In situ XAS of Pt Monolayer Model Fuel Cell Catalysts: Balance of Nanostructure and Bimetallic Interactions

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Introduction and Objectives

Bimetallic catalyst materials are of great interest due to the tunability of their (electro)catalytic properties, which is particularly important for oxygen reduction reaction (ORR) electrocatalysts in fuel cells, where a significant reduction of Pt loading is needed to achieve economic viability. Density functional theory (DFT) calculations have successfully predicted a volcano-type relation between ORR activity and the bond strength of the "descriptor" adsorbate atomic oxygen (O_{ad}).[1] Using x-ray absorption spectroscopy (XAS) at the Pt L_3 edge on a well-defined Pt model catalyst consisting of one monolayer Pt on a Rh(111) single-crystal substrate, we overcome the incompatibility between the high penetration depth of an *in situ* technique and the required surface sensitivity, because only surface Pt atoms and their interactions with oxygen-containing species from the electrolyte are probed. By combining the High Energy Resolution Fluorescence Detection (HERFD) technique and *ab initio* multiple-scattering calculations, we can establish unambiguous spectral fingerprints for the differentiation of chemisorbed oxygen-containing species and surface oxide formation.[2,3] Here, we show our recent HERFD XAS results on two different Pt/Rh(111) model catalysts prepared by two different techniques that result either in a uniform two-dimensional Pt monolayer (2D Pt/Rh(111)) or in three-dimensional Pt islands (3D Pt/Rh(111)). Furthermore, we present an extensive DFT study on 3D Pt/Rh(111) where, in addition to the well-known strain and ligand effects, we identify an additional effect of under-coordinated Pt atoms near corners and edges of islands, which can strongly affect the overall ORR activity.

Results and Discussion

During sample preparation and subsequent characterization using EXAFS, we found that Pt evaporation in UHV onto a heated (600 K) Rh(111) substrate results in formation of 2D Pt/Rh(111) as already reported by Duisberg et al.,[4] while a 3D island morphology was

determined when Pt was deposited in a wet-chemical route[5] using the galvanic displacement of a Cu monolayer.

Both samples were studied with *in situ* HERFD XAS in 0.01 M $HClO_4$ electrolyte over a broad potential range, and the shape and intensity of the Pt 2*p* → 5*d* resonance ("white line") was carefully analyzed to identify spectral signatures of chemisorbed species H_{ad} and O/OH_{ad}, as well as Pt oxide. Most remarkably, we found that both H_{ad} at low potentials as well as O/OH_{ad} at high potentials could not be detected at all on 2D Pt/Rh(111). This result may appear surprising for a Pt electrode, but can be explained with the strong ligand and strain effects of the Rh substrate which destabilize O_{ad} by ~0.6 eV. On 3D Pt/Rh(111), the spectral signatures of H_{ad} and O/OH_{ad} can both be detected, although the potential range of the adsorbate-free or H_2O-covered surface is still wider than on Pt(111). Using DFT calculations on individual fcc threefold hollow adsorption sites, we estimate the effects of island thickness and under-coordination near edges and corners, which both stabilize O_{ad} and therefore shift 3D Pt/Rh(111) back towards pure Pt.

Conclusions

When HERFD XAS is applied to a well-defined monolayer model electrocatalyst, sufficient spectral resolution and surface sensitivity can be achieved to obtain the weak spectral signatures of chemisorbed oxygen-containing species. We have applied this technique to two Pt/Rh(111) model catalysts with different morphologies. The destabilization of O_{ad} on 2D Pt/Rh(111) due to strain and ligand effects can be compensated to a large extent by changing the morphology of the Pt monolayer to that of small 3D islands. For individual adsorption sites near island edges, this compensation effect can be sufficient to reach up to ~9.5 times higher contribution to the ORR activity than a midterrace-site on Pt(111). We propose that tailored nanostructuring of size-and shape-selected islands could maximize this effect and make the choice of elements in a bimetallic system less dependent on ligand and strain effects.

References

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