



The colour gradient reflects the transition from rock-salt to spinel structure in all figures. (a) XRD and XPS show the gradual transition of ALD deposited cobalt nickel oxide films from the 2+ oxidation state rock-salt phase (NiO , 43.3° XRD feature) to the mixed 2+/3+ oxidation state spinel structure (Co_3O_4 , 44.8° XRD feature) upon tuning the chemical composition.

(b) XPS measurements indicate that rock-salt films form a thick hydroxide layer (M-OH bond) after electrocatalytic testing whilst spinel films largely retain their oxide (M-O bond) form. This is also illustrated by the O1s XPS spectra in the inset.

(c) Rock-salt films are the most OER active after activation as schematically indicated. Yet correction of the overpotential for the increase in ECSA shows that spinel films are intrinsically the most active.