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Surface Characterization of Pt Electrodes Using Underpotential Deposition of H and Cu

V. Characterization of BD Pt Catalyst Surface

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The cyclic voltammetric characterization of commercial platinum catalysts is discussed with regard to experimental variables such as nature and concentration of electrolyte and choice of sweep rate. Information available from electrochemical experiments such as surface area and distribution of hydrogen adsorption sites is obtained for BD Pt, a commercial platinum catalyst. The distribution of hydrogen adsorption sites at BD Pt is shown to be similar to that at smooth polycrystalline Pt. Also, underpotential deposition of copper is shown to be useful for surface area measurements under the proper conditions. A maximum copper coverage of 417 μC per real cm^2 is obtained at BD Pt.

INTRODUCTION

The importance of the characterization of electrocatalyst surfaces cannot be overestimated. Some important techniques for measurement of surface area include physical adsorption of inert gas (also used to determine porosity) and chemisorption of species such as H or CO, both electrochemically and from the gas phase. Crystallite size distributions can be obtained from X-ray analysis and/or electron microscopy. The application of these techniques to the characterization of electrocatalysts has recently been reviewed by Kinoshita and Stonehart (*1*).

Many studies have established the utility of cyclic voltammetry for surface area measurements of platinum catalysts (*2–9*). Usually the charge passed due to hydrogen adsorption or desorption is used to obtain real surface area, but oxidation of adsorbed CO has also been shown to be useful (*7*). In addition, foreign metals deposited at potentials positive to the reversible potential (*10*) have been suggested (*1*) for surface area measurement. One aim of the present paper is to explore the conditions under which copper deposited at underpotentials gives accurate surface area measurement of a high-area Pt catalyst.

Several authors have explored the dependence of electrocatalytic reactions on catalyst morphology (*11–28*). In the case of demanding reactions (*29*) the design of better electrocatalysts will be facilitated by knowledge of whether the structural dependence is due to interaction with support material, impurities present on the catalyst surface, or a dependence on the distribution of adsorption sites of different geometry, which varies with crystallographic orientation. In general, if breaking a surface–adsorbate bond is rate-determining, as, for example, in methanol (*30–33, 36*b) or formic acid (*34–37*) oxidation, a dependence on site geometry is expected. To study this dependence, single crystals at which the geometry of adsorption sites is well defined are used (*30, 33, 36–39*). If in these studies one type of site is determined to be more active for a given reaction, the next step is to try to

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build a practical catalyst enriched in that particular site. Thus it will be important to be able to characterize the distribution of sites on a wide variety of supported and nonsupported materials. Understanding of the dependence of the hydrogen adsorption reaction at platinum on site geometry (*40–49*) has advanced to the point where this reaction can yield a useful characterization of adsorption sites at Pt catalysts.

This paper focuses on the information available from cyclic voltammetry at Pt catalysts in aqueous acid, i.e., surface area and distribution of adsorption sites. Experimental considerations such as choice of electrolyte and sweep rate are critically evaluated. Characterization of a commercial catalyst, BD Pt, provides the framework for the discussions.

"BD" is a trade name for a series of catalysts manufactured by Alloy Surfaces Company, Wilmington, Delaware, from which the BD Pt gauze used in this study was obtained. The BD catalysts are prepared using a proprietary process, which is briefly described elsewhere (*50*).

BD Pt was chosen for this study for two reasons. It is a high-surface area commercial catalyst and therefore provides a useful challenge for the electrochemical characterization technique described in this paper. Also, the unique method of preparation might have been expected to result in a distribution of hydrogen adsorption sites different than that observed at smooth polycrystalline Pt. The results described below clearly show that this is not the case.

METHODS

An electrode was fabricated from a small piece of BD Pt screen by spot welding to a polycrystalline wire which was sealed in soft glass. The BD Pt electrode was pretreated by potential cycling at 10 mv/s for at least 0.5 hr between hydrogen evolution and oxygen evolution potentials (for example, −0.2 to +1.2 V vs saturated calomel electrode (SCE) in 0.5 *M* H_2SO_4). This pretreatment results in a clean surface, as evidenced by the lack of spurious peaks in the double-layer region (+0.1 to +0.55 V) and in the potential region (+0.9 to +1.2 V), where hydrocarbon surface contaminants undergo oxidative desorption (*51*) (see Fig. 1).

The smooth polycrystalline electrode (geometric area = 0.14 cm^2) was polished to 1 μm using standard metallurgical techniques and cleaned by potential cycling.

The preparation of Pt single-crystal electrodes has already been described (*47*). The single-crystal electrodes were annealed 0.5 hr in a gas–air flame, quenched in 0.1 *M* $HClO_4$ + 0.005 *M* H_2SO_4 and subjected to 15 cyclic potential scans between −0.225 and +1.05 V at 50 mv/s.

Electrolytes were prepared from concentrated sulfuric acid (A. C. S. Mallinckrodt), perchloric acid (70%, double distilled from Vycor, G. Frederick Smith), or copper sulfate (anhydrous, Allied Chemical) and distilled deionized water. The cell was constructed from glass and provided a separate compartment for the reference electrode. The potential of the working electrode was sensed using a Luggin capillary, and the auxiliary electrode was Pt wire coiled about the base of the Luggin. The sweep generator and three-electrode potentiostat were of conventional design and were constructed in-house.

All experiments were performed in unstirred nitrogen-saturated solution.

RESULTS

Hydrogen Adsorption Experiments

The cyclic voltammogram of the BD Pt catalyst electrode obtained in 0.5 *M* H_2SO_4 at a sweep rate of 5 mv/s is shown in Fig. 1. The charge passed due to hydrogen deposition (Q_H) is 0.0049 C. This value is obtained by linear extrapolation of the double-layer region and integration to the current minimum just before molecular hydrogen evolution, as shown in Fig. 1. This procedure may underestimate Q_H. Woods (*9*) has shown that integrating to the current minimum yields only 77% of the true hydrogen

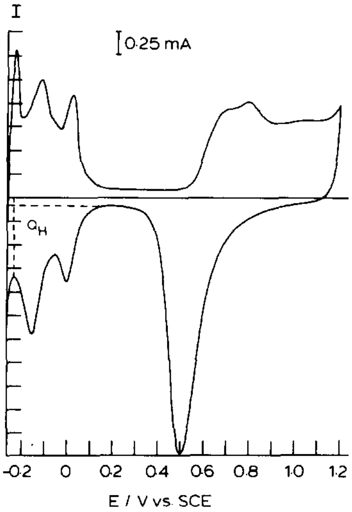

FIG. 1. Cyclic voltammogram for BD Pt catalyst electrode in 0.5 *M* H_2SO_4. Sweep rate = 5 mv/s. The area integrated to give the hydrogen adsorption charge is labeled Q_H.

adsorption charge at smooth electrodes. However, at the BD Pt catalyst electrode molecular hydrogen evolution is shifted to more negative potential, probably because diffusion of hydrogen gas away from the surface is restricted by the pore structure. This effect has been noted at platinized platinum electrodes (*6*). The result is better separation of the most negative hydrogen adsorption wave and the onset of molecular hydrogen evolution than is observed at smooth electrodes and hence a better estimate of Q_H. Accepting 0.0049 C as Q_H, the real surface area of the BD Pt catalyst electrode is 230 cm^2 based on 210 $\mu C\ cm^{-2}$ (*5*). The geometric area of the electrode is approximately 0.1 cm^2, giving a roughness factor (real area/geometric area) of 2300.

No attempt was made to measure surface area of the BD Pt catalyst by gaseous H_2 or CO titration for comparison to the cyclic voltammetric results. However, Bett *et al.* (*7*) found that surface areas of both supported and unsupported Pt catalysts determined by gas-phase techniques were in good agreement with the results obtained by cyclic voltammetry in H_2SO_4 electrolyte, using 210 $\mu C\ cm^{-2}$ real Pt area. There is no reason to suspect any deviation would occur in the case of BD Pt.

It is important to realize the consequences of the relatively large currents passed at this and other high-surface area electrodes. When using a three-electrode potentiostat a potential control error occurs equal to the current times the uncompensated portion of the solution resistance. Hence to avoid distortion of the voltammetric waves it is necessary to use low sweep rates (minimizes cell current) and high electrolyte concentrations (minimizes solution resistance, including the uncompensated portion). These conditions are often unsatisfactory when using smooth electrodes due to increased diffusion of electrolyte impurities to the surface. Fortunately, the electrolyte trapped within the pore structure of high-area electrodes is purified during pretreatment (for example, by oxidation of hydrocarbon impurities to CO_2), enabling clean experiments to be done.

It is appropriate at this point to consider the information other than surface area available from the hydrogen adsorption–desorption waves.

The origin of the multiple hydrogen waves observed at polycrystalline Pt electrodes has been a controversial subject. The crystallographic orientation of the surface has a profound impact on the hydrogen waves (*40–49, 52*), but it is equally clear that additional waves can appear corresponding to states induced by adsorbed anions (*48, 52–54*). Also, adsorbed anions can obscure certain hydrogen waves by shifting them into other, less anion-sensitive waves. For example, sulfuric acid anions in sufficiently high concentration (approx. 0.05 *M*) have been shown to shift the more anodic of the two waves characteristic of the Pt(110) − (1 × 2) surface into the less anodic wave (*45, 48, 52*). Therefore, high sulfuric acid concentrations, although most commonly used in platinum electrochemistry, are not entirely suitable for the determination of the number and character of the hydrogen waves.

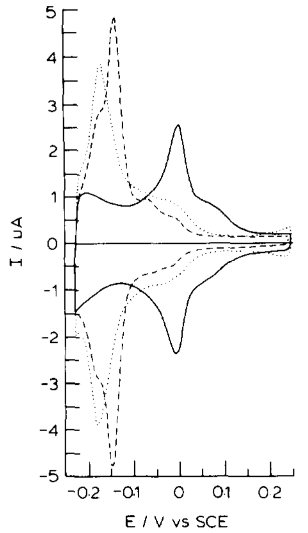

FIG. 2. Cyclic voltammograms for three low-Index Pt single crystals in 0.1 *M* $HClO_4$ + 0.005 *M* H_2SO_4. Sweep rate = 50 mv/s. (——) Pt(100); (---) Pt(110); (···) Pt(111).

Perchlorate anion has a much weaker influence on the hydrogen waves (*45, 48, 55*), and no shifting of the waves is apparent at $HClO_4$ concentrations of 0.1 *M* or lower. Cyclic voltammograms for three low-Miller Index Pt single crystals in 0.1 *M* $HClO_4$ + 0.005 *M* H_2SO_4 are shown in Fig. 2. The small amount of sulfuric acid sharpens the peaks (*56*), making them easier to distinguish, yet is insufficient to cause complete overlap of any of the waves. On the basis of the single-crystal cyclic voltammograms in Fig. 2 and earlier work (*45, 47–49*), the following peak assignments are made for smooth polycrystalline Pt (Fig. 3b): −0.013 V, Pt(100) sites; −0.15 V, Pt(110) sites; −0.18 V, Pt(111) sites. The peak at −0.073 V on the anodic scan is a nonequilibrium state of hydrogen adsorption characteristic of Pt(110) and related surfaces, as discussed elsewhere (*52, 57*).

These peak assignments require further elaboration. It is significant that although the randomly oriented microcrystals composing polycrystalline Pt would be expected to display a variety of stable low- and high-Miller Index structures (*58*), only three quasi-equilibrium hydrogen waves are exhibited in the presence of minimal anion effects. Apparently the fourfold sites (*59*) characteristic of Pt(100) adsorb hydrogen at approximately the same potential as the fourfold sites of identical geometry that occur in terraces and monoatomic steps on certain higher-Index surfaces (*60*). Thus hydrogen adsorbed from solution is a probe of local surface structure, i.e., the geometry of the adsorption site.

Pt(110) has been shown to display a reconstructed (1 × 2) surface consisting of tilted (111) microfacets (*45, 48, 61*). The (111) microfacets give a peak at the same potential as the Pt(111) single crystal, consistent with the arguments presented above. In addition, the reconstructed (110) surface contains fourfold "trough" sites which probably give rise to the peak at −0.15 V. These sites are also found on stepped [*m*(111) × *n*(111)] surfaces (*62*), and the −0.15-V peak at smooth polycrystalline Pt contains contributions from the step sites at several such structures.

In summary, the cyclic voltammogram for the smooth polycrystalline disk can be represented by a weighted sum of the three low-Index voltammograms, the three quasi-

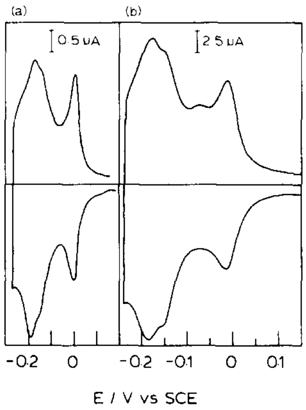

FIG. 3. Comparison of cyclic voltammograms for BD Pt catalyst electrode (a) and a smooth polycrystalline Pt electrode (b) in 0.1 *M* $HClO_4$ + 0.005 *M* H_2SO_4. Sweep rates are 7.7 mv/min for BD Pt electrode and 50 mv/s for the smooth electrode. Note the different current and potential scales in the two voltammograms.

equilibrium peaks representing three sites of different geometry: fourfold sites characteristic of Pt(100), fourfold "trough" or step sites characteristic of Pt(110), and threefold sites characteristic of Pt(111).

Characterization of the BD Pt catalyst electrode in perchloric acid is more difficult. Due to increased solution resistance, a much lower sweep rate must be used. Figure 3a shows the cyclic voltammogram obtained at a sweep rate of 7.7 mv/min. From Fig. 3a it can be seen that, at least qualitatively, the distribution of hydrogen adsorption sites at BD Pt is similar to that at smooth polycrystalline Pt. (The nonequilibrium peak is missing from the anodic scan only because of the very low sweep rate used (*63*).) We emphasize that use of a faster sweep rate in this electrolyte results in distortion (broadening and shifting) of the voltammetric waves, preventing a proper comparison of the two different surfaces.

Copper Deposition Experiments

The underpotential deposition of copper at BD Pt was explored both for surface area determination and as a probe of surface structure. The copper concentration typically used in studies of smooth electrodes (1 m*M*) was insufficient to accomplish any copper deposition at BD Pt during a 5 mv/s sweep. This is due to slow diffusion of Cu^{2+} in the pore structure. The anodic portion of the cyclic voltammogram (hereafter referred to as the stripping profile) obtained after deposition at 0.0 V for a few seconds in 0.05 *M* $CuSO_4$ + 0.5 *M* H_2SO_4 is shown in Fig. 4. This stripping profile has several interesting features. Only a very small peak is observed near +0.2 V. This peak, which is usually prominent at polycrystalline electrodes (*64*, *65*), has been associated with Pt(S)-[*m*(111) × *n*(111)] structures (*48*, *66*). Also, the charge passed due to stripping of underpotentially deposited copper is only 213 μC cm^{-2}, far below the 540 μC cm^{-2} reported for smooth polycrystalline platinum (*67*) and 420 μC cm^{-2} (i.e., one copper per hydrogen adsorption site) reported for platinized platinum (*68*). Despite the fact that full monolayer coverage is not achieved under the conditions of Fig. 4, "bulk" copper stripping peaks appear at approximately +0.1 V, a situation not usually observed at smooth electrodes (*67*, *69*).

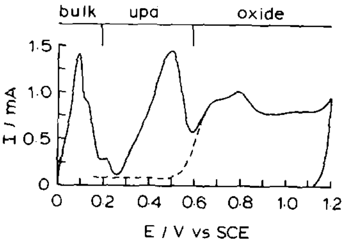

FIG. 4. Voltammogram (anodic portion only) for BD Pt catalyst electrode in 0.05 *M* $CuSO_4$ + 0.5 *M* H_2SO_4 after a several second wait at 0.0 V. Sweep rate = 5 mv/s. The dashed line represents the response obtained in 0.5 *M* H_2SO_4 with no copper added. The potential regions corresponding to stripping of bulk copper, stripping of monolayer copper, and Pt surface oxidation are labeled bulk, upd, and oxide, respectively.

There are several possible explanations for the small +0.2-V copper stripping peak. One is that BD Pt is deficient in [*m*(111) × *n*(111)] structures relative to smooth polycrystalline Pt. However, the hydrogen wave characteristic of the step sites associated with such structures is clearly evident as a shoulder on the positive potential side of the most negative wave in the cyclic voltammogram for BD Pt (Fig. 3a), just as it is in the cyclic voltammogram for smooth Pt (Fig. 3b). Another possibility is that the step sites are more accessible to the proton than to the larger Cu^{2+} ion. However, Fig. 5 shows the effect of increasing deposition time at +0.05 V on the stripping profile; after sufficiently long times (approx. 12 min), the peak at +0.2 V is fully developed. Under these conditions the copper coverage is 417 μC cm^{-2}, more in line with previous studies. The same maximum coverage at BD Pt is attained in 0.25 *M* Cu^{2+} solution.

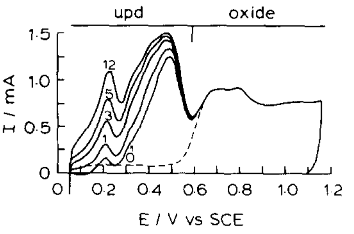

FIG. 5. Voltammograms (anodic portions only) of BD Pt after waiting various periods of time (number of minutes indicated in figure) at +0.05 V in 0.05 *M* $CuSO_4$ + 0.5 *M* H_2SO_4. Sweep rate = 5 mv/s.

Figure 4 indicates that the [*m*(111) × *n*(111)] step sites are not occupied (small +0.2-V peak) until significant copper coverage is attained on the rest of the BD Pt surface. This is an interesting observation because it could be an indication that the step sites are less accessible, i.e., buried deeper within the pore structure. To investigate this point, copper deposition studies were performed on a Pt(110) electrode. A very low copper concentration was used in order to simulate the slow diffusion in the BD Pt pore structure. Pt(110) − (1 × 2), whose surface structure can be designated Pt(S) − [3(111) × 2(111)], gives two copper monolayer copper stripping peaks (*48*), a more positive potential peak associated with the (111) microfacets and a less positive potential peak associated with the "trough" sites. Figure 6 shows that the (111) microfacets are completely covered (the stripping peak at +0.48 V reaches maximum height) before any deposition occurs at the "trough" sites (+0.27-V peak). Because the microfacet and "trough" sites should be equally accessible at the smooth surface, this result indicates that surface diffusion is rapid enough to allow preferential occupation of the sites at which copper is more strongly bound.

Evidently this preferential occupation of the sites at which copper is more strongly bound also occurs at BD Pt, although to a somewhat lesser extent. (Compare the effect of increasing deposition time at BD Pt (Fig. 5) and at Pt(110) (Fig. 6); at BD Pt the peak associated with [*m*(111) × *n*(111)] step sites does appear before the more positive potential peaks reach maximum height.) Therefore, none of the copper deposition experiments necessarily indicate a nonuniform distribution of any type of site throughout the pore structure.

One other aspect of Fig. 6 merits attention. The large peak at +0.13 V in curve 11 (t = 60 min) corresponds to stripping of "bulk" copper, which is rapidly deposited once the first monolayer is complete. If the deposition time were increased beyond 60 min, the "bulk" copper stripping peak would further increase, unlike the monolayer peaks, which have reached a maximum. (The peak corresponding to [*m*(111) × *n*(111)] sites, occurring at +0.28 V in Fig. 6, would appear to increase only because of overlap with the "bulk" stripping peak.) Note that at the Pt(110) surface, as at smooth polycrystalline platinum (*67, 69*), significant "bulk" copper deposition does not occur before the first monolayer is complete. However, at BD Pt significant "bulk" deposition *does* occur before the first monolayer is complete. While a completely satisfactory explanation of this behavior cannot be given at this time, it may be that restricted Cu^{2+} diffusion in the

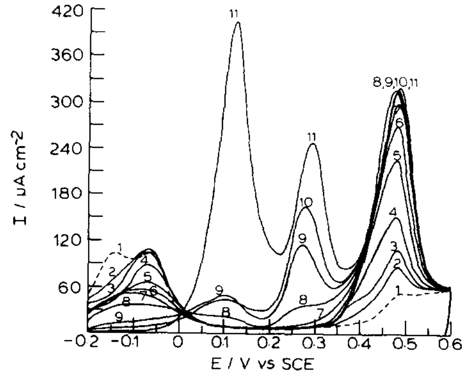

FIG. 6. Voltammograms (anodic portions only) of Pt(110) after waiting various periods of time at −0.21 V in 0.1 *M* $HClO_4$ + 3 × 10^{-5} *M* $CuSO_4$. Sweep rate = 100 mv/s. (1) 0 sec; (2) 10 sec; (3) 20 sec; (4) 40 sec; (5) 2 min; (6) 5 min; (7) 10 min; (8) 20 min; (9) 30 min; (10) 40 min; (11) 60 min.

pores and on the BD Pt surface leads to patches of completed monolayer onto which "bulk" deposition can occur.

DISCUSSION

An important point brought forth in this work is that experimental considerations such as nature and concentration of electrolyte and potential sweep rate profoundly affect the conclusions that can be drawn from voltammetric surface characterizations. Because the magnitude of potential control errors increases with increasing current, a given sweep rate may not be equally suitable for characterization of supported catalysts with widely varying degrees of dispersion. Examination of the recent literature reveals that this fact is not universally appreciated.

Cyclic voltammograms show that the distribution of hydrogen adsorption sites at BD Pt is qualitatively the same as at smooth polycrystalline Pt. (Although not done in the present work, the cyclic voltammograms could be decomposed to give a quantitative estimate of each type of site.) This similarity may seem surprising in view of the obvious morphological differences between the two surfaces. However, hydrogen adsorption from solution is primarily sensitive to local structure, i.e., the geometry of the two, three, or four-Pt atom adsorption site. Thus two macroscopic surfaces could be composed of microcrystalline domains of very different sizes and still give similar hydrogen adsorption profiles. It would be interesting to explore the underpotential deposition of various foreign metals, which are more sensitive to longer-range structure (*49, 70*), for the characterization of Pt catalyst surface structure. Gold surfaces have been studied in this way by Hamlin *et al.* (*71*) using underpotentially deposited lead. Due to slow diffusion, copper is of limited usefulness in the determination of Pt catalyst surface structure. However, to the extent that electrocatalytic reactions of small molecules are sensitive to local site geometry, adsorbed hydrogen is an excellent structural probe in these studies.

Finally, the present work shows that electrodeposited copper is useful for the determination of real surface area of practical Pt catalysts (417 μC cm^{-2}), provided that care is taken to achieve a complete monolayer while avoiding "bulk" copper deposition.

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