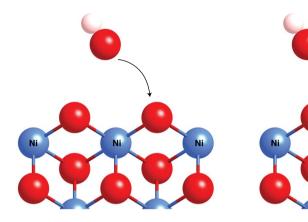
research highlights

OXYGEN EVOLUTION REACTION

Iron makes it special

Angew. Chem. Int. Ed. https://go.nature.com/2W9Lv2z (2019).



Hydrogen can be generated — and then used as a fuel — with zero carbon emissions from water electrolysis powered by renewable electricity. Considerable efforts are still necessary to improve the efficiency of water electrolysers. The catalysis research community is prominently focused on the design of more active and inexpensive electrocatalysts for the half-reaction taking place at the anode — the oxygen evolution reaction (OER). In alkaline electrolyte, the most promising OER catalysts, due to their high activity and low cost, are iron-doped nickel-based materials, such as the NiFe layered double hydroxide (LDH). While it is well established that the active phase forms under reaction conditions upon oxidation of NiFe hydroxide to NiFe oxyhydroxide, the precise nature of its active sites and those in related non-Fe-doped materials is still under debate.

Now, Xile Hu and co-workers at EPFL provide evidence, by means of in situ Raman measurements and isotope labelling experiments on Ni, NiCo, NiFe and

NiCoFe LDHs, that the presence of iron alters the OER mechanism and active site, while increasing the activity. By labelling the catalyst with ¹⁸O and subsequently immersing it in ¹⁶O labelled electrolyte, a striking difference is observed among the materials. While Ni and NiCo LDHs swiftly exchange the ¹⁸O lattice oxygen by ¹⁶O, the Raman signatures show no evidence of isotope exchange for NiFe and NiCoFe LDHs. These results show that lattice oxygen participates in the OER for the Fe-free catalysts - via a mechanism in which NiOO⁻ is oxidised to O_2 and replaced by oxygen atoms from the electrolyte - but not for those containing Fe. This also suggests that, for the latter, NiOO- is not a precursor to O_2 and that Fe is likely the active site. A series of control experiments further support the hypothesis.

Marcal Capdevila-Cortada

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