Degree of Span Control to Determine the Impact of Different Mechanisms and Limiting Steps: Oxygen Evolution Reaction over Co_3O_4 as a Case Study

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ABSTRACT

We use density functional theory (DFT) calculations to perform a facet-dependent evaluation of Co_3O_4 model electrodes for the oxygen evolution reaction (OER). To this end, we construct surface Pourbaix diagrams to identify the surface structure of antiferromagnetic Co_3O_4 under anodic polarization conditions. We observe that mixed *OH/ *O coverages are thermodynamically stable under OER conditions, which coincides with experimental reports that oxyhydroxides are the active phase of Co-based materials for oxygen evolution.

Based on the identified *OH/ *O-covered Co_3O_4 surfaces, we present a dedicated mechanistic study of the OER. In contrast to previous studies, we consider a plethora of different reaction mechanisms, including Walden-type mechanisms with concerted bond-breaking at bond-making [1], into the analysis of free-energy diagrams along the reaction coordinate, evaluated by descriptor-based analysis [2,3]. We use the OER over Co_3O_4 surfaces as a model system to introduce a new descriptor, namely the degree of span control [4], which enables determining the impact of various mechanisms and limiting steps on the OER over Co_3O_4 by going beyond the prototypical discussion of a single rate-determining reaction step.

References

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