PROJECT ABSTRACT *April 20, 2016*

Directed surfaces structures and interfaces for enhanced electrocatalyst activity, selectivity, and stability for energy conversion reactions

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In this project, we have employed a systematic approach to develop active, selective, and stable catalyst materials for important electrochemical reactions involving energy conversion. In particular, we have focused our attention on developing active catalyst materials for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).

HER: We have synthesized and investigated several highly active and acid stable non-precious metal HER catalysts, including: $[Mo_3S_{13}]^{2-}$ nanoclusters (*Nature Chemistry*, 2014) and molybdenum phosphosulfide (MoP|S) (*Angewandte Chemie*, 2014). We have also aimed to engineer these catalyst formulations in a membrane electrode assembly (MEA) for fundamental

studies of water electrolysis at high current densities, approximately 1 A/cm^2 (*ChemSusChem*, 2015). We furthermore investigated transition metal phosphide (TMP) catalysts for HER by a combined experimental–theoretical approach (*Energy & Environmental Science*, 2015). By synthesizing different TMPs and comparing experimentally determined HER activities with the hydrogen adsorption free energies, ΔG_H, calculated by density functional theory, we showed that the TMPs follow a volcano relationship for the HER. Using our combined experimental–theoretical model, we predicted that the mixed metal TMP, $Fe_{0.5}Co_{0.5}P$, should have a near-optimal ΔG_H. We synthesized several mixtures of Co and Fe phosphides alloys and confirmed that $Fe_{0.5}Co_{0.5}P$ exhibits the highest HER activity of the investigated TMPs (*Energy & Environmental Science*, 2015). The understanding gained as to how to improve catalytic activity for the HER, particularly for non-precious metal materials, is important to DOE targets for sustainable H_2 production.

OER: We have developed a $SrIrO_3/IrO_x$ catalyst for acidic conditions (*submitted*, 2016). The $SrIrO_3/IrO_x$ catalyst significantly outperforms rutile IrO_2 and RuO_2, the only other OER catalysts to have reasonable stability and activity in acidic electrolyte, and in fact demonstrates the best activity for any known OER catalyst measured in either acidic or in alkaline electrolyte. For alkaline conditions we have demonstrated that the combined effect of cerium as a dopant and gold as a metal support, significantly enhances the OER activity of electrodeposited NiO_x films. This $NiCeO_x$-Au catalyst delivers high OER activity in alkaline media, and is among the most active OER electrocatalysts reported to date (*Nature Energy*, accepted 2016). These studies of new catalysts for the OER, both in acid and in base, are fundamental to enabling new technologies of interest for the DOE, including the production of sustainable fuels and chemicals.

ORR: One method to significantly reduce the Pt loading in fuel cell devices is to increase the ORR activity of Pt based systems. To this end we have synthesized a high surface area supported meso-structured Pt_xNi alloy thin film with a double gyroid morphology that both exhibits high activity and stability for the ORR (*submitted*, 2016). We have furthermore developed a Ru-core, Pt-shell system that improves the per Pt site activity by more than a factor of 2 (*ChemElectroChem*, 2014). Further refinement, optimizing Pt-shell thickness and reducing particle sintering during processing, enabled us to obtain a mass activity that is 2 times higher than commercial Pt/C from TKK. These are important contributions to the DOE goal of reducing Pt loading since an improved understanding of how to increase mass activity and stability helps enable low Pt content fuel cells.

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PROJECT DESCRIPTION

INTRODUCTION

Electrochemical processes are promising for sustainable energy applications as they can be directly coupled to renewable electricity (e.g., wind and solar) to produce important fuels and chemicals, including H_2. [1, 14] Electrochemical processes can also be used to directly convert chemical energy to electricity, useful for both stationary and transportation applications. [11, 12, 15]

We have investigated three electrochemical transformation reactions: (1) the hydrogen evolution reaction (HER), (2) the oxygen evolution reaction (OER), and (3) the oxygen reduction reaction (ORR). There is significant room for improvement even for today's state-of-the-art materials. New strategies and approaches are needed to improve HER, OER and ORR catalysts in order to enable economical hydrogen fuel generation and utilization.

RESEARCH RESULTS

Catalyst development for the HER

Hydrogen (H_2) is one of the world's most important chemicals mainly used for petroleum refining and synthesizing ammonia-based fertilizers. Catalyzing the electrochemical hydrogen evolution reaction (HER) coupled to renewable energy sources, e.g., wind or solar, is a potential sustainable source of H_2. Platinum is the most effective HER catalyst, but high cost and scarcity may inhibit its wide spread use. We have investigated several non-precious metal HER catalysts.

Thiomolybdate $[Mo_3S_{13}]^{2-}$ clusters for HER

We synthesized catalytically active thiomolybdate $[Mo_3S_{13}]^{2-}$ nanoclusters, that bridge molecular and solid-state electrocatalysis when supported on carbonelectrode surfaces. [13] The

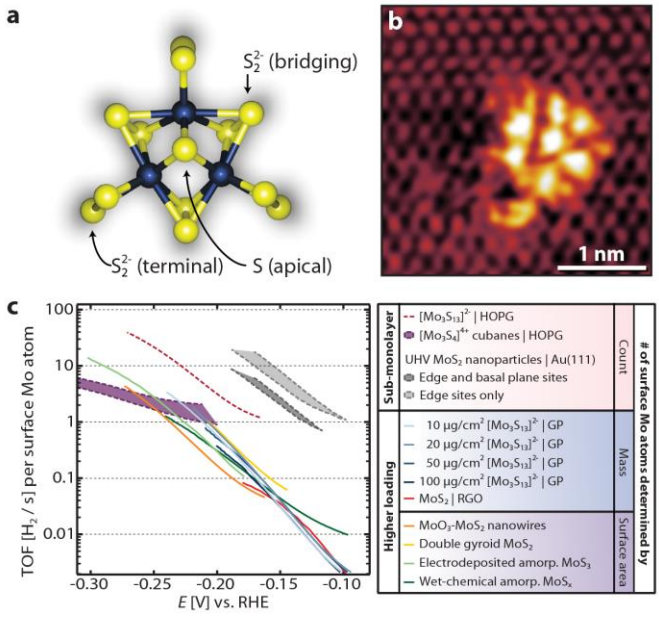

Figure 1: $[Mo_3S_{13}]^{2-}$ for HER.

(a) Model of a single $[Mo_3S_{13}]^{2-}$ cluster containing 3 different types of sulfur ligands. **(b)** Atom-resolved STM image of a single $[Mo_3S_{13}]^{2-}$ cluster revealing an ordered atomic-scale structure. **(c)** Plot displaying the turnover frequency of $[Mo_3S_{13}]^{2-}$ clusters together with several other molybdenum sulfide-based HER catalysts. The $[Mo_3S_{13}]^{2-}$ clusters exhibit the highest HER turnover frequency of any molybdenum sulfide catalyst synthesized by scalable route. [9, 13]

$[Mo_3S_{13}]^{2-}$ nanoclusters exhibited excellent HER activity and stability in acid and imaging at the atomic-scale with scanning tunneling microscopy (STM) allowed for direct observation (see Fig. 1) and quantification of the clusters which enabled determination of the turnover frequency (TOF).

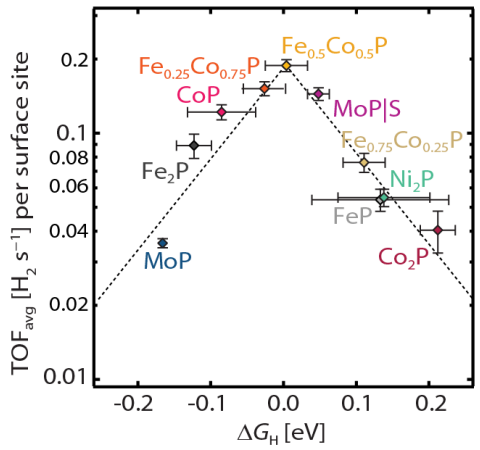

Figure 2: Activity volcano for transition metal phosphides.
Activity volcano for the HER showing the average TOF at an overpotential of 100 mV as a function of ΔG_H. [1-7]

Transition metal phosphides for HER

Recently, transition metal phosphides (TMPs) have also emerged as highly active for the HER. [16-20] However, trends in activity are not well understood. We have provided a new level of understanding through a combined theory-experiment approach. We synthesized different TMPs and correlated experimentally determined HER activities with the hydrogen adsorption free energies, ΔG_H, calculated using DFT, and showed that this correlation follow a volcano relationship (see Fig. 2). [1] Using our combined experimental-theoretical model, we further predicted that the mixed metal TMP, $Fe_{0.5}Co_{0.5}P$, should have a near-optimal ΔG_H. We synthesized and confirmed that, indeed, $Fe_{0.5}Co_{0.5}P$ exhibits the highest HER activity of the investigated TMPs.

Molybdennum phosphosulfide (MoP|S) for HER

We have furthermore shown that in the case of molybdenum phosphide (MoP), it is possible to improve both the HER activity and stability by introducing sulfur in the surface region to form a molybdenum phosphosulfide (MoP|S). [10, 21]

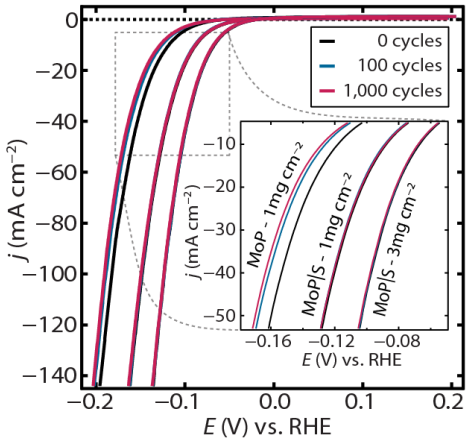

Figure 3: MoP|S for HER.
Accelerated stability test. Initial and post-potential-cycling linear sweep voltammograms of MoP and MoP|S. Whereas MoP experiences a slight decrease in current density upon increased potential cycling, MoP|S remains perfectly stable. [10]

Catalyst development for the OER

Oxygen evolution reaction (OER) is the complementary half-reaction to the HER in electrochemical water splitting, and similarly provides a source of protons for other processes such as electrochemical CO_2 reduction. To overcome the significant kinetic limitations for the OER, we have used a combination of theory and experiment to investigate and better understand catalysts function.

$SrIrO_3/IrO_x$ catalyst for OER

One example is identification of a promising $SrIrO_3/IrO_x$ catalyst.[22] This material was synthesized using pulsed laser deposition resulting in very flat, crystalline films for a well-controlled study of intrinsic catalyst activity.[8] The measured activity for this catalyst was even higher than predicted by theory and was also higher than any known OER catalysts previously reported in acid or base (see Fig. 4). [2-7] In addition to showing excellent stability over 30 hours of testing with no measurable degradation. Investigation of the catalyst surface after electrochemical testing revealed Sr leaching which likely leads to formation of a primarily IrO_x terminated surface. Theory efforts within SUNCAT have helped to elucidate plausible surface structures for the catalyst.

Gold-supported, nickel cerium oxide for OER

One of the most promising catalyst systems we recently discovered for use in basic electrolyte is a gold-supported, nickel cerium oxide ($NiCeO_x$/Au) thin film which outperforms the best known OER catalysts reported in base, including fully precious metal systems (see Fig. 4). Based on experimental observations and theoretical modeling, we ascribe the activity enhancement to a combination of electronic, geometric and support effects, where highly active under-coordinated sites at the oxide-support interface are modified by the local chemical binding environment and by doping the host Ni-oxide with Ce. This new high-performance catalyst is further demonstrated in a device context by pairing it with a nickel-molybdenum hydrogen evolution catalyst in a water electrolyzer, which delivers 50 mA consistently at 1.5 V over 24 hours of continuous operation.

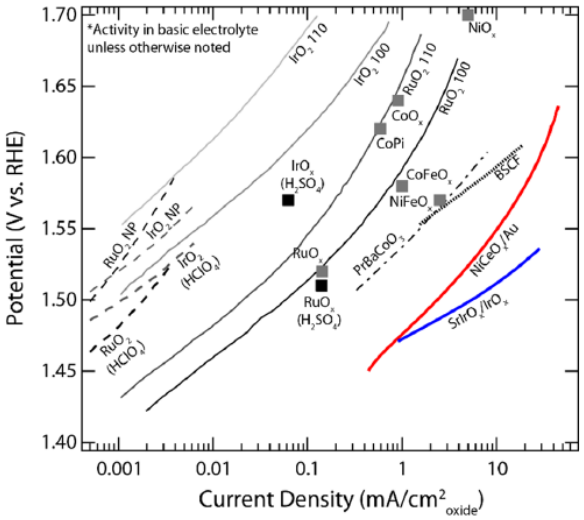

Figure 4: $SrIrO_3/IrO_x$ and $NiCeO_x$/Au for OER. OER performance of our $SrIrO_3/IrO_x$ and $NiCeO_x$/Au catalysts. Specific activity normalized to actual surface area of the metal oxide catalysts. [2-10]

Catalyst development for the ORR

Oxygen electrochemistry also plays a key role in fuel cells; the oxygen reduction reaction (ORR) is a major source of efficiency limitations due to sluggish kinetics. Improving both the activity and stability of the cathode catalyst in platinum-based polymer electrolyte fuel cells is a key technical challenge for next generation sustainable-energy conversion technologies.

Double gyroid Pt_xNi for ORR

To this end we have synthesized a high surface area supported meso-structured Pt_xNi alloy thin film with double gyroid (DG) morphology that both exhibits high activity and stability for the ORR (see Fig. 5). [11] The DG Pt_xNi represent the first ever reported fully contiguous large area supported thin film of a highly ordered mesoporous metal alloy. Our studies of ORR catalysis on these thin films show that the DG meso-structure remains intact and maintains good activity even after intensive accelerated stability testing.

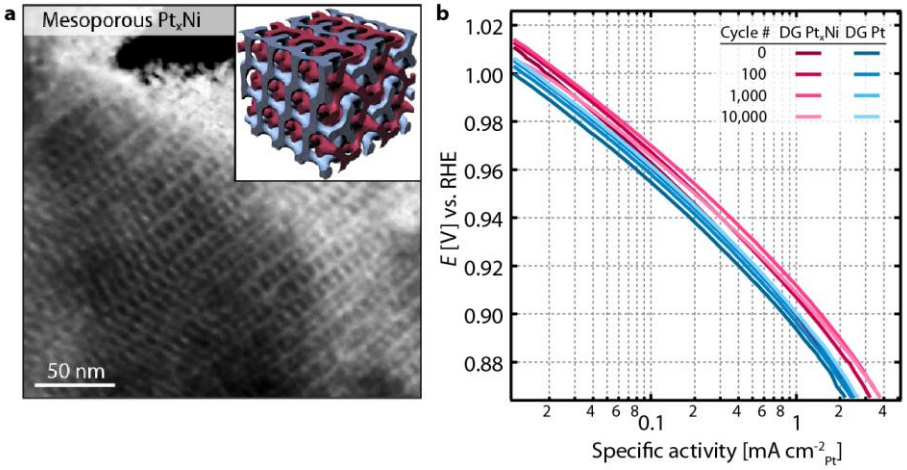

Figure 5: Double gyroid Pt_xNi for ORR.

TEM image and model of the bi-continuous mesoporous PtxNi with double gyroid morphology. Initial and post potential cycling Tafel plot of the kinetic current densities of DG Pt_xNi (Pt: 17 µg cm^{-2}) and DG Pt (Pt: 40 µg cm^{-2}). [11]

Core-shell Ru@Pt nano-particles for the ORR

Additionally, through a combined theory-experiment approach, we identified and developed highly active Ru@Pt core-shell nano-particles for the ORR. [12] Following theoretical predictions of improved oxygen binding on many sites for the Ru@Pt system compared to those of Pt(111), core shell structures (see Fig. 6) were synthesized using a scalable polyol synthesis method. Experimental optimization led to the creation of a highly active and stable Ru@Pt catalyst which outperformed state-of-the-art commercial Pt/C (TKK) nanoparticles and exceeded the DOE 2017 target for mass activity. [23]

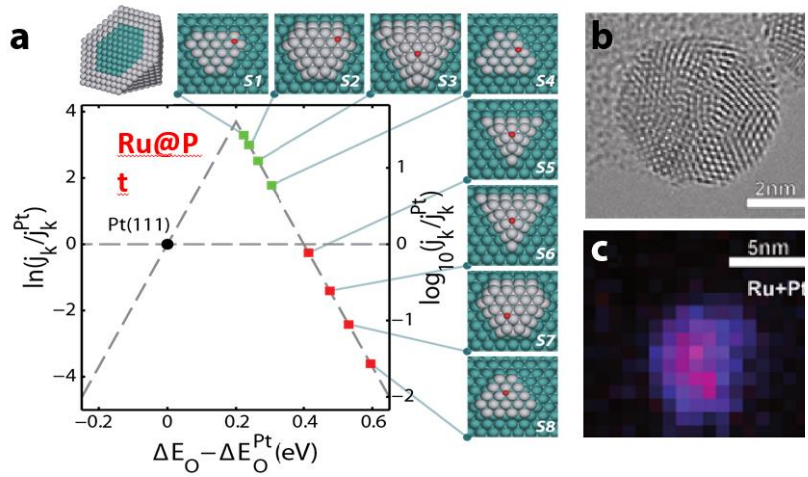

Figure 6: Core-shell Ru@Pt for ORR.

Theoretical oxygen reduction reaction activity volcano plotted as a function of oxygen binding energy. The core-shell strategy allows one to take advantage of two effects: weakening oxygen binding energies by means of thin-film overlayers, and strengthening oxygen binding energies through nano-scale effects. **(b)** and **(c)**, TEM image and EDS map of Ru@Pt core-shell nanoparticle, respectively. [12]

DESCRIPTION OF SPECIAL RECOGNITIONS RECEIVED BY THE PI

- Volkswagen/BASF Science Award Electrochemistry, 2014.
- Resonate Award, Resnick Sustainability Institute at the California Institute of Technology, 2014.
- 2014 *Energy & Environmental Science* Readers' Choice Award and Lectureship

STATEMENT OF UNSPENT FUNDS FOR THE YEAR

There are no unspent funds.

COMPLETE LIST OF PUBLICATIONS:

J. Kibsgaard, T. F. Jaramillo, F. Besenbacher
Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate $[Mo_3S_{13}]^{2-}$ clusters.
Nature Chemistry **6**, 248-253 (2014).

J. Kibsgaard, C. Tsai, K. Chan, J.D. Benck, J.K. Nørskov, F. Abild-Pedersen, T.F. Jaramillo
Designing an Improved Transition Metal Phosphide Catalyst for Hydrogen Evolution using Experimental and Theoretical Trends.
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J. Kibsgaard, T. F. Jaramillo
Molybdenum Phosphosulfide: An Active, Acid-Stable Earth-Abundant Catalyst for the Hydrogen Evolution Reaction.
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Polymer Electrolyte Membrane Electrolyzers Utilizing Non-precious Mo-based Hydrogen Evolution Catalysts.
Chemsuschem **8**, 3512-3519 (2015).

L.C. Seitz, C.F. Dickens, K. Nishio, Y. Hikita, J. Montoya, A. Doyle, C. Kirk, A. Vojvodic, H.Y. Hwang, J.K. Nørskov, T.F. Jaramillo
A Highly Active and Stable $SrIrO_3/IrO_x$ Catalyst for the Oxygen Evolution Reaction.
Submitted, (2016).

J.W.D. Ng, M. García-Melchor, M. Bajdich, C. Kirk, P. Chakthranont, A. Vojvodic, T.F. Jaramillo
Leveraging Electronic, Geometric and Support Effects in Electrocatalyst Development: Au Supported $NiCeO_x$ for Water Oxidation
Nature Energy (Accepted, 2016).

J. Kibsgaard, A. Jackson, T. F. Jaramillo
Mesoporous platinum nickel thin films with double gyroid morphology for the oxygen reduction reaction.
Submitted, (2016).

A. Jackson, V. Viswanathan, A.J. Forman, A.H. Larsen, J.K. Nørskov, T.F. Jaramillo
Climbing the Activity Volcano: Core-Shell Ru@Pt Electrocatalysts for Oxygen Reduction.
ChemElectroChem **1**, 67-71 (2014).

(g) Multi-year publication spreadsheet per attached Excel template

See the associated Excel file.

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[1] J. Kibsgaard, C. Tsai, K. Chan, J. D. Benck, J. K. Nørskov, F. Abild-Pedersen and T. F. Jaramillo, *Energy and Environmental Science*, **8**, 3022-3029 (2015).

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