

Operando X-Ray Diffraction Studies of Co₃O₄ Catalysts during Oxidation Reactions

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The search for economically viable catalysts for the oxygen evolution reaction (OER), which is the bottleneck of electrochemical water splitting, is a key challenge in the worldwide transition to renewable energy systems. Transition-metal oxides such as Co₃O₄ are among the best precious-metal-free electrode materials for the anodic OER in alkaline electrolysis [1]. Moreover, these spinel-type transition metal oxides are an important class of catalysts for the selective oxidation of organic compounds in the liquid phase. Here, we present studies of OER model catalysts, consisting of thin epitaxial Co₃O₄(111) films electrodeposited on Au(111), by *operando* surface X-ray diffraction measurements. This technique can be performed simultaneously with electrochemical measurements (e.g. cyclic voltammetry and electrochemical impedance spectroscopy) and therefore enables direct structure-reactivity-correlations. Previous results have shown reversible changes in the oxide's structure, in particular the formation of a sub-nm CoO_x(OH)_y skin layer in the pre-OER potential range [2]. Detailed analysis revealed a clear correlation of the OER activity with the average skin layer thickness, indicating that the entire skin layer is an OER-active region in Co oxide catalysts [3]. Furthermore, studies of ethylene glycol (EG) oxidation on Co₃O₄ films revealed similar structural changes, even though they appear to be less pronounced under alcohol oxidation conditions, especially at higher EG concentrations. In addition, thermal annealing of the Co₃O₄(111) films leads to the complete absence of potential-dependent structural changes, indicating that no reversible skin layer is formed, as well as a different influence on the catalyst activities for OER and EG oxidation.

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