Investigating Solid/Liquid Interfaces with Ambient Pressure Hard X-ray Photoelectron Spectroscopy

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Historically, most solid/liquid electrolyte interfaces are probed in an *ex situ* fashion which prevents the ability of directly capturing metastable and transition states, or the properties of an interface undergoing a (photo) electrochemical reaction. Up to now our physical/chemical insight into complex interfacial processes involving energy and charge transfer is limited and often based on simple, pre-defined models. Therefore, there is the need for molecular-level information to provide a more rational approach to material optimization through the direct investigation of electrified solid/liquid interfaces.

In the recent years, many *in situ* or *operando* techniques have been developed with the aim of addressing such a crucial aspect. Among the different approaches explored so far, ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) has emerged as an effective tool to study electrified solid/liquid interfaces under realistic working conditions [1]. The use of hard X-rays (in the range of 2.0 and 10.0 keV) leads to high photoelectron kinetic energies, allowing the probe of the sample surface and near-surface region buried by thin liquid electrolyte layers (in the order of tens of nanometers). The main advantages of using a *photon in-electron out* technique are constituted by the fact that the detected particles, i.e. photoelectrons, carry information about the chemical state of the elements present at the interface (i.e. oxidation state) [2, 3] as well as potentials localized at the solid/liquid junction [4]. Moreover, the detection of photoelectrons allows to perform core-hole-assisted spectroscopies such as resonant photoemission (ResPES) and core-hole-clock (CHC) spectroscopy in an unprecedented *in situ* or *operando* approach. Finally, the limitation imposed by low photoionization cross sections arising from the high photon energy used in such experiments is nowadays efficiently overcome by the combination of AP-HAXPES with novel and optimized photoelectron kinetic energy analyzers and high-brilliance sources such as III generation synchrotrons.

In this talk, we will focus on the creation of a liquid layer on the sample surface via the so-called "dip&pull" technique [5], developed at the Advanced Light Source at Berkeley Lab. We will discuss in detail the physical basis of such technique, emphasizing the advantages and limitations of front X-ray illumination when coupling the "dip&pull" technique with AP-HAXPES. We will then show some recent results obtained using this novel approach, drawing the potentialities and the possible improvements in future perspectives.

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