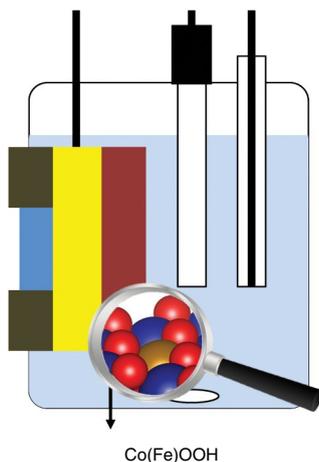


OXYGEN EVOLUTION REACTION

Iron holds it tight

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The (photo)electrolysis of water is expected to be one of the main sources of hydrogen production in the near future, but a number of issues still prevent its large-scale deployment. One of the main hurdles in the optimization of water electrolyzers is finding efficient catalysts at the anode to drive the evolution of molecular oxygen with the minimum overpotential. Iron-incorporated nickel and cobalt (oxy)hydroxides are considered the state-of-the-art electrocatalysts for the oxygen evolution reaction in alkaline electrolyte. Despite the extensive research devoted to the study of these catalysts during water oxidation, there is no clear consensus about the site responsible for the reaction. Several works seem to conclude that iron is the active site in Fe-doped NiOOH, although recent reports suggest a synergy between both nickel and iron sites.

For Fe-doped CoOOH the results have even been less conclusive.

Now, Shannon Boettcher, Maytal Caspary Toroker and co-workers show, by means of operando spectroscopy and density functional theory calculations, that iron is involved in the active site in Fe-doped CoOOH for the oxygen evolution reaction. Operando X-ray absorption spectroscopy, performed in alkaline electrolyte at potentials before and after the reaction onset, manifests the increase in iron's oxidation state ($>3+$) and the shortening of the Fe–O bond length during water oxidation. Cobalt ions, on the other hand, do not experience any change in oxidation state or Co–O bond length. These results differ from those on Fe-free CoOOH, which show an increase in Co oxidation state — no change in the Co–O length is observed, which is likely to be due to the lower fraction of Co being oxidized compared with Fe in Fe-doped CoOOH. All these observations are supported by the computational analysis of Fe-free and Fe-doped CoOOH on the adsorption of water and the different reaction intermediates.

The results suggest that water oxidation follows a different mechanism in the presence and absence of iron, which for the former involves iron as the active site, contributing to the fundamental understanding of a primal process and shedding light on a key aspect of its state-of-the-art catalyst.

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