# Operando methods for the elucidation of electrolyte effects in electrocatalysis

Kolmeijer, K.E.; Mom, R.V.

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Review Article

# *Operando* methods for the elucidation of electrolyte effects in electrocatalysis

Kees E. Kolmeijer and Rik V. Mom

The electrolyte pH, ion composition, and solvent are important design parameters in electrocatalytic systems, which directly impact the system's catalytic activity, selectivity and stability. However, the relationship between the electrolyte composition and electrocatalytic performance is complex, and at present difficult to predict. To elucidate the underlying principles that govern electrolyte effects in electrocatalysis, *operando* techniques capable of resolving the active site structures at the electrode–electrolyte interface play a crucial role. Here, we review the current capabilities of these *operando* techniques and analyze how they can be used to find the rules of the game for electrolyte engineering.

**Addresses**
Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC, Leiden, the Netherlands

Corresponding author: Mom, Rik V. (r.v.mom@lic.leidenuniv.nl)

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## Introduction

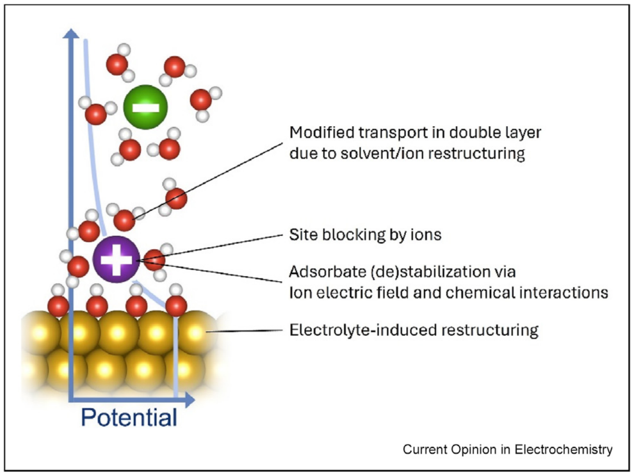
In electrocatalytic processes such as water electrolysis, chlorine production, or the conversion of $CO_2$ to useful chemicals, the catalytic turnover almost invariably occurs at the electrode–electrolyte interface. From this, it follows that the interfacial electrolyte is an integral part of the active sites, which can be used to modulate the activity, stability, and selectivity of electrocatalytic systems. Indeed, it has been found that the choice of ions [1–8], pH(9–12), and solvent [13–15] in the electrolyte has a significant impact on the catalytic performance of a wide variety of reactions, including the oxygen evolution reaction [2,3,11,16], oxygen reduction reaction [6,8], hydrogen evolution reaction [4,7,12], nitrate reduction reaction [5], methanol oxidation reaction [6], and $CO_2$ reduction reaction [1,13,15,17].

While this makes it clear that electrolyte engineering is a useful tool to optimize electrochemical reactions, the electrolyte effects on performance show a complex dependence on the electrolyte composition and electrode structure. For example, the effect of cations on the hydrogen evolution reaction (HER) can be inhibiting or promoting, depending on the pH of the electrolyte [10]. Similarly, the optimal choice of cations depends on the choice of electrode material, showing a performance trend of $Cs^+>K^+>Na^+>Li^+$ for Pt electrodes, but $Li^+>Na^+>K^+>Cs^+$ for Au electrodes [17]. This interrelation between practical design parameters creates a complex parameter space, making electrolyte optimization a trial-and-error process. To create simple, generally applicable design rules to navigate the parameter space in electrolyte engineering, it is therefore important to understand the underlying molecular-level mechanisms that cause electrolyte effects in electrocatalysis.

The main challenge in identifying these mechanisms is that the structure of the interfacial electrolyte strongly deviates from that of the bulk electrolyte, due to the electrostatic and chemical interactions of the interfacial electrolyte species with the electrode surface [18]. These interactions generally result in the attraction of either cations or anions towards the surface, forming an electric double layer (Figure. 1). Meanwhile, also the solvent restructures at the interface in order to optimally solvate both the interfacial ions and the electrode surface [18,19]. Lastly, the interfacial electrolyte structure has an interplay with the electrode surface structure [20,21]. At present, no model can fully capture this ion–solvent-surface restructuring. Therefore, a key challenge is to analyze how the choice of bulk electrolyte composition translates into changes in the active site structure during electrocatalytic reactions, and in turn how tuning this active site structure affects the catalytic performance.

To address this challenge, *operando* techniques capable of resolving (parts of) the electrode–electrolyte interface structure under operating conditions play an essential role. Using *operando* spectro-electrochemistry, structural details such as the interfacial hydrogen bonding network [19,22], interfacial electric field [23], and ion-adsorbate coordination [24,25] have been identified as critical parameters, which can be indirectly

**Figure. 1**



Interfacial electrolyte structure and its potential effects on electrocatalytic performance.

tuned via the bulk electrolyte composition. These structural features can influence the catalytic performance in several ways, as summarized in Figure. 1. Here, we summarize the current capabilities of *operando* techniques in resolving the nature of electrolyte effects. We will focus on vibrational spectroscopy, X-ray spectroscopy, and surface X-ray diffraction, which have been used under true *operando* conditions, i.e. while electrocatalytic turnover is taking place at the interface. However, we note that *in situ* techniques, which only probe the double layer under static, non-catalytic conditions, such as laser-induced current transient (LICT) [3,9] and scanning probe microscopy (AFM/STM) [26—28] have also delivered valuable insight to the topic.

## Vibrational spectroscopy

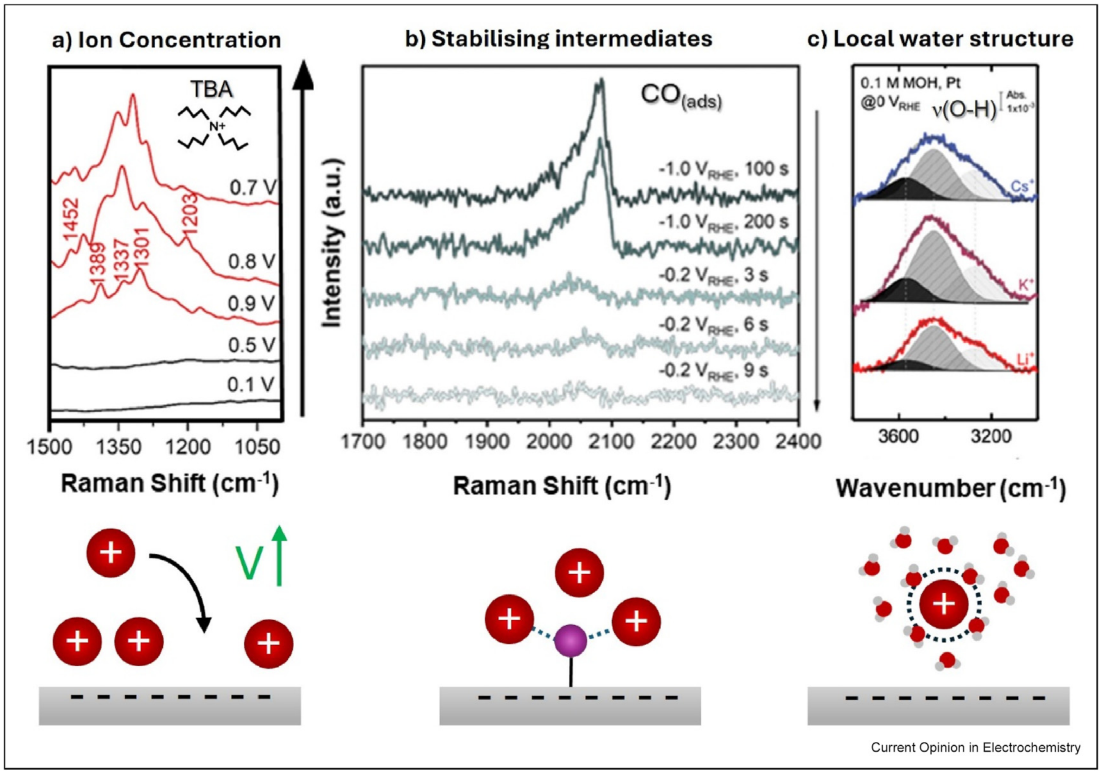
The vast majority of spectro-electrochemical studies on electrolyte effects have been carried out using vibrational spectroscopies. Indeed, vibrational techniques are comparatively easy to use and can be applied to a variety of electrochemical systems. To create interface sensitivity in the measurements, the vibrational signal is locally enhanced at the electrode surface using plasmonic hotspots, facilitating the detection of surface and near-surface species [29—34]. Ag, Cu, or Au electrodes with nanometer-scale roughness have suitable plasmonic properties for this purpose and are therefore widely used in surface-enhanced Raman spectroscopy (SERS) and surface-enhanced infrared spectroscopy (SEIRAS) [30,34—36]. For non-plasmonic electrodes, core—shell nanoparticles with tailored plasmonic properties can be utilised as implemented in shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) [33,37—39]. An alternative approach is infrared reflection absorption spectroscopy (IRRAS) using polarised light at grazing incidence. By subtractive normalisation of spectra obtained with s- and p-polarised light, a highly interface-sensitive interferogram is obtained [40—43]. Lastly, high interface sensitivity can also be achieved by non-linear spectroscopic techniques with symmetry-breaking selection rules, such as second or third harmonic generation, sum/difference frequency generation and 2D IR spectroscopy [44—49].

These interface-sensitive techniques make it possible to track reaction intermediates, electrolyte species and interfacial water-based features (Figure. 2). Changes in the intensity and position of ion or adsorbate peaks as a function of potential provide a rough indication of the surface concentration and local electric field strength (Figure. 2a) [41,47,50,51]. Meanwhile, tracking the intensity of adsorbate peaks can be used to probe the (de) stabilising effect of interfacial ions on reaction intermediates [10,32,39,52—54]. For example, a time-resolved CO2RR SERS study by Lee et al. showed the requirement of cations to capture a $CO_{(ads)}$ reaction intermediate (Figure. 2b) [54]. Another essential aspect that vibrational spectroscopy techniques can resolve is the effect of ions on the local water structure, often determined through the deconvolution of water-based features [12,33,53,55]. In an *operando* SHINERS study on a Pd single crystal, Wang et al. showed the increased contribution of water coordinated to cations at the electrode—electrolyte interface when approaching hydrogen evolution potentials, which facilitate hydrogen evolution by their closer proximity to the electrode [33]. This cation-induced water restructuring is affected by the identity of the cation. Huang et all. showed that smaller cations with large hydration shells create a rigid local water structure as opposed to larger cations that allow for more free water close to the electrode's surface (Figure. 2c) [12]. As revealed in recent studies, these subtle differences can majorly impact surface-reactions that require hydrogenation steps [12,32,53].

As discussed above, vibrational spectroscopy is highly capable of resolving structural trends to explain electrolyte effects in electrocatalysis. Its dominance in *operando* electrolyte effect studies originates from its comparatively simple instrumentation, which is compatible with almost any electrolyte and electrocatalytic process. Another advantage of vibrational spectroscopy is the time resolution. In optimised configurations, spectral acquisition times can reach sub-second to sub-picosecond intervals, which is excellent for resolving complex reaction mechanisms and determining the presence and role of adsorbates with short lifetimes and their interactions with electrolyte species [30,34,48,49,56,57].

However, vibrational spectroscopy techniques also have limitations. For example, substrates with the

**Figure. 2**



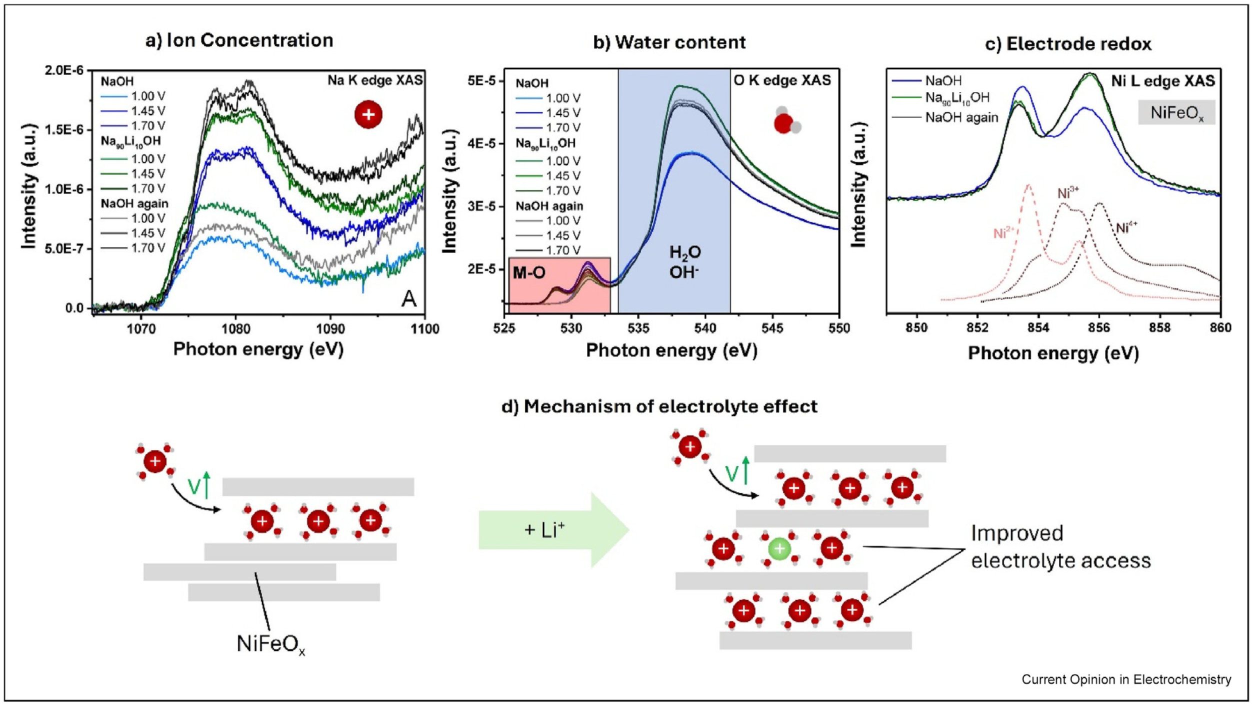
**a)** Potential dependent *in situ* SHINERS spectra of Pt(111) in TBAOH pH 12 electrolyte (figure adapted from Ref. [51]. **b)**, Time resolved *operando* CO2RR SERS spectrum after changing the potential from −1.0 V to 0.2 V vs RHE in $CO_2$ saturated 0.1 M $KHCO_3$ electrolyte. Figure adapted from Ref. [54]. **c)** Deconvoluted OH stretching peak at 0 V vs RHE into three components: Ion coordinated water (3570 $cm^{-1}$), weakly hydrogen-bonded water (3450 $cm^{-1}$) and free water (3270 $cm^{-1}$) from in-situ SEIRAS spectra on Pt. Figure adapted from Ref. [12].

appropriate plasmonic properties are usually limited to gold, silver and copper. To achieve sufficient enhancement, the surface of these metals must consist of nanostructures with specific sizes (50—100 nm) [58,59], preventing the use of smaller nanoparticles or flat surfaces such as single crystals. While the SHINERS strategy provides an attractive approach for using a wider range of substrates, synthesising intact thin-shelled particles is challenging. Improperly isolated particles can give an unwanted contribution to the electrochemical process of interest. In addition, the created plasmonic hotspots that dominate the recorded signal might not represent the whole electrode surface. Another limitation for electrolyte studies is that the direct measurement of cations is limited to complex ion structures, as traditionally used alkali cations don't have any vibrational mode that can be excited.

## X-ray spectroscopy

While X-ray spectroscopies are widely used in electrochemistry to track changes in the oxidation state and ligand environment in electrodes [60], their application to electrolyte effects has only recently begun [11,20,25,61—63]. The main attractive feature of this branch of techniques is their element-sensitivity, which makes it possible to separately inspect the interfacial chemistry of ions [20,25,61,64,65], water molecules [20,66—68], and the electrode surface [11,60,62,69—71] based on the different elements they contain. This is exemplified using a recent study from van der Heijden et al. [20], in which the promoting effect of small amounts of $Li^+$ in NaOH for the oxygen evolution reaction on $NiFeO_x$ was investigated. Using Na K-edge, O K-edge, and Ni L-edge X-ray absorption spectroscopy, the authors were able to simultaneously track the $Na^+$ ions, interfacial water molecules, and Ni catalyst atoms (Figure. 3). In this way, they were able to show that the addition of $Li^+$ induces better electrolyte penetration into the layered $NiFeO_x$ structure, as evidenced by the increased $Na^+$ and $H_2O$ signals (Figure. 3a and b). This improves the mass transport of reactants within the catalyst layer, and makes more Ni sites available for catalysis, as evidenced by the increased fraction of Ni in the active 3+/4+ state observed in the Ni L-edge (Figure. 3c). The study thus shows the capability of X-ray spectroscopy to unravel the interplay between different electrode—electrolyte interface components. On a more detailed level, X-ray absorption spectroscopy can also be

**Figure. 3**



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*Operando* soft X-ray absorption spectroscopy showing the interplay between ions, water, and electrode during the oxygen evolution reaction on $NiFeO_x$ at pH 13. **a)** Na K-edge spectra showing potential dependent $Na^+$ intercalation, which increases upon $Li^+$ addition. **b)** O K-edge spectra showing increased water uptake into the catalyst film upon $Li^+$ addition. **c)** Ni L-edge spectra showing an increased fraction of Ni in the active $Ni^{3+/4+}$ state upon $Li^+$ addition. a-c adapted from Ref. [20]. **d)** Overall effect of $Li^+$ addition inferred from X-ray spectroscopy and activity measurements.

used to resolve interfacial water structures [66,68], the hydration shell structure of ions [25,72,73], and the ion protonation state (e.g. $HSO_4^-$ vs $SO_4^{2-}$) [74,75].

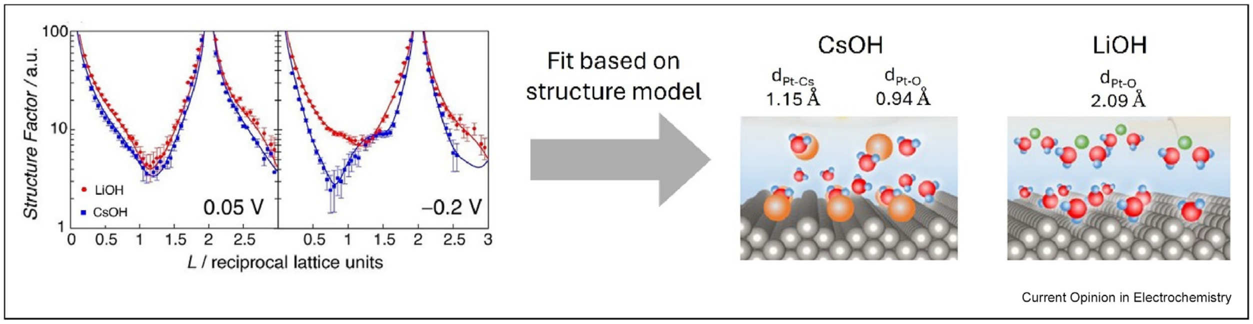
Complementary to X-ray absorption spectroscopy, a recent development in the field is *operando* X-ray photoelectron spectroscopy (XPS) [64,76,77]. *Operando* XPS offers the possibility to see not only the concentration and chemical state of all components of the electrode—electrolyte interface, but also the potential they experience [64,67,69,78]. Favaro et al. showed that this can be used to extract the potential profile of the double layer [67]. In the context of electrocatalysis, Hübner et al. recently used *operando* XPS to resolve the role of $K^+$ ions in the 2- electron oxygen reduction reaction on carbon electrodes [61].

Compared to the more widely used vibrational spectroscopies, X-ray spectroscopy offers a few pros and cons. On the upside, X-ray spectroscopies are in principle compatible with all electrode materials and electrolytes. It also has the capability to resolve all components of the electrode—electrolyte interface in one experiment, including mono-atomic ions (e.g. $Na^+$) that are invisible to vibrational spectroscopy. The downsides of *operando* X-ray spectroscopy are its risk of beam-damage (most pronounced for systems containing organics) and its technical complexity. In general, interface-sensitive X-ray spectroscopy experiments require specialized setups that make use of grazing incidence X-rays [71] or vacuum-based spectroscopic techniques [64] with an advanced spectro-electrochemical cell design. While these methodologies are becoming increasingly mature and user-friendly, for the moment *operando* X-ray spectroscopy studies on electrolyte effects require some level of specialism.

## Surface X-ray diffraction

Using surface X-ray diffraction, it is possible to derive the atomic positions of water molecules and ions at the interface between single crystals and electrolytes [21,24,40,79–83]. The technique is primarily sensitive to the position of (heavy) ions, but can also resolve the distance between the electrode and the first water layer [40,80,82]. In situations where the interfacial ions form an ordered structure, also the in-plane positions of the ions can be obtained [80,82]. In the context of electrolyte effects, this information can be very useful to judge how interfacial ions influence electrocatalytic reactions. For example, Strmnik et al. [24] used the measured ion-electrode distance to determine whether the hydration shell of the interfacial ions opens up, so

**Figure. 4**



*Operando* surface X-ray diffraction on Pt(110) during the hydrogen evolution reaction at pH 13. Specular crystal truncation rod data is shown on the left, while the right side shows the structural parameters extracted using curve fitting. Data and ball model adapted from Ref. [80].

that the ions can directly interact with the reaction intermediates on the surface, modulating their reactivity. In a similar way, the formation of an ordered $Cs^+$ overlayer with a short distance to the Pt(110) substrate was identified by Tanaka et al. as a barrier for water transport/dissociation during the hydrogen evolution reaction in CsOH(80) (Figure. 4). Surface X-ray diffraction also provides insight into how ions affect the electrode surface structure. For example, Kumeda et al. [21] found that $Li^+$ ions reduce the surface roughening that develops during the surface oxidation of Au(111).

The structural information in these examples is extracted by fitting crystal truncation rod curves using a structural model. From this, three challenges arise: 1) Recording crystal truncation rod curves with a sufficient signal-to-noise ratio is time consuming, meaning that only a few electrolytes can be tested per synchrotron beam time. 2) A model for the interfacial electrolyte must be built and systematically varied to find the optimal fit. While software exists to aid with this (e.g. ROD [84]), the procedure requires expertise. 3) Light atoms such as the oxygen from water have a relatively small influence on the fitting curve due to their low X-ray scattering probability. Therefore, determining their position is comparatively difficult, putting further demands on the quality of the data and analysis. Due to these experimental and analytical challenges involved in surface X-ray diffraction studies on interfacial electrolytes, only a few groups have published on this topic so far. However, given the promise of the technique, several groups are currently picking up the gauntlet.

## From structure to mechanism

A critical step in the analysis of electrolyte effects using *operando* techniques is to understand the link between the structure that is measured and the observed catalytic performance. The most widespread methodology adopted for this is to create structure−performance correlations, i.e. to link differences in the *operando* interface structure in different electrolytes to differences in catalytic performance. For example, the much more ordered, ion-rich structure observed in CsOH in Figure. 4 compared to LiOH was linked to the lower catalytic activity in the hydrogen evolution reaction [80]. However, the interpretation of such correlations can be challenging, because a structural change can affect catalysis in many ways. For example, if more cations are attracted to the surface, this influences the transport of reactants though the double layer, the interfacial electric field (activation energy), and in some cases also ion-adsorbate interactions (activation energy). To distinguish these effects, an attractive method is to also consider *how* the activity is affected by the structure change. In the case study in Figure. 3, the onset potential in NaOH and NaOH + LiOH was the same and differences only appeared at higher overpotential, clearly indicating that the cation effect was related to transport [20]. In contrast, the necessity of a cation-containing electrolyte to attain any conversion during $CO_2$ reduction implies an effect on the activation energy [54,85].

An alternative methodology to solidify the analysis is to combine *operando* measurements with theory. Through simulated spectra, energetics, and atomic structures, calculations aid in both the assignment of spectral features and in the identification of the mechanisms through which the identified structures influence the catalysis. Both aspects are very well exemplified by a recent study from Li et al. [19]. By calculating the vibrational density of states of water at the Pt(111)-electrolyte interface, they were able to assign the water vibration peaks in their SEIRAS spectra. Meanwhile, the atomic structures identified in the same calculations provided a rationalization for the relationship between the spectroscopically observed H-bonding and the activity through the identification of an H-bond gap that limits proton transport to the electrode during the hydrogen evolution reaction.

## Outlook

Over the past years, the combination of *operando* spectroscopy, systematic experiments and theory has revealed many key mechanisms through which the interfacial electrolyte influences electrocatalysis. An important next step will be to understand under what conditions which mechanism dominates, or if multiple mechanisms occur simultaneously [86]. The latter is a particularly pressing question for complex reactions such as $CO_2$ reduction, because the many adsorbates and electrolyte species involved lead to interrelated effects. *Operando* spectroscopy can play a key role in untangling these, but an increased focus on resolving the chemistry of *all* components of the electrode−electrolyte interface is necessary. For example, in the $CO_2$ reduction reaction, tracking of the adsorbates, electrode surface structure, interfacial pH, cation positions/concentration and water structure is key, as it is now clear that each of these components plays a role in the activity and selectivity, but not how the components work together to create the activity/selectivity effects. Collaborative efforts to combine multiple spectroscopy, diffraction, and microscopy techniques may prove to be essential to achieve this.

From a more practical point of view, the next frontier for the field will be to move from explaining electrolyte effects after the fact, towards (roughly) predicting electrolyte effects given a combination of electrode, electrolyte and reaction. This requires a more generalized understanding of 1) how the bulk electrolyte composition relates to the electrolyte structure formed at the interface and 2) how the interfacial electrolyte structure affects the electrocatalysis. With the increasingly large volume of case studies available in the literature, the field is now moving closer to attaining such a more general view.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rik Mom reports financial support was provided by Dutch Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

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

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** of outstanding interest

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