

# Operando X-Ray Photoelectron Spectroscopy of solid-liquid interfaces: characterization of metal nanoparticles during OER

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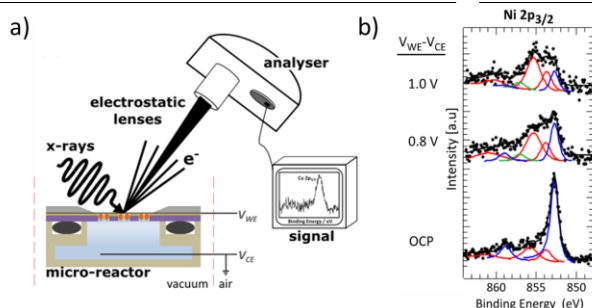
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Water electrolysis is a promising energy vector and a serious alternative to batteries, especially when combined with fuel cells for the on-site generation of electricity. However, one of the involved processes -the Oxygen Evolution Reaction- suffers from sluggish kinetics due to its 4-electron transfer process. Transition metals (e.g., Co, Ni, Fe) are an inexpensive alternative to precious metal catalysts (e.g., Pt), but there are still open questions about their mechanism to catalyze the OER. Optimizing the OER electrocatalysts must be a top priority for advancing this vital technology. To this end, X-ray photoelectron spectroscopy (XPS) is arguably one of the most powerful techniques for probing solid-liquid interfaces. However, this element-specific and surface-sensitive technique requires high vacuum conditions. Over the last two decades, ambient pressure XPS (AP-XPS) has been developed, extending the operating range to the mbar region [1]. The so-called “graphene-capping approach” can be easily used under *operando* conditions at X-ray lab sources. Graphene is strong enough to sustain the large pressure difference but still thin enough to allow sufficient photoelectrons to pass through. In this contribution, we demonstrate the successful application of the graphene-capping approach in a micro-electrochemical reactor [2]. Pt is used here both as a counter and reference electrode, and graphene acts as a working electrode (Fig. 1a). Ni NPs are deposited on the backside of graphene, and their changing oxidation state is monitored in a mildly alkaline aqueous solution under electrochemical control. The sensitivity of XPS to the chemical state and environment of the sample allows us to differentiate the oxidation/reduction of Ni and graphene (Fig. 1b). Moreover, using synchrotron radiation facilities opens the possibility of using XPS in conjunction with Near Edge X-Ray Absorption Fine Structure (NEXAFS). NEXAFS is also sensitive to the bonding environment, so it can provide information about the geometry, bonding distances, and neighboring atoms. These proof-of-concept experiments show that a similar signal-to-noise ratio can be obtained compared to other studies in the literature that use synchrotron radiation, making our approach more versatile and easily adaptable to any lab-based X-ray source facility and many model reactions.

## References

- [1] M. Salmeron, R.Schlögl. *Surf. Sci. Rep.*, 63 (2008)169-200.
- [2] B.-O. Shalom, Miguel A. Andrés, et al. *Electrochem. Commun.*, 142 (2022) 107375.
- [3] B.-O. Shalom, Miguel A. Andrés, Manuscript submitted for publication.

## Figures



**Figure 1:** a) Schematic of our micro-electrochemical reactor. b) *Operando* XPS measurements conducted under electrochemical reaction conditions, showing the Ni 2p<sub>3/2</sub> region.