Exploring the electrode-electrolyte interface of a nickel electrocatalyst during hydrogen oxidation/evolution reactions

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The electrode-electrolyte interface – small world of a few nanometers span – is the region of interest for electrochemists, where most electrochemical processes happen. However, its exploration is quite challenging due to its small dimensions and potential- and time-dependent nature. It thus requires **surface-sensitive techniques** that can be used during operation of the catalyst, as the properties of the electrode and electrolyte (*e.g.* surface state, local pH) at the interface will be modified by the reaction conditions.

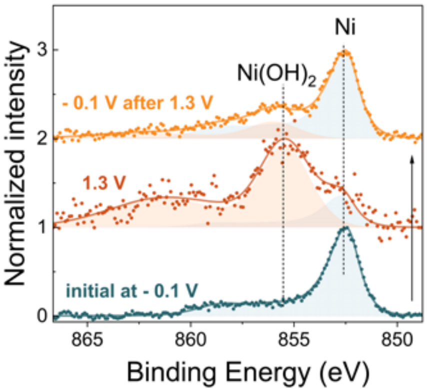

Figure 1. Ni $2p_{3/2}$ dip-and-pull X-ray photoelectron spectra showing the evolution of the surface composition of a flat polycrystalline Ni electrode in 0.1 M KOH under oxidative (1.3 V_{RHE}) and reductive (- 0.1 V_{RHE}) conditions.

On the electrode side, especially when non-noble metals are used as the catalyst, the combination of applied potential and local pH can affect the thermodynamic stability of surface species, leading to changes in the performance. In particular, the activity of nickel towards hydrogen evolution (HER) and oxidation (HOR) reactions depends on the oxide coverage of its surface, with an optimum of around 30% of the surface covered by NiO_x (NiO or β-$Ni(OH)_2$).[1] Assessing how this ratio evolves *operando*, and how these changes can be correlated to the electrode-electrolyte interface properties, is pivotal. In this work, we used **Dip-and-Pull X-ray Photoelectron Spectroscopy (XPS)** [2] to probe the surface state of a model polycrystalline nickel electrode as a function of applied potential, in 0.1 M KOH. This technique allows analyzing a flat electrode covered by a thin film of electrolyte under polarization. It enabled for the first time a direct observation of a metallic Ni surface under *operando* conditions (**Figure 1**). Starting from this initially metallic surface, the thickness of the oxide layer was followed by XPS as a function of the applied potential (**Figure 2**). The metastable nature of this NiO_x layer formed under anodic polarization was confirmed by the observation of a significant reduction of the surface when exposed to HER (- 0.1 V_{RHE}) conditions (**Figure 1**). The resulting Ni/NiO_x composition of the active surface during the HER was shown to depend on the conditions of the oxidation pre-treatment, suggesting new avenues for refining the properties of the Ni-based electrocatalysts.

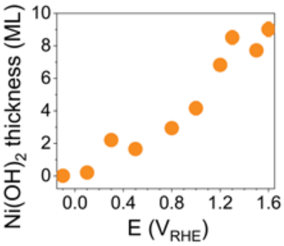

Figure 2. Calculated thickness of surface $Ni(OH)_2$ as a function of the applied potential.

On the electrolyte side, the interfacial generation/consumption of protons/hydroxides during HER/HOR leads to **local pH** conditions that can differ greatly from the bulk pH. Here we probed local pH using **confocal laser scanning microscopy (CLSM)** combined with pH-sensitive fluorescent dyes. The objective was to assess the changes in local pH during HER/HOR as a function of the potential and bulk pH, identifying conditions in which nickel oxidation state could be thermodynamically modified owing to the interfacial pH values.

References:
[1] A. G. Oshchepkov, A. Bonnefont, E. R. Savinova, *Electrocatalysis* **2020**, *11*, 133–142.
[2] S. Axnanda, E. J. Crumlin *et al.*, *Sci Rep* **2015**, *5*, 9788.

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