

ADSORPTION OF ACETYLENE ON POLYCRYSTALLINE AND SINGLE CRYSTAL GOLD ELECTRODES IN ACID MEDIA

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Abstract

Electro-oxidation and electroreduction reactions of acetylene adsorbates on gold were studied in 0.1 M HClO₄. It was found that acetylene forms chemisorbates in a wide potential range. On-line electrochemical mass spectrometry (DEMS) was used for the detection of the reaction products on porous polycrystalline gold electrodes. Only CO₂ was detected during the oxidation of the adsorbates, whereas acetylene and ethylene were identified as products of adsorbates reduction. The oxidation and reduction of the chemisorbates on single crystal faces display distinctive differences. The oxidation charge (Q_{ox}) required to oxidize acetylene adsorbed species completely to CO₂ depends on the adsorption potential (U_{ad}). The shape of the curve Q_{ox} vs U_{ad} is also affected by the structure of the gold surface.

Introduction

The interaction of small organic molecules with gold in acid solutions is characterized by a weak adsorption except for species containing sulphur atoms [1]. However, in previous studies it was observed that acetylene adsorbs strongly on gold surfaces forming stable chemisorbates. These chemisorbed species remain on the surface after complete electrolyte exchange [2-5]. Thus, acetylene appears to be an appropriate model system for studying the interaction of unsaturated organic molecules containing a C≡C group with gold surfaces.

In the present paper, the adsorption of acetylene and the surface reactions of the adsorbates are comparatively discussed on polycrystalline and single crystal gold electrodes. Oxidation and reduction products of the adsorbed intermediates are detected on porous gold by means of Differential Electrochemical Mass Spectrometry (DEMS) [6]. The influence of the surface structure on the adsorption is also studied by varying

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the adsorption potential.

Experimental

Experiments were carried out in 0.1 M HClO₄ (Merck p.a.) using Millipore-MilliQ[®] water. Saturated solution of C₂H₂ (Linde) was obtained by bubbling the purified gas [3,4] through the electrolyte previously deaerated with argon.

DEMS studies were performed in a small flow cell attached to the vacuum chamber with the mass spectrometer (Balzers QMG 412). The working electrode was a porous gold layer sputtered on a microporous PTFE membrane (Scimat 200/40/60). The geometric area of the electrode was 0.5 cm² and the roughness factor was 5-6. For the adsorption experiments the 0.1 M HClO₄ solution saturated with C₂H₂ was introduced in the cell at different adsorption potentials (U_{ad}). After that, the C₂H₂ containing solution was replaced by pure electrolyte solution. Cyclic voltammograms (CVs) and mass spectrometric cyclic voltammograms (MSCVs) were recorded simultaneously. Details about the experimental procedure are given in [4].

Measurements with the single crystals were done in a conventional electrochemical flow cell using the hanging meniscus method. The geometric area for the single crystal faces was 0.78 cm². The adsorption experiments were performed introducing the gas through a small capillary just in front of the raised meniscus as described in [5].

In all studies a Au wire was served as counter electrode and the reference was a reversible hydrogen electrode (RHE) in the electrolyte solution. The experiments were performed at room temperature.

Results and Discussion

Oxidation and reduction reactions of acetylene adsorbates on gold

The only oxidation product of acetylene adsorbates detected through DEMS was CO₂ (m/z = 44, [CO₂]⁺) as it can be seen in Figure 1b for U_{ad} = 0.60 V. The onset potential for the oxidation is approximately 0.90 V, attaining an anodic peak at 1.27 V with a small contribution at 1.50 V (Figure 1a). The inset in Figure 1b shows that the electroreduction of the adsorbates leads to the formation of C₂H₂ (m/z = 26, [C₂H₂]⁺) and C₂H₄ (m/z = 28, [C₂H₂]⁺). This process reveals a cathodic peak centered at 0.31 V in the CV (inset in Figure 1a).

Dependence of the voltammetric characteristics of the adsorbates on the structure of the gold surface

The voltammetric characteristics of acetylene chimisorbates during the electro-oxidation and electroreduction processes depend strongly on the structure of the gold

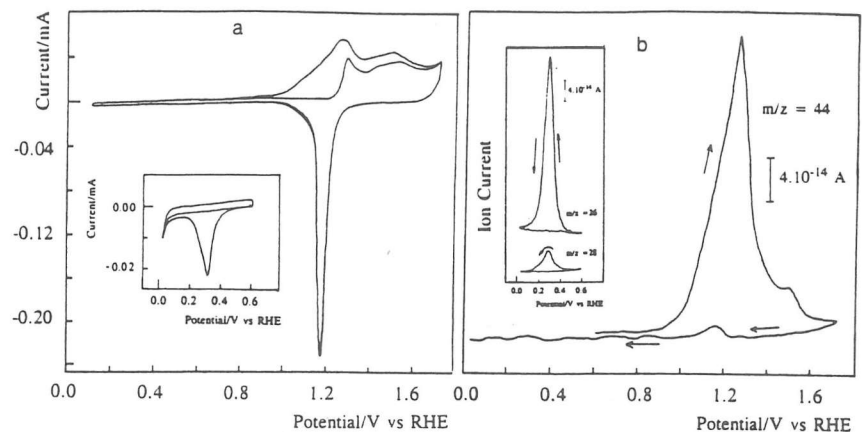


Figure 1. Electro-oxidation and electroreduction of acetylene adsorbates in 0.1 M HClO₄ on porous Au ($v = 0.01$ V/s; $U_{ad} = 0.60$ V, $t_{ad} = 5$ min). a) CV for the first and second potential cycle after adsorption starting with a positive-going scan from U_{ad} (adsorbates oxidation). Inset: reduction of the adsorbed species starting with a negative-going scan from U_{ad} . b) MSCV for the oxidation to CO₂ ($m/z = 44$). Inset: MSCVs for the reduction to C₂H₂ ($m/z = 26$) and C₂H₄ ($m/z = 28$). First potential cycle after adsorption.

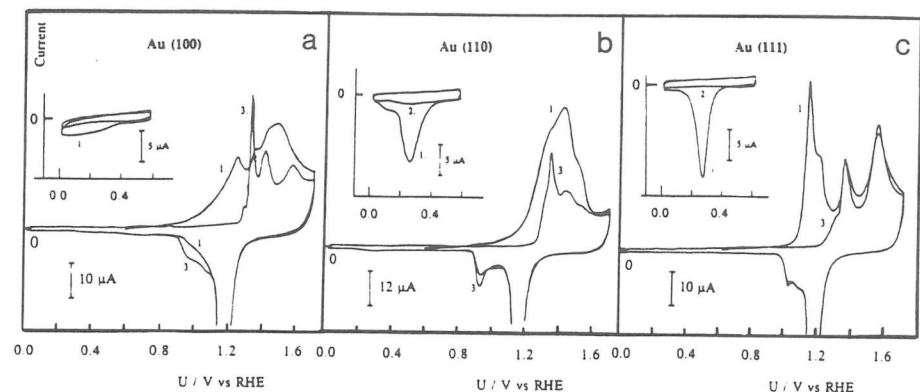


Figure 2. Oxidation of acetylene adsorbates in 0.1 M HClO₄ on a) Au(100), b) Au(110) and c) Au(111) ($v = 0.02$ V/s; $U_{ad} = 0.60$ V; $t_{ad} = 5$ min). First and third potential cycles. Inset: adsorbates reduction starting with a negative-going scan from U_{ad} .

surface. Thus, for the oxidation in the case of Au(100) two distinct potential ranges are observed: the first one between 0.78 V and the potential of the gold oxide formation, and the second in the AuO region (Figure 2a). On the other hand, for Au(111) acetylene adsorbates are mostly oxidized at potentials below the formation of gold oxide (Figure 2b). The oxidation on Au(110) commences at 0.85 V and displays a maximum at 1.41 V together with two shoulders at 1.32 V and 1.52 V (Figure 2c).

The electroreduction shows also remarkable differences when the three single crystal faces are compared. For Au(111) and Au(110) the onset potential for the reduction is observed to be at about 0.42 V, and a peak is apparent between 0.23 V and 0.27 V. The shape of the curve is broader for Au(110) compared to Au(111). 90% of the adsorbate is reduced during the first negative-going potential scan on Au(111) and Au(110). However, in the case of Au(100) only a small cathodic current contribution is observed and 50% of the adsorbates remains on the surface after reduction.

Dependence of acetylene adsorption on U_{ad}

The charge density required for the complete oxidation of the adsorbed species to CO_2 , Q_{ox} , was calculated by integrating the difference in the anodic current between the first and the second potential cycle. Figure 3a shows the corresponding plots of Q_{ox} vs U_{ad} (full line) and the integrated ion current for $m/z = 44$ vs U_{ad} (dashed line) for a porous polycrystalline gold electrode. The electro-oxidation charge increases for $U_{ad} > 0.20$ V attaining a maximum at about 0.70-0.80 V, followed by a decrease for $U_{ad} > 0.90$ V. A similar behaviour is observed for the integrated ion current for CO_2 mass signal ($m/z = 44$). The parallel shape of both curves in Figure 3a confirms the experimental finding that CO_2 is the sole oxidation product of acetylene adsorbates.

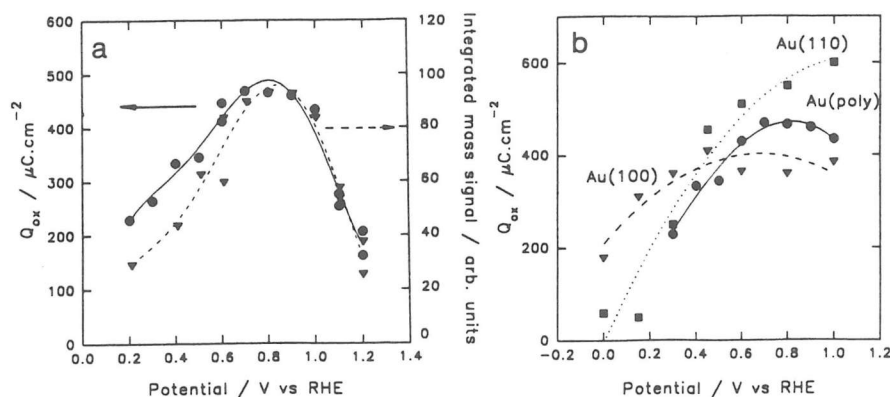


Figure 3. Oxidation charge for acetylene chemisorbates previously formed at different U_{ad} . a) Porous gold; full line: Q_{ox} vs U_{ad} (●); dashed line: integrated ion current for $m/z = 44$ vs U_{ad} (▼). b) Q_{ox} vs U_{ad} for Au(poly), Au(110) and Au(100).

The plot Q_{ox} vs U_{ad} is also dependent on the structure of the surface as it can be seen in Figure 3b. With respect to polycrystalline gold, the adsorption on Au(110) shows higher values of Q_{ox} for $U_{ad} > 0.30$ V. In the case of Au(100) the adsorption commences at lower potentials than on Au(poly) and Au(110), but Q_{ox} is approximately constant in the range 0.20-1.00 V. For $U_{ad} > 0.50$ V the oxidation charge is lower for Au(100) than on Au(poly).

Concluding Remarks

Acetylene turns out to be an interesting model system for chemisorption studies of unsaturated organic molecules on gold in acids. The adsorption, electro-oxidation and electroreduction processes depend strongly on the adsorption potential as well as on the structure of the surface. In order to get a deeper insight into the adsorption process, the structures of the adsorbates formed and their surface reactions, further investigation using electrochemical and spectroscopic methods are required.

References

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