Detroit ECS Student Chapter:
Trailblazers in Electrochemistry
(Vision 2020)

Thursday, November 5th, 2020 @ 2:00 pm ET

Water Dissociation Catalysis

Prof. Shannon Boettcher
Department of Chemistry and Biochemistry and the Materials Science Institute
Director, Oregon Center for Electrochemistry
University of Oregon, Eugene, OR, 97403

Water is arguably the most-important molecule to humanity due to its ubiquitous role in biological, industrial, and environmental processes. Reactions of water typically involve breaking the H-O bond. The simplest reaction is heterolytic water dissociation (WD), $H_2O \rightarrow H^+ + OH^-$, the understanding of which has been a focal point of experiment and theory for decades. Related dissociative adsorption reactions occur on surfaces and are important when water is used as a reactant for thermochemical processes, such as the water-gas-shift reaction. In biological systems, metalloenzymes such as carbonic anhydrase dissociate water to catalyze, for example, CO_2 equilibria. In the context of energy conversion, WD is a fundamental step in many electrochemical processes. For example, the WD step is thought to be rate-limiting for the hydrogen evolution reaction (HER) under alkaline conditions and thus modification Pt HER catalysts with metal hydroxides, that presumably accelerate WD, lead to large increases in HER activity. While measurements of dissociative water adsorption are often made using the tools of surface science under vacuum conditions, the WD reaction has not been systematically studied under electrochemical conditions. We use a bipolar-membrane (BPM) electrolyzer (where WD is driven in the region between a hydroxide-exchange membrane and a proton-exchange membrane by an applied potential) to study WD kinetics across a range of materials. We find that the local pH is a critical, but previously unrecognized, variable affecting WD kinetics and a pH-dependent proton-transfer WD mechanism is proposed. Combining WD catalysts efficient in locally acidic conditions with those efficient in basic conditions, nearly eliminates the WD overpotential in BPM electrolyzers operating at 20 mA cm^{-2}. The catalysts enable continuous BPM operation at 0.5 A cm^{-2} with a total applied electrolysis potential of ~ 2 V – substantial improvements over the state of the art and suggesting new applications for BPMs. We further discovered that the WD kinetics measured in the BPM correlate with HER kinetics under conditions where WD is an important elementary step. We discuss the design of bifunctional electrocatalysts based on the insight into the underlying WD steps.

President: Ruchiranga Ranaweera
Fourth Year Graduate Student
Luo Lab
Department of Chemistry
Wayne State University
Detroit, MI, 48202
trranaweera@wayne.edu

Vice President: Samji Samira
Fifth Year Graduate Student
Nikolla Lab
Department of Chemical Engineering
Wayne State University
Detroit, MI, 48202
ssamira@wayne.edu

Treasurer: Chaturanga Hewa
Fourth Year Graduate Student
Luo Lab
Department of Chemistry
Wayne State University
Detroit, MI, 48202
hewa@wayne.edu

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Biography: Shannon Boettcher is an Associate Professor in the Department of Chemistry and Biochemistry at the University of Oregon. He holds a B.A. in Chemistry with a minor in Physics from University of Oregon. He then obtained his Doctoral degree in Inorganic Chemistry from University of California Santa Barbara (UCSB) in 2008. Subsequently, he was awarded the Kavli Nanoscience Institute Prize Postdoctoral Scholar Award and joined Caltech to work with Professor Harry Atwater and Nathan Lewis. His research is at the intersection of materials science and electrochemistry, with a focus on fundamental aspects of energy conversion and storage. He has been named a DuPont Young Professor, a Cottrell Scholar, a Sloan Fellow, and a Camille-Dreyfus Teacher-Scholar. In 2019, he was included as an ISI highly cited researcher (top 0.1% over past decade). In 2019, he founded the Oregon Center for Electrochemistry.

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