II.G.17 Joint Center for Artificial Photosynthesis: Benchmarking Electrocatalysts for the Oxygen Evolution Reaction

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Objectives

The JCAP benchmarking project involves the development and implementation of uniform protocols for characterizing the performance of catalysts for the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), and carbon dioxide reduction reaction (CO_2RR) under standard conditions relevant to the design of a water-splitting device. To this end, the benchmarking team identifies standard reaction conditions relevant to integrated solar fuels devices, determines standard measurement protocols that adequately and efficiently test catalytic activity and stability, and present pertinent data to the community in a concise and transparent way. By employing standard measurement protocols, unbiased evaluation by the JCAP benchmarking team will provide comparisons that are as accurate as possible between electrocatalytic materials under a uniquely defined set of conditions.

Technical Barriers

The identification of efficient electrocatalysts for the oxygen evolution reaction remains an important challenge in the development of integrated solar-fuels generators.[1-3] However, objective evaluation of the efficiency of OER catalysts is complicated by a lack of standardization both in the measurement and reporting of electrocatalytic data. The protocol we have developed in this study has allowed us to evaluate and compare 10 different non-noble metal catalysts for OER.

Abstract

We have developed a procedure for evaluating the activity, stability, electrochemically-active surface area, and Faradaic efficiency of electrodeposited catalysts for the oxygen-evolution reaction (OER). The primary figure of merit used is the overpotential necessary to achieve 10 mA cm^{-2} current density, roughly the current density expected for a 10% efficient integrated solar-to-fuels device under 1 sun illumination.[4-6] This benchmarking protocol was used to examine the oxygen-evolution activity of the following representative set of Ni- and Co-based metal oxide catalysts in acidic and alkaline solution: CoO_x,[7] CoP_i,[8,9] $CoFeO_x$,[7] NiO_x,[10] $NiCeO_x$,[10] $NiCoO_x$,[11] $NiFeO_x$,[7] and $NiLaO_x$.[10] An electrodeposited IrO_x catalyst was also investigated for comparison.[12,13] We have developed a graphical representation of relevant electrocatalytic parameters in order to facilitate the comparison of catalytic performance of multiple catalysts. Two general observations were made from comparing the performance of these catalysts: 1) every system but IrO_x was unstable under oxidative conditions in acidic solution and 2) every non-noble metal system achieved 10 mA cm^{-2} current density at similar operating overpotentials between 0.35 and 0.43 V in basic solution.

Progress Report

We have developed a procedure for evaluating the activity, stability, electrochemically-active surface area, and Faradaic efficiency of electrodeposited catalysts for the oxygen-evolution reaction (OER) shown in Figure 1. Rotating disk voltammetry (RDV) is used to explore the electrocatalytic activity of electrodeposited catalysts. Rotating the electrode in solution ensures rapid product removal and minimizes bubble formation at the electrode surface. All measurements are made at 1600 rpm under 1 atm O_2 using a commercial saturated-calomel reference electrode and a carbon-rod auxiliary electrode. Ferrocenecarboxylic acid at pH 7 is used as an external reference. The activity and stability of each catalyst system is measured at room temperature in two of the solutions relevant to an integrated solar water-splitting device: 1 M H_2SO_4 and 1 M NaOH. The figure of merit for electrocatalytic activity is the overpotential η required to achieve a 10 mA cm^{-2} current density per geometric area.

The procedure for measuring electrocatalytic activity is as follows: first, the solution resistance is estimated

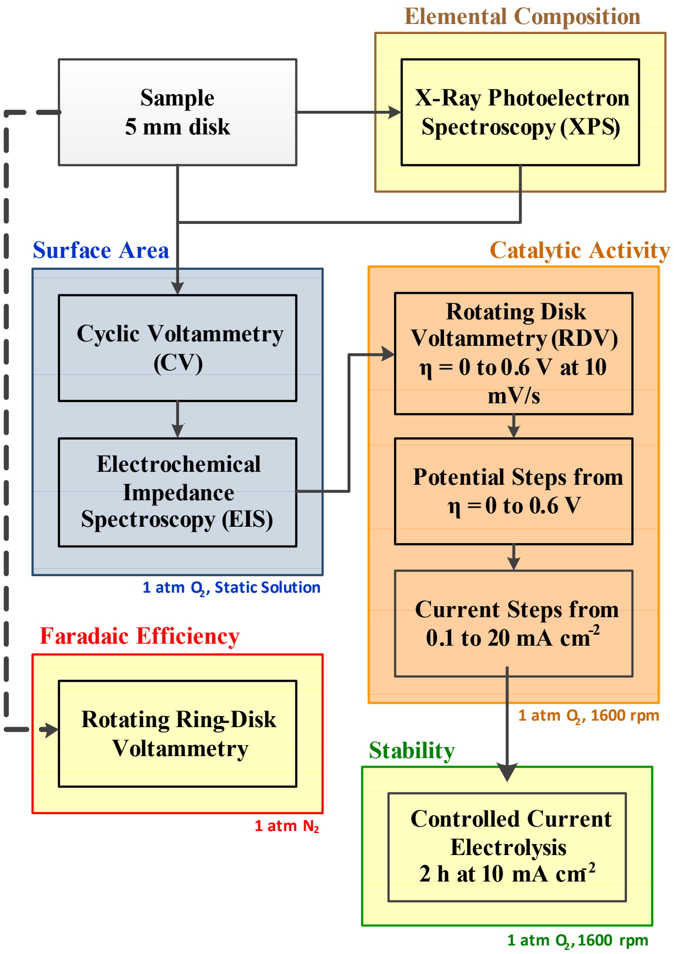

FIGURE 1. Protocol for measuring the electrochemically-active surface area, catalytic activity, stability, and Faradaic efficiency of heterogeneous electrocatalysts for OER. (Reprinted with permission from McCrory, C.C.L.; Jung, S.; Peters, J.C.; Jaramillo, T.F. *J. Am. Chem. Soc.* 2013, *135*, 16977-16987. Copyright 2013 American Chemical Society.)

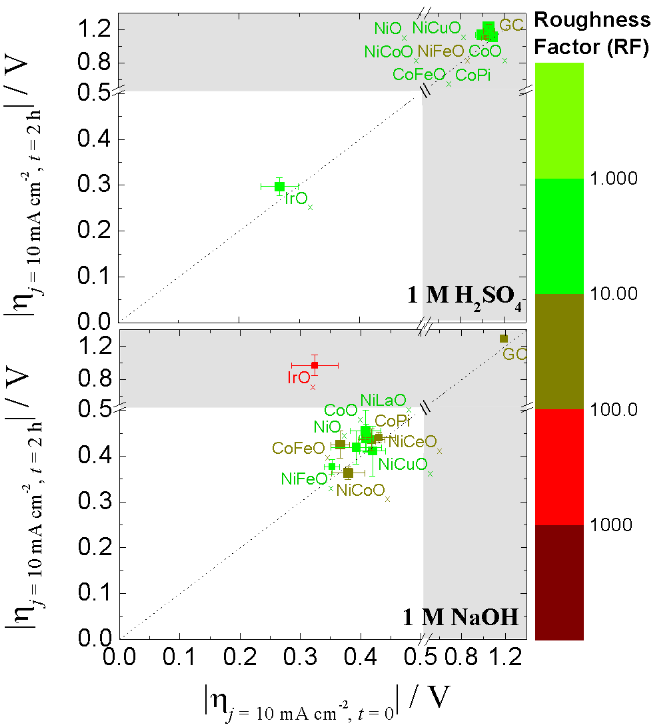

FIGURE 2. Comprehensive plots of catalytic activity, stability, and electrochemically-active surface area for OER electrocatalysts in acidic (top) and alkaline (bottom) solutions. The x-axis is the overpotential required to achieve 10 mA cm-2 per geometric area at time t = 0. The y-axis is the overpotential required to achieve 10 mA cm^{-2} per geometric area at time t = 2 h. The diagonal dashed line is the expected response for a stable catalyst. The color of the each point represents the roughness factor (RF) of the catalyst with a bin size of one order of magnitude with light green representing RF = 1, and dark red representing RF > 10^3. The size of each point is inversely proportional to the standard deviation in the ECSA measurements. The region of interest for benchmarking is the unshaded white region of the plot where the overpotential required to achieve 10 mA cm^{-2} per geometric area at time t = 0 and t = 2 h is less than 0.5 V. There is a break and change in scale in both axes at overpotentials > 0.5 V, and the corresponding region of the plot is shown in gray. (Reprinted with permission from McCrory, C.C.L.; Jung, S.; Peters, J.C.; Jaramillo, T.F. *J. Am. Chem. Soc.* 2013, *135*, 16977-16987. Copyright 2013 American Chemical Society.)

from a high-frequency impedance measurement and every subsequent measurement is IR compensated at 85%. This is followed by a set of activity measurements including linear sweep voltammograms at 0.01 V/s, current steps from 0.01 to 20 mA cm^{-2} per geometric area, and potential steps. Short-term stability measurements are conducted by stepping and holding the current at 10 mA cm^{-2} per geometric area for 2 h and observing the change in operating potential as a function of time. A comprehensive plot that contains information regarding catalyst activity, stability, and specific activity is shown in Figure 2. In general, the best catalyst are expected to achieve 10 mA cm^{-2} current densities at low overpotential, maintain constant activity over time, and have low surface roughness (i.e. high specific activity). Here, the surface roughness is estimated from measuring the non-Faradaic capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammograms[14,15] and from measuring the frequency-dependent impedance of the system using electrochemical-impedance spectroscopy (EIS).[16-18]

Two general observations are made from comparing the performance of these catalysts. First, every system investigated with the exception of IrO_x was unstable under oxidative conditions in acidic solution. Although this study focused on a comparatively small subset of OER catalysts, nevertheless this result highlights the need for additional research towards the discovery of non-noble metal acid-stable OER catalysts. Secondly, every non-noble metal system studied achieved 10 mA cm^{-2} current density per geometric area at similar operating overpotentials between 0.35 and 0.43 V in 1 M NaOH. This suggests that several existing OER catalysts may be attractive for incorporation into devices from an activity and stability standpoint, although the measurements here do not take into account other considerations such as thickness and absorptivity of the catalysts which may have a significant impact on the performance of an integrated catalyst-semiconductor photoanode.

Future Directions

The procedure reported here was initially used to compare the performance of 10 OER catalysts. We are currently expanding the scope of this work to compare the activity and stability of roughly 50 electrocatalysts for HER and OER. This includes developing extended-stability tests for select catalysts that show particular promise based on the initial activity and stability measurements. Moreover, we are currently developing protocols to benchmark the activity, stability, and product distribution of CO_2RR electrocatalyst and integrated semiconductor-catalyst photoelectrodes for HER and OER.

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Publication list (including patents) acknowledging the DOE grant or contract

1. McCrory, Charles C.L.; Jung, Suho; Petres, Jonas C.; Jaramillo, Thomas F.; Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *Journal of the American Chemical Society* **2013**, *135* (45), pp 16977-16987.