ON THE ACTIVITY OF ELECTROLYTICALLY MIXED DEPOSITS OF PLATINUM AND RUTHENIUM IN THE REACTION OF ELECTRO-OXIDATION OF METHANOL

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Abstract

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ON THE ACTIVITY OF ELECTROLYTICALLY MIXED DEPOSITS OF PLATINUM AND RUTHENIUM IN THE REACTION OF ELECTRO-OXIDATION OF METHANOL

(Presented by Academician A. N. Frumkin on 6 VIII 1964)

Recently a number of studies have been carried out comparing the activity of platinum-group metals in electro-oxidation reactions ([1,2]). It seemed expedient to us to test, for these purposes, electrolytically mixed deposits (e.m.d.) of various platinum metals, since in some cases the activity of mixed catalysts proves to be higher than the activity of the components (see, for example, ([3])).

Initially, e.m.d. of platinum and palladium were studied ([4])*. At low palladium content in the deposit, the activity of the electrodes in the reaction of electro-oxidation of ethanol was close to that of platinum, while at high palladium content the overvoltage of electro-oxidation of the alcohol increased markedly.

Considerably more interesting results were obtained in the study of platinum-ruthenium catalysts. A detailed study of the platinum-ruthenium system was undertaken because the literature contains indications of the high catalytic activity of platinum-ruthenium alloys with a small percentage content of ruthenium in certain catalytic processes ([5,6]). The adsorption and catalytic properties of a ruthenium electrode have been studied by an electrochemical method in ([7]).

E.m.d. of platinum and ruthenium were obtained by electrodeposition from 1% solutions ($H_2PtCl_6 + K_2RuNOCl_5$) with different Pt : Ru ratios, at a current density of 2 ma/cm^2, on a platinum plate with a visible surface area of 2 cm^2. Determination of the composition of the deposits with the aid of $K_2RuNOCl_5$ containing Ru^{106} showed approximate agreement between the weight percent content of ruthenium in the solution and on the electrode**.

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

The measurement procedure was analogous to that used in ([8]). The potentials φ_r are given relative to the reversible hydrogen electrode in the same solution; current densities are calculated per 1 cm^2 of visible surface. The measurements were carried out at room temperature, 20 ± 2°.

In Fig. 1 the charging curves are compared for electrodes of platinized platinum

Fig. 1. Charging curves

Figure 1: Fig. 1. Charging curves

(Pt/Pt), ruthenium, and e.m.d. of platinum and ruthenium at Pt : Ru = 9 : 1. The charging curve of e.m.d. Pt : Ru = 9 : 1 practically coincides with the charging curve of the Pt/Pt electrode, while the course of the charging curve of the e.m.d. at Pt : Ru = 77 : 23 is analogous to that of the charging curve of the e.m.d. at Pt : Ru = 9 : 1. Introduction of ruthenium into the deposit decreases the energy of the bond of adsorbed hydrogen with the electrode surface. The course of the charging curve in the middle part becomes flatter, which apparently indicates the presence, in the "double-layer" region, of adsorbed gases and earlier oxidation of the surface. In contrast to the Pt/Pt electrode, the charging curves of the electrolytically mixed deposit (e.m.d.) (Pt : Ru = 9 : 1) in 1 N H_2SO_4 and in 1 N KOH prove to be close. On the ruthenium electrode the amount of 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 alkaline solution, in contrast to platinum.

Fig. 1. Charging curves (dashed line—cathodic run) on a platinized platinum electrode (1), an electrolytically mixed deposit of platinum and ruthenium at Pt : Ru = 9 : 1 (2), and on a ruthenium electrode (3) in 1 N H_2SO_4 (a) and 1 N KOH (b). Current density 10^{-4} A/cm^2.

We studied the activity of e.m.d. of platinum and ruthenium in the reaction of electrooxidation of methanol by measuring potential-shift curves when alcohol was brought into contact with an electrode stabilized at 500 mV, steady-state polarization curves, and curves of electrooxidation of substances chemisorbed when the electrode was in contact with a methanol solution. The study showed that the activity of the deposits in the electrooxidation reaction, as a function of the ruthenium content in the deposit, passes through a maximum and markedly exceeds the activity of platinized platinum. The transition to electrodes with the highest activity occurs at a ruthenium content in the deposit between 5 and 10%, which agrees with the results of studies of the activity of platinum-ruthenium alloys in other works (5). The measurements were carried out with a methanol content in the solution of 0.6 M.

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* The work was carried out jointly with the Indian trainee Hira Lal. Its results will be set forth in detail in a special communication.

** Measurements with the radioactive isotope of ruthenium were carried out jointly with V. Kazarinov. The results of these experiments, as well as studies of the properties of e.m.d. of platinum and ruthenium, are being prepared for publication.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The potential-shift curves obtained when alcohol is brought into contact with the electrode characterize the rate of electrooxidation of methanol on a surface free of chemisorbed substances. On an electrode with 5% ruthenium, the potential shift in the cathodic direction is only slightly faster than on the Pt/Pt electrode. At a Ru content of 10%, the change in potential is considerably faster; after ~ 1 h, φ_r reaches values of $\sim$ 30-40 mV and continues to change in the cathodic direction at a rate of about 0.1 mV/min, whereas on the Pt/Pt electrode after 1 h φ_r reaches only $\sim$ 80-100 mV (9). On going to an electrode with 23% Ru, the rate of potential shift changes only insignificantly, whereas at 30% Ru the potential shifts only slowly in the cathodic direction and after 1 h reaches $\sim$ 200 mV. On a ruthenium electrode practically no potential shift is observed upon introduction of methanol either in acid or in alkaline solution; i.e., on ruthenium in the potential region studied, methanol is practically not oxidized. Measurement of polarization curves in methanol solutions on the ruthenium electrode leads to an analogous conclusion.

Stationary polarization curves characterize the rate of electrooxidation on a surface whose coverage by the chemisorbed substance practically does not change with time. The results of measuring stationary polarization curves on a Pt/Pt electrode and on an electrolytically mixed deposit, at Pt : Ru = 9 : 1, are shown in Fig. 2. In 1 N H_2SO_4 the overvoltage of electrooxidation on the electrolytically mixed deposit is approximately 150 mV lower than on the Pt/Pt electrode. The slope of the Tafel straight lines is ~60 mV in the case of Pt and ~50 mV on the electrolytically mixed deposit. The polarization curves on the electrolytically mixed deposit, unlike those on the Pt/Pt electrode, practically coincide in 1 N H_2SO_4 and 1 N KOH, whereas on the Pt/Pt electrode the overvoltage in alkali is noticeably lower, and the slope of the Tafel dependence is ~85-100 mV. On the electrolytically mixed deposit in 1 N KOH, the overvoltage of electrooxidation of methanol is 60-70 mV lower than on Pt/Pt at a current density of 2.5 mA/cm^2.

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

Fig. 3. Curves of electrooxidation of substances chemisorbed during polarization of electrodes in methanol solutions, on platinized platinum (1) and on an electrolytically mixed deposit of platinum and ruthenium (2) at Pt : Ru = 9 : 1 in 1 N H_2SO_4 (*a*) and 1 N KOH (*b*). Current density 10^{-4} A/cm^2. The dashed

lines show the direct course of the charging curves.

Figure 3 presents curves of the electrooxidation of substances chemisorbed during polarization of the electrode in methanol solutions, on the electrolytically mixed deposit at Pt : Ru = 9 : 1, and compares them with the corresponding curves for the Pt/Pt electrode. As can be seen from the figure, appreciable differences are observed in the potentials at which oxidation begins, in the character of oxidation, and in the potentials of complete oxidation of the chemisorbed substances on platinum and on the electrolytically mixed deposit. The overvoltage of oxidation of the chemisorbed substances in the case of the electrolytically mixed deposit is lower by 200 mV than on the Pt/Pt electrode in 1 N H_2SO_4. The electrooxidation curves on the electrolytically mixed deposit in acid and alkaline solutions are close to one another. It is characteristic that the overvoltages of oxidation of the chemisorbed substance and of the oxidation process under stationary conditions on the electrolytically mixed deposit in the presence of methanol in solution practically coincide. This

means that the rate of the process is determined by the rate of removal of chemisorbed substances.

On the basis of the data obtained in the present work, it may be concluded that the electrooxidation of methanol on electrolytically mixed deposits of platinum and ruthenium at Pt : Ru = 9 : 1 obeys simpler kinetic regularities than on platinized platinum.

In conclusion, I consider it my pleasant duty to express my deep gratitude to Academician A. N. Frumkin for suggesting the topic, for his constant interest in the work, and for valuable advice in discussing the experimental data.

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Note: Figure translations are in progress. See original paper for figures.