Tracking catalyst redox states and reaction dynamics in Ni-Fe oxyhydroxide oxygen evolution reaction (OER) electrocatalysts: The role of catalyst support and electrolyte pH

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Abstract

Ni-Fe oxyhydroxides are the most active known electrocatalysts for the oxygen evolution reaction (OER) in alkaline electrolytes and are therefore of great scientific and technological importance in the context of electrochemical energy conversion. Here we uncover, investigate, and discuss previously unaddressed effects of conductive supports and the electrolyte pH on the Ni-Fe oxide catalyst redox behavior and catalytic OER activity, combining operando UV VIS spectro-electrochemistry, operando electrochemical mass spectrometry (DEMS), and in-situ X-ray absorption spectroscopy. Supports and pH >13 strongly enhanced the pre-catalytic voltammetric charge of the Ni-Fe oxyhydroxides redox peak pairs, shifted them more cathodically, and caused a 2-3 -fold increase in their catalytic OER activity. A non-monotonic super-Nernstian pH dependence of the redox peaks with increasing Fe content – displaying Pourbaix slopes as steep as -120 mV/pH - suggested a 2 proton- 1 electron transfer. DEMS-based faradic oxygen efficiency analyses and electrochemical UV-VIS studies consistently confirmed our voltammetric observations evidencing both a more cathodic O₂ release and a more cathodic onset of Ni oxidation at higher pH. On the other hand, both in-situ cryo X-ray absorption spectroscopy (XAS) and UV VIS data suggested a larger fraction of oxidized Ni^{3/4+} in supported Ni-Fe/C catalysts, but confirmed the unresolved paradox of a reduced metal redox activity with more Fe content, despite higher kinetic OER rates. We explain and discuss the experimental pH effects using refined coupled (PECT) and decoupled proton transfer -electron transfer (PT/ET) schemes involving negatively-charged oxygenate ligands generated at Fe centers. Together, we offer new insight in the catalytic reaction dynamics and associated catalyst redox chemistry of the most important class of alkaline OER catalysts.