

Capturing the Local Potential Variations of Ionic Liquid Devices by XPS under DC and/or AC Modulations

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Electrochemical cells are based on the fundamental process of ion motion and accumulation on surfaces. A complex interplay of molecular properties of ions and cell dimensions control the entire process and determine the overall dynamics of the system. Although traditionally X-ray photoelectron spectroscopy (XPS) operates at high vacuum, it has also been utilized for investigation of the vacuum/liquid and liquid/solid interfaces, since almost its introduction. In this chapter, we briefly summarize historical developments of the technique for the characterization of liquid interfaces by showcasing some exemplary case studies from the published literature. We, then, present our work on electrified solid/liquid interfaces of electrochemical cells using liquids with sufficiently low volatility. Such procedure reveals localized electrical potential developments, through binding energy shifts of the atomic core levels, in a chemically specific fashion. Combining it with impedance like Square-Wave AC electrical potential modulation, the information can be extended to the time domain for investigating ionic liquid based electrochemical cells configured as coplanar capacitors in macro-dimensions. Through our analysis, the nonlinear time-resolved voltage profiles across the cell emerge as spatially nonuniform electrical double layer formation on electrode surfaces. The coplanar capacitor has extremely slow time response, which is mostly controlled by IL film thickness. XPS measurements capture the ion dynamics in tens of seconds to microseconds range, and reveal that ionic motion is all over the device, including those on metallic electrode regions. Such a behavior can only be attributed to motion in more than one dimension. The ion dynamics can also be simulated by using a modified PNP equation, only after taking into account steric effects, and device dimensions. Measurements on two devices with different dimensions corroborated with and validated the simulation results.¹

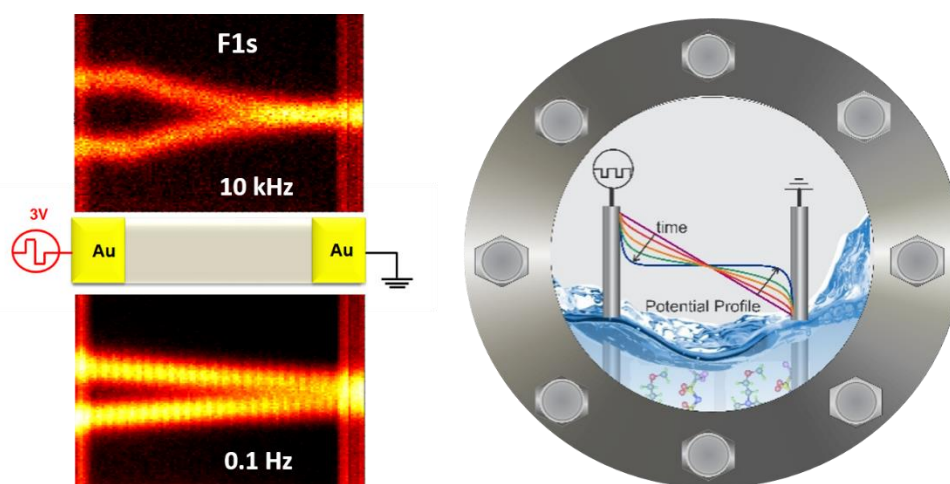


Fig. 1. XPS data recorded under impedance like AC electrical potential allow extracting dynamics of non-faradaic processes

[1] Merve Taner Camci, Pinar Aydogan Gokturk, Mustafa Başaran, Burak Ulgut, Askin Kocabas, Coskun Kocabas, Sefik Süzer., Chapter in Encyclopedia of Solid-Liquid Interfaces, Volume 8, 80026. <https://doi.org/10.1016/B978-0-323-85669-0.00097-0>