Activity descriptors and reaction mechanisms of the oxygen evolution reaction on perovskite oxide electrocatalysts

Livia Giordano

University of Milano-Bicocca, Milano, Italy

e-mail: livia.giordano@unimib.it

Understanding the nature of the active site and the reaction mechanisms is crucial for the design of cost-effective and highly efficient (electro)catalysts for the energy transition. Despite its relevance, the complexity of catalytic systems and the time scale of (electro)chemical reactions hinder gaining atomic level insights on the reaction intermediates under the catalyst operating conditions. In this talk we show how by combining first principles calculations with experimental characterization it is possible to unambiguously identify the active sites and the reaction intermediates at the surface of perovskite oxide ABO_3 catalysts. Specifically, we show how by tuning the oxide electronic structure with A-site substitution, the reaction mechanism for the oxygen evolution reaction (OER) can be modified from a mechanism centered on the B-site to a mechanism involving the lattice oxygen, and we discuss the implication for the oxide electrocatalytic activity and stability [1, 2]. Moreover, we further demonstrate that the OER activity on the metal site of Co-based perovskites can be increased by incorporating an ordered array of oxygen-vacancies in the oxide. Specifically, $La_3Co_3O_8$ ($LaCoO_{2.67}$) showed a remarkable enhancement of electrocatalytic properties over the parent compound $LaCoO_3$, which we attribute to a smaller gap between Co 3d and O 3p bands centers [3]. These results show the critical role of the catalyst electronic structure in determining reaction mechanisms and catalytic activity, providing a framework for the rational design of novel oxide catalysts.

References

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