Towards Designing Interfacial Reactivity Across the Scales : From Operando Spectroelectrochemistry to In Situ Surface Science Techniques.

Controlling interfacial reactivity at metallic surfaces remains a major challenge, particularly in the context of material degradation. Most protection strategies still rely on the empirical selection of inhibitors rather than their predictive design. In this context, measuring and quantifying, in real time, the reactivity of metals and alloys in the presence of inhibitors, combined with a molecular-scale understanding of inhibition mechanisms, is of utmost importance. This talk introduces a multiscale analytical strategy that bridges macroscopic operando techniques with molecular-scale insights to enable the rational design of metallic interfaces. To illustrate this approach, two studies will be presented. First, Atomic Emission Spectroelectrochemistry (AESEC) will be introduced as a tool for the real-time monitoring of metal and alloy dissolution and electrodeposition kinetics. AESEC combines an electrochemical flow cell with an inductively coupled plasma optical emission spectrometer, enabling the quantitative, element-resolved measurement of dissolution and deposition rates during electrochemical experiments. This technique provides unique insights into how each element, whether originating from the electrolyte or the substrate, participates in electrochemical reactions. The second study will demonstrate how in situ surface-science techniques using electrospray ionisation coupled with X-ray Photoelectron Spectroscopy (XPS) and Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) can elucidate the reactivity of metals toward complex molecules such as ionic liquid (ILs). XPS provides detailed information on the reactivity of both the ionic liquid and the substrate under controlled conditions, while PM-IRRAS probes molecular orientation, self-assembly, and interfacial bonding mechanisms. Beyond corrosion inhibition, this multiscale approach offers a framework for controlling metallic surface reactivity in a wide range of applications, including electrocatalysis and heterogeneous catalysis.