STUDY OF ELECTRODE REACTIONS BY THE USE OF TRIANGULAR VOLTAGE PULSES IN CONJUNCTION WITH A ROTATING DISC ELECTRODE AND A RING

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A rotating disc electrode with a ring has been used with triangular voltage pulses to examine the reduction mechanism for surface oxides on platinum and the ionization of molecular oxygen.

It has been reported [1-3] that oxidation of platinum in anodic polarization requires a larger charge than does the corresponding reduction, which has been explained in terms of the reduction of the surface oxides to hydrogen peroxide [1, 2]. The reduction of these oxides is examined in detail here.

It has been shown recently [4-6] that a rotating electrode can be used in kinetic studies on electrode reactions. The method we have used is as follows. A smooth platinum disc 0.6 cm in diameter was supplied with triangular pulses of fixed amplitude at a controlled rate. A lightly platinized ring (internal diameter 0.65 cm, external 0.82 cm) was kept at 1.2 V (oxidation potential of hydrogen peroxide). The current associated with the reduction of surface oxide when the rate of rise of voltage on the disc is 10 V/sec should be comparable with the current arising from the ionization of molecular oxygen when the disc rotates at 2000-2500 rpm. Nekrasov and Myuller [5, 6] have shown that the hydrogen peroxide made by reduction of molecular oxygen at the disc is readily detectable at the ring; so the current to the ring should be 6-7 μA if only 1% of the surface oxide is reduced to hydrogen peroxide, and this is just detectable by the disc-ring method. A rate of rise of 100 V/sec would raise this current to 100 μA, and this is readily measured.

The tests were done with KOH (0.1 or 1 N) and N H_2SO_4.

Triangular pulses (100 v/sec) of variable amplitude (extreme cathode value of 0.1 V, anode value between 0.9 and 1.5 V) gave no detectable hydrogen peroxide in an argon atmosphere. Disc speeds up to 6000 rpm were used. One might expect the hydrogen peroxide to be oxidized if it were formed under these conditions if the anode potential were to attain the point on the i vs. φ curve corresponding to that oxidation; but calculation indicates that the time needed for the hydrogen peroxide to migrate from disc to ring at 6000 rpm is about 10^{-3} sec, whereas the duration of a pulse of range 0-1 V with a rise rate of 100 V/sec is 10^{-2} sec.

It is thus clear that the reduction of oxygen chemisorbed on platinum does not give rise to hydrogen peroxide. This compound was also not detected when the amplitude was raised to 2 V, i.e., to the point at which the compound can be formed by oxidation of water.

The above method can also be used to examine the effects of the state of the surface on the kinetics of the reduction of oxygen, because the oxidizing capacity can be adjusted via the extreme anode value of the pulse.

We have examined the effects of this oxidizing capacity on the amount of hydrogen peroxide formed by ionization of molecular oxygen. Figure 1 shows the relation of ring current to pulse height for a rise rate of 100 V/sec (abscissa anode value of height, extreme cathode value 0.1 V, potential relative to hydrogen electrode in same solution). The ring current was measured 5 min after applying the pulses to the disc.

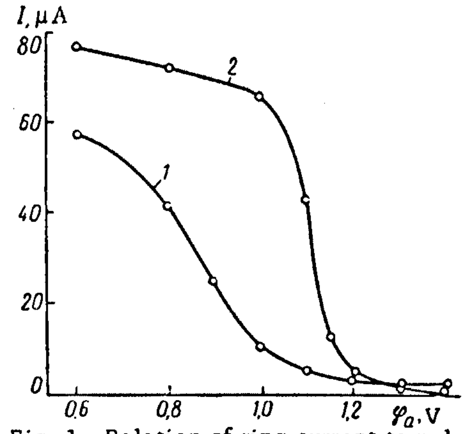

Fig. 1. Relation of ring current to pulse height for a speed of 2250 rpm. 1) 0.1 N KOH; 2) N H_2SO_4.

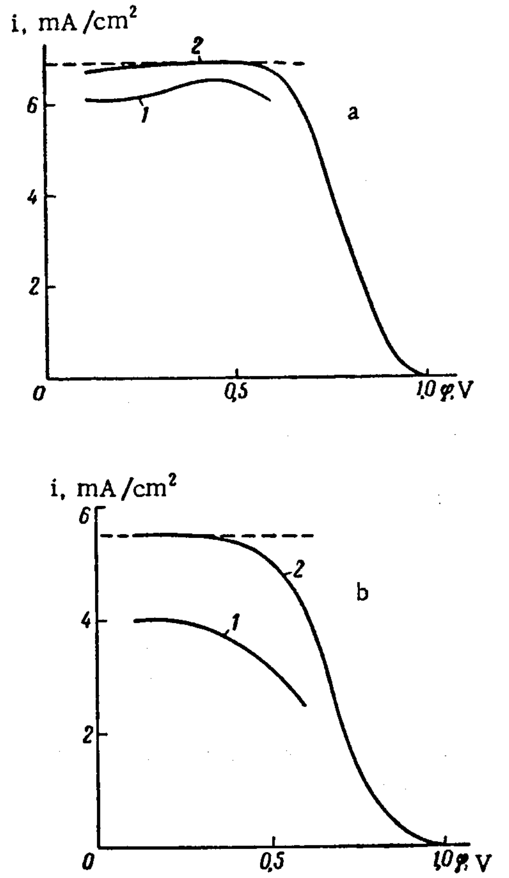

Fig. 2. Polarization curves for the reduction of molecular oxygen; a) 0.1 N KOH; b) N H_2SO_4. Pulse amplitudes: 1) 0.1-0.6 V; 2) 0.1-1.2 V.

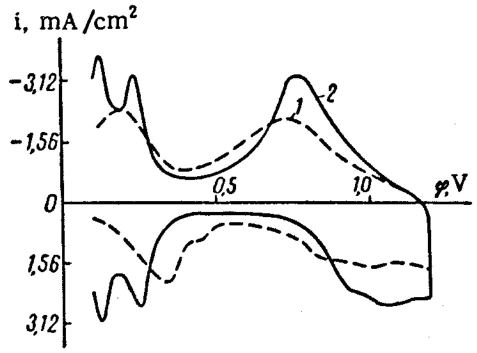

Fig. 3. i vs. φ in argon for rise rates of 1 V/sec: 1) 0.1 N KOH; 2) N H_2SO_4.

Figure 1 shows that the ring current falls as the oxidizing cappacity (anodic amplitude) increases, no matter whether the medium is acid or alkaline. The same result was obtained at lower rise rates. The limiting current at the disc increased with the anode value of the pulses (Fig. 2a and b). The results indicate that the amount of hydrogen peroxide is lowered and show that the second stage in the ionization of oxygen is accelerated by the surface oxides, which is in agreement with the published evidence [5].

The Levich-Ivanov formula [7] for the ring-disc system shows that the ring detects 40% of the hydrogen peroxide formed at the disc;, this enables us to correct the cathode curve for the reduction of oxygen. Correction of the curves of Fig. 2a for the current corresponding to the unreacted hydrogen peroxide (e.g., by 0.1 V) gives the limiting diffusion current for the ionization of molecular oxygen (a four-electron process); similar results have been derived for curve 2 of Fig. 2b. The disc current in the case of curve 1 of Fig. 2b is partly of kinetic type, perhaps on account of anion effects; it requires further examination.

Curves 1 and 2 of Fig. 1 are markedly different. The ring current in the acid medium falls only very slightly when the extreme anode potential is raised from 0.6 to 1.0 V, but further increase in that potential causes a sharp fall in the amount of hydrogen peroxide detected at the ring; whereas 0.1 N KOH gives a gradual fall in ring current as the anode potential is raised from 0.6 to 1.2 V. The curves of i vs. φ in Fig. 3 (for argon) confirm what has often been shown before, namely that the electrode becomes oxidized earlier in alkali, which is probably responsible for the difference in the relation of current to pulse height for acid and alkaline media.

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