ELECTROCATALYTIC PROPERTIES OF MICROCRYSTALS OF PLATINUM METALS, DEPOSITED ON INERT CARRIERS

II. ADSORPTION AND EVOLUTION OF HYDROGEN, AND ADSORPTION AND OXIDATION OF METHANOL, ON PLATINIZED GOLD

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

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Our first communication [1] dealt with the catalytic properties of platinum microcrystals, deposited on smooth pyrocarbon. It was found that the rate of electrochemical evolution of hydrogen per unit of true platinum surface increases markedly with decreasing coverage of the carbon surface by platinum. In our opinion, this is due to the effect of platinum on the catalytic properties of the adjoining carbon sectors. It was therefore interesting to study the properties of electrodes with platinum microcrystals, deposited on a substrate, whose properties differ markedly from those of carbon. It was found that gold is a suitable material for this purpose, because the rate of hydrogen evolution [2, 3] and of methanol oxidation [4] on it is at least one order of magnitude less than on platinum.

The electrodes were gold rods of diameter 3 mm, pressed into a Teflon tube. From a 0.5 M solution of Na_2PtCl_6, we deposited potentiostatically on the electrode an amount of platinum sufficient to cover only part of the gold surface. A marked shortcoming in the deposition of very small amounts of platinum on a gold substrate is the fact that platinum deposition from the solution takes place by contact (although fairly slowly). Therefore, in these experiments we could not accurately assess the amount of deposited platinum in contrast to a carbon base), and we measured only its surface. The rest of the procedure was the same as in [1]. All the experiments were performed in 1 N H_2SO_4 at 20°C.

The surface of the deposited platinum was determined from the difference between the areas below the potentiodynamic (i, φ) curves in the hydrogen region for platinized and unplatinized electrodes (calculating that 1 cm^2 of platinum corresponds to 0.21 mC). It is known [5, 6] that platinum forms two-phase alloys with gold, the gold-rich phase, like pure gold, adsorbing virtually no hydrogen, while the platinum-rich phase adsorbs practically the same amount of hydrogen as pure platinum. Since deposition of platinum on gold was followed by a very marked increase in hydrogen adsorption in our experiments, we inferred that platinum does not diffuse rapidly into gold with alloy formation. Of course, the metals could exert a mutual effect at the points of contact of the platinum crystals with gold, and from the value of hydrogen adsorption we could measure not only the surface of pure platinum, but also the surface with properties similar to a platinum-rich alloy. However, as will be seen below, alloy formation could not exert a marked effect on the results.

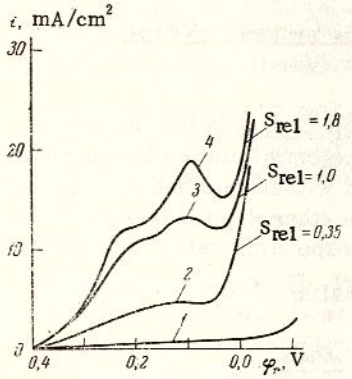


Fig. 1. Cathodic potentiodynamic (i, φ) curves on pure (1) and platinized (2-4) gold (v = 10 V/sec).

Figure 1 shows the characteristic shape of the (i, φ) curves on pure and platinized gold. With increasing ratio of the surface of deposited platinum to the geometric area of the electrode (S_{rel}), the shape of the curves becomes increasingly similar to that of the (i, φ) curves on pure platinum. In contrast to platinized carbon electrodes,

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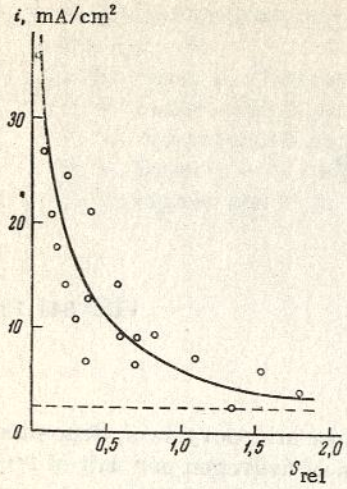


Fig. 2. Density of hydrogen evolution current vs coverage of gold surface by platinum at $\varphi_r = -0.025$ V; dashed line denotes smooth platinum.

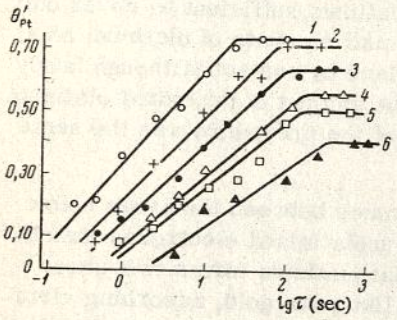


Fig. 3. Kinetic isotherms of adsorption of methanol on platinum (1) and platinized gold (2-6) at different S_{rel}: 2) 1.5; 3) 1.8; 4) 1.0; 5) 0.4; 6) 0.15.

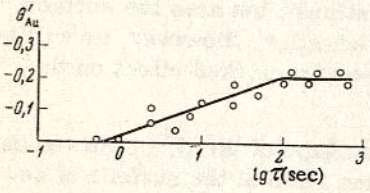


Fig. 4. θ'_{Au} vs time.

on gold and platinized gold electrodes the quantity of electricity, found by integrating the (i, φ) curves in the hydrogen region, is independent of the rate of imposition of the potential v in the range 0.2-20 V/sec. It was found that the most suitable rate was 10-20 V/sec.

The steady rate of hydrogen evolution was determined by recording the potentiostatic (i, φ) curves at a sweep rate of 0.01 V/sec. The currents on gold were 1-30% of those on deposited platinum, and this background current was subtracted from the measured currents on platinized gold. In the φ_r range from -0.015 to -0.050 V, the Tafel plot, with a slope of 40-50 mV, is closely maintained on both pure gold and platinized gold. Extrapolation of the hydrogen evolution current on pure gold to $\varphi_r = 0$ gives a value of about 10^{-4} A/cm², which agrees satisfactorily with data of Breiter and Clamroth [2].

Figure 2 compares the activities (for hydrogen evolution) of electrodes with different degrees of coverage of gold by platinum. The activity per unit true surface of platinum increases with decreasing coverage of the gold base by platinum, as in the case of platinum deposited on pyrocarbon [1]. This increase in activity cannot be attributed to formation of a Pt–Au alloy, because the rate of hydrogen evolution on Pt–Au alloys is intermediate between the rates on the pure metals [4]. The higher activity of deposited platinum in comparison with smooth platinum might be due either to the dependence of the process rate on the size of the platinum crystals, or to the effect of platinum on the catalytic properties of the adjoining gold sectors.

We studied adsorption and oxidation of methanol on electrodes obtained by this method. Methanol adsorption was measured by the method of cathodic potentiodynamic pulses at a sweep rate v = 20 V/sec, using the procedure in [7]. Figure 3 shows the kinetic adsorption isotherms obtained at 20°C and $\varphi_r = 0.425$ V in a solution of 1 N H_2SO_4 + 1 M CH_3OH. The adsorption time τ is plotted on the horizontal axis; the coverage of the platinum surface by methanol θ'_{Pt}, obtained from the equation

$$\theta_{Pt}' = \frac{[{}_sQ_{H(Pt/Au)} - {}_sQ_{H(Au)}] - [{}_RQ_{H(Pt/Au)} - {}_RQ_{H(Au)}]}{{}_sQ_{H(Pt/Au)} - {}_sQ_{H(Au)}} \quad (1)$$

is plotted on the vertical axis; here ${}_sQ_{H(Pt/Au)}$ is the quantity of electricity consumed on the change in potential and on hydrogen adsorption on platinized gold in a solution without methanol; ${}_RQ_{H(Pt/Au)}$ is the same quantity for adsorption of methanol for a specific time; and ${}_sQ_{H(Au)}$ and ${}_RQ_{H(Au)}$ are the corresponding values for pure gold.

Figure 4 plots the change in the value

$$\theta_{Au}' = \frac{{}_sQ_{H(Au)} - {}_RQ_{H(Au)}}{{}_sQ_{H(Au)}} \quad (2)$$

vs the residence time of the gold electrode in a methanol solution. In calculating θ'_{Pt}, the values of ${}_RQ_{H(Au)}$ for each adsorption time was found from the curve of θ'_{Au} vs log τ (Fig. 4) from the known time-independent value of ${}_sQ_{H(Au)}$.

The kinetic adsorption isotherm of methanol may be expressed [8] by the equation

$$\theta_{Pt}' = A + \frac{1}{\alpha f} \ln \tau, \quad (3)$$

TABLE 1

Specimen No.	S_{rel}	θ'^{max}_{Pt}	αf	$v_a \cdot 10^3$ at $\theta'_{Pt} = 0{,}35$, mA/cm^2	k_a mA/cm^{-2} liter	k_a' mole^{-1}	v_{ox}, mA/cm^2
1	Pt_{sm}	0,74	8,0	23	0,380	0,380	0,410
2	1,8	0,72	8,8	7,6	0,162	0,189	0,165
3	1,5	0,65	9,8	3,0	0,090	0,210	0,160
4	1,0	0,58	10,2	1,2	0,042	0,210	0,040
5	0,4	0,52	10,9	0,73	0,034	0,376	0,070
6	0,15	0,43	12,4	0,12	0,010	0,420	0,019

where α is the transport coefficient, f is the factor of surface heterogeneity, and A is a constant. Equation (3) results from the fact that the rate of adsorption of methanol on platinum is not described [8] by the Roginskii-Zel'dovich equation

$$v_a = k_a C \exp(-\alpha f \theta_{Pt}') \tag{4}$$

(C is the volumetric concentration of methanol), from which we can determine the adsorption rate constant k_a.

Table 1 gives the values of αf, v_a, and k_a, calculated from Eqs. (3) and (4). It will be seen that with decreasing degree of coverage of gold by platinum, the adsorption rate v_a and the adsorption rate constant k_a fall very markedly. Simultaneously, the limiting coverage of the deposited platinum surface by methanol θ'^{max}_{Pt} (Fig. 3) also decreases. This may be one of the causes of the change in the adsorption rate.

To determine whether the difference in the adsorption rate constants on different specimens is due only to the different values of θ'^{max}_{Pt}, we calculated the adsorption rate constant k_a', reduced to limiting coverage of smooth platinum by methanol ($\theta'^{max}_{sm\ Pt}$)

$$k_a' = k_a \exp[\alpha f(\theta'^{max}_{smPt} - \theta'^{max}_{Pt})]. \tag{5}$$

It will be seen from Table 1 that the reduced rate constant does not fluctuate markedly from one specimen to another. This would suggest that the adsorption rate depends on the difference $\theta'^{max}_{Pt} - \theta'_{Pt}$, and that the decrease of the adsorption rate on different specimens of platinized gold electrodes might be due to a decrease in the number of sites on which methanol is adsorbable on the platinum surface. On the other hand, it is possible that the surface properties affect θ'^{max}_{Pt} and k_a independently, as may be inferred, for example, from data of Khazova et al. [9], who observed a decrease in k_a at constant θ'^{max}_{Pt} in going from smooth platinum to platinized platinum. Further investigations will be required to solve this problem.

The final column of Table 1 gives the steady oxidation rate of methanol, v_{ox}, in a solution of 1 N H_2SO_4 + 1 M CH_3OH at 20°C and $\varphi_r = 0.7$ V. It will be seen that there is a tendency for the oxidation rate to increase with increasing coverage of gold by platinum.

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