

Hydrogen Reactions on Pt supported on Au, Cu and HOPG

– The Influence of the Substrate on Electrocatalytic Activity

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Introduction

A challenge in the development of electrocatalysts is to understand important design parameters which can have a strong influence on electrocatalytic activity. These parameters are particle size, inter-particle distance and influence of the substrate material. Since commercial catalysts are rather complex systems, the purpose is to study and control structural parameters. Until now the interaction of nanoparticles with the support plays not an important role in applications; it seems that the substrate has a direct influence on the catalytic activity.

Recently, the electrocatalytic activity of Pd- and Pt-nanoislands on Au(111)-electrode towards hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) was investigated [1-3]. The specific current density of platinum (current density related to the electrochemical active area of Pt) is enhanced by up to three orders of magnitude as compared to Pt(111) [3]. Such significantly enhanced activity may be discussed in terms of: i) The lattice of the Pt nanoislands is strained due to larger lattice constant of the Au(111) support, which increases the binding energy to the adsorbed hydrogen [2-5]. ii) Low coordinated atoms such as atoms on steps or defects may cause an increased specific activity [6]. iii) An enhanced mass transport for small particles due to hemispherical diffusion in contrast to planar diffusion may lead to higher current densities.

In order to better understand the involvement of the substrate material, we systematically varied the properties of the substrates. HOPG surfaces have a much weaker interaction with Pt as compared to gold as substrate. Copper was chosen as substrate since the lattice constant is smaller as compared to gold which leads to a compression of pseudomorphic Pt-layer overlayers.

Materials and Methods

Potentiostatic pulses were used to perform a defined electrochemical deposition of Pt islands on Au and HOPG, the deposition of Pt on Cu was done electroless. These nanostructured electrodes were characterized with hydrogen adsorption, CO monolayer oxidation and the integration of the Faradaic charge during the deposition procedure. All above mentioned electrochemical methods agree well with the determination of the coverage with STM or AFM. The reactivity was investigated by cyclic voltammetry or short potentiostatic pulses in hydrogen saturated 1M HClO₄.

Results and Discussion

We found that the specific catalytic activity of platinum on Au(111) is enhanced by up to a factor of 1000 as compared to Pt(111). The observed enhancement for the Pt/Au(111) system may be caused by one or a combination of the following explanations:

- I.) a direct influence of the support;
- II.) high reactive steps and defect sites or;
- III.) an enhanced mass transport.

Comparing the Pt/Au(111) system with other systems such as the investigated Pt/Cu and Pt/HOPG systems a similar enhancement effect was not found. The difference between the specific current density of Pt/Au and Pt/HOPG is at least two orders of magnitude. A similar behavior shows a Pt-monolayer deposited on copper. A significantly lower activity than Pt-multilayers is found, which also hints to a disadvantageous influence of the substrate material for HER and HOR. Furthermore, also submonolayers of Pt deposited on copper show no enhanced specific activity towards HER.

Significance

We are reporting unusually high current densities for hydrogen reactions on Pt/Au(111). This is in clear contrast to the behavior of Pt deposited on HOPG or Cu regarding the hydrogen reactions. Possible explanations will be presented and discussed

References

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