

Overcoming challenges of fundamental electrochemical kinetic studies under dilute-reagent conditions

by

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Electrochemical reactions show promise for decarbonizing the chemical industry through distributed, local chemical synthesis; replacement of hazardous, atom-inefficient, and emissions-heavy precursors and processes with benign reagents and electrical potential; the storage of intermittent renewable energy in chemical bonds; and the direct conversion of CO₂ into value-added chemicals. Before electrochemical technologies can be deployed, however, they must go through many stages of development. Different electrochemistries have different needs prior to deployment. In this thesis, we focus on lab-scale, fundamental kinetic studies of select electrochemistries for which fundamental kinetic study is a need – particularly those chemistries for which dilution or mixing phenomena are of practical concern.

We first discuss electrochemical CO₂ reduction – a chemistry that is very well studied in the lab environment, but has yet to reach deployment stage. In particular, we address the questions: what happens if one does not have access to a pure CO₂ gas feed? Is electrochemical CO₂ reduction tolerant to common CO₂ impurities such as N₂ and O₂? Through mechanistic study, we demonstrate that neither the rate nor the mechanism of CO₂ reduction is affected by the presence of O₂, but that the cathodic co-reduction of O₂ at relevant potentials represents a parasitic current – an energetic trade-off for tolerance to feed impurity which should be considered in techno-economic analyses of CO₂ reduction systems.

Next, we consider mixtures not in the gas phase but in the liquid phase: blended aqueous-nonaqueous electrolytes. Such mixtures are often used to bring organic substrates into contact with water as a co-reactant, for example in O-atom transfer chemistries. We describe complexities of working in such systems, such as nonideal solution thermodynamics and ill-defined potential scales, and develop methods to account for these complexities, for instance by direct measurement of species thermodynamic activity through vapor pressure measurements. We report the first measurement of the water dependence of nonaqueous alkaline hydrogen evolution, accounting for such nonidealities, and find that the reaction is ~2.8-order with respect to water. To explain this high-order dependence, we propose molecular explanations for water's nonideal behavior and hypothesize many roles water can play in blended electrolytes. We extend the usefulness of our activity correction to O-atom transfer chemistries, demonstrating the generality of the approach. In addition, we discuss the molecular origins of nonideal solution thermodynamics and present early snapshots of water's structure in blended electrolytes, as achieved through collaborative work in molecular dynamics simulations.

Finally, we use such a blended electrolyte to develop an approach to direct benzylic C-H oxidation for the production of commodity chemicals. Through xylene partial oxidation as a case study, we demonstrate that electrochemical benzylic C-H activation can take place on carbonaceous anodes with fair selectivity (Faradaic efficiencies ~40-50%). The reaction yields primarily p-tolualdehyde, a 4-electron oxidation product. Our results indicate that the reaction may proceed through a coupled proton-electron transfer (CPET) to yield a radical intermediate prior to further oxidation.

High dependence of the reaction on water (~3-4 order) is suggestive that, as in the case of hydrogen evolution, CPET chemistries may be very sensitive to electrolyte water content. Future development of the benzylic C-H oxidation reaction scheme may allow for the partial oxidation of xylene to more cleanly synthesize products such as terephthalic acid, which is used in the production of PET plastic and is currently made in a harsh, corrosive environment conducive to the undesired co-generation of CO₂.

We hope this work represents a useful step toward the understanding and deployment of these relevant electrochemical systems.

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