

Facet Dependence of the Oxygen Evolution Reaction on Co-Based Epitaxial Thin Film Electrocatalysts

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The efficiency and durability of OER electrocatalysts are crucial for advancing green hydrogen production. While transition metal oxides show promise, atomic-scale processes remain largely unexplored.¹ Thus, in this study we investigate the structure-composition-reactivity correlations of epitaxial Co_3O_4 , CoFe_2O_4 , and Fe_3O_4 thin-film electrocatalysts, focusing on the (001) and (111) surface facets. Using LEED, XPS, STM, and EC-AFM, we quantitatively compared these materials to elucidate the impact of iron incorporation and facet orientation on OER performance. Our findings emphasize the crucial role of structural inhomogeneities and surface defects on OER reactivity. We identified key descriptors governing the behavior of (oxy)hydroxide skin layers, which are critical to the OER process. The thickness of these layers remains below 1 nm, influenced by composition and facet orientation, with iron leading to thinner layers. Facet-dependent reactivities were observed, with Co_3O_4 more reactive on the (001) facet, and Fe-containing oxides more active on the (111) facet. Iron modifies the reactivity of skin layers formed at sub-OER potentials compared to those formed under OER conditions, enhancing the latter's activity for Fe_3O_4 and FeCo_2O_4 . Tafel plots indicate that (001) facets exhibit more favorable reaction kinetics, and iron consistently lowers the Tafel slopes, suggesting improved potential-dependent kinetics.² Additionally, operando EC-AFM studies on Co_3O_4 facets grown on Au reveal hydroxide particle formation on the (001) facet, indicating possible surface reconstruction and disorder under anodic conditions due to oxyhydroxide phase formation. These findings underscore the impact of structural defects on reactivity, highlighting the need for further detailed investigation and contribute to a deeper understanding of the atomic-scale processes in OER electrocatalysts, providing a robust experimental basis for optimizing catalyst design for improved water-splitting efficiency.

[1] Davis, E. M. *et al.*, Nat Commun, 2023, **14**, 4791 DOI: <https://doi.org/10.1038/s41467-023-40461-0>

[2] Davis, E. M. *et al.*, J. Am. Chem. Soc., 2024, **146** (20), 13770-13782, DOI: [10.1021/jacs.3c13595](https://doi.org/10.1021/jacs.3c13595)