ELECTRODEPOSITED PLATINUM AND PLATINUM-LEAD ELECTROCATALYSTS

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Finely divided Pt and Pt-Pb black powders have been used for some time as anode catalytic materials for the oxidation of hydrocarbons and hydrocarbons containing oxygen in fuel cells. These blacks have been prepared by a number of different methods with the end result that each preparative method and even variations within a given method yield catalysts of different activity. The subject of this paper is a study of the microstructural and electrochemical surface area characteristics of Pt and Pt-Pb electrodeposited blacks prepared under different electrochemical conditions and is part of an over-all program on electrocatalytic materials.

EXPERIMENTAL APPROACH

Three important aspects of preparing catalysts by electrodeposition were studied. These were the effects of the electrode surface microstructure upon which the catalyst nucleates and grows, the current density during electrodeposition and the Pb ion concentration in the plating solution. Earlier in the program, it was observed that the electrochemical surface area and activity of electrolytically prepared Pt blacks varied with different surface treatments of the electrode substrate prior to electrodeposition. Replication electron microscopy in conjunction with electrochemical surface area measurements were performed to establish whether or not differences in nucleation and growth of Pt and Pt-Pb blacks could account for such differences. Cross-sections of the electrodeposited layers were also examined.

The extent of electrochemical surface area was investigated in regard to the deposition parameters, current density and Pb concentration of the plating solution. These results were correlated with catalytic activity for the electrode oxidation of hydrocarbon fuels studied in other parts of the program. The surface areas were measured using a charging method which involves the measurement of the number of coulombs required to remove a monolayer of adsorbed hydrogen by electrochemical oxidation from the surface of the catalyst. The influence of the concentration of Pb upon the character of the catalytic deposit was studied both microscopically and electrolytically employing the same methods as mentioned above.

DISCUSSION OF EXPERIMENTAL RESULTS

Microscopy of the Nucleation and Growth of Pt and Pt-Pb Electrodeposits

Electron Microscopy: Replication electron microscopical techniques were used to study the nucleation and growth of Pt and Pt-Pb electrodeposits on Pt electrodes which were purposely chemically pretreated to alter the electrode topography to ascertain what effects topography had upon structural and physical properties of the deposit. The surfaces examined were, untreated, metallographically

polished, sandblasted and etched by heat, molten sodium carbonate and aqua regia. Figure I contains electron micrographs illustrating the effect of each treatment on the topography. Pt was electrodeposited on a series of 1 cm^2 area pretreated electrodes at different time intervals from a 2% aqueous solution of H_2PtCl_6 at a current density of 100 ma/cm^2. Each electrode was electrochemically cleaned and reduced before electrodeposition. Figure II shows the nucleation and growth of Pt on untreated Pt surfaces. The electrodeposit appears first as randomly distributed particles which enlarge laterally with plating time until the electrode surface becomes covered. Further deposition appears to occur primarily in the surface asperities and the deposits become smoother. Deposition on other surfaces follows the same general pattern with minor variations.

Pt-Pb blacks were electrodeposited on untreated, annealed and sandblasted surfaces at current densities of 10 and 100 ma/cm^2 from 0.1 M H_2PtCl_6, 2 x 10^{-3} M $PbOOCCH_3$ solutions. The electrodeposits formed at 10 ma/cm^2 on the various surfaces as fine nuclei randomly dispersed over the surface. These nuclei grew laterally into a thin smooth grayish deposit. The electrodeposits prepared at the higher current density were different from those prepared at 10 ma/cm^2 in that the nuclei formed more rapidly and were coarser in appearance. Each pretreated surface showed some difference in mode of nucleation. Figure III shows the nucleation and growth on untreated Pt surfaces. The same general growth pattern persists in this case as those described in the previous experiments. However, these deposits were much more fragile than those previously discussed.

Light Microscopic Surface Analysis: Light microscopic examinations of Pt and Pt-Pb electrodeposits prepared at 100 ma/cm^2 revealed only rough appearing surfaces without any distinguishing features. The same examinations for Pt-Pb blacks deposited at 10 ma/cm^2 did reveal some distinguishing features and are shown in Figure IV. This figure contains a series of photomicrographs for deposits on annealed substrates showing first the smooth deposit followed by cracking defects and some interesting secondary growth phenomena as the electrodeposition time was advanced.

Cross-Sectional Microscopical Analysis: Electron and light microscopic studies show only the topographical features of the deposits. Cross-sections of these deposits were prepared to give some concept as to the structural characteristics of the catalyst interior. Figure V contains cross-sections of deposits prepared at 10 and 100 ma/cm^2 for Pt and Pt-Pb black deposits. Both types of deposits prepared at 10 ma/cm^2 and the Pt deposit prepared at 100 ma/cm^2 appear as solid films with vertical cracks. The Pt-Pb deposit prepared at 100 ma/cm^2 is significantly different and is characteristic of dendritic type structure.

Deposit Thickness Growth Rates

Cross-sectional analysis also afforded as a means to obtain information regarding deposit thickness growth rates and the compactness of the deposit from deposit thickness measurements, deposition times and deposit weights. The two types of deposits were prepared on untreated Pt electrodes at time intervals and average film thicknesses and deposit weights were measured.

Linear thickness growth rates were observed for Pt and Pt-Pb deposits prepared at 10 ma/cm^2 and 100 ma/cm^2 respectively. The respective rates are 2 x 10^{-4} and 2.8 x 10^{-3} mm/sec. Pt discharged at 100 ma/cm^2 was not linear and was found to

obey the relation:

$$\ell = bt^m$$

where ℓ is the deposit thickness and b and m are constants. The Pt-Pb black deposited at 10 ma/cm^2 shows an initial rapid thickness growth rate which tapers off and appears to become linear after approximately 200 seconds deposition time.

Surface Area of Electrodeposits

Surface Area of Pt Blacks Prepared on Pretreated Electrode Surfaces: The surface area of Pt electrodeposits precipitated at 100 ma/cm^2 on the pretreated Pt electrodes is shown graphically vs deposition time in Figure VI. These data indicate the influence of surface pretreatment on electrochemical area. An expression was found which relates surface area with deposition time for deposition at 100 ma/cm^2 for the first 400 seconds of plating time, it is:

$$\theta = mt(1-e^{-\alpha t}) \qquad (1)$$

where θ is the electrochemical surface area, m is the slope at high values of time in θ vs t plots, such as Figure VI. α is obtained by solution of (1) after substitution of m and an experimental point θ, t. α and m are different for each of the deposits on the differently treated electrodes.

Surface Area of Pt-Pb Deposits on Pretreated Pt Surfaces: The surface area of these deposits was found to increase linearly with time or deposit weight for depositions at 100 ma/cm^2. Furthermore, the pretreatment of the substrate electrode did not influence the surface area of the deposit. Surface area vs deposit weight plots have average slopes of 21.5 mC/mg deposit. The average weight of deposit which builds up was found to be 0.05μ g/sec. From this information, the following equation was derived for calculating deposition times to prepare catalysts of approximate desired surface areas;

$$t_{sec} = \frac{\theta\, mC/cm^2}{1.07} \qquad (2)$$

This equation assumes no loss of catalyst due to flaking off from the electrode.

Deposition of this codeposit at 10 ma/cm^2 did not show any linear relationship between surface area and deposit time or weight. The amount deposited per unit time varied with electrode pretreatment and the rate of increase in surface area was observed to decrease with deposition time. The experimental data were found to obey the following equation:

$$\theta = b\beta\,(i/t)^{m/2} \qquad (3)$$

b and m are constants dependent upon the nature of the substrate surface and are obtained from graphical plots of experimental data. i is defined as the current density. Figure VII shows the experimental and calculated surfaces areas using equation (3).

The Effect of Current Density on Surface Area: Since codeposits prepared at the two current densities varied so widely, experiments were conducted to

determine the effect of variations in current density on the surface area of the codeposit. The same number of Faradays were discharged in the preparation of each codeposit. The results of the experiment on untreated Pt electrodes is shown in Figure VIII. This plot is essentially the same for each of the treated surfaces. A plot of deposit weight vs current density has the same shape as in Figure VIII.

The surface area was found to be related to the current density by the following:

$$\theta / \beta = bt(i/t)^m \qquad (4)$$

where each symbol has the same definition as given before. Figure IX shows agreement between experimental and calculated surface areas.

Composition of Electrocodeposits

The Effect of Current Density on Deposit Composition: Electrodeposits formed in the same manner as in the previous section were found to give the same shape curve as Figure VIII when %Pb is plotted versus current density. Consequently the form of the equation which related surface area and current density will serve to relate %Pb found in deposit vs current density; it is:

$$\%Pb = bt(i/t)^m \qquad (5)$$

Again, b and m are constants and are obtained from linear plots of equation (5) using experimental data.

Effect of Pb Ion Concentration in the Plating Solution Upon the Structure and Physical Properties of the Electrodeposit

Effect Upon Surface Area: The electrochemical surface areas were measured for a series of Pt-Pb deposits prepared from plating solutions containing different amounts of Pb ion at a current density of 100 ma/cm^2. The surface area per unit weight of the electrodeposit was found to decline upon increased additions of Pb ion. The concentrations studied ranged between 1×10^{-4} and 5×10^{-2} moles/liter.

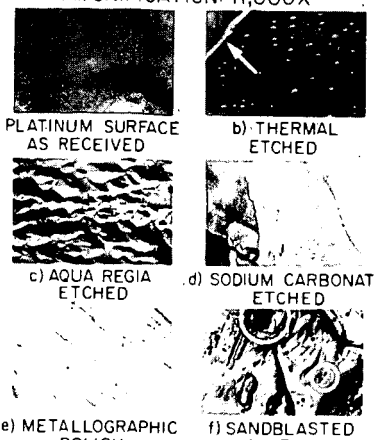
Effect on Deposit Structural Properties: Cross sectional and surface photographs were taken of the deposits prepared from solutions containing different amounts of Pb ion at 100 ma/cm^2. Cross sectional studies revealed a transition from a closely packed deposit prepared from a solution containing 1×10^{-4} moles/liter Pb ion to a dendritic type deposit from a solution containing 1×10^{-2} moles/liter Pb ion Surface photographs show a corresponding transition in texture from fine grains to a coarse open structure for the lower and higher concentrations of Pb ion respectively.

CONCLUDING REMARKS

This study has demonstrated that replication electron microscopy in conjunction with cross-sectional optical microscopy can be applied to the characterization of the morphology and mode of nucleation of Pt or Pt-Pb electrodeposits. The analysis has also shown that by closely controlling the microstructure through judicious changes in the cell plating conditions, large variations in the properties of the deposit can be obtained. The quantity of nuclei deposited from solutions containing Pt and Pb was greater than that observed with solutions containing only Pt under similar conditions. An increase in the surface area of the Pt-Pb codeposits was found to be dependent on the weight of the deposit, the electrodeposition time, and the current density.

ELECTRODE SURFACES BEFORE AND AFTER TREATMENT

MAGNIFICATION: 11,000X



a) PLATINUM SURFACE AS RECEIVED

b) THERMAL ETCHED

c) AQUA REGIA ETCHED

d) SODIUM CARBONATE ETCHED

e) METALLOGRAPHIC POLISH

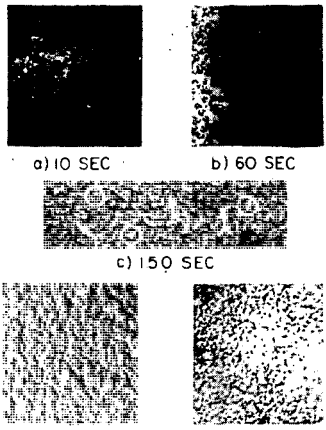
f) SANDBLASTED SURFACE

FIGURE 1.

Pt BLACK ELECTRODEPOSITION

SUBSTRATE: Pt

MAGNIFICATION: 11,000 X



a) 10 SEC

b) 60 SEC

c) 150 SEC

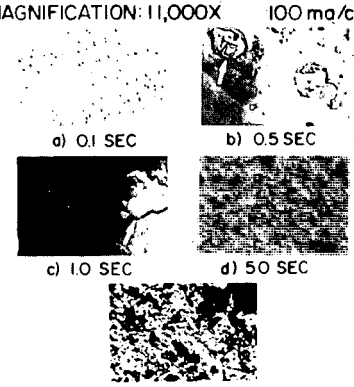
d) 300 SEC

e) 600 SEC

FIGURE 2

NUCLEATION AND GROWTH OF PLATINUM-LEAD CODEPOSITS ON AS RECEIVED PLATINUM SUBSTRATES

MAGNIFICATION: 11,000X 100 ma/cm²



a) 0.1 SEC

b) 0.5 SEC

c) 1.0 SEC

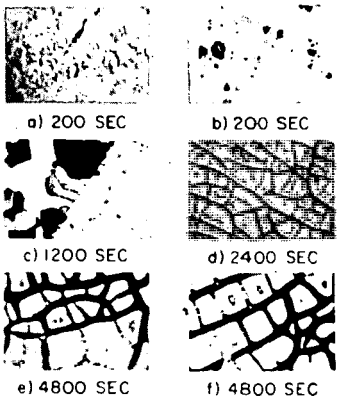
d) 50 SEC

e) 60 SEC

FIGURE 3

GROWTH OF PLATINUM-LEAD CODEPOSITS ON ANNEALED PLATINUM SUBSTRATES

MAGNIFICATION 200X 10 ma/cm²



a) 200 SEC

b) 200 SEC

c) 1200 SEC

d) 2400 SEC

e) 4800 SEC

f) 4800 SEC

FIGURE 4

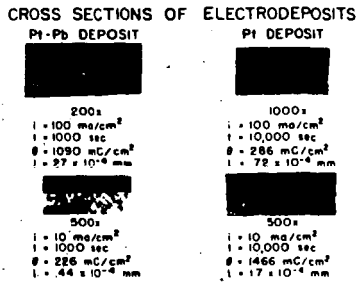


FIGURE 5

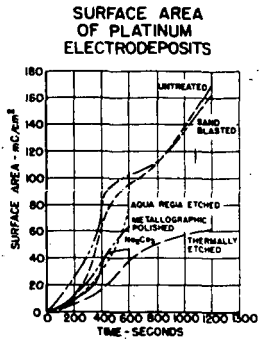


FIGURE 6

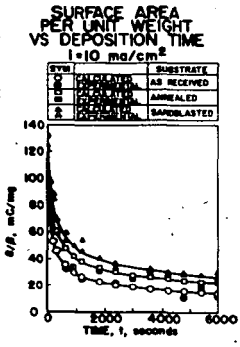


FIGURE 7

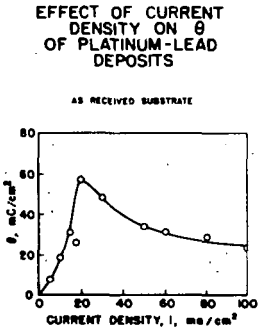


FIGURE 8

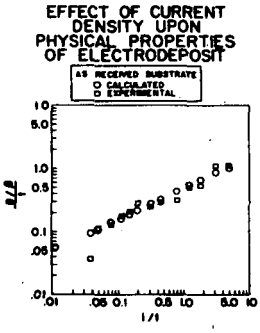


FIGURE 9