Osmium adlayers spontaneously deposited on the Pt(111) electrode: a structure and function study

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One of the obstacles to overcome in making direct methanol fuel cells (DMFC) practical is the lack of efficient poison-tolerant anode catalysts. In the oxidation of methanol on Pt, surface CO is formed as a stable intermediate, which blocks catalytic sites and inhibits further methanol oxidation. Therefore, a good anode catalyst for DMFC should easily transform the poisonous CO to CO2 – using oxygen atoms available in water on the electrode surface, or water decomposition products like adsorbed OH species – to release surface sites for subsequent methanol oxidation. In this project, Pt surfaces have been modified with various metals such as Ru and Os to change the CO surface binding properties, and lessen the effect of CO poisoning. Since the most active methanol oxidation catalysts are known so far to be ternaries or even quaternaries, and contain osmium as one of such catalysts components (Pt/Ru/Os and Pt/Ru/Os/Ir), the role of osmium in methanol oxidation electrocatalysis needs to be fully understood. We therefore report the formation of Os islands on Pt(111) electrodes by spontaneous deposition studied by in-situ STM, and Os oxidation states on Pt(111) by ex-situ x-ray photoemission spectroscopy (XPS) and in-situ Grazing Incidence Fluorescence X-ray Absorption Spectroscopy (GIF-XAS).

The spontaneous deposition of Os on Pt(111) was carried out by: (1) immersing a clean and ordered Pt(111) into 1 mM $OsCl_3$ + 0.1 M H_2SO_4 solution without electrode potential control, (2) rinsing the electrode with water and (3) voltammetrically cycling in the potential range between 0.08 V and 0.9 V (vs. RHE). The in-situ STM work reveals that monoatomic (or nearly monoatomic) height islands of Os are formed, and are in a round shape and in 2-5 nm diameter, and confirms our previous STM results observed in air. The ex-situ XPS data demonstrate the dependence of the oxidation states of Os on the electrode potential. Namely, there are three oxidation states: metallic Os ($4f_{7/2}$ core level binding energy of 50.8 eV), Os(IV) (51.5 eV) and Os(VIII) (52.4 eV). Predominantly metallic layer of Os exists in the potential region below 500 mV (vs. RHE) but osmium is oxidized to Os(IV) above 500 mV at the expense of metallic Os. Stripping of osmium does not begin until the potential reaches 900 mV, but then, at higher potentials, the dissolution occurs simultaneously with platinum oxide formation. Notably, above 1000 mV, the oxidation state of the residual Os increases to VIII.

The in-situ GIF-XAS results support the presence of the three oxidation states of Os on Pt(111) that were identified as a function of electrode potential. The x-ray energy at maximum absorption appeared at 10.8765 keV below 400 mV, was gradually shifted to higher values in the potential range between 500 mV and 1000 mV, and reached the limiting value of 10.8793 keV. Other GIF-XAS parameters related to the oxidation state of Os, like normalized peak height and peak width will be reported, as they show tendencies consistent with the XPS measurements. In addition, the variation of the raw edge jump height of Os, equivalent to the surface concentration, reveals that the electrochemical stripping of Os begins at 1000 mV, as expected from voltammetry. Both qualitatively and quantitatively, the results from ex-situ XPS and in-situ GIF-XAS appear uniquely consistent. The observed results are discussed regarding the development of poison-tolerant catalysts for use in the direct methanol oxidation fuel cell. We present results on osmium adlayers that are much comprehensive than before, and have much more pronounced in situ components due to our in situ STM and GIF-XAS measurements. Convergence of the in situ and ex situ data is one of the main research outcomes of this project.