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Microgravimetric and voltammetric study of Zn underpotential deposition on platinum in alkaline medium

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Abstract

The microgravimetric and voltammetric responses of a polycrystalline Pt electrode in 0.1 mol L^{-1} NaOH solution in the presence and the absence of 1.6×10^{-4} Zn^{2+}, at 0.1 V s^{-1} were analyzed. During the positive potential sweep, the water molecules are progressively substituted by OH^- ions, prior to PtO formation. The voltammetric charges obtained under the Zn_{ads} dissolution peaks suggest that 0.7 monolayers are deposited, with each Zn ad-atom occupying one active site and transferring two electrons. The total loss of mass due to the dissolution of the Zn ad-layer was 136.6 ng cm^{-2} and the mass increase due to PtO formation was found to be only 12 ng cm^{-2} less than the theoretical ones, 157.5 and 37.4 ng cm^{-2}, respectively, indicating that both processes are overlapped. In this way it is proposed that an adsorbed by-layer of Zn and OH^- ions is formed.

Keywords: Electrochemical quartz crystal microbalance; Zn UPD; Hydroxyl ion adsorption; Ad-atoms

1. Introduction

Zinc is used in a wide range of technological applications, such as a component in cathodes for water electrolysis [1–3], in energy storage devices [4–6], in semi-conductive layers in photovoltaic devices [7–9] and in alloys used for corrosion protection [10,11], amongst others. This wide range of applications is reflected in the exceedingly high number of scientific papers that describe the behavior of Zn during its deposition from acid or alkaline medium [12–15]. Several studies of the electrodeposition behavior are dedicated to the initial stages of phase formation, in the so-called underpotential deposition (UPD) region [16–21], mainly in acid media.

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One of the best "in situ" techniques for such observations is a combination of cyclic voltammetry (CV) with the electrochemical quartz crystal microbalance (EQCM) technique [23–25]. The simultaneously acquired current and mass variation data can provide insights into the electroactive or non-electroactive interactions that occur at the electrode surface.

The utilization of CV-EQCM coupled techniques for the study of the electrochemical deposition of Zn began with the work of Aramata et al. [22]. The authors analyzed Zn UPD on polycrystalline Pt surfaces by FTIR and EQCM in $0.1\,\mathrm{mol\,L^{-1}}$ KH_2PO_4 solutions at pH 4.6. It was concluded that Zn ad-atom coverage reached a maximum value of 0.75 at 0.05 V in a UPD process involving a two-electron transfer. The EQCM data gave the value of phosphate coverage as 0.27. Moreover, with the addition of Zn^{2+} to the electrolyte the intensity of the FTIR bands at 990, 1044 and $1090\,\mathrm{cm^{-1}}$ increased and the electrode potential shifted towards more negative values. These results suggest that phosphate species (in the form of HPO_4^{2-}) adsorb on the UPD Zn on Pt. In this situation at least one of the three P—O groups seem to be bound to the Zn adlayer on the Pt surface.

Wang et al. [23] used CV-EQCM techniques to study the electrodeposition and corrosion of tin–zinc coatings. A 70%Sn–30%Zn layer was deposited from a neutral non-cyanide bath. This layer was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) and characterized as Sn and Zn phases. Using the EQCM technique, the plating current efficiency was determined. Moreover, the EQCM experiments were also able to measure the corrosion rate when the coating was exposed to a $0.5\,\mathrm{mol\,L^{-1}}$ Na_2SO_4 (pH 3.6) solution under open circuit potential conditions. Under such conditions, it was demonstrated that the Zn dissolution reaction is the main process occurring.

In a recent publication Giménez-Romero et al. [24] studied the electrochemical reduction of Zn(II) ions by CV-EQCM and electrochemical impedance spectroscopy (EIS) in moderately acidic medium. Data obtained by both electrochemical techniques suggests that zinc reduction, in 0.010 $\mathrm{mol\,L^{-1}}$ $ZnSO_4$ + $0.32\,\mathrm{mol\,L^{-1}}$ H_3BO_3 + 0.26 $\mathrm{mol\,L^{-1}}$ NH_4Cl + $1.33\,\mathrm{mol\,L^{-1}}$ Na_2SO_4, pH 4.4, is characterized by the simultaneous reaction of two processes, zinc reduction and proton reduction. On the other hand, the zinc oxidation occurs in two steps: the first process is a heterogeneous reaction where the product is not on the electrode surface nor is detected by EQCM, whereas the second process is a homogeneous reaction.

As far as can be found in literature, applications of CV-EQCM in studies of Zn underpotential deposition are limited to acid or neutral media. However, many industrial electrodeposition baths for Zn and its alloys are alkaline. Thus, the use of CV-EQCM techniques to study the formation of the first Zn_{ads} layer becomes interesting. The CV-EQCM techniques can be used in order to evaluate the co-adsorption processes of the metallic ions and OH^- on the electrode surface and its influence on the degree of Zn ad-atom surface coverage.

Therefore, the objective of this present study is to analyze UPD Zn at Pt electrodes by CV-EQCM techniques in alkaline medium.

2. Experimental

The electrolytes used in this work were prepared with P.A. grade NaOH (Mallinckrodt), ZnO (Mallinckrodt) and purified water (Milli-Q system). Before each experiment, the solutions were deaerated by passing N_2 (SS White Martins) for 20 min. All experiments were conducted at room temperature (25 ± 1 °C).

A conventional, three electrode, Pyrex® glass electrochemical cell with a Teflon® cover and a capacity of 50 mL, was used in the experiments. The working electrode was a platinum disc mounted on an AT-cut quartz crystal (with a resonance frequency of 9 MHz) supplied by Maxtek Inc. The electroactive area was calculated at $0.35\,\mathrm{cm^2}$, using the hydrogen desorption charge method [26]. The experimental sensitivity of the quartz crystal Pt electrode was determined by potentiostatic silver electrodeposition [27–29] as being $830\,\mathrm{Hz\,\mu g^{-1}}$. A $1\,\mathrm{cm^2}$ platinum foil was used as the auxiliary electrode while the reference