7. Mechanistic insight into the electrocatalytic reduction of CO_2 via *operando* spectroscopy and microscopy methods

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Status

In this contribution, we will assess whether an electrocatalyst's morphology under reaction conditions is the same as in its pre-catalyst state, or if drastic structural and chemical changes are likely to occur. This aspect has been beautifully exemplified in the literature related to Cu materials, the premier catalyst for the electrochemical CO_2 reduction (CO_2RR) to C_{2+} hydrocarbons and alcohols. In particular, the selectivity of Cu-based materials is known to be strongly affected by different environmental factors which determine the evolution of their surface structure and composition such as the electrolyte and the applied potential [1],[2]. Furthermore, these changes are expected to be more severe at high current densities in industrial CO_2 flow electrolyzer applications [3]. To date, our fundamental understanding of a catalyst morphology is still largely rooted in descriptors derived from surface science thermal catalysis studies, with the operating temperatures influencing surface atomic diffusion and the most stable morphology. Such descriptions are unlikely to hold for electrocatalysts that operate in an electrolyte, under applied potential and mostly at ambient temperatures, which can lead to thermodynamically unfavourable motifs. These dynamical motifs are, however, non-trivial to investigate because of the challenges associated with characterizing samples in a "vacuum-incompatible" liquid environment. Moreover, the critical features can be lost once the catalysts are removed from the reaction conditions.

To enable direct studies during reaction, significant efforts have been invested in recent years to develop electrochemical cell designs that can circumvent the limitations of conventional surface science methods [4]. Some analytical techniques where such setups have been implemented for electrocatalysis studies are summarized in Figure 1. *Operando* spectroscopy is the more established approach, where a broad probe beam is used to interrogate the samples and their averaged properties are measured. For example, Raman spectroscopy can track the surface binding of reaction intermediates during CO_2RR [5], whereas X-ray absorption spectroscopy (XAS) allows us to probe the catalyst structure, composition and oxidation state [6]. The use of *operando* microscopy to track nanoscale structural [7] and surface [8] changes that occur under CO_2RR reaction conditions using specialized electrochemical reaction cells, comparatively, in its infancy. Examples of *operando* work describing the behaviour of cubic Cu_2O catalysts during CO_2RR are provided in Figure 2. Ideally, the experiments will also be coupled with online monitoring of the reaction products for structure-property correlation, although examples of such implementations are still very scarce.

For more details on the use of in-situ spectroscopy to probe the structure of the electrochemical double layer, we refer readers to Section 8; conversely, Section 9 elaborates on the use of in-situ spectroscopy to probe adsorbed intermediates.

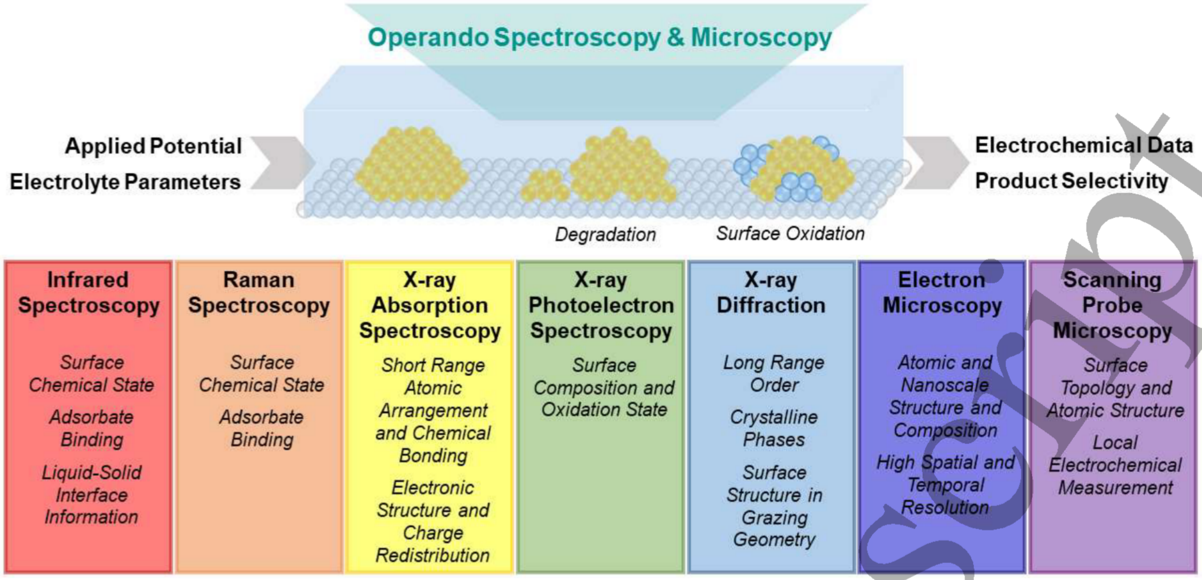

Figure 1. Common analytical techniques used for *operando* spectroscopy and microscopy investigations of CO_2RR electrocatalysts and their respective features.

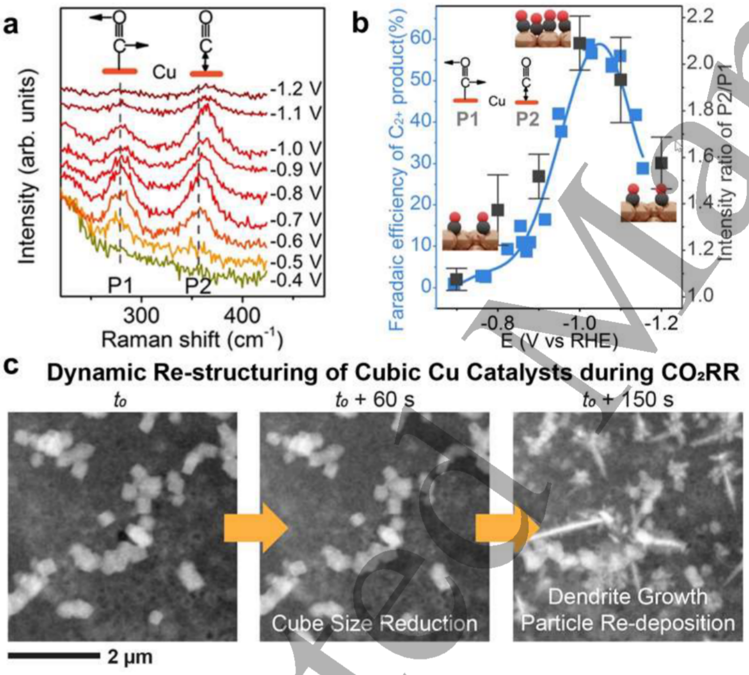

Figure 2. Examples of *operando* investigations of CO_2RR electrocatalysts. (a) *Operando* Raman spectra of Cu_2O nanocubes acquired during CO_2RR in 0.1 M $KHCO_3$ showing the restricted rotation of adsorbed CO (P1) and Cu–CO stretching (P2) from −0.4 to −1.2 V_{RHE}. (b) Potential-dependent intensity ratio of P2 to P1 peaks and C_2+ Faradaic efficiency. (c) Electrochemical transmission electron microscopy image sequence showing the time-resolved evolution of Cu_2O in CO_2-saturated 0.1 M $KHCO_3$0.1 M $KHCO_3$ at -0.7V versus a pseudo-Pt reference. Figures are modified from [5] and [7] with permissions from the American Chemical Society, 2021 and Springer Nature, 2020 respectively.

Current and Future Challenges

There are several challenges associated with *operando* spectroscopy and microscopy studies to probe the dynamic behaviour of electrocatalysts. First, high temporal resolution is needed in electrochemical CO_2RR to resolve the rapid changes in morphology and oxidation state observed in Cu during fast or pulsed potential sweeps. Furthermore, in a system with significant gas evolution, the formation of bubbles on the working electrode can also lead to unstable local electrolyte conditions on the timescale of the measurements. Within the different techniques described in Figure 1, there is already considerable spread in their temporal resolution, ranging from ms resolution in advanced quick X-ray absorption setups, subsecond resolution in surface-enhanced Raman spectroscopy and surface X-ray diffraction and a few seconds in electron microscopy. A number of scanning probe approaches [9] allow monitoring electrochemical reactions locally, but their temporal resolution is still insufficient to track fast intermediate reaction steps taking place during CO_2RR. In many cases, the changes in the catalyst morphology are already probed at higher time resolution compared to the accumulation times (typically tens of minutes) required for the analysis of the reaction products from CO_2RR using, for example, gas chromatography, making the impact of these changes on the catalyst functionality difficult to decouple. The generally slow response of the product measurements is another significant bottleneck for advancing the mechanistic understanding we can derive from *operando* studies of CO_2RR electrocatalysts.

In addition, the cell geometry or materials need to be optimized for each technique and these compromises often mean that the experimental conditions applied in different experiments do not exactly match, making the generalization of the results sometimes complicated. Each technique also has its limitation, where, for example, most *operando* spectroscopy techniques are ensemble-averaging and, hence, only sensitive to the majority species in the sample. The role of minority and spectator species is difficult to decouple from such studies. *Operando* microscopy studies, on the other hand, suffer from limited statistics due to the narrow view associated with the high spatial resolution imaging. It should be also noted that most *operando* techniques employ energetic probes (high energy electrons, X-rays, lasers), which can alter the state of the catalysts being studied. Beam damage effects are especially critical in synchrotron-based spectroscopic/diffraction studies and high-resolution transmission electron microscopy where radiolysis can lead to the formation of reductive/oxidative species or alter the local pH of the sample environment. While such issues are generally mitigated with low radiation dose methods and comparative control experiments, one cannot keep reducing the dose without running into signal-to-noise ratio issues or sacrificing temporal resolution with longer acquisitions.

As *operando* methods become more common and the instrumentation improves, data management becomes a looming problem. In this aspect, there are already emerging challenges in both the processing and interpretation of large *operando* datasets, and in the compilation of data streams from different instruments. In this respect, machine learning approaches would become increasingly important in the analysis and interpretation of *operando* microscopy and spectroscopy data [6].

Advances in Science and Technology to Meet Challenges

We envision that future technical advances in *operando* spectroscopy and microscopy will mostly be associated with improving the spatial and temporal resolution of these methods, including enabling online product analysis of the electrolyte stream. The latter is essential to correlate the catalyst selectivity with its corresponding structure. There is also a considerable gap between the nanoscale morphological data that can obtained from electron and scanning probe microscopy with the microscale probe sizes of the different *operando* spectroscopy techniques. Here, improving the spatial resolution of scanning methods such as scanning X-ray microscopy and confocal Raman spectroscopy will allow us to bridge the results obtained using different methods. Future developments in the *operando* characterization of electrocatalysts will also involve the use of multiple techniques simultaneously, or, when the requirements of the different methods do not allow it, to employ transferrable reactor cells that are compatible with the different experimental setups.

Tracking electrochemical transformations and detecting elusive transient species and reaction intermediates that might be intermittently present on the catalyst surface or in its vicinity will require improving the temporal resolution of the different techniques through more sensitive detectors. The improvement required in this case is not limited to the tracking of structural changes. Compositional maps obtained, for instance, using energy dispersive X-ray spectroscopy within an electron microscope can provide extremely valuable information about a catalyst made up of different elements. The time resolution of such investigations must be, however, drastically improved to follow the rapid transformations of electrocatalyst under potential control. Other improvements will involve incorporating more capabilities into the reactor cells, such as including local pH measurement close to the working electrode, where pH effects remain one of the more challenging issues to rationalize in CO_2RR [10].

Lastly, the interpretation of *operando* spectroscopy data can be enhanced by better theoretical support, such as using calculations to understand the features in the Raman or infrared spectra and how they relate to different adsorbates and modelling of near-edge or extended X-ray absorption data [5]. Here, machine learning approaches are expected to significantly aid these efforts [11].

Concluding Remarks

We envision that the knowledge that will be extracted from *operando* spectroscopy and microscopy studies will aid the rational design of a new generation of active but even more importantly, highly selective and durable CO_2RR catalysts. Clearly, it is not sufficient to only enable better data collection, the data must be processed and weaved together into a consistent picture. We expect future efforts to focus on combining multiple *operando* techniques to mitigate the weaknesses of a single technique, i.e., where electron microscopy provides the morphological detail needed for interpreting spectra from ensemble-averaging techniques such as Raman or X-ray absorption spectroscopy. How to merge such data meaningfully, especially for complex reactions like CO_2RR, with multiple possible underlying processes or a multi-element material remains a largely unsolved problem, specially when each technique uses a different electrochemical cell configuration. This is especially critical if, for example, confinement and mass transport limitation effects in such cells lead to artifacts in the data and result in findings that are not representative of the processes in benchtop or industrial electrochemical experiments. Finally, we see significant promise in the use of data science, thanks to recent breakthroughs in machine learning methods, for providing an effective solution for analysing and combining several complementary large operando spectroscopy/microscopy datasets.

Acknowledgements

We appreciate funding by the European Research Council (ERC-725915, OPERANDOCAT) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – project no. 406944504 – SPP 2080.

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