

# Strictly potentiostatic current oscillations during bulk CO electro-oxidation on platinum in the presence of inhibiting anions

Souradip Malkhandi, Antoine Bonnefont, Katharina Krischer \*

*Physik-Department E19, Technische Universität München, James-Frank-Str. 1, D - 85748 Garching, Germany*

Received 4 April 2005; received in revised form 19 April 2005; accepted 19 April 2005

Available online 26 May 2005

## Abstract

We investigate bulk CO electrooxidation on a rotating Pt disk electrode in concentrated acidic electrolytes containing small amounts of  $\text{BF}_4^-$  anions with cyclic voltammetry and potentiostatic measurements. Under potentiodynamic conditions, the average reactivity decreases with increasing  $\text{BF}_4^-$ -concentration. For fixed applied potential strictly potentiostatic current oscillations were observed. Both observations are reproduced with a mean field model for CO electrooxidation in which the anions are assumed to competitively adsorb on free electrode sites while the electrode potential is treated as a parameter. Bulk CO electrooxidation on Pt in the presence of inhibiting anions is thus an example of an electrochemical oscillator with purely chemical feedback loops. © 2005 Elsevier B.V. All rights reserved.

*Keywords:* Carbon monoxide oxidation; Oscillations; Tetrafluoroboric acid; Anion adsorption; Cyclic voltammetry

## 1. Introduction

When adsorbed on an electrode, carbon monoxide is a poison for many electrocatalytic reactions, most notably hydrogen oxidation and the oxidation of small organic molecules, such as formic acid or methanol (see, e.g. [1,2] and references therein). Electrode poisoning by adsorbed CO is also a major problem concerning the anode reaction in low-temperature  $\text{H}_2/\text{O}_2$  or direct methanol fuel cells. In the former type of fuel cells, the  $\text{H}_2$  feed gas might be contaminated with CO owing to the reformer process, which is the main source of  $\text{H}_2$ . During methanol oxidation on Pt, CO is formed as an intermediate, leading thus to a self-poisoning of the electrode. Understanding the mechanism of CO electro-oxidation is therefore essential to be able to minimize the poisoning effect of CO in electrocatalysis, and much

work has been devoted to fundamental studies of CO electro-oxidation on noble metals under various conditions (for reviews, see e.g. [1–5]).

An important result of these studies is that CO is oxidized through the Langmuir-Hinshelwood mechanism, i.e., the formation of  $\text{CO}_2$  is preceded by the adsorption of both reactants, CO and an oxygen-containing species which compete for the same reaction sites [6,7]. On Pt electrodes, the reactive oxygen species are formed through the oxidative chemisorption of water, which takes place only at potentials considerably more positive than the reversible oxidation potential of hydrogen or methanol. Hence, the extent of poisoning by CO should be reducible when providing an oxygen source at lower potentials. Most of the efforts along these lines aimed at ‘decorating’ or alloying Pt catalysts with other noble metals, which form oxides at lower potentials than Pt [8]. Ru was found to be a promising metal in this respect.

However, not only the anode material but also the nature of the supporting electrolyte influences the

\* Corresponding author. Tel.: +49 89 289 12535; fax: +49 89 289 12530.

*E-mail address:* [Krischer@ph.tum.de](mailto:Krischer@ph.tum.de) (K. Krischer).

overall reaction rate and thus has to be incorporated when one wishes to obtain a complete picture of the mechanism of CO electro-oxidation. Consequently, more recently also the influence of different anions on the oxidation rates of CO and of small organic molecules has been studied. In the course of such studies, an unusual anion effect was reported by Schell and coworkers [9–11]. These authors observed a remarkable enhancement in the oxidation rate of formic acid [9,10] and of methanol [11] when replacing a small amount of perchloric acid base electrolyte with HBF<sub>4</sub>. They offer an intriguing explanation for the enhancement effect, which could be described as the anionic counterpart to the metal-promoted oxide formation at low potentials: in aqueous solutions BF<sub>4</sub><sup>-</sup> is in equilibrium with BF<sub>3</sub>OH<sup>-</sup> ions, which in turn can, directly or indirectly, adsorb on the electrode negative to the onset of oxidation of chemisorbed water. Schell et al. suggest that the OH-group of adsorbed BF<sub>3</sub>OH<sup>-</sup> reacts with adsorbed CO, keeping thus the electrode reactive for the direct oxidation of formic acid or methanol at potentials at which it is poisoned by CO in a BF<sub>4</sub><sup>-</sup>-free electrolyte.

In this paper, we study bulk CO electro-oxidation on a rotating Pt disk electrode in perchloric and sulfuric acid containing different amounts of HBF<sub>4</sub> as well as in 0.5 M HBF<sub>4</sub> solution to test the above described hypothesis.

## 2. Experimental

The working electrode (WE) was a polycrystalline platinum (99.999%) disk electrode embedded in a Teflon block. The home-built electrode system was attached to a Pine instrument rotator. The electrode had a geometrical surface area of 0.1975 cm<sup>2</sup> and a roughness factor of about 1.65. Note that below we normalize the current density to the geometrical surface area. Prior to each experiment the electrode was pretreated in the following way: three times in a row, it was first immersed in a 1:1 mixture of H<sub>2</sub>SO<sub>4</sub> (96%) and H<sub>2</sub>O<sub>2</sub> (30%) for 5 min, and then in Millipore water for 5 min. Both steps were done in an ultrasonic bath. Thereafter, the electrode was thoroughly rinsed with water and transferred to the electrochemical cell with a water droplet on the electrode surface. It was immersed in the electrolyte under potential control close to 0 V RHE. The counter electrode was a Pt wire bent to a ring and was placed symmetrically to the WE in the main compartment of the cell (for details see [12]). The reference electrode (RE) was a sat. Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode and kept in a separate compartment. All potential values below are given with respect to this reference electrode.

All water used in the experiments was obtained from a Millipore MilliQ system. The electrolytes were prepared from HClO<sub>4</sub> (70%, Suprapure Merck) or H<sub>2</sub>SO<sub>4</sub>

(96%, Suprapure Merck), and HBF<sub>4</sub> (50%, Aldrich, 'Purum'). The glass cell as well as all other glass items used were cleaned in H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> 1:1 solution. The potentiostat employed was built by the Electronic Laboratory of the Fritz-Haber-Institut der MPG, Berlin, Germany and worked in parallel with a Sun Solaris based Real Time data acquisition system.

Prior to the measurements with CO, the quality of the WE was checked by recording a cyclic voltammogram (CV) in an Ar (Linde, 99.999%) saturated electrolyte. Therefore, the electrolyte was purged with Ar for at least 30 min, during which the potential was scanned between -660 and 600 mV (vs. sat. Hg/Hg<sub>2</sub>SO<sub>4</sub>). After switching to CO (Air Liquide, 99.99%) bubbling, the electrode was cycled for approximately 25 min between -640 and 400 mV to guarantee saturation of the electrolyte with CO before CVs were recorded. Also in the further course of the experiments CO was continuously bubbled through the electrolyte. In all experiments shown the WE was rotated with 1200 rpm.

## 3. Results

Fig. 1 shows asymptotic cyclic voltammograms of Pt in CO-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different amounts of BF<sub>4</sub><sup>-</sup> ions. The solid curve was obtained in pure supporting electrolyte, the dashed, dotted and dot-dashed curves in electrolytes containing 5, 10 and 20 mM HBF<sub>4</sub>, respectively. The CVs are all qualitatively similar and agree with those from the literature. During the positive scan, they exhibit a low current, CO-poisoned state up to approximately 250 mV, at which the onset of the oxidation of the CO monolayer manifests itself in an ignition peak. For more positive

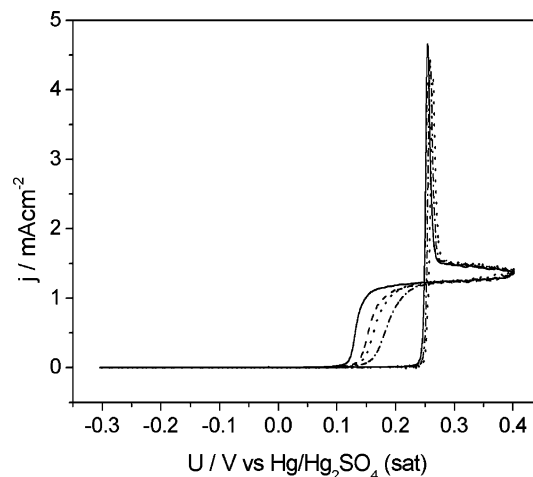


Fig. 1. Cyclic voltammograms of a rotating Pt disk electrode in CO saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0 (solid curve), 5 (dashed curve), 10 (dotted curve) and 20 (dash-dotted curve) mM HBF<sub>4</sub>; scan rate 50 mV/s; rotation rate 1200 rpm.

Download English Version:

<https://daneshyari.com/en/article/10267154>

Download Persian Version:

<https://daneshyari.com/article/10267154>

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