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Insights into Electrochemical Reactions from Ambient Pressure Photoelectron Spectroscopy

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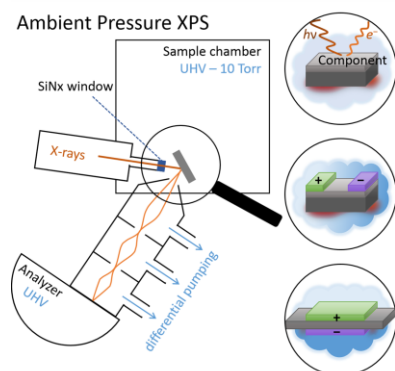
Conspectus

The understanding of fundamental processes in the bulk and at the interfaces of electrochemical devices is a prerequisite for the development of new technologies with higher efficiency and improved performance. One energy storage scheme of great interest is splitting water to form hydrogen and oxygen gas, and converting back to electrical energy by their subsequent recombination with only water as a by-product. However, kinetic limitations to the rate of oxygen-based electrochemical reactions hamper the efficiency in technologies such as solar fuels, fuel cells, and electrolyzers. For these reactions, the use of metal oxides as electrocatalysts is prevalent due to their stability, low cost, and ability to store oxygen within the lattice. However, due to the inherently convoluted nature of electrochemical and chemical processes in electrochemical systems, it is difficult to isolate and study individual electrochemical processes in a complex system. Therefore *in situ* characterization tools are required for observing related physical and chemical processes directly at the places where and while they occur, and can help elucidate the mechanisms of charge separation and charge transfer at electrochemical interfaces.

X-ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis) has been used as a quantitative spectroscopic technique that measures the elemental composition, as well as chemical and electronic state of a material. Building from extensive *ex situ* characterization of electrochemical systems, initial *in situ* studies were conducted at (near) UHV conditions ($\leq 10^{-6}$ Torr) to probe solid-state electrochemical systems. However through the integration of differential-pumping stages, XPS can now operate at pressures in the Torr range, comprising a technique called ambient pressure XPS (AP-XPS).

In this Account, we briefly review the working principles and current status of AP-XPS. We use several recent *in situ* studies on model electrochemical components as well as operando studies performed by our groups at the Advanced Light Source (ALS) at Lawrence Berkeley National Lab to illustrate that AP-XPS is both a chemically and electrically specific tool since photoelectrons carry information on both the local chemistry and electrical potentials. The applications of AP-XPS to oxygen electrocatalysis shown in this Account span well defined studies of (1) the oxide/oxygen gas interface, (2) the oxide/water vapor interface, and (3) *operando* measurements of half and full electrochemical cells. Using

specially designed model devices, we can expose and isolate the electrode or interface of interest to the incident X-ray beam and AP-XPS analyzer to relate the electrical potentials to the composition/chemical state of the key components and interfaces. We conclude with an outlook on new developments of AP-XPS endstations, which may provide significant improvement in the observation of dynamics over a wide range of time scale, higher spatial resolution, and improved characterization of boundary/interface layers (solid/solid and liquid/solid).



Introduction

Interactions at the interface between metal oxides and gas or liquid play a crucial role in determining the properties in a wide variety of systems and applications, for instance environmental and geochemistry, production and storage of energy, and heterogeneous catalysis. Such interactions are especially dynamic in chemical and electrochemical reactions that play an important role in energy conversion and storage. In particular, we are motivated by the use of hydrogen or metals as energy carriers—coupled to the evolution of oxygen gas upon storage and oxygen reduction upon subsequent conversion back to electrical energy. However, kinetic limitations to oxygen-based electrochemical reactions hamper the efficiency in promising technologies such as solar fuels,¹⁻² fuel cells,³⁻⁴ and electrolyzers.^{1, 5-6}

By employing a catalyst, the rate of reactions can be increased by lowering the activation energy. Metal oxides are used extensively to catalyze oxygen-based reactions due to their stability, low cost, and ability to store oxygen within the lattice.⁷⁻¹⁰ As catalysis is an interfacial process, the activity is determined by the surface composition under reaction conditions. To build an understanding of the reaction mechanism and rate-limiting steps, *in situ* characterization of

adsorbed intermediates and electron transfer is required.^{4, 11-12} However, at pressures approaching those of practical relevance, characterization with surface science techniques is challenging. Furthermore, the study of oxide catalysts also comes with difficulty in distinguishing between different oxygen-containing species in the liquid/gas phase, adsorbed on the surface, and within the lattice.

We focus here on the use of X-ray photoelectron spectroscopy (XPS), which can probe chemical composition at a depth of several nanometers,¹³ identify oxidation states, and provide insights into the electronic structure of a catalyst surface.¹⁴ XPS measures the binding energy of ejected core-level electrons. The binding energy is characteristic of different elements, which enables quantification of surface stoichiometry. This allows one to monitor changes during electrochemical cycling, such as the formation of oxygen vacancies¹⁵ and cation segregation.¹⁶ In addition, for a given element, shifts in binding energy can reflect change in the local electrical potential (e.g. due to an applied bias) or chemical shifts arising from changes in speciation or electronic structure. Furthermore, near-edge X-ray absorption fine structure (NEXAFS) can be recorded by scanning the incident photon energy across the absorption edge of the element of interest, where the differentially-pumped photoelectron analyzer is used as a partial electron yield (PEY) detector, elucidating surface-sensitive information about the unoccupied states complementary to that about the occupied states probed by XPS.

Ambient Pressure X-ray Photoelectron Spectroscopy

Due to the short inelastic mean free path (IMFP) of photoelectrons in condensed matter, XPS is surface sensitive (probing the top few nanometers) with the use of soft X-rays (<1500 eV).¹⁷ In standard cases, this short IMFP also limits the technique to ultra-high vacuum due to (in)elastic scattering of electrons in the gas phase, which reduces the path length of photoelectrons in high

pressure conditions. This problem is overcome in ambient pressure XPS (AP-XPS), which allows measurement in the Torr range or above.¹⁸⁻¹⁹ A typical instrument (Figure 1) consists of a high-pressure cell/chamber, separated from the electron analyzer—which remains in high vacuum—by a differentially pumped electrostatic lens system and series of apertures.²⁰⁻²¹ Such instruments are found at synchrotrons around the world²²⁻²⁷ and are being increasingly used with lab X-ray sources as well, which will further empower the field in the years to come.

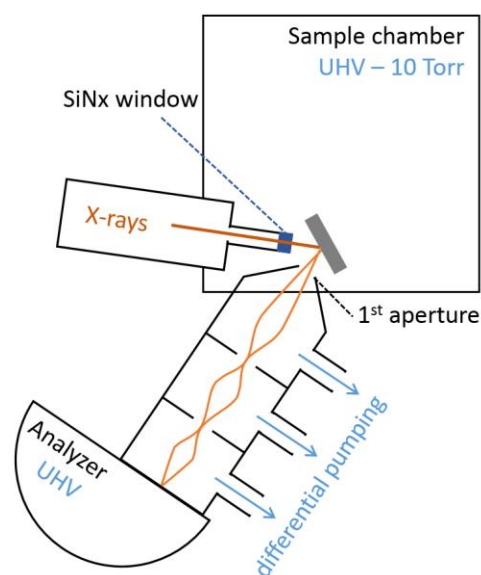


Figure 1. Schematic of the ambient pressure X-ray photoelectron spectroscopy (AP-XPS) instrument at ALS beamline 11.0.2, with set of differentially pumped electrostatic lenses/apertures between the sample chamber and the electron analyzer. Figure adapted from ref. 28 with permission from Elsevier.

AP-XPS probes the surface chemistry of catalysts at elevated pressures,²⁹ identifying and quantifying adsorbates in equilibrium with the gas. Furthermore, AP-XPS can detect photoelectrons from the gas itself when pressures exceed ~ 0.05 Torr,³⁰ using their binding energy to evaluate changes in the sample work function.^{18, 31} The shift in apparent binding energy of an electron under an applied bias is a direct measure of the local surface potential compared to the

open circuit voltage (OCV), enabling correlation of surface chemistry with local potentials.³²⁻³⁴ The combination of these features makes AP-XPS an excellent tool for studying electrochemical reactions at the catalyst surface.

There are, however, some constraints on the maximum pressure, which limits the ability to reach some of the conditions relevant to catalysis. The pressure differential between the sample chamber and the electron analyzer is, among other factors, governed by the aperture size. The first aperture radius also fixes the minimum sample-aperture distance to approximately twice the radius to achieve 95% the measured chamber pressure at the sample surface.²⁰ Factors that determine the attenuation of the electrons by gas molecules also affect the pressure limit, including the photoelectron kinetic energy and the types of gases used in the experiment.²⁷ Assuming a case of 100 eV kinetic energy photoelectrons and an aperture radius of 150 μm , the maximum allowable pressure (where the signal is reduced to 13% of that in vacuum) is 5 Torr in an oxygen environment.³⁰

Systems can be designed with increasing complexity to approach operating conditions, working within the pressure constraints of AP-XPS. As a first step, changes in chemical potential can be applied in the study of model systems via gas pressure and temperature, investigating surfaces and interfaces of electrochemical cell components (e.g. cathode, anode, or solid electrolyte). As a second step, an electrochemical potential gradient can be created by applying a voltage. Studies are often simplified to conditions which remain net-constant in chemistry, with the products of the working electrode acting as reactants of the counter (termed a “half-cell”). To consider a galvanic cell capable of supporting its own Nernst potential, two volumes are required for separate reactions to occur simultaneously (“full-cell”). A table of electrochemical and related AP-XPS studies of oxides performed at synchrotrons worldwide is provided in the Supporting Information.

We will discuss the use of AP-XPS in the context of oxygen electrocatalysis, focusing on model systems of the oxide/O₂ gas interface, oxide/H₂O vapor interface, and *operando* studies of electrochemical devices. The focus falls primarily on perovskite oxides, which are of interest as electrocatalysts in aqueous environments and solid oxide fuel cells (SOFCs). In addition, we will discuss CeO₂ for high temperature solid oxide electrolysis cells (SOECs).

The Oxide/O₂ Gas Interface

We first discuss studies of the oxide/O₂ gas interface, important for a number of applications ranging from pollution control, to sensors, to (electro)catalysis. Knowing and controlling the surface composition of the oxide during operation is crucial to enhance device performance. For instance, surface secondary phases can form during operation, the amount and composition of which can change as a function of temperature, oxygen partial pressure, humidity, and applied electrical potentials,³⁵⁻³⁸ affecting oxygen surface exchange in SOFCs. The presence of such secondary phases can greatly influence the activity for oxygen electrocatalysis, as observed in the La_{1-x}Sr_xCoO_{3-δ} series.³⁹⁻⁴¹ We have studied the segregation of Sr in epitaxial La_{1-x}Sr_xCoO_{3-δ} thin films at elevated temperatures and oxygen pressures relevant to SOFC operating conditions.⁴²⁻⁴³ Non-destructive depth profiling of surface and bulk spectral features can be obtained by tuning the incident photon energy for a given core level, where changes in the resultant kinetic energy modify the information depth. Using this method, surface features of the Sr 3*d* were determined to be the higher binding energy components⁴²⁻⁴³ and were found to decrease in relative intensity with increasing temperature in 0.67 Torr O₂ (Figure 2). By normalizing the intensity to the photoionization cross-section, changes in the elemental composition can be assessed. Sr within the perovskite (“lattice” component) phase was found to enrich toward the film surface (Figure 2 b). Both of these observations are in contrast to that for a polycrystalline La_{1-x}Sr_xCoO_{3-δ} pellet (Figure

2 a), which showed no change in surface chemistry with temperature. These spectroscopic observations have led us to propose that the ability to reduce surface secondary phases and develop Sr-enriched perovskite surfaces of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ film contributes to its enhanced activity for oxygen electrocatalysis relative to powder-based electrodes.⁴³ Combining the chemical information gleaned from photoelectron spectroscopy with the structural information from parallel *in situ* X-ray reflectivity (XRR) can elucidate further information of oxide catalyst surfaces.⁴⁴ Heating the bare perovskite above 350 °C leads to partial transformation at the surface, and then small reversible changes in Sr speciation upon subsequent thermal cycling (Figure 2 c).

Figure 2. AP-XPS elucidates the enrichment of elements in SOFC catalysts *in situ*. (a) Secondary phases evident as a “surface” Sr peak in a polycrystalline pellet of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ under operational conditions are more prominent, in contrast to (b) a $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ thin film, where “surface” Sr is reduced in intensity. Adapted from ref. 43 by permission of The Royal Society of Chemistry. (c) Heating a $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskite surface leads to partial transformation at the surface, and then small reversible changes in Sr speciation (shown relative to initially at 520 °C) upon subsequent thermal cycling. Adapted with permission from ref. 44. Copyright 2013 American Chemical Society.

The Oxide/H₂O Vapor Interface

In aqueous oxygen electrocatalysis at room temperature, the interactions of catalysts with water as a reactant, intermediate, and product play a key role in the reduction and evolution of oxygen.⁴⁵⁻

⁴⁶ The reactivity of surfaces with water vapor or liquid dictates their hydroxylation, which changes their reactivity and adsorptive properties.

To obtain a deeper understanding of oxide catalysts, the surface chemistry in H₂O vapor has been explored using AP-XPS.⁴⁷ By performing isobaric and/or isothermal measurements to access a range of relative humidities, the oxygen spectra of model oxide surfaces have been deconvoluted into hydroxyls (OH⁻), oxy-carbonaceous species such as carbonate (CO₃²⁻), bulk oxygen, and adsorbed water (H₂O). Using a multilayer electron attenuation model,⁴⁸⁻⁵⁰ the coverage of each species can be deduced. In the case of TiO₂, the relation between the coverage of OH⁻ and Ti³⁺ sites suggests hydroxylation of the surface proceeds by dissociation of water molecules, where the OH⁻ group fills an O²⁻ vacancy and the remaining H⁺ binds to a bridging O²⁻, forming a second OH⁻ group. This coverage remains constant as a function of H₂O chemical potential, and subsequent H₂O adsorbs molecularly.⁵¹ In contrast, for Fe₂O₃, the OH⁻ coverage formed at low H₂O chemical potential increases in line with water adsorption at higher relative humidities.⁵²

Moving beyond binary oxides, the activity for oxygen electrocatalysis can be enhanced through the use of complex oxides, such as perovskites.⁵³⁻⁵⁴ For oxygen reduction, the proposed mechanism in basic solution involves the displacement of adsorbed OH⁻ groups by O₂, and subsequent reduction leads to a final step in which water re-protonates the oxidized surface.^{46, 53} Thus the binding and coverage of OH⁻ can play an important role in the oxygen reduction activity.⁴⁵ The quantity of OH⁻ measured in the presence of water vapor gauges the relative affinity of the surface toward hydroxylation. Greater OH⁻ coverage, indicative of an increased binding strength of OH⁻, can lower ORR activity by hindering the displacement of OH⁻ by molecular oxygen, which is considered to be rate-limiting for the oxygen reduction reaction (ORR).⁵³

In a study of model epitaxial LaCoO₃ (001) films, the surface reacts with water, forming OH⁻ species as the relative humidity increases (Figure 3 a). Of further interest is a surface peak present in all H₂O chemical potentials not observed in the case of simple oxides, attributed to the change

in Madelung potential at a polar surface, which could lead to species such as undercoordinated oxygen. The shift in the gas phase water peak to ~ 1 eV higher binding energies with increasing relative humidity (decreasing temperature) is indicative of a decrease in work function, dictated by the net change in surface dipole. Due to the affinity of La-based perovskites for carbon, any trace CO_2 in the chamber will react with the surface,⁵⁵ forming CO_3^{2-} species over time. As coverage increases – deduced by the model in Figure 3 b – these CO_3^{2-} species compete with OH^- for surface sites (Figure 3 c), suggesting that in an aqueous environment, oxy-carbonaceous species may play a role as spectator or poison in oxygen electrocatalysis. However, the coverage of OH^- compared amongst different LaMO_3 surfaces ($M = \text{Cr-Ni}$) correlated with calculations of the free energy of hydroxylated surfaces, indicating the technique can assess the relative affinity toward hydroxylation.⁴⁵ The adsorption of water and its relation to hydroxylation also bears important ramifications to the hydrogen bonding network present at the catalyst surface under reaction conditions.

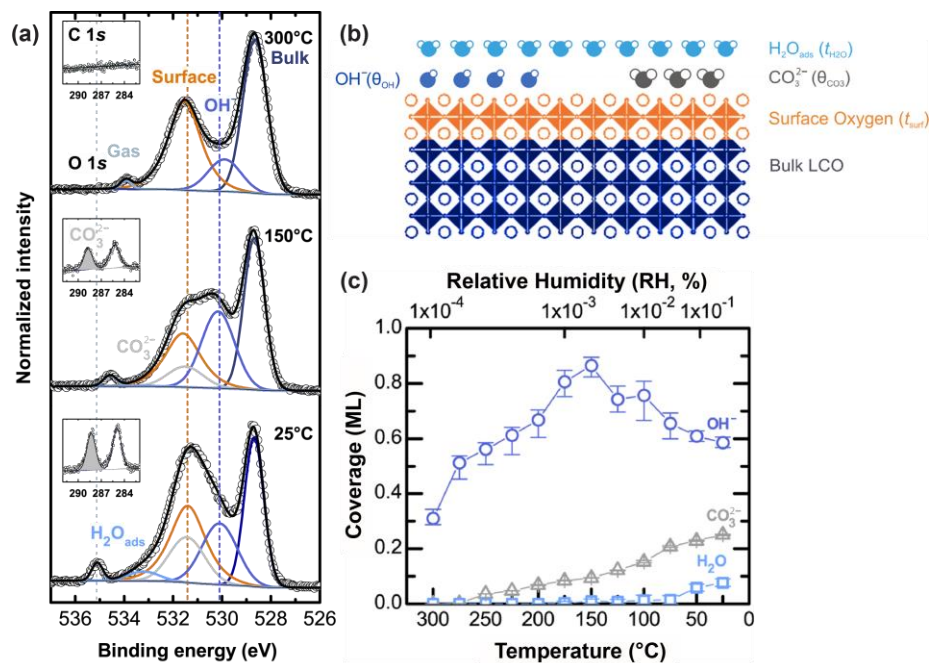


Figure 3. A LaCoO_3 perovskite film surface hydroxylates in the presence of water vapor. (a) O 1s spectra illustrating the contribution of various surface species in 100 mTorr H_2O , where the relative humidity is increased by cooling the sample. While a clean film shows only “bulk” oxygen, “surface” oxygen, and OH^- , cooling leads to the formation of CO_3^{2-} and adsorption of water. (b) Schematic of the multilayer electron attenuation model used to determine the coverage in monolayers (ML) in (c). Adapted with permission from ref. ⁴⁷. Copyright 2014 American Chemical Society.

Insights from *Operando* Electrochemical Measurements

The most direct relation to realistic operating conditions can be obtained by *operando* measurements of model electrochemical cells. For instance, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskite films decorated with the Ruddlesden-Popper phase, which have higher activity for the ORR than undecorated films,⁴⁰ showed an increase in lattice Sr with polarization. This change paralleled an increase in oxygen located in the terminal lattice layer (surface, but not adsorbed O_2) not observed for the bare perovskite, which may reflect active surface vacancy sites which have become occupied after oxygen dissociation.¹⁶ Alternatively, the increase of an oxygen species located at higher binding energy with applied potential could suggest a reduction of surface oxygen during cathodic polarization. Such an accumulation of negative charge on the oxygen is supported by the upward shift in the Fermi level observed for the decorated film, in contrast to the bare perovskite film, which remains unchanged with polarization.¹⁶ In a recent study of Fe and Fe-Co perovskite electrodes with mixed La^{3+} and alkaline earth (2+) cations (such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$), changes in the oxygen K-edge PEY-NEXAFS with applied potential suggested anionic redox is involved in SOFC and SOEC operation.⁵⁶ Changes in intensity of the feature reflecting covalency between the Fe and O with cathodic polarization were consistent with the population of electronic

states near the Fermi level. Such a change in the electron density takes place in parallel with a reduction of the perovskite and a raising of the Fermi level, similar to that observed in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$.¹⁶

An additional strength of AP-XPS is its ability to act as a non-contact probe of changes in the local potential through the use of focused X-ray beams and/or spatially resolving detectors. For a cell applying a potential across the surface in a uniform gaseous environment, the voltage drop which occurs at the electrode/electrolyte interface and the resultant chemistry can be probed with spatial resolution on the order of 20-50 μm .^{15, 21, 34} This can provide spatially resolved information regarding the electrochemically driven, surface charge-transfer processes under relevant chemical environments, promoting the development and validation of microscopic and molecular theories and of detailed interfacial models of electrochemical systems.

One such instance is the study of CeO_{2-x} for SOEC, where water is split into hydrogen and oxygen anions at high temperature. AP-XPS has been used to monitor changes in Ce oxidation states, measure local surface potentials in-plane across the SOEC, and measure local overpotentials of operating devices in far-from-equilibrium conditions.^{32, 57} The active regions have been found to extend $\sim 150 \mu\text{m}$ from the current collectors and are thus not limited by the three phase-boundary interfaces. The persistence of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ shifts within this active region suggests that the surface reaction kinetics and lateral electron transport on the thin ceria electrodes are co-limiting processes.³² Building upon this work, the relation of Ce redox to oxygen speciation was recently investigated, in order to “observe” charge separation at an SOEC gas–solid interface and monitor changes in chemical intermediates involved in the electrochemical process. Within the electrochemically active region of the SOEC, a separation of local surface potentials of adsorbed

OH^- and incorporated O^{2-} ions due to a build-up of surface Ce^{3+} was observed, proposed to be a result of rate-limiting charge transfer processes.¹⁵

In contrast to cell designs which apply a potential in-plane across the surface, employment of two isolated gas chambers separated by an electrolyte enable the potential of each half cell to be independently controlled. The perovskite cathode $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) has been studied in an operable SOFC during turnover of the ORR (Figure 4 a).⁵⁸ A rigid shift was observed in the binding energy of gas phase O_2 core levels relative to the Fermi level of the analyzer, as well as changes in chemical speciation and valence state. Comparing the overall O 1s spectra at open circuit to that when the potential is reduced by 0.6 V (conducting a current limited by the oxygen reduction rate), the total oxygen intensity is seen to decrease (Figure 4 b). This suggests that oxygen is being depleted from the cathode surface. This change in stoichiometry is corroborated by changes in the Fe valence state of BSCF, probed by fluorescence-based NEXAFS within the same ambient pressure chamber (Figure 4 c). The Fe L edge NEXAFS arises from electronic transitions between the occupied Fe 2p and unoccupied Fe 3d states. The shift in spectral weighting toward lower photon energy upon reducing the cell potential indicates that the average valence state of iron decreases with increased cell current (limited by oxygen reduction).⁵⁹

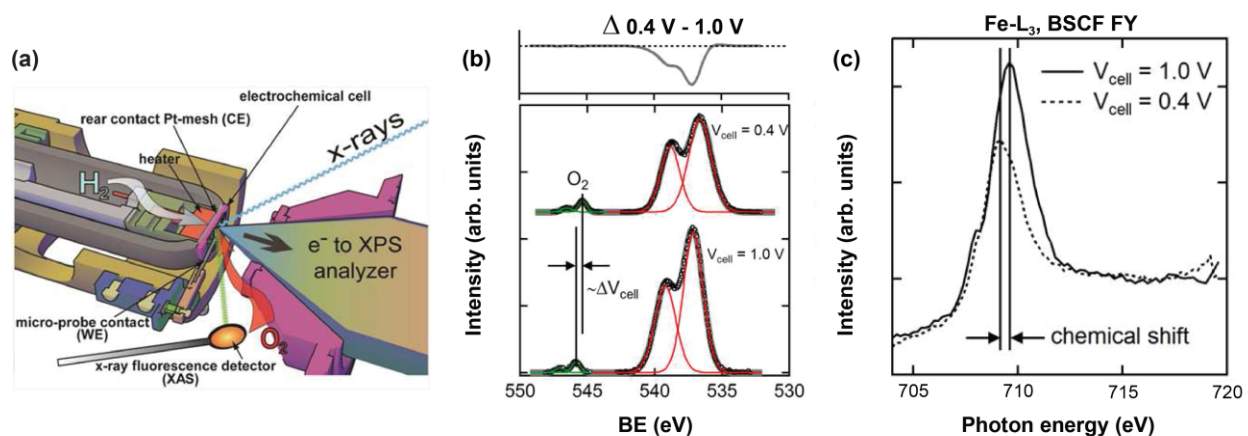


Figure 4. (a) Schematic of the custom-designed vacuum chamber and manipulating stage. The electrochemical cell is patterned onto an electrolyte membrane and then sealed to a ceramic tube using a specially formulated glass. (b) Normalized O 1s XPS measured for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (BSCF) at open circuit (1.0 V) and at a cell potential of 0.4 V, with the difference between the normalized O 1s spectra taken after aligning the gas-phase O₂ peaks to correct for the change in surface potential. (c) Normalized Fe-L₃ X-ray absorption edge measured at open circuit (1.0 V) and 0.4 V show the average valence of Fe decreases with increased cell current. Reprinted with permission from ref. ⁵⁸. Copyright 2013, The Electrochemical Society.

Conclusions and Outlook

In summary, the highlighted applications in this Account so far demonstrate the power of soft X-ray AP-XPS to investigate surfaces and interfaces of interest for oxygen electrocatalysis. One of the main characteristics is the surface sensitivity, tunable by photon energy at synchrotron sources for depth profiling, in elucidating chemical shifts and quantifying stoichiometry. However, the limited probing depth generally constrains the technique to the gas/solid or gas/liquid interface, while buried interfaces (solid/solid or liquid/solid) remain inaccessible. With the development of high spatial resolution instruments as well as hard (>7 keV) and “tender” (2-7 keV) X-ray photoelectron endstations,⁶⁰ it will be increasingly possible to probe buried interfaces in the near future. Recent demonstrations observed the oxidation of platinum in KF/H₂O⁶⁰ and Ni in a KOH electrolyte⁶¹ *in situ*, probing through 10-30 nm of electrolyte. Further development of hard/tender X-rays will provide valuable information on the electrochemical double layer which forms at solid/liquid interfaces. Other efforts are ongoing to increase the pressure limit and spatial resolution through changes in the cell/end station geometry and lenses, with large strides being made at synchrotrons around the world to reach close to atmospheric pressures.⁶²⁻⁶³ An additional

approach includes the use of X-ray lenses to produce standing waves, increasing the depth resolution of sample/interface analysis.^{61, 64} Finally, novel pump-probe techniques using AP-XPS coupled to laser systems (and the free-electron laser) can also provide unique time-resolved information.⁶⁵ Such studies can help assess the presence and energetics of reaction intermediates and further build further mechanistic insight in electrocatalysis.

ASSOCIATED CONTENT

Supporting Information. Table of electrochemical and related AP-XPS studies of oxides performed at synchrotrons worldwide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Ethan J. Crumlin obtained his MS and PhD in Mechanical Engineering from MIT, and was a Postdoctoral Fellow at the Advanced Light Source (ALS). He currently is a Research Scientist at the ALS at Lawrence Berkeley National Laboratory (LBNL), where his research focuses on *in situ* and *operando* AP-XPS to understand interfaces for energy systems.

Hendrik Bluhm obtained his PhD in Physics from the University of Hamburg. He worked on the development of synchrotron-based AP-XPS during his Postdoc at LBNL and at the Fritz Haber Institute in Berlin. He currently is a Senior Scientist in the Chemical Sciences Division at LBNL and an Adjunct Professor at the Department of Chemistry & Biochemistry at the University of Maryland, College Park, MD, focusing on the interfacial chemistry of liquid and solid surfaces under environmentally relevant conditions.

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