

# Hydrogen-evolution and -oxidation on Ag(1 1 1) covered by Pt

Ralf Tölle, Andreas Otto \*

*Lehrstuhl für Oberflächenwissenschaft, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany*

Available online 3 August 2005

## Abstract

Physical vapour deposited Pt on Ag(1 1 1) forms inhomogeneous films, leaving access to the Ag(1 1 1) surface, as proven by electroreflectance. The overpotential of the hydrogen evolution reaction at Ag(1 1 1) by water splitting in neutral perchlorate and sulphate electrolytes and by  $\text{H}_3\text{O}^+$  discharge in acidic perchlorate and sulphate electrolytes is considerably reduced by the Pt coverage, but does not vanish. The transfer coefficient for water splitting is more than 50% lower than for  $\text{H}_3\text{O}^+$  discharge. In  $\text{H}_2$ -saturated neutral electrolytes, the potential gap between hydrogen evolution by water splitting and  $\text{H}_2$ -oxidation decreases with the increasing number of Pt monolayers. In acidic electrolytes, this gap does not exist. Here, the absolute current densities of  $\text{H}^+$ -reduction and  $\text{H}_2$ -oxidation grow with the number of Pt monolayers. In the neutral electrolytes, sulphate strongly inhibits the  $\text{H}_2$ -oxidation (by a factor of about 25 with respect to perchlorate).

© 2005 Elsevier B.V. All rights reserved.

## 1. Introduction

At a platinum electrode in a given electrolyte both the hydrogen-evolution-reaction (HER) [1] and  $\text{H}_2$ -oxidation reaction (HOR) set in at the thermodynamic  $\text{H}_2/\text{H}^+$  redox potential in this electrolyte, whereas for the noble metals there exist a hindrance of the HER, and the HOR is completely inhibited. The hindrance of the HER may be either quantitatively characterized by a low exchange current (as for instance in [2]) or by the

overpotential  $\eta_{\text{H}}$ , approximately given by  $\eta_{\text{H}} = E_{\text{Pt}}(j_{\text{H}}) - E_{\text{noble}}(j_{\text{H}})$ , where  $E_{\text{Pt}}$  and  $E_{\text{noble}}$  are the electrode potentials of the Pt and the noble metal working electrodes in the same electrolyte at the same small current density  $j_{\text{H}}$  of the HER. A common theory is to relate  $\eta_{\text{H}}$  by  $\eta_{\text{H}} = \text{pzc}(\text{Pt}) - \text{pzc}(\text{noble})$  to the difference of the potential of zero charge (pzc) of the electrodes in the same dilute electrolyte. The relation reflects the hypothesis, that the HER sets in for all metal electrodes negative of the pzc at the same negative value of the “surface charge”.

In the thesis work [3] we have tried to test this model of  $\eta_{\text{H}}$ , choosing bulk silver electrodes and

\* Corresponding author. Tel.: +49 2673 1205.  
E-mail address: [otto@uni-duesseldorf.de](mailto:otto@uni-duesseldorf.de) (A. Otto).

under-potential and over-potential deposition of Ag on Pt(111). In order to comply with the rules of the research program “fundamentals of electrochemical nano-technology”, also small quantities of Pt on Ag(111) were investigated. Here we expected, that the physical vapour deposited Pt forms “clusters” on Ag(111). Though recent research focuses mainly on the HER by proton discharge, see [4] and references therein, we also present work on HER in neutral aqueous electrolytes, where the HER involves the splitting of water, following the work in our laboratory on HER at silver electrodes by splitting water with hot electrons [5,6]. Of course, it was mandatory to investigate as well, how the HOR developed with the quantity of Pt on Ag(111) in H<sub>2</sub> saturated electrolytes.

## 2. Experiment

The Ag(111) crystals were prepared by mechanical polishing down to 0.25 μm, chemical etching in a 1:1 mixture of NaCN and H<sub>2</sub>O<sub>2</sub>, transferred to a NaCN aqueous solution to remove insoluble AgCN by formation of soluble Ag(CN)<sub>2</sub><sup>-</sup>, washed in deionized water and dried in a stream of nitrogen gas. Then it was annealed 3 times for 10 s in the reducing hydrogen flame with directly following cooling in a stream of N<sub>2</sub>. After this repeated treatment X-ray diffraction in the Bragg–Brentano mounting yielded strong and narrow (111) reflexes. The quality of the crystals is indicated by the deep minimum of reflectivity near 316.2 nm (3.92 eV) [7], see Fig. 1, as explained below.

Platinum was deposited on the samples in two ways.

In the first method it was deposited by thermal evaporation (physical vapour deposition PVD) in a vacuum below 10<sup>-8</sup> mbar with 0.1 ML/s. The quartz balance was positioned directly besides the substrates. The second method was electrochemical deposition (ECD) at 0 V from H<sub>2</sub>[PtCl<sub>6</sub>] with 0.1 ML/s; the thickness of the Pt layer was controlled by taking the sample out of the Pt-salt electrolyte after various times and inserting it into a Pt-free electrolyte.

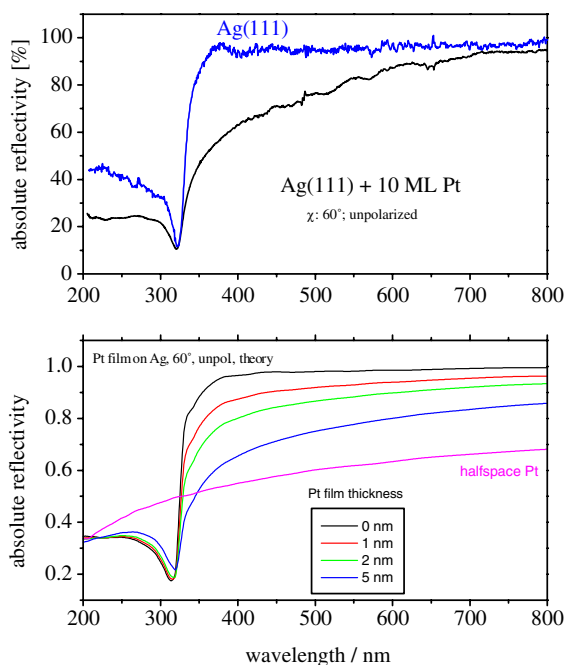


Fig. 1. Above: Absolute reflectivity of a Ag(111) crystal and a Ag(111) crystal covered by 10 ML of PVD Pt. Angle of incidence 60°, unpolarized incident light. Below: Calculated absolute reflectivity of a silver halfspace covered with homogeneous stratified layers of Pt of various values of film thickness, compared to a halfspace of Pt.

The orientation of Pt(111) single crystal was checked by Bragg–Brentano X-ray scattering. The crystal was cleaned in a reducing hydrogen flame and cooled in nitrogen gas.

Gold films of 40 nm thickness were deposited by thermal evaporation on boro-float glass in a high vacuum of less than 5 × 10<sup>-8</sup> Torr. It was heated slowly in a hydrogen flame and brought to red glow [8]. The comparison with cyclic voltammograms from smooth Au(111) electrodes [9] showed very good (111) orientation of the films.

Acidic (0.1 M HClO<sub>4</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub>) and neutral electrolytes (50 mM KClO<sub>4</sub>, 50 mM K<sub>2</sub>SO<sub>4</sub>) electrolytes were prepared with Millipore, direct, -Q3, 18.2 MΩ water. The reference electrodes (either SCE or Ag/AgCl) were separated by a Haber–Luggin capillary from the electrolytes, which were deaired by nitrogen bubbling.

Silver underpotential (first and second monolayer) and overpotential deposition on Pt(111)

Download English Version:

<https://daneshyari.com/en/article/9594757>

Download Persian Version:

<https://daneshyari.com/article/9594757>

[Daneshyari.com](https://daneshyari.com)