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CO electrooxidation on a polycrystalline Pt electrode: A wall-jet EQCN study

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Abstract

Pre-adsorbed and bulk (continuous) CO oxidation on a polycrystalline Pt electrode were examined in a wall-jet electrochemical quartz crystal nanobalance (EQCN) setup, using both differential and integral evaluation of the EQCN data, to get further insights into the kinetics and mechanism of this important fuel-cell related electrocatalytic reaction. The hydrogen underpotential adsorption–desorption features in the base cyclic voltammogram of a Pt film are accompanied by significant changes in the electrode mass due H-upd induced desorption–adsorption of anion. In the double-layer region small capacitive currents are accompanied by comparatively large reversible mass changes indicating anion adsorption/desorption (96.5 g mol^{-1} assigned to bisulfate). OH and oxygen electrosorption from water at potentials more positive of 1.0 V result in relatively small variations in the electrode mass (16 g mol^{-1} for PtOH and ca. 9 g mol^{-1} for PtO formation, respectively). The CO-adlayer stripping first leads to the electrode mass decrease in the "pre-peak" region, followed by a fast mass increase within the main stripping peak due to re-adsorption of bisulfate anion (91 g mol^{-1}). A mass-transport limited current for bulk CO oxidation under continuous flow of CO-saturated electrolyte leads to negligible mass changes ($0–1 \text{ g mol}^{-1}$) in the PtO region, suggesting that bulk CO oxidation is mediated by electroformed PtO.
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1. Introduction

Electrooxidation of adsorbed CO on Pt and bimetallic Pt alloys is one of the fundamental problems related to practical application of low temperature polymer electrolyte fuel cells (PEFCs), including direct methanol fuel cell (DMFC) [1]. Under fuel cell operating conditions the anode catalyst surface is progressively blocked by strongly adsorbed CO species, which is present in the hydrogen feed at the trace amounts (PEFC), or is developed due to catalytic methanol dehydrogenation (DMFC). As a result the poisoning CO_{ad} species hinder the access of the fuel to the catalyst surface and its electrooxidation at the anode,

leading to severe fuel cell performance losses. Electrooxidation of adsorbed CO can be achieved at potentials of OH electrosorption and the surface reaction between neighboring CO_{ad} and OH_{ad} species via Langmuir–Hinshelwood mechanism on Pt (or bifunctional mechanism [2] for bimetallic electrodes). Therefore, a detailed understanding of kinetics and mechanism of CO electrooxidation is required to improve the activity of anode catalysts and their tolerance toward the CO poisoning. This has stimulated extensive research efforts, applying numerous in situ and ex situ techniques for the electrode|electrolyte interface probing [3,4]. Notably, due to a low concentration of dissolved gasses in aqueous solutions, an enforced mass-transport to the electrode surface is required for the suppression of diffusion limitations in the kinetic studies, which is usually achieved in a rotating (ring) disk electrode (R(R)DE) setup [5–7]. Alternatively, a well-defined mass-transport when studying electrocatalytic reactions can be established using other

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hydrodynamic voltammetry techniques – either wall-jet disk electrode (WJDE) [8–12], or thin-layer flow-cell (TLFC) [13–23] configuration.

Electrochemical quartz crystal nanobalance (EQCN), being a sensitive probe to detect the electrode mass changes in nanogram range, have been widely employed to study various processes occurring at the solid|liquid interface [24]. However, up to now, only several attempts have been made to monitor the electrode mass variations during electrocatalytic oxidation of small C-1 molecules, such as formic acid [25–27], methanol [28–30], and formaldehyde [31,32] on Pt and bimetallic (Pt alloys [29,30] or underpotentially-modified Pt [27]) electrodes. Electrooxidation of CO has been studied using EQCN from both pre-adsorbed CO-adlayer state in the supporting electrolyte [15,33,34], and bulk (continuous) oxidation of the dissolved CO gas [34]. However, bulk CO oxidation rate is largely hindered due to diffusion limitations at low (ca. 1 mM at room temperature) concentration of CO-saturated solutions.

To overcome diffusion limitations, an enforced and well-defined mass-transport to the electrode surface is required, which can be achieved for the EQCN in a RDE configuration [35–37], WJDE [38–44] or TLFC [45,46] design. Although all three of these hydrodynamic EQCN designs were demonstrated to operate successfully for different systems [35–46], none of them have been applied, so far, to study continuous oxidation of CO under controlled mass-transport conditions. In the present contribution, we have employed a WJDE-EQCN design to study bulk oxidation of CO on Pt electrode under well-defined mass-transport. For comparison, the EQCN response of Pt electrode and pre-adsorbed saturated CO adlayer oxidation in a quescient supporting electrolyte (0.5 M H_2SO_4 solution) was studied. Similar measurements were reported recently [15,17] when studying pre-adsorbed and bulk CO oxidation on electrodeposited Pt and PtRu electrodes, and on carbon-supported Pt catalyst using a thin-layer EQCN/DEMS flow-cell.

For the mechanistic and kinetic analysis of the EQCN data in the present study, both charge/total frequency (mass) change ($\Delta q/\Delta f$), and current/frequency (mass) change rate ((dq/dt)/(df/dt)) plots vs. the electrode potential were employed. The former case corresponds to the integral moiety – the *amount* of adsorbed/desorbed (deposited/dissolved) species when passing a certain charge through the circuit, which is equivalent to a traditional (classical) coulometric gravimetry. The second case corresponds to the differential moiety – the *rate* of adsorption/desorption (deposition/dissolution) process, measured independently using EQCN through the Faraday current (voltammograms) and frequency (mass) change rate (voltmassograms) [47]. For the Faradaic reactions of a known stoichiometry, the frequency (mass) change rate can be directly converted to the current units and used for the extraction of partial reaction currents in complex processes [41–44]. It should be noted, however, that a common presentation of the EQCN data usually involves "mixed" differential/integral (voltammetric/total mass change) plots.

In the following after a brief description of experimental details, we will present and discuss the EQCN results for Pt electrode in the supporting electrolyte and electrooxidation of pre-adsorbed CO adlayer on Pt in a quescient electrolyte, and bulk CO oxidation in a WJDE-EQCN configuration, using both differential and integral EQCN data evaluation in order to gain further insight into the kinetics and mechanism of these important electrocatalytic reactions.

2. Experimental

The wall-jet EQCN flow-cell design has been described in detail elsewhere [44]. Briefly, AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelemetrics Ltd., UK) home-evaporated by thin Pt layers (thickness ca. 500 nm) from both sides were connected to a home-built oscillator. The exposed geometric area of the working electrode was 0.636 cm^2. Pt films evaporated on quartz crystals from both sides were attached to the Pt contact wires and pressed in-between two silicone rubber *o*-rings, which were placed between the holder and a glass cell body, respectively, at the bottom of the cell of a working volume of ca. 2 ml. The upper part of the cell contained the Pt-wire counter electrode, joints for the electrolyte inlet and Luggin capillaries, and the electrolyte outlet tube (the inner diameter of the inlet capillary was 0.8 mm, the distance to the electrode ∼2 mm). A wall-jet cell, equipped with two separate inlet bottles (either CO or Ar-saturated), allowed either conventional EQCN measurements in a quescient solutions (a base CV/EQCN of Pt electrode in the supporting electrolyte, pre-adsorbed CO monolayer stripping after solution exchange back to supporting electrolyte), or bulk CO electrooxidation, impinging CO-saturated (1 mM) electrolyte (0.5 M H_2SO_4) at a constant flow rate (1 ml s^{-1}), driven by the hydrostatic pressure in the supply bottles. Analytical grade sulfuric acid and triply distilled water were used to prepare the solutions, purged before use by Ar (Elmemesser, 99.999%) or CO (Elmemesser, 99.997%) gases, respectively.

The EQCN measurements were carried out using a precision frequency counter Ch3-64 and two digital voltmeters B7-46 (Russia) connected to a PC through the IEEE 488 interface. A programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia) were used (the potential sweep rate was 10 mV s^{-1}). The electrode potential was measured with respect to Ag/AgCl/KC1$_{sat}$ reference electrode and is referred below vs. a standard hydrogen electrode (SHE). A Pt-wire served as a counter electrode. The measured electrode potential, the Faradaic current and the frequency were transferred to the PC every 1.3 s. Differential EQCN data (the frequency/mass change rate df/dt) were found as the difference between two frequency measurements per 1 s and compared with the reaction rate (Faradaic current) as a function of the electrode potential. For the integral presentation of the EQCN data, the total frequency (electrode mass) plots were compared with the coulometric