



# PhD Thesis Defense: Investigation of Dynamic Catalyst -Electrolyte Interfaces in Electrochemical Systems for Establishing Activity Correlations

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November 02, 2026

10:00

Auditorium

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Rising atmospheric CO<sub>2</sub> levels, driven primarily by anthropogenic emissions, are a central contributor to global climate change and environmental instability. Electrocatalytic reactions provide a promising pathway for CO<sub>2</sub> emission reduction through electricity-driven conversion of CO<sub>2</sub> and/or water into value-added chemicals and fuels. In this context, catalysts are widely recognized as the key determinants of performance. This thesis takes the discussion a step further by examining how, in specific reactions, not only the catalyst itself but also the surrounding environment becomes crucial in defining performance matrices. More specifically, it investigates dynamic catalyst-electrolyte interfaces in water electrolysis

and direct bicarbonate reduction, with a particular emphasis on interfacial dynamics and their correlation with activity.

The thesis first outlines the fundamental aspects of water electrolysis and bicarbonate reduction, and then presents new concepts and findings on the role of dynamic catalyst-electrolyte interfaces in these systems. To do so, several in situ and operando techniques are employed, including Raman spectroscopy, X-ray absorption spectroscopy, electrochemical impedance spectroscopy, and quantitative bubble analysis, complemented by other electrochemical methods to establish correlations with performance.

In the case of water electrolysis, the thesis focus on the oxygen evolution reaction, which represents the largest energetic penalty in the system. Correlations spanning atomic to microscale features are identified, collectively shaping the performance landscape of the reaction. Using complementary in situ probes, these correlations are shown to go beyond simple cause-and-effect relationships, highlighting the importance of uncovering the underlying mechanisms rather than relying solely on performance metrics.

In direct bicarbonate reduction, performance is strongly influenced by the availability of CO<sub>2</sub> at the interface, which is in turn linked to the local pH. Through operando Raman spectroscopy, a descriptor for the interfacial buffering state is identified, providing indirect insight into instantaneous CO<sub>2</sub> availability. This hypothesis is further validated by engineering the catalyst-electrolyte interface to actively tune this descriptor, resulting in a threefold improvement in performance. This demonstrates how mechanistic understanding of the catalyst-electrolyte interface can guide informed hypotheses that are ultimately deterministic, reducing the experimental parameter space and improving optimization efficiency.

Overall, the thesis emphasizes the importance of understanding why performance improves, rather than simply attributing progress to *“better catalysts”*. A deeper understanding of these systems, especially at high current densities, can lead to more coherent design principles and challenge existing assumptions about major factors governing the electrochemical performance. The results show that the catalyst surface cannot be considered a static entity, but rather a dynamic system whose structure and reactivity are continuously modulated by external factors. These insights provide a more detailed mechanistic picture of electrochemical interfaces and help identify key descriptors for catalyst design.

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