EC Cell for Operando XAS investigations on X-ray opaque supports



Unraveling the photoelectrocatalytic OER on ultra-thin Y-Ni_xFe₂O₃ films

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INTRODUCTION

Investigating the structural and electronic dynamics of a catalyst under *operando* conditions has a crucial role in the development of more performant electrochemical devices. A special importance is to be assigned to the catalyst/electrolyte interface, whose understanding leads to improved electrochemical processes. X-ray absorption spectroscopy (XAS) is one of the most powerful techniques to this end. However, probing an absorption edge below 10 keV in the presence of a layer of liquid electrolyte is quite challenging. This obstacle is usually overcome by depositing the sample on a conductive and x-ray transparent support (e.g. thin graphite foil or Si_3N_4 membrane) then probing the sample from the substrate side. However, this geometry not only limits the sensibility to the electrode/electrolyte interface but precludes the study on non-transparent supports. Sample can also be probed from the electrolyte side by shrinking the liquid layer thickness.

Ni-doped Maghemite for OER

The sluggish kinetics required by the OER makes it essential to find high-efficiency and earth-abundant catalysts.

We designed an electrochemical flow cell that allows to carry on XAS experiment under *operando* conditions, probing the sample in fluorescence mode, from the electrolyte side. The thin, homogeneous liquid layer flowing on top of the sample (~17 µm) grants an excellent *photon-in photon-out* efficiency, without compromising the quality of the electrochemical measurement. This cell is now available at the SAMBA beamline in SOLEIL synchrotron, and allow for excellent XAS spectra even down to the Ti K-edge, as detailed in our recent publication (F. Paparoni et al., Phys. Chem. Chem. Phys., 2024,26, 3897-3906). This poster present an investigation on **Ni-doped maghemite ultra-thin film (~5 nm)**, epitaxially grown **(111) on Pt (001)** single crystal. Samples with different Ni content were prepared via oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and probed with XAS under a 0.1 M solution of KOH.

Promising results have been shown by 3d transitional metal oxides.

Recent studies show that the photoelectrochemical activity for the OER of Fe_2O_3 can be tailored with n-type doping. The 2 eV band gap of this material makes it a suitable candidate as PEC photoanode. The doping is expected to Improve the solar-to-hydrogen conversion efficiency of the material by improving its poor charge transport.

OPERANDO X-RAY ABSORPTION SPECTROSCOPY



Ni/Fe

- 0.02 - 0.04

> - 0.07 - 0.14

- 0.2 - 0.4 Fe K-edge



Operando XAS Setup at the SAMBA beamline

- EC-Cell (2): X-ray fluorescence is measured with a Si drift detector (3) from the electrolyte side. High *photon-in photon-out* efficiency (75% Fe K-edge, 43% Ti K-edge). Three-electrode system, with Pt counter and a leak-free Ag/AgCl reference electrodes, Compatible with both alkaline and acid environment.
 Cell is connected to a Bio-Logic SP-300 potentiostat (5).
- The renovation of the electrolyte (6) and the and bubbles removal is facilitated by a

peristaltic pump (4). If required, inert gas can be flown.

★ (1) A solar simulator (1000 W Xe Arc Lamp), equipped with IR filter and optical

chopper, illuminate the sample.

Operando XAS: Effect of the potential

When the applied potential is above the OER onset, the **adsorption of OH**⁻ **into the O-vacant sites** increases the population of unoccupied states, resulting in a moderate white line intensity increases at both edges, while the pre-edges flattens. The effect is relatively stronger on the sample with lower Ni content. This is confirmed by the electrochemical data (Fig. a,b): while all Ni-doped samples show a lower OER onset then the pristine material, the **lowest overpotential and Tafel slope is found in the sample with the lowest Ni content (red)**, due to the **highest concentration of O vacancies**.



Structural effect of Ni insertion

The insertion of Ni within the maghemite structure increases the structural disorder. Our results suggest a replacement of octahedral Fe³⁺ by Ni²⁺, with concurrent formation of O-vacancies. With higher content of Ni, the structure gradually reorder towards $NiFe_2O_4$.





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Fixed Energy X-ray Absorption Photo-Voltammetry (FEXRAPV)

While all samples show a stable photocurrent density, with a maximum for a 0.07 Ni/Fe dopant ratio, the exposure to light does not clearly change the sample structure. The very small modulations observed at the XANES when the sample is illuminated are difficult to interpret.

To follow the rapid, reversible effects, we measured in FEXRAPV mode, probing a single energy point, synchronizing the acquisition with an optical chopper and a potentiostat in chronoamperometry mode, applying a constant potential (1.55 V vs RHE). The fluorescence signal was folded using the chopper period (0.5 s). The measurement was repeated at different energy points. The only signal coming out of the noise level was at **the Fe K white line energy**. This preliminary encouraging result must be confirmed in a further experiment; however, it correlates the white line intensity which is a function of the density of empty states of Fe, with the expected **accumulation of holes on the surface of the illuminated photoanode**. This technique could provide real-time element specific information on the dynamics of hole accumulation in addition to short range structural information.