

# The Oxygen-Evolving State of Co-based Electrocatalysts: Size effects and the Role of Fe Decoration

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Oxidation electrocatalysis is playing an increasingly important role in realizing the industrial and societal transformation towards a carbon-neutral, sustainable scheme.<sup>1</sup> Here, water electrolysis based on abundant and inexpensive transition metal oxides is a key technology for producing green hydrogen by converting electrical energy from renewable power sources. Co-based electrocatalysts are known to be highly active and stable under alkaline reactions. Earlier studies showed that the oxygen evolving state of  $\text{Co}_3\text{O}_4$  electrocatalysts involve a structural transformation in the near-surface induced by the oxidative reaction conditions and the change in Co oxidation state and Co-O coordination.<sup>2,3</sup> Furthermore, independently from the initial state, Co (oxyhydr)oxides experience a unification towards an octahedral  $\text{Co}^{3+}\text{-O}$  coordination under OER conditions and the catalytic activity benefits from distinct reducible  $\text{Co}^{3+}\text{-O}$  sites.<sup>4</sup> In this framework, the role of the nanoparticle size on the catalytic activity and the oxygen evolving state was unclear. Additionally, the beneficial role of Fe surface decoration or bulk incorporation of Co oxide OER electrocatalysts is established but they underlying processes not unravel. I will present insights which lead to a unifying picture of OER catalyzed by Co oxide pre-catalysts.

We prepared a series of size-selected  $\text{CoO}_x$  nanoparticles (NP) between 1-9 nm using the inverse micellar encapsulation route. To study the role of Fe decoration on  $\text{Co}_3\text{O}_4$ , we utilized an ensemble of cubic and non-cubic  $\text{Co}_3\text{O}_4$  nanoparticles and electrochemically decorated with electrolyte  $\text{FeO}_x$  species. The samples were tested electrochemically and comprehensively characterized. To identify the key properties of the oxygen-evolving state, we applied a broad set of operando methods including operando high energy XRD and XAS – bulk sensitive at the metal K-edges as well as interface-sensitive using photoelectron-yield at the metal L- and O K-edges. The link between the surface chemical state and the Co-O building blocks were studied using DFT+PBE0 calculations.

Our investigations of the size-selected Co oxide nanoparticles (NP) showed that the specific activity of sub-5 nm NPs is significantly higher than that of larger bulk-like NP.<sup>5</sup> During OER, the electrocatalysts are reversibly oxidized leading

to a size-dependent Co-O contraction as revealed by operando X-ray spectroscopy. These findings allowed us to extract quantitative information on the oxygen-evolving near-surface structure. A comparison with DFT+PBE0 calculations suggests pronounced charge reorganization in the hybridized Co 3d and O 2p orbitals, leading to the formation of oxyl surface species under OER conditions. Our insights contrast with the commonly assumed high-valence of the metal ions during OER and furthermore emphasize the catalytic importance of the surface oxygen chemistry.

Our investigations of the Fe decorated  $\text{Co}_3\text{O}_4$  revealed a link of the termination-dependent Fe decoration to the activity enhancement and to a significantly stronger  $\text{Co}_3\text{O}_4$  near-surface (structural) adaptation to the reaction conditions. The near-surface Fe-O species accumulate oxidative charge and undergo a reversible bond contraction during the catalytic process. Moreover, our work demonstrates the importance of low coordination surface sites on the  $\text{Co}_3\text{O}_4$  host to ensure an efficient Fe-induced activity enhancement, providing another puzzle piece to facilitate optimized catalyst design.

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