Hard X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy as new approach for surface properties analysis

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Energy storage is pivotal for a swift implementation of a renewable energy economy, but still awaits a technically and economically feasible large-scale solution. Alkaline water electrolysis represents a promising method used for hydrogen production particularly due to robustness, efficiency, durability and cost.[1] These advantageous have their in origin in the use of a simple setup and the use of abundant and cheap materials, e.g., Ni (alloys) as electrode material. The peculiarity of Ni can be related to its ability to form various compounds with hydrogen and oxygen (e.g., NiH_x, NiO, $Ni(OH)_2$, NiOOH).

X-ray photoelectron spectroscopy is the ideal tool to probe the chemical and electronic structure of surfaces, including electrodes. However, standard methods are restricted to ultra-high vacuum conditions; and even near ambient pressure photoelectron spectroscopy [2] may deliver falsified results of the surface during operando conditions, because the great number of (secondary) photoelectrons excited during photoexcitation. We therefore propose a different strategy to probe the extended surface post-mortem by photoemission, and link the thus obtained materials characterization to the true operando technique electro-chemical impedance spectroscopy (EIS) performed in parallel. A sophisticated sample station attached to an X-ray photoelectron spectrometer with standard (XPS: Al-Kα radiation) and hard X-ray excitation (HAXPES: Cr-Kα radiation) allows the preparation and monitoring of oxide/hydroxide layer thickening as a function of potential and time, from which an improved understanding of the properties of electrode surfaces can be drawn. The above- introduced Ni and nickel oxide/hydroxides surface serve as a relevant example of this approach.

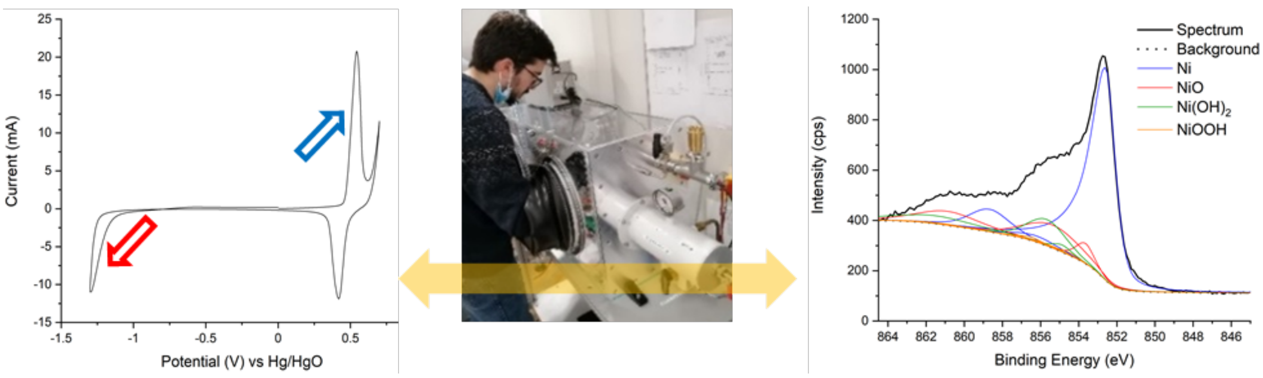

Figure 1: Cyclic voltammogramm (left) of Ni in 1M KOH prepared in an Ar-glove box attached to an XPS/HAXPES instrument (right panel: HAXPES of cycled Ni-electrode).

[1] D.M.F. Santos, C.A.C. Sequeira, *Quim. Nova* **2013**, 36, 1176–1193.

[2] Z. Novotny et al., *Rev. Scientific Instr.* **2020**, 91,023103.

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