IONIZATION OF HYDROGEN ON A SECTIONAL AND ROTATING ELECTRODE IN SULFURIC ACID

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With ionization of molecular hydrogen on platinum in acid solutions, the polarization curves display limiting currents of order 2-5 mA/cm^2, and in some cases maxima which, under different experimental conditions (solution composition, state of the platinum surface, speed of mixing), may be due either to diffusion or kinetic limitations [1-5].

On a semiimmersed electrode the diffusion limitations may be partly removed [6]. Assuming, in accordance with data of Will [6], that the bulk of the current is generated in a thin film of electrolyte above the meniscus at a distance of approximately 3 mm, Povarov and Lukovtsev [7] calculated that the true current density in the film is approximately 6.4 mA/cm^2.

The aim of our work was direct measurement of the true current density on smooth platinum in the film zone and comparison of the results with data obtained for a rotating electrode under the same experimental conditions.

EXPERIMENTAL

We used a rotating electrode (720-9400 rpm) and a cell of usual type with a hydrogen comparison electrode. The working electrode was a platinum wire of diameter 1 mm (the metal was of "Ékstra" grade), sealed into a glass tube of external diameter 5 mm. The electrode was made S-shaped (at about 10 mm from the lower end it was bent at 90° away from the axis of rotation, then bent back at 90° in a plane perpendicular to this axis). In absence of rotation the ground end of the tube, perpendicular to the electrolyte surface, was used as a sectional electrode, placed in different zones of the film, because, depending on the electrolyte level, the meniscus may be formed either on the glass (above or below the platinum) or at the level of the platinum [8].

The feed conditions of a substance to disc electrodes of different configurations (including S-shaped electrodes) were studied by Nekrasov [9], who showed that, at the same rate of rotation of the pulley, an S-shaped electrode makes mixing several times more effective than an ordinary disc electrode.

To establish the coefficients relating the measured number of rotations of an S-shaped electrode to the effective velocity (i.e., the nominal rate of rotation of an ordinary disc electrode, leading to the same conditions of convective diffusion), we plotted the cathodic polarization curves in a solution of 0.0097 N H_2SO_4 + 0.1 N K_2SO_4. The experimental values of the limiting currents and the knowledge of all the values in the Levich equation ($\nu = 1.2 \cdot 10^{-2}$ cm^{2}sec^{-1}, $D = 2.05 \cdot 10^{-5}$ cm^{2}sec^{-1}) enabled us to find the effective rates of rotation. It was found that $m_{ef} \cong 7m_{pul}$. Up to a pulley speed of about 3000 rpm (corresponding to a Reynolds number of about 30,000) the measured value of the limiting current was proportional to $m^{1/2}$. At a pulley speed greater than 3000 rpm, which corresponded to effective speeds greater than 20,000 rpm, laminar mixing was impaired, so higher speeds could not be used.

Preparation of the electrode consisted in grinding with fine emery paper, etching in nitric acid or hot sulfuric acid, and repeated washing in doubly distilled water. We also performed individual experiments in which the electrode was pretreated with permanganate (by the Yeager method [4]) or by preliminary cathodic polarization at a current density of 3 mA/cm^2 [3]. The electrode roughness factor was determined from

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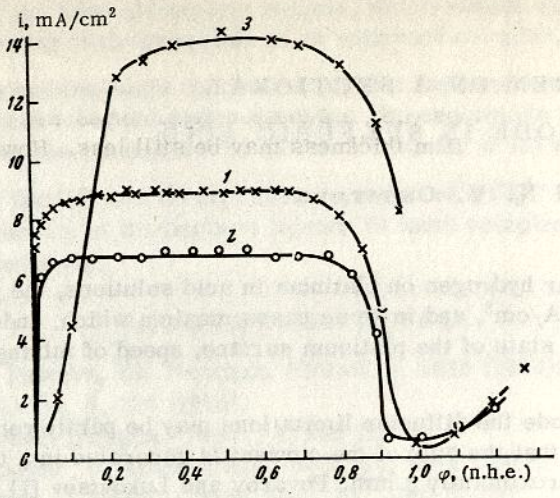


Fig. 1. Hydrogen ionization current versus potential in 1 N H_2SO_4 on a rotating S-shaped electrode (1 m_{ef} = 20,000 rpm, 2 m_{ef} = 11,600 rpm) and on a sectional electrode (3).

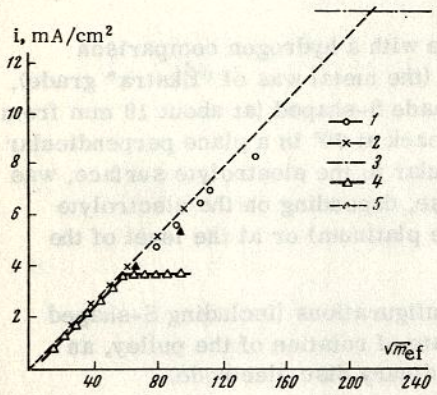


Fig. 2. Limiting hydrogen ionization current versus $\sqrt{m}$ in 1 N H_2SO_4: 1) S-shaped electrode; 2) ordinary disc electrode; 3) sectional electrode; white triangles data of Aikazyan [1]; black triangle data of Yeager [4].

hydrogen adsorption by the potentiodynamic method by a TsLA oscillographic polarograph (model 02A) at a potential application rate of 20 V/sec.

The electrolyte was 1 N H_2SO_4, twice distilled after purification by cathodic polarization for a day. The criterion of solution purity was the absence of a fall in the maxima on the potentiodynamic charging curves at 0.4-0.0 V for not less than 5 min. The temperature was −20°C. When we plotted the hydrogen ionization potentiostatic curves, before each point was obtained standard activation was performed: 30 sec at 1.2 V (n.h.e), 30 sec 0.0 V (n.h.e), with residence for 3 min at the given potential.

RESULTS AND DISCUSSION

A. Rotating Electrode. To compare the experimental and literature data, we assessed the electrode activity $1/R_\eta$, i.e., the ratio of cathode density to polarization at very low polarizations ~10-15 mV. The value of R_η was 2.36 Ω/cm^2, i.e., the same as in [1].

The character of the polarization curves on a rotating electrode (Fig. 1) coincides with that of the curves in [2, 4], i.e., there is a marked rise in the current at potentials up to 0.050 V and a fall at 0.850-1.1 V, followed by a gradual rise due to evolution of oxygen. Despite the indirect method of determining the effective electrode rotation rates, the limiting currents at the different rotation rates lie on the calculated curve of i versus $k\sqrt{m_{ef}}$ up to m_{ef} = 20,000 rpm (Fig. 2).

With the exception of cathodic treatment, the different methods of surface preparation had no effect on the curves. Electrodes subjected to prolonged cathodic polarization (5-8 h) displayed a marked fall in activity and instability of the values at potentials less than 0.050-0.100 V; the fall on the polarization curves, observed in [1, 2], was absent in every case. The authors of [1, 2] apparently used very reduced platinum, which explains the marked effect of the anions and impurities [3]. However, this assertion requires more precise definition.

In addition to data obtained on a S-shaped electrode, for this comparison we used a number of polarization curves for three disc electrodes of normal shape. The shapes of the curves were the same and the experimental points of the i, $k\sqrt{m}$ curve lie on the calculated curve throughout the range of m values from 720 to 9400 rpm.

B. Sectional Electrode. When rotation of the electrode was stopped and the solution level gradually fell, at a specific position of the meniscus we obtained current values which greatly exceeded the maximum values obtained at m_{ef} = 20,000 rpm (Fig. 1, curve 3). With extrapolation of the maximum current density of 14 mA/cm^2 at 0.500 V on to the calculated curve, we find that this current corresponds to a mixing speed of about 50,000 rpm and to a film thickness (i.e., a diffusion layer) of about $3 \cdot 10^{-4}$ cm. If kinetic limitations have a partial effect at this current, the film thickness may be still less. However, bearing in mind the purely diffusion character of the limiting current up to m_{ef} = 20,000 rpm, we can assume that the kinetic current during hydrogen ionization on platinum must greatly exceed that obtained on a sectional electrode. This shows that we can obtain very high current densities on smooth platinum at 0.3-0.7 V. At the same time, the shape of the polarization curve on the sectional electrode indicates marked ohmic losses in the film, which are absent on the disc electrode. In our experiments we determined the roughness factor; it was ~2. Under these experimental conditions the maximum current is limited by diffusion, not by kinetic factors, so the results must be independent of the roughness factor (within certain limits, at least). This agrees with data in [1, 6] and is also confirmed by measurements on platinized electrodes with roughness factors of 15 and 1600. On the first electrode the maximum current does not differ from the current on a smooth electrode; on the second electrode the maximum current (without rotation) increases to 25 mA/cm^2 (on the visible surface), probably owing to the appearance of marked roughness, comparable with the thickness of the diffusion layer.

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