

Perspective

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# Shining light on electrochemistry: a synchrotron-based X-ray spectroscopic interrogation

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## Abstract

Over the last few decades, synchrotron radiation has experienced a flourishing growth, fueled by cutting-edge spectroscopic techniques that have empowered its remarkable ability to probe down to the atomic level. Indeed, this advancement has been inspiring, unlocking powerful insights and capabilities in the realm of electrochemistry community. This perspective showcases recent ground-breaking efforts and remaining challenges with respect to X-ray spectroscopy, as well as their implications for ongoing research.

**Keywords:** Synchrotron radiation, electrochemistry, X-ray absorption/emission spectroscopy, interface

Synchrotron radiation, electromagnetic emission from relativistic charged particles traveling along a circular trajectory, was first discovered in the late 1940s<sup>[1]</sup>. Once known as a notorious by-product in high-energy physics, synchrotron radiation has come a long way and is now on the cusp of a new era - an unprecedented brilliant, tunable and short pulsed light source<sup>[2,3]</sup>. Over the enduring decades, synchrotrons have revolutionized our ability to probe and understand the matter with the motto “making visible the invisible”<sup>[4,5]</sup>. This perspective aims to provide an overview of synchrotron-based X-ray spectroscopic interrogation in the realm of electrochemistry, which has inspired accumulative research outputs in this community spanning classical electrochemistry, electrocatalytic and spectroscopic aspects. An additional note is that we focus exclusively on the synchrotron-based studies here, and we refer the reader elsewhere for other independent excellent contributions.



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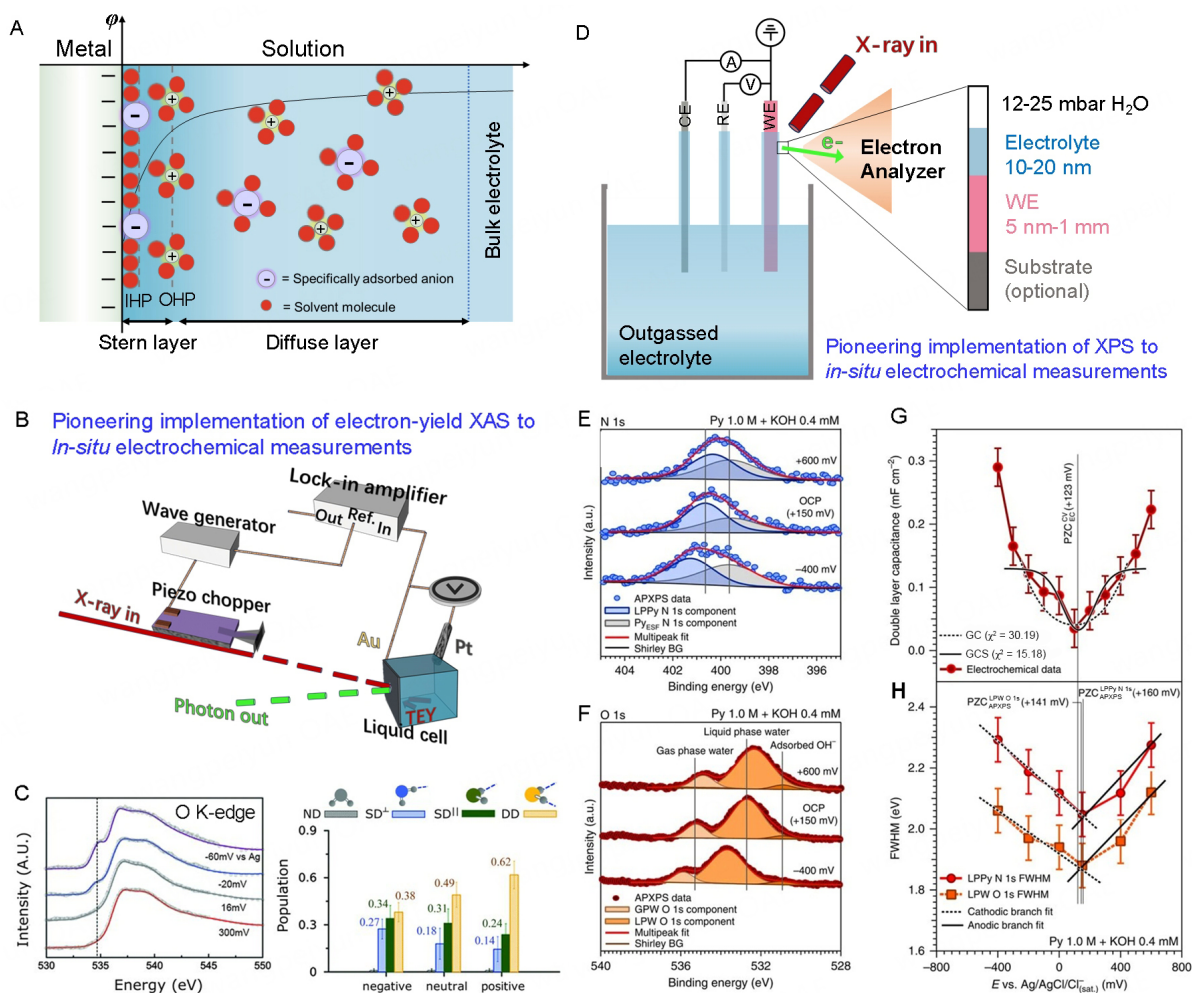


## CLASSICAL ELECTROCHEMISTRY: ELECTRICAL DOUBLE LAYER

In electrochemistry, a typical scenario involves an electrified surface in contact with an electrolyte solution [Figure 1A]. The electrical double layer (EDL), also known as the Stern layer and the diffuse layer, is a micro-region of a few nanometers in thickness and is spatially concealed between the two bulk phases of solid and liquid<sup>[6]</sup>. For the imbedded interface, there is increasing consciousness that its molecular-level characteristics, to a large extent, underpin the critical functions and properties relevant in many electrochemical processes, while these characteristics remain hitherto elusive. Electron-yield X-ray absorption (XAS) and X-ray photoemission spectroscopy (XPS) offer a promising solution to this old yet current enigma, benefiting from their inherent surface sensitivity. By virtue of instrumental innovation, Velasco-Velez *et al.* pioneered the extension of soft XAS (sXAS) to *operando* electrochemical measurements in 2014<sup>[7]</sup>. They applied a modulated (piezo-actuated chopped) incoming X-ray and lock-in amplifier to extract the neat total electron yield (TEY) signal under electrical bias and experimentally identified the evolved water orientation once the electrode potential deviates from the potential of zero (free) charge (pzfc) [Figure 1B and C]. This finding serves as a paradigm for the argument on the interfacial electrical field-driven water reorganization behavior, which accounts for large kinetic pH effect in hydrogen evolution reaction<sup>[8]</sup>. In alkaline media, the significant cathodic shift of electrode bias with respect to the pzfc leads to a stronger interfacial electric field and, therefore, an increased water reorganization barrier to accommodate charge transfer. The initial XPS studies were conducted using immersed electrodes under static conditions, with a particular focus on the specific adsorption of ions at the inner Helmholtz plane<sup>[9,10]</sup>. The investigation of bias-dependent probing of EDL was not accessible until the introduction of the “dip and pull” method [Figure 1D]<sup>[11]</sup>. The creation of a stable nanometer-thick electrolyte layer on the surface of the working electrode showcases compatibility with *in-situ* measurements and provides direct access to the potential drop within the EDL and the pzfc by means of ambient pressure XPS [Figure 1E-H]<sup>[12]</sup>. Here, it is worth pointing out that the co-presence of cations/anions in alkaline/acidic electrolytes significantly complicates the EDL of interest. Prior studies emphasize the non-covalent interactions with reactants/intermediates<sup>[13-16]</sup>, while Li *et al.* very recently argued that the near surface concentrated Na<sup>+</sup> exerts noticeable statistical effects on the hydrogen bond network connectivity in the EDL<sup>[17]</sup>. Hitherto, the critical role and diversity between various ions remain not well documented. Future work will continue devoting to these remaining details (partially solvated alkaline cations, cation-surface distances and concentrations), and we anticipate correlative X-ray-based techniques, such as surface X-ray scattering<sup>[18]</sup> and sXAS, would provide additional spectroscopic evidence to shed light on this topic and offer further insights.

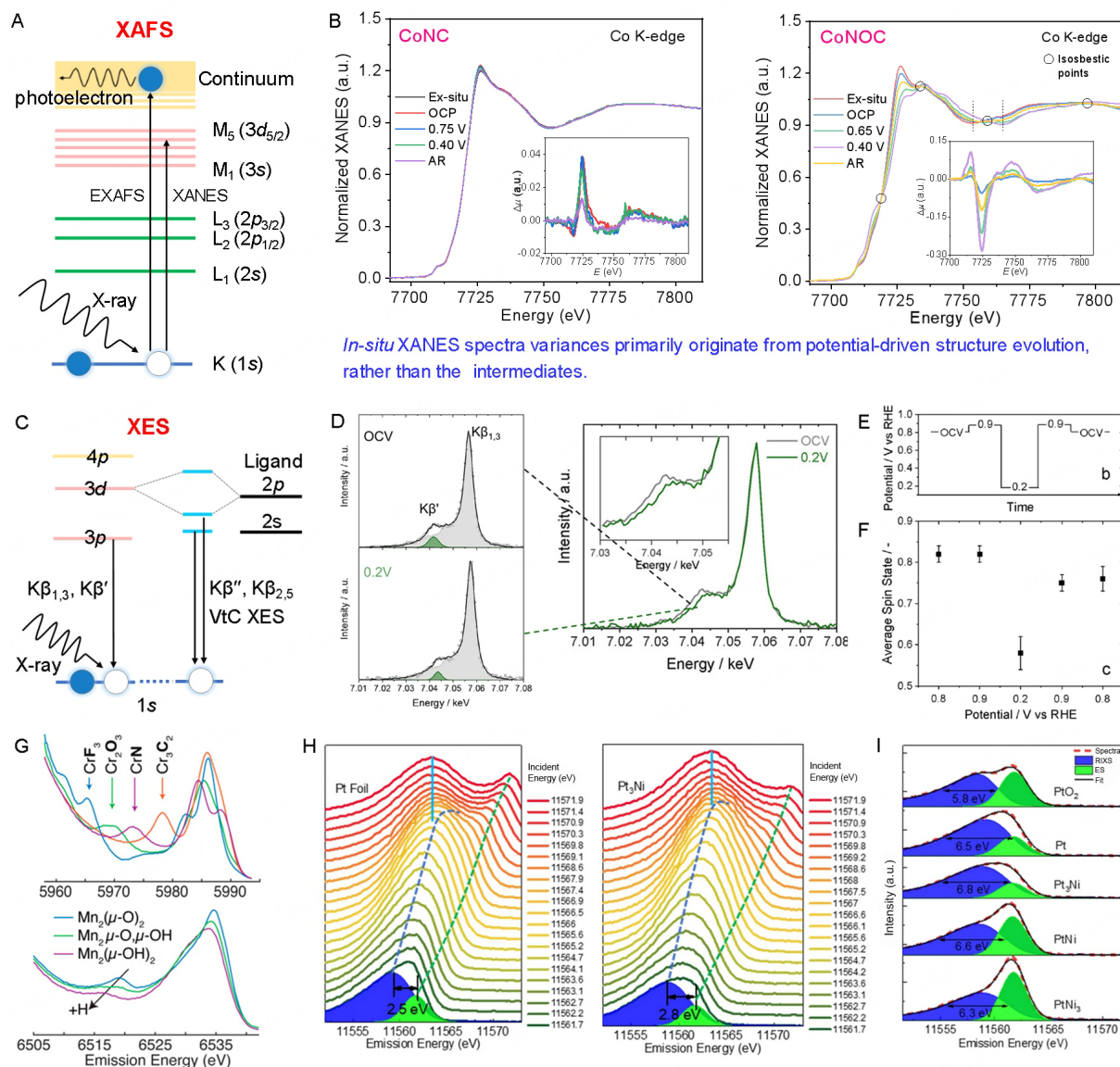
## MODERN ELECTROCATALYSIS

Recent decades have witnessed a remarkable flourishing of electrocatalysis that extends beyond classical electrochemistry. X-ray absorption fine structure (XAFS) spectroscopy, with its unique combination of both element specificity and local structure sensitivity<sup>[19]</sup>, experiences highly productive advancements driven by the growing demands of nanocatalysts for electrochemical applications. It provides comprehensive insights into electronic state and local structure of reactive centers, including quantitative information at the atomic level with respect to the photo-absorbing atom, i.e., near-neighbor species (the accuracy of determining the atomic number  $Z$ ,  $\pm 5$  or so) and interatomic distance, symmetry and coordination number [Figure 2A]. Particularly, the spectral characteristics bring new opportunities to build on progressive guidelines for predictive activity and rational design of target catalysts, in striking contrast to the sophisticated theoretical ones. For instance, Huang *et al.* developed experimental Sabatier plot for Pt-alloy oxygen reduction reaction (ORR) catalysts based on tangible descriptors of strain and asymmetry factor<sup>[20]</sup>. Besides, the XAFS



**Figure 1.** Imbedded interface-the electrical double layer. (A) schematic of the classical Gouy-Chapman-Stern model. The IHP, OHP and diffuse layer are indicated. The potential  $\phi$  is shown with respect to the distance from the surface. The yellow and purple denote the cations and anions, respectively; (B) schematic of the modulation setup consisting of piezo-actuated chopped incoming X-ray and lock-in amplifier to extract neat TEY XAS signal under electrical bias; (C) the bias-dependent TEY O K-edge NEXAFS spectra of water collected at the Au electrode. The intensified pre-edge peaks at around 535 eV under negative bias (-20, -60 mV vs. Ag) fingerprint the SD orientation of water molecules (single donor parallel and perpendicular toward the gold surface), namely the dangling hydrogen bonds. These figures are quoted with permission from Velasco-Velez *et al.*<sup>[7]</sup>; (D) schematic of the "dip and pull" setup for ambient pressure XPS measurements. WE, RE, and CE correspond to the working electrode, reference electrode, and counter electrode, respectively; (E and F) normalized bias-dependent N 1s and O 1s core-level peaks collected in KOH aqueous solution containing a spectator molecule pyrazine; (G) double-layer capacitance as a function of applied potential; (H) spectral broadening of liquid phase LPPy N 1s and LPW O 1s components as a function of applied potential. The pzc of +160 mV, +141 mV extracted from the minimum of indicated N 1s, O 1s V-shaped plots aligns well with that (+123 mV) of a double-layer capacitance method. This figure is quoted with permission from Favaro *et al.*<sup>[12]</sup>. IHP: Inner Helmholtz plane; OHP: outer Helmholtz plane; XAS: X-ray absorption; TEY: total electron yield; XPS: X-ray photoemission spectroscopy; NEXAFS: near-edge X-ray absorption fine structure.

technique is completely compatible with *in-situ/operando* studies. Measurements under realistic working conditions empower us to monitor the potential-driven valence oscillation<sup>[21]</sup> and dynamic active sites (phase transformation<sup>[22]</sup>, metal-ligand distortion/displacement<sup>[23]</sup>, *etc.*), propelling the fundamental understanding to new heights. We refer the reader to excellent reviews on the utilization of various *in-situ* electrolyte cells<sup>[24]</sup>, which represent an important technical aspect of the applicability of X-ray techniques and accurate data acquisition under working conditions. Achieving satisfactory signal-to-noise ratios in XAFS spectra often necessitates the use of high catalyst loadings, which, in turn, introduce significant



**Figure 2.** Hard XAS/XES for electrocatalysts characterization. (A and C) representative energy level diagrams depict the origin of the spectral features. The XAS involves the excitation of core-level electron to the unoccupied states or into the continuum, serving as a probe of the unoccupied orbitals of chemical species and local atomic structure. In contrast, the XES monitors the decay of core holes (fluorescent X-rays associated with electron from higher-lying orbitals decay to fill the core hole) and, therefore, probes the occupied valence states in an atom-specific projection; (B) *in-situ* Co K-edge XANES study on CoNC and CoNOC during oxygen reduction reaction operation. Comparative study reveals the stable and rigid in-plane embedded  $\text{Co}_1\text{N}_x$  moiety and the flexible edge-hosted  $\text{Co}_1\text{N}_2$  sites. The observed changes in the XANES spectra are primarily dictated by potential-driven structure evolution, whereas the adsorption of oxygenated intermediates exerts only a negligible effect. These figures are quoted with permission from Hu *et al.*<sup>[27]</sup>; (D) comparison of *in-situ*  $\text{K}\beta$  mainline XES spectra recorded on DW21 catalyst in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  at OCV and 0.2 V vs. RHE, along with corresponding fit results. The inset shows a magnified view of the  $\text{K}\beta'$  region; (E) the time course of applied bias in the *in situ* XES measurements, whereby each potential hold lasted 10 min; (F) Average spin states at each corresponding potential. These figures in (D-F) are quoted with permission from Saveleva *et al.*<sup>[31]</sup>; (G) valence-to-core XES of various chromium-based compounds exhibiting sensitivity of the  $\text{K}\beta''$  feature to the light atom identity (upper); Intensity and energy of Valence-to-core XES correlates to protonation state of ligands in manganese dimers (below). These figures are quoted with permission from Cutsail *et al.*<sup>[33]</sup>; (H) valence-to-core X-ray emission spectra of Pt foil (left) and  $\text{Pt}_3\text{Ni}$  (right) collected at the Pt  $L_3$ -edge. The energy difference between the resonant inelastic scattering (RIXS, blue dash line) and the elastic scattering (ES, green dash line) is labeled for each sample, with the full width at half maximum of the inelastic peaks summarized in (I). These figures are quoted with permission from Chen *et al.*<sup>[34]</sup>. XAFS: X-ray absorption fine structure; XANES: X-ray absorption near-edge structure; XES: X-ray emission spectroscopy; OCV: open circuit; RHE: reversible hydrogen electrode; XAS: X-ray absorption.

limitations in terms of ion and mass transport<sup>[25]</sup>. In light of this, the author suggests an appropriate catalyst layer thickness while also adopting the common practice of multiple scans to improve data acquisition. Moreover, the author would like to reiterate that the behavior of reactive species on surfaces can hardly be captured by conventional XAFS measurements owing to their extremely short lifespan within the timescale. This argument is solidly supported by recent publications on prototypical single-atomic Co-N-C electrocatalysts<sup>[26,27]</sup>. The comparative *in-situ* Co K-edge X-ray absorption near-edge structure (XANES) spectra of CoNC (in-plane embedded Co sites) and CoNOC (edge-hosted cobalt sites) unequivocally reveal that the spectral change during ORR operation is primarily dictated by potential-driven structure evolution, whereas the adsorption of oxygenated intermediates exerts only a negligible effect [Figure 2B]. As far as we are concerned, the issue on a holistic view of the reaction process can be best addressed by the correlative infrared/Raman spectroscopy<sup>[28,29]</sup>, which offers complementary information to XAFS study.

Commissioning third/fourth-generation synchrotrons demonstrate unique opportunities to advanced spatial and energy-resolved spectroscopic techniques. Heterogeneous electrocatalysts are inherently non-uniform, where the nanoscale variations in atomic structure, composition, and accessibility do impact their reactivity. We highlight recent insights into site-specific reactivity in electrocatalysis by conducting high spatial-resolved studies instead of ensemble-averaged measurements. Remarkably, Mefford *et al.* resort to *operando* scanning transmission X-ray microscopy (STXM) to disentangle the sequential dehydrogenation process from  $\beta$ -Co(OH)<sub>2</sub> to  $\beta$ -CoOOH through the single platelet particle during the oxygen evolution reaction operation<sup>[30]</sup>. To date, the compositional encyclopedia of electrocatalysts mostly encompasses the transition metal-based systems. Direct probing of metal *d*-states is of immense significance and has long been plagued by either forbidden dipole electronic transition or core-hole lifetime broadening of conventional XANES. In contrast, X-ray emission spectroscopy (XES) emerges as a promising alternative to provide complementary information with respect to the electron structure (local charge- and spin-density) and local environment of the emitting species via monitoring the intensity of a fluorescence line associated with a specified excited state decay process using a narrow energy resolution [Figure 2C]. A notable application of this method is demonstrated by Saveleva *et al.* through *operando* K $\beta_{1,3}$  XES, where they provide compelling evidence of the decrease in the average spin state of iron atoms during ORR [Figure 2D-F]<sup>[31]</sup>. Additionally, the spinoff valence-to-core (VtC) emission lines, corresponding to de-excitation from occupied valence states to the nascent core-hole, offer particular insight into the frontier orbital populations within a molecular orbitals picture<sup>[32]</sup>. In this context, its sensitivity to ligand identity (i.e., C, N, O, or F) and protonation state (O<sup>2-</sup>, OH<sup>-</sup>, or H<sub>2</sub>O) is of great interest<sup>[33]</sup> [Figure 2G]. Chen *et al.* experimentally identified the shift of Pt *d*-band centroid away from the Fermi level upon Ni alloying, based on the energy difference between the resonant inelastic scattering and the elastic scattering<sup>[34]</sup> [Figure 2H and I]. Currently, the metal-enzyme systems are most frequently investigated<sup>[35,36]</sup>, and the characterization on artificial electrocatalysts has not kept pace. Nevertheless, it is foreseeable that the new-emerging precision synthesis would soon fuel a race towards the scope extension. Last but not least, the increased brightness of synchrotron sources comes with the potential risk of damaging the samples under X-ray beam irradiation. To examine the radiation damage, it is advisable to record and compare the spectra under various experimental conditions, such as different photon fluxes, beamsizes, and sampling times. To mitigate the damage effects, common practices may include time-resolved techniques, such as quick-XAFS (QXAFS) and energy-dispersive XAFS/XES for data recording.

## OUTLOOK

Modern electrochemical cells are increasingly dependent on the membrane electrode assembly-based electrodes, which no longer stick to the ubiquitous solid-liquid interface in the past. Instead, there is a growing demand for deep insight into the new-emerging solid/polymer/gas interface. Synchrotron-based

X-ray spectroscopies are expected to be progressive and continue to inspire scientists for interdisciplinary research today as they did in the early 20th century.

## DECLARATIONS

### Authors' contributions

The author contributed solely to the article.

### Availability of data and materials

Not applicable.

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### Conflicts of interest

The author declared that there is no conflict of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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