Journal of The Electrochemical Society

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Journal of The Electrochemical Society, 2020 **167** 054509

Perspective

Perspective—Outlook on Operando Photoelectron and Absorption Spectroscopy to Probe Catalysts at the Solid-Liquid Electrochemical Interface

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Operando X-ray Photoelectron and Absorption Spectroscopy (XPS and XAS) using soft (up to 2 KeV) and tender (2–10 KeV) X-rays applied to study functional materials for energy conversion has gone through great development in the last years and several approaches to different cell designs combined with instrumentation development now allow successful characterization of electrode-electrolyte interfaces under working conditions. An overview of the current state and challenges are presented along with an outlook into the direction that future development should take, which we expect would allow us to expand and complete our understanding of the liquid-solid electrochemical interfaces.

 [DOI: 10.1149/1945-7111/ab68d2]

Manuscript submitted October 21, 2019; revised manuscript received December 1, 2019. Published January 20, 2020. *This paper is part of the JES Focus Issue on Heterogeneous Functional Materials for Energy Conversion and Storage.*

The growing interest in new energy conversion and storage systems has triggered over the last decades the fast development of new techniques to study electrochemical interfaces to gain understanding in systems such as batteries,[1] fuel cells,[2] and electrochemical water electrolysers[3] among others. The main motivation to use Near Ambient Pressure (NAP) X-ray spectroscopies under operando conditions is that it allows us to investigate the (reversible or irreversible) changes of a working electrode. The changes in electronic structure of a working electrode allow us to describe the true working chemistry of an active interface, which cannot be accomplished otherwise due to the limitations of solely electrochemical tools. However, one must be able to tell apart changes corresponding to an active interface from other processes such as material corrosion and dissolution, and to characterize the electrochemical performance of the material under investigation. For this, investing in additional improvements beyond the current state of the art methodology and infrastructure of NAP spectroscopies is necessary.

Several techniques allowing the electrochemical interface characterization have been used to study adsorbed species at the interface and the surface catalysts state under reaction conditions. Infrared (IR) and Raman Spectroscopy have been extensively used to study the adsorbed surface species of reactants, intermediate and products on electrocatalysts' surfaces under operation.[4] With electrochemical nuclear magnetic resonance both the catalyst state and adsorbed species can be studied.[5,6] With electron paramagnetic resonance free radicals present under reaction conditions can be detected when radical decay and radical formation kinetics are such to keep the concentration above the detection limit.[7] X-ray diffraction at grazing angles allows characterization of the surface structure of catalysts under reaction conditions[8,9] (crystalline phases only). Electrochemical transmission electron microscopy can be used to collect imaging and diffraction data at the nanoscale having high spatial and temporal resolutions.[10] Scanning probe microscopies such as scanning tunneling and atomic force microscopies allow us to study catalysts surfaces under working conditions.[11,12] Other techniques and more detailed information on each one of them as well as the related challenges for operando measurements can be found elsewhere.[10,13–16]

Despite all the mentioned techniques to probe reaction intermediates and products, information on the electronic structure of electrocatalysts under working conditions are still necessary to achieve a mechanistic understanding at the atomic level and provide insights into a rational design of new and better electrocatalysts. X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS) provide unique tools to study the catalyst electronic structure. XAS is bulk sensitive when measured in Fluorescence Yield (FY) due to the high attenuation depth of soft X-rays (micrometer range), where electrodes with high surface/bulk ratio are needed to provide detectable contribution of surface species. Higher surface sensitivity is achieved by measuring XAS in electron yield due to the lower inelastic mean free path (IMFP) of electrons. Secondary electrons emitted by the sample can be collected close to the sample or by measuring the sample to ground current giving the Total Electron Yield (TEY). Additionally, emitted electrons can be measured using the spectrometer (specific kinetic energy) as for Auger electrons, known as Auger Yield (AY).[17]

Great advances in the understanding of electrocatalytic materials were achieved through surface science techniques where often ex situ characterization of electrocatalysts has been performed, ideally through the direct transfer between and electrochemical cell and a UHV chamber (no air exposure).[18,19] Despite the insights brought by ex situ characterization it has been shown that metastable species might only be present under reaction conditions.[20,21] Thus, ex situ post-analysis might leave behind metastable species that remain hidden when not analyzed during operation.

To gain knowledge about the dynamics of an interface using surface science spectroscopic techniques that typically needed UHV (10^{-8}–10^{-10} mbar), required the development of new setups able to measure at higher pressures and in the presence of liquid environments. In the 1970s–1980s Siegbahn et al.[22,23] used differential pumping stages that progressively reduce the pressure to a low-pressure range at the electron analyzer to perform for the first time XPS studies of liquids. Over the last decade, the development of new approaches to probe solid-liquid and solid-gas interfaces by photons under more realistic conditions and using synchrotron radiation has become a predominantly growing field of research.[3,13,24] With the development of Near Ambien Pressure (NAP) spectroscopies it is possible now to perform measurements under reaction conditions. Moreover, using synchrotron facilities enables the combination of XAS and XPS to probe the electrochemical interface.[3,25] By tuning

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the photon energy nondestructive depth profiling of chemical composition and relevant surface species can be studied (when beam-induced effects are absent or negligible). The combination of both XAS and XPS techniques using synchrotron radiation is a powerful tool to investigate electrocatalysts under reaction conditions, delivering new insights to the fundamental knowledge on the electrode-electrolyte interface at the atomic level.

In the next sections we discuss the present state and direction of the development of synchrotron operando XPS and XAS addressing the technical challenges focused on the characterization of catalysts at the (water-based) electrolyte-electrode interfaces. Moreover, we give an overview on the necessary next steps to consider for further development.

Current Status

To get information on the electronic structure of an electrocatalysts under reaction conditions different strategies can be used. XAS and XPS may be recorded by detecting photons or electrons from an electrode-electrolyte interface. Hard X-rays (also called tender X-rays when the photon energy is below 10 KeV) have been commonly applied to study electrocatalysts under reaction conditions (for solid-liquid interfaces). For instance, the use of a 15-nm-thick Si membrane which separates vacuum from the liquid as a working electrode (WE) in contact with a small volume of liquid has been reported.[26] X-rays (6 KeV) from a synchrotron radiation source (irradiated from the vacuum side of the membrane) were used to reach the solid/liquid interface. Photoelectrons emitted from the Si side exposed to the solution could pass through the thin Si membrane (and be detected) due to the high IMFP of the high kinetic energy (KE) photoelectrons.[26]

For first-row transition metals where the L-edges (2p-3d transitions) probe directly the unoccupied valence states (making it sensitive to the interaction with adsorbed species) measurements are done by using soft X-rays (energy range typically up to 2 KeV). Moreover, within this range L and M edges of most of the transition metals can be measured, and light elements (N, C, O, etc) can be probed under reaction conditions. For K-level based transitions, XAS can be measured by AY which is dominant for elements with $Z < 15$ while for L- and M-level transitions, AY can be measured for elements up to $Z = 50$.[27]

For the soft X-ray energy range UHV is typically required due to the low penetration depth of soft X-rays in air.[28] Thus, an X-ray transparent membrane (placed as close as possible to the sample, e.g. $\sim$ 1 cm) is used to separate the UHV of the X-ray source from the NAP-chamber[17] where higher pressures are used in the sample environment. This has made possible the investigation of solid-gas and solid-liquid interfaces using soft X-rays.[17]

To study electrocatalysts in operando conditions, one approach has been to use an electrochemical cell where the WE consists of an electrocatalyst of interest placed over a proton exchange membrane (PEM), where electrolyte flowing through the cell diffuses trough the membrane and reaches the electrocatalyst on the other side, which is kept at a 0.1 mbar of water pressure[20,29] (Fig. 1a). Although in this case the water on the WE is present as water vapor the cell design allows XAS and XPS measurements with soft X-rays and the detection of electrochemical reaction products formed at the WE, such as evolving gases, by a quadrupole mass spectrometer (QMS) directly attached to the XPS chamber.[20,29] A recent modification was reported for this cell where a Graphene layer is added on top of the catalyst (facing the vacuum side) which allows liquid water to be trapped between the membrane and the Graphene, forming a liquid film at the WE.[21,30] The investigation of IrO_x under reaction conditions by changes induced in the O K-edge using the PEM-cell design has unveiled the nature of the reactive oxygen species forming at the electrocatalyst surface during oxygen evolution reaction (OER).[20,21]

Another approach to measure operando XAS with soft X-rays has been to use 3-electrode flow cells using a Si_3N_4 membrane as a WE[31, 35–37] in direct contact with the liquid electrolyte (Fig. 1b). This interface resembles better the conventional electrochemical cell. XAS can be measured in FY (bulk sensitive) thought the X-ray transparent Si_3N_4 membrane. FY spectra obtained for materials with high surface/bulk ratio will be more sensitive to changes at the active surface. Moreover, secondary electrons that are generated near the electrode-electrolyte interface can be collected as TEY signal. This can be done by using the WE electrode as a collector of the secondary electrons emitted by the catalyst at the interface,[31,38,39] providing surface sensitive information of the active material (see Refs. 31,38,39 for detailed information).

To be able to measure XPS a holey Si_3N_4 grid (a window with an extensive arrays of holes) and an electron transparent bilayer graphene (BLG) membrane that separates the vacuum chamber from the electrolyte inside the cell, can be used as a WE[32] (see Fig. 1c). In this case the electrocatalyst of interest can be deposited directly on the BLG and can be studied with soft X-rays by XAS and XPS under reaction conditions, since the BLG allows photoelectrons coming from the interface to pass through and reach the analyzer.[32] XAS in FY and TEY (measured at the WE) can also be used to get bulk and surface sensitive information, respectively (as described above). Additionally, TEY can be collected outside the sample from the vacuum side of the BLG[32] giving information on the interface between the deposited material and the BLG.[32] A different cell for operando XAS measurements has been recently reported where an "out of chamber" electrochemical cell operates in a He atmosphere and XAS is measured by Fluorescence Yield.[33] The electrochemical cell is placed inside a He-flow box. The WE consist of an 4 μm Ultralene® (water thigh) with a 50 nm titanium-film/carbon-film for electrical contact. The studied material can be drop-casted onto this WE and measured trough the film[33] (see Fig. 1d). The approach allows the use of a more conventional electrochemical cell geometry and electrode assembly, and fast sample exchange.

A different method to measure XPS on an electrode under applied bias has been a "dip-pull" method where a thin liquid film of a few nm is created over a WE by immersing it in electrolyte and then pulling it out forming a meniscus across the WE surface (see Fig. 1e).[34] By this approach, using NAP-XPS spectra can be measured trough the thin liquid film using tender X-rays (since higher photon energy is necessary to probe the interface trough the water film). This configuration is preferred for the study of photoelectrochemical (PEC) interfaces, which require thicker active material films due to the diffusion length of the excited charge carriers.[40] It also allows investigation of the electrical double layer where the BE shift and the broadening of the XPS peaks of the solvent and a spectator specie in the solvent can be used to probe the potential drop across the interface.[41]

The liquid thin layer formed with the "dip-pull" method undergoes instability for faradaic reactions involving consumption of the electrolyte, as in OER, due to the mass transport limitations imposed by the thin-electrolyte film.[42] However, the thin layer can be partially stabilized by the addition of a supporting electrolyte of non-interacting salt enabling the study of electrocatalysts for gas evolution reactions to some extent.[42]

An important aspect to consider during operando investigations of liquid-solid interfaces using NAP-spectroscopy is that significant number of radicals might be produced by water radiolysis due to the interaction with the beam.[43] These radicals may react with the studied catalyst or interfere with the reaction being studied. The degree of radiolysis and interference of radiolytic products (which for water are H_2 and H_2O_2) depends strongly of the system under investigation and the volume of solution that is irradiated. Thus, it will be different for different cell designs.[43] This can be minimized by using a small volume flow cell where the electrode-electrolyte interface can be continually renewed.[43] Here, a flow cell design using Si_3N_4 as a substrate for the catalyst (like in Figs. 1b and 1c) provides the required geometry to minimize radical interaction with the WE. The different types of cell have different characteristics and are summarized in Table I.

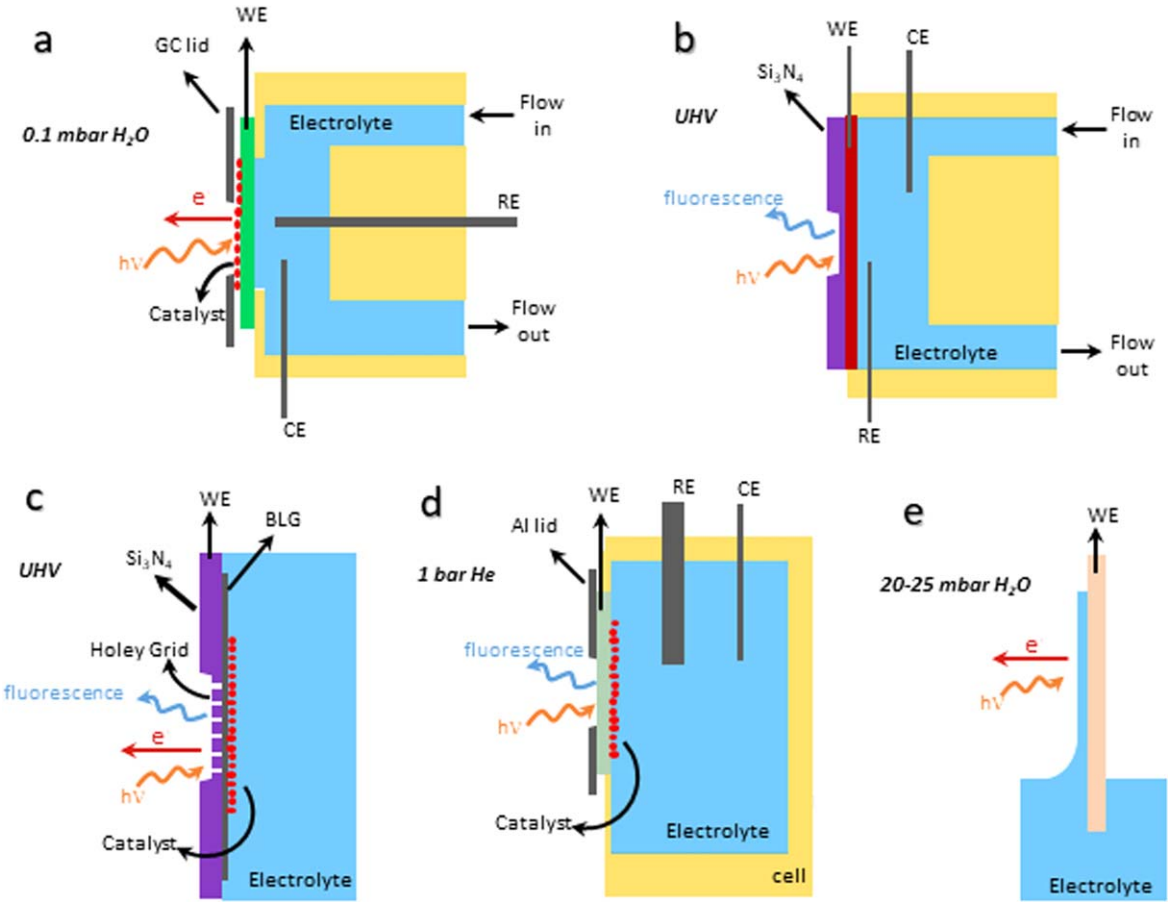

Figure 1. Schematic representation of a 3-electrode (small volume) flow-cell (a) where the WE consists of a catalyst deposited on a PEM that separates the electrolyte from the NAP-chamber, with the catalyst on the NAP side under 0.1 mbar water vapor (as in Ref. 20), (b) where the WE consists of a thin film on a Si_3N_4 membrane (that separates the liquid from UHV), with the film in direct contact with the electrolyte (as in Ref. 31), (c) a WE consisting of NPs deposited on a BLG placed on a Si_3N_4 holey grid (that separates the liquid from UHV), with the catalyst in direct contact with the electrolyte (as in Ref. 32). (d) A static "out of chamber" cell where the WE consist of a catalyst deposited on to a watertight 4 μm Ultralene® film with a 50 nm titanium-film/carbon-film for electrical contact, with the catalyst in direct contact with the electrolyte (as in Ref. 33) and the cell placed in a He flow-box. (e) A WE of a 3-electrode "dip-pull" static cell (as in Ref. 34) where the catalyst is in contact with a thin-liquid film (*the thin-liquid film is only showed on one side of the WE*) under 20–25 mbar water vapor.

The flow cell design with a holey Si_3N_4 grid and a BLG as a WE compiles several positive characteristics: i) It resembles a regular 3-electrode electrochemical cell (WE in direct contact with the electrolyte); ii) the continuous flow allows constant removal of radiolitic products and iii) both XPS and XAS can be measured using soft and tender X-rays. For this reason, in the next section we focus on this type of flow-cell design.

Future Needs and Prospects

For some electrolytes, slightly different cell geometries and reference electrodes (REs) might give slightly different over potentials for the same surface processes.[44] For a complete picture the next logical step is the upgrading of the electrochemical cell to a suitable design to perform kinetic studies using the same cell geometry and WE as in the NAP spectroscopy setup. With the current cell-geometries this kind of studies is not possible because these cells do not have well-defined hydrodynamics at the WE.[45] New cell designs that fulfill this requirement (for details see Ref. 45) would provide *genuine operando* measurements where spectroscopic information can be readily linked to the more conventional and well-established electrochemical experiments (describing reaction performance). This is a main necessary step to develop better understanding of reaction mechanisms, enable rational design of new catalysts and contribute to the development of new technologies.

Secondly, on-line reaction products analysis implemented to operando XPS and XAS should also be considered to get combined electrocatalytic activity and selectivity with electronic structure information. Combination of XPS and XAS measured under reaction conditions with techniques such as Gas Chromatography (GC), High-performance liquid chromatography (HPLC), Differential Electrochemical Mass Spectrometry (DEMS), depending on the reaction studied and cell geometry, seem feasible candidates to complement and expand our understanding of the electrode-electrolyte interface under operation. The combination with IR or Raman spectroscopies, although challenging regarding instrumental design and geometry, seem also an attractive option. It would allow us to probe surface intermediates of the electrochemical reaction along with the catalyst surface electronic state.

The combination of synchrotron-based spectroscopies and product analysis is particularly useful for a better understanding of the relation between catalyst surface species and its activity/selectivity. For this, having enough surface area to detect products with the current existing electrode and cell designs remains a challenge. The use of dispersed NPs[20,21] or other high surface area materials (e.g. mesoporous)[46,47] could provide the required surface area for product detection.

An important challenge is the improvement of the chemical stability of the BLG at the WE. For certain reactions like OER the evolving oxygen may react with the BLG by oxidizing it.[3] Moreover, radiolitic products may attack the BLG creating defects

Table I. Summary of different types of electrochemical cells for soft and tender X-ray operando XPS and XAS.

Type of cell and use	Type of measurement	Cell characteristics	
Catalyst/PEM/Graphene flow cell.[20]	XPS and XAS (TEY and PAY) Catalyst characterization. Soft X-rays.	WE: Thin films and nanoparticles. On-line QMS. Charge transport limitations through the membrane. Anodic corrosion of Graphene.	Suitable for gas evolution reactions and electrodeposition studies.
Catalyst/Si3N4-window flow cell.[31]	XAS (TEY and FY). - Interface and catalyst characterization. Soft X-rays.	WE: thin films and nanoparticles.	Removal of radiolitic products by continuous flow[a)]
Catalyst/BLG/Si3N4-holey window flow cell.[32]	-XPS and XAS (TEY and FY). Catalyst Characterization. Soft X-rays.	WE: thin films and nanoparticles. Anodic corrosion of Graphene.	
''dip-pull" thin liquid film cell.[34]	XPS Double layer/Interface and Catalyst characterization. Tender X-rays.	WE: Solid material of any thickness. Mass and charge transport limitations (*parallel to the liquid thin-film*).	Suitable for PEC interfaces, adsorbate studies and electrical double layer
''out of chamber" cell.[33]	XAS (FY) Catalyst characterization. Tender X-rays.	WE: Nanoparticles disperse in high surface area supports.	Suitable for gas evolution reactions[a)]

a) On-line gas/liquid product analysis can potentially be implemented.

and holes, allowing the liquid into the UHV chamber.[43] Therefore, lowering the water-beam interaction is also a key necessity, particularly in the case of higher-flux beam lines. For this, technical improvements on equipment's performance are needed, such as faster acquisition of XPS and XAS combined with better electron analyzers of higher sensitivity to minimize the time of exposure of the electrolyte to the beam and allow faster data acquisition with reliable signal/noise ratio. In general, this would also allow better evaluation of beam-sensitive materials. In this sense, further instrumentation development (e.g. superior analyzers with improved acceptance angle and detectors) would meet the requirements for an improved setup to study the dynamics of liquid-solid electrochemical interfaces. Current developments include laser-pump/X-ray-probe (called "pump–probe") for time-resolved XPS[48] and NAP-XPS.[49] When fast measurements are not possible however, minimizing exposure and continuous displacement of the sample (so that fresh different spots are measured) seem to be an effective strategy to make beam damage effects small or negligible[17,21,30] (homogeneity/heterogeneity of the sample must be considered).

Additionally, other materials might be found to be good candidates to replace the BLG in the WE. Plenty of 2D materials have been synthesized or theoretically predicted however, some requirements need to be fulfilled to replace the BLG in an electrochemical liquid flow cell for NAP spectroscopies applications. These include good electrical conductivity (for a monolayer or bilayer), electron transparency (for XPS measurements), mechanical resistance and elasticity (to resist separating liquid electrolytes from UHV), and good chemical resistance (to be used under harsh electrochemical conditions in different types of electrolytes). One possible candidate is the predicted[50] and later synthesized,[51] borophene, a single layer of boron atoms. The different phases of borophene that have been synthesized up to now show metallic properties and due to the structural polymorphism of borophene, unique mechanical properties have been found.[52] Despite its tendency to oxidation due to its high surface activity, several approaches have been studied to improve stability of borophene and numerous potential applications in the energy field have been investigated.[52] Detailed information on the state-of-the-art challenges for synthesis, characterization and potential applications of borophene can be found elsewhere.[52]

A second yet less developed candidates are the recently discovered two—dimensional (2D) early transition metal carbides, nitrides and carbonitrides, called MXenes, of the formula $M_{n+1}X_nT_x$, (where M is a transition metal, X is C and/or N, and T_x denotes surface functionalization).[53] First time reported in 2011,[54] MXenes have gained attention due to their metallic character, high-temperature stabilities, and good mechanical properties. MXenes are produced by the selective etching of the groups III −VI elements layers from MAX phases (layered, hexagonal early-transition-metal carbides and nitrides). Their high potential comes from their diversity, since more than 70 different MAX phases exist experimentally,[53] from which at least 20 different types of MXenes have been already obtained and several more have been theoretically predicted.[55] In MXenes, $n+1$ layers of M cover n layers of X in an $[MX]_nM$ arrangement. The simplest MXene has then M_2X structure with 3 atomic layers predicted.[55] This makes single layers of MXenes, in the context of replacing a BLG, better candidates to be considered for high photon flux and tender X-rays synchrotron applications.

For practical applications, large-scale experimental growth and transfer of a single layer to the desired substrate has still to be improved for both borophene[52] and MXenes.[55] Moreover, the interaction between the active material and these 2D material has yet to be considered and studied (the active material under investigation needs to be stable under reaction conditions when deposited onto the 2D material). Thus, BLG remains still the material of choice for NAP spectroscopy applications.

Finally, we want to emphasize that the combination of experiments with theoretical studies is mainly necessary to reach an understanding at the atomic level. The current state and challenges of theoretical modeling applied to the electrochemical interfaces has been recently addressed and can be found elswhere.[56] Further use and growth of computational spectroscopy is a necessary and key element in the interpretation of experimental operando spectroscopic data due to the complexity of the investigated materials and the dynamic electrochemical interfaces. Many examples of the relevance of computational spectroscopy can be found in the literature. Particularly notable has been its utilization in the investigations of IrO_x-based materials under electrochemical reaction conditions.[20,21,57,58]

Summary

The current state of the art in instrumental and technical development of synchrotron radiation-based operando XAS and XPS makes it possible to study electrochemical interfaces under working conditions. However, some improvements are still necessary to build a complete picture of operating electrocatalysts at the solid-liquid interface. The summary of necessary next steps is as follows:

- Development of a new cell compatible with a NAP setup to perform off-line kinetic studies using same cell geometry and WE as in the NAP spectroscopy setup, to make a direct link between reaction performance and spectroscopic measurements (genuine operando).
- Technological improvement of analyzers to lower the water-beam interaction by developing faster data acquisition and higher sensitivity to reduce beam induced radiolysis and beam damage.
- On-line reaction products analysis (according to the reaction under investigation and cell geometry) to combine with operando XPS and XAS measurements.
- Improvement on the chemical and mechanical stability of the layer (BLG or other possible 2D material candidates) at the WE.
- Improve the mass and charge transport for the thin-liquid film configuration and PEM -based cell configuration.

Acknowledgments

The authors gratefully acknowledge the Max-Planck Gesellschaft for generous founding and Helmholtz-Zentrum Berlin for providing support of the in situ electron spectroscopy activities of the Fritz Haber Institute (FHI) at BESSY II beamlines.

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