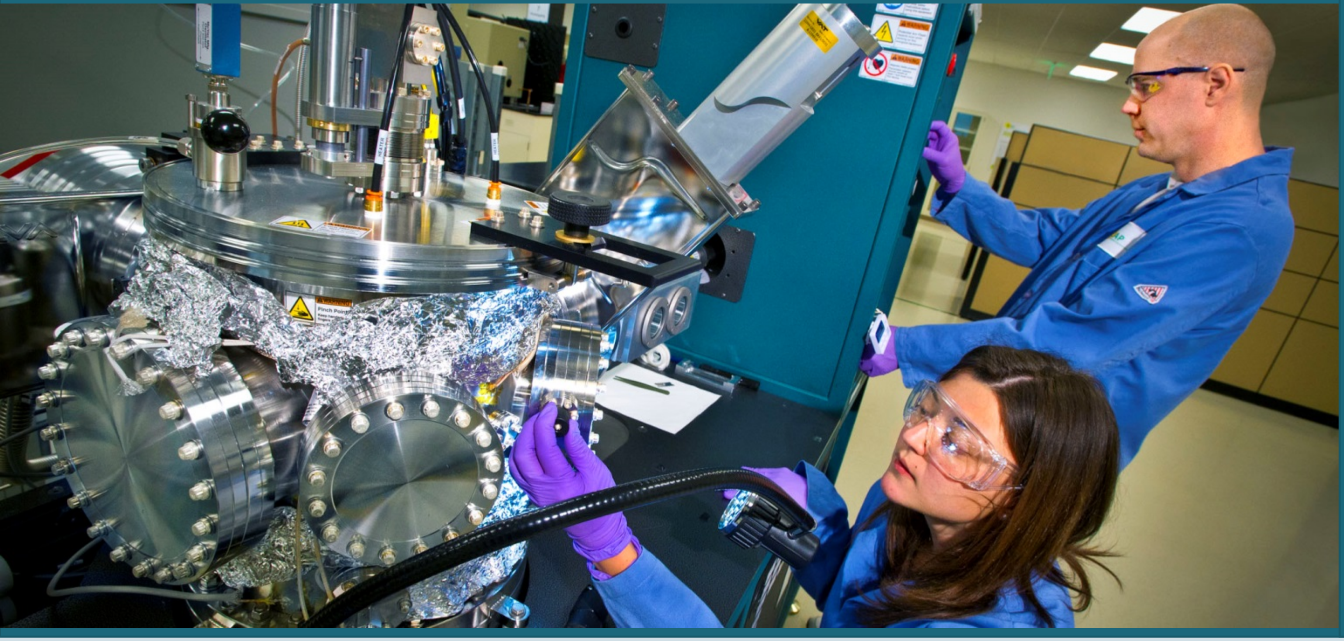
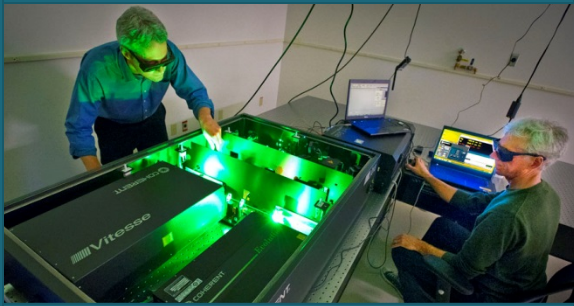
JCAP Research Overview for HTAC





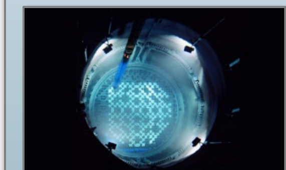
Carl Koval, Director

October 30, 2013

DOE Energy Innovation Hubs

All five DOE Energy Innovation Hubs have challenging goals

Consortium for Advanced Simulation of Light Water Reactors (CASL)



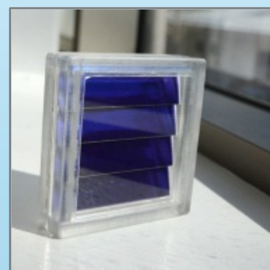
Objective: *Develop computer simulation models that enhance the safety, reliability, and economics of nuclear energy.*

Energy Efficient Buildings Hub (EEBHub)

Objective: *Improve energy efficiency of buildings in the Philadelphia metropolitan area by 20% by 2020.*

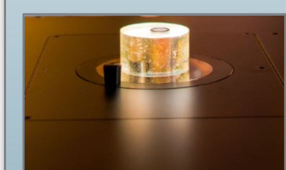
Joint Center for Artificial Photosynthesis (JCAP)

Objective: *Develop an efficient, scalable and robust prototype that generates fuel from sunlight, water, and carbon dioxide.*



Joint Center for Energy Storage Research (JCESR)

Objective: *Increase the energy density of batteries by a factor of five within five years at one-fifth of the cost.*



Criticial Materials Institute (CMI)

Objective: *Identify approaches to reduce supply risk of rare-earth elements that are critical to clean energy technologies.*

The Joint Center for Artificial Photosynthesis – At a Glance

5 Leading Research Institutions

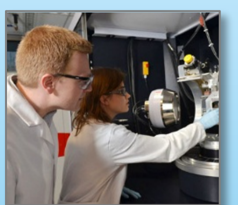
California Institute of Technology · Berkeley Lab (Lawrence Berkeley National Laboratory) · SLAC · University of California, Irvine · University of California, San Diego

Two Dedicated Research Laboratories

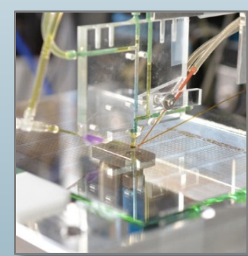
Jorgensen Laboratory

Solar-Energy Research Center

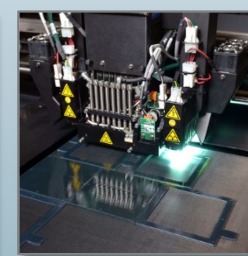
140 Scientists and Engineers



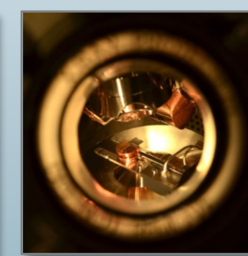
Instruments & Unique Capabilities



High throughput electrochemistry



Rapid prototyping systems

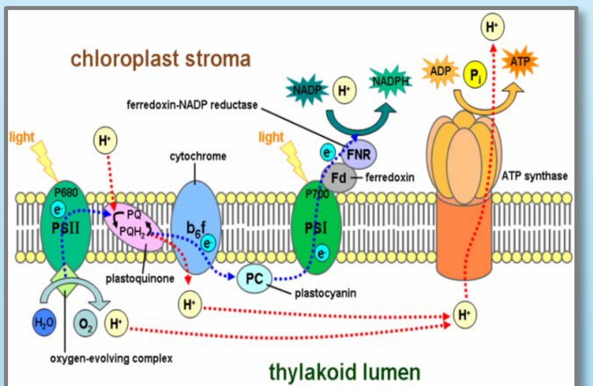


Advanced surface characterization

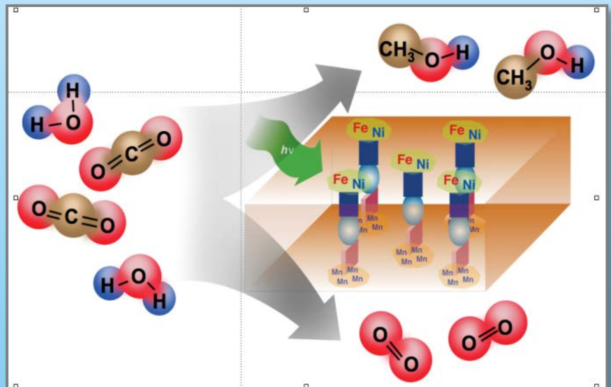
JCAP 5-YEAR GOAL

Discovery of robust, Earth-abundant light absorbers, catalysts, linkers and membranes; and scale-up science required to assemble the components into a complete photosynthetic system.

NATURAL PHOTOSYNTHESIS



ARTIFICIAL PHOTOSYNTHESIS



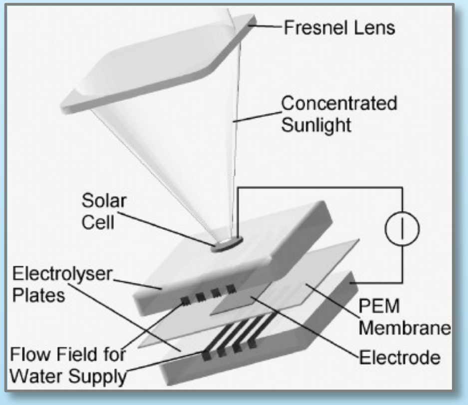
"It is time to build an actual artificial photosynthetic system, to learn what works and what does not work, and thereby set the stage for making it work better"

Melvin Calvin (1961 Nobel Laureate)

JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

General Approaches to Artificial Photosynthesis

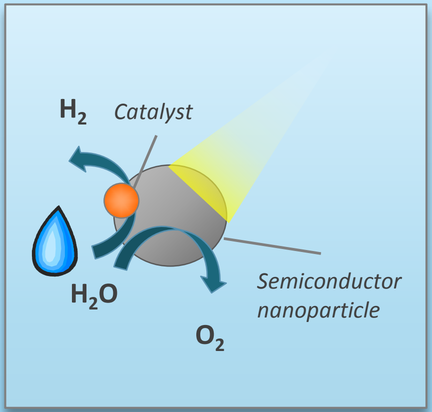
Discrete Photovoltaic Wired to Electrolyzer



Advantages: Operational system has already been demonstrated with 18% efficiency.[1]

Challenges: Demonstrated system demands expensive components; lack of integration further reduces cost efficiency.

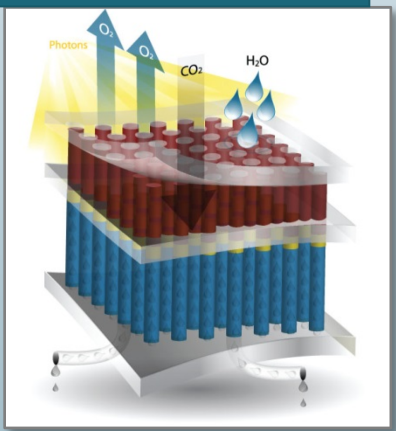
Solar-Fuel Generating Particle Dispersions



Advantages: Offers a simple architecture with the potential for low materials cost.

Challenges: Co-generation of fuel and oxidizer pose operational safety issues.

Integrated Photoelectrochemical Solar-Fuel Generator



Advantages: Potentially lower component costs than a discrete system with reduced complexity.

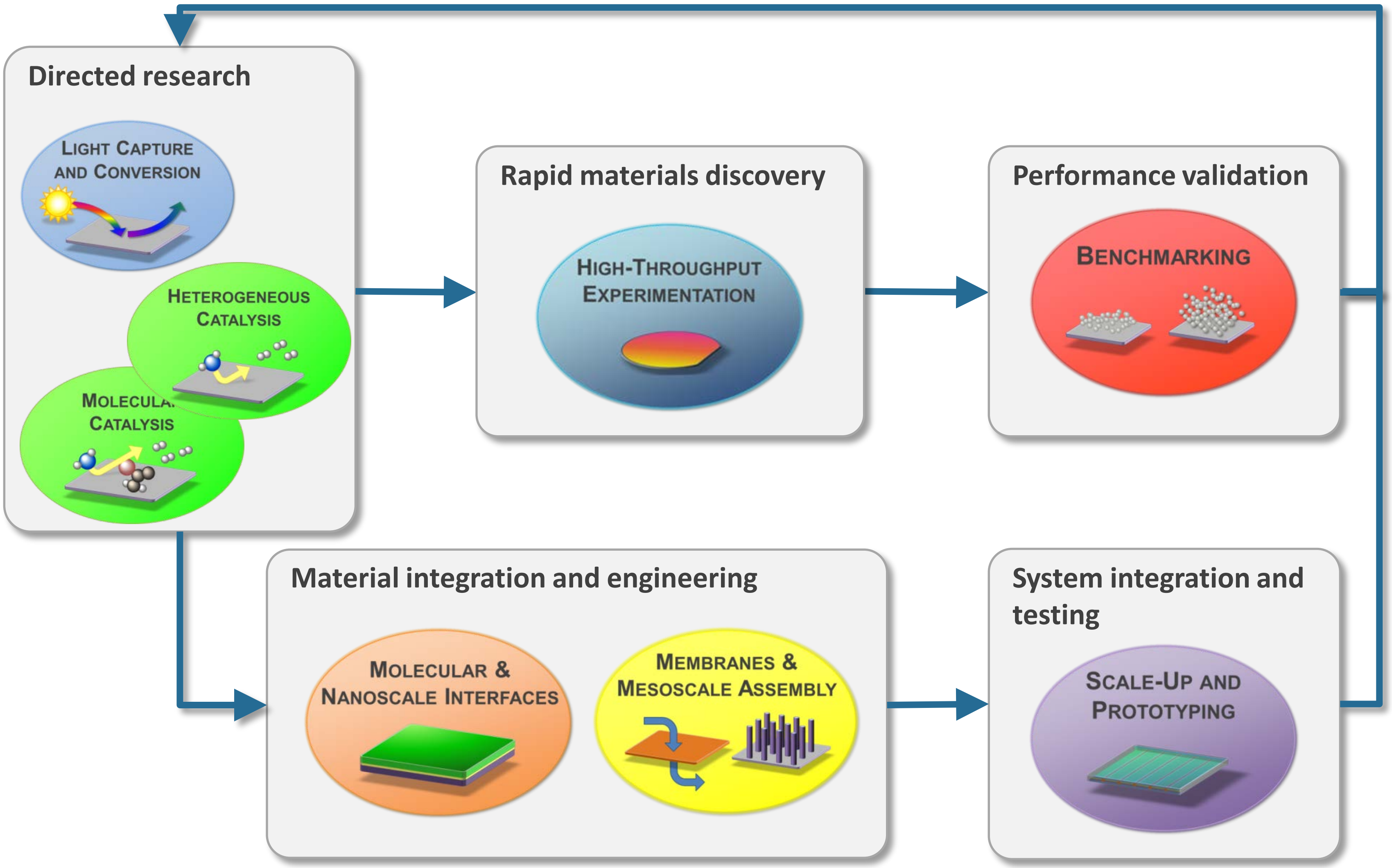
Challenges: Requires that semiconductor, catalysts, and membranes operate efficiently under identical conditions.

[1] G. Peharz, F. Dirmouth, and U. Wittstadt *Int. J. of Hydrogen Energy* **2007**, *32*, 3248-3252 (DOI: 10.1016/j.ijhydene.2007.04.036)

JCAP Joint Center for Artificial Photosynthesis

JCAP APPROACH TO ARTIFICIAL PHOTOSYNTHESIS

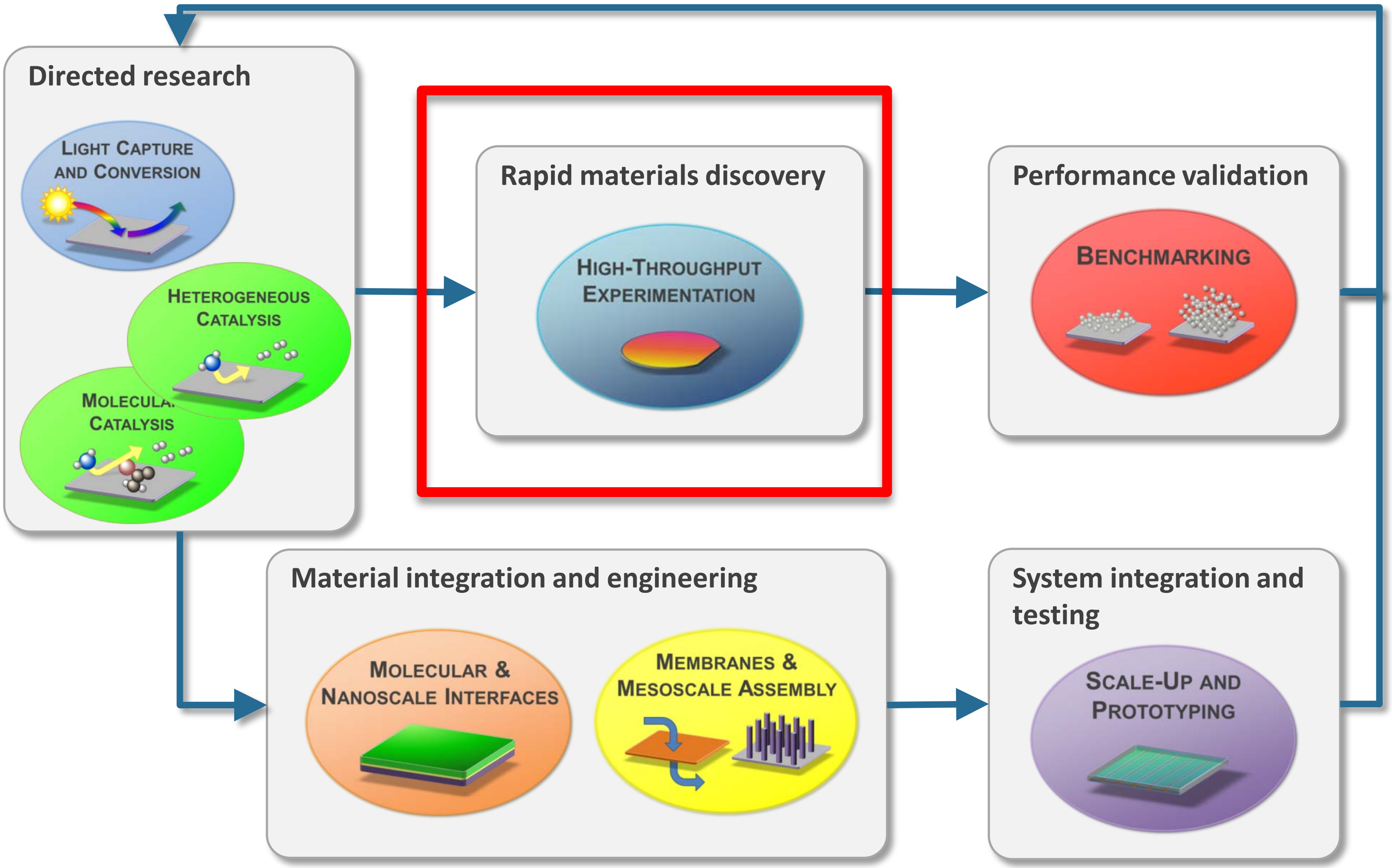
Projects are coordinated to accelerate materials discovery and prototype development



JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

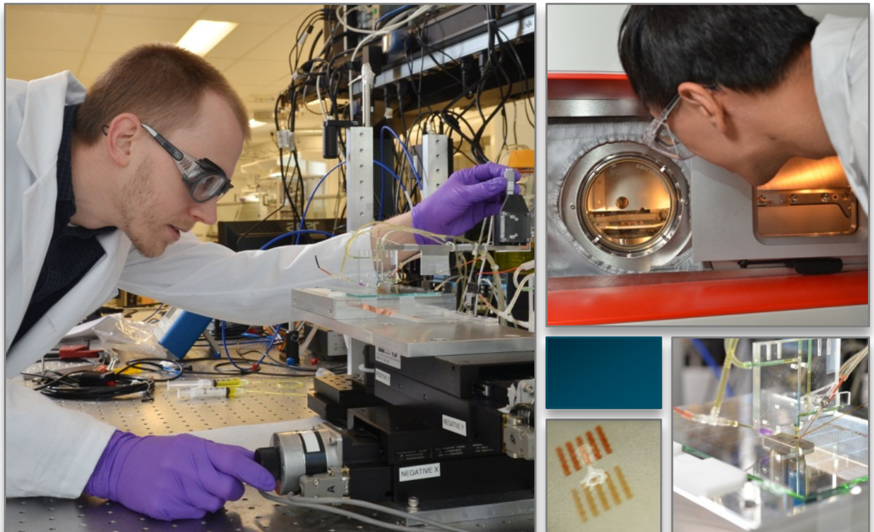
JCAP Approach to Artificial Photosynthesis

Projects are coordinated to accelerate materials discovery and prototype development



JCAP
Joint Center for Artificial Photosynthesis

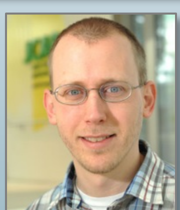
OVERVIEW OF THE HIGH-THROUGHPUT EXPERIMENTATION PROJECT



OBJECTIVES

JCAP's High-Throughput Experimentation (HTE) Project focuses on automated, high-throughput discovery of light absorbers and heterogeneous catalysts. The project employs combinatorial techniques that can produce new alloys from Earth abundant elements, rapid screening methods that can identify high-performing light absorbers and catalysts, and surface-science analysis tools that can characterize the structure and composition of promising materials.

PROJECT LEADER

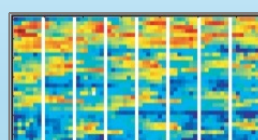


John Gregoire

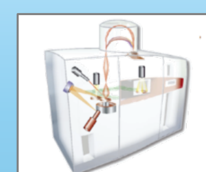
APPROACH

Combinatorial materials synthesis

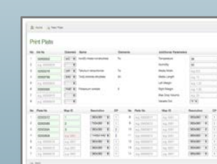
High-throughput screening



High-throughput characterization



Planning and analysis



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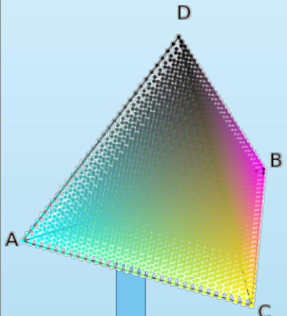
Combinatorial Materials Synthesis

Discrete composition libraries are produced using ink jet printers

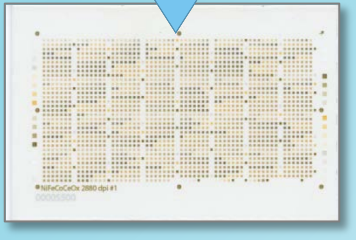
Mapping of Composition Space



- 4-element space
- 3.33% intervals.
- 5456 samples ($1mm^2$) on 3 plates

Ink Formulation and Printing

Calcination

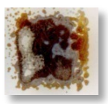


Material libraries consisting of pseudo- binary, tertiary, and quaternary compositions can be produced with unprecedented throughput using inkjet printers

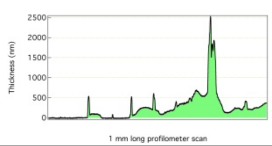
High-throughput inkjet printing required extensive development

Technical gaps

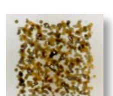
Non-reproducibility
Step-wise, multi-pass printing reduces throughput and reproducibility



Non-uniform thickness
Printing on glass substrates produces highly non-uniform film thicknesses

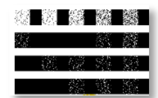


Poor mixing
Standard inkjet printing techniques result in poor mixing of components



Key innovations

Bitmap printing
An automated bitmap printing routine was developed that uses randomized, overlaid patterns

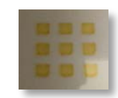


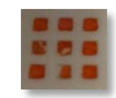
Substrate treatment
JCAP developed an agarose-gel based surface treatment that reduces surface tension of glass substrates

Hydration patterning
JCAP discovered that priming of substrates with patterned water droplets improves mixing.

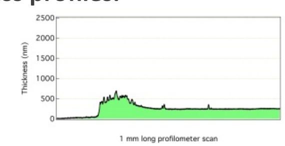
Achievements

Consistent, high-throughput printing
Printed ink spots can now be printed consistently with higher throughput at constant volumes.





Uniform thickness
Inkjetted films now exhibit uniform thickness profiles.

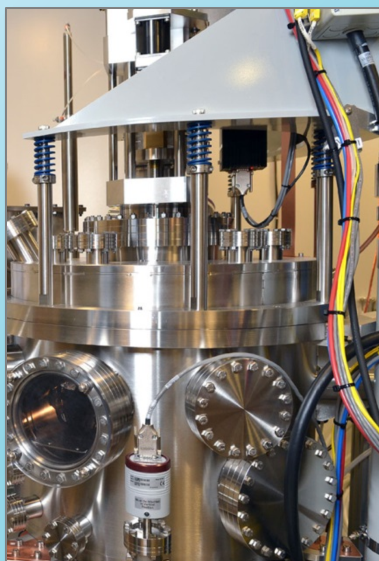


Homogeneous mixing
Printed spots now exhibit good thickness uniformity

COMBINATORIAL MATERIALS SYNTHESIS

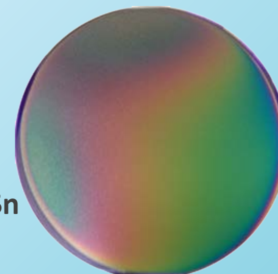
Continuous composition libraries can be produced using physical vapor deposition

OFF-AXIS SPUTTERING SYSTEM



TERNARY LIBRARY EXAMPLES

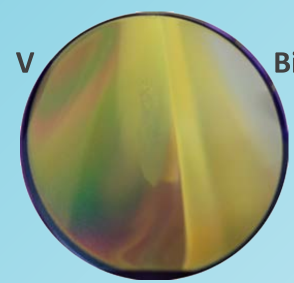
Zn



Sn Si

Metal nitride library

V Bi



Fe

Metal oxide library

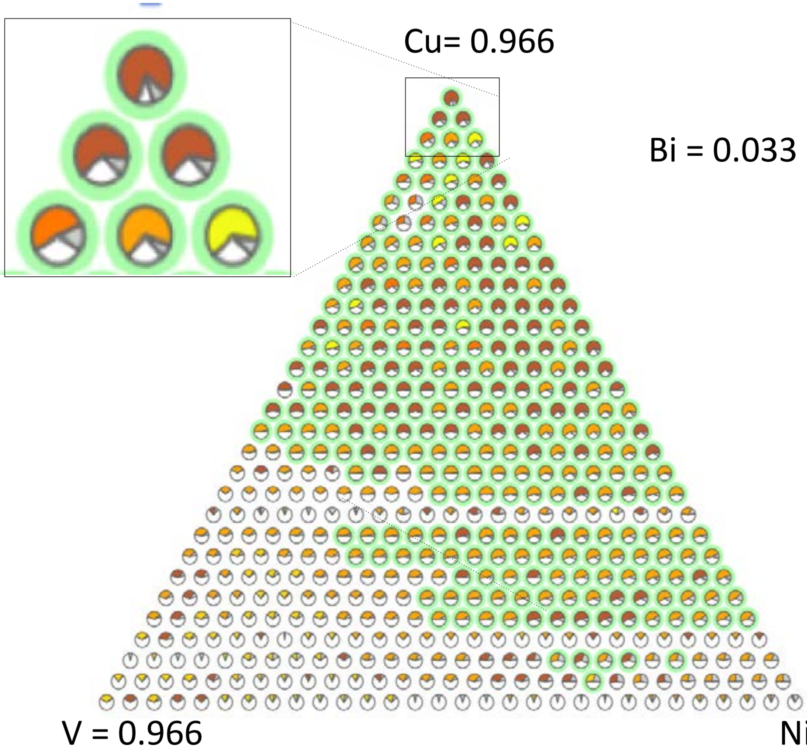
Material libraries consisting of pseudo- binary, tertiary, and quaternary compositions can be produced with physical vapor deposition methods

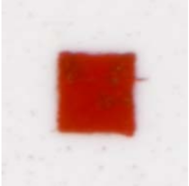
Color mapping: Highly parallel photoabsorber screening

Materials synthesis → Light-absorber screening / Electrocatalyst screening → Characterization → Data informatics and distribution

- Optical absorption
- Band gap
- Quantum efficiency
- Aqueous echem.
- Band energy

In **Hue – Saturation – Lightness** color space, histograms reveal continuity, homogeneity



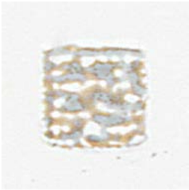


continuity GOOD
homogeneity GOOD

screen bandgap
screen absorptivity

continuity BAD
homogeneity GOOD

screen bandgap
semiquantitative absorptivity



continuity BAD
homogeneity BAD

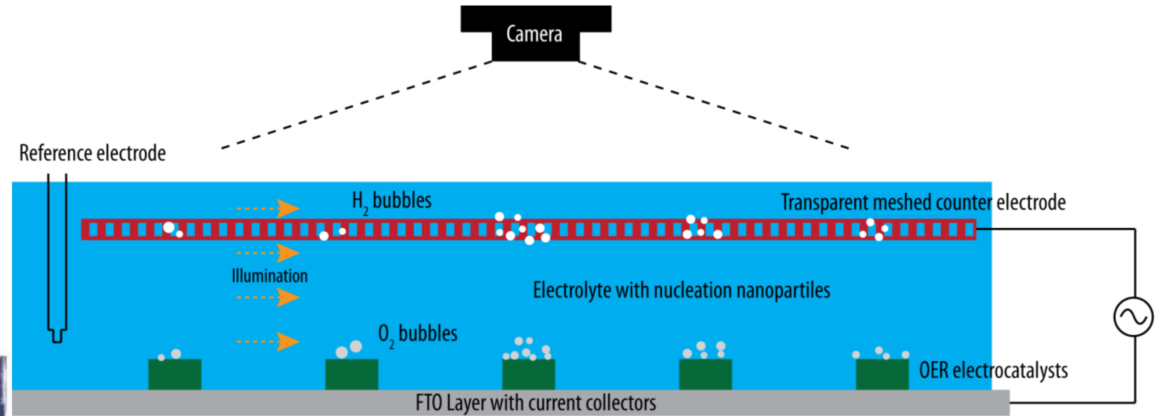
do not scan bandgap
do not screen absorptivity

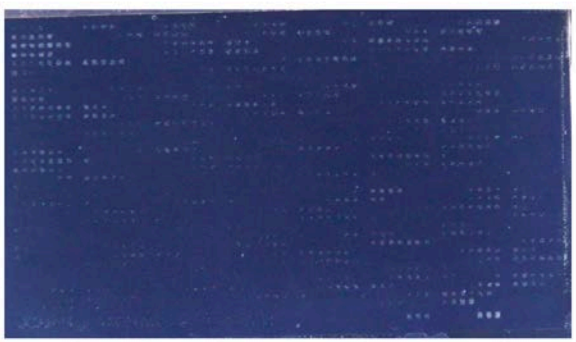
Color image processing → Smart Sampling & Database Integration → Increased UV-Vis Throughput

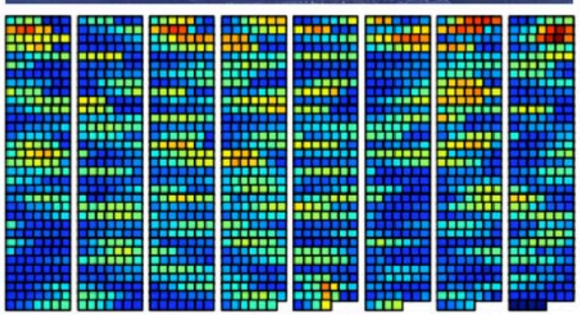
Bubble imaging: Highly parallel electrocatalyst screening

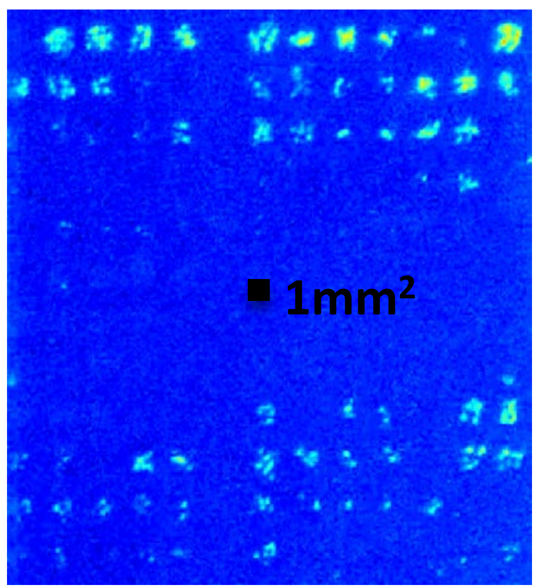
Materials synthesis → Light-absorber screening / **Electrocatalyst screening** → Characterization → Data informatics and distribution

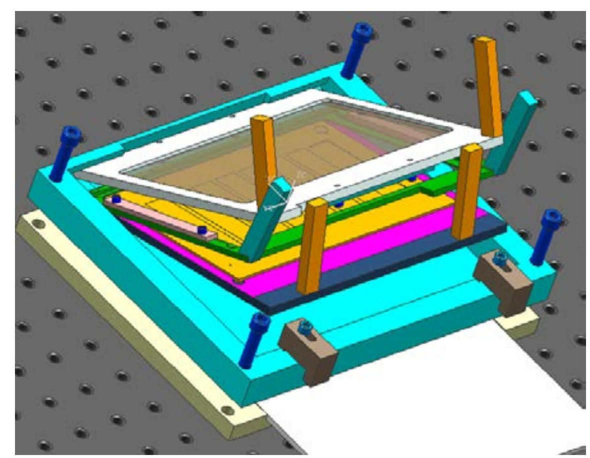
- Chemical Stability
- **Gas production**
- Current vs. Overp.
- Voltage Stability
- Faradaic Efficiency



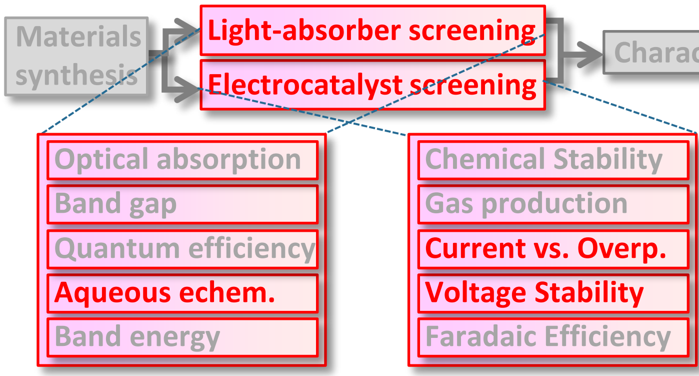




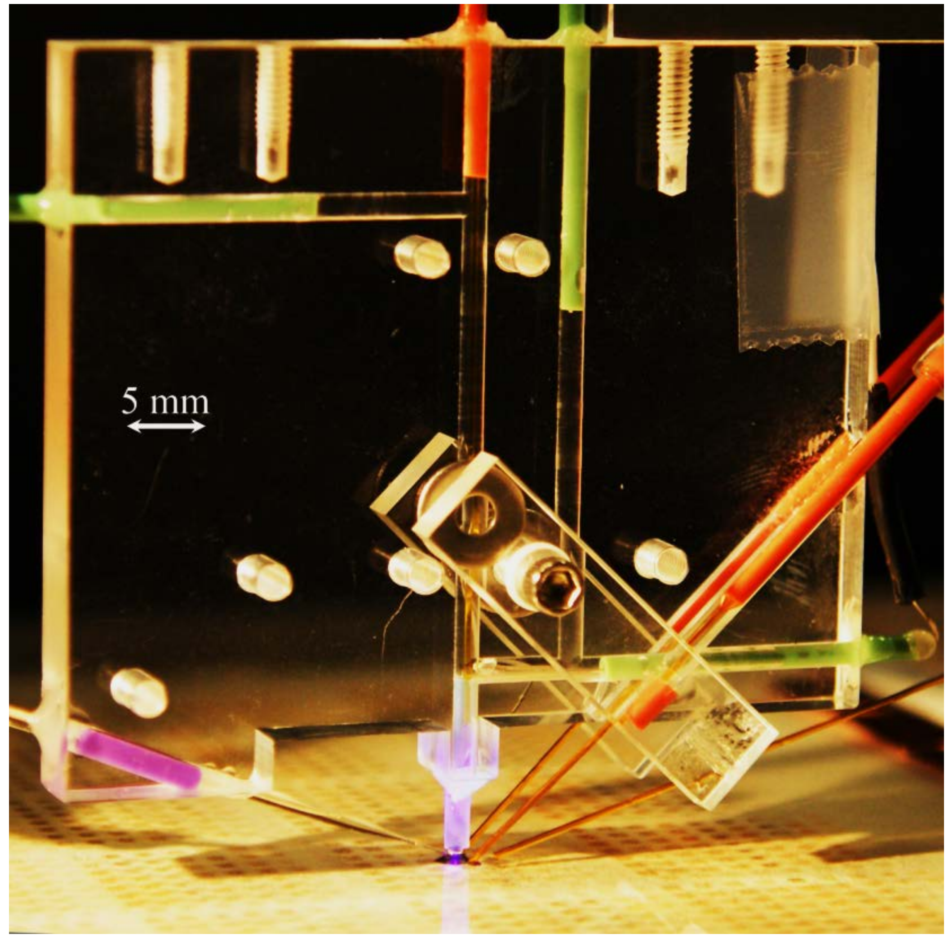




Scanning Drop Cell



- Establishes 3 electrode cell for each sample
- Gasket-free for rapid, on-demand rastering
- Low uncompensated resistance for rapid scanning and data interpretation
- Fiber-coupled for photoelectrochemistry
- Flow cell eliminates cross contamination
- Demonstrated 1V CV at 4s per sample, **~50x faster than any previous scanning instrument**
- Complete software automation and real-time analysis

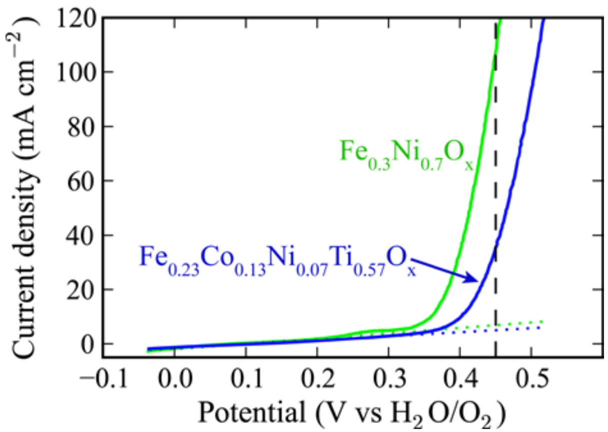


J. M. Gregoire, C. Xiang, X. Liu, M. Marcin, J. Jin, Rev. Sci. Instrum. 84, 024102 (2013)

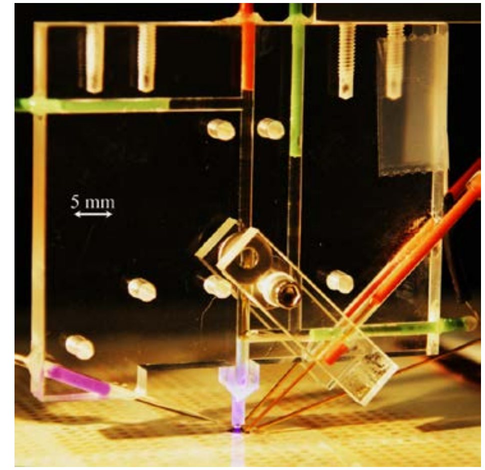
Scanning Droplet Cell: OER Electrocatalysis

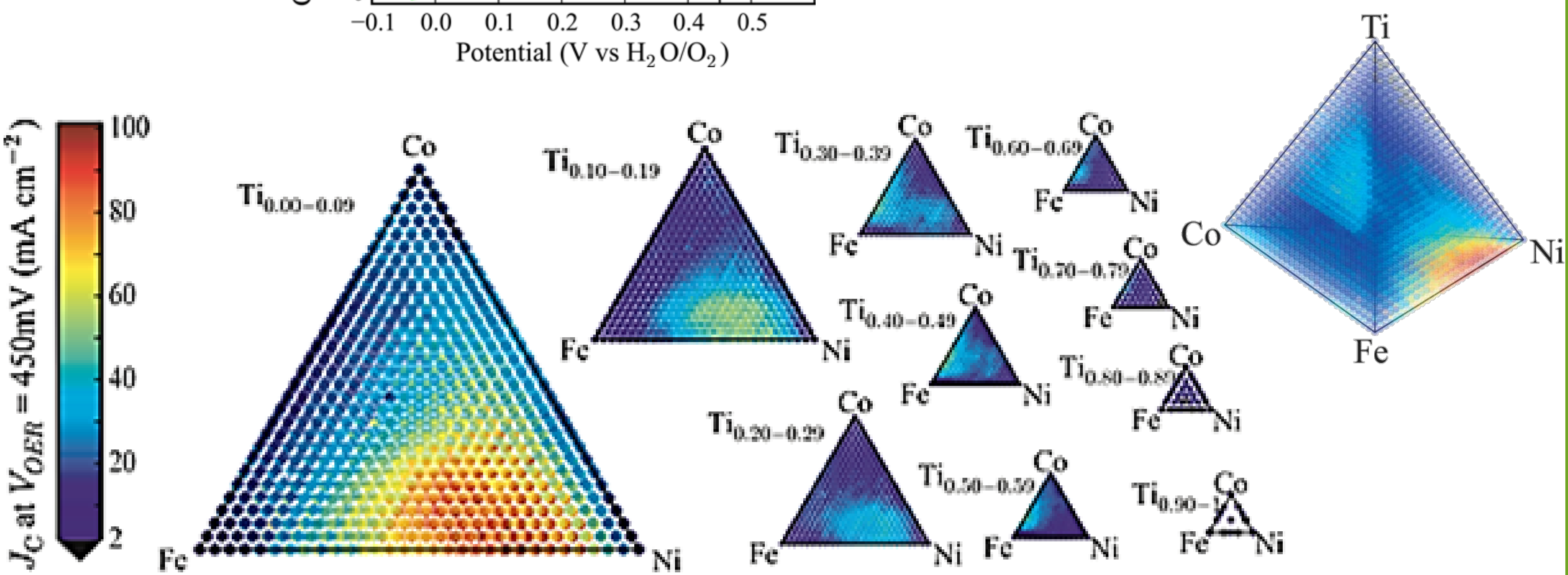
Materials synthesis → Light-absorber screening / **Electrocatalyst screening** → Characterization → Data informatics and distribution

- Chemical Stability
- Gas production
- **Current vs. Overp.**
- Voltage Stability
- Faradaic Efficiency

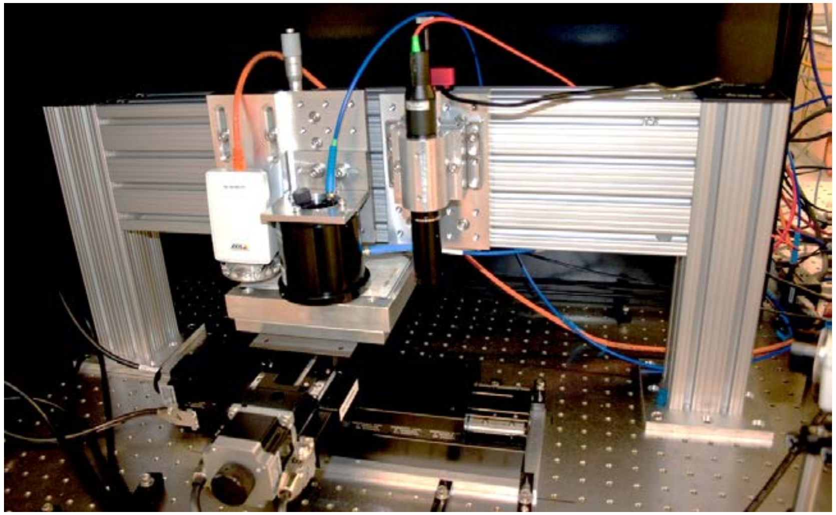


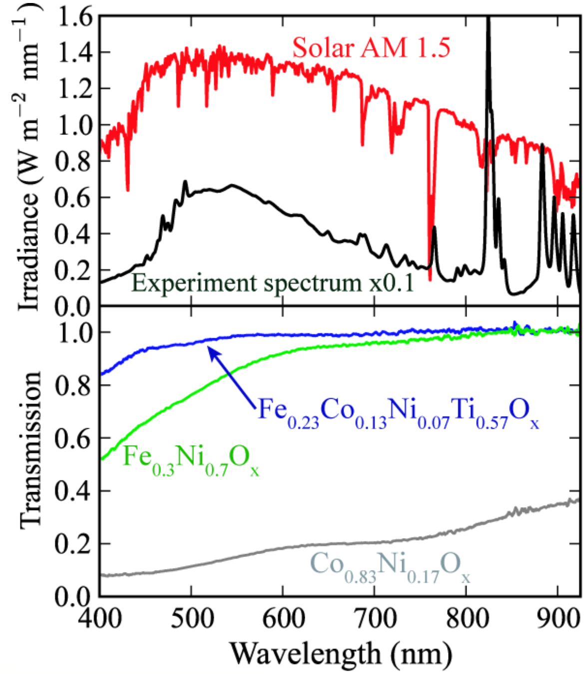
Perform CV on every sample, map current at selected overpotential



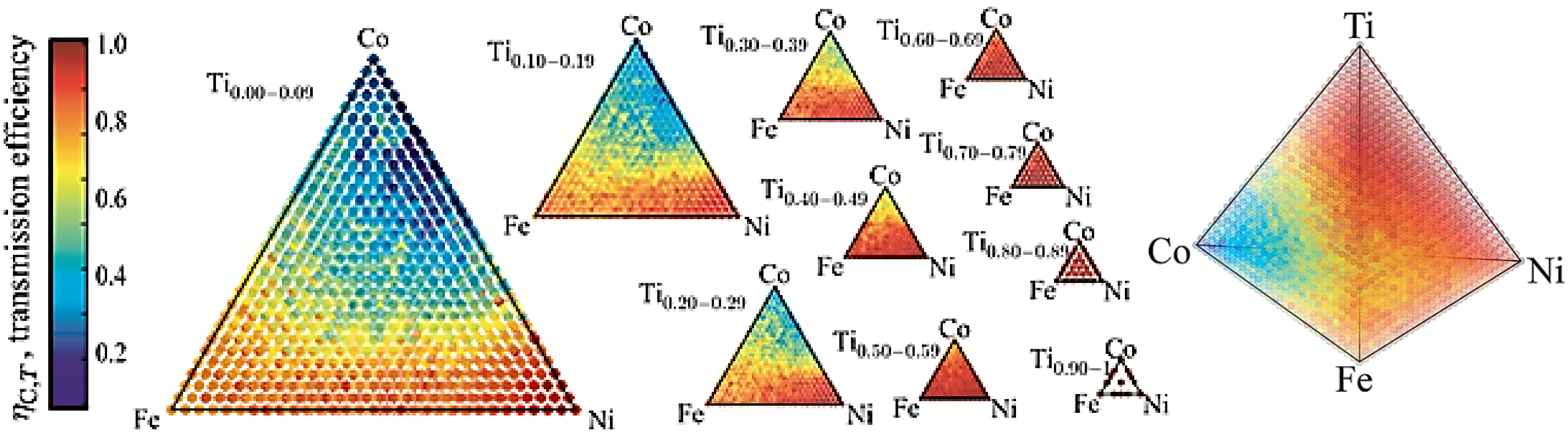


Optical Screening, In This Case For OER Transparency





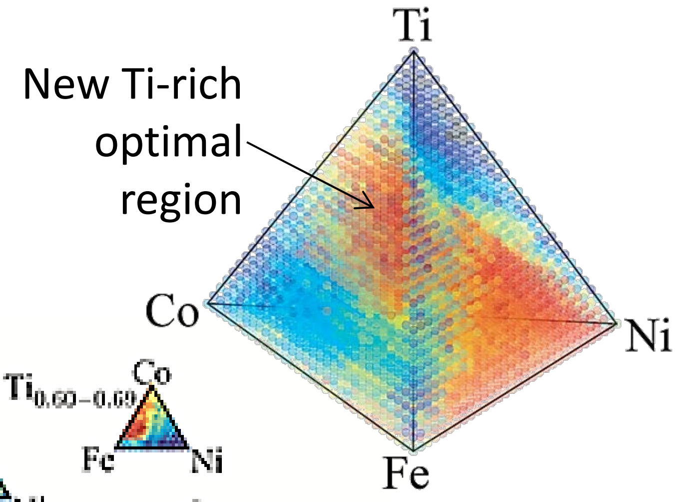
What fraction of the solar energy is transmitted through the catalyst?



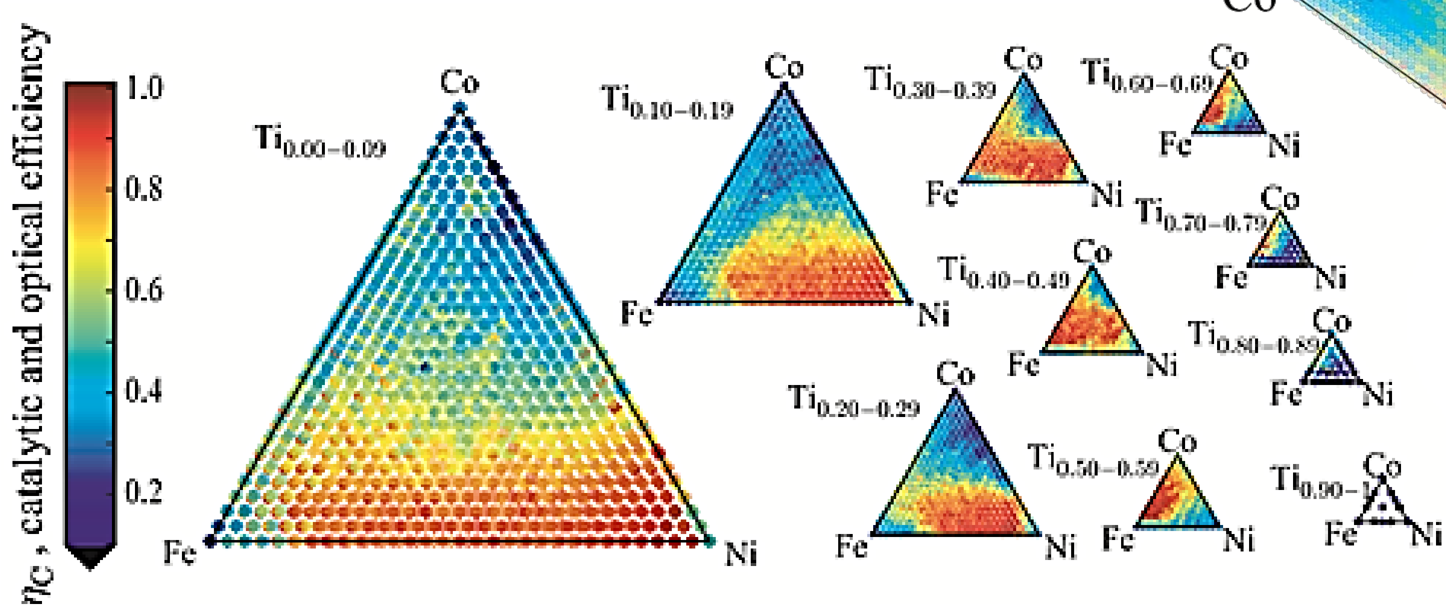
User-Defined Efficiency Model -> Database Generated Figure of Merit

Describe your light absorber device:

- Device operating at pH 14
- Photoabsorber stack using all solar radiation between 400 nm and 900 nm
- Photoanode voltage is 450 mV positive of O_2/H_2O
- Photocurrent produced is 23 mA/cm^2



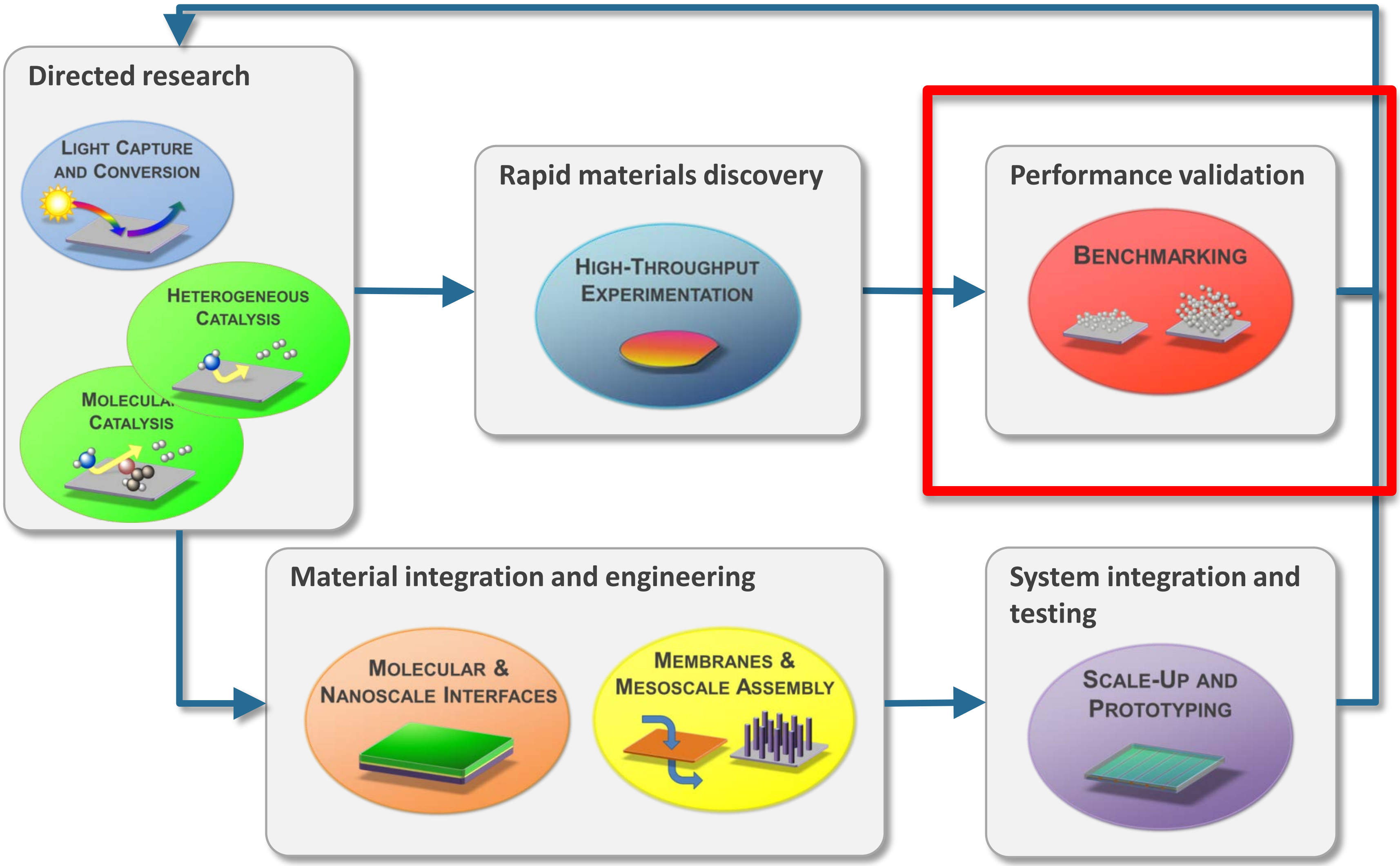
Here is your customized catalyst efficiency:



JM Gregoire, C Xiang, S Mitrovic, X Liu, M Marcin, EW Cornell, J Fan, J Jin
J. Electrochem. Soc. 160, F337-F342. (2013)

JCAP APPROACH TO ARTIFICIAL PHOTOSYNTHESIS

Projects are coordinated to accelerate materials discovery and prototype development



OVERVIEW OF BENCHMARKING PROJECT




OBJECTIVES

The Benchmarking Project serves as a community resource for the performance validation of electrocatalysts and photocatalysts. By employing a standard set of measurement protocols, unbiased evaluation by the Benchmarking Project provides comparisons that are as accurate as possible between materials/devices coming from different laboratories.

PROJECT LEADERS

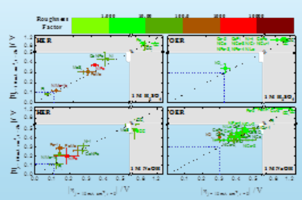
Jonas Peters

Tom Jaramillo

APPROACH

Design of benchmarking standards and protocols

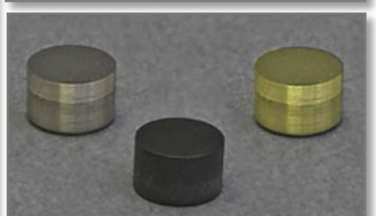
Benchmarking of electrocatalysts



Benchmarking of light absorbers

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

Benchmarking Standards and Protocols for



Electrolyte Solutions:
Acidic: 1 M H_2SO_4, Alkaline: 1 M NaOH
HER preelectrolysis at -0.8 V vs SCE with sacrificial carbon

Working Electrode:
Glassy Carbon Disk (0.195 cm^2)
Polished with 9 µm, 6 µm, 1 µm, and 0.1 µm diamond suspension

Auxiliary Electrode:
Carbon Rod or B-doped Diamond Plate
Separated from main solution with fine-porosity glass frit

Reference Electrode:
Saturated Calomel Electrode (SCE)
Externally referenced to ferrocenecarboxylic acid in 0.2 M Phosphate Buffer at pH 7 (0.28 vs SCE)

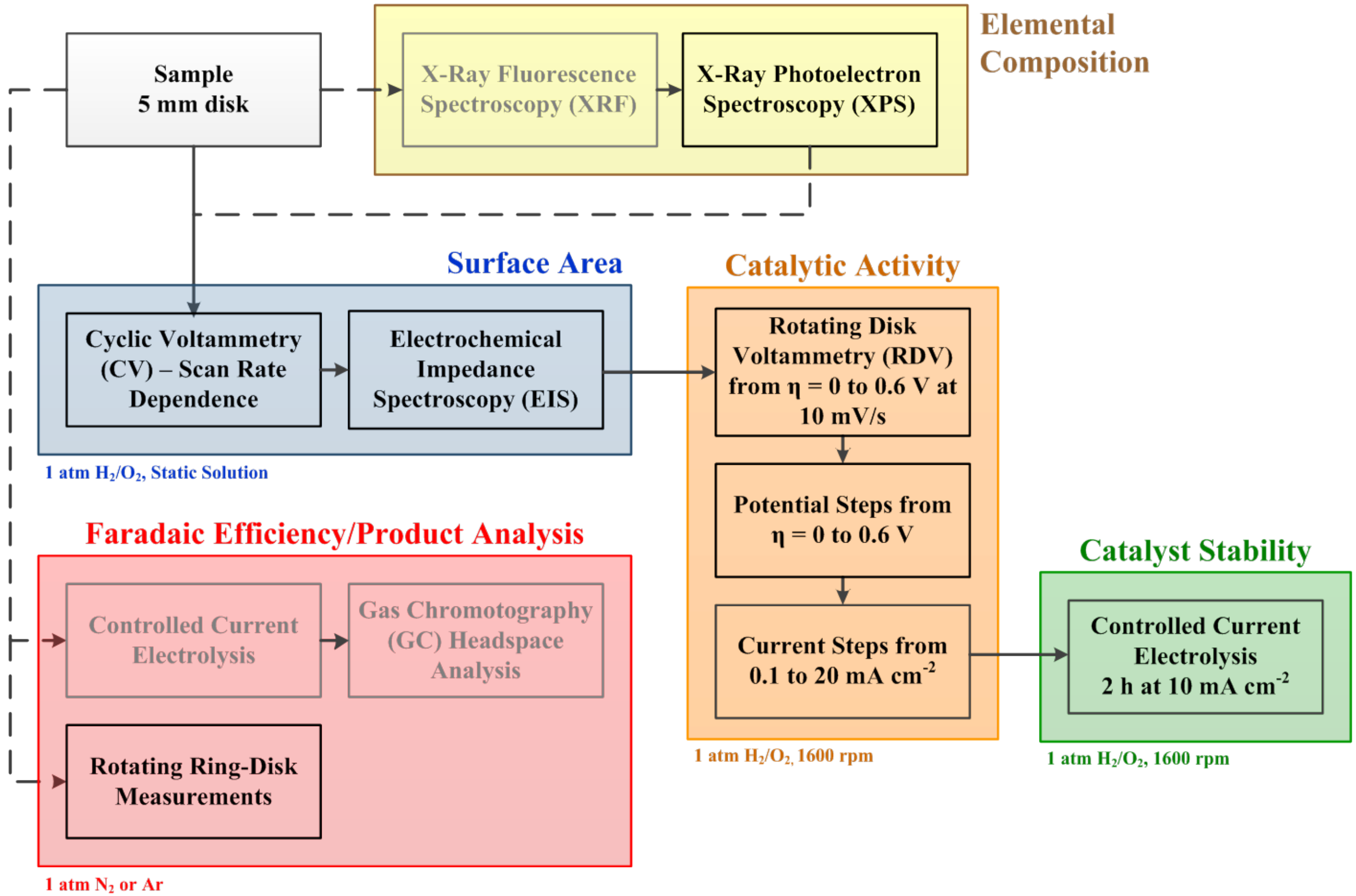
Primary Figure of Merit:
Overpotential required to achieve 10 mA cm^{-2} per geometric area

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

Benchmarking Methodology

Benchmarking protocols and standards have been established for electrodeposited catalysts

Benchmarking Flowchart



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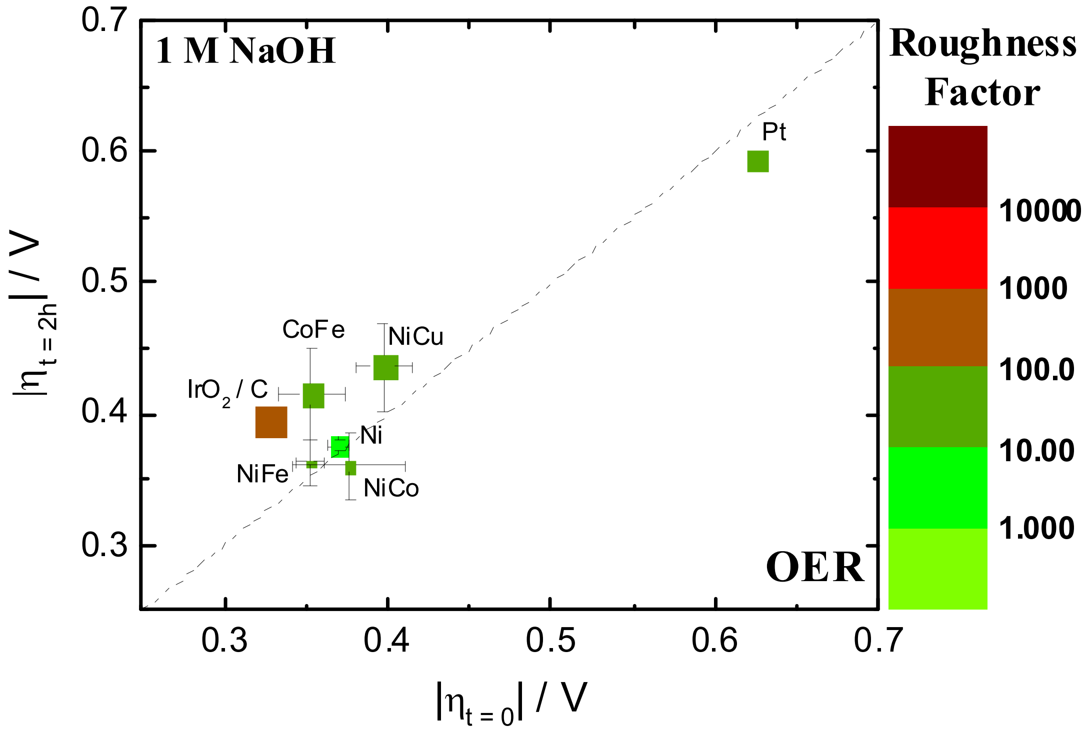
Benchmarked Oxygen Evolution Catalysts

Catalysts are now readily comparable on standardized plots

Catalysts for Oxygen Evolution Under Alkaline Conditions



Catalytic activity and stability can now be assessed by measuring electrochemical behavior under standardized conditions

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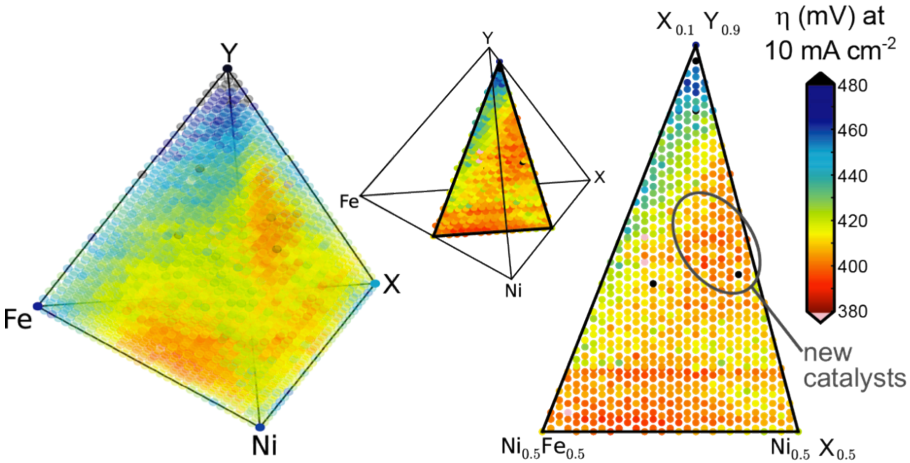
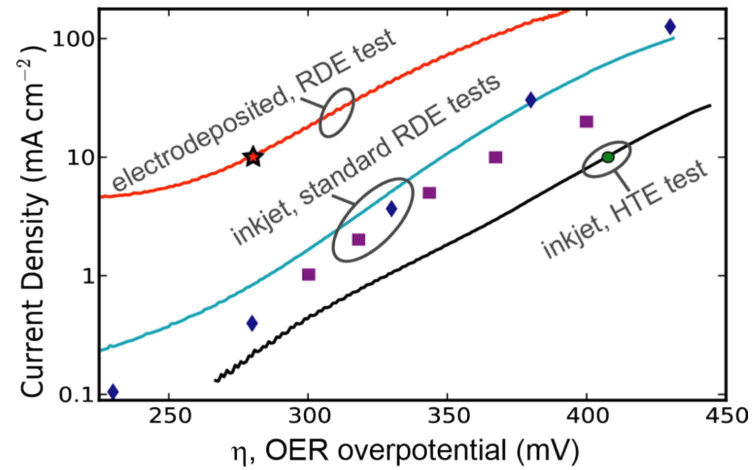
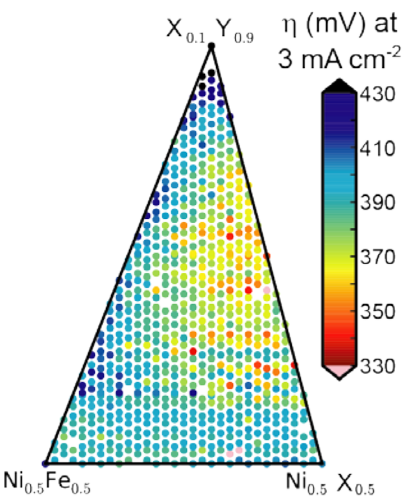
Discovery and Rapid Technological Development of a new Oxygen Evolution Catalyst

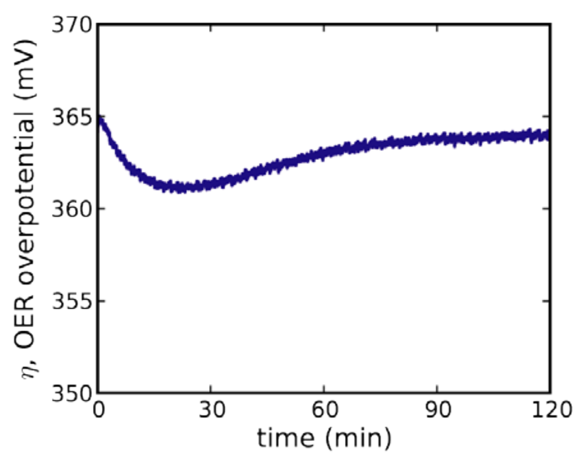
Scientific Achievement

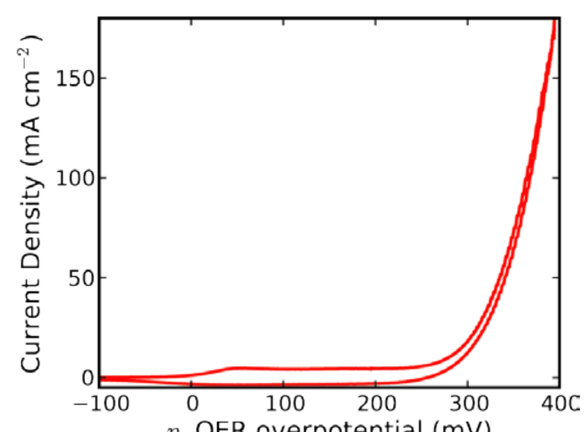
Using high throughput experimentation (HTE), JCAP discovered a new family of electrocatalysts for the oxygen evolution reaction (OER). The catalytic activity observed via high throughput synthesis and screening was reproduced using traditional electrodeposition synthesis and traditional electrochemical experiments. Using a testbed system, solar-powered water splitting with the new OER catalyst was demonstrated for 100 hours.





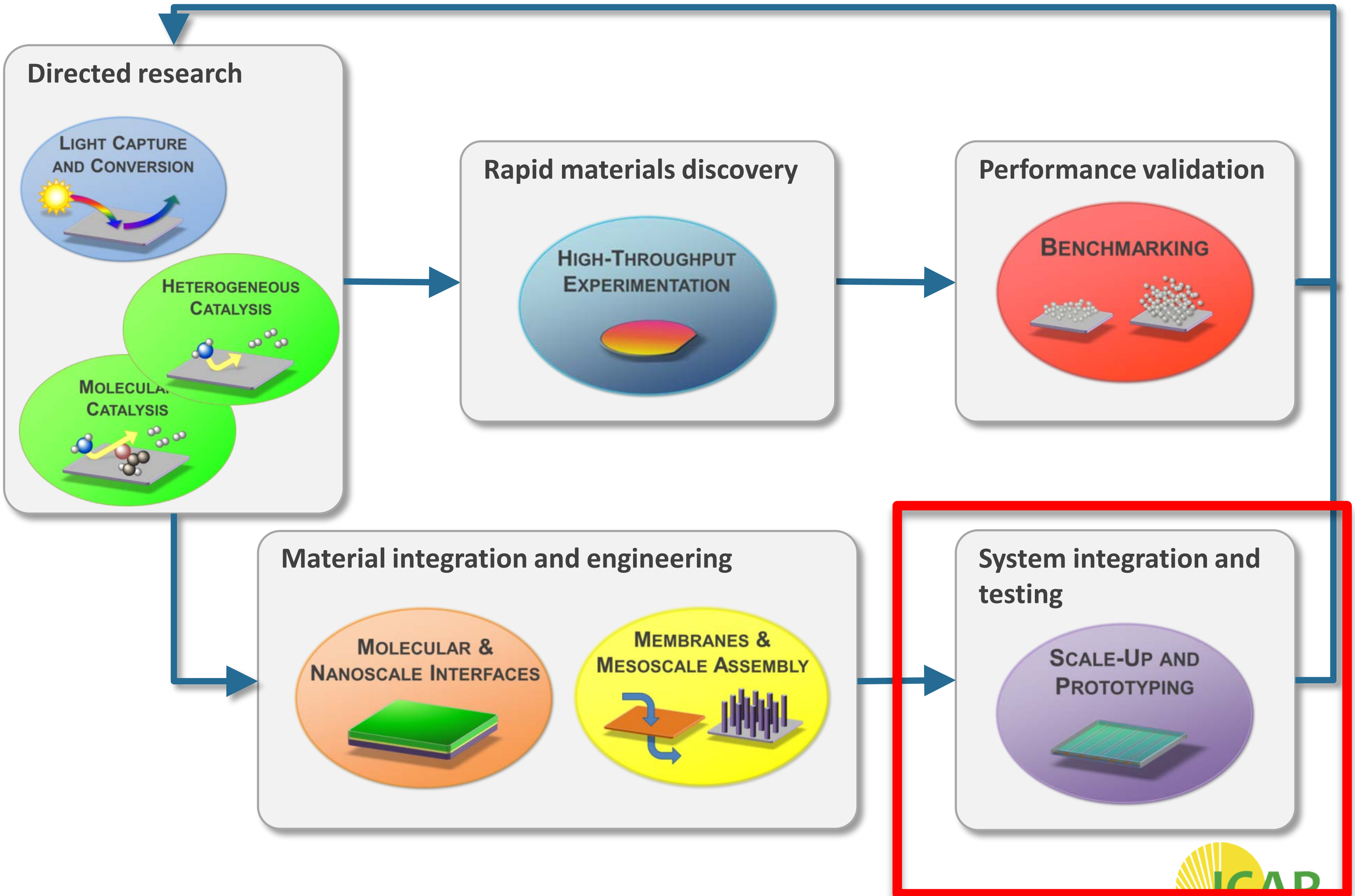






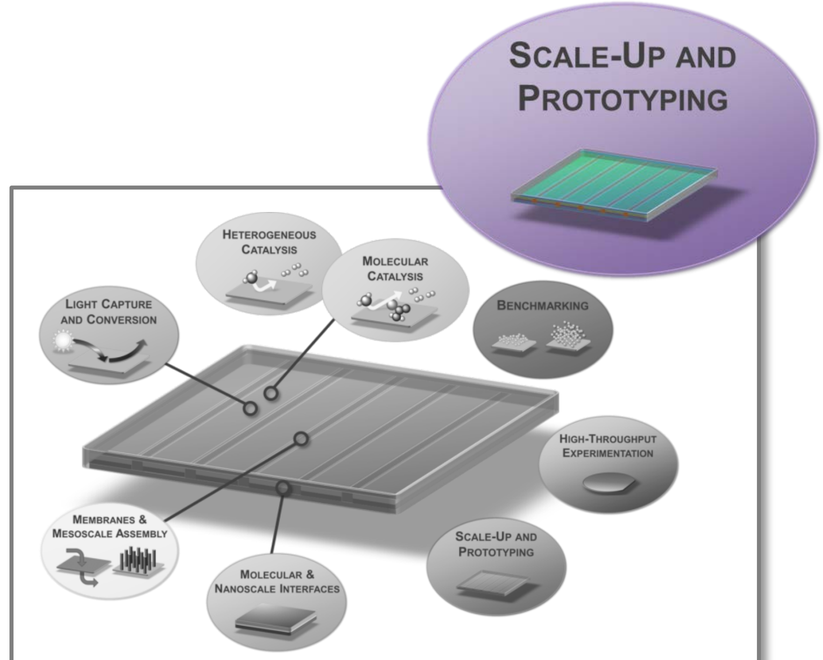
JCAP Approach to Artificial Photosynthesis

Projects are coordinated to accelerate materials discovery and prototype development



Project Overview – Scale-up and Prototyping

The goal of the Scale-up and Prototyping project is to develop robust, high-performance, scalable solar-fuels generators by implementing systems engineering methodologies and actively integrating newly discovered robust and Earth-abundant materials and components.



Project Leaders

Jian Jin

Will West

JCAP
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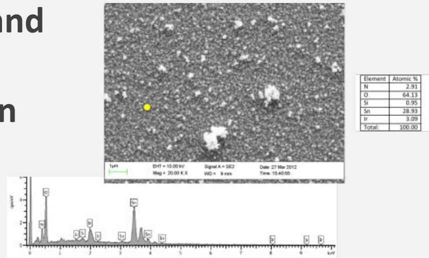
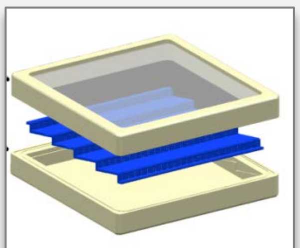
JCAP Approach to System Integration of Solar-Fuels Generators

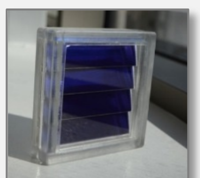
Material and process integration



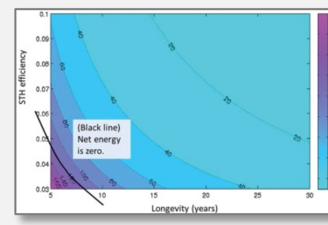
Early design test beds and feasibility studies



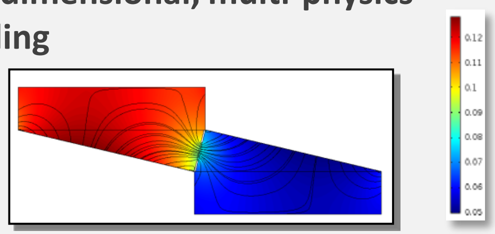
Fabrication and characterization of prototypes



Investigations of manufacturing, scale-up, and sustainability

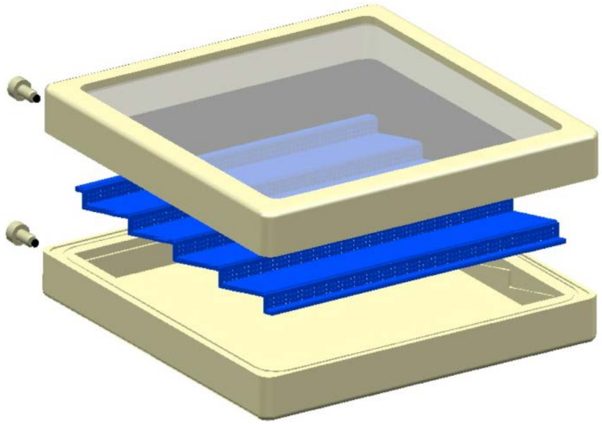


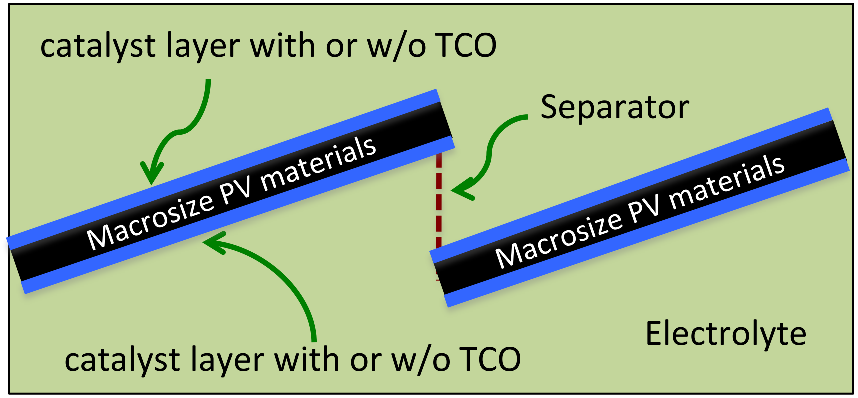
Multi-dimensional, multi-physics modeling



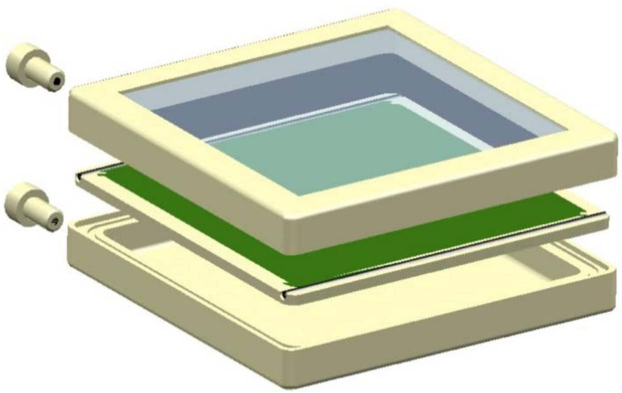
Prototype Designs for a Solar-Driven Water-Splitting Device

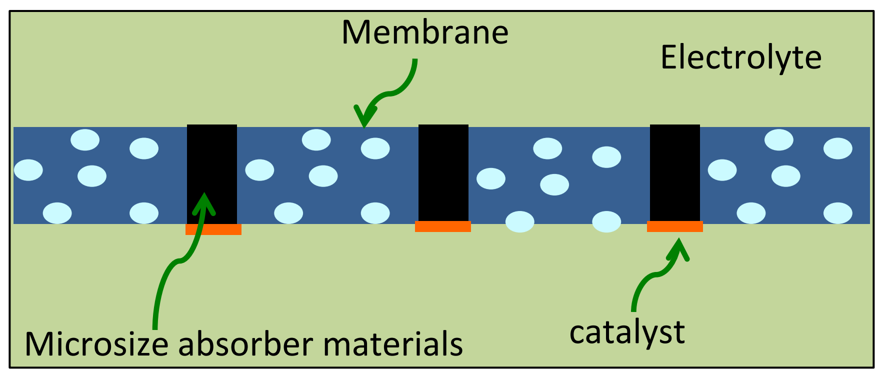
Louvered prototype





Absorber-in-membrane prototype





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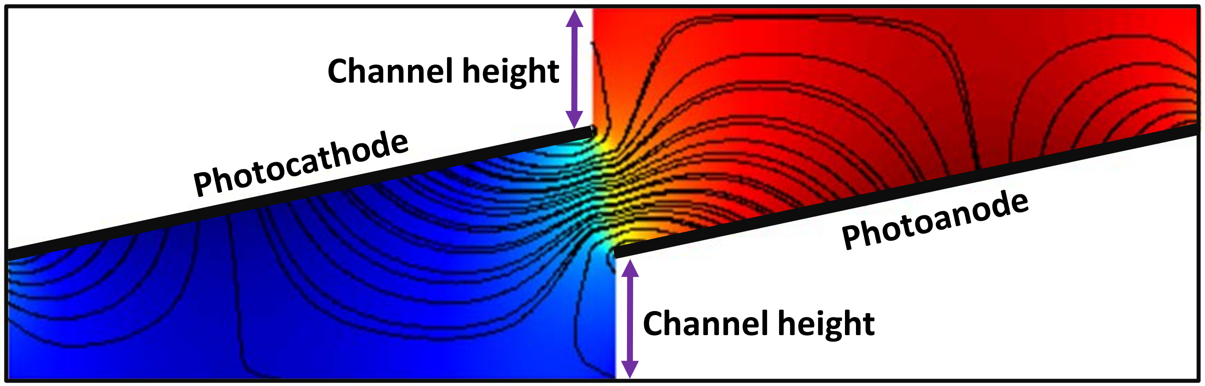
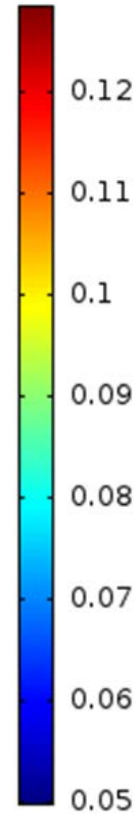
Research Highlight: Modeling of Resistive Losses

Electrolyte potential (V) and current density (stream lines) for the louvered prototype design

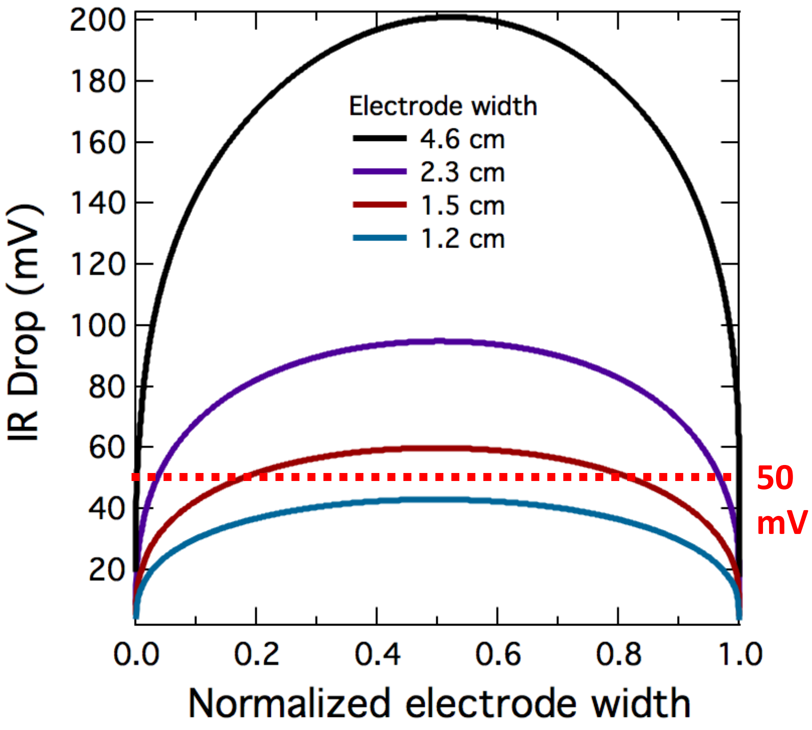


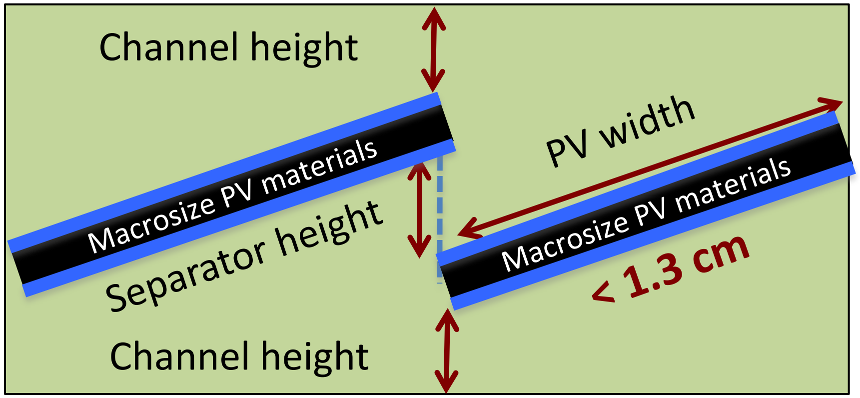


Semiconductor width = 2 cm
Nafion height = 4 mm
Channel height = 4 mm

> **Computational modeling using Poisson's equation solver in COMSOL Multiphysics provides electrical potential and current distributions**

Research Highlight: Optimization of Electrode Geometries





not to scale

Separator height = 4 mm
Channel height = 4 mm

For the louvered prototype design, the electrode width cannot exceed 1.3 cm for a 50 mV potential drop

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JCAP Modeler

Welcome to JCAP Modeler

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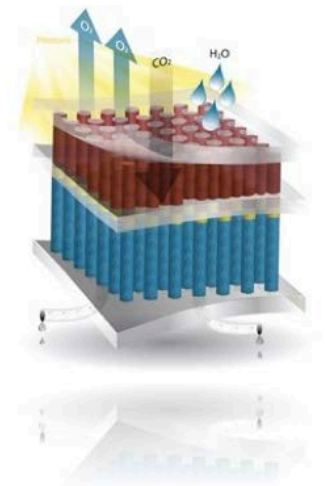
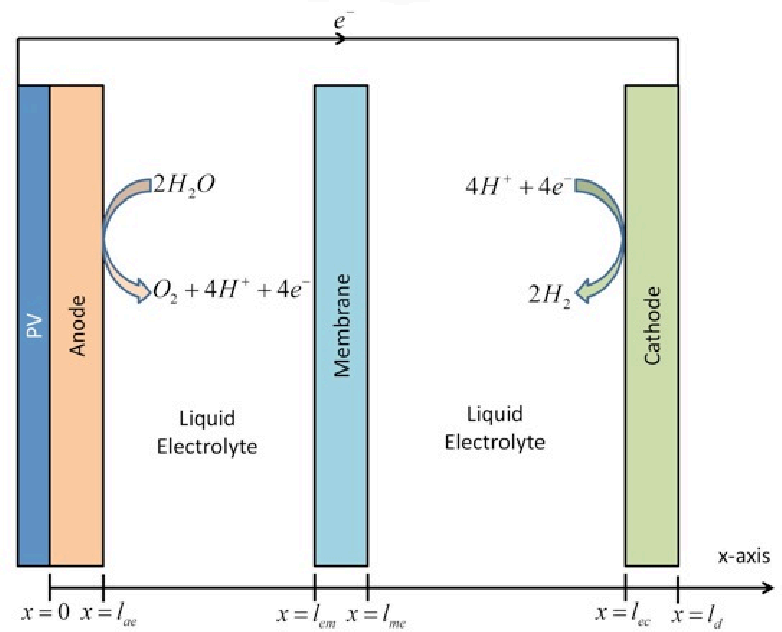


Modeling using JCAP Modeler

JCAP Modeler is a web application to study the behavior of various photoelectrochemical water-splitting devices. Description of each model and associated parameters are given on a designated webpage. Currently, the JCAP Modeler is capable to simulate:

Description of 1D Model

Schematic Diagram



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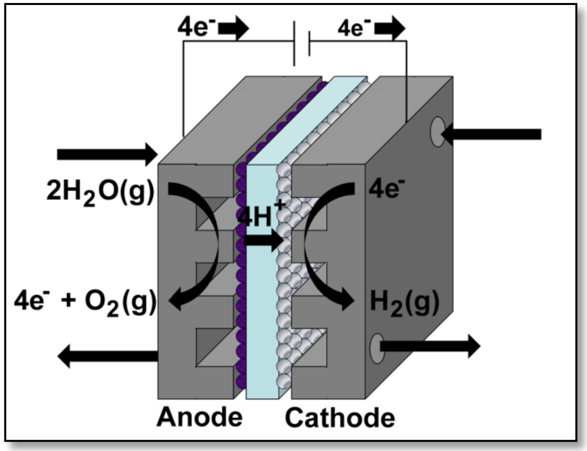
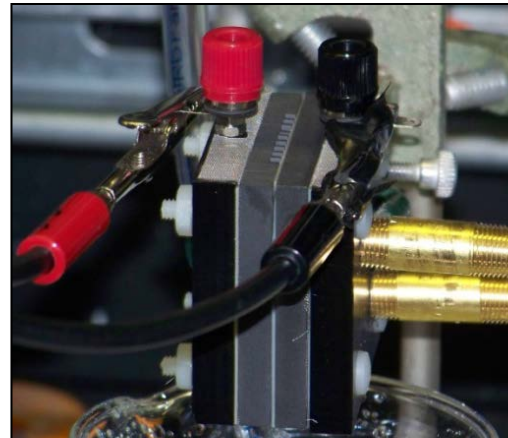
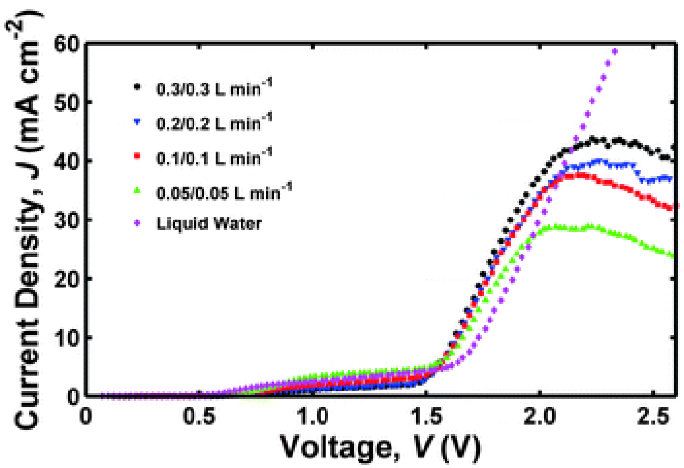
Research Highlight: Solar-Fuels Generation Using Water Vapor





Test set-up for proton exchange membrane electrolysis by water vapor.



An efficient solar photoeletrolyzer can be operated using water vapor in place of liquid water

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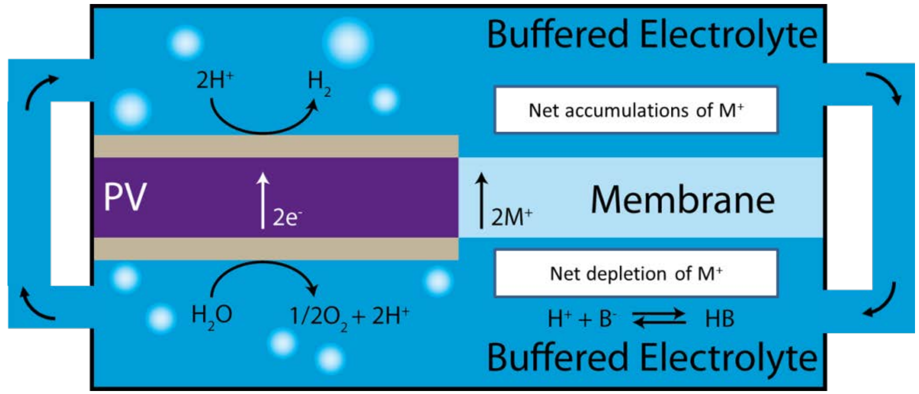
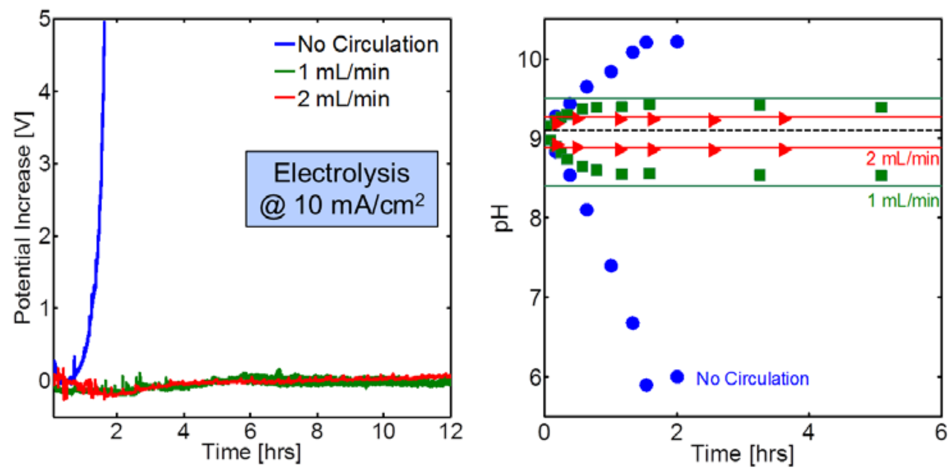
DEVELOPMENT AND TESTING OF A RECIRCULATING PROTOTYPE

(1) Membrane separation of H_2 and O_2 compartments necessitates either high or low pH solutions
(2) Corrosion has been identified as a key life-limiting mechanism
(3) Buffered pH systems yield vast improvements in semiconductor/catalyst lifespan, but shut down due to membrane transport limitations
(4) A design was explored to allow for buffered mid-pH solutions
   (1) Leveraged direct technical input from JCAP Membrane team members (Led by Miguel Modestino)
   (2) Includes a membrane with a bypass recirculation system
   (3) Explosive gas mixtures are avoided by engineering recirculation physically distant from electrodes
(5) Demonstrated that with minimal recirculation, can avoid concentration gradients over diurnal cycles at relatively low recirculation rates

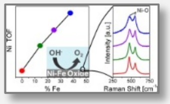




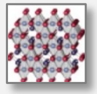
Recirculation Model design (above) and electrolysis data as a function of recirculation rate (below).

Overview of Recent Discoveries in the Joint Center for Artificial Photosynthesis

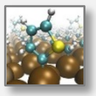
Underpinning Discovery Science



The way the best earth-abundant oxygen producing catalysts work is now known, letting better ones be designed.

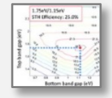


The electrochemical environment for O_2 production has identified a route to higher efficiency

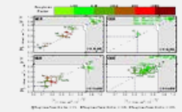


Semiconductor/ linker interfaces can be tuned for optimal efficiency using newly discovered principles

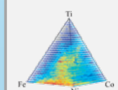
Accelerated Materials Discovery



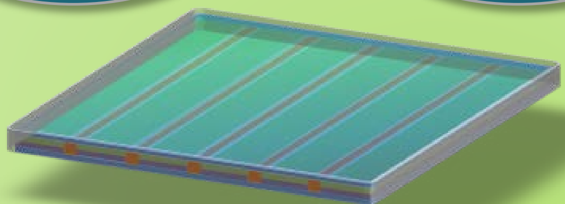
Criteria for optimal light-absorbing materials are determined



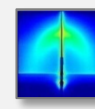
For the first time, the efficiency of solar fuels catalysts is compared in a standardized way



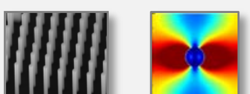
World's fastest high-throughput synthesis and screening system for catalyst discovery



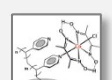
Component Assembly and Optimization



Key design criteria for safe and more efficient membranes are identified



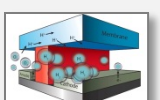
Nanowire –based systems are developed that capture light with more than 90% efficiency



An active catalyst is successfully surface-attached, increasing catalyst options

Scale-up and System Integration

Hydrogen gas is produced with more than 7% efficiency using optimized materials



Custom systems for rapid evaluation of new materials combinations are in routine use

Analysis of solar-fuel generators shows early energy payback of core device

JCAP
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The Joint Center for Artificial Photosynthesis (JCAP) is the nation's largest research program dedicated to the development of an artificial solar-fuel generation technology. Established in 2010 as a U.S. Department of Energy (DOE) Energy Innovation Hub, JCAP aims to find a cost-effective method to produce fuels using only sunlight, water, and carbon-dioxide as inputs. JCAP is led by a team from the California Institute of Technology (Caltech) and brings together more than 140 world-class scientists and engineers from Caltech and its lead partner, Lawrence Berkeley National Laboratory. JCAP also draws on the expertise and capabilities of key partners from Stanford University, the University of California campuses at Berkeley (UCB), Irvine (UCI), and San Diego (UCSD), and the Stanford Linear Accelerator (SLAC). In addition, JCAP serves as a central hub for other solar fuels research teams across the United States, including 20 DOE Energy Frontier Research Center.

For more information, visit http://www.solarfuelshub.org.

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