Multimodal *Operando* XRD, PDF and XAS Reveal the Structural Evolution of Layered Ni OER Catalysts

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Tracking the structural evolution of synthesised pre-catalysts into active electrocatalysts under operating conditions requires a dedicated approach for characterizing materials in real time under electrochemical environments. Active catalysts for the oxygen evolution reaction (OER), a critical reaction for achieving green hydrogen production, are typically based on Ni layered double hydroxides (LDHs) doped with transition metals, though many aspects of the active catalyst structure remain unresolved. [1,2] The misunderstanding of these materials largely stems from the complex, anisotropic structure of LDHs, which are highly susceptible to stacking faults and other defects, [3] complicating structural elucidation via diffraction alone. The transition from the pre-catalyst LDH into the active OER catalyst involves an anisotropic structural transformation coupled with redox changes, and tracking this transition therefore requires simultaneous insight into layer stacking, intralayer structure, and oxidation states of Ni and dopant metals during electrochemical operation.

Here we present a unique *operando* electrochemical cell with an integrated fluorescence detector, enabling multimodal X-ray diffraction (XRD), total scattering/pair distribution function (PDF), and X-ray absorption spectroscopy (XAS) measurements within a single integrated experiment. This setup provides complementary structural information across multiple length scales, while simultaneously tracking electrochemical activity and metal oxidation states, allowing for a complete description of active catalyst formation in state-of-the-art Ni OER catalysts.

By gradual stepping into and out of the OER region for Ni LDHs doped with Mn, Fe, Co, and Cu, we have fully characterized the pre-catalyst, activation process, reversible active catalyst formation, and post mortem catalyst. Correlated analysis of diffraction, local structure, oxidation states, and current density reveals that interlayer vs intralayer structural distortion occur independently, and that only some dopant metals become oxidised with increased potential, subsequently impacting the local structure of the active catalyst. The structural changes are largely reversible, although delayed when stepping out of the OER region, and electrolyte-driven interlayer rearrangements leave the post-mortem structure distinct from the initial pre-catalyst. Together, this multimodal *operando* approach resolves the structural evolution of layered Ni catalysts under working conditions, and links it directly to catalytic activity.

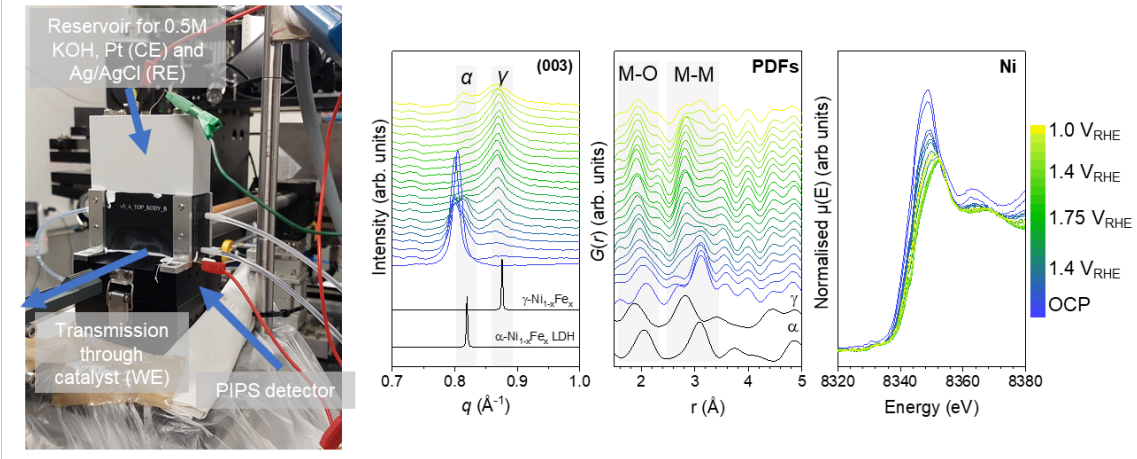


Figure 1. *Operando cell in use at the ESRF (BM31), and an overview of XRD, PDF and Ni XANES during catalysis.*

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[2] O. Aalling-Frederiksen, et al. Small (2025). 21, 2411211.
[3] W. A. Sławiński, et al. Inorg. Chem. (2016). 55, 12881-12889.