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Preparation and electrochemical characterization of low-index rhodium single crystal electrodes in sulfuric acid

Qinqin Xu [a,b], Udo Linke [b], Renata Bujak [c], Thomas Wandlowski [a,*]

[a] Departement of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
[b] Institute of Bio- and Nanosystems IBN 3, Research Center Jülich, 52425 Jülich, Germany
[c] Institute of Construction Science "Eduardo Torroja", CSIC, C/Serrano Galvache 4, 28033 Madrid, Spain

ABSTRACT

The electrochemical properties of low-index phase Rh(1 1 1), Rh(1 1 0) and Rh(1 0 0) single crystal bead electrodes, prepared by a novel technique combining electron beam heating with inductive annealing in a controlled atmosphere, have been characterized in 0.1 M H_2SO_4 by cyclic voltammetry and chronoamperometry. Hydrogen and sulfate adsorption as well as surface oxidation depend strongly on the crystallographic orientation of the surface. The potentials of zero total charge (E_{pztc}) of all three Rh electrodes in 0.1 M H_2SO_4 were determined by the combination of charge displacement and voltammetric experiments. The charge balance reveals unambiguously that the ($\sqrt{3} \times \sqrt{7}$) adlayer on Rh(1 1 1) is composed of specifically adsorbed sulfate ions eventually coadsorbed with water molecules. Hydrogen-sulfate coadsorbed with hydronium ions could be excluded. The kinetics of sulfate ion desorption followed by the adsorption of hydrogen at less positive potentials could be represented by a nucleation and growth mechanism coupled with a parallel first order process.

The electro-oxidation of irreversibly adsorbed carbon monoxide monolayers was also investigated and revealed distinct structure sensitivity. The reaction pathway on all three low-index phases of Rh proceeds according to a Langmuir–Hinshelwood mechanism and is controlled by nucleation of OH_{ads} at steps and other defect sites followed by a complex growth process on terrace sites. The low surface mobility of CO_{ads} leads to a slow and incomplete CO monolayer electro-oxidation on Rh(1 1 1). The high density of step sites on Rh(1 1 0) and the reversible formation of oxygenated species on Rh(1 0 0) at rather low potentials significantly enhance the electro-oxidation activity leading to the following reactivity sequence: Rh(1 1 1) $\ll$ Rh(1 1 0) $\sim$ Rh(1 0 0). The shape of the experimental transients and attempts to model them demonstrate the occurrence of at least two processes occurring in parallel. The long-term response represents clearly a process involving a slow surface-diffusion step.

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1. Introduction

The use of well-defined electrode surfaces, such as single crystals [1], epitaxially grown thin metal films [2,3] or custom-designed nanoparticles [4,5] represents a powerful approach to explore structural aspects in interfacial electrochemical reactions. The introduction of the flame annealing technique for preparing high-quality single crystal platinum surfaces by Clavilier [6,7] stimulated a large number of electrochemical studies on correlations between interfacial structure and reactivity, specifically in electrocatalysis to investigate fundamental properties of fuel cell reactions. Clavilier's method was applied to Au [8], Ag [9], Ir [10], Pd [11–13] and Rh [14,15]. More recent developments aimed to prepare

well-defined single crystal electrodes of "reactive" metals involve resistive [14,16], inductive [13,17] or electron beam annealing [13] as well as combinations of the various approaches.

Among the platinum group metals rhodium is characterized by its hardness, chemical inertness in acidic solutions [18], low resistance and advanced catalytic properties for a wide range of heterogeneous reactions [19]. Rhodium is often used as an alloying agent with platinum, which leads to important applications such as the three-way automotive catalyst to convert CO and NO [20], or in petroleum refining to crack hydrocarbons [21].

Compared with Pt single crystal surfaces only a limited number of electrochemical experiments have been published for low-index Rh single crystals, which is most likely due to the difficulties in their preparation [22]. Meretskii et al. [23] reported the first polarization curves of Rh(1 1 1) in an electrochemical environment. Wieckowski and co-workers published in a series of papers voltammetric profiles of Rh(1 1 1) and Rh(1 1 0) employing ultrahigh vacuum (UHV)-based preparation techniques [24,25], or flame annealing

* Corresponding author.
  E-mail address: thomas.wandlowski@dcb.unibe.ch (T. Wandlowski).
  URL: http://www.dcb-server.unibe.ch/groups/wandlowski/ (T. Wandlowski).

in combination with cooling in oxygen-free nitrogen-containing iodine vapor followed by CO replacement and subsequent electrochemical oxidation of CO (iodine–CO replacement technique) [14,26–30]. These authors investigated the potential-dependent specific adsorption of (hydrogen-) sulfate [24–29], the reduction of ClO_4^- [27,30] as well as CO adlayers on Rh(poly), Rh(1 1 1) and Rh(1 0 0) [25] by combination of cyclic voltammetry with radio-tracer labeling studies [28,29] and UHV characterization employing electron energy loss spectroscopy, Auger electron spectroscopy and low energy electron diffraction [25]. Sung et al. [25] resolved, depending on adsorption time and potential, a main and a splitted (2 × 2) CO structure on Rh(1 1 1) in CO-saturated 0.5 M H_2SO_4 solution.

Weavers group adopted the iodine–CO replacement technique and carried out a series of experiments employing infrared reflection absorption spectroscopy (IRAS) of CO chemisorption and electro-oxidation on the low-index phases of Rh single crystals [31–36]. These studies revealed a distinct dependence of CO adsorbed in atop and bridge sites on potential, coverage and surface structure. A combined IRAS and in situ scanning tunneling microscopy (STM) study revealed the existence of two distinctly different potential-dependent adlayer structures for a CO saturated adlayer on smooth Rh(1 1 1) in aqueous electrolyte [37]. Roughening of the bare Rh(1 1 1) electrode by oxidation/reduction cycles enhances significantly the activity towards CO electro-oxidation [32,38]. Chang and Weaver proposed based on voltammetric and IRAS experiments with a Rh(1 0 0) electrode that the electro-oxidation of CO proceeds at the periphery of preformed CO islands according to a nucleation and growth process [36].

Clavilier et al. [15,38] and Feliu et al. [39] pointed out that the iodine–CO displacement technique [14] leads to a certain surface disorder with prominent effects on interfacial reactivity of these electrodes. As an alternative preparation technique these authors proposed a combination of flame annealing with cooling in a hydrogen–argon gas mixture and subsequent transfer of the electrode into the electrochemical cell with a protecting droplet of ultrapure water [15,39]. Gomez et al. employed this method and reported high-quality (fast-scan, 50 mV s^{-1}) voltammograms of well-ordered Rh(1 1 0) [40], Rh(1 0 0) [41] and Rh(1 1 1) [42] single crystal electrodes in 0.5 M H_2SO_4. Wan et al. [43] demonstrated by in situ STM that the entire double layer region of a Rh(1 1 1) electrode in H_2SO_4 is covered by a long-range ordered ($\sqrt{3} \times \sqrt{7}$) adlayer, which was attributed to a hydrogen-bonded network of co-adsorbed (hydrogen-) sulfate ions and water molecules. These authors also reported structure details of the rough "rolling hill" morphology of a Rh(1 1 1) surface after electrochemical activation by single and multiple oxidation/reduction cycles [44]. Shingaya and Ito examined the double layer structure and the adsorption of (hydrogen-) sulfate ions on Rh(1 1 1) by in situ IRAS and ex situ LEED [45,46].

Recently, Housmanns et al. published a series of papers on CO electro-oxidation on "ordered" and "disordered" Rh [n(1 1 1)–(1 1 0)] single crystal electrodes [47–51]. Based on chrono-amperometric transients [48,49] and a dynamic Monte Carlo simulation [50] these authors proposed that the overall mechanism of the CO electro-oxidation reaction on Rh[(n(1 1 1)–(1 1 0)] electrodes follows a Langmuir–Hinshelwood-type nucleation and growth mechanism controlled by the slow surface mobility of adsorbed CO.

The studies on relationships between surface structure and interfacial reactivity with massive single crystal electrodes are complemented by investigations employing bimetallic alloy electrodes
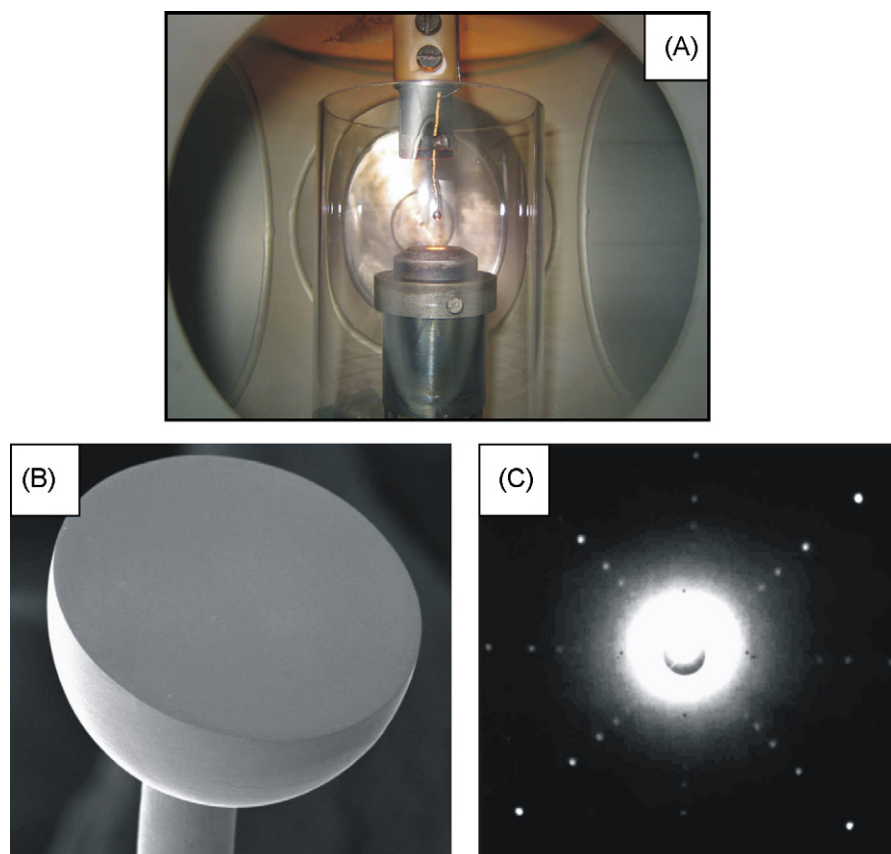

Fig. 1. (A) Assembly for the preparation of bead crystals employing an electron beam set-up, (B) SEM image and (C) Laue X-ray diffraction pattern of a high-quality Rh(1 0 0) bead electrode. Diameter of the polished surface: 2.5 mm.