# CO oxidation on stepped Rh[$n$(1 1 1) × (1 1 1)] single crystal electrodes: Anion effects on CO surface mobility

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## Abstract

The influence of anion adsorption on the CO electrooxidation reaction on stepped Rh[$n$(1 1 1) × (1 1 1)] electrodes was investigated by comparing voltammetric and chronoamperometric data obtained in 0.5 M HClO$_4$ with previously published results obtained in 0.5 M H$_2$SO$_4$. Compared to sulfuric acid media, complete stripping of the CO adlayer requires fewer cycles in perchloric acid and the resulting stripping voltammetry peaks are shifted to considerably lower potentials, attesting to the reduced influence of more weakly adsorbed anions. The absence of a shoulder prior to the main oxidation peak and the higher symmetry of the main peaks implies that the electrooxidation reaction in perchloric acid is not only faster than in sulfuric acid but probably also not diffusion limited, which suggests the mean field approximation as the best mathematical model for the reaction kinetics rather than nucleation and growth. The chronoamperometric transients recorded at various potentials show only a single oxidation peak with a slight tailing at longer times. Only the Rh(1 1 1) transients display tailing, which is Cottrellian in nature. The surface diffusion coefficient of CO deduced from the Cottrell plots is more than four orders of magnitude larger in perchloric than in sulfuric acid (HClO$_4$: $1 \times 10^{-12} < D < 2 \times 10^{-11}$ cm$^2$ s$^{-1}$ vs. H$_2$SO$_4$: $1 \times 10^{-16} < D < 8 \times 10^{-16}$ cm$^2$ s$^{-1}$), which also suggests a mean field model for HClO$_4$ rather than nucleation and growth. Apparently, specific anion adsorption on rhodium surfaces not only affects the rate, but also the dynamics of the CO electrooxidation reaction. Thus, by varying the adsorption strength of the anion, we could, in principle, influence the diffusion rate of adsorbates on the surface and, therefore, the reaction dynamics and the overall reaction rate.
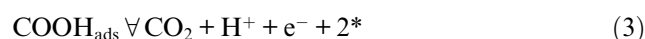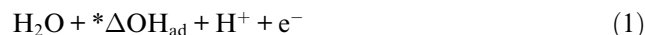© 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Understanding the overall reactivity of surface-catalyzed reactions requires insight into the mobility of adsorbed species. In a Langmuir–Hinshelwood type mechanism, the overall rate of the reaction depends critically on the extent to which reactants are mixed on the surface and, thus, on their respective rate of diffusion [1]. In electrocatalysis, the issue of surface mobility has recently received considerable attention in relation to the mechanism of CO electrooxidation [2–12].

The oxidation reaction of CO on noble metal surfaces is generally accepted to be of Langmuir–Hinshelwood type with the overall mechanism represented by the following steps [13]:

$$H_2O + * \rightleftharpoons OH_{ad} + H^+ + e^- \tag{1}$$

$$CO_{ads} + OH_{ads} \rightarrow COOH_{ads} \tag{2}$$

$$COOH_{ads} \rightarrow CO_2 + H^+ + e^- + 2* \tag{3}$$

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where "*" denotes a free surface site, reactions 1 and 3 are assumed to be fast, and reaction 2 is rate determining (at relatively high overpotentials).

Since the rate of reaction 2 depends on the spatial distribution of the reactants, the surface mobility of the adsorbates is of great importance. Analytical expressions for the total reaction rate can be obtained in two limiting cases, namely the mean-field approximation and the nucleation and growth model. The mean-field approximation assumes perfectly mixed reactants and a reaction rate that is proportional to the average coverages of the reacting species [1], implying a surface diffusion rate higher than the reaction rate. In the nucleation and growth model reacting species are assumed to be immobile on the surface. The reaction nucleates by adsorption of OH at "special" sites, usually defects or steps, and proceeds only at the interface between two reacting phases, causing the formation and growth of islands [14].

A noble metal to have recently gained renewed interest with respect to CO electrooxidation is rhodium [15–17]. Even though rhodium may not be a particularly attractive metal for application in low-temperature fuel cells, it displays CO oxidation characteristics, which deviate considerably from those of platinum and which, therefore, make it an interesting surface to study, especially in relation to the still much debated issue of CO surface mobility [18]. Recently, we studied this reaction on stepped $Rh[n(111) \times (111)]$ electrodes in 0.5 M $H_2SO_4$ and concluded that, contrary to what was reported for stepped Pt electrodes [2], the kinetics of the reaction can best be described by the nucleation and growth model rather than the mean-field approximation due to a low CO surface mobility [16,19]. Moreover it was suggested that the low mobility of CO on rhodium might be caused by the influence of the strongly adsorbed (bi)sulfate anion.

In this paper, we investigate in more detail the influence of specifically adsorbing anions on the catalysis of the CO electrooxidation reaction on stepped rhodium electrodes of $[n(111) \times (111)]$ orientation. CO stripping and chronoamperometric experiments were performed in 0.5 M $HClO_4$ and the results will be compared to those obtained previously in 0.5 M $H_2SO_4$ [16,19]. Results presented herein show that, like the electrooxidation of CO on Pt surfaces, the rate of the oxidation reaction is higher in perchloric acid than in sulfuric acid [20,21]. However, contrary to sulfuric acid, current–time transients recorded in perchloric acid display only a single oxidation peak followed by a tail at longer times. For Rh(111) this tail is Cottrellian in nature (similar to sulfuric acid media), which in principle could be taken as evidence for a surface diffusion limited reaction. We will interpret these results in terms of an anion-dependent CO surface diffusion coefficient.

## 2. Experimental setup

The working electrodes used in this study were rhodium bead-type single crystal electrodes of $Rh[n(111) \times (111)]$ (identical to $Rh[(n-1)(111) \times (110)]$) orientation (Rh(331), Rh(553), Rh(554), and Rh(111) with $n = 3$, $n = 5$, $n = 10$, and $n = 200–500$, respectively). The electrodes were prepared as described in [22], and oriented, cut and polished according to the Clavilier method [23]. Prior to each measurement the single crystal electrode was flame annealed and cooled down to room temperature in an argon (Hoekloos, N50)-hydrogen atmosphere (ratio 3:1), after which it was transferred to the electrochemical cell under protection of a droplet of deoxygenated water.

A special electrochemical cell, described in [3], contained a small movable spoon over an electrolyte reservoir, which allowed dosing of CO at open circuit potential (ocp) from a saturated CO solution without dissolving CO in the blank electrolyte. The CO coverage was checked by cycling in the hydrogen adsorption/desorption region. The electrochemical cell was cleaned by boiling in a 1:1 mixture of concentrated sulfuric and nitric acid, followed by repeated boiling (four times) with ultra-pure water (Millipore MilliQ gradient A10 system, 18.2 M$\Omega$ cm, 2 ppb total organic carbon). The blank electrolyte, 0.5 M $HClO_4$, was prepared with concentrated perchloric acid (Merck, "Suprapur") and ultra-pure water. During measurements the blank electrolyte was deoxygenated with argon (N50) and the electrolyte in the container above the spoon was saturated with CO gas (Hoekloos, N47).

A coiled platinum wire was used as a counter electrode and the reference electrode was a reversible hydrogen electrode (RHE) connected via a Luggin capillary. Measurements were performed at room temperature (22 °C) with a computer-controlled Autolab PGSTAT20 potentiostat.

## 3. Results and discussion

### 3.1. Cyclic voltammetry in absence of CO

In sulfuric acid media it is difficult to establish the system cleanliness and surface quality of a $Rh[n(111) \times (111)]$ electrode from the blank cyclic voltammogram (BCV) due to the absence of well-defined, reversible anion and hydrogen adsorption/desorption peaks [16,19]. However, in perchloric acid the cyclic voltammogram of Rh(111) is characterized not only by the reduction of perchloric acid at low potentials but also by a "butterfly" at approximately 0.64 V vs. RHE [24–29]. This butterfly is ascribed adsorption and desorption of perchloric acid and oxygen containing species ($OH_{ads}$) in the same manner as (bi)sulfate on Pt(111). Similar