COMPARISON OF THE PROPERTIES OF COMPACT AND DISPERSE PLATINUM-RUTHENIUM ELECTRODES

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Compact alloys of Pt and Ru, with ruthenium contents of 10, 20, 30, and 40% by weight, were obtained by melting definite proportions of Pt and Ru powders, compressed into tablets, in an electrical oven in a helium atmosphere. The Pt and Ru used were of 99.96% and 99.87% purity, respectively, and contained as impurities mainly other metals of the platinum group. The alloys obtained were diffusion annealed for three hours in an evacuated oven at 1400-1600°C (depending on the composition of the alloy). Electrolytically mixed deposits (e.m.d.) of Pt and Ru were obtained by the method of [1]. Powdered Pt + Ru catalysts were precipitated from solutions of H_2PtCl_6 and $H_2[Ru(NO)Cl_5]$ with sodium borohydride [2]. Measurements were conducted at 20±2°C in 1 N H_2SO_4. The potentials φ_r presented are with respect to the reversible hydrogen electrode in the same solution.

Anodic and cathodic potentiostatic curves are shown in Fig. 1a for compact 10 and 40% Pt + Ru alloys and for a platinum electrode in a solution of 1 N H_2SO_4. Curves for alloys containing 20 and 30% Ru lie between the curves for the 10- and 40% alloys. Even with a 40% Ru content, the potentiostatic curves are extremely close in shape to the curve for the platinum electrode. The only differences are the heights of the peaks and the increases of the anodic currents with increase in Ru content when φ_r is in the "double layer" region. In contrast with this, in the case of e.m.d. of Pt and Ru, the introduction of Ru in the deposits caused a strong change in the nature of hydrogen and oxygen adsorption (Fig. 1b). There is an especially significant change in the cathodic curve: with the 30% alloy, the regions of oxygen reduction and hydrogen adsorption combine. These results testify to the earlier oxidation of the surface in the presence of Ru and to the more substantial and irreversible adsorption of oxygen. The nature of hydrogen and oxygen adsorption on the powdered alloys is the same as on the e.m.d.

There is also a strong contrast in the behavior of the e.m.d. of Pt and Ru and compact Pt + Ru alloys in the electrolytic oxidation of methanol. In order to measure the methanol dehydrogenation currents i_d on compact electrodes, we used a method in which we measured the I, t curves after a right-angle switch of the potential from 1.1 V to the selected value of φ_r [3]. In the case of disperse alloys, the measurements of methanol dehydrogenation currents were conducted as in [4].

We show in Fig. 2 the log i_d, φ_r curves for smooth alloys of Pt and Ru (1a) and for e.m.d. (2a), for comparison with the results for smooth platinum (1b) and Pt/Pt (2b) electrodes. For compact Pt + Ru electrodes, the curves practically coincide, and match those described in the literature for smooth Pt [3], while in the case of the deposited electrodes, the curves for Pt + Ru and Pt electrodes are noticeably different. We have already discussed the reasons for the differences in the shape of the curves for disperse electrodes [11]. According to Fig. 2, there are also differences in the process rates on the smooth and deposited electrodes. However, these differences are immaterial for the questions discussed in this paper. They can be connected with the different conditions of measurement of the nonsteady-state methanol oxidation currents. During operation with smooth electrodes, the surfaces were brought to a potential of 1.1 V, corresponding to the oxygen region, before the measurement of each point. In the case of the deposited catalysts, the electrode was subjected to the base electrolyte for extended time at the selected φ_r; this could cause a stronger adsorption of anions, which would hinder the process.

It is known from [1] that the overvoltage for oxidation of methanol in steady-state conditions is lower by some 150 mV when 10-15% Ru is introduced into the platinum deposit. Although measurement of steady-state polarization curves at low φ_r on smooth electrodes with small surfaces is difficult, a difference in the electrolytic oxidation of methanol on compact and disperse Pt + Ru electrodes can be established in the following measurements. To the increase in the process rate on the Pt + Ru alloy there corresponds a shifting of the maximum and the descending branch of the curve showing the potential dependence of the surface filling θ toward a φ_r more cathodic with respect to Pt/Pt [5]. We studied the dependence of methanol adsorption on smooth electrodes by a method using cathodic

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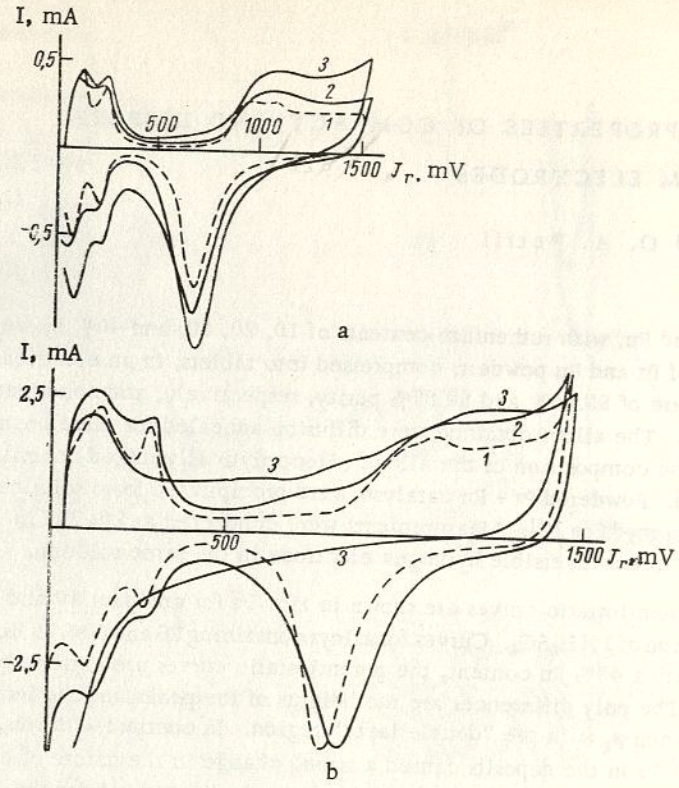

Fig. 1. Potentiostatic curves for compact (a) and disperse (b) platinum (1) and platinum-ruthenium electrodes with Ru contents of 10 (2) and 40 (3) % in 1 N H_2SO_4. The sweep rates were 500 mV/sec (a) and 5 mV/sec (b).

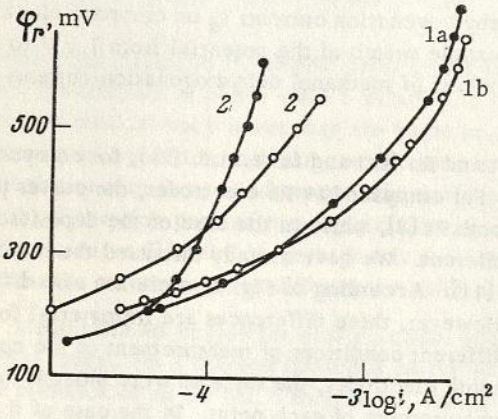

Fig. 2. Dependence on electrode potential of rate of dehydrogenation of methanol in 1 N H_2SO_4 on smooth (1) and electrolytic deposits (2) of Pt + Ru (a) and Pt (b) electrodes; C_{CH_3OH} = 2 M.

potentiostatic pulses [6]. In the case of compact electrodes, the maximum and the descending branch of the θ, φ_r curves practically coincide (Fig. 3), which is apparently due to the closeness of the rates of electrolytic oxidation of methanol on Pt + Ru and Pt electrodes. The potentiostatic curves we measured on compact electrodes in methanol solutions were practically coincident in shape and current magnitude with those described in the literature for smooth platinum [7].*

The lattice constants of the compact and powdered alloys were obtained from x-irradiation to ascertain the reasons for the different behaviors of smooth and electrolytically or chemically deposited electrodes. With increase of Ru content in the alloy, the lines of the x-ray photographs become diffuse, making difficult a highly accurate determination of the lattice constants. Lines corresponding to ruthenium were found on x-ray photographs for alloys with 40% Ru. The following lattice constants are for powdered (a) and compact (b) alloys of Pt and Ru: 10% Ru (a) -3.885 ± 0.005 Å; (b) -3.90 ± 0.01 Å; 30% (b) -3.860 ± 0.005 Å; 40% (b) -3.83 ± 0.02 Å. The lattice constants of the e.m.d. and compact alloys of Pt and Ru are insignificantly different for the same Ru content, and the observed differences cannot, apparently, be identified as the reason for the difference in their properties. The x-ray data are in good agreement with [9] and somewhat different from [2]. The different behavior of compact and disperse Pt + Ru

* In a recently published paper [8], even a slight decrease in the methanol oxidation rate was obtained in the change from Pt to compact alloys of Pt + Ru.

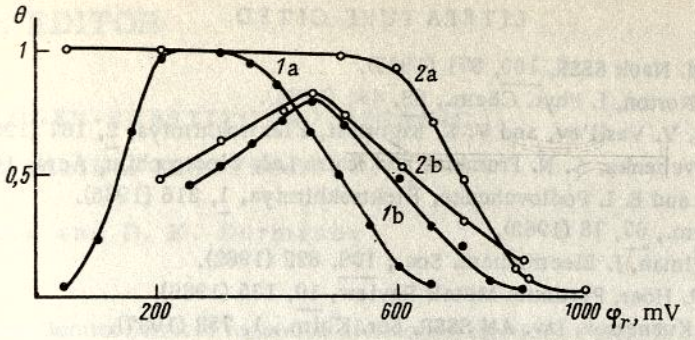

Fig. 3. Dependence of the surface covering of disperse (a) and compact (b) Pt + Ru (1) and Pt (2) electrodes on the potential, in a solution of 0.05 M CH_3OH + 1 N H_2SO_4.

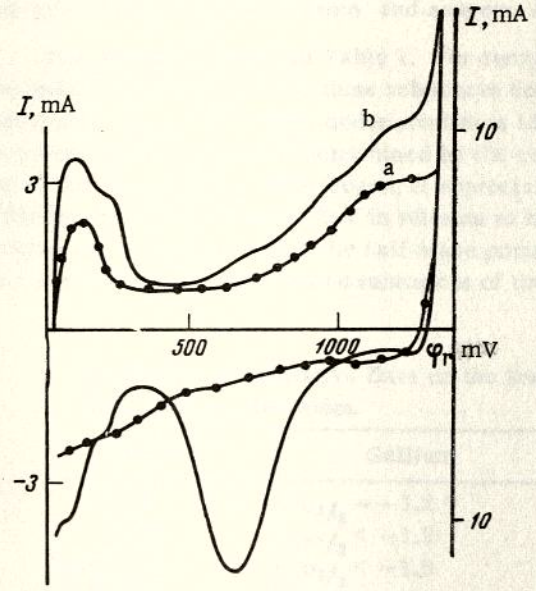

Fig. 4. Potentiostatic curves for 40% powdered Pt + Ru alloy before (a) and after (b) heating for three hours at 850°. The axis at the right is for the curve a.

alloys can be associated with the different states of their surfaces on account of the treatment of the compact alloys at high temperature. To verify this assertion, e.m.d. with a 30% Ru content were heated for three hours at 600° in an argon atmosphere in a quartz test tube. The properties of the alloy changed significantly with the contraction of the surface, and the potentiostatic curve after heating was in complete agreement with the curve for Pt. Similar experiments were conducted with the 40% powdered alloy. In this case also, the properties of the alloy approximated those of platinum after heating of the powder for three hours at 850° (Fig. 4).

Heating of the electrode may cause changes in its surface microstructure (in the number and nature of surface defects and orientation of crystallographic boundaries) and changes in the composition of the surface layer. The assumption of a role for defects is made in works on catalysis. The compact alloys were subjected to the deformation of cold rolling, which must have increased the number of defects. The magnitude of the deformation reached 40%. The potentiostatic curves in a 1 N H_2SO_4 solution, however, practically did not change. Data on the behavior of electrodes of platinum [10], prepared in various manners, and of compact and disperse ruthenium, indirectly refute the assumption of a defect role. In the case of the individual metals, the history of the electrode shows no strong influence on the adsorption and electrochemical properties of the metal, as in the case of the alloys.

The absence of important differences between compact Pt and Pt + Ru alloys, and the approximate matching of the properties of disperse alloys after heating with the properties of platinum can be explained by the assumption that ruthenium diffuses from the surface layer to the interior of grains to vacant lattice sites, and thus the properties of the surface layer approximate those of platinum. Such a process is energetically favorable, since ruthenium has a higher melting temperature and must thus have a higher surface tension than platinum. Attempts were made to remove the surface layer from a compact Pt + Ru alloy by mechanical treatment, by dissolution in aqua regia, by anodic polarization at +2.8 V in hydrochloric acid, and by treatment with basic molten nitrate. The electrode properties, however, remained practically independent of treatment, and thus no direct experimental evidence of the assumption was obtained. Although further study is necessary to explain the observed phenomena, the very fact that the properties of the alloys depend strongly on the method by which they were obtained is of interest.

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