

The role of alcohols in the surface structure disordering on electrode Pt(111) in acid medium

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Abstract

The oxide growth on Pt(111) in aqueous media at high potentials prompts a surface structure changing. However, when glycerol is added in the electrochemical system, this behavior is suppressed since the adsorbed species from glycerol electrooxidation reaction seems to prevent the surface disorder caused by the formation of platinum oxide. Our results show that the presence of alcohol plays an important role in surface structure ordering.

Introduction

The platinum oxidation and reduction has been studied exhaustively by the scientific community¹⁻⁴. The study of platinum single-crystal surfaces are limited to low potentials due to superficial reconstruction caused by oxidation and reduction during cycling.

Björling and co-workers suggest a superficial disordering of Pt(111) terraces. This changing has a dominant feature of (110)-defects sites while (100)-defect sites act as intermediate.^{2,3}

However, the study of these processes in the presence of organic molecules in the electrochemical environment is difficult since it is not possible to separate the contributions of the molecule and the surface oxidations. In this way, it is usually supposed that surface oxidation happens the same way as in the pure electrolyte.

This is particularly important since the electrooxidation of small organic molecules takes place in the same potential range as the surface oxidation. In this work we studied the surface oxide formation using an ordered Pt(111) electrode and evaluated the extent of surface disordering in presence and absence of glycerol.

Results and Discussion

Figure 1 presents the voltammetric profile of Pt(111) electrode before (black) and after 30 cycles up to 1.3V (red). The peak at 0.12 V evince the creation of surface defects with (110) symmetry orientation. The extension of disordering can be evaluated by the intensity of this peak, the decrease in peak at 0.48V ((111) domains) and increase in oxidation/reduction charges. When glycerol is

present in the electrolyte, (110) peak is smaller if compared with result recorded in the absence of glycerol.

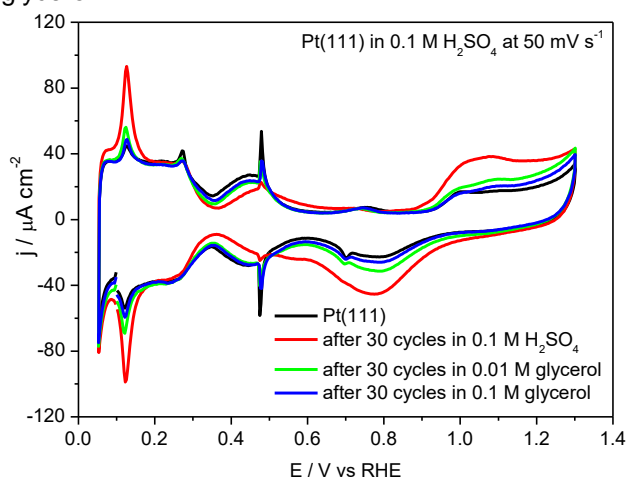


Figure 1. Voltammetric profile of Pt(111) in 0.1 M H₂SO₄ before (black) and after 30 cycles in absence (red) and presence (0.01M – green and 0.1M – blue) of glycerol. Scan Rate: 50 mV s⁻¹.

The glycerol presence seems to protect the surface disordering even when the electrode is subjected to potentials where is known to produce irreversible surface reconstruction due to place exchange process¹⁻³. This behavior can be related to the competition for OH adsorbed species that both Pt and glycerol need to oxidation.

Conclusions

The results here presented indicate a surface structure changing of Pt (111) after oxide growth. However, glycerol molecules inhibit this changing due to the competition for OH_{ads} species.

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