Prospects for electrochemical X-ray photoelectron spectroscopy as a powerful electrochemical interface characterization technique

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Review Article

Prospects for electrochemical X-ray photoelectron spectroscopy as a powerful electrochemical interface characterization technique

Sheena Louisia, Marc T. M. Koper and Rik V. Mom

Abstract
X-ray spectroscopies provide a powerful way to disentangle the roles of the different elements in electrochemical systems. Within this family of spectroscopies, electrochemical X-ray photoelectron spectroscopy (EC-XPS) has recently emerged as a technique that can specifically probe the heart of any electrochemical process: the electrode−electrolyte interface. Here, we discuss the current state-of-the-art of EC-XPS and review the practical implementation of the measurements. We identify three principal categories of EC-XPS approaches: quasi-in situ, thin electrolyte, and thin electrode. As each presents distinct advantages and drawbacks, we highlight the importance of matching the electrochemical system of interest with the most suitable approach.

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Introduction

Electrochemical devices are showcases of multi-element chemistry. For example, $LiNiMnCoO_2$ cathodes are commonly used in lithium-ion batteries [1], PtCo alloy particles are state-of-the-art in hydrogen fuel cells [2], and NiFeOx is the industry standard as the anode in alkaline electrolyzers [3]. From the electrolyte side, the cations, anions, and solvent molecules add further elements to the mix. To disentangle the role of each of these components in the operation of an electrochemical device, element-specific measurements are key. X-ray spectroscopies are highly suitable techniques to achieve this since they can provide direct insight into the oxidation states and bonding environments of every element except H. In this way, X-ray spectroscopies perfectly complement vibrational spectroscopies that are commonly used in electrochemistry to obtain insights into chemical bonds instead of element-specific information. Consequently, a wide variety of X-ray spectroscopies have been used in electrochemistry research, including X-ray emission spectroscopy [4,5], X-ray absorption spectroscopy [6], inelastic X-ray scattering [7,8], and photoelectron-based techniques [9]. From these, hard X-ray (>10 keV) absorption spectroscopy (XAS) has been by far the most popular, as it is experimentally the least challenging and can readily be used for *operando* measurements [6]. Using hard XAS, one can measure the average oxidation state of selected elements and characterize the structure of the coordination shell around the absorbing atoms. This has proven instrumental in obtaining insight into the active site structure of electrocatalysts under operation. However, the technique does have some relevant limitations in the context of electrochemistry research. First, XAS is not a surface-sensitive technique. Since electrochemical activity often only involves the few atomic layers around the electrode−electrolyte interface, i.e. those from the electrode surface and the electrical double layer that directly participate in electron transfers and their mediation, the subtleties of surface chemistry can be obscured by the large bulk contribution to the XAS signal. In addition, it is usually impossible to obtain XAS spectra of all the elements in the electrochemical system in one experiment. This makes unraveling the interplay between different elements under operating conditions challenging.

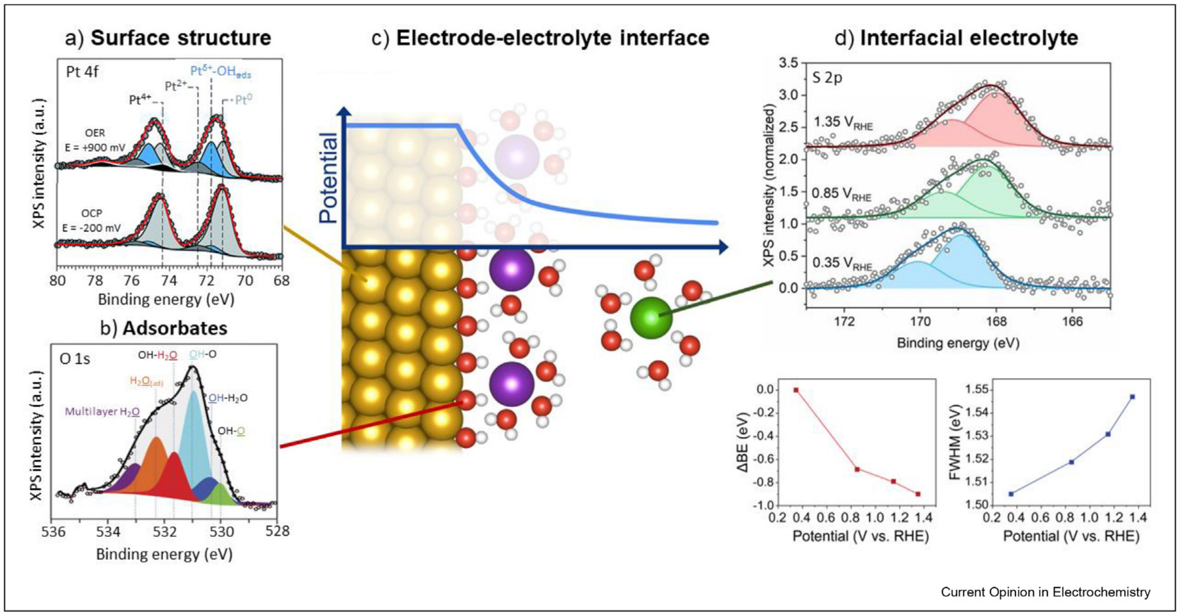
Electrochemical X-ray photoelectron spectroscopy (EC-XPS) is an emerging technique that can complement hard XAS in this respect. Although EC-XPS experiments are more complex than *operando*-hard XAS, as we will discuss later in this review, they can specifically detect the electrode−electrolyte interface and provide a chemical fingerprint for every element in a single experiment [10,11]. Unlike traditional ex situ XPS that are carried out under ultra-high vacuum (UHV) conditions, EC-XPS gathers a variety of approaches meant to preserve the electrochemically relevant surface and sometimes interface as efficiently as possible. This review aims to provide electrochemists with an overview of the current state-of-the-art of EC-XPS. As a general category, EC-XPS is a technique that spans over measurements carried out in quasi-in situ, in situ, or in-operando conditions. Using examples from the literature, we will first highlight the powerful capabilities of the technique. Then, we will discuss the practical aspects of the measurements in various configurations sorted into three categories: quasi-in situ, thin electrolyte film, and thin electrode/window. We will conclude with a brief outline of future perspectives.

Capabilities of electrochemical X-ray photoelectron spectroscopy

So far, the primary application of EC-XPS has been the characterization of the surface structure of the electrode. As an example, Figure 1a shows the $Pt^{\delta+}/Pt^{2+}/Pt^{4+}$ oxide film formed at the top ∼2.5 nm of a Pt foil during the oxygen evolution reaction (OER) in 1 M KOH [12]. This mixture of oxidation states is different from a Pt^{4+}-only state that is otherwise thermodynamically expected under these conditions, underlining the importance of kinetic limitations in the oxides formed on platinum. Similar studies conducted in acid electrolytes and at lower potentials, i.e. under fuel cell-relevant conditions, showed that the formation of mixed $Pt^{\delta+}/Pt^{2+}/Pt^{4+}$ oxides is a universal phenomenon on Pt electrodes, but the oxide thickness is limited to 1 monolayer at lower potentials [13,14]. From a technical point of view, these results highlight two key aspects of EC-XPS: (1) its surface sensitivity, which makes it capable of characterizing ultrathin oxide layers; and (2) its capability to provide detail beyond the average oxidation state of an element.

Similarly, EC-XPS is also capable of detecting adsorbates. Casalongue et al. highlighted this in their study of adsorbed O, OH, and H_2O on Pt nanoparticles during the oxygen reduction reaction (ORR) [15] shown in Figure 1b. They reported that OH and O adsorbates are present on the surface in a hydrated or less hydrated form, depending on the applied potential. Density functional theory calculations indicate that these different forms have very different reactivity in the ORR. While this example shows the potential for using EC-XPS in mechanistic studies, it should be noted that the detection of adsorbates is generally challenging due to the peak overlap with other components in the system. In fact, more recent studies have since identified water, polymer electrolytes (e.g. Nafion), and adventitious carbon as adsorbates likely to interfere with the signal of surface O and OH species [14,16]. These works reinforce

Figure 1



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Overview of the capabilities of EC-XPS. **a**) Pt 4f spectra showing the surface oxidation of a Pt foil under OER conditions in 1 M KOH [12]. **b**) O 1s spectra of the adsorbates on a Pt/C hydrogen fuel cell cathode at 0.9 V_{SHE} in 0.8 Torr O_2 [15]. **c**) Atomic representation of the electrode−electrolyte interface and the electrostatic potential drop that occurs across the interface. **d**) S 2p spectra of sulfate ions from 0.1 M H_2SO_4 in the vicinity of a RuO_x electrode at various potentials [9]. The bottom two panels show the ΔBE shift (left) and FWHM (right) variation as a function of applied potential, which is due to the electrostatic potential drop across the electrode−electrolyte interface. EC-XPS, electrochemical X-ray photoelectron spectroscopy; OER, oxygen evolution reaction; ΔBE, binding energy; FWHM, full width at half maximum.

the importance of carrying out a careful and comprehensive peak analysis when considering such complex systems.

Besides the electrode, the interfacial electrolyte can also be probed using EC-XPS. Although studies on this topic are still scarce, one of the exciting developments is the application of EC-XPS as a sensitive probe for the electrostatic potential in the double layer [9,17]. As illustrated in Figures 1c-d, if an atom experiences a local electrostatic potential that differs from that of the grounded working electrode, it directly translates into a shift in the binding energy (ΔBE) for this atom. As depicted in Figure 1c, the double layer formed in the interfacial electrolyte displays such a deviating local electrostatic potential. Figure 1d shows how this affects XPS spectra for the case of the S 2p peak of sulfate ions near a RuO_x electrode [9]. As the potential is increased, the potential drop across the double layer also increases, resulting in an increasing ΔBE of the S 2p peak. Furthermore, the right bottom panel of Figure 1d indicates that the width (FWHM) of the S 2p peak also increases with applied potential. This is due to the gradient in the electrostatic potential in the double layer, which in turn causes a corresponding gradient in the binding energy of the S 2p electrons from the sulfate ions. At 1.35 V_{RHE}, there is a large potential drop at the interface, resulting in a larger electrostatic potential gradient and, thus, a larger peak width than at lower potentials. As demonstrated in this work, the potential dependent variation of FWHM can be analyzed to estimate the thickness of the double layer, here <1 nm. These results highlight how the high energy resolution accessible with EC-XPS enables an in-depth investigation of the electrochemical interface at the nanoscale.

Electrochemical X-ray photoelectron spectroscopy in practice

EC-XPS instrumentation deviates significantly from standard XPS setups because the measurement principle of XPS is not directly compatible with electrochemical environments [9,18,19]. At the core of any XPS experiment lies the soft/tender (<10 keV) X-ray source that illuminates the sample and the electron analyzer that measures the kinetic energy of the photoelectrons ejected from the sample. Since both soft X-rays and electrons are strongly scattered by gases, liquids, and solids [20–22], XPS experiments are traditionally performed in vacuum. In EC-XPS, this vacuum is interfaced with the wet or gaseous environments used in electrochemistry. Various approaches have been developed to this end, each with its pros and cons. To provide some overview, we have divided the EC-XPS approaches into (1) quasi-in situ, (2) thin electrolyte film, and (3) thin electrode approaches (Figure 2).

Quasi-in situ

In quasi-in situ EC-XPS, an electrochemical cell is attached to a standard vacuum XPS system [23–28]. After exposing the working electrode to a desired electrochemical condition in the cell, the electrode is pulled out of the electrolyte under potential control (Figure 2a). The electrode is then rinsed and moved to the vacuum chamber, where XPS measurements are carried out using an in-vacuum transfer mechanism that prevents air exposure. This method's key assumption is that the electrode surface's in situ state is preserved during this procedure. Although there is no guarantee that this assumption holds, some validation is provided by the match between quasi-in situ EC-XPS and other measurements. For example, the onset of Pt^{4+} formation on Pt nanoparticles was observed above ∼1 V_{RHE}, consistent with various other in situ measurements [19].

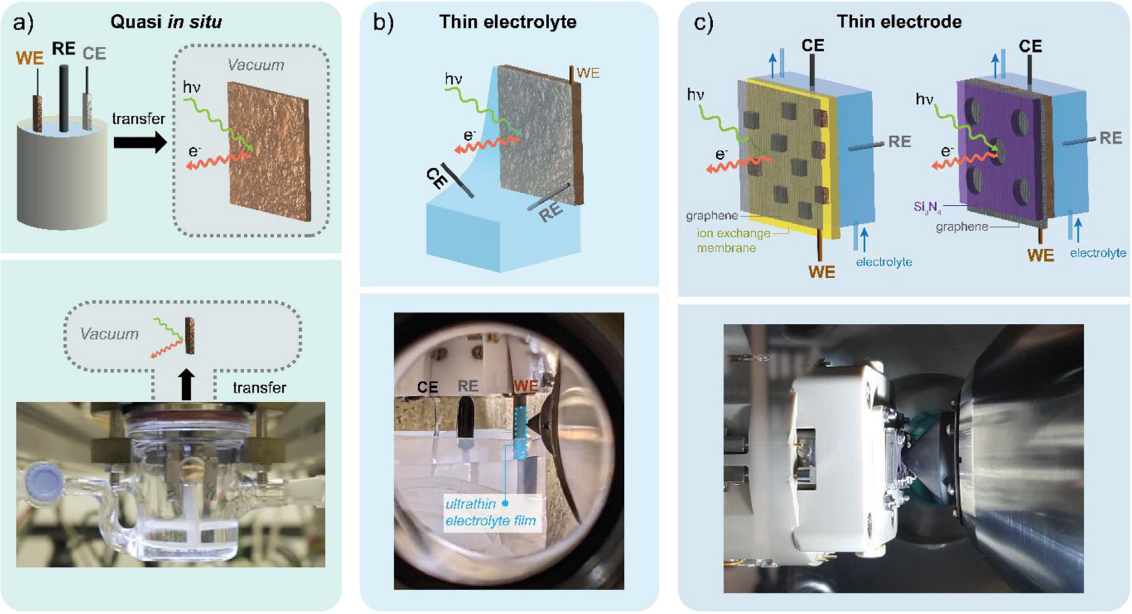
Due to the separation of electrochemistry and XPS measurements, quasi-in situ EC-XPS can be applied to almost any electrochemical system, except membrane-electrode assemblies used in fuel cells and electrolyzers. In addition, no sacrifice has to be made on the spectroscopic quality. This is illustrated by the recent work of Arán-Ais et al. where the oxidation states of a Cu electrode are monitored at different intervals during pulsed CO_2 electrolysis [25]. Using high-quality Cu LMM spectra, they were able to quantify sub-monolayer quantities of Cu_2O formed during the anodic part of the pulses, some of which remained during the cathodic parts of the pulses where the CO_2 reduction reaction occurred (Figure 3a). These oxide remnants were suggested to significantly impact the selectivity of the reaction.

To obtain further insights into highly reactive surface adsorbed species, a few studies have also employed cryogenic XPS as a way to preserve sensitive species at the solid–liquid interface. In addition, unlike regular quasi-in situ XPS, cryogenic XPS can preserve the integrity of an assembled system such as a coin cell, thus allowing the expansion of eligible samples [29].

Thin electrolyte film

For true in situ studies, the electrochemical cell has to be placed inside the XPS vacuum chamber so that electrochemistry and spectroscopy can be performed at the same time. This requires adaptations in both cell design and XPS instrumentation (see Refs. [9,16,18] for technical details). One design approach for the in situ cell makes use of an ultrathin electrolyte film on the working electrode (Figure 2b) [11,18,30–32]. If the electrolyte film is thinner than the photoelectron inelastic mean free path (1–20 nm) [33], photoelectrons can escape through the liquid film, after which they can travel to and be detected by the electron analyzer

Figure 2



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Schematics (top) and photos (bottom) of the three EC-XPS approaches. **a**) The quasi in situ approach, where electrochemistry is performed in a regular glass cell with working (WE), counter (CE), and reference electrodes (RE), before transferring the WE to the vacuum chamber for XPS. The cell is attached to the XPS system (image from Ref. [19]), facilitating a clean transfer via washing, purging with inert gas, and pumping down to vacuum. **b**) Thin electrolyte approaches involve the formation of an ultrathin electrolyte film on the working electrode, which is sufficiently thin to enable X-rays to reach the electrode and photoelectrons to escape to the vacuum chamber, where they are detected using the electron analyzer. During the measurement, the wet working electrode remains in electrochemical contact with the reference and counter electrodes positioned in a shared electrolyte (see bottom panel). **c**) In thin electrode approaches, the electrode is nanostructured so that the electrode–electrolyte interface can be probed right at the surface of the cell. The electrode is supported on an ion exchange membrane (left) or a holey SiNx membrane (right). Graphene is often used to separate the wet electrochemical environment from the vacuum of the XPS chamber. This also permits the use of closed-flow cells inside the vacuum chamber (bottom panel).

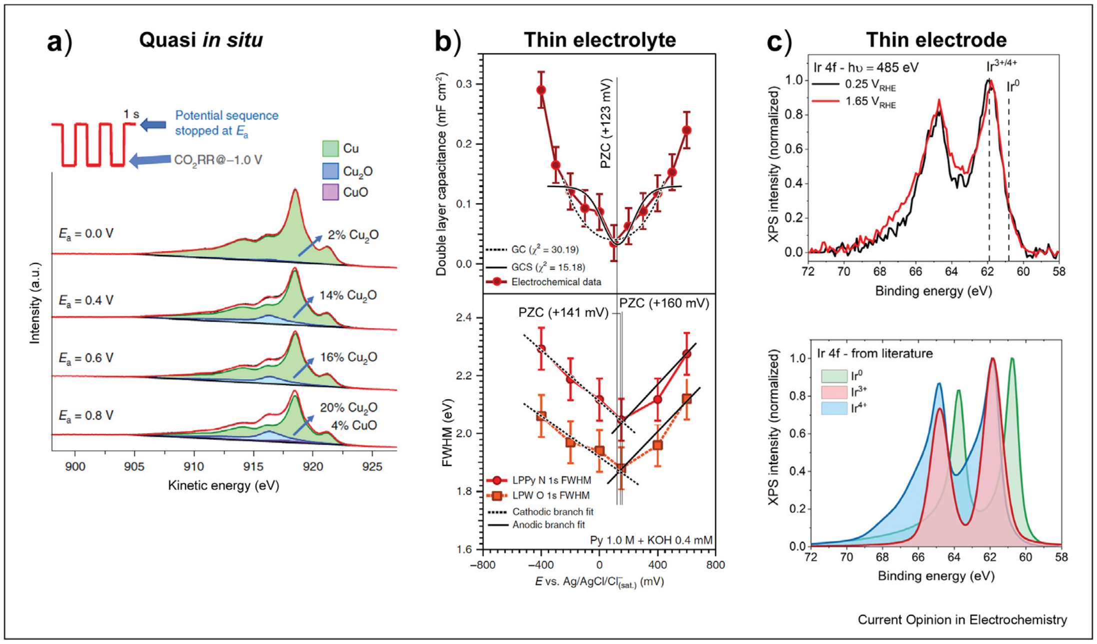
[16,18]. Although the formation of ultrathin electrolyte films may seem unlikely based on the classical wetting theory [34], in practice, the phenomenon of electrowetting likely enables 5–20 nm films to readily form on a variety of electrode materials [16,30,35–37].

Among the different adaptations of the thin electrolyte approach, the dip-and-pull geometry is the most popular [16,18]. In this approach, the electrode is first subjected to an applied bias before being partially pulled out of an electrolyte-filled container to form the ultrathin electrolyte film. In such a configuration, the electrode remains electrochemically connected with the rest of the cell, allowing for true in situ conditions. Other approaches to form the ultrathin film are the “tilted sample” approach [30,32], which relies on the spontaneous formation of the electrolyte film on a reclined sample, and the “offset droplet” method [11,31], where the electrolyte is introduced through a capillary and partially pulled back to form the electrolyte film. While these approaches do not require the ∼4 cm-long samples that are needed for the dip-and-pull method, they put more constraints on the electrochemistry.

Although the spectroscopic quality of the thin electrolyte approach cannot match that of quasi-in situ EC-XPS, it enables a direct view of the electrode–electrolyte interface. On the electrode side, changes in surface oxidation state have been studied for a variety of materials (e.g. Figure 1a) [12,39–42]. Perhaps even more interesting is the possibility of studying the interfacial electrolyte [9,17]. The most explicit study of the double layer was achieved by using pyrazine, an electrochemically inert spectator molecule, to probe the change of potentials experienced by the molecule through its N 1s core level (Figure 3b) [17]. This study successfully demonstrated that the dip-and-pull geometry provides a clear correlation between the presence of cations and the double-layer capacitance as a function of applied potential.

The main drawback of the thin electrolyte approach remains the mass transport limitation through the electrolyte film that restricts the current density at the measurement spot to a few hundred nA/cm^2, as calculated in the work of Favaro [43] and experimentally confirmed by Velasco-Vélez [9]. Therefore, this

Figure 3



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Representative examples of the three EC-XPS approaches. **a**) Quasi-in situ Cu LMM Auger spectra obtained after 1 h of pulsed electrolysis with −1.0 V vs RHE as the lower limit and various anodic potentials (E_a) as the upper limit. The electrode was removed at potential E_a [25]. **b**) Top: Double layer capacitance measured on a Au electrode in 1.0 M Py and 0.4 mM KOH as a function of applied potential. The electrochemical data are fitted using the GC model (dotted line) and the GCS model (full line). Bottom: N 1s FWHM of LPPy and O 1s FWHM of LPW as a function of applied potential [17]. **c**) Ir 4f spectra of semi-crystalline IrO_x supported on Nafion and covered with graphene (geometry as in Fig. 2c, left panel). At 1.65 $V_{RHE,}$ several mA/cm^2 of OER current could be measured during the recording of the spectrum [38]. EC-XPS, electrochemical X-ray photoelectron spectroscopy; PY, pyrazine; GC, Gouy Chapman; GCS, Gouy Chapman Stern; FWHM, full width at half-maximum; LPPy, liquid phase pyrazine; LPW, liquid phase water; OER, oxygen evolution reaction.

approach is best applied to situations without faradaic current, which is realistic for batteries and supercapacitors, for example.

Thin electrode/window

The use of ultrathin or porous electrodes provides an alternative to the ultrathin electrolyte approach (Figure 2c). For example, membrane electrode assemblies (MEAs) such as those used in fuel cells can be directly used in EC-XPS experiments [44–47]. At the surface of an MEA, (polymer) electrolyte and electrode are mixed, which means that photoelectrons can escape directly from the electrode–electrolyte interface without the need to travel through the electrode or electrolyte. To operate the MEA inside the XPS chamber, the only requirement is to have the polymer electrolyte wetted with water to activate ionic conductivity. This can be done by dosing water vapor into the XPS chamber. Unfortunately, the required water vapor pressure can be as high as ∼20 mbar [45], which causes significant scattering of the photoelectrons along their way to the electron analyzer. As an alternative, the MEA can also be wetted from the backside using a liquid electrolyte [14,48,49]. To minimize evaporation in the vacuum chamber, the electrode may be covered with an electron-transparent graphene window [14,48]. This strategy has allowed conducting *operando* studies on faradaic processes at current densities of several mA/cm^2 [9,38]. Figure 3c shows an example of IrO_x nanoparticles during the OER [38]. As the potential is increased, the particles are found to gradually undergo Ir^{3+}/Ir^{4+} redox. This redox is intimately linked with the conversion of OH to O moieties in the oxide, which is necessary to activate the structure for OER.

Although EC-XPS using MEAs provides good opportunities for *operando* studies, not all electrochemistry can be captured in an MEA cell. For electrochemical systems involving ions or molecules that do not readily diffuse through a polymer electrolyte, the holey SiN_x approach provides the opportunity to measure the interface between an electrode and bulk liquid electrolyte [50]. In this configuration, the working electrode consists of nanoparticles deposited on graphene. This catalyst/graphene film is placed on a SiN_x chip with holes of ∼1 μm (Figure 2c). During the EC-XPS measurements, the catalyst/graphene–electrolyte interface can be probed through these holes. Although the graphene/SiNx assembly is fragile and somewhat challenging to prepare, carefully constructed samples have been shown to survive even under OER conditions

[51,52]. Most importantly, in this configuration, EC-XPS distinguishes the oxidation state of the surface from the bulk. Ir^{V} and electron-deficient O^{I-} species were found to predominate at the surface and identified as most active for OER. The higher surface area-to-bulk ratio of IrO_x NPs makes them more electrocatalytically desirable than IrO_x thin films. For battery systems based on Si electrodes, 15 nm Si windows have been used instead of the graphene/holey SiNx. In this case, Si can be used as both a window and an electrode, facilitating the in situ study of the lithiation and delithiation processes in Li batteries [53,54]. Although the Si windows are fragile, this approach shows how a window approach can be extended to a wider variety of materials.

Future perspectives

With its capability to dissect both the elemental and chemical composition of the electrode—electrolyte interface, EC-XPS has displayed the potential to claim an important spot in the electrochemist's toolbox. Using the different approaches that have been developed, a wide variety of electrochemical processes can now be studied. Progress in the development of new cell components and measurement geometries will undoubtedly further broaden the scope of the method in the coming years. Perhaps more important, however, is that EC-XPS finds its way from the spectroscopy specialists to the wider electrochemistry community. To this end, a shift of focus towards user-friendliness and clean electrochemistry will be important. Finally, more widespread access to EC-XPS equipment will be crucial. The recent development of the first laboratory EC-XPS set-ups and the commercialization of the equipment are two important first steps in this direction.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data were used for the research described in the article.

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An upgraded adaptation of the offset droplet is presented in this work. A thin electrolyte film is maintained on the working electrode's surface with a capillary, which also contains the counter and reference electrodes. This adaptation of the *thin electrolyte* configuration is presented as more adaptable than the dip-and-pull approach, given the broader range of eligible electrodes (e.g. single crystals) it can measure.

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This study identifies the different surface oxygen species formed on Pt during OER using EC-XPS in a dip-and-pull geometry. This work highlights how the *thin electrolyte* EC-XPS can enable the analysis of a complex mixture of oxidation states that bears electrocatalytically relevant information.

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In this article, a Pt nanoparticle-based polymer electrolyte (PEM) fuel cell is studied with EC-XPS and identifies a variety of oxygen surface species relevant to ORR. Supported by density functional theory calculations, this work identifies the electrocatalytic importance of non-hydrated OH as a key surface species for ORR on Pt.

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This study demonstrates the successful application of EC-XPS in a dip-and-pull geometry to investigate in situ the potential drop across the double layer formed at an Au aqueous interface. This work highlights a potential dependent change in the binding energy of an electrochemically inert spectator molecule that is consistent with the double layer capacitance measured for this interface.

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In this study, *quasi-in situ* EC-XPS is used to study Pt nanoparticles deposited on Co_3O_4(111)/Ir(100) films, revealing the changes in the distribution of Pt oxidation states after exposing the sample to different potentials. The protected transfer of the sample from the electrochemical cell to the XPS vacuum chamber is sufficient to corroborate the onset potential of Pt^{4+} formation also observed in situ.

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