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Structural Effects in Electrocatalysis: Oxidation of Ethylene Glycol on Single Crystal Gold Electrodes in Alkaline Solutions

Studies of chemical reactions on well-defined surfaces provide fundamental data on surface reactivity and guidelines for the understanding and design of catalytic materials. Few such studies have been made in electrocatalysis. It is likely that structural effects will be observed in many cases since the adsorption of the reactant, adsorbate migration, adsorbate chemical reaction and product desorption should be structure-sensitive. It is only recently that studies of the oxidation kinetics of HCOOH (*1–4*), CH_3OH (*2, 4*), CH_2O (*2*), and oxygen reduction (*5*) have shown a dependence of the kinetics of these reactions on the crystallographic orientations of the surface.

Ethylene glycol is a potential fuel of practical interest whose electrooxidation has not been studied in detail, although interest for this reaction is growing ((*6, 7*), and references therein). This is a complex reaction whose mechanism is far from being understood. It has been proposed for acid solutions that the oxidation involves adsorption and dehydrogenation according to the following reactions (*6, 8*):

$$HOCH_2\text{—}CH_2OH \rightarrow (HOC\text{—}COH)_{ads} + 4H_{ads} \quad (1)$$

$$4H_{ads} \rightarrow 4H^+ + 4e^- \quad (2)$$

The adsorbed molecule may suffer further transformation and the splitting of C—C bonds may occur (*6*). Under steady state conditions a stepwise oxidation may occur giving various products, including oxalate, glycol aldehyde and CO_2 (*7*). Some evidence of a possible existence of C—OH, the strongly bound intermediate in the oxidation of HCOOH and CH_3OH, has been found for this reaction, too (*6*). It has been suggested that in alkaline solutions the reaction stops at the oxalate stage (*7*).

It is quite clear, however, that some kind of strongly bound intermediate is formed in the oxidation of ethylene glycol on platinum. This is indicated also by the effects of foreign metal adatoms covering a part of the Pt surface. Thus, pronounced catalytic effects of Pb (*9*), Tl and Bi (*10*) have been observed in alkaline solutions and these are partly based on a suppression of formation and/or adsorption of strongly bound intermediates.

In this work the oxidation of ethylene glycol on gold single crystals with the (100), (110) and (111) orientations has been studied with the aim of investigating whether there is structural sensitivity in this reaction. Structural sensitivity, as well as the role of AuOH species formed on surfaces, could be of interest for both electrocatalysis and catalysis.

The single crystal electrodes were obtained from Metal Crystal Ltd., Cambridge, and were oriented to better than 1° and cut. The details of the electrode preparation have been given elsewhere (*3*). The structure of the surfaces has been checked by LEED and their purity by Auger electron spectroscopy. The electrolyte was 0.1 *M* NaOH solution prepared from triply distilled water and Analar NaOH. The counterelectrodes were gold and platinum plates. The reference electrode was Hg/HgO, OH^-. All potentials are given vs this reference electrode. Nitrogen was bubbled through the electrolyte before measurements. All measurements were carried out at room temperature. Ethylene glycol was

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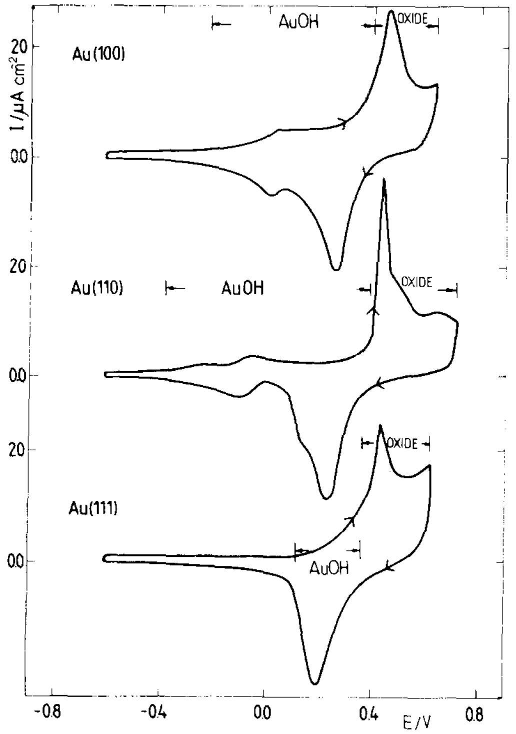

FIG. 1. Voltammetry curves of single crystal gold electrodes in 0.1 *M* NaOH. Sweep rate 50 mV/s.

added to the electrolyte in the concentration of 0.1 *M*.

The state of the electrode surface has been checked by LEED after the electrochemical preparation procedure (*5*). Immediately after introduction into the UHV chamber it was easy to obtain characteristic LEED patterns for the surfaces used. This means that the preparation gives a clean and ordered surface. Such surfaces showed characteristic voltammetry curves, and these were used to check the state of the surfaces before the oxidation of ethylene glycol.

Figure 1 shows the voltammetry curves for the three Au single crystals in 0.1 *M* NaOH obtained with a 50 mV/s sweep rate. There is considerable difference between the curves. A formation of AuOH, the oxide precursor, is seen on the Au(100) and Au(110) surfaces in the potential region before the oxide formation. It has been shown recently that the cycling of potential in the range encompassing the oxide formation on gold removes the (5 × 20) reconstructed surface giving (1 × 1) symmetry (*11*). Therefore, under these experimental conditions the Au(100) − (1 × 1) structure was used. Besides the difference in the potential of AuOH formation for the Au(100) and Au(110) faces, a difference in the shape of voltammetry curves in the region of OH^- chemisorption is seen (Fig. 1). This is due to a different lateral interaction of $(OH^-)_{ads}$ which is caused most probably by a different partial charge of this species on the two surfaces. The formation of AuOH may be best represented by the following partial charge transfer reaction (*5*):

$$\mathrm{Au} + \mathrm{OH}^- - \lambda e \rightarrow \mathrm{AuOH}^{(1-\lambda e)-} \quad (3)$$

It is surprising that there is apparently no formation of AuOH on the Au(111) face before oxide formation. It is known that the

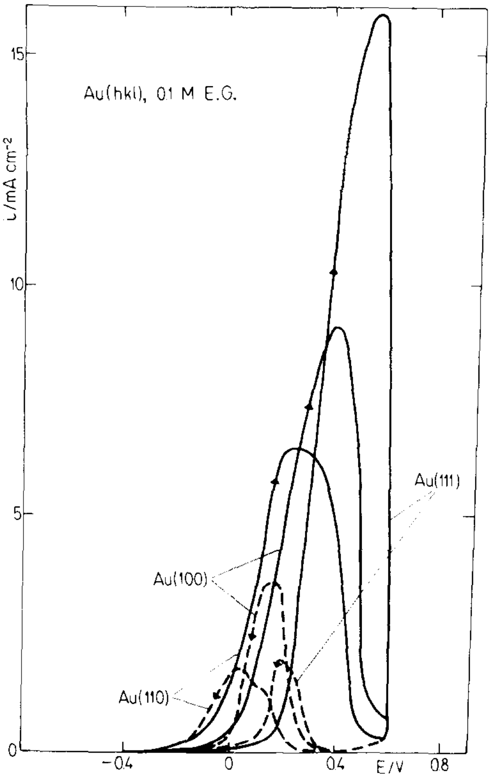

FIG. 2. Oxidation of ethylene glycol (0.1 *M*) on single crystal gold electrodes in 0.1 *M* NaOH. Sweep rate 50 mV/s.

TABLE 1

Incipient Potentials for AuOH Formation and Ethylene Glycol Oxidation on Gold, and Peak Currents and Peak Potentials for the Oxidation of EG in 0.1 *M* NaOH as a Function of the Crystallographic Orientation of the Gold Surface

Surface	E_{AuOH} (V)	E_{ox} (V)	i_p (mA/cm^2)	E_p (V)
Au(100)	−0.20	−0.20	7	+0.35
Au(110)	−0.35	−0.35	4	+0.20
Au(111)	+0.10	+0.05	14	+0.45

(111) orientation exhibits a lower reactivity than the other low-index faces, which is in this case quite pronounced. The interaction of H_2O and hydroxyl formation has been studied with a number of metal surfaces in the gas phase (*11*), but to our knowledge not with gold.

Figure 2 shows the oxidation of ethylene glycol on gold single crystal electrodes. A pronounced sensitivity on the crystallographic orientation is seen. The reaction commences at the most negative potentials on the Au(110) surface. The peaks obtained in the cathodic-going sweeps also show the effect of crystallographic orientations. They are displaced to more negative potentials due to the irreversibility of oxide reduction. Consequently, the currents associated with them are lower. Table 1 gives a comparison of the incipient potentials of the EG oxidation, the peak potentials and the currents at the peak for the three surfaces.

Table 1 shows that there is a direct parallelism between the incipient potential of AuOH formation and the incipient potential of EG oxidation. The peak potentials follow the same trend. It is reasonable to assume that AuOH is the active species in the oxidation of EG. There is no OH^- adsorption on the Au(111) face clearly separated from the oxide formation. It occurs, if at all, at a narrow potential region, just before the oxide formation.

The peaks in the current–potential curves are produced less by a depletion of the reacting species but, to a larger extent, by a formation of a strongly bound species formed in the reaction. This means that the peak current at the most active surface, Au(110), occurs at the most negative potentials. The lowest current is associated with it because of the lowest overpotential for the reaction. The highest currents are associated with the Au(111) surface because of the highest overpotential and probably because of the reaction of some intermediate with gold oxide.

The implications of these experimental findings are the following:

—Ethylene glycol is not oxidized on the $AuOH^-$, or oxide-free, metallic gold surface in alkaline solutions. AuOH or Au oxide are necessary for the reaction to take place.

—A pronounced structural sensitivity of the oxidation of EG on Au is observed, which comes predominantly from the structural dependence of the formation of Au(OH).

—The evidence of participation of the AuOH species in the oxidation of EG allows us to write with more confidence at least one step in the mechanism of the oxidation of EG on Au electrodes. This agrees with the scheme proposed for Pt (*13*). In the case of Au, however, there is evidence of the role of OH^- adsorption, which was only assumed in the case of Pt. On the basis of the above data one can write

$$C_2H_4(OH)_2 + Au + OH^- \longrightarrow Au - C_2H_3(OH)_{2_{ads}} + H_2O + e^- \quad (4)$$

$$Au + OH \xrightarrow{\text{fast}} AuOH + e^- \quad (5)$$

$$Au - C_2H_3(OH)_{2_{ads}} + AuOH \xrightarrow{\text{r.d.s.}} \text{products} \quad (6)$$

There is no evidence for the oxidation of some strongly bound intermediate by AuOH. Further work is needed to obtain more kinetic and mechanistic information on this reaction, which would be helpful for a deeper understanding of its structural sensitivity.

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