

The nature of the electrified solid/liquid interface during CO₂ and water electro-activation

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The interface between a charged metal and an aqueous electrolyte is the most commonly studied junction in electrochemical surface science, as its properties determine the reactivity of many systems relevant for technological applications. More specifically, in the electrocatalytic conversion of energy, the activity, selectivity and efficiency are determined by the charge transfer between electrolyte and electrode, which is governed by the interfacial properties of the system investigated. Hence, a fundamental understanding of the interplay between applied potential and surface/interface properties is pivotal to further advance in energy conversion and storage technology, as well as in electrocatalysis, in general.

CO is a key intermediate in the electro-oxidation of energy carrying fuels. Single-crystal Cu^[1] and Au^[2] model catalysts can efficiently electro-oxidize CO in alkaline media, where strong surface structural changes are observed under reaction conditions. We have shown that the concomitant presence of high-energy undercoordinated Cu structures at the surface is a prerequisite for its high activity. The CO electro-reduction and the hydrogen evolution reaction (HER) are found to proceed on strongly reconstructed surfaces as well, which was studied with bare and modified Cu single-crystal electrodes in alkaline media.^[3]

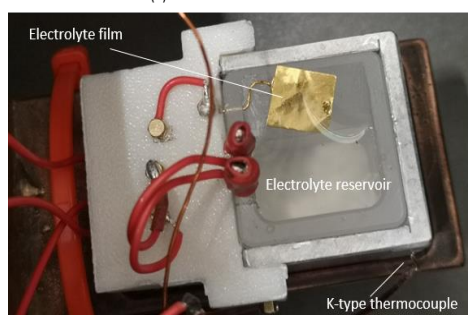


Figure 1. EC-XPS cell. ^[4]

The changes of the interface properties of electrode surfaces are intimately related to the electric field at the solid/liquid interface and to their electrocatalytic activity. This talk will discuss all these interfacial aspects, analyzed with a combination of *in-situ* analytics, with view on the electrocatalytic reactivity towards CO and water activation at (modified) copper (Cu) and gold (Au) electrodes. The interfacial changes are tracked *in-situ*, with analytical focus on

electrochemical scanning tunneling microscopy (EC-STM), and lab-based electrochemical X-ray photoelectron spectroscopy (EC-XPS, see Fig. 1) to monitor the structure and chemistry of the electrified interface during the reactions.

References:

- [1] A. Auer, M. Andersen, E.M. Wernig, N.G. Hörmann, N. Buller, K. Reuter, J. Kunze-Liebhäuser, *Nature Catal.* 3, 797 (2020).
- [2] H. Kita, H. Nakajima, and K. Hayashi, *J. Electroanal. Chem.*, 190, 141 (1985).
- [3] A. Auer, F.J. Sarabia, D. Winkler, C. Griesser, V. Climent, J.M. Feliu, J. Kunze-Liebhäuser, *ACS Catal.* 11, 10324 (2021).
- [4] C. Griesser, D. Winkler, T. Moser, L. Haug, M. Thaler, E. Portenkirchner, B. Klötzer, S. Diaz-Coello, E. Pastor, J. Kunze Liebhäuser, *Electrochem. Sci. Adv.* (2023) e2300007.