has a
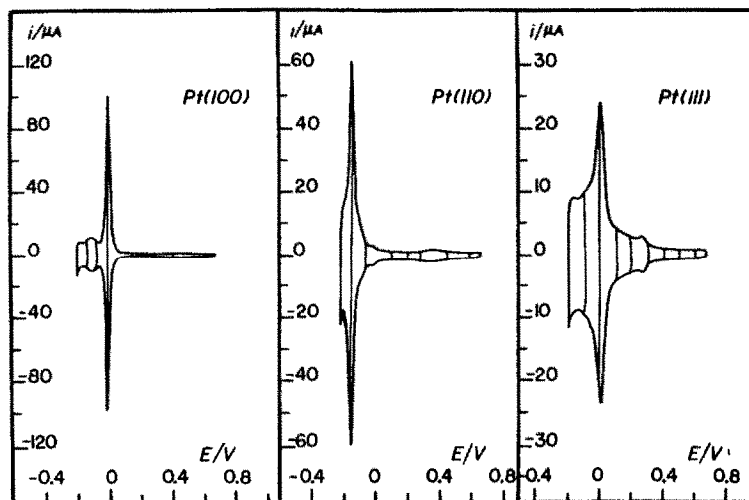
Fig. 10. Cyclic voltammetry for flame-annealed Pt single crystals in 0.1 M HCl. Sweep rate: 50 mV s^{-1}; electrode area: 0.283 cm^2.

significant effect only for HCl concentrations higher than 1×10^{-5} M. Hydrogen adsorption is shifted in the negative direction in the presence of 1×10^{-4} M Cl$^-$.

Figure 9 shows the voltammetric curves for Pt (111) in 0.1 M HClO$_4$ with and without varying amounts of Cl$^-$. Traces of Cl$^-$ change the voltammetric curves dramatically in the potential region between 0.4 and 0.8 V. The sharp reversible peak at $+0.5$ V is shifted positively and with increasing Cl$^-$ concentration becomes more irreversible and smaller in size. In the double-layer region, Cl$^-$ adsorption and desorption is observed.

In contrast to Pt (100) and Pt (110), traces of Cl$^-$ have much less effect on the hydrogen adsorption in the voltage range -0.2 to $+0.1$ V on the Pt (111) surface. Even in the presence of a small concentration of Cl$^-$, the pzc for Pt (111) is probably still quite positive to the hydrogen adsorption region, and thus specific adsorption of Cl$^-$ should be small in this region.

Increasing the Cl$^-$ concentration beyond 10^{-3} M makes the cyclic voltammograms for all three surfaces exceptionally symmetrical. Figure 10 shows the voltammetric curves for the surfaces in 0.1 M HCl. In the presence of high Cl$^-$ concentrations, the hydrogen adsorption–desorption peaks become very sharp, indicating a coupling between the H and Cl$^-$ adsorption–desorption processes. More details about the effect of specific adsorption of Cl$^-$ will be reported in a future publication.

In conclusion, large Pt single crystals prepared by H$_2$ + O$_2$ or H$_2$ + air flame annealing followed by cooling in H$_2$ gas yield similar hydrogen absorption–desorption behavior to that of crystals prepared in the UHV. Examination of flame-annealed crystals in the UHV with LEED, AES, and XPS will be performed to verify

the quality of these surfaces. If they prove to be of good quality, this new ex vacuo preparation method should provide a faster and easier technique for the preparation of large, clean, well characterized Pt single crystals. This would be potentially useful for kinetic and mechanistic studies which would involve difficult experimental procedures using UHV methods.

Results on the flame-treated electrodes show that H adsorption–desorption behavior in dilute acids is strongly affected by the crystallographic orientation of the Pt single crystals. Very small concentrations of anions can induce profound changes in the H electrosorption isotherm.

ACKNOWLEDGEMENT

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