

Short communication

## Electrochemical quartz crystal microbalance study of the electrodeposition of Co, Pt and Pt–Co alloy<sup>☆</sup>

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### Abstract

The electrochemical deposition of Co, Pt and Pt–Co alloy are studied with the electrochemical quartz crystal microbalance (EQCM) on a gold substrate. Co is deposited from acidic sulphate bath containing boric acid. Different processes are identified in this bath. Electrodeposition of Co on Au substrate is observed at potentials above redox potential, underpotential deposition, most probably due to formation of a Co–Au alloy. At more cathodic potentials, below  $-0.5$  V, metallic Co is formed. The film is completely dissolved at positive potentials during the anodic scan, probably mediated by  $\text{Co}(\text{OH})_2$ . The electrodeposition of platinum from acidic  $\text{PtCl}_6^{2-}$  bath occurs below the thermodynamic potential (0.74 V) with almost 100% efficiency. At potentials negative from 0.0 V the efficiency decreases due to parallel water reduction. The codeposition of Co and Pt is also studied in acidic bath. Here, the decrease of pH due to water reduction on Pt deposits gives rise to precipitation of  $\text{Co}(\text{OH})_2$ , together with the deposition of metallic Pt and Co. The films contain as major component the  $\text{Pt}_3\text{Co}$  alloy.

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### 1. Introduction

The electrodeposition of metal and alloys is a technique that may have special interest for the synthesis of electrocatalysts for proton exchange membrane fuel cells (PEMFC). It is low temperature and non-vacuum technique, easily applied on different scales, from micrometric to macroscopic areas [1]. It also allows for a good control of the amount of electrocatalyst, and can be used to deposit films or particles of metals, alloys and compounds. For particles deposition, it is used the pulse deposition variant [2–6]. With respect to PEMFC catalysts, the principal electrocatalyst used at present is platinum and its binary alloys, that may enhance the activity towards water reduction and favour tolerance to CO in the anode [7,8]. Two main issues of major importance for PEMFC deployment, are the durability and cost of the electrocatalyst [9]. The electrodes with standard performance ( $0.5 \text{ W cm}^{-2}$ ) require about  $0.5 \text{ mg cm}^{-2}$  of platinum, which contributes to fuel cell cost with about  $\text{US\$ } 40 \text{ kW}^{-1}$  (above 70% of stack cost) according to present plat-

inum prize [10]. This charge would probably be increased in case of massive production of fuel cells, requiring a significant part of world-wide platinum resources.

Electrodeposition, due to its particularities, may help in the preparation of electrodes with higher stability, using lower platinum content, as well as the synthesis of alternative catalysts based on new platinum forms, like incorporated in polymer films [11–13], platinum alloys [14,15], or new non-platinum catalysts [16]. During electrodeposition of platinum on carbon, the growth of hemispheric particles take place by the transfer of electrons from the electrode substrate to dissolved Pt(IV) species. Particles will deposit preferentially on electrochemically more active sites, like graphene edges (steps) and kinks, or surface oxygenated groups of carbon (aldehydes, alcohols and ketones), giving rise to a strong interaction with the substrate and more stable particles.

In this work, the deposition of Pt, Co and co-deposition of both are studied with the electrochemical quartz crystal microbalance (EQCM). Pt–Co alloys have shown enhanced kinetics towards oxygen reduction [17], and acceptable stability [18,19] which is of interest for the synthesis of more efficient electrocatalyst with lower Pt content. Co may be alloyed with Pt by direct electrodeposition in acidic [20,21] and basic ammonia solution [22,23]. Solid solution alloys can be obtained with

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