ALS SCIENCE HIGHLIGHT

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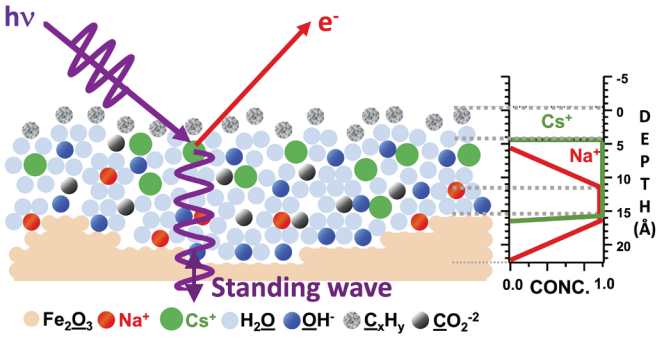
New Technique Gives a Deeper Look into the Chemistry of Interfaces

A new technique developed at the ALS offers sub-nanometer resolution of every chemical element to be found at heterogeneous interfaces, such as those in batteries and fuel cells. The technique, Standing-Wave Ambient-Pressure Photoelectron Spectroscopy (SWAPPS), combines standing-wave photoelectron spectroscopy (SWPS) with high-ambient-pressure photoelectron spectroscopy (APPS). The result is a technique that enables researchers to study a host of surface chemical processes under realistic pressure conditions. The technique is very promising for measuring such interfaces, which are critical components in energy research, heterogeneous catalysis, electrochemistry, and atmospheric and environmental science.

Solid/gas, liquid/gas, and solid/liquid interfaces play a major role in many important areas of science and technology, for example, in energy generation, electrochemistry, corrosion, environmental science, and information technology, but pose experimental challenges for the investigation of their chemical and structural properties on the molecular scale. The electrical double layer in batteries and fuel cells, for example, has been studied for over 100 years and yet is not fully understood. Characterizing such interfaces requires enhancing the signal from the narrow interfacial regions over those originating from the layers on either side of them.



By utilizing x-ray standing waves to excite photoelectrons, SWAPPS delivers vital information about all the chemical elements at the heterogeneous interfaces found in batteries, fuel cells, and other devices.

A key to the success of this study was the use of x-ray standing waves to excite the photoelectrons. A standing wave is an oscillatory pattern created when two waves of identical wavelength interfere with one another: one is the incident x-ray and the other is the x-ray reflected by a mirror. By suitable rotation of the sample, the x-ray standing wave can be scanned through the interface, with the photoelectrons excited by it revealing much about the depth distributions of each chemical species in a sample. Tailoring the x-ray wave field into a standing wave can thus be used to achieve much greater depth sensitivity in photoelectron spectroscopy.

SWAPPS therefore provides all the advantages of the widely used technique of x-ray photoelectron spectroscopy, including element and chemical-state sensitivity, and quantitative analysis of relative concentrations of all species present. However, SWAPPS does not require the usual ultrahigh-vacuum environment around the sample, which means researchers can measure the interfaces between volatile liquids and solids. SWAPPS can deliver vital information about the structure and chemistry of liquid/vapor and liquid/solid interfaces, in particular the electrical double layer.

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Research conducted by: S. Nemšák, C. Conlon, A. Keqi, A. Rattanachata, and C.S. Fadley (UC Davis and Berkeley Lab); A. Shavorskiy, O. Karslioglu, I. Zegkinoglou, F. Salmassi, E. Gullikson, and H. Bluhm (Berkeley Lab); P. Greene, E. Burks, and K. Liu (UC Davis); and S. Yang (IBM Almaden Research Center).

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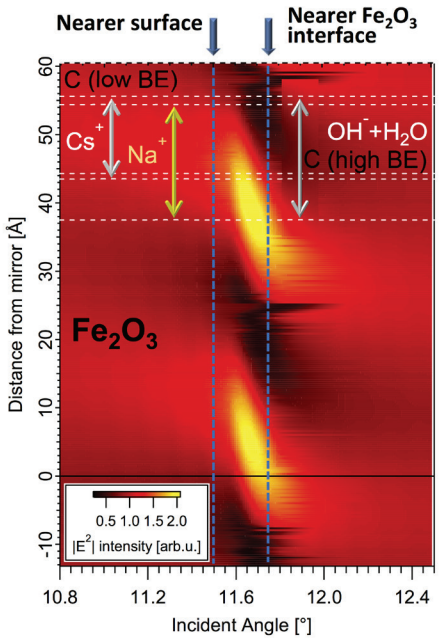
SWAPPS Role in Chemical Imaging

In terms of energies and wavelengths, x-rays serve as excellent probes of chemical processes. In the alphabet soup of x-ray analytical techniques, two in particular stand out for the study of chemistry at the interface where layers of two different materials or phases of matter meet. The first is SWPS, developed at the ALS, which made it possible for the first time to selectively study buried interfaces in a sample with either soft or hard x-rays. The second is APPS, also developed at the ALS, which made it possible for the first time to use x-ray photoelectron spectroscopy under pressures and humidities similar to those encountered in natural or practical environments.

Heterogeneous processes at solid/gas, liquid/gas, and solid/liquid interfaces are ubiquitous in modern devices and technologies, but often difficult to study quantitatively. Full characterization requires measuring the depth profiles of chemical composition and state with enhanced sensitivity in narrow interfacial regions at the nanometer scale. By combining features of SWPS and APPS techniques, SWAPPS is able to measure the elemental and chemical composition of heterogeneous interfaces with sub-nanometer resolution in the direction perpendicular to the interface.



SWAPPS measures the depth profiles of chemical elements with sub-nanometer resolution in the direction perpendicular to the interface utilizing an x-ray standing-wave field that can be tailored to focus on specific depths, i.e., near the surface or near the iron oxide interface.

ALS researchers have used SWAPPS to study a model system in which a nanometer layer of an aqueous electrolyte of sodium hydroxide and cesium hydroxide was grown on an iron oxide (hematite) solid. The spatial distributions of the electrolyte ions and the carbon contaminants across the solid/liquid and liquid/gas interfaces were directly probed and absolute concentrations of the chemical species were determined. The observation of binding-energy shifts with depth provided additional information on the bonding and/or depth-dependent potentials in the system.

They were able to determine that the sodium ions were located close to the iron oxide/solution interface, while cesium ions were on average not in direct contact with the solid/liquid interface. They also discovered two different kinds of carbon species, one hydrophobic, which is located exclusively in a thin film at the liquid/vapor interface, and a hydrophilic carbonate or carboxyl that is evenly distributed throughout the liquid film.

The SWAPPS combination of an oscillatory standing-wave field and the exponential decay of the photoelectron signal at each interface gives researchers unprecedented depth resolution. Future time-resolved SWAPPS studies using free-electron laser or high-harmonic generation light sources would also permit, via pump-probe methods, looking at the time scales of processes at interfaces on the femtosecond time scale. Many future applications of this technique thus seem possible.