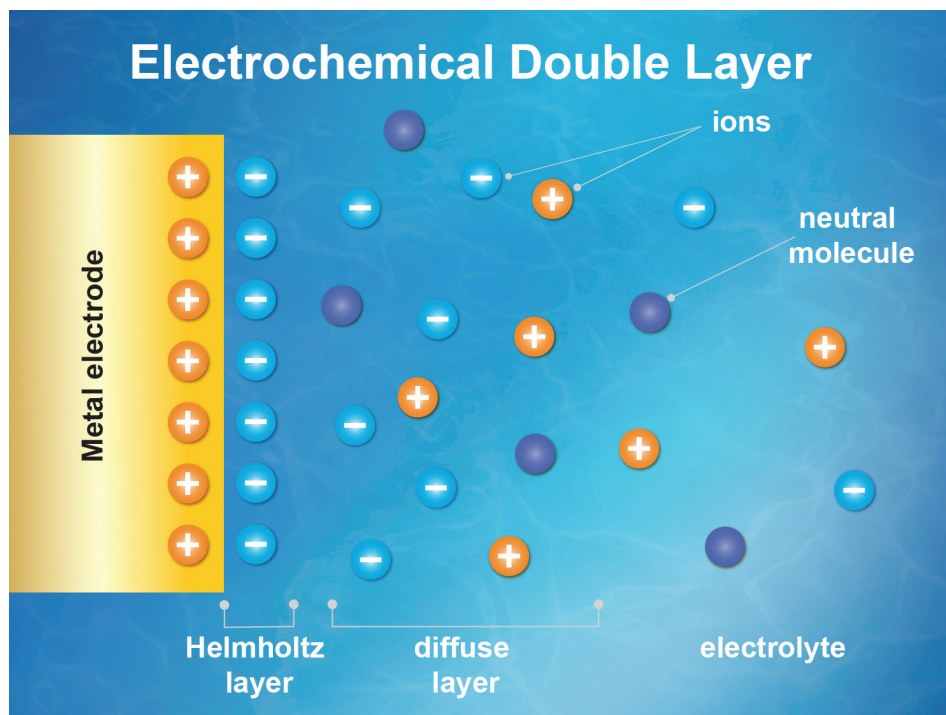


# Tender X-Rays Map the Double-Layer Potential



Stylized representation of an electrochemical double layer, the heart of solid/liquid chemical interactions such as those occurring around a battery's electrode. The double layer consists of a Helmholtz layer of ions adsorbed on the electrode surface and a diffuse layer extending into the electrolyte. In this experiment, pyrazine molecules (dark blue) were added to the electrolyte as a neutral probe. (Credit: Zosia Rostomian/Berkeley Lab)

In a first-of-its-kind experiment, ALS researchers demonstrated a new, direct way to study the inner workings of a phenomenon in chemistry known as an “electrochemical double layer” that forms where liquids meet solids—where battery fluid meets an electrode, for example. Scientists can now directly probe this previously elusive layer of chemistry thanks to a unique x-ray toolkit developed at the ALS. These x-ray tools and techniques could be extended to provide new insight into battery performance and corrosion, a wide range of chemical reactions, and even biological and environmental processes that rely on similar chemistry.

The problem of understanding electrified solid/liquid interfaces has been known for many years, but researchers trying to explain what's at work have mostly been limited to running computer simulations and modeling. In a battery, for example, the electrochemical double layer describes the layer of charged atoms or molecules in the battery's fluid that are drawn in and cling to the surface of the electrode because of their opposite electrical charge—an essential step in battery operation—and a second and closely related zone of chemical activity that is affected by the chemistry at the electrode's surface. The complex molecular-scale dance of charge flow and transfer within a

## Getting to the Bottom of Battery Basics

How fast can batteries be recharged? How much more energy can be stored in a battery of a given size? Billions of dollars can be gained or lost depending on the answers, not to mention the safety concerns raised as high-energy-density batteries become commonplace in homes, on roads, and in the air. Yet, our ability to find answers has been limited by a lack of tools capable of studying basic battery function at the molecular level under operating conditions. The electrochemical double layer, for example, is a fundamental concept in electrochemistry and an essential feature of all batteries. Since the idea was first advanced by Hermann von Helmholtz over a century ago, many theoretical refinements have been proposed, predicting in detail the double layer's structural and electrical organization. Those predictions could never be directly experimentally verified—until now. The experiments performed by Favaro et al. can be done under operating conditions, in a working electrochemical cell. With these methods, researchers hope to understand how processes involving solid/liquid interfaces in general behave down to the level of electrons and atoms.

battery's double layer is central to its function, and the ability to directly probe any attribute of the double layer would be a significant advancement.

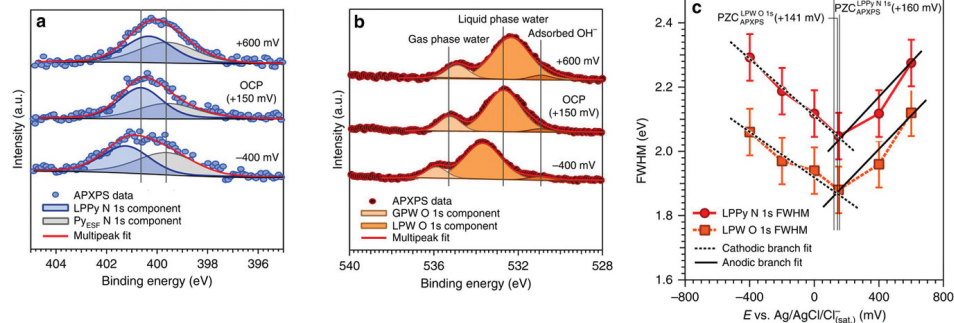
A team of researchers from Berkeley Lab and Shanghai have now demonstrated the ability to measure changes in the electric potential within the double layer under

operating conditions. Essentially, they can now create a direct map, independent of a model, showing how the potential within the double layer changes with respect to other key parameters.

An important breakthrough enabling this experiment was the ability to combine ambient-pressure x-ray photoelectron spectroscopy (APXPS) at ALS Beamline 9.3.1 with “tender” x-rays, which are intermediate in energy between soft and hard x-rays. Tender x-rays provide the right penetrating power to the escaping photoelectrons, allowing measurement of the electric potential profile for water and pyrazine molecules across the solid/liquid interface in response to changes in the electrode potential and the electrolyte concentration.

To do this, the researchers used a gold electrode and an aqueous electrolyte containing a neutral spectator molecule called pyrazine ( $C_4H_4N_2$ ), introduced as a uniformly distributed, independent molecular probe. In addition to being element- and chemical-specific, XPS provides information about the local potentials of atoms that undergo photoionization. By measuring the shifts in core-level binding energies of the elements in the liquid layer (such as N 1s from pyrazine and O 1s from water) as a function of the applied potential at the electrode, it is possible to determine local potentials within the liquid layer. Moreover, the width of the core-level peaks broaden as the potential in the double layer increases, providing a key spectroscopic parameter to directly measure double-layer properties.

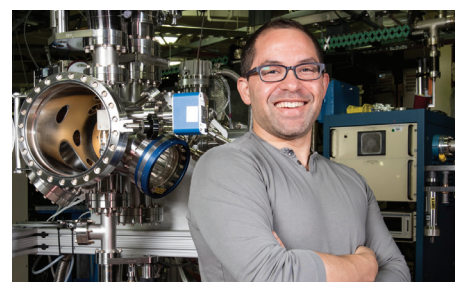
The data provided a precise measure of the drop in the electric potential within the double layer. The measurements also enabled determination of the potential of zero charge (PZC), the value of applied potential at which no net charge density is present at the electrode surface. These results help narrow the list of candidate models explaining the double layer. Importantly, the technique is well suited to active chemistry, and there are plans to add new capabilities to make this



**Spectral broadening of core-level peaks for (a) pyrazine (N 1s) and (b) water (O 1s) at different applied potentials (OCP = open circuit potential; LPPy = liquid-phase pyrazine; Py<sub>ESF</sub> = pyrazine at the electrode surface; GPW = gas-phase water; LPW = liquid-phase water). (c) LPPy N 1s and LPW O 1s full-width at half-maximum (FWHM) trends as a function of the applied potential within the double-layer region (PZC = potential of zero charge; Ag/AgCl/Cl<sup>-</sup><sub>(sat.)</sub> = reference electrode).**

technique more robust for studying finer details during the course of (electro) chemical reactions and to bring in other complementary x-ray techniques.

Solid/liquid interfaces are key for all kinds of research, from batteries and fuel cells to artificial photosynthesis. The information gained by applying these new tools will provide guidance for theoretical models as well as materials design and the development of improved electrochemical, environmental, biological, and chemical systems.



**Berkeley Lab's Ethan Crumlin, working with other researchers, found a new way to study chemical processes at work in batteries and in other chemical reactions using a specialized x-ray toolkit developed at the ALS. (Credit: Marilyn Chung/Berkeley Lab)**

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