UNDERPOTENTIAL OXIDATION PEAK (UPO) AND POTENTIODYNAMIC EVALUATION OF KINETICS FOR ANODIC ALDEHYDE BEHAVIOR

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Introduction

A substantial question imposes whether the reversible peak of primary oxide (M-OH) growth and desorption really arises bonded for certain fixed potential, or as a highly fast reaction in both directions,

$$M + 2\,H_2O \Leftrightarrow M\text{-}OH + H_3O^+ + e^- \qquad (1)$$

can precede and exceed such value along potentiodynamic axis. Namely, in basic acidic and alkaline solutions such distinctly reversible peak arises quite fixed for constant potential values (Pt, Au. Ag). Meanwhile, it has been observed long ago[1] that anodic oxidation of aldehyde group and simple alcohols starts immediately after desorption of H-adatoms even within rather negative potentials and all along the double layer charging range. Thus, the scanning of entire voltammograms between hydrogen and oxygen evolving limits in the presence of simple and some specific aldehydes, as well as various mono saccharides on typical different electrode materials (Au, Pt, Pd, Ag, Ni) has been of substantial significance to assess some mechanistic questions and enter in the substance of some specific potentiodynamic occurrences.

Experimental

Experimental evaluation has been performed in typical three compartment glass cell on a common way of measurements, but the specific feature of solubility of many aldehydes and monosaccherides in aqueous media practically in all ratios, allowed a rather broad concentration range from 0.01 to 5 M and even higher contents to investigate the effect of the latter.

Results and Discussion

A rather broad ***underpotential oxidation peak*** (*UPO*) starts immediately after H-adatom desorption, and depending on aldehyde concentration, extends deep within anodic potential range, even shifts oxygen evolving limit and proceeds together with the latter (Fig. 1 and 2). At the beginning of cyclic voltammetry age this peak was usually named 'electrocatalytic'. However, every hold of potential scan at any point sharply leads to rather low values of currents characteristic for surface oxide growth. Such behavior is known from plentiful of the *UPD* scans in metal deposition, bears imprinted all such features and allows us to introduce such a new term (*UPO*) in potentiodynamic properties. Namely, any further recontinuation of potential scan, brings voltammogram typical for basic solution with irreversible oxide desorption, but after hydrogen adsorption and desorption, there again arises typical potentiodynamic spectra characterized by the *UPO* for aldehyde group. Since generation of M-OH (Eq. (1)) is a rather fast reaction, as long as there is enough mass-transfer aldehyde approach to the electrode surface, its consumption for the anodic oxidation, as a typical irreversible electrode process,

$$M\text{-}CHO + M\text{-}OH + H_2O \Rightarrow$$
$$\Rightarrow M\text{-}COOH + M + H_3O^+ + e^- \qquad (2)$$

extends longer along potential (time) axis. The reaction rate at rater high aldehyde contents delineates enormous peak values and behaves similarly as the spillover effect in heterogeneous catalysis. Stepwise scanned voltammograms (Fig. 3) clearly show the absence of surface oxide growth, and consequently, the irreversible oxide desorption reduces to rather small charge capacity areas. As the consequence of the latter, there arises clear and ***distinct renewable peak*** of anodic aldehyde oxidation even during the reverse cathodic scan towards hydrogen evolving limits.

Conclusions

In concluding remarks one can state that as long as there is enough consuming species (aldehyde, alcohol), M-OH is able immediately to oxidize them and prevent surface oxide growth until oxygen evolving limits and even further. The mechanism involves direct anodic oxidation (Eq. (2)) of available species, but this is a typical ***dynamic*** process, which immediately ceases under steady state conditions, when O-adatoms at potentials of their molecular evolution, finally become available for their oxidation. On the contrary, as long as there is present even a submonolayer oxide coverage, anodic aldehyde oxidation ceases.

References

1. R. R. Adzic, A. V. Tripkovic, i W. E. O'Grady, ***Nature***, **296**, 137 (1982).

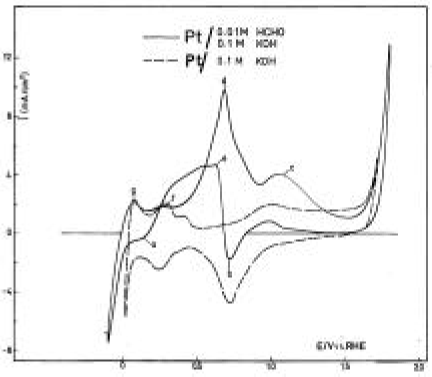

Fig. 1, 2 & 3. Cyclic voltammograms of Au and Pt in alkaline solutions of formaldehyde and manose.