

Traversing catalytic contexts for interrogation and design of carbon conversion electrocatalysts

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Driving chemical reactions with voltage provides an opportunity to perform thermodynamically difficult reactions at mild temperatures and pressures. One useful chemistry to perform electrochemically is CO₂ conversion. Converting CO₂ into value-added chemicals could be one strategy for abating atmospheric carbon, and electrochemistry is well-suited to provide the driving force required for CO₂ conversion reactions that tend to be highly endergonic. However, amidst the physical complexity of electrified interphases, both mechanistic inquiry and rational catalyst design remain challenging. In this work, we leverage concepts from fields outside of electrocatalysis to establish new strategies for both the interrogation and design of promising electrocatalysts.

We first discuss strategies for interrogating electrocatalytic reaction mechanisms. This is described in the context of CO₂ reduction reaction (CO₂RR) to carbon monoxide (CO) at immobilized metal tetrapyrroles. We detail how collecting and quantitatively analyzing reaction rate data over a wide range of reaction conditions illuminated new details of the CO₂RR reaction mechanism at cobalt phthalocyanine (CoPc). Specifically, we found that there is mixed control between concerted and sequential proton-electron transfer pathways, as well as catalyst poisoning from the bicarbonate anion. Such mechanistic analysis strategies are often used in heterogeneous thermocatalysis, and this work illustrates the depth of mechanistic information that can be gained when they are applied to electrocatalysis. We also report a robotic system that automates collection of reaction rate data to improve this kinetic analysis workflow. We report how the robotic system was used to expand our CO₂RR mechanistic analyses to additional metal tetrapyrroles such as cobalt tetraphenyl porphyrin. Together these works establish a foundation for applying more rigorous kinetic analyses in the space of electrocatalysis.

We next discuss strategies for designing electrocatalytic active sites. We show how a new electrochemical C–C bond formation catalyst was developed by sequentially electrifying known hydroformylation catalysts. We show that electrification of a known organometallic catalyst leads to mechanistically distinct, voltage-driven reactivity. Notably, we find one advantage of the new voltage-driven reaction is that it can proceed at milder operating conditions: at 25 °C, the electrochemical reaction is over an order of magnitude faster than the original thermochemical reaction. This work pioneers a design paradigm of using known reactivity from thermal catalysis as a direct experimental starting point for developing new electrocatalysts.

Together, these works provide new interdisciplinary approaches for interrogating and designing electrocatalytic interphases. In the context of carbon conversion, this work has contributed insight on reaction mechanisms of known CO₂RRs, and, demonstrated new catalysts that further upgrade common products of CO₂RR for greater value-add.