

Platinum/Osmium as a Catalyst for Ethanol Oxidation

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Introduction

The SPE-based fuel cells fed with liquid fuels are very attractive for mobile application. Such cells offer advantages in the storage of fuel, but currently show rather low power densities when compared with H_2/O_2 system. A variety of liquid fuels, such as methanol, ethanol, glycol, formaldehyde, hydrazine, etc are, in principle, suitable for this purpose. Methanol has become the most carefully studied of the liquids listed above, while, ethanol is a more promising fuel, as it can be readily produced from renewable biomass. Also it is less toxic than methanol. The electrooxidation of ethanol on platinum is feasible, although the poisoning problems are more complex in this case. The electrochemistry of this process is unfortunately sluggish and efficient catalysts for the fuel oxidation are still far from satisfactory. To improve the oxidation rate, considerable efforts have been directed towards the development of high surface activity catalysts. This study presents the effort to develop a new catalyst for ethanol oxidation based in the modification of well oriented surface platinum by deposition of controlled amounts of osmium, in order to form two-dimensional surface islands.

Experimental

Pt(111) and Pt(100) single crystals were used as substrate for osmium deposition. The deposition of ultra-thin films of osmium on platinum single crystals was carried out from 1×10^{-3} M solution of H_2OsCl_6 in 0.1 M H_2SO_4 . Two different ways of deposition were used: (i) the spontaneous deposition by simple immersion of the electrode into H_2OsCl_6 solution for different time (the open circuit potential was 0.79 V), and (ii) constant potential electrolysis at 0.05 V and 0.15 V for different time. The ethanol oxidation reaction was studied using such prepared surfaces under voltammetric and chronoamperometric conditions in 0.5 M C_2H_5OH + 0.1 M H_2SO_4 .

Results and Discussion

Figure 1 shows the cyclic voltammograms for Pt(100) in H_2SO_4 before and after osmium spontaneous deposition in different time. It is obviously seen that the H_{ads}/H_{des} peaks decreases as the deposition time increases. The osmium coverage was estimated from the quantitative analysis of the charges involved in the H_{des} peaks in a broad range of deposition time and by considering the following equation: $\theta_{Os} = 1 - \theta_H$. The calculated values for θ_{Os} as a function of the deposition time are shown in Figure 2. Below coverage of ca. 0.5 ML, the electrolysis yield was ca. 100 %. Above this limit, it was observed a significant drop in the electrolysis yield, to approximately 10 %. This shows that osmium nucleates relatively fast and efficiently at the deposition beginning, that is, on osmium free platinum, or on the surface sparsely populated by osmium, but the nucleation slows down at the higher coverage. This behavior can, be related to the presence of osmium oxides easily formed during the osmium deposition, and to the difficulty in the Os layer growth on a Os/OsO_x covered electrode.

Typical anodic voltammetric profiles in 0.1 M H_2SO_4 + 0.5 M ethanol, for Os deposited at 0.05 V, is presented in Figure 3. The peak in 0.65 V appears for

ethanol oxidation on Pt/Os surface where only a small shoulder is observed for pure Pt. The maximum intensity of this peak is observed for 0.48 ML of Os, indicating that after this time the relation Os sites/Pt sites is beyond from the ideal value. Since the peak observed for pure Pt is more positive than that observed for Pt/Os, this suggests that the ethanol is easier oxidized on the modified surfaces. The chronoamperometric measurements of ethanol oxidation on the Pt(hkl)/Os surfaces are shown in Figure 4, for Os deposited at 0.15 V. Overall, a strong catalytic effect for ethanol oxidation is observed for the surfaces modified by osmium, showing an increase in the oxidation current of between one and two orders of magnitude. This fact is highly significant and promising.

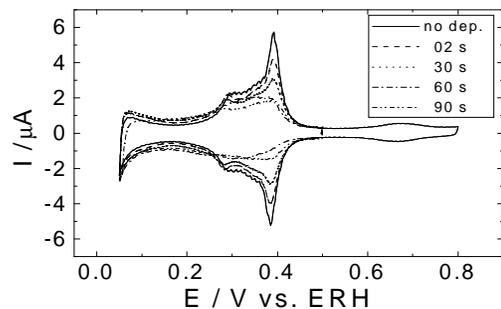


Fig. 1. CV for Pt(100) before and after Os modification.

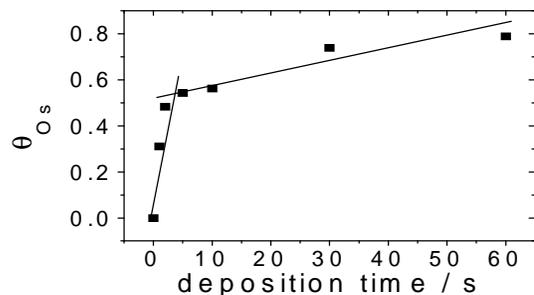


Fig. 2. Variation of θ_{Os} on Pt(100) deposited at 0.05 V.

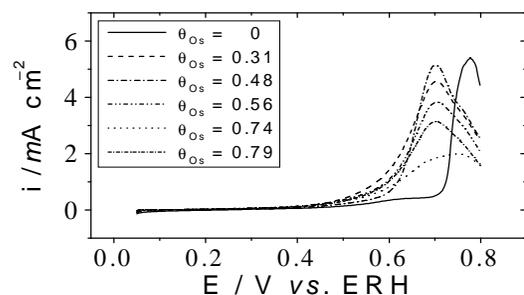


Fig. 3. VC for the ethanol oxidation on Pt(100)/Os

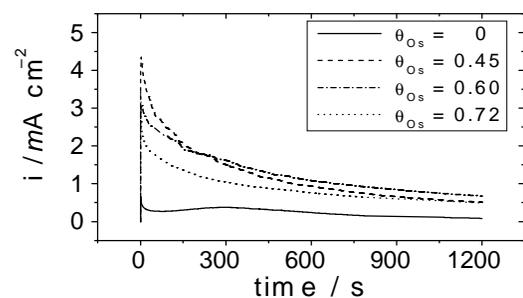


Fig. 4. I vs. t for ethanol oxidation in 650 mV on Pt(100).

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