

## In-situ SXRD structural study of PtZn electrochemical alloying

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An important problem in material science is the search for a suitable catalyst for the oxygen reduction reaction (ORR). Bimetallic surfaces have been shown to be more active than single element materials [1]. Unfortunately, such materials are unstable and dissolution of the less noble metal is observed at reaction conditions. Therefore, a significant effort has been made to understand the processes taking place on those surfaces during catalysis (in the electrochemical environment) in order to improve the performance of the catalyst in fuel cell applications [2]. Various techniques have been used to observe catalysis in an electrochemical environment, but in-situ structural information of bimetallic surfaces during catalysis is scarce. Only two techniques are suitable for this purpose in an electrochemical environment: surface x-ray diffraction (SXRD) and electrochemical STM.

In this set of experiments, we study the alloying and dissolution process of ORR active PtZn surface alloy [3]. The PtZn surface is prepared in an electrochemical cell by Zn deposition on Pt(111) and Pt(110) surfaces from sulphate solution at potentials negative to the AgCl reference electrode. The surface rods, reflectivity, and powder pattern are measured during the deposition and stripping. To obtain the structural reference information, we first measure the clean surface in Zn free 0.01 M MgSO<sub>4</sub> electrolyte. As the potential decreases from 125 mV to -850 mV we observe surface roughening, lattice expansion, and change in reflectivity.

The Zn is deposited on the surface at various potentials negative to 125 mV. Zn is adsorbed as soon as -200 mV and the deposition is followed by immediate diffusion to the bulk (alloy formation). Depositing Zn on the surface inhibits the surface roughening which was observed in Zn free 0.01 M MgSO<sub>4</sub>. We also found no evidence of an ordered Zn UPD monolayer which precedes the bulk diffusion and for both surface orientations, the PtZn alloy has the same characteristic diffraction ring pattern. When the alloy is formed by slow sweep to negative potentials, the resulting structure is an ordered monocrystal. Contrary, when the alloy is formed by stepping the potential to -750 mV, the resulting structure is a polycrystal. The alloy dissolution is a significantly slower process than the alloy formation. The main difference between the Pt(111) and Pt(110) substrate is the kinetics of the alloy formation and dissolution. The alloy forms significantly faster on a more open Pt(110) surface.

The in-situ measurement of the alloy dissolution is also discussed for different potentials and during

different chemical reactions. The oxygen reduction reaction has no effect on the speed of dissolution while adsorbing CO on the surface changes significantly the dissolution kinetics. In case of adsorbed CO, zinc from first few alloy monolayers dissolve rapidly at the beginning of the process, while at the later stages the dissolution rate constant decreases (Fig.1).

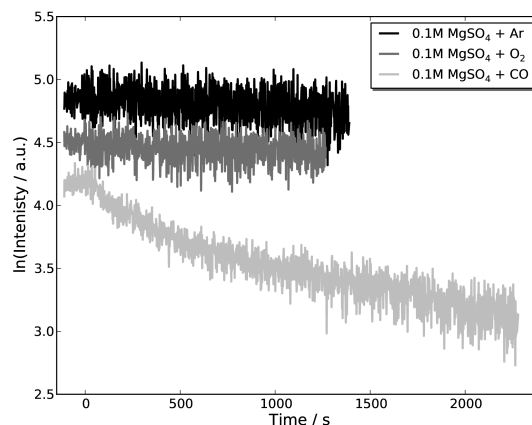


Fig.1 Alloy dissolution at 200 mV vs. Ag/AgCl for different chemical environments.

### References:

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