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Conference Note (Invited)

The Crystallographic Orientation and Surface Modification Effects in Electrocatalysis*

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INTRODUCTION

A paramount role of surface structure and composition on the kinetics of electrocatalytic reactions has been realized with the establishment of electrocatalysis as a science. Consequently, a variation in the surface structure, and a modification of surface composition is expected to result in a considerable alternation of the electrocatalytic properties of electrodes. Reliable data on the role of surface structure have not been obtained until recently in the work with the single crystal surfaces. The effect of crystallographic orientation of electrode surfaces on kinetics of electrochemical reactions has been definitely established in the oxidation of small organic molecules¹⁻⁴ and oxygen reduction^{5,6} on well-prepared single crystal surfaces. A modification of surface properties by foreign metal adatoms, obtained by the underpotential deposition, has been shown to produce striking catalytic effects on various electrode reactions (Ref. 7 and references therein). This is a simple way to modify surface properties, which may have an applicative potential.

Oxidation of Organic Molecules

The oxidation of HCOOH^{1-4} , $\text{CH}_3\text{OH}^{2,4}$ and $\text{HCHO}^{2,4}$ on Pt shows a pronounced dependence on the symmetry of surface atoms. It has been emphasized that not only kinetics, but also the mechanism of the oxidation of HCOOH , depend on the surface structure. The Pt(111) surface showed the highest activity for the oxidation of HCOOH , because it is not blocked by

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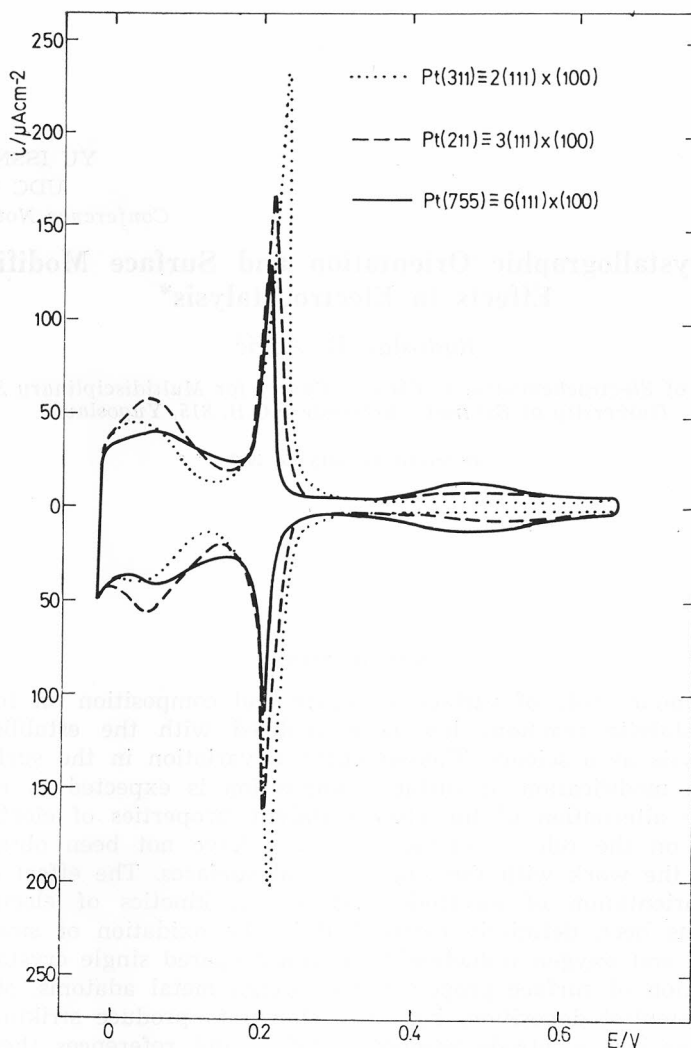


Figure 1. Hydrogen adsorption on platinum single crystal stepped surfaces in 0.05 M H_2SO_4 showing the role of the step density. Sweep rate 50 mVs^{-1} .

strongly bound intermediates. The other two surfaces, the Pt (100) and Pt (100) are totally blocked up to 0.9 V and 0.8 V respectively. Upon activation, they show higher activity than the (111) face. Unfortunately, that activity has no practical significance. Similar conclusions pertain to the behaviour of the other two molecules.

Most recently, this reaction has been studied on five single-crystal Pt stepped surface⁸ from the (110) and (011) zones. It showed a sensitivity to the terrace orientation, the density of steps and to the step orientation. The surface which are blocked for the main reaction by intermediates, as the

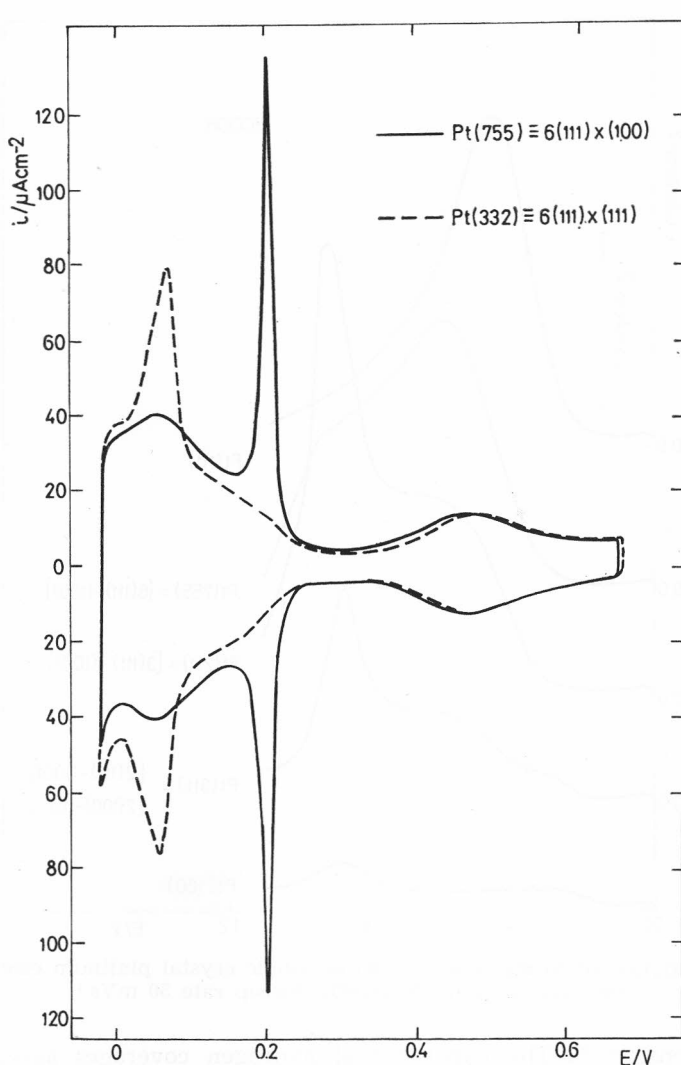


Figure 2. Effect of step orientation. Other data as in Figure 1.

Pt (100) and Pt (110) surfaces are, become more active upon introduction of steps. The surface which are not blocked, i. e., the Pt (111) surface, becomes less active upon introduction of steps, because more active steps increase their activity for the »wrong« reaction — the formation of blocking intermediates.

Hydrogen adsorption is one of the most frequently studied electrode reactions. It shows a pronounced dependence on the surface orientation.⁶⁻¹⁰ It appears that this reaction shows extremely interesting features on stepped single crystal surfaces. Figures 1. and 2. give the data for three surfaces from the [011] zone. It is also sensitive to the terrace orientation, step orientation

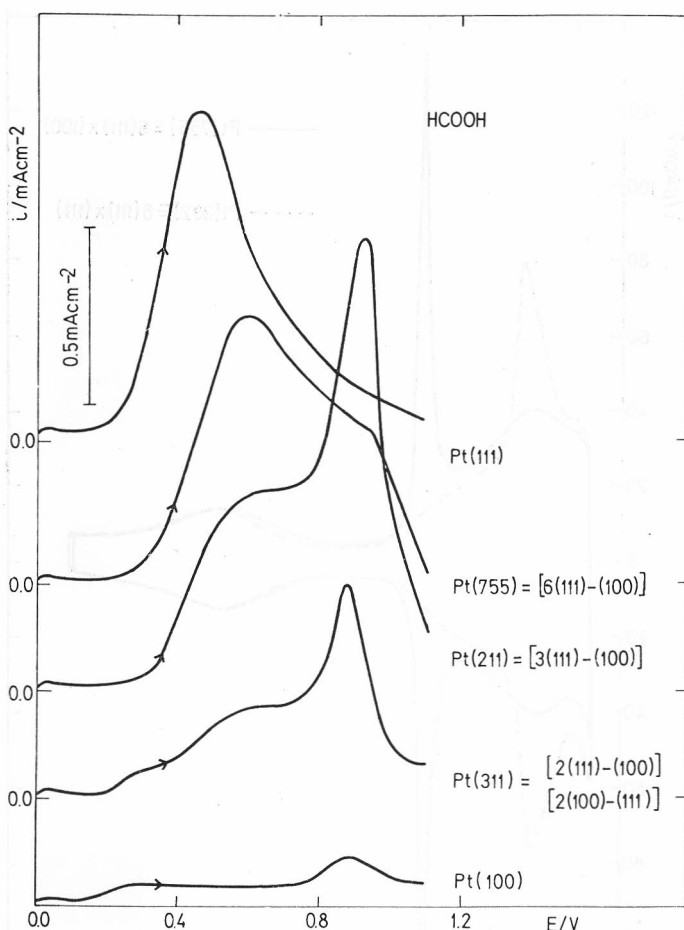


Figure 3. Oxidation of formic acid (0.3 M) on single crystal platinum electrodes from the [011] zone 0.5 M H_2SO_4 . Sweep rate 50 mVs^{-1} .

and step density^{11,12}. The experimental hydrogen coverages agree with the coverages calculated assuming one to one adsorption. It appears that the shape of voltammetry curves can be used to identify a structure of these surface¹². The oxidation of formic acid on these surface is shown in Figure 3. The most active surface for the oxidation of formic acid appears Pt(111), while Pt(100) is blocked in the anodic-going sweep. The intermediate stepped surfaces from the [011] zone show a gradual evolution of one feature with a gradual vanishing of the other, depending on the step density of a given orientation. The results show a possibility of following on an atomic level the changes in surface structure through the current-potential relationship for the hydrogen adsorption and the oxidation of HCOOH . Therefore the investigation of electrocatalytic reactions on stepped single-crystal surfaces appears as a promising way of studying these reactions and of searching for the best catalyst.

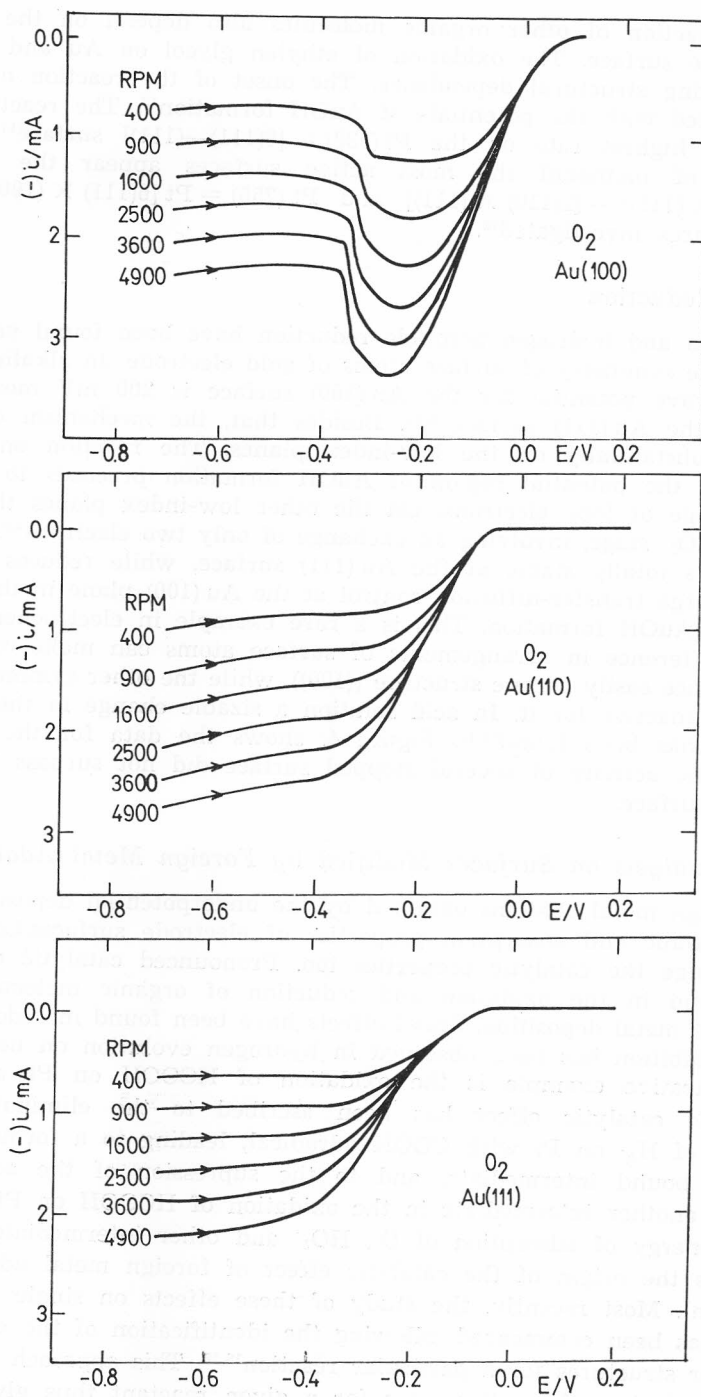


Figure 4. Oxygen reduction on rotating single crystal gold electrodes in 0.1 M NaOH. Sweep rate 50 mVs^{-1} , rotation rate is given in the graph. Potential given vs Hg/HgO, OH^- reference electrode.

The reaction of other organic molecules also depend on the structure of electrode surface. The oxidation of ethylen glycol on Au and Pt shows an interesting structural dependence. The onset of the reaction on Au can be correlated with the potentials of AuOH formation¹³. The reaction on Pt shows the highest rate on the Pt(332) = [6(111)—(111)] surface¹⁴. For the oxidation of methanol the most active surfaces appear the Pt(331) = Pt [3(111) × (111)] = [2(110) × (111)] and Pt(755) = Pt [6(111) × (100)], among the structures investigated¹².

Oxygen Reduction

Oxygen and hydrogen peroxide reduction have been found very dependent on the symmetry of surface atoms of gold electrode. In alkaline solution the half-wave potential for the Au(100) surface is 200 mV more positive than for the Au(111) surface^{5,6,15}. Besides that, the mechanism of reaction differs substantially on the low-index planes. The reaction on the (100) surface in the potential region of AuOH formation proceeds to OH⁻ with an exchange of four electrons. On the other low-index planes the reaction stops at HO₂⁻ stage, involving an exchange of only two electrons^{5,6}. Hydrogen peroxide is totally stable at the Au(111) surface, while reduces under the mixed charge transfer-diffusion control at the Au(100) plane in the potential region of AuOH formation. This is a rare example in electrochemistry that only a difference in arrangements of surface atoms can make one reaction to take place easily on one structure ((100)), while the other symmetry, ((111)), is totally inactive for it. In acid solution a sizable change in the half-wave potential has been found^{16,17}. Figure 4. shows the data for the low index planes. The activity of several stepped surface did not surpass that of the Au(100) surface.

Electrocatalysis on Surfaces Modified by Foreign Metal Adatoms

Foreign metal adatoms obtained by the underpotential deposition change the electronic and adsorption properties of electrode surfaces. Consequently, they change the catalytic properties too. Pronounced catalytic effects have been found in the oxidation and reduction of organic molecules, oxygen reduction, metal deposition. Small effects have been found in redox reactions, while inhibition has been observed in hydrogen evolution on noble metals⁷. An illustrative example is the oxidation of HCOOH on Pt and Pt/Pb_{ad}. A sizable catalytic effect has been ascribed to the elimination of the reaction of H_{ad} on Pt with COOH adradical, leading to a formation of the strongly bound intermediate, and to the suppression of the adsorption of C(OH)₂, another intermediate in the oxidation of HCOOH on Pt⁷. A change of the energy of adsorption of O₂, HO₂⁻ and other intermediates, has been found as the origin of the catalytic effect of foreign metal adatoms in O₂ reduction⁷. Most recently, the study of these effects on single crystal electrodes has been commenced, allowing the identification of the most suitable overlayer structures for a particular reaction^{18,19}. This approach might facilitate a tailoring of reaction sites for a given reactant thus giving grounds for a predictive base of electrocatalysis.

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SAŽETAK

Kristalografska orijentacija i efekti površinske modifikacije u elektrokatalizi

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Na primerima oksidacije mravlje kiseline, metanola i metaldehida na platini prikazan je uticaj kristalografske orijentacije na kinetiku elektrohemijske reakcije. Redukcija kiseonika razmatra se u ovisnosti o simetriji površinskih atoma zlatne elektrode. Na oksidaciju mravlje kiseline također se može utjecati adsorbiranim atomima olova.