

Controlling structural transformations of cobalt spinel catalyst surfaces under electrochemical conditions towards a mechanistic understanding of the alkaline oxygen evolution reaction

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One of the most promising approaches to hydrogen production is the use of non-precious metal oxide catalysts for electrochemical water splitting. Many research groups have focused on the study of the oxygen evolution reaction (OER), as this anode reaction requires a significantly higher overpotential than the cathodic branch. Since electrocatalysts for anodic processes are exposed to highly oxidizing conditions, the development of catalysts can be advanced by researching the corresponding (unavoidable) structural transformation and its (cor-)relation to catalytic properties. In this study, cyclic voltammetry with scan rate variation was used to trigger different electrochemical transformations of electrocatalytic cobalt spinel surfaces. Their electrocatalytic activity and structural properties were investigated using *i. a.* Raman spectroscopy.

In-situ and *operando* studies described the transformation of electrocatalytic surfaces in alkaline media during OER.^{1, 2} Normal cobalt spinel Co₃O₄ transforms in cyclic voltammetry already in a potential range more negative than the OER onset.^{3, 4} Accordingly, this opens the possibility of observing changes or even tuning the composition, average cobalt oxidations state, *etc.* of cobalt spinel catalysts by electrochemical activation, aiming for improved electrocatalytic activity towards OER.⁵

The present study explores the impact of anodic and cathodic charge imbalances induced on Co₃O₄ nanoparticles during cyclic voltammetry within the pre-OER potential range. To this end, Raman spectroscopy has been used to investigate the structural changes of Co₃O₄ nanoparticles.⁶

Interestingly, both cases of excess, where either more cathodic conversion charge is measured during closed cyclo-voltametric sweeps or more anodic current flows, lead to a significant decrease in the electrocatalytic activity compared to preconditioning with balanced conversion charges. *Operando* and *ex-situ* Raman measurements revealed significant spectral differences between the electrochemically pre-treated samples. For a more detailed analysis of the structural changes in the cobalt oxide-based catalyst, theoretical simulations of Raman spectra and corresponding DFT calculations were performed.

Insight into the electrochemical transformation processes at or near the surface of electrocatalysts paves the way for a mechanistic understanding of how such catalysts work.

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