

Crystal-facet-dependent surface transformation dictates the oxygen evolution reaction activity in lanthanum nickelate

Achim Fungerlings¹, Marcus Wohlgemuth², Denis Antipin³, Emma van der Minne⁴, Ellen Marijn Kiens⁴, Javier Villalobos³, Marcel Risch³, Felix Gunkel², Christoph Baumer⁴, and Rossitza Pentcheva¹

¹Department of Physics University of Duisburg-Essen, Duisburg, Germany; ²Peter Gruenberg Institute and JARA-FIT, Forschungszentrum Juelich GmbH, Juelich, Germany; ³NWG Gestaltung des Sauerstoffentwicklungsmechanismus, Helmholtz-Zentrum Berlin fur Materialien und Energie GmbH, Berlin, Germany; ⁴MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, Enschede, Netherlands

E-Mail presenting author: achim.fuengerlings@uni-due.de

In a combined experimental and theoretical study using electrochemical measurements, X-ray spectroscopy, and density functional theory calculations (DFT) with a Hubbard U -term we explore the effect of surface transformation on the water oxidation activity of $\text{LaNiO}_{3-\delta}$ electrocatalyst with (001), (110) and (111) surface orientation. We reveal that the overpotential of the (111) facet is $\approx 30\text{--}60$ mV lower than for the other facets. While a surface transformation into oxyhydroxide-like $\text{NiOO}(\text{H})$ may occur for all three orientations, it is more pronounced for (111). A structural mismatch of the transformed layer with the underlying perovskite for (001) and (110) influences the ratio of Ni^{2+} and Ni^{3+} to Ni^{4+} sites during the reaction and thereby the binding energy of reaction intermediates, resulting in the distinct catalytic activities of the transformed facets. [1]

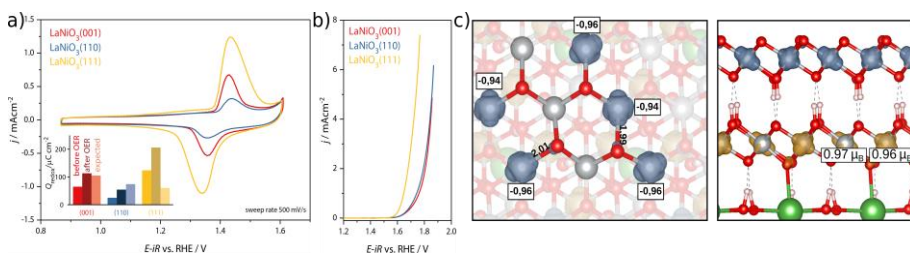


Figure 1: a) Redox peak before OER onset and b) facet-dependent OER activity of $\text{LaNiO}_{3-\delta}$, c) Spin density of the transformed (111) facet from DFT+ U showing stripes of low and intermediate spin Ni. Adapted from [1].

[1] A. Fungerlings *et al.*, Nat. Commun., 2023, **14**, 8284, <https://doi.org/10.1038/s41467-023-43901-z>