STUDY OF ADSORPTION PHENOMENA ON PLATINUM BY THE POTENTIOSTATIC METHOD

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References [1-4] deal with the specific adsorption of cations on the properties of platinum. Combination of different methods (charging curves, adsorption potentials, and labeled atoms) revealed a specific relation between the electrode potential and the amount of specifically adsorbed cations and hydrogen. However, these methods did not provide information on the effects of cations on the qualitative state of the adsorbed gases.

To elucidate this problem we used a new nonstationary potentiostatic method [5]. The measurements were performed on a platinized Pt electrode with visible surface 2 cm^2, on which 0.195 ± 0.003 g of platinum was deposited. The solutions of sulfuric acid, zinc, cadmium, and thallium sulfate were prepared from reagents of cp grade in doubly distilled water and were further purified on a large Pt electrode at 0.5-0.6 V in a current of argon [6]. The (U, φ) curves were recorded at potential 0.06-1.2 V (relative to a reversible hydrogen electrode in the same solution) in a current of argon at 28, 40, and 60°C at sweep rate 18 mV/sec on a TsLA PE-5611 potentiostat (made in the USSR).

Figure 1 plots (I, φ) anode curves for 1 N sulfuric acid and zinc sulfate solutions at 28°C. In sulfuric acid the curve has a characteristic appearance [5, 8]. The hydrogen part of the curve (0.06-0.4 V) has two maxima at 0.18 and 0.3 V, characterizing hydrogen adsorbed on different faces of the platinum. The heights of the maxima indicate that the amount of hydrogen with high bond energy on the platinum is much less than that with medium bond energy. In the double-layer region the current falls markedly and the curve is parallel to the x axis (0.4 to 0.8 V), after which we observe evolution of oxygen.

In the presence of 0.01 N $ZnSO_4$ the shape of the (I, φ) curve is practically unchanged, but the heights of the maxima in the hydrogen and oxygen sectors decrease. A further increase in the zinc sulfate concentration (0.1-1 N) distorts the curve shape in the hydrogen part. At potential 0.12 V we observe a new step, which indicates the appearance of weakly combined hydrogen on the modified surface of the platinum. In our opinion, the maximum at 0.12 V is due to molecularly adsorbed hydrogen, weakly linked to the surface, so that its atomization is impeded. Simultaneously the current maximum at 0.18 V falls markedly and is displaced by 0.02 V towards the positive side, whereas the height of the peak at 0.3 V even increases in comparison with the curve in 0.01 N $ZnSO_4$. This increase is probably due to superposition of the current consumed on Zn desorption on the hydrogen ionization current. In 1 N $ZnSO_4$ this effect is even more marked.

The (I, φ) curves, recorded in cadmium sulfate solutions, exhibit a new current maximum in the double-layer region at 0.7 V, corresponding to ionization and desorption of cadmium, specifically adsorbed on the platinum (Fig. 2). In [3] Balashova and Kazarinov showed by the labeled atoms method that cadmium is completely desorbed at 0.8 V. The fact that cadmium desorption takes place as an electrode process indicates its atomic state on the Pt surface and confirms our hypothesis that the cations are discharged during their specific adsorption on metals of the Pt group.

With an increase in the cadmium sulfate concentration to $5 \cdot 10^{-2}$ and 10^{-1} N, the (I, φ) curves are markedly distorted. The hydrogen sector contains only one small peak at 0.18 V, indicating the presence of hydrogen. The nature of the second hump at 0.35 V is probably due to desorption of cadmium, which begins at potentials more positive than 0.2 V. The curves therefore do not have a distinct double-layer region, and Cd desorption occurs throughout (its rate depending on the potential). This characterizes the energetic nonuniformity of the adsorbed cadmium.

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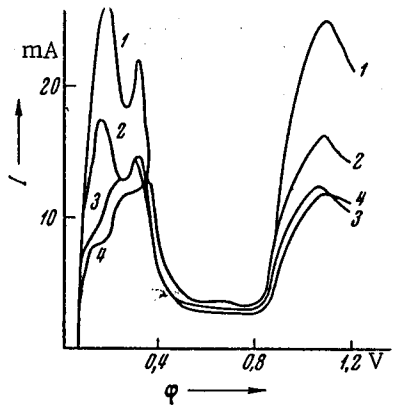

Fig. 1. Potentiostatic curves of a platinized Pt electrode at 28° in zinc sulfate solutions: 1) 1 N H_2SO_4; 2) 10^{-2} N $ZnSO_4$ + 1 N H_2SO_4; 2) 10^{-1} N $ZnSO_4$ + 1 N H_2SO_4; 4) 1 N $ZnSO_4$ + 1 N H_2SO_4.

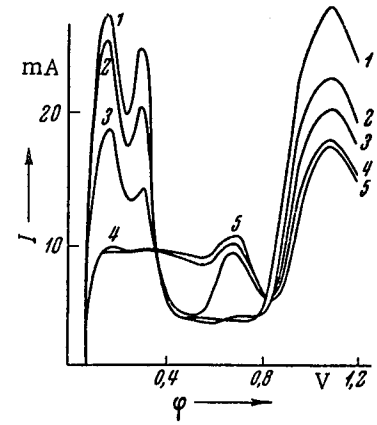

Fig. 2. Potentiostatic curves of platinized Pt electrode at 28°C in cadmium sulfate solutions: 1) 1 N H_2SO_4; 2) 10^{-3} N $CdSO_4$ + 1 N H_2SO_4; 3) 10^{-2} N $CdSO_4$ + 1 N H_2SO_4; 4) $5 \cdot 10^{-2}$ N $CdSO_4$ + 1 N H_2SO_4; 5) 10^{-1} N $CdSO_4$ + 1 N H_2SO_4.

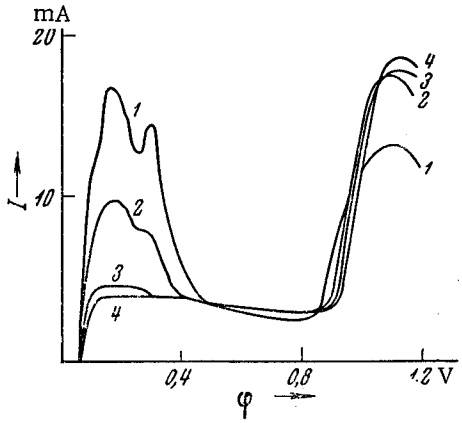

Fig. 3. Potentiostatic curves of platinized Pt electrode at 28°C in thallium sulfate solutions: 1) 1 N H_2SO_4; 2) 10^{-3} N $TlSO_4$ + 1 N H_2SO_4; 3) $5 \cdot 10^{-3}$ N Tl_2SO_4 + 1 N H_2SO_4; 4) 10^{-2} N Tl_2SO_4 + 1 N H_2SO_4.

The specific adsorption of the cations also greatly reduces the amount of adsorbed oxygen.

Figure 3 plots the (I, φ) curves obtained in 1 N H_2SO_4 and acid solutions of thallium sulfate at 28°. The reader will see that in the presence of 10^{-3} N Tl_2SO_4 the amount of adsorbed hydrogen is virtually halved, and in 10^{-2} N Tl_2SO_4 decreases almost to zero. In the oxygen sector the current maximum increases markedly in comparison with 1 N H_2SO_4 because in this sector the currents consumed on thallium desorption and on oxygen desorption are added together. Therefore modification of the Pt surface by specifically adsorbed cations leads to increasing nonuniformity of the adsorbed hydrogen, with an accompanying increase in the amount of molecular weakly-combined hydrogen and a reduction in that of strongly bonded hydrogen. Note that adsorption of cadmium and thallium takes place primarily on the most active Pt centers; this leads mainly to a decrease in the peak at 0.3 V, characterizing the hydrogen with maximum bond energy. In the case of zinc we observe a marked reduction of the maximum at 0.18 V, i.e., Zn adsorption takes place on the medium-active centers.

LITERATURE CITED

1. A. D. Obrucheva, ZhFKh, 32, No. 9, 2155 (1958); Dokl. Akad. Nauk SSSR, 120, No. 5, 1072 (1958).
2. A. N. Frumkin, Advances in Electrochemistry and Electrochemical Engineering, Vol. 3, New York-London (1963).
3. N. A. Balashova and V. E. Kazarinov, Usp. Khim., 34, 10, 1721 (1965).
4. G. D. Zakumbaeva and D. V. Sokol'skii, "Liquid-phase hydrogenation catalyst," Tr. Inst. Khim. Nauk AN KazSSR, 14, "Nauka" (1966).
5. F. C. Will and C. A. Knorr, Zs. Electrochem. Ber. Bunsenges Phys. Chem., 64, 258 (1960).
6. R. V. Marvet and O. A. Petrii, Élektrokhimiya, 3, 5, 591 (1967).
7. D. V. Sokol'skii, Vestn. Akad. Nauk KazSSR, No. 11, 47 (1951).
8. M. W. Breiter and B. Kennel, Zs. Electrochem., 64, 10, 1180 (1960).