THE ACTIVITY OF ELECTROLYTICALLY MIXED DEPOSITS OF PLATINUM AND RUTHENIUM IN THE ELECTROOXIDATION OF METHANOL

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In recent years there have been many investigations comparing the activity of metals in the platinum group in electrooxidation reactions [1, 2]. It seemed to us to be of interest to test electrolytically mixed deposits (e.m.d.) of various platinum metals in this way, because in some cases, the activity of mixed catalysts is higher than the activity of the components (see, for example, [3]).

An e.m.d. of platinum and palladium was first investigated [4].* With a low palladium content in the deposit, the activity of the electrodes in the electrooxidation of ethanol was similar to the activity of platinum, but with high palladium contents the electrooxidation overpotential of alcohol was considerably increased.

When platinum-ruthenium catalysts were studied, much more interesting results were obtained. A detailed study of the platinum-ruthenium system was undertaken because in the literature there are indications that alloys of platinum and ruthenium with small ruthenium contents have a high catalytic activity in several catalytic processes [5, 6]. The adsorption and catalytic properties of a ruthenium electrode were investigated by an electrochemical method in previous studies [7].

E.m.d of platinum and ruthenium were obtained by electrodeposition from solutions of 1% (H_2PtCl_6+$K_2RuNOCl_5$) with different Pt: Ru ratios with a current density of 2mA/cm^2 on the platinum plate with an apparent surface area of 2cm^2. The composition of the deposits was determined by the use of $K_2RuNOCl_5$ containing Ru^{106} and this showed approximate agreement with the wt. %. ruthenium content in the solution and on the electrode.†

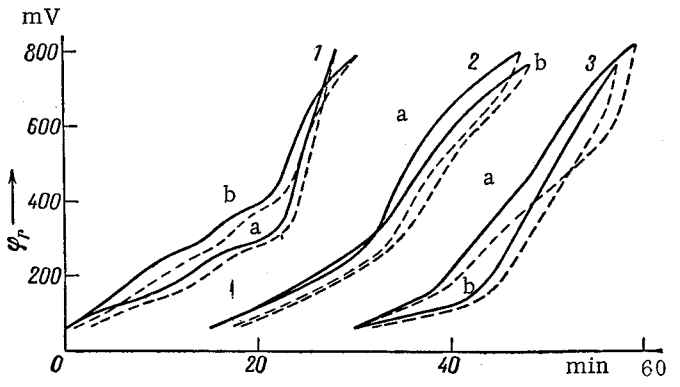

Fig. 1. Charge curves (dotted lines—cathodic curves) on a platinized platinum electrode (1), electrolytically mixed deposit of platinum and ruthenium with a Pt:Ru ratio of 9:1 (2), and on a ruthenium electrode (3) in 1N H_2SO_4 (a) and 1 N KOH (b). Current density 10^{-4} A/cm^2.

Electrodes with a ruthenium content of 5, 10, 23, and 30 wt. %. were prepared. The ruthenium electrode was obtained by electrodeposition from 1% $K_2RuNOCl_5$.

The method of measuring was similar to that used in [8]. The potentials φ_r were relative to a reversible hydrogen electrode in the same solution and the current density was calculated for 1cm^2 apparent surface area. Measurements were carried out at room temperature, 20 ± 2°.

Charging curves for electrodes of platinized platinum (Pt/Pt), ruthenium and e.m.d. of platinum and ruthenium with a Pt:Ru ratio of 9:1 are given in Fig. 1. The charge curve for an e.m.d. with Pt:Ru = 9:1 practically coincides with the charge curve for a Pt/Pt electrode, and the charge curve for an e.m.d. with Pt:Ru = 77:23 is similar to the

*This work was carried out together with an Indian student Khir Lal. His results will be presented in detail in a special article.

†Measurements with the radioactive isotope of ruthenium were carried out by V. Kazarinov. The results of these experiments and also of a study of the properties of e.m.d. of platinum and ruthenium are being prepared publication.

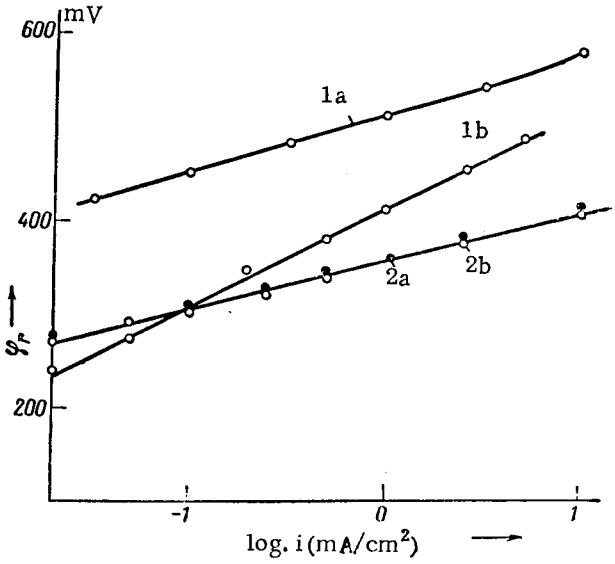

Fig. 2. Polarization curves for electrooxidation of methanol in stationary conditions on platinum (1) and on an electrolytically mixed deposit of platinum and ruthenium (2) in 1N H_2SO_4 (a) and 1N KOH (b).

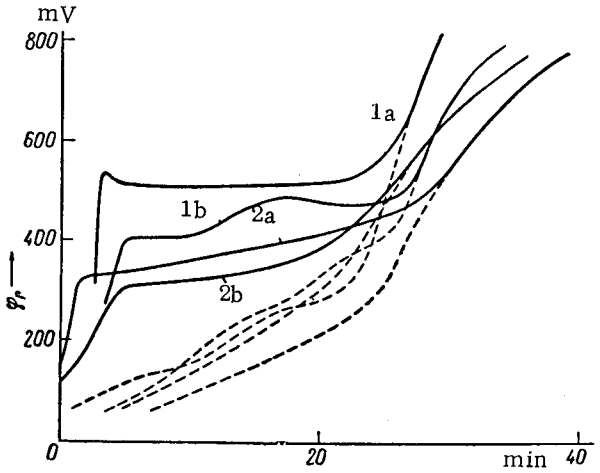

Fig. 3. Curves for the electrooxidation of materials chemisorbed during the polarization of electrodes in methanol solutions on platinized platinum (1) and on an electrolytically mixed deposit of platinum and ruthenium (2) with Pt:Ru = 9:1 in 1N H_2SO_4 (a) and 1N KOH (b). Current density 10^{-4} A/cm^2. Dotted lines—direct charge curves.

charge curve for an e.m.d. with Pt:Ru = 9:1. The introduction of ruthenium into the deposit decreases the energy of the bond between the adsorbed hydrogen and the electrode surface. In the middle portion, the charge curve has a greater slope which obviously indicates the presence of adsorbed gases in the "double layer" region and the earlier oxidation of the surface. In contrast to the Pt/Pt electrode the charge curves of the e.m.d. (Pt:Ru = 9:1) in 1N H_2SO_4 and in 1N KOH are close to each other. On the ruthenium electrode, the quantity of a adsorbed hydrogen in alkali is greater than in acid in agreement with [7]. The transition from the hydrogen region to the "double layer" region is more sharply expressed in an alkaline solution, in contrast with platinum.

We investigated the activity of e.m.d. of platinum and ruthenium in the electrooxidation of methanol by measurements of the curves for the displacement of potential on introducing alcohol into contact with the electrode stabilized at 500 mV, stationary polarization curves and curves for electrooxidation of the materials which were chemisorbed on contact with the electrode with the methanol solution. The investigation showed that the activity of the deposits in the electrooxidation plotted against the ruthenium content in the deposit passed through a maximum and was considerably greater than the activity of platinized platinum. The electrodes with the highest activity are those with a ruthenium content in the deposit of between 5 and 10%, which agrees with the results of studies of the activity of platinum-ruthenium alloys in other investigations [5]. Measurements were carried out with a methanol content in the solution of 0.6 M.

The curves for the displacement of the potential on putting alcohol in contact with the electrode characterized the rate of electrooxidation of methanol on a surface free from chemisorbed material. On the electrode with 5% ruthenium, the displacement of the potential in the cathodic direction was somewhat more rapid than on the Pt/Pt electrode. With a ruthenium content of 10%, the change in potential was considerably more rapid and after approximately 1 h φ_r reached ~ 30–40 mV and continued to change in the cathodic direction at a rate of about 0.1mV/min., whereas on the Pt/Pt electrode after 1 h φ_r reached a value of only ~80-100mV [9]. On changing to the electrode with 23% Ru, the rate of change of potential was slight and with 30% Ru the potential only slowly changed in the cathodic direction and 1 h reached ~ 200mV. On the ruthenium electrode there was observed practically no displacement of potential on the addition of methanol either in acid or in alkaline solution, i. e., on ruthenium in the studied range of potentials methanol was practically not oxidized. Measurement of polarization curves in methanol solutions on a ruthenium electrode leads to the same conclusion.

Stationary polarization curves characterized the rate of electrooxidation on a surface, the coverage of which by chemisorbed material shows practically no change with time. The results of measurements of stationary polarization curves on a Pt/Pt electrode and an e.m.d. with Pt:Ru = 9:1 are shown in Fig. 2. In 1N H_2SO_4, the overvoltage for electrooxidation on the e.m.d. is approximately 150 mV lower than in the Pt/Pt electrode. The gradients of the Tafel straight lines are ~ 60 mV in the case of Pt and ~ 50 mV on the e.m.d. Polarization curves on the e.m.d., in contrast to the Pt/Pt electrode, practically coincide in 1N H_2SO_4 and 1N KOH whereas on the Pt/Pt electrode the overvoltage in alkali is considerably lower and the gradient of the Tafel relationship is ~ 85–100 mV. On the e.m.d. in 1N KOH, the overvoltage for electrooxidation of methanol is 60–70 mV lower than on Pt/Pt, at a current density of 2.5 mA/cm^2.

The curves for the electrooxidation of materials chemisorbed during the polarization of the electrode in methanol solutions on a e.m.d. with Pt:Ru = 9:1 are given in Fig. 3 together with the corresponding curves for a Pt/Pt electrode for comparison. As can be seen from the figure there are marked differences in the potentials of the beginning of oxidation, the character of the oxidation, and the potentials of complete oxidation of chemisorbed materials on platinum and on the e.m.d. The overpotential for the oxidation of chemisorbed materials is lower in the case of the e.m.d. by 200 mV than on a Pt/Pt electrode in 1N H_2SO_4. The curves for electrooxidation on the e.m.d. in acid and alkaline solutions are close to one another. The overpotential for oxidation of chemisorbed materials and the process of oxidation in stationary conditions on the e.m.d. in the presence of methanol in the solution practically coincide. This indicates that the rate of the process is determined by the rate of removal of chemisorbed material.

On the basis of the data obtained in the present work it can be concluded that the electrooxidation of methanol on an e.m.d. of platinum and ruthenium with Pt:Ru = 9:1 obeys simpler kinetic relationships than on platinized platinum.

In conclusion I should like to express my thanks to Academician A. N. Frumkin for suggesting the theme, for his constant interest in the work and for valuable advice during discussions of the experimental data.

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