

# *In situ* spectroscopy and diffraction to look inside the next generation of gas diffusion and zero-gap electrolyzers

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Electrolyzers allow for the sustainable conversion of chemical waste (e.g. nitrous oxides,  $\text{NO}_x$ , or carbon dioxide,  $\text{CO}_2$ ) into valuable chemicals or building blocks (e.g. ammonia or hydrocarbons). There is a constant search for new and improved materials (electrocatalysts) that can facilitate these complex chemical reactions with optimized activity, selectivity, and stability. In order for electrolyzers to become economically feasible, it is of utmost importance that they perform at high current density  $> 100 \text{ mA/cm}^2$  (activity), since this scales with chemical reaction rate. However, if high current density is only achieved for a short period of time (stability), the electrolyzer has to be regenerated, which is a costly endeavor. For this purpose, chemical engineers have focused on gas diffusion electrodes (GDE) or membrane electrode assemblies (MEA) in recent years, but these cell configurations are prone to rapid deactivation and salting. *In situ* spectroscopy and diffraction techniques can shed light on the parameters that influence catalyst (de)activation, but application of the technique of choice depends heavily on the reaction conditions and hence is not straightforwardly applied to electrolyzers that operate at high current density. This review addresses the recent developments within the community for *in situ* characterization of GDE and MEA electrolyzers, and opportunities for future studies are highlighted, which are aimed to stimulate discussion and advancement of the field.

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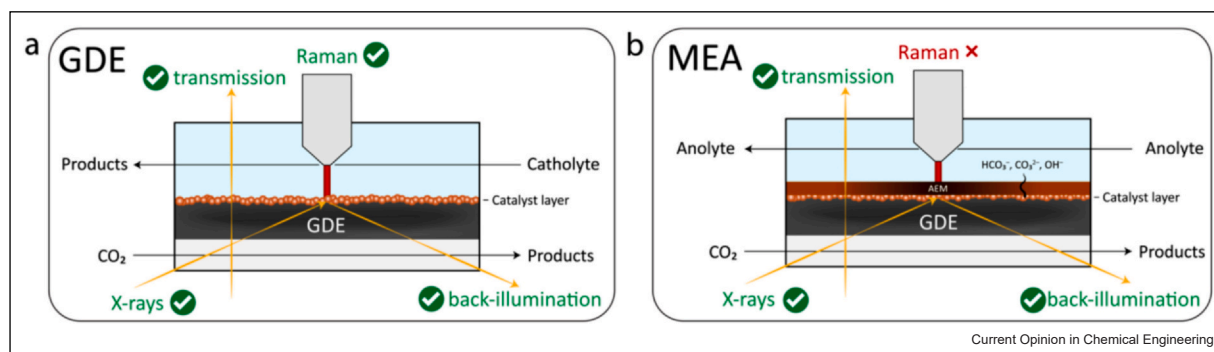
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## Introduction

Electrolyzers promise to play a pivotal role in the energy transition, and have already shown tremendous potential for the production of renewable hydrogen and other valuable compounds [1,2]. For example, electrochemical  $\text{CO}_2$  reduction (e $\text{CO}_2$ R) is a promising method of re-using atmospheric  $\text{CO}_2$  to sustainably produce chemical building blocks as a means to store (excess) renewable energy in chemical bonds [3,4]. In recent years, significant progress has been made in terms of two main descriptors of catalysis: electrocatalytic activity (current densities 10–100  $\text{mA/cm}^2$ ) and selectivity (approaching unity) of electrolyzers [5]. It has been shown that activity and selectivity are heavily influenced by catalyst design strategies, such as grain boundaries, nanoparticle morphology, and electrocatalyst composition [5–8]. However, in order for the technological development and implementation of electrolyzers to take flight, the production rates have to be scaled up to current densities of 500–1000  $\text{mA/cm}^2$  for prolonged operation time ( $> 500$  hours) [9–11]. In order to reach these higher current densities, recent cell design strategies are being explored to go beyond traditional H-shaped electrochemical cells [12–14]. Porous gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) have gained extra attention, because they circumvent mass transport limitations associated with the low solubility of  $\text{CO}_2$  in aqueous media [15,16]. Owing to their high  $\text{CO}_2$  availability and relatively low cell resistance [17], GDEs and MEAs can run at elevated current densities ( $> 100 \text{ mA/cm}^2$ ), which translates into more efficient  $\text{CO}_2$  conversion into chemicals [18]. However, despite their increased performance, the presence of a delicate gas–solid (MEA) or gas–solid–liquid (GDE) interface has a detrimental effect on the third descriptor of catalysis: stability [19–22]. It is observed that GDEs and MEAs deactivate rapidly, often ascribed to problems such as flooding, carbonate salt formation, or catalyst deactivation [17,23–25].

To investigate the degradation mechanisms of GDEs and MEAs, *in situ/operando* spectroscopy and characterization are necessary as they can increase our understanding of (de)activation events on/in the porous electrodes during e $\text{CO}_2$ R and other electrochemical reactions of interest [26]. However, we have to realize that *in situ* characterization at high current densities poses

Figure 1



Schematic representation of the potential of *in situ* vibrational and X-ray spectroscopy for detailed characterization of (a) GDE and (b) MEA electrolyzers. We hypothesize that the cell design of typical GDE electrolyzers allows for the application of Raman spectroscopy, as well as XRD and XAS in transmission and back-illumination mode, whereas the ‘sandwich structure’ of solids in a MEA cell limits the use of possible *in situ* vibrational spectroscopy methods to study the active gas–solid interface between the CL and the AEM. In this review article, recent advances in and guidelines for *in situ* characterization of GDE and MEA electrolyzers will be discussed.

additional challenges that potentially influence the measurements, such as substantial heating and bubble formation [27]. Next to that, this might also induce faster (de)activation of the electrocatalyst, highlighting the need for increased spatiotemporal resolution of the characterization method of choice. Therefore, *in situ* characterization of GDEs and MEAs is a whole different game compared with *in situ* characterization in small-scale electrolyzer cells (area 1–10 cm<sup>2</sup>, current density 10–100 mA/cm<sup>2</sup>), and the rules of the game tend to change during the measurement.

In general, *in situ/operando* spectroscopy and diffraction have already proven to be successful in revealing and understanding electrocatalyst properties by probing adsorbed intermediates and monitoring surface reconstruction [26,28–30]. For example, previous work has shown that vibrational spectroscopy (Raman and infrared) and X-ray-based techniques (X-ray diffraction, XRD, and absorption spectroscopy, XAS) are viable options for *in situ* characterization of both surface and bulk events during eCO<sub>2</sub>R in small-scale electrochemical cells (area 1–10 cm<sup>2</sup>) [31–35]. However, applying the same techniques to GDEs and MEAs requires delicate cell engineering to maximize the detected signal and minimize attenuation of the incoming and outgoing beam, and is therefore not an easy endeavor [36]. Furthermore, the presence of porous (carbon) layers potentially complicates the measurements even more. At present, only a few articles in the electrocatalysis community report *in situ* characterization of MEAs, whereas *in situ* spectroscopic investigations of GDEs have not been reported to the best of our knowledge.

In this perspective, we highlight recent advances in *operando* and *in situ* characterization of MEAs at high

current densities (> 100 mA/cm<sup>2</sup>) and hypothesize that for porous GDEs, both Raman and X-ray characterization techniques can be readily applied from a technological and engineering point of view, as pictured in Figure 1a. However, for MEA-based systems, the layered sandwich structure of solids can complicate vibrational spectroscopy methods, making XRD/spectroscopy techniques a more attractive option. We highlight recent reports on *in situ* XRD and XAS characterization of MEAs, and provide guidelines for the application of *in situ* characterization techniques beyond XRD and XAS, both at synchrotrons and in the lab [37]. The first highlighted article shows by synchrotron-based grazing incidence XRD and clever cell design that carbonate salts form at the gas–solid interface, which has a drastic influence on the potential and the Faradaic efficiency, and subsequently causes deactivation of the MEA [38]. The second article discusses the effects of unwanted cations near the cathode surface, to show how the catalyst structure during eCO<sub>2</sub>R can be assessed by *in situ* X-ray spectroscopy [39]. The third article shows the use of soft X-ray spectroscopy to study the composition and active phase of Zn-modified Cu catalysts [40]. Based on these recent reports, we envision how *in situ/operando* characterization of GDEs and MEAs can aid the energy transition by revealing the (de)activation of the active electrocatalyst in these promising electrolyzer cell designs, allowing these architectures to reach their full potential.

### Investigating gas diffusion electrode deactivation with X-ray scattering and diffraction

GDEs can reach very high current densities > 100 mA/cm<sup>2</sup> because it decouples the CO<sub>2</sub> supply from the CO<sub>2</sub> solubility limitations in the aqueous electrolyte [15,16]. In GDEs, the CO<sub>2</sub> gas is fed through the back of a porous

electrode, after which a three-phase boundary is formed at the gas–liquid–solid interface, resulting in high conversion rates (i.e. current density). It is well-known that the deactivation of MEAs and GDEs is due to flooding of the gas compartment with aqueous electrolyte and salt deposition in the GDE [17,41], but there is limited knowledge as to how or why this happens and how to prevent it from happening. Multiple studies have hypothesized that flooding occurs because of increased wetting of the GDE, instigated by cathodic potentials (electrowetting) or loss of hydrophobicity due to, for example, oxidation of the carbon gas diffusion layer (GDL) or delamination of the catalyst layer (CL) [42,43]. Subsequently, carbonate salt crystals can form in the pores of the GDL, potentially causing irreversible structure changes and hindering CO<sub>2</sub> availability [44,45].

To elucidate the deactivation mechanism, the Seger group recently performed a study on a MEA system using *operando* X-ray analysis, which enabled them to closely study the water and salt content in the GDE [38] (Figure 2). Using wide-angle X-ray scattering (WAXS), they were able to correlate the change in signal from amorphous phases to the change in GDE electrolyte content, by exploiting the fact that the other amorphous phases did not change during the measurement. Because of this, the electrolyte content could be mapped from the membrane to deep (~100 μm) inside the GDE by continuously measuring on a vertical line at different positions during eCO<sub>2</sub>R. Simultaneously, the GDE salt content was determined from the WAXS pattern, the Faradaic efficiency was tracked using gas chromatography, and the voltage was monitored during the experiment. Combining these data resulted in new insights into MEA deactivation: the carbonate salt formation seemed to precede the flooding of the GDE. We envision that other aspects of such MEAs can be investigated in different measurement geometries and through combinations of (X-ray) techniques. For example, in transmission X-ray characterization geometry, the full MEA stack can be analyzed simultaneously (Figure 1b). For this purpose, high-energy X-rays are necessary to ensure proper penetration through the MEA stack, but we anticipate that comparing and combining different measurements will enable researchers to draw a more complete picture of electrolyzer (de)activation. For example, XAS and XRD can be readily combined in such a transmission configuration to probe catalyst structure (XRD) and composition (XAS) simultaneously, for which the design of a proper *in situ* cell is a challenging endeavor.

### Investigating catalyst structure and composition with hard X-ray spectroscopy

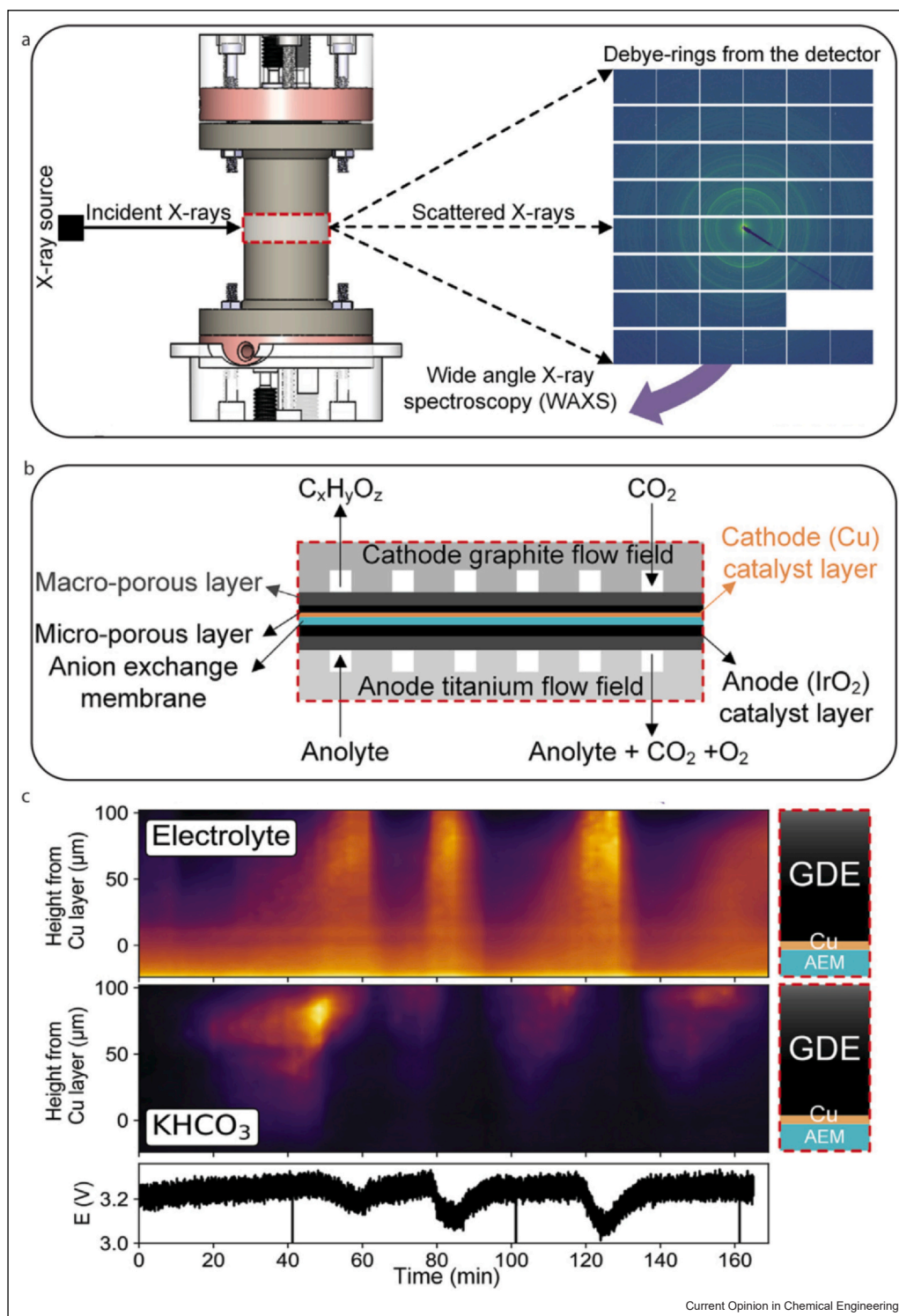
Considering that carbonate salt formation is a cause for GDE performance degradation, there is a strong

incentive to further investigate the reason why carbonate salt formation happens [44]. For carbonate salts to form, CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> ions require the presence of cations (K<sup>+</sup>) in order to precipitate in the pores of the GDE. In MEA-based systems, the use of an anion-exchange membrane (AEM) and a zero-gap configuration can make it easy to overlook or even disregard the influence of cations near or in the GDE. In this light, the Mayer group recently investigated cation effects at the cathode in a catholyte-free MEA-based system [39]. Using a range of different anolyte concentrations (0.05–1.0 M KOH, and pure aqueous electrolyte), they used *in situ* XAS at the Cu K-edge to track the copper catalyst and its chemical composition during eCO<sub>2</sub>R. All resulting spectra closely resembled metallic copper, which indicates that the catalyst is completely reduced during eCO<sub>2</sub>R. However, since XAS is a bulk technique [28], the acquired data did not describe the events on the surface of the catalyst and are therefore inconclusive as to what happens at the active site. To gain a better understanding of cation effects on catalyst structure, *quasi in situ* X-ray photoelectron spectroscopy (XPS) was used as a complementary surface-sensitive technique. It is noted that *in situ* XPS measurements are virtually impossible because of the need for ultrahigh vacuum, and the very short mean-free path of photoelectrons, which makes it impossible for XPS to investigate ‘buried’ interfaces [26,47]. Instead, the authors have taken samples and handled them inside an inert glovebox to prevent oxidation and mimic their representative oxidation state during eCO<sub>2</sub>R as much as possible. Interestingly, this approach inferred a correlation between increasing anolyte concentration and the presence of Cu<sup>0</sup> at the surface. This means that despite the use of an AEM, cations are still able to migrate from the anolyte to the GDE surface and affect the catalyst structure during eCO<sub>2</sub>R. This highlights the complexity of *in situ* characterization of MEA electrolyzers, which obviously depends on multiple parameters (e.g. electrolyte concentration, current density) over various length scales (e.g. surface versus bulk) that are ideally all probed simultaneously through clever cell design and combinations of characterization techniques (Figure 3).

### Guidelines for cell design

We wish to note that (unfortunately) one size does not fit all in the case of cell design for *in situ* characterization of GDE and MEA electrolyzers. The cell design strategy depends largely on the scientific question that needs to be answered, and the related characterization technique of choice. For example, when the scientific question can only be answered by soft X-ray spectroscopy techniques [47], the experimentalist has to pay special attention to the cell design and cannot straightforwardly use the cell design described above for *in situ* WAXS (Figure 2) [46]. Luckily, a recent study showed that it is possible

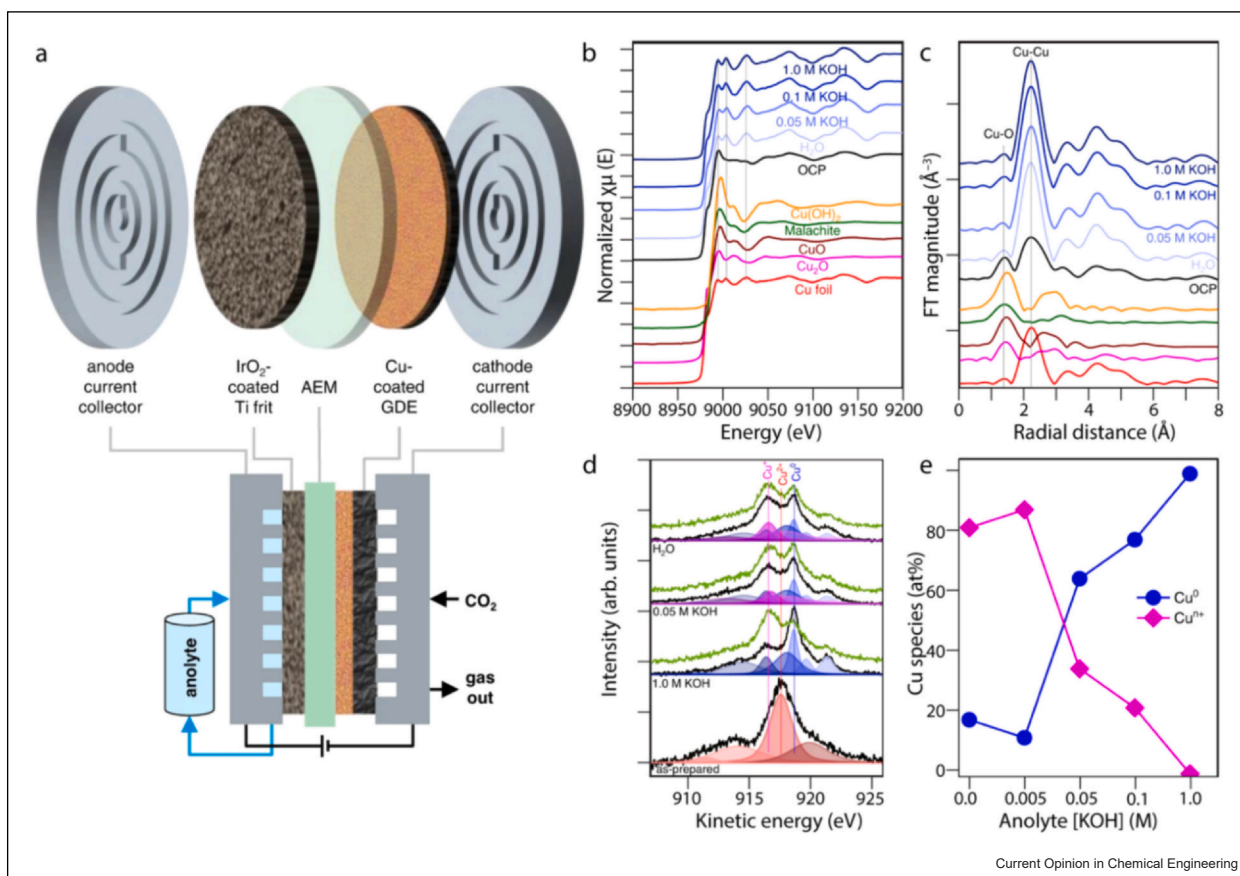
Figure 2



Operando wide-angle X-ray scattering study of electrolyte content in membrane electrode assemblies. **(a, b)** Custom *in situ* XRD and scattering GDE cell used to monitor the gas–solid interface with WAXS and **(c)** results showing water oscillations during electrolyzer operation. Figure adapted with permission from Refs [3,4]. Copyright © 2023, Joule.



Figure 3



*In situ* X-ray spectroscopy characterization of copper-based MEA cells reveals bulk and surface Cu oxidation state in different anolyte compositions through *in situ* XAS at the Cu K-edge and quasi *in situ* XPS. **(a)** Schematic of the MEA electrolyzer. **(b)** *In situ* X-ray absorption near-edge structure (XANES) spectroscopy at the Cu K-edge in different concentrations of anolyte, including reference spectra of common compounds. **(c)** Radial distribution function of the data in **(b)**. **(d)** Quasi *in situ* XPS data in different anolyte concentrations, and **(e)** the quantitative result of the at% Cu species from the XPS fitting.

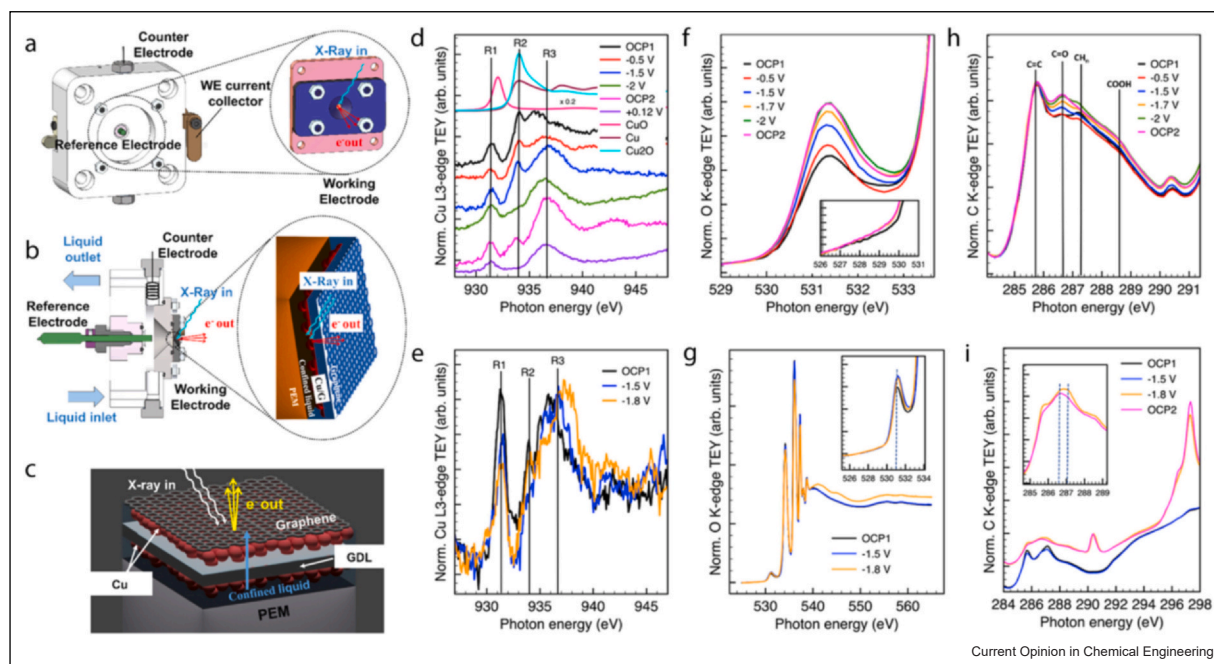
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to engineer such a cell to successfully perform *in situ* soft X-ray spectroscopy on zero-gap MEA electrolyzers (Figure 4) [40]. In this cell design, the interaction with the aqueous electrolyte was minimized through a graphene sandwich structure, which allowed for measurements in fluorescence mode at the front of the CL. The soft X-rays allowed the researchers to study the Zn-doped Cu electrocatalyst at the Cu L-edge as well as the O and C K-edges, thereby revealing the origin of the role of Zn on the electrocatalytic activity. It was found that Zn is initially doped in the oxidized Cu electrocatalyst, but after *in situ* activation, Cu and Zn form alloyed structures in the presence of stabilized Cu(I)-O species. This example opens up avenues for *in situ* investigation of active electrocatalysts through a variety of soft X-ray spectromicroscopic techniques that are not commonplace in the electrocatalysis community, including but

not limited to resonant inelastic X-ray spectroscopy [47] and ptychography [48]. Based on the recent studies that were highlighted in this short review article and our own insights, we have drafted guidelines for *in situ* characterization of GDE and MEA electrolyzers. We strongly encourage the community to include complete descriptions of their *in situ* setups, including detailed schematics of the cells used. Such details are often lacking in the literature, and could facilitate follow-up work by other groups to move the field toward standardization of techniques.

1. Decide on the characterization technique(s) based on the scientific question(s).
2. Determine the energy-dependent penetration of the X-rays through the electrolyte, porous GDL, membrane, and CL (transmission mode).

Figure 4



Soft X-ray spectroscopy of MEA electrolyzer. (a,b) Cell design, (c) schematic of the measurement mode. (d–i) *In situ* near-edge X-ray absorption fine structure (NEXAFS) at Cu L-edge, O K-edge, and C K-edge.

Figure adapted with permission from Ref. [38]. Figure adapted with permission from Ref. [37]. Copyright © 2023, ACS.

- Determine the energy-dependent penetration of the X-rays through the GDL and catalyst (back-illumination mode).
- Maximize the signal-to-noise ratio based on 2/3, for example, by using thinner carbon GDL.
- Ensure sufficient electrocatalytic performance by minimizing mass transport limitations and other kinetic effects, for example, by choosing a larger catholyte chamber based on 2/3. For best practices of GDE and MEA, see Ref. [11].
- Monitor common deactivation descriptors for GDE and MEA electrolyzers, such as flooding and salting.
- Account for potential beam damage, and adjust acquisition time to maximize signal-to-noise ratio.
- Quantify the liquid and gaseous reaction products during the spectroscopy or diffraction measurements (online), or offline in the same cell using standard product quantification techniques (e.g. chromatography).

### Characterization of gas diffusion electrodes and membrane electrode assemblies beyond the state-of-the-art

The recent work highlighted in this review shows the potential of X-ray-based techniques (especially XRD and absorption) as powerful methods to investigate MEA and GDE systems *in situ/operando*. However, we wish to note that all discussed experimental work

involving X-rays was performed at a synchrotron facility. Because of the limited time and space at these locations, this significantly hinders further development of such techniques for stability assessment of electrolyzers at high current densities, which is necessary for the large-scale implementation of electrolyzers ( $m^2$  electrolyzers). Therefore, we state that it is imperative that more accessible, in-house experiments are designed in order for electrolyzers to be implemented on industrial scale and take the next step in their technological development. For this purpose, chemical engineers are required to develop dedicated *in situ* cells that (1) optimize signal-to-noise ratio and (2) allow for the combination of characterization techniques while (3) operating at high current densities ( $> 100 \text{ mA/cm}^2$ ) and prolonged operation time for stability assessment at low-energy lab-based X-ray sources. It is our vision that only then the next generation of electrolyzers can be implemented on a large scale to aid the energy transition.

Furthermore, (X-ray) techniques beyond the state-of-the-art (XRD and XAS) have to be considered to draw a more complete picture of electrocatalyst (de)activation at high current densities. We should also not stare ourselves blind on the workhorse techniques, because despite the fact that they do give high-quality information on catalyst (de)activation, they have their own specific requirements and limitations (e.g. crystallinity for XRD).

Since catalyst (de)activation is a multiscale event, it is necessary to think outside the paved pathways and investigate the application of uncommon techniques with optimal spatiotemporal resolution. Examples include, but are not limited to, small-angle X-ray scattering (to elucidate size and shape), [49] pair distribution function analysis (to investigate amorphous structures) [50], and X-ray microscopy (to investigate composition in porous structures) [48]. We urge the community to reach out to other disciplines where these techniques have been widely applied (e.g. heterogeneous catalysis, nanomaterials science), and investigate ways to bring them to the electrocatalysis community in order for electrolyzers to take the next step toward the development of stable performance at high current density.

## Data Availability

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

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ward van der Stam reports financial support was provided by Dutch Research Council.

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