

# Probing The Electrode-Liquid Interface Using *Operando* Total-Reflection X-ray Absorption Spectroscopy

A. Grespi<sup>1</sup>, A. Larsson<sup>1</sup>, G. Abbondanza<sup>1</sup>, J. Eidhagen<sup>2</sup>, J. Manidi<sup>4</sup>, D. Gajdek<sup>5</sup>, J. Pan<sup>3</sup>, L. R. Merte<sup>5</sup>, E. Lundgren<sup>1</sup>

<sup>1</sup> Division of Synchrotron Radiation Research, Lund University, 221 00 Lund, Sweden.

<sup>2</sup> Alleima (former Sandvik Materials Technology), Sandviken, Sweden.

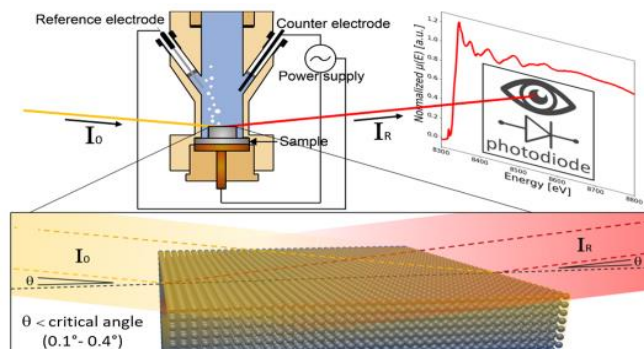
<sup>3</sup> KTH Royal Institute of Technology, Division of Surface and Corrosion Science, Stockholm, Sweden.

<sup>4</sup> Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering, G. Natta, 20133 Milano, Italy.

<sup>5</sup> Materials Science and Applied Mathematics, Malmö University, 20506 Malmö, Sweden.

andrea.grespi@sljus.lu.se

Traditional *operando* methods to study electrochemical (EC) processes, although successful, are based on EC measurements, lacking in direct sensitivity of chemical and structural surface changes. These EC reactions take place at the electrode-electrolyte interfacial regions, but several surface sensitive techniques are often limited to *ex situ* conditions, owing to the need of Ultra High Vacuum (UHV) environments [1,2]. On the contrary, synchrotron-based hard x-rays provide an extremely focused and intense, energetic source that can penetrate the electrolyte without undergoing significant attenuation. Furthermore, surface sensitivity can be increased up to a few nanometers when the incident angle is set below the critical angle for total external reflection (TER), characterized by the occurrence of an evanescent wave confined at the surface [3,4]. In this contribution, we performed *operando* Grazing Incidence X-ray Absorption Spectroscopy (GI-XAS) in total external reflection (TER) mode (Fig. 1) at P64 (DESY, Hamburg) and Balder (MAX IV, Lund). The experiment was performed using our EC setup designed for multimodal synchrotron studies, which allowed us to measure both fluorescence signal and totally reflected beam as a function of the incident beam energy. We investigated Au(111) surface electro-oxidation at its initial stage and during oxygen evolution reaction (OER), measuring Au L3-edge XANES and EXAFS in real-time while performing a cyclic voltammetry (CV) in 0.05M H<sub>2</sub>SO<sub>4</sub>. Furthermore, we studied the surface passive film development and breakdown of Ni-Cr-Mo corrosion resistant alloys in 1M NaCl under constant EC polarization. Despite the presence of bulk electrolyte and PEEK walls of the EC cell, 1-3 nm thick surface oxides film can be detected in TER mode using energies down to 8 keV. Advantages and challenges of this method will be discussed, showing experimental results.



[1] O. Diaz-Morales *et al.*, Chem. Sci., vol. 4, n. 6, pag. 2334, 2013.

[2] A. Larsson *et al.*, Applied Surface Science, vol. 611, Part A, 2023.

[3] H. Abe *et al.*, Phys. Chem. Chem. Phys., vol. 22, pag. 24974, 2020.

[4] Gajdek *et al.*, J. Phys. Chem. C, vol. 126, n. 7, pag. 3411, 2022.