“X-ray Spectroscopy of Energy Materials under *In situ/Operando* Conditions”

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Abstract

A perspective and brief review of *in situ/operando* X-ray spectroscopic techniques with focus on energy materials is presented, including discussion on current status, choice of cells and suitable X-ray energy range. Initial discussion focuses on the scientific advancement achieved using ambient pressure X-ray photoelectron spectroscopy (APXPS) at the solid/gas interface, and then progresses through the techniques evolution to probe the liquid/vapor and the emerging solid/liquid interface. This is followed by an overview of soft X-ray adsorption spectroscopy (sXAS) for energy science using both window and windowless cell configurations. Concluding remarks provide a future outlook for where the authors believe these techniques and class of science will progress towards.

1. Introduction

X-ray photoelectron spectroscopy (XPS) and soft X-ray adsorption spectroscopy (sXAS) have traditionally been considered and utilized as ultra-high vacuum (UHV) surface sensitive techniques. A driving factor for the UHV environment has been the attenuation induced from the ejected photoelectrons colliding with gas as well as sample cleanliness for specific class of experiments. However, this constraint never stopped researchers from further pushing the boundary. With the emergence of synchrotron radiation sources providing high brightness X-rays, high-resolution sXAS became accessible while several new aspects for XPS became possible. Now that the X-ray photon energy can be easily tuned across a wide range of energies, several different types of XPS science are enabled. Using low energy photons (<1 keV) to generate low kinetic energy photoelectrons (~100 eV) are the most surface sensitive,¹⁻³ increasing the photon energy range into the ‘tender’ regime (~2 keV to 6 keV)⁴ enables the non-destructive study of interfaces, and upon further increasing the energy range, high energy X-rays (>6 keV) can be used to study deeper into the bulk of materials.⁵ These three probing depths are depicted in **Figure 1**, used SESSA v1.3⁶ to simulate and determine the normalized intensity of a 1 nm gold

layer at the surface (bare gold), thin interface (underneath 10 nm of carbon), and bulk (gold underneath 50 nm of carbon) is shown as a function of the photon energy. This simulation helps demonstrate what energy range is ideal to use for each class of science. While APXPS probes the binding energies of the interested core-level electrons, sXAS corresponds to the unoccupied conduction band electronic states with the existence of core-holes. Often APXPS and sXAS provide complementary information of the chemical and physical properties of the material surfaces and interphases. Technically, compared with XPS, *in situ/operando* sXAS provides the opportunities of detecting the unoccupied states in a real-world device with a much deeper probe depth (>100 nm) in the photon-in-photon-out mode.

These characterization capabilities have been extended even further due in large part to the coupling of synchrotrons variable photon energy ranges, high brilliance, and new endstation designs. For sXAS, the integration of improved detector efficiencies combined with the use of thin photon transparent windows, pioneered the way for *in situ/operando* sXAS.^{7,8} In particular for ambient pressure XPS (APXPS) the development of differential pumping, electron pre-lens, and sample environment designs lead to the rapid proliferation of science at the solid/gas interface. Thus enabled significant scientific advancements to many research fields, in particular the environmental and catalysis communities.¹ As APXPS of the solid/gas interface has transitioned from being new and novel to routine, a significant body of work has been generated and extensively reviewed in the referenced literature.^{1,8,9} As these solid/gas interface based APXPS experiments continue to grow at an exponential rate¹ to this day, an evolution for the UHV spectroscopy technique towards *in situ/operando* spectroscopy science has emerged.^{8,10}

Figure 1: Normalized Au 4f 7/2 intensity for a simulated 1 nm gold layer that is bare, underneath 20 nm and 50 nm of carbon to depict ideal photon energies for surface, interface, and bulk sciences, respectively. This simulation utilizes SESSA v1.3⁶ to predict the intensity as a function of photon energies. The data is then smoothed for ease of viewing.

This emergence of *in situ/operando* spectroscopy science will be the focus of this review, highlighting the techniques and findings that have largely centered around energy sciences such as batteries,^{8,11-15} solid oxide fuel cells,^{10,16-25} solar cells²⁶ and other electrochemical devices.^{27,28} Heterogeneous catalysis and environmental *in situ* using APXPS will not be discussed in this review as they have been comprehensively reviewed by Starr et al.¹ In principal as long as the surface of interest can be both active (chemically, thermally, electrochemically) and can be exposed to the incoming and outgoing photons and electrons respectively, *in situ/operando* surface/interface techniques can be utilized. The focus of this work will be to initially review the *in situ/operando* APXPS at the solid/gas interface using soft X-rays, then progress to the strategies for probing of the solid/liquid interface. Followed by a review of various *in situ/operando* sXAS studies and the strategies to conduct those experiments. Lastly, will conclude with an outlook for where we foresee the future of *in situ/operando* spectroscopy progressing. Ultimately providing a comprehensive overview of the past, present, and future of core-level spectroscopy of energy materials under *in situ/operando* conditions.

2. In Situ/Operando Solid/Gas Interface APXPS

Many electrochemical devices comprised of two electrodes (typically metals and or mixed electronic and ionic conducting oxides) separated by a solid ionic conducting electrolyte, such as naion for low temperature proton exchange membranes^{27,28} or yttria-stabilized zirconia (YSZ) for high temperature solid oxide electrochemical cells (SOEC)/solid oxide fuel cells (SOFC),^{16,17,22,23,29} are the primary systems utilizing *in situ/operando* solid/gas interface APXPS, **Figure 2.** SOECs are non-liquid based electrochemical cell systems are ideal candidates for studying the solid/gas interface properties as they are completely operational in solely gas environments and using soft X-rays to specifically probe the outermost surface species. Specially designed cells that expose an electrode or electrode/electrolyte interface to a gas environment while facing the X-ray beam and the analyzer can be attached to a potentiostat using an electrical feedthrough to facilitate an applied bias. Having the ability to provide electrochemical polarization enables one to directly study the solid/gas interface, gaining information about the surface reaction species while under operation.

In situ/Operando Solid/Gas Interface APXPS

Figure 2: Examples of *in situ/operando* solid/gas interface APXPS for a) SOEC¹⁷ b) scanning photoelectron microscopy (SPEM) studies of SOECs,^{30,31} c) polymer electrolyte membrane fuel cell (PEMFC),^{27,28} and d) solid-state lithium-air battery.^{14,15}

SOEC was the first *operando* electrochemical solid/gas interface APXPS experiment thanks in large part to its thin film architecture, ability drive current with both electrodes exposed to the same gas environment, and do not require a liquid/humidified electrolyte.^{8,10} The Eichorn group and collaborators helped pioneer this class of science by investigating undoped ceria oxide, in particular to observing the interface and changing surface potentials along a lateral electrode surface,^{19,23-25,32} and later used the same techniques to probe CO₂ electrolysis.³³ This work paved the pathway for others, such as Chueh et al,¹⁶ who combined *in situ* electrochemical impedance spectroscopy and APXPS to reveal that the surface of Sm-doped CeO₂ stabilized several orders of magnitude more reduced Ce³⁺ species than the bulk (nearly fully oxidized Ce⁴⁺) when exposed to relatively oxidizing environments. In a follow up study by the Chueh et al.,²⁹ further probed this system to specifically track the oxygen-ion incorporation pathway by simultaneously tracking oxygen vacancies, electrons, and adsorbates during electrochemical polarization at 0.3 Torr H₂/H₂O/Ar (8:1:4 ratio). They were able to determine that the surface oxygen-ion transfer,

mediated by oxygen vacancies, is fast and identify the roles the surface oxygen vacancy and electron defects play in determining surface incorporation reactions.

Focusing on the high temperature oxygen reduction reaction (ORR), Shao-Horn et al. studied high activity epitaxial grown thin-films of perovskite (ABO_3) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC_{113})¹⁸ and Ruddlesden-Popper (A_2BO_4) $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_{4\pm\delta}$ (LSC_{214})³⁴ which have shown significant increases in ORR activity when creating a heterostructured interface between the two oxides ($\text{LSC}_{113/214}$), **Figure 2a**.³⁵ Using APXPS as a function of temperature in 760 mTorr enabled the observation of Sr enrichment in the near surface region of the epitaxial thin films helping to explain the enhanced activity compared to polycrystalline bulk LSC_{113} .¹⁸ By applying potentials to the epitaxial thin films of LSC_{113} , LSC_{214} , and $\text{LSC}_{113/214}$, electrochemically induced strontium segregation and active ‘polarized induced’ oxygen surface sites in the materials termination layer were observed by APXPS. This electrochemically-induced response is most pronounced on the material with a heterostructured $\text{LSC}_{113}/\text{LSC}_{214}$ interface (**Figure 2a**), which is also known to be the most active, thus providing insight into the features of a highly active ORR electrocatalysts.¹⁷ In a separate study the surface strontium concentration was shown to be systematically reversible with applied potentials.²²

With the integration of a zone plate, order sorting aperture and scanning the sample stage, microscopy capabilities become available. At ELETTRA, SOEC’s can operate in low-pressure gas environments and applied potentials while obtaining two-dimensional spatial photoelectron spectroscopic (otherwise referred to as scanning photoelectron microscopy, SPEM) information with a resolution ~ 50 nm in size, seen in **Figure 2b**.^{30,31} Using this technique facilitated the ability to clearly probe the interface of a nickel/YSZ/manganese SOEC system.³¹ With the installation of a needle nozzle with a pulsed controlled valve they are able to inject a high gas pressure environment isolated to a small region near the sample surface.³⁰ This would allow them to extend the local operating pressure regime while still being able to perform microscopy with the same spatial resolution.

After significant progress and success was made with SOECs in APXPS investigations, sample holder geometries advanced to support low temperature proton exchange membranes fuel cells (PEMFC), **Figure 2c**.^{27,28} By creating a water reservoir²⁷ or flow cell geometry²⁸, the membrane was able to be sufficiently hydrated to support electrochemical reactions while the other side of the cell facing the X-ray beam and analyzer is exposed to the ambient pressure gas environment.

The flow cell geometry was used to study the ORR on a platinum electrode and determined hydroxyl intermediates on the cathode change as a function of applied potentials. Experimental data that was used to corroborate density functional theory calculations.²⁸ The water reservoir cell configuration probed the oxygen evolution reaction (OER) during water electrolysis. From this work, observed the coexistence of multiple platinum oxidations on the surface of the electrode during oxygen evolution.²⁷

Batteries have also been able to benefit from *in situ/operando* APXPS.^{10,14,15} Specially designed solid-state lithium-air batteries were constructed to probe the solid/gas interface between the mixed ionic and electronic conducting vanadium oxide electrode and gas environment, **Figure 2d**. In the foundation study, a direct comparison between the battery operating in UHV environment and oxygen gas environment was made.¹⁵ While operating in UHV clear evidence for the lithiation is observed with changes to the vanadium valance state and shifting covalence of the oxygen lattice species within the V 2p and O 1s respectively. Upon introducing oxygen gas into the chamber, the formation and decomposition of new lithium species, Li_2O_2 and Li_2O were observed at distinct applied potentials during charge and discharge respectively.¹⁵ In a follow up study, the same technique was utilized to probe the irreversible reactions that occur from the native carbon species on the surface of the electrode (such as adventitious carbon) as well as from exposure to low CO_2 partial pressures.¹⁴ This study provided direct evidence for the batteries sensitivity to even simple and seemingly innocuous common carbon contaminants (such as adventitious carbon), thus helping to reinforce the importance for lithium-air batteries to develop strategies for how to deal with its high reactivity to carbon.

Lastly, using the *in situ* solid/gas interface APXPS science, has demonstrated the ability to measure the work function, a fundamental properties of a materials surface, in its gas environment/operating condition.³⁶ By measuring the core level binding energy shift of non-reactive argon gas that is acting as a tracer element, one can determine the relative changes in work function between the different materials. After performing a calibration using a highly ordered pyrolytic graphite (HOPG) substrate and monitoring the argon gas binding energy shift with an applied potential, one can then determine a given materials work function, which is useful for the engineering applications like photovoltaic/solar cells and semiconductor devices. This technique can even work when different reacting gases and/or temperature are exposed to the material of interest.³⁶

3. *In situ/operando Operando* Liquid/Vapor and Solid/Liquid Interface APXPS

Expanding upon the success from *in situ/operando* solid/gas interface APXPS, a natural progression is to study liquids, liquid/vapor and solid/liquid interfaces, **Figure 3**. Liquids, liquid/vapor, and solid/liquid interfaces play a major role in many atmospheric and environmental chemistries, both as catalysts for heterogeneous reactions, and as sinks and sources for atmospheric trace gases,³⁷ as well as energy sciences.³⁸ Up to now little is known about the concentration of solution phase species at the liquid/vapor interface, which can significantly differ from the bulk solution concentration and is an important quantity in the modeling of heterogeneous reactions at liquid/vapor interfaces. A direct measurement of the rate of chemical reactions at the liquid/vapor interface under atmospherically and environmentally relevant conditions is difficult due to the lack of quantitative experimental techniques that are surface-sensitive, chemically specific, offer temporal resolution and can operate at elevated pressures in the Torr range. A promising strategy is the combination of APXPS with a liquid jet initially developed by Siegbahn et al.,^{39,40} (**Figure 3a**). This technique creates a continuously flowing liquid jet that would pass in front of the analyzer and X-ray beam to collect spectra from both the surface of the liquid and vapor phases. By changing the relative position of the liquid stream to the analyzer/X-ray beam they could effectively tune the relative liquid to vapor photoelectron contribution to be more liquid or vapor sensitive.⁴⁰ This technique facilitated the probing of a wide range of liquid solutions including water,⁴¹ alcohols,⁴¹ organic solvents,^{40,42} salt concentrated solutions,⁴³ and acids.⁴⁴

Figure 3: Examples to probe liquids, liquid/vapor, and liquid/solid interfaces. a) liquid-jet: liquid and liquid/vapor, b) droplet train: liquid and liquid/vapor, c) liquid-jet with nanoparticles: solid/liquid interfaces, d) windowless methods to study liquid and solid/liquid interfaces, e) window-based methods to study liquid and solid/liquid interfaces.

This liquid jet configuration was later adapted from continuous stream to a continuously flowing stream of discrete droplets at intervals from sub-milliseconds to many milliseconds, referred to as ‘droplet train’, **Figure 3b**. The advantage of this technique is the ability to study the liquid/vapor interface at varying reaction times to a gas environment based on the frequency of the droplet train. Utilizing an aqueous methanol solution in a proof-of-principle experiment, this droplet train technique has demonstrated that methanol segregates to the surface of this water mixture.⁴⁵

As the understanding of liquids and liquid/vapor interfaces increased from technical experimentation challenges to scientific contributions, efforts extended to probing the solid/liquid interface. Siegbahn et al again established the foundation techniques to probe the solid/liquid interface, and later others continued to develop additional strategies.^{39,46,47} Creating a liquid suspension of nanoparticles and leveraging the liquid-jet APXPS setup previously discussed (**Figure 3c**), a solid/liquid (as well as vapor) interface was investigated.^{48,49} This work led to the understanding of tin oxide nanoparticles spatial distribution at the water/air interface,⁴⁸ as well as the influence of silica colloid nanoparticles surface charge densities ability to regulate its adsorption to the interface.⁴⁹ A similar approach can also be used to investigate gas phase reactions with solid aerosol particles through the combination of an aerodynamic lens with APXPS.⁵⁰

To enable *operando* solid/liquid APXPS capabilities a new method needed for creating the solid/liquid interface with the abilities to conduct electrochemistry, had to be developed. With the generation of new APXPS chambers capable of operating at pressures approaching 100 Torr, water with a vapor pressure of 20 Torr at room temperature, can remain in liquid phase.⁴ Additionally, using synchrotron beamlines with photon energies in the ‘tender’ X-ray regime, facilitates the ability to probe through a liquid up to 10’s of nanometers in depth. Thus enabling investigations of solid/liquid interfaces. Using a simple technique of placing a beaker of aqueous electrolyte inside the chamber at 20 Torr (at room temperature) and immersing a flat hydrophilic substrate (such as platinum foil) into the electrolyte, and slowly partially removing the substrate to create a thin exposed electrolyte film (with regions near the top that are several 10’s of nanometers thick) that is electrochemically connected to the remaining electrolyte within the beaker. This method has been labeled the ‘dip and pull’ method, (**Figure 3d**) with the detailed steps portrayed in **Figure 4a**.⁴

By including reference and counter electrodes, electrochemical experiments can be performed while simultaneously probing the solid/liquid interface directly. The inherent elemental and chemical sensitivity of APXPS thus permits full characterization of the substrate, liquid and interfacial regions providing a novel pathway to measure, e.g., the structure of the electrical double layer at the solid/liquid interface (e.g., inner vs. outer sphere adsorption of solution ions), as well as the chemical nature of the solid interface with the liquid, including oxidation state changes due to charge-transfer reactions across the solid/liquid interface and protonation/de-

protonation of interface oxygen in metal oxides as a function of pH. Since photoelectron spectroscopy probes the electrons, band bending and alignment can also be probed through rigid shifts of the peak positions of all core and valence band levels across the interface.⁴ As a proof of concept, the ‘dip and pull’ method was first used to probe electrochemical solid/liquid interface between a polycrystalline platinum foil and 6 M KF aqueous electrolyte. As shown in **Figure 4b**,⁴ is the Pt 4f spectra detected through an electrochemically active thin electrolyte layer formed on the platinum foil electrode. Since the platinum electrode is grounded, it does not change with applied potentials, however the O 1s liquid (dark blue) shifts linearly 1:1 with the applied potential change from -0.8 V to -0.4 V verse the Ag/AgCl reference electrode. Upon further increasing the applied potentials to 1.2 V verse the Ag/AgCl reference electrode, the platinum oxidation can clearly be observed.⁴

Figure 4. a) ‘dip & pull’ procedures: *i*) collecting spectra of the hydrated working electrode, *ii*) submerged to conduct electrochemistry, and lastly, *iii*) partially pulling out the electrodes leaving a thin active electrolyte layer; b) Pt 4f and O 1s spectra at -0.8 V to -0.4 V verse the Ag/AgCl reference electrode, depicting the linear shift in O 1s liquid phase (dark blue) and vapor phase peak (light blue) shifting in the same direction.⁴

This technique was further adapted to obtain even higher probing depth resolution, on the order of angstroms by Fadley et al.^{51,52} They developed a new technique, standing wave ambient pressure photoelectron spectroscopy (SWAPPS).⁵¹ In SWAPPS the solid substrate of interest is deposited onto a synthetic multilayer mirror. X-rays with a small divergence are incident on the sample at the first-order Bragg angle of the multilayer mirror (e.g. $\sim 4^\circ$ for 2.5 keV X-rays and a multilayer periodicity of 3.4 nm). This leads to the formation of a standing wave above the mirror with a wavelength close to the mirror periodicity. The SW extends above the mirror, and can be scanned vertically by changing either the incidence angle (rocking curve) or photon energy around the Bragg condition, thus selectively probing the interfaces, the bulk solid, or bulk liquid. SWAPPS is still in its infancy and has so far been used to investigate the preferential adsorption of sodium

over strontium ions in an ultrathin NaOH/CsOH solution layer on hematite,⁵¹ and the oxidation of Ni under anodic potentials in the presence of a KOH solution.⁵²

In attempts to bypass the pressure gap required to study liquids at non-UHV pressures several groups have developed X-ray and electron transparent windows, **Figure 3e**.⁵³⁻⁵⁵ Using a window helps to facilitate the investigation of even some of the highest vapor pressure liquids. A graphene oxide window was one of the earliest windows used for probing the solid/liquid interface of an aqueous salt solution and gold nanoparticles at photon energies < 1.4 keV.⁵³ This was later extended to the use of graphene windows.⁵⁴ A 15 nm silicon window was created to conduct *operando* APXPS, demonstrating the oxidation of silicon with applied potentials at a photon energy of 5.95 keV.⁵⁵

All these solid/liquid techniques have various advantages and disadvantages. Focusing on the window⁵³⁻⁵⁵ and windowless^{4,51,52} techniques, there are several inherent attributes that need to be considered. For techniques that are using a window, the materials photon and electron optical properties, thickness, chemical compatibility, and area need to be taken into careful consideration to ensure maximum signal (from both the X-ray beam, emitted photons and electrons) as well as the mechanical/chemical stability to ensure it will not break, react and/or interfere with the spectroscopy. Additionally, by default, when using a window to study a liquid, you will be simultaneously probing the solid/liquid interface between the window material (or its coating) and the solution. This can be good if the interface is what you are interested in studying, however if obtaining signal only from the liquid is desired, this interface will be an unavoidable contribution and attenuation to the signal.

When using a windowless, it offers a large flexibility for the solid substrate that can be used, as it does not need to be photon and electron transparent. If the liquid thin-film is too thick ($> \sim 30$ nm) probing the interface will be a challenge.⁴ One must be cognizant of the liquids vapor pressure, as high vapor pressures can make it difficult to maintain a stable liquid thicknesses and UHV pressures in the analyzer. As the current ‘dip and pull’ method relies on gravity and the hydrophilic interaction between the solid and liquid, working with hydrophobic electrodes in this current configuration will be a challenge. Lastly, the thin electrolyte layer has a high mass transport resistance, which currently prevents the system's ability to support investigations at high current densities in the probing area. However, one could also take advantage of this resistance to

slow down the reaction rate to a time scale (of minutes and hours) that would allow the *operando* APXPS to actually observe the transitions as a function of time.

To more clearly see the influence of windowless, graphene and silicon windows similar to those previously discussed^{4,51-55} on the probing of a particular solid/liquid interface, SESSA⁶ was used to simulate each scenario. This simulation will demonstrate the relative intensity of a solid/liquid interface layer (represented by a 1 nm gold layer in this model) of a metallic electrode (such as platinum), **Figure 5**. For this simulation, we are assuming that a 10 nm platinum electrode is deposited onto the graphene and silicon windows to ensure sufficient electrical continuity. From this simulation, the windowless configuration provides the largest relative intensity of the 1 nm Au interface being probed at a photon energy of about 4 keV. The graphene window is actually very X-ray and electron transparent, however the platinum electrode significantly attenuates the interface intensity and shifts the optimal photon energy up to about 5.5 keV. Lastly, using a silicon window with platinum electrode provides the largest attenuation of the interface, suggesting it will be very challenging to probe and also will require much higher photon energies, > 6 keV. Pushing into the hard X-ray regime. This simulation hopefully helps reinforce and guide the reader to match the type of science to be studied, with the appropriate method, and photon energy range.

Figure 5: Comparing different configurations for probing a 1 nm Au interface using the windowless ‘dip & pull’,⁴ graphene window,⁵³ and Si window.⁵⁵

4. *In situ/Operando* soft XAS

The absorption of synchrotron photons results in the excitation (need to obey the dipole selection rule) of a core electron to an unoccupied state above the Fermi level. Thus soft X-ray absorption spectroscopy (sXAS) provides the information on the unoccupied electronic structure in the vicinity of the Fermi level, with the existence of core holes. sXAS can be performed through two primary modes, total electron yield (TEY) and total fluorescence yield (TFY), with different probing depths of several nanometers and hundreds of nanometers, respectively. Alternative methods are also being developed, such as the utilization of hard X-ray in-soft X-ray out techniques, which have been utilized to explore a charging lithium ion battery.⁵⁶ In order to achieve sXAS of samples under real-world conditions, typically, a soft X-ray window made of ~100 nm thick silicon nitride is utilized to separate the sample environment from the soft X-ray UHV chamber. The last decade has witnessed rapid progress on designing and manufacturing different *in situ* cells for use in synchrotron based sXAS, **Figure 6**.^{26,57-70}

While *in situ* sXAS experiments based on TEY mode have just been demonstrated in electrochemical cells,⁷¹ most of the *in situ* sXAS experiments are performed through TFY modes due to the fact that TFY is a photon-in-photon-out (PIPO) technique and thus able to probe the bulk regime. Different types of *in situ* cells for sXAS PIPO techniques have been designed and fabricated at synchrotron facilities. The static gas cell enables studies of molecular gases at gas pressure ranging from a few hundred millitorr to approaching 20 Torr,⁷²⁻⁷⁷ or solid-state materials in a gas environment.^{67,78} For example, Guo *et al.* successfully utilized static liquid cells for studying the hydrogen bonding in liquid water and organic solvent.^{68,69}

the sample temperature ranging from liquid-nitrogen temperature to several hundred degrees for catalytic reactions, and the pressures approaching 1 atm.⁸¹ Currently attempts are underway to increase this limit up to 10 atm. These soft X-ray *in situ* cells and their many derivatives have been widely utilized for studying materials for energy and environmental applications, such as corrosion effects,^{64,66} catalytic reactions,⁵⁷ semiconductor solar cells,⁵⁸ and batteries.⁶²

In situ potentiostatic sXAS experiments were designed to gain deeper insights into the interface between the electrode and the electrolyte during deposition.^{11,79,80} **Figure 6a** shows the X-ray transparent *operando* sXAS cell, electrochemical data taken using the cell, and sXAS data taken at three potentials, -0.1 V, -0.2 V and -0.4 V versus Mg reference electrode (RE), **Figure 6b**. The potential $V = -0.2$ V is the start of Mg deposition, and -0.1 V and -0.4 V represent potentials before and after Mg deposition, respectively. The presence of a sXAS signal $V = -0.1$ versus Mg RE is an interesting result because the additional edge is observed before Mg deposition should occur (at $V = -0.2$ V versus Mg RE). The sXAS results indicate that the presence of the Mg species besides the Mg-dimer is required before the deposition of Mg. The exact stoichiometry and structure of the species at the interface of Mg deposition remains unknown, but one can infer additional structural information from the extended X-ray absorption fine structure analysis. Previously, energy-induced intermediates have been seen with sXAS. Considering the current sXAS data and analysis that compliment previous studies, a direct electrochemical reduction of the Mg-dimer is an unlikely route to form Mg metal.

Using a gold-coated silicon nitride window flow-cell *operando* sXAS system, fundamental properties of the structure of water at the gold interface were unraveled, **Figure 6c**.⁷¹ For an unpolarized (neutral) gold surface, a majority of the water molecules at the interface have the hydrogen atoms pointing towards the gold surface. As the gold electrode is polarized more negatively, the number of water molecules in the interface with hydrogen atoms pointing towards the surface increases. While going more positive, the hydrogen atoms orient away from the gold.⁷¹ A similar cell design was also utilized to probe a hematite photoanode during photoelectrochemical water splitting (**Figure 6d**),²⁶ demonstrating the wide range of *operando* sXAS can probe using this window architecture.

Similarly to APXPS, sXAS has extended its capabilities to utilize windowless techniques. Cathode materials sit in the heart of modern battery researches, partially because there is still no perfect candidate that can maintain high-power and stable cycling with capacity comparable to

that of the anodes.^{82,83} Although various systems, such as conversion-type and organic cathodes, have recently garnered much attention, the present Li-ion technology is based on intercalation chemistry with insertion/extraction of Li-ion into/from the electrode materials. Most intercalation type cathode materials are 3d transition metal (TM) compounds with certain lattice structures, such as layer (LiCoO_2), spinel (LiMn_2O_4), and olivine structures (LiFePO_4), as the host framework for (de)lithiation process. sXAS at TM *L*-edge detects the transition from 2*p* core level to 3*d* unoccupied states, thus reveals directly the valence states of TM 3*d* electrons. By virtue of the sensitivity to the valence electron states, sXAS could be utilized to obtain the quantitative values of the oxidation states of the 3*d* TMs in battery electrodes.^{12,84} In addition to the information on the evolution of electronic states at different electrochemical stages, because TM-3*d* states are localized, sXAS spectra are also highly sensitive to the local lattice distortions.

The *in situ* sXAS experimental setup for studying Li-ion batteries is shown in **Figure 6e** as developed by Yang et al.¹³ A sophisticated battery fabricated by utilizing polymer electrolyte and current collector with detection windows carved by a high-precision laser system. This technique empowers researchers to monitor the electron state evolution of electrodes in real-time with the electrochemical cycling. The surface sensitivity of sXAS enables position dependent studies on the distinct charge dynamics in different cathode electrodes. For $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{CoO}_2$ (NMC) electrode, the *in situ* results show the real time response of Ni oxidation states between Ni^{2+} and Ni^{4+} to the state-of-charge (SOC) with cycling voltage below 4.2 V, which is consistent with *ex situ* studies. On the contrary, the LiFePO_4 (LFP) electrodes do not exhibit such a real-time response, although the cell fabrication and cycling are the same as that of the NMC cell. The Fe oxidation states do not change until a certain period of relaxation is achieved, which depends on the active material (i.e. LFP) concentration in the electrode, as well as the temperature of the cell. Furthermore, the position-dependent studies of the LFP electrodes through *ex situ* sXAS at a “locked” state of charge (before a long relaxation), verifies that the delithiation process starts from the region close to the current collector where the electrons originate. The comparative studies between different electrode systems and between *in situ* and *ex situ* sXAS results demonstrate the power of sXAS for revealing the charge dynamics in battery electrodes.¹³

Lastly, an interesting adaptation of the APXPS chambers is that, they can also be configured to collect ambient pressure sXAS (APXAS), by collecting the ejected photoelectrons as the incident photon energy sweeps through an elements edge of interest. Known as the partial electron yield

(PEY). This technique was utilized to study high temperature electrochemical oxygen evolution and reduction reactions of cobalt and iron perovskites, **Figure 6f**. By probing the X-ray adsorption spectrum from both the transition metal cations and oxygen anions, they were able to demonstrate that the oxygen anions near the surface of the electrode were the dominant redox-active centers, not the transition metal anions.²¹

This windowless APXAS design has also been used with a liquid jet system similar to the one previously discussed for the APXPS experiments (**Figure 3c**). In this work it was utilized to conduct sXAS measurements on silica nanoparticles of varying sizes in aqueous solutions at different pH.⁸⁵ With this technique they were able to observe the changes in the Si K-edge of the Si 1s $\rightarrow$ t₂ (Si 2p-3s) adsorption induced from how the nanoparticles silanol protonation state would change at the surface from different pH solutions. Thus using APXAS to allow them to demonstrate that the silica nanoparticle size was inversely proportional to the protonation state.

5. Future Outlook

The configuration for this class of science is currently separated to individual beamlines and endstations as depicted in **Figure 7a**. Where *in situ/operando* XPS, sXAS and scanning transmission X-ray microscopy (STXM, a XAS technique capable of performing nanometer spatial resolution microscopy and have been used to study battery and fuel cell related materials^{86,87}) were conceived as separate techniques to provide specific scientific insight related to their particular instrumentation capabilities. However, with reflection of the types of *in situ/operando* science that this review highlights, and the natural evolution of science and instrumentation that has taken place, it is evident that these various techniques have overlapping scientific interest, provide complementary information, and in some situations even share the same physical hardware (such as APXPS and APXAS). This merging of techniques lays the foundation for the future development and scientific direction, supporting the continued convergence of these different approaches, solving scientific challenges with a multi-modal approach. This multi-modal scientific approach is the precipice for the Advance Light Source (ALS) at Lawrence Berkeley National Laboratory to develop ‘Advanced Materials Beamline for Energy Research’ (AMBER), an integrated beamline to simultaneously facilitate *in situ/operando* XPS, sXAS, and STXM is shown in **Figure 7b**.

Figure 7: Future progression for endstation development to support the synergy/multimodal scientific approach from where we are a) now, b) through an ‘AMBER’ approach, and c) looking towards the future of a fully integrated multi-modal highway approach, to support all classes of *in situ/operando* research.

AMBER would integrate all the *in situ/operando* soft X-ray spectroscopic tools that have been developed at the ALS for energy research over the last ten years, including APXPS, sXAS, and *in situ* STXM. The new beamline and its three endstations (shown in **Figure 7b**) will be optimized for the *in situ/operando* understanding and tailoring the properties of novel materials that are suitable for energy sciences such as, solar energy conversion and energy storage. By using a universal sample mount/transfer system, we will be able to seamlessly interface, exchange, and study samples at each endstation. AMBER would enable the ALS to tackle the basic research needs described in the DOE’s recent “America’s Energy Future” report,⁸⁸ providing strong and timely support for ALS general users, DOE Energy Hubs, and industrial users. Through this beamline, the ALS would engage a large number of users affiliated with universities, national laboratories and industries in investigations of photon–electron conversion, ionic-electronic transport, and the interplay between materials chemistry and physical phenomena. Technical innovations in the proposed AMBER beamline include: high throughput with the least number of reflections by using brightness-preserving, high-precision optics in the beamline design; complete polarization control; submicron focusing with K-B optics and the option of nanofocusing with a zone plate; all under *in situ/operando* environment and characterization tools that can measure surfaces, interfaces (including the solid/liquid interface), and bulk characteristics. This similar approach has also been or is currently being pursued at the Diamond Light Source (I06), Shanghai Synchrotron Radiation Facility, and BESSY II (EMIL).⁸⁹

Looking even further into the future, an ultimate vision to strive for, will be the development of a ‘multimodal highway’, **Figure 7c**. One beamline with a wide range of *in situ/operando* X-ray

characterization techniques including XPS, sXAS, STXM and photoelectron diffraction, as well as *in situ/operando* non-X-ray techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. All connected to each other, and an integrated sample preparation systems such as sputtering, pulsed laser deposition (PLD), and glove box sample treatment center by an enclosed sample transfer ‘highway’. Currently the need for a multimodal approach is already in great demand, and is the motivation behind AMBER. However the future scientific discovers will require this level of integration to push even further, centralizing the scientific process and discoveries all the way from sample growth to complete characterization, in one multi-modal highway.

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