Aggregation Effects on the Electrocatalytic Activity of Platinum

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Chlorine evolution is used as a test reaction to investigate the electrocatalytic activity of platinum in various states of aggregation. Ti, implanted with Pt ions, Ti with electrodeposited Pt, massive Pt, Ti–Pt composites, and dilute Ti–Pt alloys are examined. Use of a non-steady-state technique enables results to be expressed on a true surface area basis. Though the implanted and electrodeposited species are initially most active, both tend to lose activity with time although specific activity increases. Massive Pt is least active. Loss of activity is shown to be at least in part due to Pt loss from the surface. The results are discussed in terms of aggregate size and loss of metallic character with diminishing size.

INTRODUCTION

While a substantial body of electrochemical data now exists relevant to the electrocatalytic behavior of massive metals as catalysts, much less information is available relating to the catalytic behavior, in electrochemical systems, of dispersed or "diluted" platinum or other catalytically active metals dispersed in an electrically conducting but otherwise inert matrix. Such data as have been published have recently been reviewed elsewhere (1). Many important questions, and in particular those relating to the concept of "facile" or "demanding" reactions in an electrochemical context, remain unanswered. In an attempt to pursue such questions, the work reported here was carried out using the chlorine evolution reaction as a "test reaction." This process was studied on electrocatalysts of massive Pt, and also on alloys in which Pt was present in small amounts, using these electrodes in com-

parison with others based on Pt electrodeposition on Ti and lastly Pt implanted into the Ti matrix. This last technique is of interest because the metal is deposited atomically in a nonequilibrium condition by bombardment of the matrix (in this case Ti) by a beam of Pt+ ions. It has been used by Voinov et al. (2) and Grenness et al. (3), and Ref. (1) contains a review of their findings. In addition to their work, some striking "negative" results have been recorded though never published. Both Grenness (4) and Brooman (5) implanted doses of 10^{16} ions into graphite and gold matrices, respectively, and failed to detect any significant change in activity for the hydrogen evolution reaction, although (at least in the case of Brooman's work) Rutherford back-scattering studies showed the Pt to be present at or close to the surface of the metal. SIMS (secondary ion mass spectrometry) also confirmed the presence of Pt, at or close to the surface.

88

EXPERIMENTAL

1. Electrode preparation. The implanted electrodes were prepared from titanium blanks (1 cm square) implanted with 10^{16} platinum ions/cm². Control electrodes were made by implantation of argon (at the same beam current). Electrodes implanted with platinum showed a golden color, but implantation with argon produced no color change.

The implanted electrode was spot-welded on to a titanium wire similar to the ones described below. The back of the electrode and the weld area on the front were covered with Alkathene (courtesy I.C.I. Ltd.) by applying the hot, molten, plastic with a spatula.

The electroplated electrodes were prepared by plating on to titanium wire electrodes from a 4% solution of chloroplatinic acid at current densities of 0.2–1.0 mA cm⁻², for periods of 10 or 20 sec. Based on 100% current efficiency for the electrodeposition process, this would correspond to 4 to 20 monolayer equivalents of platinum on the surface of the titanium. Scanning electron microscope investigations showed that the platinum was deposited as crystallites with a wide size

range. The heaviest plating produced a preponderance of particles in the 1–2 μm range. Two kinds of bulk platinum electrode were prepared. One was the usual platinum wire (Johnson Matthey, 99%), the other was platinum wire spot-welded on to titanium wire electrodes. These electrodes were designed to have areas of bulk platinum of the same order as the platinum areas of the dispersed platinum electrodes.

Alloys containing 0.01 to 5.0 atom% of platinum were prepared by vacuum arc melting of a mixture of the two metals on a water-cooled copper base. Each alloy was remelted to ensure uniform distribution.

2. Electrochemical tests. The electrodes were tested at room temperature in chlorine-saturated 2 *M* Analar sodium chloride solution in a 1-liter flange flask. The potential limits were such that there was no danger of platinum dissolving from the platinum counter electrode and depositing on the working electrode (*1*). Surface area measurements were made using the method described by Breiter (*6*). The electrolyte was Analar 1 *M* sulfuric acid at room temperature.
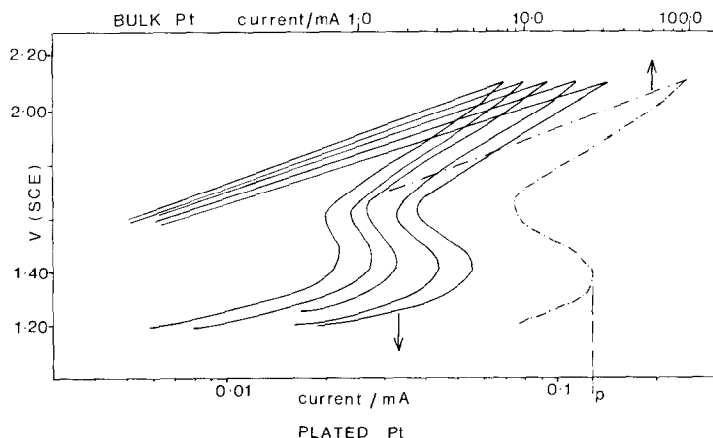

FIG. 1. Anodic polarization scans of bulk platinum (– · – · –) and electroplated platinum (——). 2 *M* NaCl; room temperature; potential sweep rate, 5 mV/sec.
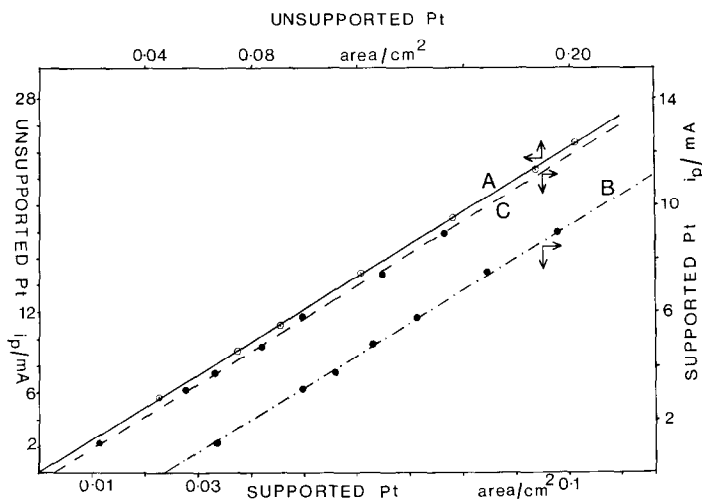
UNSUPPORTED Pt

FIG. 2. Relationship between passivation current i_p and surface area for bulk platinum. 2 M NaCl, room temperature. (A) unsupported, (B) and (C) supported on titanium wire; (B) with approximately 3 cm of titanium exposed, (C) after covering up approximately 2.5 cm of the titanium wire with polythene; potential sweep rate, 5 mV/sec.

RESULTS AND DISCUSSION

(a) Bulk Platinum

Figure 1 shows data obtained in this work for electrodes made of bulk Pt (wire). Such current-voltage plots have been obtained by other workers in the past and their overall form has been interpreted by Kuhn and Wright (7).

Because i_{crit}, the current density at the top of the passivation peak (under defined conditions of temperature, Cl⁻ concentration, and scan rate), is a unique quantity (8), we may use it to determine the "active" surface area of other samples. Thus, providing that a test electrocatalyst exhibits the current maximum and minimum described above, we may, by measuring the peak current (i_p), use the data obtained on massive platinum to estimate the exposed surface area of Pt catalyst on the test sample. A test of this is shown in Fig. 2, curve A where platinum catalyst area is plotted against i_p. The conversion factor, obtained from this graph, is 8×10^{-3} cm² per mA of indicated i_p.

Galvanostatic hydrogen stripping could not be used for surface area measurement

of the dispersed platinum electrodes because of hydrogen adsorption by the titanium matrix. This was determined using electrodes consisting of short lengths of platinum wire spot-welded on to titanium wire electrodes, the platinum areas being similar to those of the dispersed platinum electrodes. Figure 2, curve B, shows that i_p was again proportional to platinum area. The intercept on the area axis implies that the titanium matrix is also being measured.

When the titanium was covered with Alkathene, reducing the exposed area of titanium by approximately 0.75, the value of the intercept was also reduced, but by a factor of 10 (Fig. 2, curve C). Clearly the effect of the titanium matrix is considerable. It therefore seems certain that the area of the dispersed platinum would be swamped by that of the matrix, and so its measurement by the method of galvanostatic hydrogen stripping is not possible.

The activity for chlorine evolution might reasonably be expected to be proportional to the surface area of the metal. This is found to be the case for bulk platinum (Fig. 3) where a plot of $i_{2.1}$ [current registered at a potential of 2.1 V with

respect to saturated calomel electrode (SCE)] against i_p passes through the origin. The choice of this potential, while being arbitrary, is both convenient, in that it represents a potential at which a substantial current flows, and not critical, in that any similar value (1.9 or 2.3 V) might have been selected without in any way altering the conclusions drawn here.

(b) Electroplated Platinum

The behavior of electrodes prepared by electrodeposition of platinum on titanium is similar to that of bulk platinum electrodes (Fig. 1), the only difference being that the current progressively decreases with successive cycles. The loss of platinum surface area indicated by a decreasing i_p can be
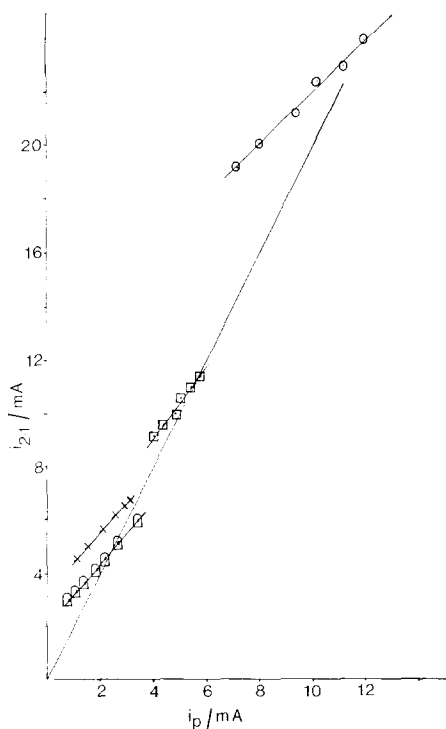

Fig. 3. Current at 2.1 V (SCE) versus passivation current i_p for various electroplated electrodes ($\odot$, $\square$, $\triangle$, $\times$) and bulk platinum (———). 2 M NaCl, room temperature. Plating was at 0.5 mA/cm² for 10 sec from 4% chloroplatinic acid solution. Potential sweep rate, 5 mV/sec.

explained either in terms of anodic dissolution of the platinum (9) or of coalescence of the platinum crystallites. Rutherford back-scattering (10) measurements were not sufficiently sensitive to distinguish between these possibilities. A plot of $i_{2.1}$ against i_p (Fig. 3) for the plated samples is also linear but with an intercept on the Y axis. The values of slope and intercept differ from one electrode to the next.

Although the variation in activity from one plated electrode to another was considerable, even for those prepared under apparently identical conditions, it was generally found that the higher the platinum loading, the higher the activity and that the specific activity of an electroplated Pt anode increased linearly as a function of the number of potentiodynamic scans to which it was exposed. The same was true of the exchange current density based on the true surface area as obtained by the procedure described above. Thus i_0 was typically 2.4 × 10⁻⁶ A cm⁻² for bulk Pt and 11 × 10⁻⁶ A cm⁻² for Pt wire supported on Ti [in good agreement with the figures quoted by Bittles and Littauer (11)], while with Pt electroplated anodes it was some two orders of magnitude higher.

(c) Implanted Platinum

The exchange current density value for the ion-implanted anodes was similar to that found for the electroplated anodes although the situation was complicated by the $\eta - \log i$ plots which showed a change of slope at approximately 1.9 V.

Tests on the Pt-ion-implanted anodes showed a distinct lack of uniformity. However, in all cases, a dramatic reduction in specific activity ($i_{2.1}/i_p$) was seen after each successive cycle up to approximately 10 cycles, after which the activity became constant. Certain of the ion-implanted anodes did not exhibit a true passivation peak, but showed a shoulder. In other cases, where a well-defined peak was seen, this

degraded during cycling to a shoulder. The currents observed with Pt-implanted samples were initially very high (from 1 to 40 mA at 2.1 V) though these decreased rapidly with cycling.

At the implantation energy and dose used in these experiments the distribution of implanted platinum is expected to depart from the usual Gaussian and to be skewed toward the matrix surface. A high concentration of platinum is expected at, or just below, the surface, and by slowly etching the matrix, this depth distribution can be explored. A series of experiments was therefore begun attempting to etch away the outer layers of metal at a very slow and controlled rate. Initially, hot concentrated HCl was used for this. However, reproducibility was very poor and there seemed to be no etch effect until substantial gas evolution (presumably H_2) was observed at which time the Pt itself was removed very rapidly, leaving in all cases a completely inactive electrode. A 0.4% HF solution was found to etch more slowly at room temperature and this was subsequently adopted. In a series of experiments in which the activity of an electrode was measured, after which it was etched, an increase in activity was invariably found, as defined both by i_p and $i_{2.1}$. However, this improvement in activity was only temporary and decreased on cycling the electrode as also occurred with the unetched electrodes. A similar improvement in activity was found by leaving the electrodes standing overnight in electrolyte solution: Whether this was due to atomic migration of Pt in the solid or some slow corrosion processes ("etching") taking place while the electrode stood was not ascertained.

Annealing of the samples in argon at 620°C for 4 hr again increased the activity, but, as before, the enhancement was temporary and did not increase i_p but only $i_{2.1}$.

Rutherford back-scattering (RBS) analysis applied to samples before and after exposure to the potentiodynamic scans showed that some 50% of the Pt atoms had been lost after electrochemical exposure.

To eliminate any effect due to cycling, steady-state experiments were performed. After the initial platinum content had been measured by RBS, the electrode was held at a potential of 2.1 V (SCE) for 1 hr; the platinum content was then again measured and found to be 40% lower. These findings are somewhat surprising since one would not expect such a high percentage of ion-implanted platinum to reside at the surface. There would seem to be only two possible explanations for these results. The first would be the very rapid migration of Pt atoms in the bulk Ti to the surface. Ion-implanted samples carry, in a small zone, concentrations of implant species which frequently exceed the limits implied by phase diagrams. Furthermore, the implanted species do not exist as discrete and defined phases as shown in the phase diagrams but rather in a highly labile state, frequently as individual atoms, interstitially or otherwise placed in the matrix. As such, their tendency to migrate may be more pronounced than classically prepared specimens of similar composition. The second would be the co-dissolution of the Ti with the Pt, thereby "rolling-back" the solid–solution interface. Titanium is known as a metal whose dissolution rate under the conditions found here is normally extremely small, and such a high corrosion rate would therefore be surprising. However, the corrosion resistance of Ti under normal conditions is due to the presence of a thin but perfect layer of the metal oxide, which is an excellent insulator. This situation may well differ in the case of implanted samples. Not only is implantation (even of Ar ions) known to increase the conductivity of insulating oxides, as found by Parker and Kelly (12) who observed an increase of some two orders of magnitude when Kr (at the 6×10^{15}-ion level) was implanted in

bulk TiO_2, but also the presence of metallic Pt would be expected to give similar or greater effects. In addition, the use of non-steady-state techniques which were necessary to characterize the surface areas of catalysts meant that the electrodes, at least transiently, found themselves at potentials where the oxide of Ti might be reduced. If this were so, the included Pt would be progressively exposed to solution and then perhaps released to solution by an undermining process.

Dearnaley et al. (13) have reported that oxide-formation characteristics of the titanium matrix depend on the electronegativity of the implanted species. Metals with an electronegativity of 1.0 (e.g., Ca) lowered the rate of thermal oxidation at 600°C, whereas those greater than 1.1 assisted the oxidation process. If this applies electrochemically, then platinum, with an electronegativity of 2.2 (14), would be expected to enhance the corrosion of the titanium matrix.

(d) Alloyed Platinum

The behavior of the alloy electrode showed marked differences from that of the other types in several ways. The initially observed rest potential could be as low as 0.3 V in contrast to the more commonly observed value of 1.1 V found with other electrode types. The alloy electrodes initially showed little activity and no passivation peak. Etching in 0.4% HF produced more anodic rest potentials until after an etch time of a few minutes the rest potential attained 1.0 V. It did not, however, reach the value of 1.1 V found with the other types of anode.

Another difference was the response to cycling. After etching, the electrode was cycled between 0 and +2.1 V, starting at 0 V. The first cycle produced a passivation peak (showing the presence of platinum at the surface) whose height depended on the duration of the etch treatment. In the
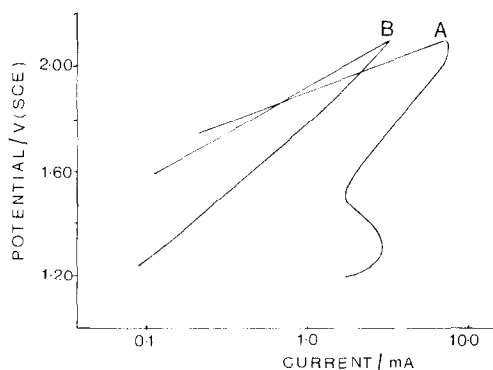

FIG. 4. Polarization curves for 2.5% alloy: (A) first scan after etching in 0.4% HF solution for 1 min; (B) second scan. 2 M NaCl; room temperature, potential sweep rate, 5 mV/sec.

case of the 1% alloy, a well-defined second peak at ca. 1.95 V was observed. The 2.5% alloy also exhibited a second peak, but much smaller, at that potential. On the second and subsequent cycles, there was no peak (Fig. 4). The current at 2.1 V ($i_{2.1}$) decreased with each cycle. The electrodes could be reactivated by further etches. The 0.05% alloy required a 5-min etch time to produce a rest potential greater than 1 V. No true passivation peak was produced, but only a shoulder (cf. implanted electrodes).

The exchange current density on the 2.5% alloy was 16×10^{-6} A cm^{-2}. This was the case after both a 1-min etch and a 2-min etch: The latter treatment exposed 26 times more platinum than the former (as indicated by the increase in i_p).

The loss of the platinum passivation peak after the first cycle implies that the platinum initially at the surface has dissolved. It also indicates that the titanium has not been corroded because this would have exposed more platinum and so produced a passivation peak.

CONCLUSIONS

Comparisons between the Pt/Ti Systems

(1) Platinum loss. Both the implanted electrodes and the alloys lost platinum

during a cycle. Since bulk platinum is known (9) to dissolve during oxide formation and reduction, it seems likely that the loss of area experienced by the plated electrodes is likewise caused by platinum dissolution. The loss of the implanted platinum was a rapid process even in the constant-potential tests where corrosion of bulk platinum is expected to be very slow (11). The fact that such a large quantity of platinum is lost implies that its distribution is more skewed than originally expected. It seems likely that the "titanium" surface is in fact rich in platinum and poor in titanium; this platinum will be in a highly disordered state and so presumably less stable anodically. Loss of this platinum could result in the undercutting and consequent loss of the surface titanium atoms, thereby exposing more unstable platinum atoms. The importance of the disorder in relation to the Pt loss rate may be indicated by the fact that the Pt loss rate for the electrodeposited samples was very much slower.

(2) *Activity for chlorine evolution.* The exchange current densities were found to have the following approximate relationship:

$$i_0 \text{ (implant)} = i_0 \text{ (electrodeposit)}$$
$$= 100 \, i_0 \text{ (bulk)}$$

and

$$i_0 \text{ (alloy)} = i_0 \text{ (bulk Pt on Ti)}$$
$$= 10 \, i_0 \text{ (bulk Pt)}.$$

The skew distribution of ion-implanted platinum could result in several monolayer equivalents of platinum at the surface, and so similarity between the implanted and electroplated electrodes might be expected.

The platinum atom concentration in the alloys was the lowest of the systems tested (2.5 atom% corresponds to a few nanograms per square centimeter). These crystallites are therefore expected to be much smaller than those of the plated electrodes. The activity is indeed lower but

is still greater than that of bulk platinum. As the etching time was increased, more platinum was exposed although its activity did not change. This is to be expected since the crystallites will be widely dispersed and fairly uniform in size. Thus, continued etching results in the exposure of an increasing number of discrete crystallites all with approximately the same activity.

The loss in platinum area of the plated electrodes with simultaneous increase in specific activity can most easily be explained by assuming that the larger crystallites are more active ·than smaller ones. This is a reasonable assumption since smaller particles have a higher surface atom/bulk atom ratio and so will suffer a greater loss in "metallic" character (16). Since smaller particles are less stable (15) they can be expected to be the first to be lost, either by dissolution or by migration and coalescence with larger particles. Both processes involve the loss of small, low-activity particles, and so the average (observed) specific activity increases. Coalescence would also actually increase the specific activity of the enlarged crystallites.

Bulk platinum, therefore, with its "infinite" crystallite size should be much more active than dispersed platinum. In fact its specific activity is very much lower. This could be due to there being an optimum crystallite size somewhere between bulk and the crystallite sizes used here, and above this size the specific activity decreases with increase in crystallite size. A more likely explanation is that there is some kind of interaction, presumably electronic, between the matrix and the crystallites. This was suggested by Urisson et al. (21) who also found that dispersed platinum on a variety of matrices had a greater specific activity than bulk platinum for several reactions (17–25). Such an interaction would explain the greater activity of the bulk platinum when supported on titanium.

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