



## Viewpoint Paper

# Precise oxygen evolution catalysts: Status and opportunities

Lena Trotochaud and Shannon W. Boettcher\*

*Department of Chemistry and Biochemistry, 1253 University of Oregon, Eugene, OR 97403, USA*

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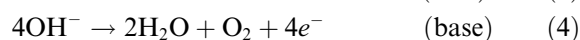
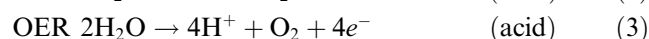
**Abstract**—This Viewpoint highlights recent advances in oxygen evolution reaction (OER) catalysis using well-defined/characterized systems and outlines a path for possible further improvements. First, we review our results on ultra-thin film catalysts and compare them to other systems, emphasizing methods that provide accurate intrinsic catalyst activities. We then discuss reports that catalysts with the highest OER activities (in base) often undergo structural and chemical changes during the OER. These findings have implications on how OER catalysts are studied and designed. We suggest opportunities to control molecular-scale interactions in hydrous layered hydroxide/oxyhydroxide catalysts as well as the control of three-dimensional nano- and microstructures using templating approaches.

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## 1. Introduction

Splitting water to generate hydrogen fuel and oxygen gas ( $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ ) could provide for clean, scalable, global energy storage [1,2]. The water splitting reaction is composed of two half-reactions: the hydrogen evolution and oxygen evolution reactions (HER and OER, respectively):



The slow kinetics of the OER limits the efficiency of both photon-driven and electricity-driven water splitting [2,3]. Generally accepted mechanisms for water oxidation include four sequential electron transfer steps. Each electron transfer is typically coupled with a proton transfer. The OER intermediates are stabilized by the catalyst; for example, as surface-bound peroxo- or oxo-species. The relative stabilities of these intermediates and the activation barriers between them dictate which step is rate-determining and thus the overall water oxidation rate [4]. The identity of the surface intermediates depends on the reaction conditions (e.g. pH) and

likely the catalyst material. Work to identify precise mechanistic pathways has been attempted [5] but conclusive evidence identifying intermediates is limited [6]. A mechanistic understanding of the rate-determining steps would provide insight into how structure and composition can be tuned to modify the energetics of the reaction intermediates and thus increase reaction rates.

One long-standing challenge in OER catalysis is that typically studied catalysts are poorly defined, which makes relating structural, compositional and electronic features to the observed activity trends difficult. Well-defined catalysts allow for accurate assessment of the intrinsic activity and are needed for improving mechanistic understanding. Single crystals, precise nanoparticles, homogeneous molecular clusters and ultra-thin films are reasonable model systems for studying catalytic processes and mechanisms, but significant challenges remain in precisely tuning composition and structure, unambiguously identifying the active sites, understanding changes to the structure in situ and maintaining long-term stability for applications.

We examine recent advances in OER catalysis using well-defined/characterized systems and propose paths for improvement. We first briefly review our research on ultra-thin film catalysts, and compare those results to other well-defined systems. The thin film geometry is advantageous for the study of heterogeneous catalysts because the deposited catalyst films are essentially “all surface”. Through these experiments we demonstrated that  $\text{Ni}_{1.0}\text{Fe}_{0.1}\text{OOH}$  has the highest OER activity

\*Corresponding author. Tel.: +1 541 346 2543; e-mail: [swb@uoregon.edu](mailto:swb@uoregon.edu)

measured to date in basic media. Second, we discuss several recent reports that many OER electrocatalysts undergo structural and chemical changes during the OER in basic solution. We describe the implications of these findings on how OER catalysts are studied and, ultimately, designed.

## 2. The need for well-defined OER catalysts and standardized measurements

Increasing the surface area of heterogeneous OER catalysts usually decreases the overpotential for a given current density by introducing more active sites per unit geometric area. The resulting materials are often poorly defined structurally and their microscopic surface area, number of active sites, active-site distribution, compositional homogeneity and electron and mass (e.g. bubble) transport properties are challenging to measure (and correct for). High-surface-area heterogeneous catalysts, while potentially of technological relevance, limit the ability to correlate experimental results with theoretical calculations [4]. For example, Trasatti and Lodi [7] identify  $\text{RuO}_2$  and  $\text{IrO}_2$  as the most active catalysts in both acid and base. This conclusion is not consistent with our work on well-defined thin films of the same materials [8], nor with other recent thin-film measurements on less well-defined but similar systems [9,10], which show a range of first row transition-metal oxides/hydroxides/oxyhydroxides to have higher activity than  $\text{IrO}_2$  in basic solution. Recently published theoretical work by Bajdich et al, however, correlates well with experimental results on well-defined catalysts systems (including our thin ultra-thin films [8]), showing an enhancement in OER activity for doped  $\text{Ni}_{0.25}\text{Co}_{0.75}\text{OOH}$  in comparison to a pure  $\beta\text{-CoOOH}$  surface [11].

To quantitatively compare the activity of catalysts and uncover true structure/composition/activity relationships, a common performance metric is required. We find that the best metric is the turn-over frequency (TOF) at steady state (i.e. after stabilization of the potential in response to an applied current). The TOF is defined as the number of times per second a single active site (which we assume to be a single metal cation) evolves an  $\text{O}_2$  molecule (by accepting four electrons from solution). Because TOFs are typically potential-dependent (based on Butler–Volmer or Tafel kinetics) [12], the overpotential at which the TOF is measured must be reported. TOFs are often not reported due to difficulties in determining the amount of active catalyst in porous electrodes. Sometimes the surface area is estimated based on the capacitance of the electrode; however, this is often inaccurate because the capacitance per unit real surface area can vary widely depending on surface chemistry and porosity [13]. Surface areas based on imaging the particle size distribution directly with an electron microscope, or obtained via gas-adsorption, are more accurate [14], as long as the catalyst is crystalline and the surface does not change under OER conditions. Such conditions, however, often do not hold (see discussion below).

Precise measurements of OER TOFs also require correct referencing to the thermodynamic potential of the

oxygen couple in the electrolyte, as well as precise measurement of, and correction for, uncompensated solution resistance  $R_u$ . Errors in applied potential of as little as 20–30 mV can lead to order-of-magnitude errors in the reported TOF, due to the exponential dependence of TOF on driving force. We find that the simplest method for determining the thermodynamic OER potential is to measure the reversible hydrogen potential (RHE) by cycling freshly cleaned Pt in a  $\text{H}_2$  sparged electrolyte solution. The point of zero current is 0 V vs. RHE, and the OER potential is 1.23 V positive of RHE.  $R_u$  can be minimized through use of a Luggin capillary and high concentrations of supporting electrolyte. Minimization of  $R_u$  is important to reduce errors associated with correction for  $R_u$ . We find that the best estimates of the  $R_u$  are obtained from high-frequency ( $\sim 10\text{--}50$  kHz) impedance measurements [8]. Under these conditions the impedance is typically resistive (phase angle near zero) and can be associated solely with the uncompensated series resistance.

For molecular catalysts, the relevant driving force for the oxidation reaction (i.e. the equivalent of the overpotential) is often not reported because chemical oxidants are used to drive the reaction instead of an electrode. However, the solution potential of oxidant couples (e.g.  $\text{Ce}^{3+/4+}$  or  $\text{Ru}(\text{bpy})_3^{2+/3+}$ ) can be measured directly vs. a reference electrode to estimate the driving force of the chemical oxidant. The lack of driving force data can lead to confusion over relative activity of molecular catalysts vs. heterogeneous ones. Relatively large ( $\sim 500$  mV) driving forces are typically applied to molecular catalysts, as highly oxidizing reagents are used.

## 3. Single-crystal electrodes

For heterogeneous catalysts, single crystals provide a useful platform for the study of catalysis on precise surfaces. The difficulty in synthesizing high quality, sufficiently conductive single crystals of the desired oxides prohibits their routine use. Single-crystal OER results are limited [15–17]. In the absence of single crystals, study of catalytic activity on specific crystal faces is enabled by epitaxial growth on appropriate lattice-matched substrates [18,19]. Epitaxial growth of oxides, however, is also difficult.

## 4. Homogeneous molecular catalysts

Soluble homogeneous catalysts composed of molecularly defined complexes/clusters are useful model systems because the OER mechanism and possible intermediates are amenable to identification using powerful molecular analysis techniques (e.g. IR, NMR, etc.). Molecular  $\text{Mn}_3\text{CaO}_4$  and  $\text{Co}_4\text{O}_4$  cubanes have been targeted for their structural similarity to the  $\text{Mn}_4\text{CaO}_5$  oxygen evolving complex (OEC) in photosystem II [20–22], although no truly functional molecular OEC mimics have been reported to date. Ru complexes have received significant attention [23], but the stability of these complexes has been questioned [24]. Organic ligands are

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