

**On the activity of electrolytic mixed platinum—ruthenium  
deposits in methanol electrooxidation reaction**

*Recommended by Academician A.N. Frumkin, August 6, 1964*

A number of recent studies were aimed to compare the activity of platinum group metals in electrooxidation reactions [1,2]. It seems reasonable to test codeposited metals of the platinum group, because the activity of certain mixed catalysts sometimes exceeds the activity of components (see in [3] for example).

Initial studies [4] of platinum—palladium codeposits<sup>1</sup> demonstrated that for low palladium content the activity towards ethanol electrooxidation is similar to platinum activity, while for higher palladium content the overvoltage increases significantly.

Much more interesting results were obtained for platinum—ruthenium catalysts. The detailed study of this system was initiated by publications [5,6] which mentioned the high activity of platinum—ruthenium alloys with low ruthenium content in certain reactions. Adsorption and catalytic properties of ruthenium electrode were studied by means of electrochemical techniques in Refs. [7].

Platinum—ruthenium codeposits (denoted below as Pt—Ru) were prepared from 1 wt % ( $\text{H}_2\text{PtCl}_6 + \text{K}_2\text{Ru}(\text{NO})\text{Cl}_5$ ) solutions with various Pt/Ru ratios under a current density of 2 mA/cm<sup>2</sup> on a platinum plate of 2 cm<sup>2</sup> geometric surface area<sup>#</sup>. The deposit composition as determined by using  $\text{K}_2^{106}\text{Ru}(\text{NO})\text{Cl}_5$ <sup>2</sup>, was found to approach that in the deposition solution (in terms of wt % Ru).

The electrodes containing 5, 10, 23, and 30 wt % Ru were fabricated. Ruthenium electrode was deposited from 1 wt %  $\text{K}_2\text{Ru}(\text{NO})\text{Cl}_5$ .

The experimental procedure was similar to that applied in Ref. [8]. The potentials  $\phi_r$  are referred to the reversible hydrogen electrode in the supporting electrolyte solution (RHE), current densities are normalized per cm<sup>2</sup> of the geometric surface area. For all measurements, temperature was 20±2°C. Methanol concentration in our studies was 0.6 M.

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<sup>1</sup> This study was carried out in collaboration with Indian PhD student Hira Lal. The results will be reported in detail in a separate communication.

<sup>#</sup> Deposition time was ca. 3 h (the author's comment in answer to translator's question).

<sup>2</sup> Radiotracer experiments were carried out jointly with V.Kazarinov. The results of these experiments, and also of the studies of codeposited platinum-ruthenium samples, are in preparation.

Figure 1 compares charging curves<sup>#</sup> of platinized platinum (Pt/Pt), ruthenium, and Pt—Ru (9:1). The charging curve of Pt—Ru (9:1) practically coincides with the curve of Pt/Pt. The charging curve of Pt—Ru (77:23) is close to the curve of Pt—Ru (9:1). The presence of ruthenium in the deposit reduces the energy of adsorbed hydrogen bonding with the electrode surface. The mid segment of the curve becomes flatter, which can be explained by the presence of adsorbed gases<sup>@</sup> in the “double layer” range and by earlier oxidation of the surface. In contrast to Pt/Pt, Pt—Ru (9:1) deposits demonstrate similar charging curves in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH. For ruthenium electrode, the quantity of adsorbed hydrogen<sup>@@</sup> in alkaline solutions is higher than in acid ones, in agreement with Ref. [7]. In contrast to platinum, the transition from hydrogen-adsorption range to “double layer” one is more pronounced in alkali.

To study the activity of Pt—Ru towards methanol electrooxidation, we used the following techniques: (1) potential shifts upon adding methanol to the cell with the electrode stabilized at 500 mV; (2) steady-state polarization curves; (3) polarization curves corresponding to oxidation of species formed in the course of methanol-electrode contact. Our study demonstrates that the activity vs. electrode composition dependence has a maximum and exceeds significantly the activity of platinized platinum. The highest activity is achieved for 5–10 % ruthenium content, in agreement with the data on platinum—ruthenium alloys reported by other groups [5].

Potential shifts measured upon introduction of methanol are typical for electrooxidation of the reactant on the surface free of chemisorbed species. For 5% ruthenium, the potential shifts in the cathodic direction only slightly faster than for Pt/Pt. For 10% ruthenium, the potential shifts much faster, reaches  $\phi_r \sim 30\text{—}40$  mV after ca. 1 h, and continues to decrease with 0.1 mV/min rate, whereas for a Pt/Pt electrode the potential reaches only 80—100 mV after 1 h [9]. For the electrode with 23% Ru, the potential decay remains virtually the same; however, the potential of 30% ruthenium shifts very slow in the cathodic directions, and after 1 h reaches only  $\sim 200$  mV. There is practically no methanol-induced potential shift for ruthenium electrodes both in acidic, and alkaline solutions, i.e. there is no evidence of methanol oxidation on ruthenium in the potential range under study. The same conclusion follows from polarization curves measured in methanol-containing solutions on ruthenium electrode.

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<sup>#</sup> Charging curves is a notion used in the Russian literature for potential versus charge curves under galvanostatic polarization (translator's note).

<sup>@</sup> “Adsorbed gases” (direct translation) should be referred to hydrogen and oxygen adatoms, i.e. the products of hydrogen and oxygen gases chemisorption (translator's note).

<sup>@@</sup> “Quantity of adsorbed hydrogen” makes sense of the total charge in the hydrogen adsorption region (translator's note).

Steady-state polarization curves correspond to electrooxidation on a surface the coverage of which with chemisorbed species remains unchanged. Figure 2 shows steady-state curves of Pt/Pt and Pt—Ru (9:1). Methanol oxidation overvoltage in 0.5 M H<sub>2</sub>SO<sub>4</sub> is ca. 150 mV lower for Pt—Ru (9:1) as compared with Pt/Pt. The Tafel slope is found to be ~60 mV for Pt and ~50 mV for Pt—Ru. The steady-state polarization curves of Pt—Ru practically coincide in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH, whereas for Pt/Pt the overvoltage is significantly lower in alkaline solution and the Tafel slope equals ~85—100 mV. For Pt—Ru, the overvoltage at 2.5 mA/cm<sup>2</sup> in 1 M KOH is 60—70 mV lower than for Pt/Pt.

Figure 3 presents chronopotentiograms of oxidation of chemisorbed species formed under electrode polarization in methanol-containing solutions. Data for Pt—Ru (9:1) and Pt/Pt are compared. One can notice essential difference which concerns the initial oxidation potentials, the whole oxidation range, and to the potentials at which the oxidation is completed. The overvoltage corresponding to the oxidation of chemisorbed species in 0.5 M H<sub>2</sub>SO<sub>4</sub> is 200 mV lower for Pt—Ru as compared with Pt/Pt. The curves measured in acidic and alkaline solutions at Pt—Ru are very close to one another. Note that overvoltages of methanol oxidation from the solution bulk and oxidation of chemisorbed methanol are practically equal. This means that the rate of the former process is determined by the rate of removal of chemisorbed species.

Data presented above demonstrate that the kinetics of methanol oxidation at Pt—Ru (9:1) is much simpler as compared with platinized platinum.

In the conclusion, I'd like to acknowledge academician A.N.Frumkin, who proposed the topic, displayed systematic interest in this study, and supported it by valuable comments when discussing the experimental data.

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## FIGURE CAPTIONS

Fig. 1. Charging curves (dashed line designates cathodic branch) on Pt/Pt electrode (1), Pt—Ru codeposit for Pt:Ru =9:1 (2), Ru electrode (3) in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) and 1 M KOH (b). Current density  $10^{-4}$  A/cm<sup>2</sup>.

Fig. 2. Steady-state polarization curves of methanol electrooxidation on Pt (1) and Pt—Ru codeposit (2) in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) and 1 M KOH (b).

Fig. 3. Chronopotentiograms of oxidation of chemisorbed species formed under electrode polarization in methanol-containing solutions for Pt/Pt (1) and Pt—Ru (1:9) (2) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) and 1 M KOH (b). Dashed line – direct branches of charging curves (Fig. 1).