

# HYSTERESIS AND INHIBITION EFFECT IN THE ANODIC OXIDATION OF *n*-PROPANOL

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Experimental results are presented demonstrating a change in the inhibition effect of sorbate and its relation to the hysteresis of the current *vs.* potential curves.

In the study of the electrochemical transformation of organic compounds the determination of current *vs.* potential relationships is of essential importance. This determination generally encounters difficulties in the case of organic substances in comparison with inorganic redox systems, owing to the fact that in organic electrochemical processes the sorption of intermediates and/or products takes place, which can hardly be controlled. Therefore, the effect of sorption on the kinetics of reaction too can be determined only with difficulty. The experimental approach is not always clear enough to meet these difficulties and the reproducibility of the various results is not sufficient. In many cases it brings about such phenomena as the hysteresis of the potential *vs.* current curves, which unambiguously shows the need to get a better understanding of the change in the sorbed layer and its effect on the current-generating process.

As an example, in this paper some features which might lead to the hysteresis of current *vs.* potential curves are discussed for the anodic oxidation of *n*-propanol.

## *Experimental*

The equipment was the same as previously described [1]. The working electrode was a platinum disc of 0.8 cm<sup>2</sup> geometric area, with a roughness factor of 4.75. It was rotated at 1000 rpm. Measurements were carried out in 1 mol dm<sup>-3</sup> HClO<sub>4</sub> solution. As reference, a hydrogen electrode in the same solution was used. *n*-Propanol of analytical purity was distilled under a reduced nitrogen atmosphere and its purity was checked by gas-chromatography. Perchloric acid of Merck "Suprapur" grade was used. The triply-distilled water was redistilled pyrolytically [2] in a system attached to the cell.

The coverage values of the electrode were determined from the change in hydrogen capacity measured by means of cathodic potential sweeps at a rate of 20 V s<sup>-1</sup>.

### Results and discussion

It is known that the strong sorption of primary alcohols is an irreversible process, and the sorbed species may not be considered as intermediates of the catalytic alcohol — aldehyde transformation [3—6].

The change in current with the growth in the amount of adsorbate can be illustrated by the current *vs.* coverage curve taken at  $E=0.4$  V (Fig. 1). It can be seen that the kinetic pattern of the time-dependence of the current does not change even over a relatively large time range (curve *a*).

After a certain period of time (700 s), if the potential is switched from 0.4 V to more positive values, the resulting current *vs.* coverage relationships at the new potentials follow the pattern shown in Fig. 2. These curves reveal that the current is not only influenced by the change in the amount of sorbed species.

The situation is similar if the change in potential is the same, but the starting value of the coverage ( $\theta^0$ ) is different before the potential step (Fig. 3). It can be seen that the current *vs.* coverage curves have two regions well distinguishable from each other. Those regions where the decrease in coverage occurs can not be considered as "stationary", although the current change in this period would imply so. These regions do not represent identical states, since at the same potential diffe-

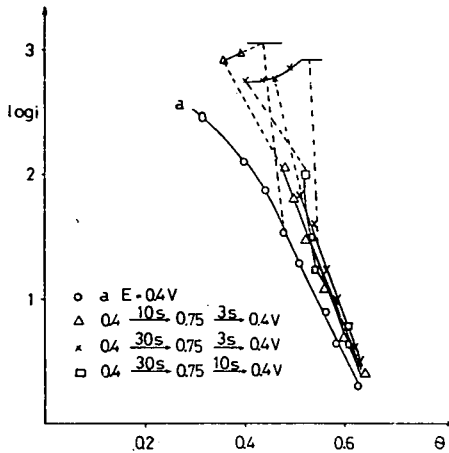


Fig. 1. Current *vs.* coverage relationships  
 $a - E=0.4$  V

$\Delta, \times, \square$  - during the potential sequences given in the Figure

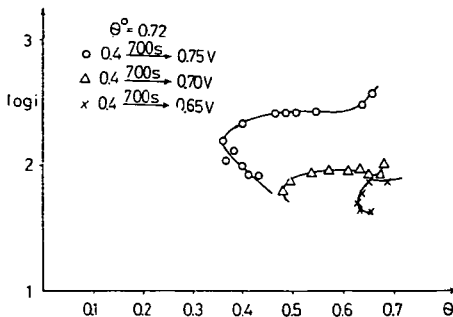


Fig. 2. Current *vs.* coverage curves after potential switchings from 0.4 V o — to 0.75 V,  $\Delta$  — to 0.70 V, X — to 0.65 V

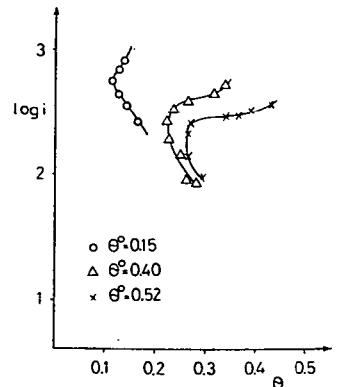


Fig. 3. Current *vs.* coverage relationships after potential switchings from 0.4 V to 0.75 V o — at  $\theta^0 = 0.15$ ,  $\Delta$  — at  $\theta^0 = 0.40$ , X — at  $\theta^0 = 0.52$

rent currents flow at the same value of the coverage, depending on the starting  $\theta^0$ .

On the basis of these observations, it is obvious that a polarisation curve recorded by means of the potential step method in the anodic direction, might show a hysteresis.

If the potential is switched back in the cathodic direction to 0.4 V, a similar difference arises (Fig. 1). At this potential no oxidation or reduction of sorbate takes place, as the charge required for its anodic oxidation is 1  $e/c$  in the whole range of sorption [7]. It follows that coming back to 0.4 V provides a conservation of the previous state of the surface. Thus, the difference in current at the same coverage might be attributed to the different inhibiting effect on the catalytic alcohol — aldehyde reaction. As Fig. 1 shows, the inhibition is smaller than without potential change.

In Fig. 4, the results in Fig. 1 are presented as a function of time. It can be seen that the effect is not temporary, showing that the substance formed at 0.75 V is indeed not converted back into its initial state at 0.4 V.

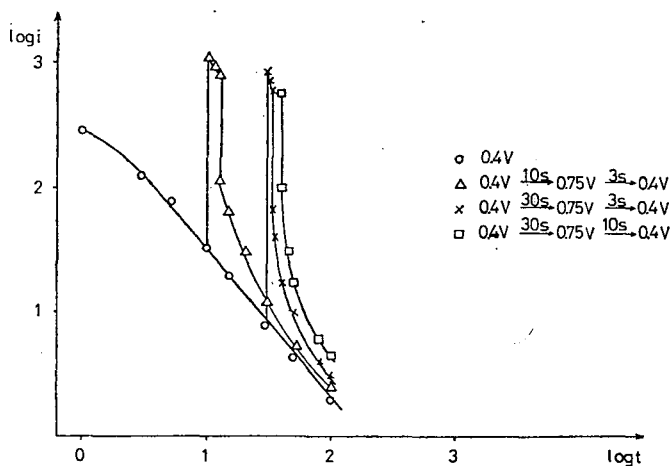


Fig. 4. Time-dependence of the current during the potential sequences given in the Figure

The reasons for the change in the inhibiting effect may be seen from measurements concerning the state of the sorbed species (Fig. 5). The oxidative desorption of the species at 0.75 V exhibits a constant charge/centre ratio, which is about 2—2.5  $e/c$ .

On the basis of all these observations, it may be concluded that

- the layer produced by oxidizing the adsorbate formed at 0.4 V shows a lower inhibition effect at 0.4 V than the original state does;
- these changes in inhibition might lead to the hysteresis of the current *vs.* potential curves generally observed in the electrochemical investigation of organic compounds.

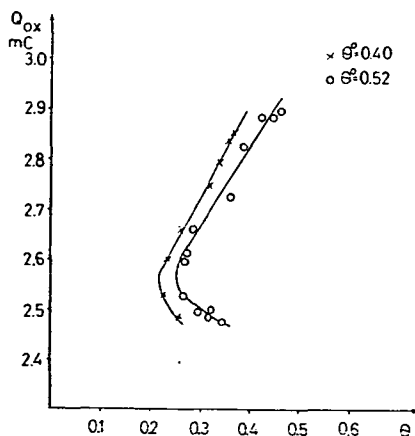


Fig. 5. Charges relating to the oxidation of sorbate as a function of coverage  
 X —  $\theta^{\circ}=0.40$ , o —  $\theta^{\circ}=0.52$

#### References

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#### ГИСТЕРЕЗИС И ИНГИБИРУЮЩИЙ ЭФФЕКТ В АНОДНОМ ОКИСЛЕНИИ *n*-ПРОПАНОЛА

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Представлены экспериментальные данные, показывающие изменения в ингибирующем действии сорбата и его связи с гистерезисом на кривых электрический ток — потенциал.