Rigor and Reproducibility in Electrocatalysis – Overview and Present Status

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Current efforts to bring rigor and reproducibility to electrocatalysis date back to a benchmarking study of the oxygen evolution reaction (OER) on Ni- and Co-based catalysts and a commercial IrO_x catalyst by the Jaramillo group in 2013.[1] This study established a protocol for reporting activity of each catalyst as characterized by a consistent set of metrics: electrochemically accessible surface area (ECSA), the overpotential required for 10 mA/$\mathrm{cm}^2_{\mathrm{geo}}$ based on geometric surface area, and the Faradaic efficiencies of reaction products.

In 2018, the Bell and Jaramillo groups reported a cross-laboratory study of CO_2 electroreduction that yielded reproducible reaction rates between the two laboratories through a rigorous set of standards and protocols.[2] This work adopted a comparative study of two catalysts with two different product distributions. The idea was to obtain reproducible results for the catalyst with the simpler product distribution (H_2 and CO from a silver catalyst) to eliminate systematic errors within each group. Upon completion of the silver experiments, each laboratory examined the catalyst with a more complex product distribution (H_2, methane, and ethylene from a copper catalyst), successfully reproducing each other's results. The authors noted numerous examples where uncontrolled experimental parameters or improper procedures could affect results: (1) control of surface structure, (2) use of diamond-based rather than alumina-based polishing compounds, (3) careful selection of electrolyte anions and cations, (4) monitoring and control of mass transfer effects, (5) distinction of local and bulk pH, (6) use of pH-independent reference electrodes, (7) calibration of reference electrodes, (8) use of large area-to-volume ratio cell designs to mitigate electrolyte impurities, (9) measurement of ECSA, and (10) not using onset overpotential as a measure of catalyst effectiveness. The paper also recommended that electrocatalytic activity be based on ECSA rather than on geometric surface area.

Recently, Edgington and Seitz published a Perspective about rigor and reproducibility of catalyst degradation in oxygen evolution and water electrolyzers.[3] Oxygen evolution electrocatalysts are subject to a number of performance inhibiting (mainly site blocking) and dissolution phenomena that differ in regards to a three-electrode cell *vs.* an electrolyzer. They recommended the use of an S-number—the molar ratio of O_2 produced in OER to that of catalyst dissolution—to compare stability among a set of catalysts. They also showed how the S-number, originally developed for use with platinum group metal (PGM) catalysts, can be extended to non-PGM catalysts. For good measure, they recommended that studies of OER catalyst stability be compared with an IrOx catalyst.

Within the last ten years, there have appeared several reports that, while seemingly describing experimental artifacts of a particular system of study, cumulatively point to a discipline-wide lack of understanding of how to design and conduct rigorous and reproducible measurements. Many of these reports have been collected in a virtual issue of *ACS Energy Letters*.[4] Key topics identified in that issue (and others) include: enhancement of Ni-catalyzed OER due to trace contaminants of iron in reagent grade KOH,[5–7] dissolved glassware in alkaline media,[8,9] pitfalls in measuring pH,[5,10,11] inconsistent reporting of overpotentials,[1,11–14] lack of iR compensation,[15–17] incomplete descriptions of electrode conditioning procedures and measurement parameters,[18,19] product analysis,[20–23] selection and use of reference electrodes,[11,14,24] selection of counter electrodes,[25] measurement of ECSA,[1,5,12,13,26,27] trace metal contamination,[24] electrocatalyst stability,[3,18,25] and beam damage in X-ray measurements.[28]

Rigorous and reproducible experiments require thoughtful experiment design, effective control of experimental parameters, and thorough assessment of measured and calculated quantities. The experiment design should begin with a well-constructed, falsifiable hypothesis and include a research plan of sufficient scope to address the topic comprehensively and with enough redundancy to verify the main findings while mitigating experimental artifacts. Necessarily, each case will be unique and, as proper design and execution of a research plan is the mainstay of PhD research, is best handled by the PhD adviser. One of the goals of the Workshop is to codify the information necessary for rigorous and reproducible research as a guide in setting up a research plan.

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