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Structure-activity relationship in mixed (Fe,Ni) oxyhydroxide catalysts for electrochemical oxygen evolution

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The addition of Fe sites has been found to enhance the catalytic activity of NiO(OH) for the electrochemical oxygen evolution reaction (OER). For electrodeposited mixed (Fe,Ni) oxyhydroxide films, we found a volcano-shaped correlation between Fe content and OER activity, which is maximized near a Fe:Ni atomic ratio of 1. In order to understand the structural and electronic interplay between Fe and Ni sites and its effect on OER activity, we employed in situ x-ray absorption spectroscopy both under OER operating conditions as well as at lower potentials where the Ni(II)/Ni(III) redox transition can be observed. The high energy resolution fluorescence detection (HERFD) technique was used to obtain detailed electronic structure information from Fe and Ni *K*-main- and pre-edge features. These results are combined with extended x-ray absorption fine structure (EXAFS) measurements. We can thus probe the correlation between Fe and Ni oxidation states, Fe–O and Ni–O bond distances, and longer metal–metal distances and coordination numbers that originate from edge- or corner-sharing between (Fe,Ni)O_6 octahedra.
We propose that the observed linear increase of the Ni(II)/Ni(III) equilibrium potential with Fe content can be explained with a strain effect where Fe sites induce increased metal–oxygen bond distances which destabilize Ni(III).