ELECTROCATALYTIC PROPERTIES OF MICROCRYSTALS OF PLATINUM METALS DEPOSITED ON INERT CARRIERS

I. ADSORPTION AND EVOLUTION OF HYDROGEN ON PLATINIZED PYROCARBON

L. S. Kanevskii, V. Sh. Palanker, and V. S. Bagotskii

UDC 541.135.52-44

Catalyst research by chemical or electrochemical methods is usually performed on porous systems or monolithic smooth catalysts. In the case of porous systems, the chief difficulty in assessing the rate per unit true surface is the varying degree of accessibility of different parts of the surface due to diffusion and ohmic restrictions. In the case of a monolithic smooth catalyst, however, the possible effect of structural factors is disregarded.

A number of recent reports [1-3] compare the electrocatalytic properties of smooth and dispersed platinum, but their data are contradictory.

To study the effect of catalyst dispersity on its activity, while avoding porosity, we developed an electrode preparation method consisting in deposition of trace amounts of platinum on a smooth inert substrate. During deposition of the catalyst microcrystals (in the size range from a few to several hundred angstroms), the electrode retains the same mirror smoothness as before deposition, and it may be assumed that the surfaces of all the microcrystals remain accessible to virtually the same degree.

The inert substrates were chiefly smooth carbon materials (because they conduct electricity and are fairly inert) in the form of vitreous carbon, covered with a thin layer of compact nonporous pyrocarbon. The visible electrode surface was ~15 mm^2. The pseudocapacities of such substrates are small in comparison with that of platinum in the hydrogen region.

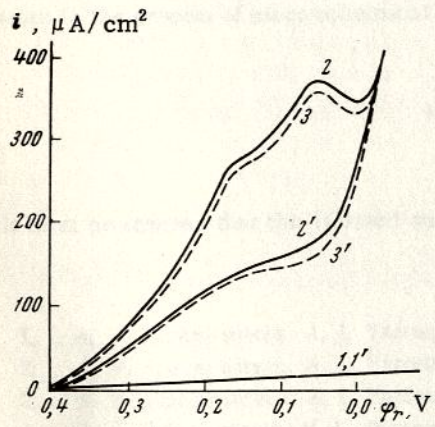


Fig. 1. Cathodic potentiostatic (i, φ) curves on nonplatinized (1, 1') and platinized (2, 2') pyroelectrodes; 3,3') difference curves. v = 20 V/sec.

Deposition of platinum on the carbon rods was effected from 0.5 M solutions of Na_2PtCl_6 or H_2PtCl_6, from which oxygen had been thoroughly removed by argon. The weight of the platinum was determined from the quantity of electricity passed during deposition. Deposition was performed potentiostatically at potentials far more positive than the reversible potential of a hydrogen electrode (φ_r = 0.3-0.5 V), which ensured a virtually 100% current yield.

All the experiments were performed in 1 N H_2SO_4 at 20°C. The solutions were prepared from specially pure H_2SO_4; they were further purified by prolonged (24 h) cathodic-anodic treatment at large platinized electrodes.

To determine the surface of the deposited platinum we recorded the cathodic potentiostatic (i, φ) curves of hydrogen adsorption on nonplatinized and platinized pyrocarbon (before the curves were recorded the electrode was subjected to standard cathodic-anodic treatment: residence time 20 sec at φ_r = 1.2 V and 20 sec at φ_r = 0.0 V). Figure 1 shows a characteristic (i, φ) curve. In contrast to the curves for platinum, those for platinized pyrocarbon do not display distinct current maxima. The cause is not yet known.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 2, pp. 271-274, February, 1970. Original article submitted June 6, 1969.

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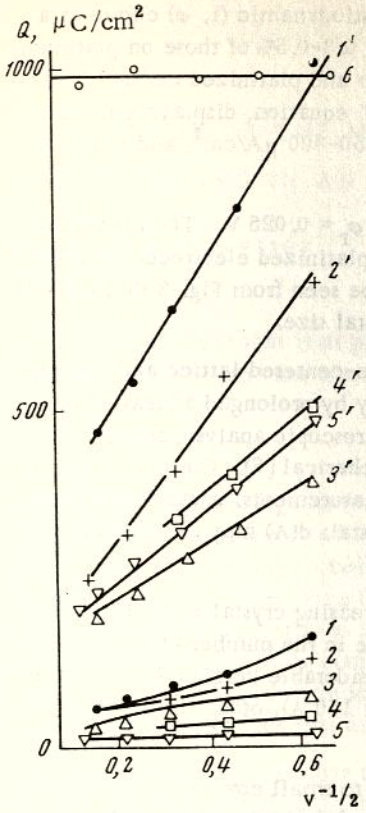


Fig. 2. Quantity of electricity (per 1 cm^2 of visible electrode surface), obtained by integrating (i, φ) curves, versus sweep rate v. 1-5) Nonplatinized pyroelectrode; 1'-5') platinized pyroelectrode; 6) smooth Pt.

For pyrocarbon we established that the quantity of electricity Q, found by integrating the (i, φ) curves in the range φ_r = 0.4-0.025 V, depends on the rate of application of the potential v. The curves plotting Q versus $v^{-1/2}$ are vitually linear (Fig. 2). This phenomenon is due to the nature of the carbon electrode, not to the arrival of any reducing ions from the solution, because at platinum electrodes in the same solutions Q is independent of v (Fig. 2). It may be assumed that the dependence of Q on v is due to the slowness of reduction of oxygen, present in different forms on the carbon surface. It will also be seen from Fig. 2 that a similar dependence is observed for platinized carbon if the base electrolyte is subtracted. This anomalous behavior of platinum on carbon may be attributed to the effect of the platinum crystals on the properties of the carrier. It is possible that adsorption of hydrogen on platinized carbon takes place on the areas adjoining the platinum, whereas in absence of the latter these areas do not adsorb hydrogen. In this case adsorption of hydrogen on the "carbon" sectors may be much slower than on platinum; this leads to the dependence of adsorption on the rate of application of the potential. A hypothesis was put forward by Burshtein et al., [4], who studied activated adsorption of hydrogen on platinized carbon from the gas phase at temperatures above 300°C.

The surface of the deposited platinum was determined from hydrogen adsorption by integrating the (i, φ) curves in the range from 0.4 to 0.025 V, assuming that adsorption of hydrogen is equivalent to 210 $\mu C/cm^2$. The value of Q for smooth monolithic platinum is independent of the rate of recording of the (i, φ) curves up to very high values (800 V/sec) [5]. If we assume that deposited platinum has the same properties, and the dependence of adsorption on the rate of application of the potential is due only to adsorption on carbon, the platinum surface may be obtained from hydrogen adsorption at high sweep rates. Extrapolation of the straight line obtained by plotting Q versus $v^{-1/2}$ to an infinite rate gives Q values 20-30% smaller than those determined at v = 20 V/sec. To calculate the platinum surface we used the experimentally determined value of adsorption at v = 20 V/sec, which gives a rather excessively high surface.

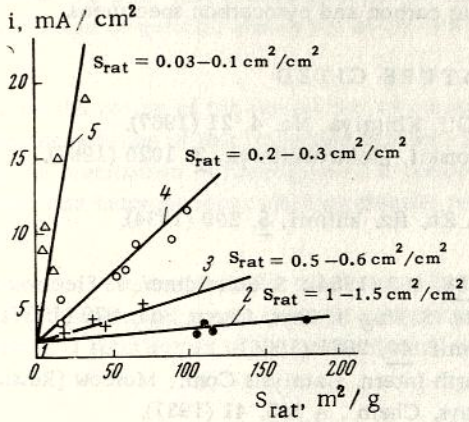


Fig. 3

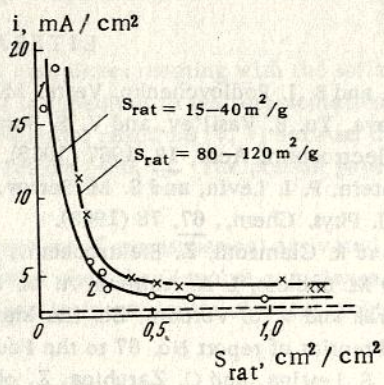


Fig. 4

Fig. 3. Current density of hydrogen evolution versus specific surface of deposited Pt.

Fig. 4. Current density of hydrogen evolution versus coverage of pyrocarbon surface by platinum. S_{rat} is the ratio of the true Pt surface to the visible electrode surface.

The steady rate of hydrogen evolution was determined by recording the potentiodynamic (i, φ) curves at a sweep rate of 0.01 V/sec. The hydrogen evolution currents on pure carbon are only 0.3-0.5% of those on platinum. In the φ_r range from -0.015 to -0.05 V the hydrogen evolution currents on platinum and platinized carbons (here and below all data relate to 1 cm^2 of true platinum surface) closely obey the Tafel' equation, displaying the same slopes. The hydrogen evolution exchange reaction current on smooth platinum is 650-800 $\mu A/cm^2$, and the Tafel' slope is from -38 to -40 mV; this coincides fairly closely with the values in [6].

We compared the activities of different electrodes for hydrogen evolution at φ_r = 0.025 V. The results are given in Fig. 3. Point 1 relates to smooth monolithic platinum, and curves 2-5 to platinized electrodes with different ratios of the true platinum surface to the geometric surface of carbon. It will be seen from Fig. 3 that the rate of hydrogen evolution increases with the specific surface, i.e., with decreasing crystal size.

If the platinum crystals have an equilibrium structure, they form a cubic face-centered lattice and are octahedral or cubooctahedral in shape. However, equilibrium crystals are obtained only by prolonged annealing at a fairly high temperature (about 500°C in the case of platinum) [7, 8]. Electron-microscopic analysis of metallic microcrystals deposited at high temperatures reveals that they are approximately spherical [8]. Our platinum was deposited at room temperature. As shown by preliminary electron-microscopic measurements, under these conditions the platinum particles are virtually hemispherical. The diameter of such crystals d(Å) may be assessed from the specific surface $S_{sp}(m^2/g)$, $d = 2800/S_{sp}$.

The proportion of atoms with small coordination numbers increases with decreasing crystal size. It is often assumed that these atoms may be the active centers of catalysts; a marked increase in the number of such atoms occurs only if the crystals are very small (< 50 Å) [7, 8]. Since we observed a considerable heightening of catalytic activity even for crystals with small specific surfaces (mean crystal diameter about 150 Å), other factors are apparently of importance in this case.

It will be seen from Fig. 4 that the process rate increases markedly as we go to small coverages of carbon by platinum, which indicates a possible effect of platinum on the catalytic properties of the carrier (the radius of action of platinum may be fairly large). For specimens 1 and 2 (Fig. 4) the specific surfaces are close (20 and 16 m^2/g), but the activities differ by a factor of 4. The mean diameter of these crystals is about 160 Å. The numbers of crystals per 1 cm^2 of carbon, calculated from the weight of deposited platinum, are $7.5 \cdot 10^9$ and $80 \cdot 10^9$, respectively. Hence we find that the distance between the crystal centers is 1200 and 350 Å, respectively, which is 7.5 and 2.2 times greater than the crystal diameter, respectively. In this case the coverage of the carbon surface by platinum is 1.5 and 16%, respectively. At such values the rate is still not independent of the degree of coverage. Research [9] on adsorption of electrolytes on platinized carbons shows that the effect of platinum may be exerted over even greater distances.

We thank Yu. B. Vasil'ev and A. M. Skundin for useful advice and are grateful to our colleagues of the Kudinov branch of the All-Union Red Banner of Labor Scientific-Research Institute of Electromechanics (VNIIÉM) D. I. Lyaks and S. M. Rabinovich, who prepared the vitreous carbon and pyrocarbon specimens.

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