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An electrochemical flow cell for operando XPS and NEXAFS investigation of solid–liquid interfaces

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Abstract

Suitable reaction cells are critical for operando near ambient pressure (NAP) soft x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) studies. They enable tracking the chemical state and structural properties of catalytically active materials under realistic reaction conditions, and thus allow a better understanding of charge transfer at the liquid–solid interface, activation of reactant molecules, and surface intermediate species. In order to facilitate such studies, we have developed a top-side illuminated operando spectro-electrochemical flow cell for synchrotron-based NAP-XPS/-NEXAFS studies. Our modular design uses a non-metal (PEEK) body, and replaceable membranes which can be either of x-ray transparent silicon nitride (SiN_x) or of water permeable polymer membrane materials (e.g. NafionTM). The design allows rapid sample exchange and simultaneous measurements of total electron yield, Auger electron yield and fluorescence-yield. The developed system is highly modular and can be used in the laboratory or directly at the beamline for operando XPS/ x-ray absorption spectroscopy investigations of surfaces and interfaces. We present examples to demonstrate the capabilities of the flow cell. These include an operando NEXAFS study of the Cu-redox chemistry using a SiN_x/Ti-Au/Cu working electrode assembly (WEA) and a NAP-XPS/-NEXAFS study of water adsorption on a NafionTM polymer membrane based WEA (NafionTM/C/IrO_x catalyst). More importantly, the spectro-electrochemical flow cell is available for user community of B07 beamlines at Diamond Light Source.

1. Introduction

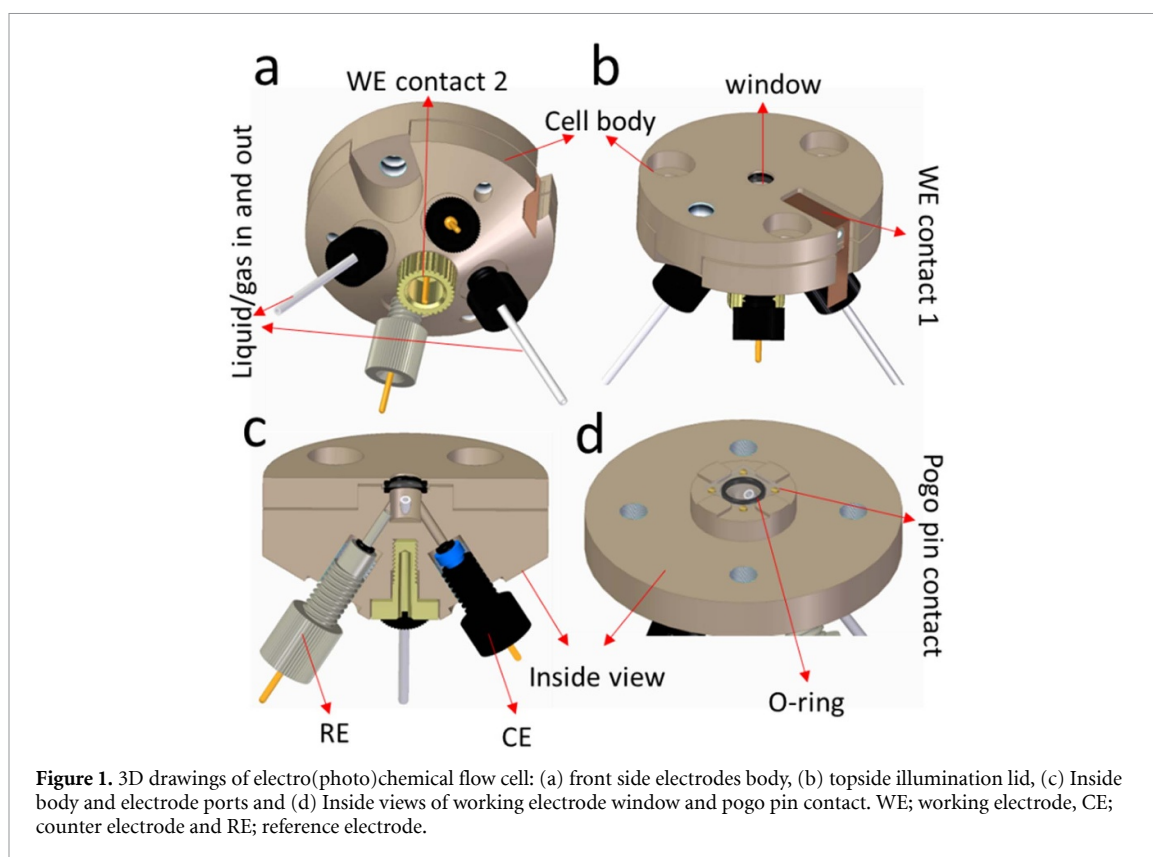
Research in heterogeneous catalysis has as one of its main objectives the derivation of structure-activity links [1]. These relationships relate catalytic performance, such as reactant conversion, product selectivity, and reaction mechanism, with physical sample composition, such as active metal distribution, pore network properties, and support shape and structure [1, 2]. By encouraging knowledge-based design and operation of catalytic processes rather than trial-and-error experimental or synthetic approaches, understanding structure-activity links is a difficult but essential step in building more effective and stable catalysts [3]. *In-situ* and operando characterization have become established as crucial ideas for obtaining such structure-activity relations in catalysis over the years [1, 4].

Electrochemical or photo(electro)-chemical conversion processes are believed to be key to overcome both the energy demand and global climate change [5, 6]. They are able to convert components of the earth's atmosphere, e.g. H₂O, N₂, CO₂, into higher-value products such as hydrogen, carbon monoxide, methanol, hydrocarbon, or ammonia, by using renewable energy at room temperature and are therefore seen as the

most cost-effective routes compared to energy intensive thermal processes [1, 5, 6]. For example, the CO₂ reduction to CO process consists of two half catalytic reactions: CO₂ reduction, e.g. $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$ and the oxygen evolution reaction (OER), $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$. Along with CO₂ activation and reduction, the oxidation half reaction is also a bottleneck that hinders the overall reaction process [7]. Electrocatalysts or photo(electro)catalysts play a key role in these energy conversion technologies because they increase the rate, efficiency, and selectivity of the chemical transformations involved [2, 8]. For this reason, in recent years, extensive work has been devoted to the development of new materials by band engineering, cocatalyst decoration, and junction construction in order to promote the electro- or photo(electro)catalytic redox reaction [9–11]. However, the lack of understanding of the sluggish kinetics of multi-electron reactions, such as CO₂ reduction and water oxidation, and the underlying redox mechanism for various products have hampered the optimization of electron-to-chemical/solar-to-chemical conversion catalysts with respect to high efficiency and product selectivity [9, 12].

Soft x-ray spectroscopies (including XPS and XAS) are powerful element selective techniques that help understand the electronic and geometric structure of (photo)electrocatalysts under operating conditions [13–15]. Although electrocatalysis itself is performed by electroactive species, other, non-electroactive ones play a critical role in electrocatalytic reactions as well. Cations, anions, solvents, and reactants all have significant effects in the efficiency of electrocatalytic reactions. X-ray absorption spectroscopy (XAS) of the K-edges of light elements, such as nitrogen, oxygen and carbon [13, 16] and the L-edges of 3d transition metals allow us to investigate the partially unoccupied 3d orbitals by acquiring information on oxidation state, geometry, spin states and the interaction with ligands (charge transfer and back bonding), which are pivotal for catalysis [16]. Different detection modes for XAS, such as direct absorption (in transmission), total/partial fluorescent yield (TFY/PFY), total/partial electron yield (TEY/PEY), or Auger electron yield (AEY) can be utilized to tailor the technique to the reaction environment and information depth required for a specific problem. In general, fluorescence is more bulk sensitive, and can be used in gas or liquid reaction environments and with many window materials, whereas electrons are more surface sensitive but will only penetrate low-pressure gas atmospheres or liquid layers of a few nm [17]. Measurements in transmission mode are limited by the need for sufficiently thin samples. Especially in the soft x-ray range this requirement can be difficult to fulfil, since attenuation lengths of solids are typically well below 1 μm . XPS, on the other hand, is one of the most widely used surface analysis techniques. It is applicable to a wide range of materials or elements and gives valuable quantitative and chemical state information from the surface of the material being examined [18]. In the case of electrocatalysis, ambient conditions are required, whereas conventional lab based XPS is mostly operated under UHV conditions, limiting its application for studying solid-liquid or solid-gas interfaces under ambient conditions (i.e. in the presence of gases and liquids). Synchrotron radiation, on the other hand, provides a multitude of features that makes it an appealing source for quantitative XPS. Among the most important are its high flux density, enabling faster data acquisition than with conventional sources, and tunable photon energy, which can be used for depth-dependent chemical analysis of catalyst materials [19].

Various reaction cells have been used for operando gas-phase and liquid-phase reactions [20–23], including photochemical reactions [24, 25], and electrochemical reactions [26, 27]. The primary obstacles in developing operando NAP-XPS/-NEXAFS cells for photocatalytic and electrocatalytic reactions are that these reactions take place at the solid-liquid interface and that the catalyst must be exposed to UV-visible irradiation and/or held at an external potential. As a result, the challenge for cell design is to limit x-ray path length in the liquid phase to minimize attenuation and allowing UV-visible light irradiation. In recent years, several experimental setups have been used to study solid/liquid electrochemical interactions [28], such as ‘dip and pull,’ [29, 30] ‘tilted sample,’ [31] ‘offset droplet,’ [32] ‘capillary,’ [33] and ‘membrane-based electrode assembly’ [34]. Membrane-based working electrodes, in particular, enable operando NAP-XPS/-NEXAFS investigations on real-world electrocatalytic systems. For example, SiN_x membranes and SiN_x membranes with graphene windows [15, 22, 35, 36] can be used to efficiently investigate model and crystalline electrocatalysts for near-edge x-ray absorption fine structure (NEXAFS), and XPS, respectively. On other hand, polymer-based membranes [37, 38] enable the investigation of more sophisticated and powder-based electrocatalysts. Here we describe a viable solution to these problems, a top-illuminated operando (photo)electrochemical flow cell that enables synchrotron-based NAP-XPS/-NEXAFS studies of surfaces and interfaces while minimizing x-ray path length in the liquid phase. More importantly, the developed system is highly modular and accommodate different membranes/windows including polymers, SiN_x, and graphene. In addition, the flow cell can be used at the beamlines as well as in the laboratory, which is of great benefit for preparation and validation of synchrotron experiments.



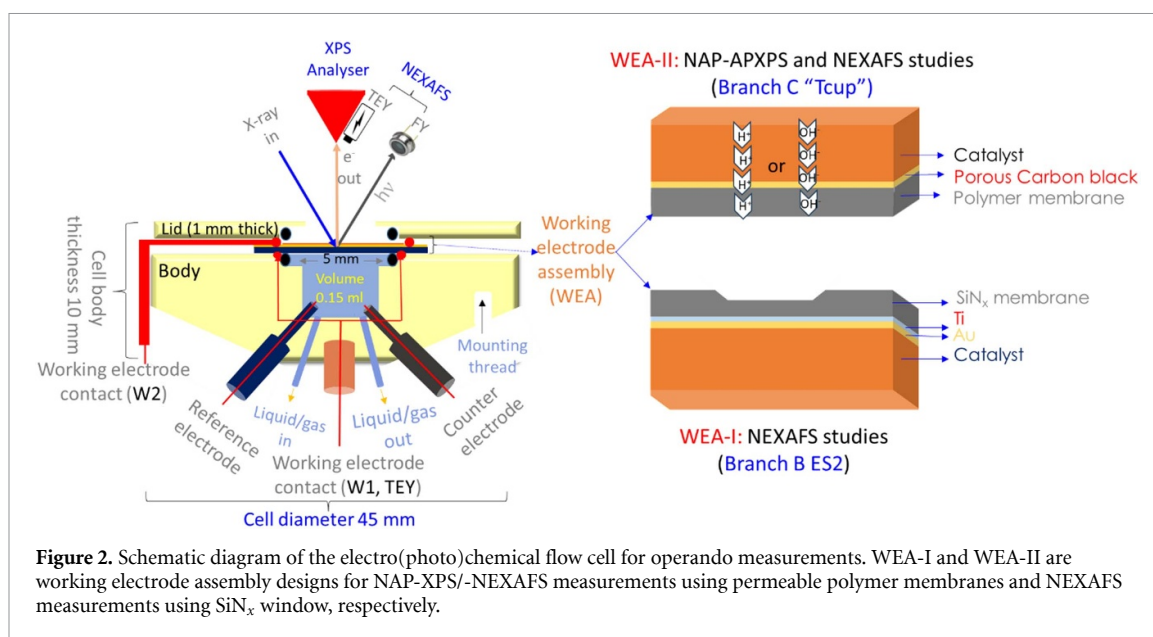
2. Design of the NAP-XPS/-NEXAFS spectro-electrochemical flow cell

2.1. Mechanical design of flow cell

The modular design of the flow cell is based on a non-metal PEEK body, and exchangeable membranes/windows, which can be either of x-ray transparent silicon nitride (SiN_x) or of water permeable polymer membrane materials (e.g. NafionTM). 3D drawings and schematic diagrams are shown in figures 1 and 2, respectively. Figure S1 displays 2D drawings of the total channel dimensions, including sections A-A and B-B, whereas figure S2 depicts photographs of the flow cell. The flow cell has an outer diameter of 45 mm and a thickness of 10 mm (figure 2) with a 5 mm diameter window on the top side (figures 1(b) and 2). The total volume of the cavity filled with liquid is 150 μl (excluding tubing). The cell can operate either in two (WE and CE) or three electrode (WE, CE and RE) configurations, and in static mode or with a constant flow. The window or membrane is coated with the catalyst or material of interest and acts as the WE. Its operating voltage is measured against a RE, which is, depending on the application, either a commercially available micro- Ag/AgCl (aqueous electrolytes) or Ag/Ag⁺ (organic electrolytes) electrode (by Redox.me). The electrolyte solution is delivered through chemical resistant and vacuum compatible 1/16" OD/1 mm ID PEEK or PTFE tubing. Standard IDEX and BNC fittings are used to connect the tubing and electrode contacts, respectively. Either SiN_x or polymer membranes (e.g. proton exchange membrane (NafionTM) or anion exchange membrane) can be used as working electrode substrate. An M4 tapped hole is integrated into the flow cell's body to allow mounting it onto the beamline's sample manipulator.

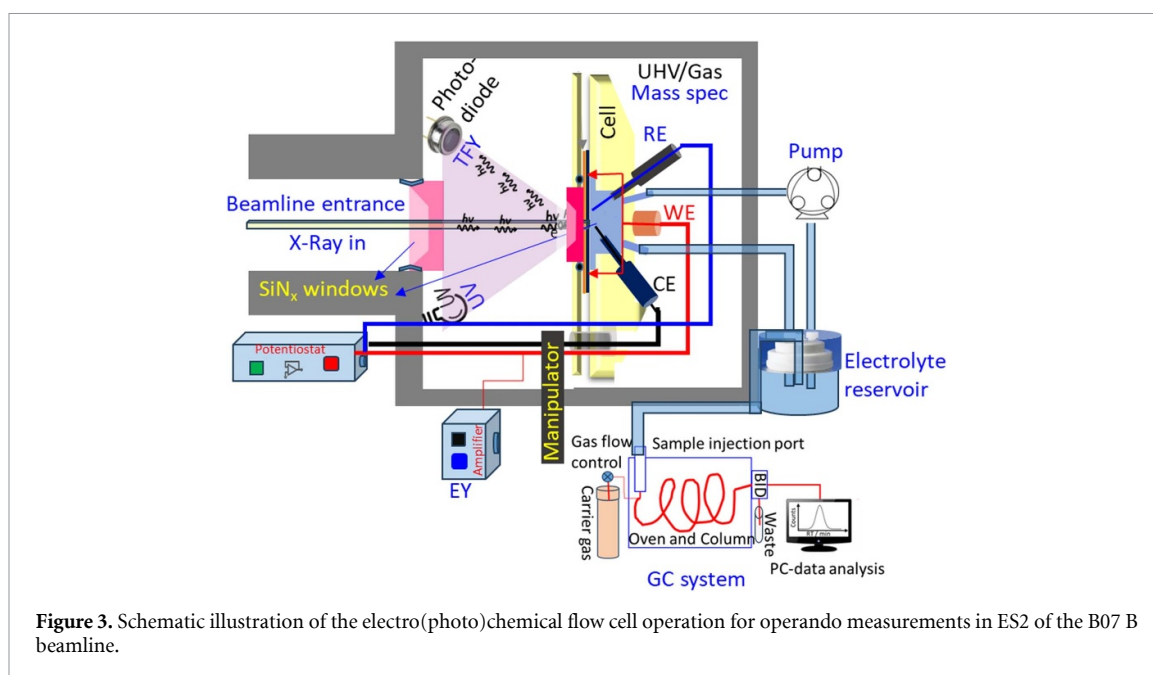
SiN_x windows of 50-200 nm thickness are sufficiently transparent for soft x-rays and stable enough to withstand the pressure of the electrolyte. These are used for XAS of surfaces and interfaces inside the cell, as shown in working electrode assembly (WEA) I in figure 2. The SiN_x window used in our measurements had a size of 1 × 1 mm² and a thickness of 100 nm. It is etched into a 7.5 × 7.5 mm² silicon frame which is 381 μm thick, holding the window in place and providing a seal to the cell with a 5 mm ID (internal diameter) O-ring and a 1 mm thick lid (figures 1(c) and (d)). Under operating conditions, with the cell in the vacuum chamber, outside pressures of 10⁻⁵-10⁻⁴ mbar can be achieved with a SiN_x window. The four spring-loaded electrical contacts seen in figure 1(c) and illustrated as WE contact (W1) in figure 2 are used as a current collector for EY operando NEXAFS measurements.

Polymer-backbone-based proton [39] or anion exchange membranes [40] can be used as support for catalysts on the outside of the cell while still enabling electrochemical contact to the electrolyte inside the cell. The schematic layout of the cell when using polymer membranes is shown in WEA-II in figure 2. This



particular assembly is used for operando XPS measurement of the solid-liquid interface. The polymer membrane (Nafion115™) used in our measurements had a diameter of 10–12 mm and a thickness of 127 μm . This polymer membrane uses an X-ring with a 4.45 mm ID (internal diameter) and 1.78 mm thickness to provide an airtight seal to the flow cell. Under operating conditions, outside pressures of 10^{-2} - 10^{-1} mbar can be achieved with polymer membranes such as proton exchange and anion exchange membranes. As expected, relatively high pressure is detected when employing a Nafion membrane over SiN_x membranes due to control leak through the membrane channels, which is required to observe the electrochemistry on the vacuum side of the membrane for XPS measurement. Pressure inside the cell is one bar (atmospheric pressure). The copper ring type electrical contacts seen in figure 1(d) and illustrated as WE contact (W2) in figure 2 are used as a drain current collector for operando NAP-NEXAFS measurements. It is important to note that these polymer membranes are not electron conducting, but they can be coated directly with conducting catalyst material or with commercially available meso-porous carbon black as an electrical contact layer prior to the deposition of the (non-conducting) catalyst material (**see the ESI for experimental details on the deposition method**). This working electrode enables not only NAP-NEXAFS measurements, but also NAP-XPS by enabling measuring of both photoelectrons emitted from the membranes or catalyst material deposited at the top side of the flow cell, as a function of reactant gas, water vapor pressure, and/or applied external potential. Furthermore, photoelectrochemical reactions can be performed and probed utilising a 365 nm UV or LED light source also available in the endstation on both branch B and branch C of B07, Versatile Soft x-ray (VerSoX), beamlines.

A flow cell is preferable to a static one because it maintains a consistent temperature throughout x-ray and/or UV irradiation, reducing potential radiation damage. Furthermore, constantly renewing the electrolyte that is affected by the x-ray radiation of consumed, e.g. during water splitting, maintains a consistent pH and releases the liquid and/or gas products. However, a high flow rate contributes to a low signal-to-noise ratio and may induce artefacts owing to flow-induced vibrations. Therefore, it is critical to keep the flow rate as low as possible of flow in between the measurement of spectra. Different electrolyte solutions with variable pH ranges can be used in the flow cell for *in-situ* or operando (photo)electrochemical studies. Using a micro-syringe (Hamilton Microlab 500 syringe pump) or peristaltic pump (SPETEC GmbH Germany, 50-60 Hz and 70 W) available at the B07 beamline the flow can be controlled down to 2 $\mu\text{l min}^{-1}$ and is supplied by 1/16" OD peek tubes, which are interlocked to pressure gauges to cut the flow in the event of the SiN_x window or polymer membrane failing. For *in-situ* or operando electrochemical experiments, an industry standard potentiostat (Ivium CompactStat) can be utilized to adjust the electrode potential and current in the ranges of ± 5 V and 30-800 mA, respectively. The applied potential or current can be controlled directly from a dedicated laptop using Ivium software (IviumSoft). More conveniently, it is also possible to apply and manage the potential or current via the beamline control systems (EPICS). Alternatively, the potential can be applied in the range ± 5 V by the biasing capability of the Stanford SR570 current amplifier. In addition, liquid or gas produced inside the cell can be detected and quantified using portable gas chromatography (Shimadzu GC-2010 Plus).



2.2. Peripheral equipment

2.2.1. The VerSoX beamline at diamond light source

The B07 beamline is comprised of two branchlines, B and C, each with its own source and monochromator. As a result, they can work simultaneously and independently. The energy range of branch C is 130–2800 eV. Branch B has a range of 45 eV–2200 eV, which includes the Li K-edge and the N 6,7 absorption edges of the sixth row Pt metals. The design criteria for both branches were to achieve maximum photon flux and good energy resolution ($E/\Delta E > 5000$) throughout a broad range of photon energies. The Plane Grating Monochromator on both branches has three gratings of 400, 600, and 1000/1200 lines mm^{-1} , designed to produce an energy resolving power $h\nu/\Delta(h\nu) > 5000$ over most. The use of incident collimated light allows for varying cff, which improves the suppression of second and higher diffraction orders [22]. A pair of refocusing mirrors, M4b/c (vertical) and M5b/c (horizontal), situated after the exit slit, direct the monochromatic beam to the sample spot. The beamline's EPICS (Experimental Physics and Industrial Control System) and GDA (Generic Data Acquisition) control environments fully integrate all motions of optical elements, shutters, diagnostics, and vacuum control [23, 24]. The near ambient pressure (NAP) XPS / NEXAFS endstation is positioned in the heart of Branch C. Branch B contains a UHV XPS/NEXAFS end station (ES-1) and a high-throughput NEXAFS endstation (ES2). However, only the NAP endstation of Branch C and ES-2 of Branch B can accommodate electrochemical and other high-pressure cells, which will be of interest to readers as long as the electrochemical cell presented in this work is concerned [19, 41].

2.2.2. Endstations

The NEXAFS ES2, on the branch B beamline is designed for XAS measurements of solid, liquid and gaseous samples with a pressure range of 10^{-7} mbar to 1 bar. The beam size at the sample position was measured to be $120 \mu\text{m}$ (H) $\times$ $40\text{--}120 \mu\text{m}$ (V) for Branch B at the second focus using a calibrated camera. A photograph of the flow cell inside ES2 is shown in figures S3(a)–(c). Figure 3 shows a schematic illustration of its operation for operando measurements. The cell can be introduced via a DN63 CF flange on the top or a quick entry door on the side of the chamber and mounted directly on flag type sample plate using a custom-made the flow cell sample holder (figure S4). The DN63 CF flange is sealed with Viton O-ring for fast sample change. Leak valves can be used to introduce water vapor and a variety of gases, depending on the needs of the experiment. The endstation is enclosed in a small radiation hutch for user safety. EY is measured via the working electrode of the flow cell by connecting the working electrode to a current amplifier and grounding the counter electrode to vice versa. But we utilize TFY rather than EY for simultaneous monitoring of the x-ray signal and electrochemical responses because our beamline does not yet have a chopper. We can, however, measure the EY using the same working electrode after a potential hold for a predetermined amount of time. We aim to have a chopper in the future, which will allow us to differentiate between an electrochemical reaction and currents from x-rays. For TFY measurements, a photodiode (AXUV-100G TF400) is utilized with a 150 nm aluminum coating to block photoelectrons and stray visible

light. Grinter *et al* [41], provides detailed information on the measuring principles for NEXAFS experiments in ES2 as well as a beamline specification.

The endstation of branch C offers a chamber with fast entry system ('Tea Cup') [19], which is also used for operando cells like the electrochemical flow cells, which can be mounted using a vacuum flange (figure S7) accommodating the cell, liquid lines, and electrode feedthroughs. It is mounted on manipulator that allows linear travel in three dimensions with respect to the analyzer. In addition, the Tea Cup has elaborate gas and water dosing facilities which can be used to expose samples up to pressures of ~ 100 mbar. This can be used in connection with polymer-membrane-based working electrode assemblies for carrying out operando studies of e.g. water oxidation or CO_2 and water reduction reactions. It is also possible to measure the gas produced inside the endstation using a mass spectrometer, which is integrated in the NAP electron analyzer of the endstation. Both GC and mass spectrometer enable real-time identification and quantification of reaction products. The beam size at the sample position was measured to be $90\text{ }\mu\text{m}$ (H) $\times$ $60\text{--}100\text{ }\mu\text{m}$ (V) for Branch C using a thin mica sheet. X-ray analysis on catalyst (sample) surfaces and interfaces can be investigated simultaneously using TEY, AEY, and TFY detection mode, which provide a useful insight on surface and interface chemistry, such as molecular adsorption [42], metal-support interactions [43], charge transfer and reaction kinetics [44–46]. Therefore, the cell can be used for the study of solids, liquids, and solid/liquid interfaces under operando conditions as function of reactant gas or water vapor pressure, applied voltage or light illumination with the possibility to carry out both XPS and XAS studies. Furthermore, time-resolved XPS and XAS measurements can be performed. A fast spectrum can be measured in 30 s. The spectrum acquisition time depends on the element and its composition, the type of XAS edges and XPS peaks, the photon energy (XAS) and kinetic energy (XPS), and the needed resolution. However, the spectrum acquisition times for measuring good XAS and XPS spectra are 2–15 and 5–30 min, respectively.

3. Preliminary results

3.1. Proof of principle of spectro-electrochemical flow cell: SiN_x membrane based WEA for NAP-NEXAFS

To validate the flow cell using a SiN_x -based working-electrode assembly, we first conducted a set of off-beamline electrochemical measurements. Figure 4 shows cyclic voltammetry (CV) and linear sweep voltammetry (LSV), respectively, of 20 nm thick sputtered Cu in 0.1 M KOH employing a $\text{SiN}_x/\text{Au-Ti}/\text{Cu}$ WEA in the flow cell and in a beaker. As shown in figure 4(a), we detected two anodic at 0.925 V and 0.64 V vs RHE, and two cathodic current peaks at 0.5 V and 0.2 V vs RHE, which are typical of a Cu surface [47] and are almost identical for both CV cycles (cell and beaker) (see the ESI for experimental details). It is worth pointing out that not only the redox behavior of the Cu electrode is similar in the beaker and cell but also the signal-to-noise ratio and current density. Figure 4(b) also shows very similar LSV behavior under identical experimental conditions, with a current density of -1.85 mA cm^{-2} at a cathodic potential of -0.28 eV vs RHE in 0.1 M KOH electrolyte at pH 12. The formed products were analyzed by gas chromatography via head space analysis of electrolyte reservoir. The total H_2 evolved from HER was consistent with a 2:1 theoretical stoichiometry of H_2 and O_2 with the actual involvement of 2 and 4 e^- to form H_2 and O_2 , respectively (figure S6). Furthermore, we measured CV and electrochemical impedance spectroscopy (EIS) (figures 4(c) and (d)) on the cell and compared the results to a lab-based beaker type cell using Au (10 nm)/Ti (10 nm) coated SiN_x as a standard working electrode, revealing that the cell has no perceptible extra resistance despite its small size and uses small volume of electrolyte. Interestingly, on the cell, we observed rapid charge transfer at the electrode interface from EIS (figure 4(d)). However, the gold shows a similar broad oxidation peak, which begins at 1.5 V vs. RHE in cell and beaker conditions (figure 4(c)). During the backward scan, a dramatic decrease peak at 1.18 V vs. RHE is noticed, indicating the reduction of the produced gold oxide layer [48].

For *in-situ* or operando investigations, the flow cell with the 10 nm Au/Ti coated SiN_x WEA, was mounted on the manipulator of the NEXAFS endstation (ES2) of the branch B beamline, as shown in figures 3 and 4. Figure 5(a) shows the O K-edge NEXAFS spectra of liquid water inside the flow cell in both EY and TFY detection modes. For EY signal, we used the working electrode drain current directly while grounding the counter electrode. The TFY signal was measured via a photodiode facing the SiN_x window. The unoccupied states probed by O K-edge NEXAFS, notably the antibonding O–H molecular orbitals and their characteristics are sensitive to the H-bonding network surrounding the probed water molecules [49]. Figure 5(a) shows the features characteristic for liquid water, the pre-edge shoulder at 535.4 eV, related to dangling O–H bonds [17], and the broad feature between 537.0 eV and 545.0 eV, related to hydrogen bonds.

Cations are coordinated with the oxygen atoms in water molecules in an electrolyte solution, while anions are coordinated with the hydrogen atoms in water molecules. As a result, understanding the hydration structure of ions in various electrolyte solutions is critical in electrochemical systems in order to optimize ionic conductivity and thus electrochemical performance. Many techniques, including XPS [50], NEXAFS [51], x-ray scattering [52], neutron diffraction [53], x-ray diffraction [54], and Raman spectroscopy [55],

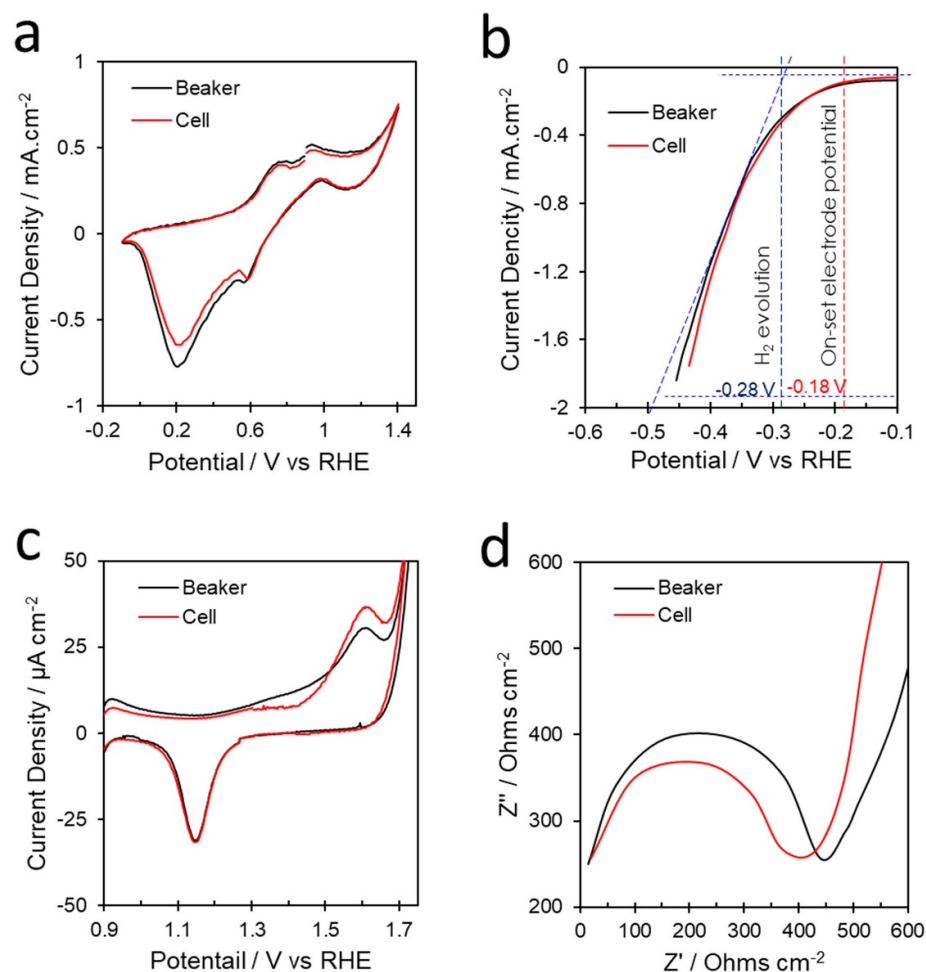


Figure 4. Cyclic Voltammetry (a) and Linear sweep voltammetry (b) of CuO_x catalyst in cell and beaker under identical experimental conditions. Cyclic Voltammetry (c) EIS (d) of Au/Ti/SiN_x working electrode in cell and beaker under identical experimental conditions. All CVs, LSVs, and EISs were recorded in 0.1 M KOH at pH 12 and at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$.

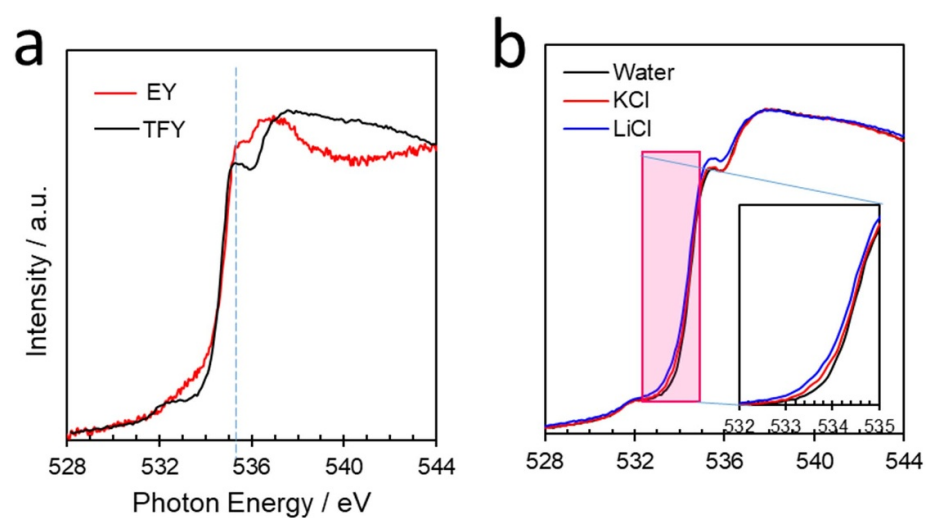


Figure 5. (a) (c) O K-edge EY and TFY NEXAFS spectra of liquid water inside the cell. Experimental conditions: Sample— $\text{H}_2\text{O/TiAu/SiN}_x$, 600 l/mm Pt, 0.1 mm exit slits, CE and WE grounded. (b) O K-edge TFY NEXAFS spectra for pure liquid water and aqueous salt solutions with different cations (0.5 M LiCl, and 0.5 M KCl) at 25°C . Inset images show the expansion of the pre-edge region of selected area of the same spectra. Experimental conditions: Sample— $\text{H}_2\text{O/TiAu/SiN}_x$.

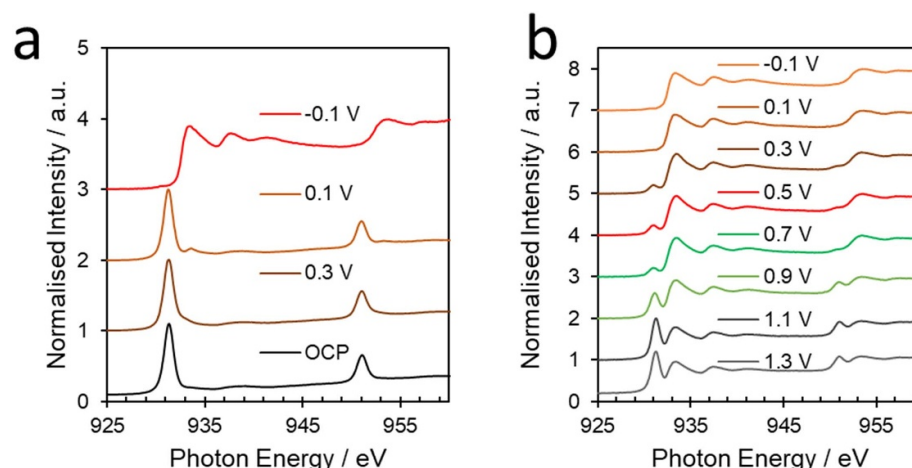


Figure 6. Cu $L_{2,3}$ -edge NEXAFS spectra as a function of applied potential during Cu reduction (a) and oxidation (b) half reactions in 0.1 M KOH electrolyte solution at pH 12. Experimental conditions: Sample— H_2O -Cu (40 nm)/AuTi/SiN_x, TFY, potential holds using Ivium potentiostat.

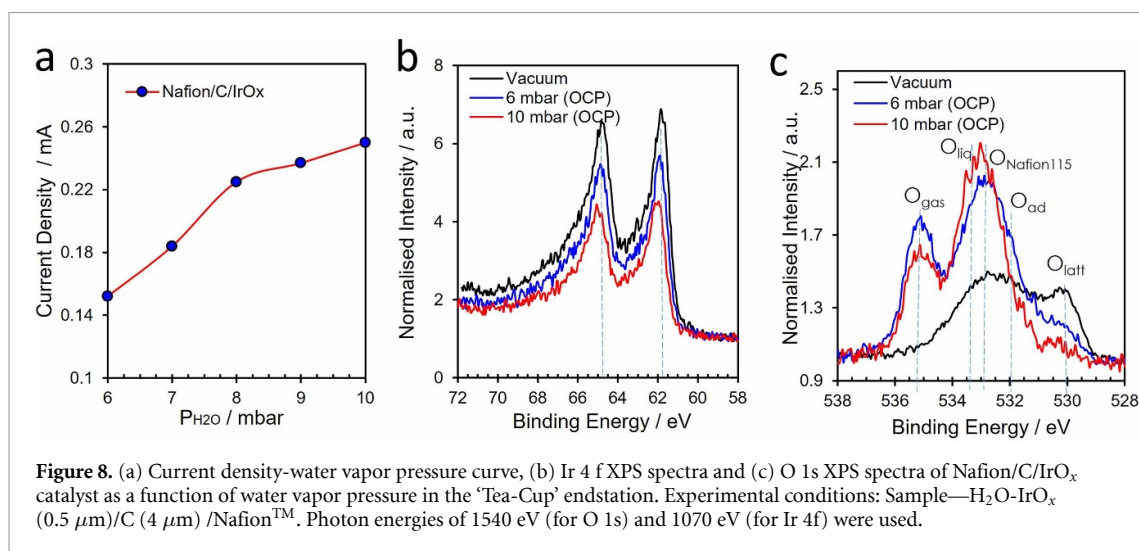
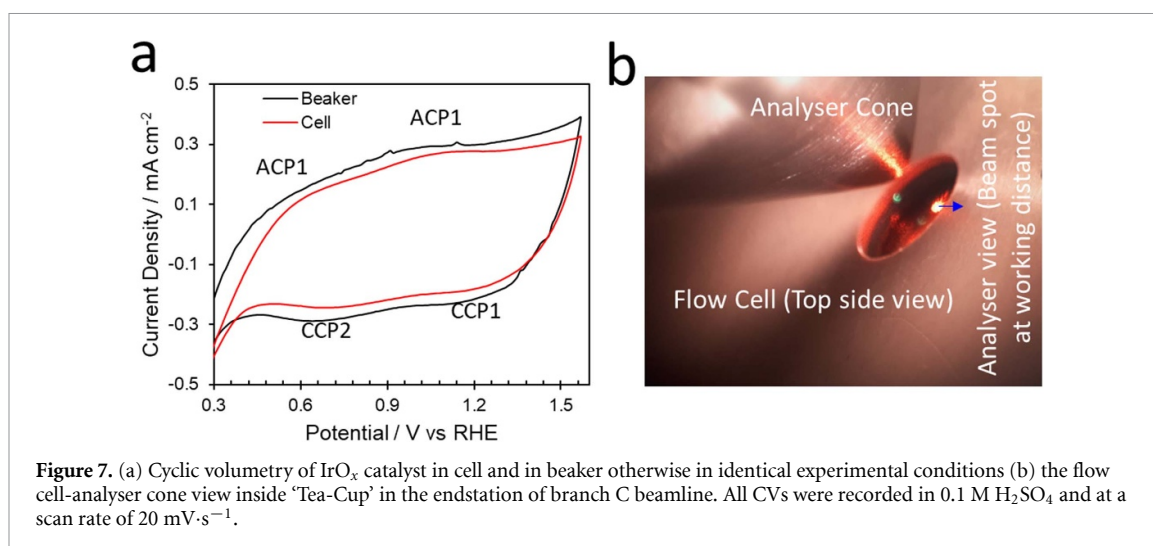
have been used to investigate the hydration structure of ions in solutions. In TFY mode, we further investigate the O K-edge XAS of aqueous solutions containing various aqueous salts. As seen in figure 5(b), the onset of the pre-edge peak of aqueous salt solutions exhibits a shift in photon energy compared to that of liquid water. This energy shift is affected by the cation, with LiCl solutions exhibiting greater shifts than KCl solutions. These results suggest that the pre-edge peak's energy shift could be caused by cations interacting with oxygen lone pairs of water [56–58]

Figure 6 shows the Cu L-edge TFY NEXAFS spectra during electrochemical reduction (figure 6(a)) and oxidation (figure 6(b)) cycle of sputtered CuO_x in 0.1 M KOH solution as a function of applied potential. Initially, the Cu L-edge spectrum shows two prominent peaks at 931.0 and 951.0 eV which are corresponding to electron transitions from $2p_{3/2}$ (L_2) and $2p_{1/2}$ (L_3) energy levels, respectively, to 3d empty states of the Cu^{2+} oxidation state, indicating the complete oxidation of the sputtered Cu [59]. When the negative reduction potential increased gradually, these two peaks decrease accompanied by the formation of new peaks characteristic of metallic copper. Surprisingly, surface Cu^{2+} was partially reduced to Cu^{1+} up to a cathodic potential of 0.1 V vs RHE; further increasing the applied reduction potential resulted in complete reduction of to Cu^0 . When the potential sweep is reversed (figure 6(b)) Cu^0/Cu^+ remained the dominant species as a function of anodic potential sweep up to +0.9 V, although some Cu^{2+} is present. Unlike during the reduction potential sweep, the surface Cu^{2+} abruptly increases from anodic potential 0.9 V–1.3 V vs RHE, but has not entirely oxidized, indicating that in basic media Cu forms a passive layer of Cu^{2+} .

3.2. Proof of principle of spectro-electrochemical flow cell: polymer membrane based WEA for NAP-XPS/-NEXAFS

Operation of the flow cell with the polymer-based WEA was also first validated with off-beamline electrochemical measurements, comparing the cell with measurements in a beaker (see the ESI for the experiment details). In this case, we used an industrial catalyst, IrO_x as a benchmark catalyst for water oxidation [60]. The electrocatalytic performance of IrO_x in the flow cell was investigated by means of CV in 0.1 M H_2SO_4 with Pt wire and micro-Ag/AgCl as the counter and reference electrodes, respectively. The IrO_x catalyst was deposited on a NafionTM/C/ IrO_x WEA as shown in the figure 2. Two oxidation and two reduction waves which are visible in the cyclic voltammogram and detected as two anodic (ACP1; ~0.6 V, ACP2; ~1.15 V) and two cathodic current (CCP1; ~0.65 V, CCP2; ~1.2 V) peaks vs RHE for both CV cycles (in cell and in beaker) as shown in figure 7(a) [61]. These peak positions and shapes, which are typical of IrO_x catalysts, are very similar for the beaker and cell measurements, also in terms of signal-to-noise ratio and current density, when the experimental conditions are the same.

For *in-situ* or operando investigations, the flow cell with the polymer based WEA, is mounted in the ‘Tea-Cup’ endstation of the NAP-XPS/-NEXAFS beamline (branch C), as shown in figure S5. The beam, analyzer cone and sample surface meet in one flange as shown in figure 7(b). The angle between the incoming beam and the sample surface and the analyzer cone is 60° on the NAP-XPS/-NEXAFS (branch C) beamline. To avoid the gas phase contribution, we can move the sample and analyzer cone along with the corresponding incoming beams using a sledge. In way, this angle is tuneable. Nafion115TM/C/ IrO_x WEA was investigated as a function of water vapor pressure in the ‘Tea-Cup’ endstation under OCP conditions because



the crystalline IrO₂ binds oxygen too strongly, resulting in the O–O bond formation step to form *OOH intermediate being rate-determining for OER [62, 63]. As shown in figure 8(a), as the water dosing pressure in the endstation increases, the current density gradually increases due to surface wetting, which enhances ionic mobility due to equilibrium between water molecules in the electrolyte solution and water molecules in the 'Tea-Cup' endstation. There is a substantial rise in current density up to 8 mbar water vapor pressure, but only a slight increase from 8 mbar to 10 mbar. As seen in figure 8(b), the peaks at 61.7 and 64.7 eV correspond to Ir⁴⁺ 4f_{7/2} and 4f_{5/2}, respectively. More intriguingly, when the water pressure rises to 10 mbar, the peaks slightly shift to higher binding energy with decreasing intensity, indicating the presence of additional oxygen related species due to partial reduction to Ir³⁺ and formation of vacancies [64, 65]. On other hand, O 1s spectra of IrO_x shows a broad feature with three maxima at 534–530 eV binding energy originates lattice oxygen (530.0 eV), adsorbed OH species (531.9 eV) and SO₃ (533.0 eV, from Nafion ionomer). A strong and sharp peak at 535.3 eV binding energy is attributed to gas phase water molecules within the excitation volume between sample and analyzer. The lattice oxygen peak at 530.0 eV in O 1s spectra eV evolves towards larger binding energy when water vapor pressure increased 10 mbar, indicating the formation of Ir–O–H bond on the surface which agrees with the shift in the Ir 4f spectra (figure 8(c)). The peak at 535.3 eV corresponds to water vapor caused by external water dosing. We also observe an evolving feature above 533.0 eV at relatively high-water vapor pressure (6 and 10 mbar), which could be due to presence of liquid water molecules (533.2 eV) [66, 67] or multi-layer water molecules. The Ir 4f and O 1s results confirm the presence of both Ir⁴⁺ and Ir³⁺ in humid environments, owing to the partial reduction of Ir⁴⁺ in crystalline IrO₂ to Ir³⁺ (IrO_x) due to the formation of electronic defects in the iridium framework, leaving two free electrons that convert neighboring Ir⁴⁺ to Ir³⁺ to ensure local charge neutrality, as similar observations reported by Pfeifer *et al* [62, 65]. Considering the decline in XPS counts as a function of water

dosing pressure, we believe 8 mbar is a good trade-off and optimal experiment conditions for operando studies on water oxidation using Nafion/C/IrO_x catalyst.

4. Conclusion

We have successfully designed and commissioned a spectro-electrochemical flow cell, which allows fast sample change and membrane replacement and user-friendly operation for synchrotron-based soft x-ray photoelectron and absorption spectroscopy measurements. The working principle of the spectro-electrochemical flow cell was demonstrated for operando NAP-XPS/-NEXAFS measurements under electrochemical reduction and oxidation conditions using CuO_x and IrO_x catalysts, as a working electrode, Pt counter electrode and micro-Ag/AgCl reference electrode, respectively. The following are the advantages of this cell design for investigating surfaces and interfaces under operando conditions are: (i) the ability to use the same flow cell for both ambient pressure NEXAFS and NAP-XPS/NEXAFS beamlines at Diamond Light Source, (ii) adoptability to different working and counter electrodes of user interests, (iii) simultaneous NEXAFS measurements using electron yield (EY), AEY and TFY, (iv) fast sample/membrane replacement (v) compatible with organic as well as aqueous electrolyte solutions, (vi) ability to perform photoelectrochemical reaction on the beamline using UV and LED light sources and (vii) ability to operando NP-XPS/-NEXAFS as function of applied potential or current. The flow cell is available for users of Diamond's VerSoX beamline B07. Furthermore, this modular design enables the flow cell to be used at other Diamond Light Source counter-part beamlines such as B22 (Infrared beamline), B18 (Hard x-ray beamline), and DESY Synchrotron's P22 (Hard x-ray Photoelectron Spectroscopy beamline), allowing for the unique exploration of scientific questions.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: CC0 Public Domain Dedication.

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References

- [1] Seh Z W, Kibsgaard J, Dickens C F, Chorkendorff I, Nørskov J K and Jaramillo T F 2017 Combining theory and experiment in electrocatalysis: insights into materials design *Science* **355** eaad4998
- [2] He J and Janáky C 2020 Recent advances in solar-driven carbon dioxide conversion: expectations versus reality *ACS Energy Lett.* **5** 1996–2014
- [3] Rao R R, Corby S, Bucci A, García-Tecedor M, Mesa C A, Rossmeisl J, Giménez S, Lloret-Fillol J, Stephens I E L and Durrant J R 2022 Spectroelectrochemical analysis of the water oxidation mechanism on doped nickel oxides *J. Am. Chem. Soc.* **144** 7622–33
- [4] Kalz K F, Kraehnert R, Dvoyashkin M, Dittmeyer R, Gläser R, Krewer U, Reuter K and Grunwaldt J-D 2017 Future challenges in heterogeneous catalysis: understanding catalysts under dynamic reaction conditions *ChemCatChem* **9** 17–29
- [5] Faunce T *et al* 2013 Artificial photosynthesis as a frontier technology for energy sustainability *Energy Environ. Sci.* **6** 1074–6
- [6] Stephens I E L *et al* 2022 2022 roadmap on low temperature electrochemical CO₂ reduction *J. Phys.* **4** 042003
- [7] Poli I, Hintermair U, Regue M, Kumar S, Sackville E V, Baker J, Watson T M, Eslava S and Cameron P J 2019 Graphite-protected CsPbBr₃ perovskite photoanodes functionalised with water oxidation catalyst for oxygen evolution in water *Nat. Commun.* **10** 2097
- [8] Liu J *et al* 2021 2021 roadmap: electrocatalysts for green catalytic processes *J. Phys. Mater.* **4** 022004
- [9] O'Mullane A P, Escudero-Escribano M, Stephens I E L and Krischer K 2019 The role of electrocatalysis in a sustainable future: from renewable energy conversion and storage to emerging reactions *ChemPhysChem* **20** 2900–3

- [10] Xu X-T, Pan L, Zhang X, Wang L and Zou J-J 2019 Rational design and construction of cocatalysts for semiconductor-based photo-electrochemical oxygen evolution: a comprehensive review *Adv. Sci.* **6** 1801505
- [11] Ran J, Jaroniec M and Qiao S-Z 2018 Cocatalysts in semiconductor-based photocatalytic CO₂ reduction: achievements, challenges, and opportunities *Adv. Mater.* **30** 1704649
- [12] Wang Y, Chen E and Tang J 2022 Insight on reaction pathways of photocatalytic CO₂ conversion *ACS Catal.* **12** 7300–16
- [13] Lange K M and Aziz E F 2013 Electronic structure of ions and molecules in solution: a view from modern soft x-ray spectroscopies *Chem. Soc. Rev.* **42** 6840–59
- [14] Wang J, Hsu C-S, Wu T-S, Chan T-S, Suen N-T, Lee J-F and Chen H M 2023 In situ x-ray spectroscopies beyond conventional x-ray absorption spectroscopy on deciphering dynamic configuration of electrocatalysts *Nat. Commun.* **14** 6576
- [15] Carbonio E A, Velasco-Vélez J-J, Schlögl R and Knop-Gericke A 2020 Perspective—outlook on operando photoelectron and absorption spectroscopy to probe catalysts at the solid-liquid electrochemical interface *J. Electrochem. Soc.* **167** 054509
- [16] Lange K M, Kothe A and Aziz E F 2012 Chemistry in solution: recent techniques and applications using soft x-ray spectroscopy *Phys. Chem. Chem. Phys.* **14** 5331–8
- [17] Frati F, Hunault M O J Y and de Groot F M F 2020 Oxygen K-edge x-ray absorption spectra *Chem. Rev.* **120** 4056–110
- [18] Oswald S 2006 X-ray photoelectron spectroscopy in analysis of surfaces *Encyclopedia of Analytical Chemistry* (Wiley) (<https://doi.org/10.1002/9780470027318.a2517>)
- [19] Held G et al 2020 Ambient-pressure endstation of the versatile soft x-ray (VerSoX) beamline at diamond light source *J. Synchrotron Radiat.* **27** 1153–66
- [20] Hannemann S, Casapu M, Grunwaldt J-D, Haider P, Trussel P, Baiker A and Welter E 2007 A versatile in situ spectroscopic cell for fluorescence/transmission EXAFS and x-ray diffraction of heterogeneous catalysts in gas and liquid phase *J. Synchrotron Radiat.* **14** 345–54
- [21] Kispersky V F, Kropf A J, Ribeiro F H and Miller J T 2012 Low absorption vitreous carbon reactors for operandoXAS: a case study on Cu/Zeolites for selective catalytic reduction of NO_x by NH₃ *Phys. Chem. Chem. Phys.* **14** 2229–38
- [22] Swallow J E N et al 2023 Revealing the role of CO during CO₂ hydrogenation on Cu surfaces with in situ soft x-ray spectroscopy *J. Am. Chem. Soc.* **145** 6730–40
- [23] Streibel V, Hävecker M, Yi Y, Velasco Vélez J J, Skorupska K, Stotz E, Knop-Gericke A, Schlögl R and Arrigo R 2018 In situ electrochemical cells to study the oxygen evolution reaction by near ambient pressure x-ray photoelectron spectroscopy *Top. Catal.* **61** 2064–84
- [24] Hocking R K, Brimblecombe R, Chang L-Y, Singh A, Cheah M H, Glover C, Casey W H and Spiccia L 2011 Water-oxidation catalysis by manganese in a geochemical-like cycle *Nat. Chem.* **3** 461–6
- [25] van Oversteeg C H M, Doan H Q, de Groot F M F and Cuk T 2017 In situ x-ray absorption spectroscopy of transition metal based water oxidation catalysts *Chem. Soc. Rev.* **46** 102–25
- [26] Cheaib K, Maurice B, Mateo T, Halime Z and Lassalle-Kaiser B 2019 Time-resolved x-ray absorption spectroelectrochemistry of redox active species in solution *J. Synchrotron Radiat.* **26** 1980–5
- [27] Gorlin Y, Lassalle-Kaiser B, Benck J D, Gul S, Webb S M, Yachandra V K, Yano J and Jaramillo T F 2013 In situ x-ray absorption spectroscopy investigation of a bifunctional manganese oxide catalyst with high activity for electrochemical water oxidation and oxygen reduction *J. Am. Chem. Soc.* **135** 8525–34
- [28] Velasco-Vélez J-J et al 2021 A comparative study of electrochemical cells for in situ x-ray spectroscopies in the soft and tender x-ray range *J. Appl. Phys.* **54** 124003
- [29] Axnanda S et al 2015 Using “Tender” x-ray ambient pressure x-ray photoelectron spectroscopy as a direct probe of solid-liquid interface *Sci. Rep.* **5** 9788
- [30] Favaro M, Clark P C J, Sear M J, Johansson M, Maehl S, van de Krol R and Starr D E 2021 Spectroscopic analysis with tender x-rays: spAnTeX, a new AP-HAXPES end-station at BESSY II *Surf. Sci.* **713** 121903
- [31] Weingarth D, Foelske-Schmitz A, Wokaun A and Kötz R 2011 In situ electrochemical XPS study of the Pt/[EMIM][BF₄] system *Electrochem. Commun.* **13** 619–22
- [32] Booth S G, Tripathi A M, Strashnov I, Dryfe R A W and Walton A S 2017 The offset droplet: a new methodology for studying the solid/water interface using x-ray photoelectron spectroscopy *J. Phys.* **29** 454001
- [33] Brummel O et al 2022 A versatile approach to electrochemical in situ ambient-pressure x-ray photoelectron spectroscopy: application to a complex model catalyst *J. Phys. Chem. Lett.* **13** 11015–22
- [34] Braglia L, Fracchia M, Ghigna P, Minguzzi A, Meroni D, Edla R, Vandichel M, Ahlberg E, Cerrato G and Torelli P 2020 Understanding solid–gas reaction mechanisms by operando soft x-ray absorption spectroscopy at ambient pressure *J. Phys. Chem. C* **124** 14202–12
- [35] Soldatov M A, Medvedev P V, Roldugin V, Novomlinskiy I N, Pankin I, Su H, Liu Q and Soldatov A V 2022 Operando photo-electrochemical catalysts synchrotron studies *Nanomaterials* **12** 839
- [36] Castán-Guerrero C, Krizmancic D, Bonanni V, Edla R, Deluisa A, Salvador F, Rossi G, Panaccione G and Torelli P 2018 A reaction cell for ambient pressure soft x-ray absorption spectroscopy *Rev. Sci. Instrum.* **89** 054101
- [37] Mom R V, Falling L J, Kasian O, Algara-Siller G, Teschner D, Crabtree R H, Knop-Gericke A, Mayrhofer K J J, Velasco-Vélez J-J and Jones T E 2022 Operando structure–activity–stability relationship of iridium oxides during the oxygen evolution reaction *ACS Catal.* **12** 5174–84
- [38] Frevel L J, Mom R, Velasco-Vélez J-J, Plodinec M, Knop-Gericke A, Schlögl R and Jones T E 2019 In situ x-ray spectroscopy of the electrochemical development of iridium nanoparticles in confined electrolyte *J. Phys. Chem. C* **123** 9146–52
- [39] Kusoglu A and Weber A Z 2017 New insights into perfluorinated sulfonic-acid ionomers *Chem. Rev.* **117** 987–1104
- [40] Du N, Roy C, Peach R, Turnbull M, Thiele S and Bock C 2022 Anion-exchange membrane water electrolyzers *Chem. Rev.* **122** 11830–95
- [41] Grinter D C, Venturini F, Ferrer P, van Spronsen M A, Arrigo R, Quevedo Garzon W, Roy K, Large A I, Kumar S and Held G 2022 The versatile soft x-ray (VerSoX) beamline at diamond light source *Synchrotron Radiat. News* **35** 39–47
- [42] Penna M J, Mijajlovic M and Biggs M J 2014 Molecular-level understanding of protein adsorption at the interface between water and a strongly interacting uncharged solid surface *J. Am. Chem. Soc.* **136** 5323–31
- [43] Li Y, Zhang Y, Qian K and Huang W 2022 Metal–support interactions in metal/oxide catalysts and oxide–metal interactions in oxide/metal inverse catalysts *ACS Catal.* **12** 1268–87
- [44] Bazant M Z 2013 Theory of chemical kinetics and charge transfer based on nonequilibrium thermodynamics *Acc. Chem. Res.* **46** 1144–60

- [45] Hu J, Al-Salihi A, Wang J, Li X, Fu Y, Li Z, Han X, Song B and Xu P 2021 Improved interface charge transfer and redistribution in CuO-CoOOH p-n heterojunction nanoarray electrocatalyst for enhanced oxygen evolution reaction *Adv. Sci.* **8** 2103314
- [46] Tang B Y, Bisbey R P, Lodaya K M, Toh W L and Surendranath Y 2023 Reaction environment impacts charge transfer but not chemical reaction steps in hydrogen evolution catalysis *Nat. Catal.* **6** 339–50
- [47] Caballero-Briones F, Artés J M, Díez-Pérez I, Gorostiza P and Sanz F 2009 Direct observation of the valence band edge by in situ ECSTM-ECTS in p-type Cu₂O layers prepared by copper anodization *J. Phys. Chem. C* **113** 1028–36
- [48] Silva Olaya A R, Zandersons B and Wittstock G 2020 Restructuring of nanoporous gold surfaces during electrochemical cycling in acidic and alkaline media *ChemElectroChem* **7** 3670–8
- [49] Myneni S et al 2002 Spectroscopic probing of local hydrogen-bonding structures in liquid water *J. Phys.* **14** L213
- [50] Winter B, Weber R, Hertel I V, Faubel M, Jungwirth P, Brown E C and Bradforth S E 2005 Electron binding energies of aqueous alkali and halide ions: EUV photoelectron spectroscopy of liquid solutions and combined ab initio and molecular dynamics calculations *J. Am. Chem. Soc.* **127** 7203–14
- [51] Schultz J W and Hornig D F 1961 The effect of dissolved alkali halides on the raman spectrum of water¹ *J. Phys. Chem.* **65** 2131–8
- [52] Mähler J and Persson I 2012 A study of the hydration of the alkali metal ions in aqueous solution *Inorg. Chem.* **51** 425–38
- [53] Mancinelli R, Botti A, Bruni F, Ricci M A and Soper A K 2007 Hydration of sodium, potassium, and chloride ions in solution and the concept of structure maker/breaker *J. Phys. Chem. A* **111** 13570–7
- [54] Megyes T, Bálint S, Grósz T, Radnai T, Bakó I and Sipos P 2008 The structure of aqueous sodium hydroxide solutions: a combined solution x-ray diffraction and simulation study *J. Chem. Phys.* **128** 044501
- [55] Smith J D, Saykally R J and Geissler P L 2007 The effects of dissolved halide anions on hydrogen bonding in liquid water *J. Am. Chem. Soc.* **129** 13847–56
- [56] Schwartz C P, Uejio J S, Duffin A M, Drisdell W S, Smith J D and Saykally R J 2010 Soft x-ray absorption spectra of aqueous salt solutions with highly charged cations in liquid microjets *Chem. Phys. Lett.* **493** 94–96
- [57] Waluyo I, Nordlund D, Bergmann U, Schlesinger D, Pettersson L G M and Nilsson A 2014 A different view of structure-making and structure-breaking in alkali halide aqueous solutions through x-ray absorption spectroscopy *J. Chem. Phys.* **140** 244506
- [58] Näslund L-Å, Edwards D C, Wernet P, Bergmann U, Ogasawara H, Pettersson L G M, Myneni S and Nilsson A 2005 X-ray absorption spectroscopy study of the hydrogen bond network in the bulk water of aqueous solutions *J. Phys. Chem. A* **109** 5995–6002
- [59] Unutulmazsoy Y, Cancellieri C, Chiodi M, Siol S, Lin L and Jeurgens L P H 2020 In situ oxidation studies of Cu thin films: growth kinetics and oxide phase evolution *J. Appl. Phys.* **127** 065101
- [60] McCrory C C L, Jung S, Peters J C and Jaramillo T F 2013 Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction *J. Am. Chem. Soc.* **135** 16977–87
- [61] Hasnat M A, Siddika M, Uddin S M N, Alamry K A and Rahman M M 2021 Fabrication of IrOx immobilized glassy carbon surface for attaining electrocatalytic ascorbic acid oxidation reactions *Electrochim. Acta* **392** 138999
- [62] Kasian O, Grote J-P, Geiger S, Cherevko S and Mayrhofer K J J 2018 The common intermediates of oxygen evolution and dissolution reactions during water electrolysis on iridium *Angew. Chem., Int. Ed.* **57** 2488–91
- [63] Rossmeisl J, Qu Z W, Zhu H, Kroes G J and Nørskov J K 2007 Electrolysis of water on oxide surfaces *J. Electroanal. Chem.* **607** 83–89
- [64] Pfeifer V et al 2016 The electronic structure of iridium and its oxides *Surf. Interface Anal.* **48** 261–73
- [65] Pfeifer V et al 2016 The electronic structure of iridium oxide electrodes active in water splitting *Phys. Chem. Chem. Phys.* **18** 2292–6
- [66] Yamamoto S et al 2010 Water adsorption on α -Fe₂O₃ (0001) at near ambient conditions *J. Phys. Chem. C* **114** 2256–66
- [67] Cordero-Edwards K, Rodríguez L, Calò A, Esplandiú M J, Pérez-Dieste V, Escudero C, Domingo N and Verdager A 2016 Water affinity and surface charging at the z-cut and y-cut LiNbO₃ surfaces: an ambient pressure x-ray photoelectron spectroscopy study *J. Phys. Chem. C* **120** 24048–55