Impact of Size and Lattice Oxygen on Water Oxidation on NiFeO_xH_y

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Hydrogen is one of the world's most important chemicals with a global production rate of approximately 50 billion kg per year. Synthesis of hydrogen using electrochemistry is very attractive as it can be produced from water in a sustainable manner. However, cost-competitive electrochemical hydrogen production is hindered by the sluggish kinetics of the oxygen evolution reaction (OER). Ni(Fe)O_xH_y are the most active catalysts for oxygen evolution in base. For this reason, they are used widely in alkaline electrolyzers. However, several open questions remain regarding the reason for their exceptionally high catalytic activity.

In this model study, we measure activity trends of mass-selected NiFe nanoparticles for oxygen evolution in 1 M KOH. We complement our activity measurements with electrochemistry-mass spectrometry, taken in operando, and transmission electron microscopy and low energy ion scattering spectroscopy, taken ex situ. Using isotope labelling experiments, we discovered that bulk lattice oxygen does not participate in the reaction. Consequently, we attribute the high activity exclusively to surface processes. On this basis, we conclusively determine that the turnover frequency is 6.2 s⁻¹ at an overpotential of 0.3 V, which is, to the best of our knowledge, the highest reported for oxygen evolution in alkaline solution.



a DC magnetron sputtering, gas aggregation, mass-selected nanoparticle source with lateral timeof-flight mass filter. **b** Transmission Electron Microscopy (TEM) images of 4 different masses of NiFe nanoparticles. **c** Size distributions for four selected masses. **d** OER mass activity for the different particle sizes.