
II.G.12 Joint Center for Artificial Photosynthesis: High Throughput Experimentation for Electrocatalyst and Photoabsorber Discovery

Principal Investigator: Carl Koval
California Institute of Technology, Pasadena, CA
Email: ckoval@caltech.edu

Names of Team Members

J.M. Gregoire (Project Lead, gregoire@caltech.edu),
J. Jin (Project Co-lead), M. Marcin, S. Mitrovic, E. Cornell,
C. Xiang, E. Soedarmadji, S. Suram, K. Kan, J. Haber,
P. Newhouse, D. Guevarra, R. Jones, N. Becerra,
M. Pesenson, L. Zhou, A. Shinde
California Institute of Technology, Pasadena, CA

DOE Program Manager: Gail McLean,
Phone: (301) 903-7807
Email: gail.mclean@science.doe.gov

Objectives

The mission of the Joint Center for Artificial Photosynthesis (JCAP) is to produce fundamental scientific discoveries and major technological breakthroughs to enable the development of energy-efficient, cost-effective, and commercially viable processes for the large-scale conversion of sunlight directly to fuels. JCAP's 5-year goal is discovery of robust, Earth-abundant light absorbers, catalysts, linkers, membranes, and scale-up science required to assemble the components into a complete artificial photosynthetic system. The High Throughput Experimentation (HTE) project develops state of the art high throughput techniques and applies them to efficient screening of earth-abundant composition spaces to identify new electrocatalyst and light absorber materials.

Technical Barriers

To identify materials that can operate in a solar fuels device, material screening must be performed under technologically-relevant conditions. High throughput instruments that adhere to these conditions must be developed and then automated to provide robust high throughput operation. This screening strategy must then be embedded in a high throughput pipeline that includes high quality materials synthesis and characterization. While operation of this pipeline can identify new promising materials and accelerated discovery, development and deployment of materials can only be attained by integrating the high throughput pipeline into a larger consortium that includes benchmarking, directed research and prototyping efforts. Successful implementation of this research paradigm

also requires interplay with theory efforts. JCAP is boldly solving these exciting technical and research integration challenges.

Abstract

JCAP-HTE performs accelerated discovery of new earth-abundant photoabsorbers and electrocatalysts through operation of a high throughput pipeline for the synthesis, screening and characterization of photoelectrochemical materials. To establish the pipeline, several new screening instruments for high throughput (photo-)electrochemical measurements have been invented. These instruments are not only optimized for screening against solar fuels requirements, but also provide new tools for the broader combinatorial materials science community. Operation of the pipeline and its embedment into the solar fuels hub has yielded the high throughput discovery, follow-on verification, and device implementation of a new quaternary metal oxide catalyst. This rapid technology development from discovery to device implementation is a hallmark of the multi-faceted JCAP research effort.

Progress Report

The widespread deployment of new energy technologies requires discovery and development of new functional materials [Energy Environ Sci 2013, 6, 1983]. Artificial photosynthesis is a promising energy technology with several substantial materials challenges [Chem Reviews 2010, 110, 6446]. Proposed designs for an artificial photosynthesis device, or solar fuel generator, involve coupling electrocatalysts to light absorbing semiconductors to provide solar-driven photoelectrochemical reactions. Successful development of such a device requires discovery of both photoabsorbers and electrocatalysts for the pertinent reactions. Desirable traits for new high performance materials include high earth abundance, facile synthesis methods and insensitivity to small variations in composition. To identify new photoabsorbers and electrocatalysts with these traits, we are building a high throughput pipeline for accelerated materials discovery.

The development of this pipeline within the solar to fuels energy innovation hub provides very powerful capabilities for accelerated discovery. The performance screening metrics employed in the pipeline are developed according to the specifications of the directed research and device prototype experts. Another important capability is the rapid incorporation of newly discovered materials into a solar fuels testbed. This capability shortens the time lapse between high

throughput discovery and technology demonstration from years to weeks.

The JCAP-HTE accelerated discovery pipeline contains 4 primary sectors as shown in Figure 1, three of which involve the development of new experimental equipment and techniques: Materials synthesis, (Light-absorber and Electrocatalyst) screening, and Characterization. The fourth sector is Data informatics and distribution and involves the data connectivity to the other sectors and to users.

Performance Screening

The heart of the high throughput pipeline is the evaluation of new materials as either electrocatalysts for solar fuels reactions or solar light absorbers. To create a high throughput screening platform, semi-quantitative parallel screening is used to rapidly identify composition regions of interest, followed by more detailed serial screening on select samples.

The JCAP-HTE parallel catalyst screening instrument is based on bubble imaging, a conceptually simple but technically nuanced technique¹. The JCAP-HTE bubble screening instrument (see Figure 2) images the oxygen and hydrogen bubbles produced by the Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER). The bubble screening method can function in all pH conditions and is suitable for the combinatorial search of catalysts for any gas evolving reaction, most notably the OER and HER solar fuels reactions.

To provide more detailed electrochemical screening, JCAP-HTE developed a scanning droplet cell (SDC)² [ENREF_2](#). The JCAP SDC provides a 3-electrode cell for an individual 1 mm² sample with no o-rings or other physical contact to the working electrode, other than the electrolyte solution. The SDC is used to provide quantitative screening



FIGURE 1. Sectors of the accelerated discovery pipeline, with the screening sector split for the 2 general material functions of light absorption and electrocatalysis.

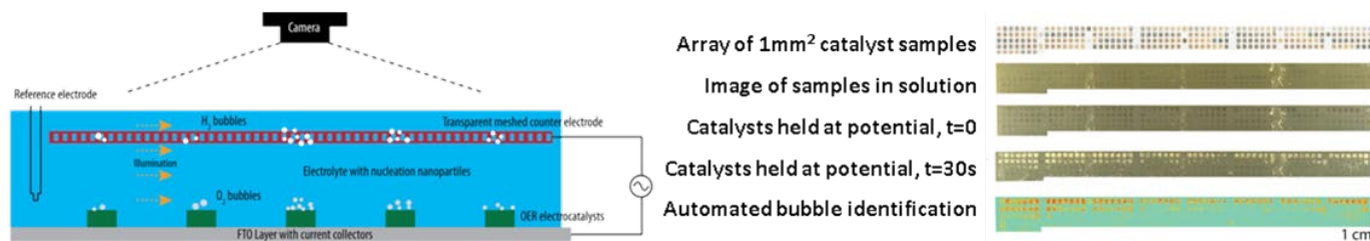


FIGURE 2. Summary of the bubble screening technique. Bubbles of evolved gas appear as white dots above active catalysts. Simultaneous imaging of all samples and automated image processing yields rapid identification of the most active catalyst compositions.

at throughput of less than 10 s per sample. Carefully designed software allows for real time data analysis so that high performance materials can be automatically evaluated with subsequent measurements, of typically longer duration, to ascertain stability.

For the screening of photoabsorbers, JCAP-HTE is continuing its development of novel instrumentation for parallel and serial screening for optical properties, but the key innovation in light absorber screening has moved beyond this to fill the technology gap between optical characterization and photoelectrochemical water splitting. With the expectation that the best photoanode absorber will not also be the best OER catalysts, a solar fuels photoanode is typically made by coupling a catalyst and absorber. To discover photoabsorbers which are not photocatalysts, a new screening tool needed to be developed. JCAP's recently published solution to this technology gap is another example of a conceptually simple but technically nuanced instrument. To alleviate the catalytic requirement, n-type/p-type photoabsorbers are screened by measuring the photo-oxidation/reduction of facile redox couples. To mitigate dark currents, a multiplexed counter electrode is coupled with the sample-indexed illumination, and to mitigate shunting of the photocurrent, a carefully engineered thin layer cell is established.

Discovery of a new class of rare earth-rich OER catalysts in unpredicted composition spaces

The discovery of Ce-rich OER catalysts was recently reported³ and followed by a detailed investigation describing its unique electrochemical performance. The pseudo-quaternary (Ni-Fe-Co-Ce)O_x library was deposited as an array of 5456 discrete compositions at 3.3 at% composition steps using inkjet printing of four separate metal precursor inks. The relative electrocatalytic performance of each composition was screened using several different figures of merit (FOM). The most informative FOM for photoelectrochemical water-splitting devices is the overpotential (η) for the OER at 10 mA/cm², which is mapped in Figure 3A for the entire composition space. The most active regions can be seen near the Ni-Fe edge and on the Ni-Co-Ce face of the tetrahedron. To visualize the

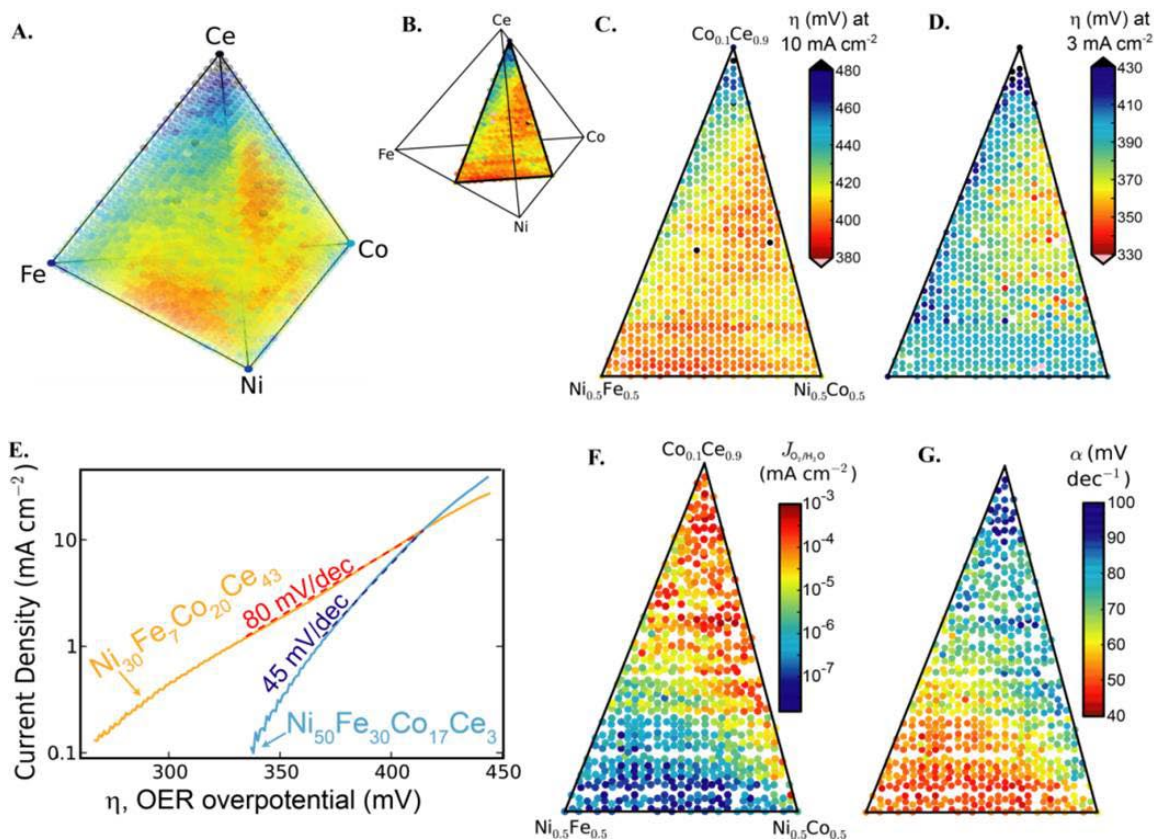


FIGURE 3. The OER overpotential for 10 mA/cm^2 is shown for the entire quaternary composition space (A) and for a pseudo-ternary cross section (B-C). A different composition trend is observed with the OER overpotential for 3 mA/cm^2 (D). This is due to the different catalytic behavior of the newly discovered high-Ce catalyst compared to known catalysts (E), prompting exploration of the trends in Tafel parameters (F-G).

relationship between these composition regions, Figure 3B demonstrates the extraction of a pseudo-ternary cross section of the data in Figure 3A, which is plotted in Figure 3C. For these same compositions, the overpotential (η) for the OER at 3 mA/cm^2 is mapped in Figure 3D. This figure demonstrates that the newly discovered high-Ce catalysts are far superior to the known Ni-Fe catalysts at low current density. To further demonstrate this relative performance, Figure 3E shows the catalytic current for representative compositions ($\text{Ni}_{0.5}\text{Fe}_{0.3}\text{Co}_{0.17}\text{Ce}_{0.03}\text{O}_x$ and $\text{Ni}_{0.3}\text{Fe}_{0.07}\text{Co}_{0.2}\text{Ce}_{0.43}\text{O}_x$), the former being a low-Ce composition similar to the known Ni-Fe catalysts, and the latter being a newly discovered high-Ce composition. Figure 3E also shows that these 2 compositions have different characteristic Tafel slopes and corresponding exchange current densities (Figure 3F-3G). Detailed composition measurements of these representative samples both before and after electrochemical testing demonstrate the fidelity of the inkjet printing synthesis and the stability of the catalysts. Using the JCAP rapid technology development platform, this catalyst and its performance have been verified by benchmarking, improved by directed research, demonstrated in a prototype device, and understood by extensive characterization.

Characterization and Data Informatics

The importance of characterization and informatics in materials discovery and understanding cannot be overstated. It is through the characterization of materials that composition-processing-structure-property relationships can be developed. Material characterization also facilitates interactions with theory efforts. Data informatics enables automated identification of unforeseen trends and completes a learning feedback loop for identification of superior materials. By developing state of the art techniques in these sectors, JCAP-HTE is foundational in using high throughput methods as tools for performing basic energy science.

Publication list

- Xiang, C.; Suram, S.K.; Haber, J.A.; Guevarra, D.W.; Jin, J.; Gregoire, J.M., A High Throughput Bubble Screening Method for Combinatorial Discovery of Electrocatalysts for Water Splitting. *ACS Comb. Sci.* **2014**, *16* (2), 47-52.
- Gregoire, J.M.; Xiang, C.; Liu, X.; Marcin, M.; Jin, J., Scanning Droplet Cell for High Throughput Electrochemical and Photoelectrochemical Measurements. *Review of Scientific Instruments* **2013**, *84* (2), 024102.

3. Haber, J.A.; Cai, Y.; Jung, S.; Xiang, C.; Mitrovic, S.; Jin, J.; Bell, A.T.; Gregoire, J.M., Discovering Ce-rich oxygen evolution catalysts, from high throughput screening to water electrolysis. *Energ Environ Sci* **2014**, *7* (2), 682-688.

4. Haber, J.A.; Xiang, C.; Guevarra, D.; Jung, S.; Jin, J.; Gregoire, J.M., High-Throughput Mapping of the Electrochemical Properties of (Ni-Fe-Co-Ce) Ox Oxygen-Evolution Catalysts. *ChemElectroChem* **2014** *1* (3) 524-528.

5. Gregoire, J.M.; Xiang, C.; Mitrovic, S.; Liu, X.; Marcin, M.; Cornell, E.W.; Jin, J., Combined Catalysis and Optical Screening for High Throughput Discovery of Solar Fuels Catalysts *Journal of the Electrochemical Society* **2013**, *160* (4), F337

6. Xiang, C.; Haber, J.; Marcin, M.; Mitrovic, S.; Jin, J.; Gregoire, J.M., Mapping Quantum Yield for (Fe-Zn-Sn-Ti)Ox Photoabsorbers Using a High Throughput Photoelectrochemical Screening System. *ACS Combinatorial Science* **2014**

7. Patent Application: Scanning Drop Sensor, May 31, 2013, J. Jin, C, Xiang, J. M. Gregoire.