

ON THE MECHANISM OF THE ELECTRO-OXIDATION OF *n*-PROPANOL

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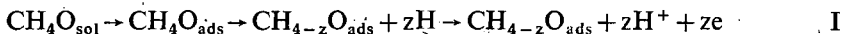
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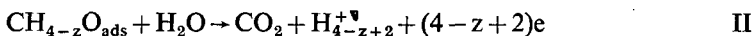
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It is concluded from the potential dependence of the non-stationary current of the electro-oxidation of *n*-propanol that the mechanism is changing with the potential. Further experimental work is in progress.

During the investigations carried out for studying the electrochemical oxidation of alcohols, methanol, one of the most promising fuel for cells, has been used [1—4]. It has been shown that, on Pt electrodes in acid solution, the oxidation takes place in two main successive steps. The first one is the process



in which slow adsorption is followed by fast dissociation and the oxidation of H atoms. The second step



is the oxidation of adsorbed particles containing C atoms, in which the water-discharge reaction



is regarded as the rate determining step (5). Both reactions are irreversible.

When the electrode comes into contact with methanol, step I occurs producing a non-stationary current until the surface coverage of organic substance, Θ , reaches its steady-state value. The rate of step II is increasing with Θ , in steady-state the rates of steps I and II are equal.

It was found [1, 2] that the kinetics of methanol adsorption can be described by the ROGINSKY—ZELDOVICH equations, which apply to an inhomogeneous adsorbent surface with a uniform distribution of the adsorption energies of the adsorption sites. As regards the composition of adsorbate, the opinions of various authors differ considerably. From his adsorption measurements, BAGOTZKY came to the conclusion that the adsorption product is a three-site bounded COH particle [1, 2]. BIEGLER [3] claims that the adsorption product can be both two-, and three-site bounded species and that its composition changes with the potential. BREITER [6]

assumes the possibility of the formation of species containing two carbon atoms as well.

Recently we have begun the investigation of the mechanism of adsorption and oxidation of *n*-propanol and related compounds. Assumably, with *n*-propanol not only the C—H but also the C—C bond will brake up similarly as in the case of propane [7].

Preliminary measurements were carried out on a smooth Pt electrode in unstirred 1 N NH_3PO_4 solutions with different propanol concentrations; the solutions were prepared from AR grade reagents and triply distilled water and were deoxygenated by CuO-purified N_2 . The temperature was maintained at 60 °C. The cell used was a conventional H-type one. The potentials are referred to NHE.

After applying the potential sequence given in Fig. 1, the electrode potential was switched to φ_{ox} , bringing about a decrease in the intensity of the current due to step I. If we plot $\lg i$ vs. $\lg t$, we get a slope of $\sim -0,3$ for the first ~ 100 s (Fig. 2).

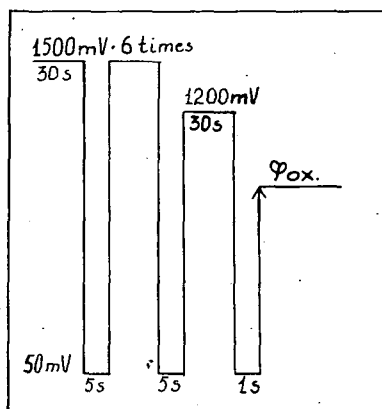


Fig. 1. Potential steps applied at the pretreatment of electrodes

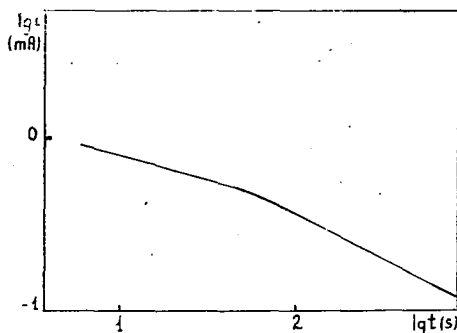


Fig. 2. Current-time behaviour at $\varphi_{\text{ox}} = \text{const}$

This value conforms to the kinetics of adsorption taking place on a surface with a logarithmic distribution of the adsorption energies of the adsorption sites [8]. Accordingly, the relationship between Θ and the adsorption time t is

$$\Theta = At^{\frac{1}{n\alpha}} \quad (1)$$

where A , n , and α are constants, $\alpha \approx 0,5$. The current is controlled by the rate of adsorption

$$i = k \frac{d\Theta}{dt} = k' t^{\frac{1}{n\alpha} - 1}, \quad (2)$$

and thus

$$\lg i = \lg k' + \left(\frac{1}{n\alpha} - 1 \right) \lg t. \quad (3)$$

For the slope we get

$$\frac{1}{n\alpha} - 1 = -0,3$$

and

$$n \approx 3,$$

Over ~ 100 s, the electrical charge Q , flowing through the electrode during time t and at potential φ might be defined formally as

$$Q = B \exp\left(\frac{z\beta F}{vRT}\right) \sqrt{t} \quad (4)$$

if it is controlled by the diffusion. In equation (4) B represents the diffusional parameters, z is the charge transfer for the overall reaction, v is the stoichiometric factor.

On determining the $m = B \exp\left(\frac{z\beta F}{vRT}\right) \varphi$ values from the $Q - \sqrt{t}$ diagram obtained from the experimental data at different potentials, and plotting their logarithms against φ_{ox} , we should get a straight line provided that B and z/v are constants, from the slope of which the z/v ratio can be calculated.

This expected line appears between 600–800 mV with a slope of 2 (Fig. 3). Thus

$$\frac{2,3z\beta F}{vRT} = 2$$

and if $\beta = 0,5$ we get

$$v = 18z.$$

This ratio is equal to the number of electrons released during the oxidation of one propanol molecule to CO_2 .

The potential range of 600–800 mV is in the double-layer region, where the whole surface is free and suitable for adsorption and oxidation. Assuming the alcohol concentration gradient to be the same in the whole potential range investigated, the decline of the curve at lower potentials might be attributed to (i) the decrease in the ability of the surface for adsorption and oxidation, (ii) the decrease and increase in the values of z and v , respectively. The decrease in the value of z might be in connection with the formation of end-products different from CO_2 .

Above 800 mV, the steep rise observable on the curve could, however, be brought about by the increase in surface area or by the decrease and increase in the values of v and z , respectively. Since in this potential range the ability of the surface for adsorption decreases due to the oxygen/hydroxide adsorption, and since the z value given above is the largest possible, the rise above 800 mV might be related to the decrease in the value of v . If this is the case, we should assume that another reac-

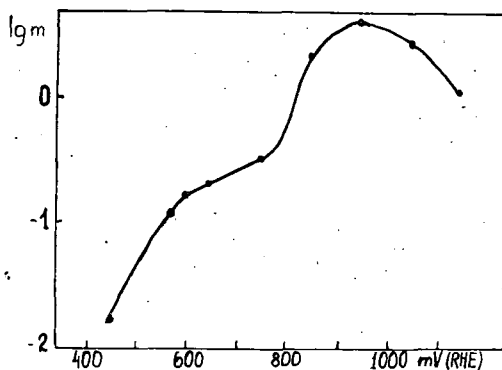


Fig. 3. Dependence of $\log m$ on φ_{ox} , [alc.] = 0,5 M. The shapes of curves have been found similar at 0,25, 0,1, and 0,04 propanol concentrations

tion will play the role of the rate determining step different from than that at lower potentials. Above 1000 mV the adsorption of organic substance greatly diminishes due to the increase in oxygen coverage [1, 2].

Investigations are in progress to determine the mechanism of adsorption and oxydation.

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О МЕХАНИЗМЕ ЭЛЕКТРООКИСЛЕНИЯ *n*-ПРОПАНОЛА

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На основе зависимости нестационарного тока от потенциала было заключено, что механизм окисления *n*-пропанола изменяется с потенциалом. Экспериментальная работа продолжается.