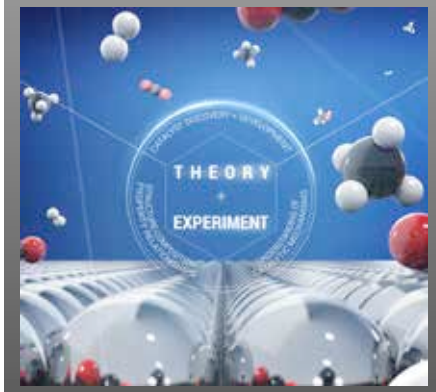
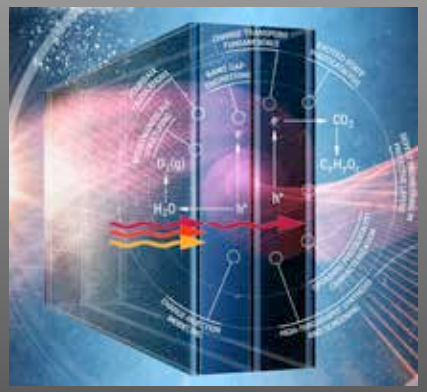
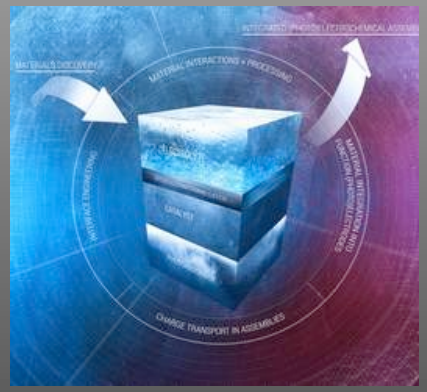
JCAP RENEWAL PROJECT







HARRY A. ATWATER

JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

BESAC MEETING

June 10th, 2016

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

THE JCAP TEAM

Solar Fuels Research
Technology Transfer
South Site Laboratory

Energy Science and Technology
Solar Fuels Research
North Site Laboratory
ALS, Molecular Foundry, NERSC

Materials Science
Catalyst Discovery and Characterization
SSRL

Laboratory and Synchrotron-based Surface Science

Synthesis and Characterization of Catalysts

The Institutional Partners have successfully worked together since 2010 to reach JCAP's current goals and will continue toward JCAP's new goals

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

Key personnel

JCAP Director

Lead Principal Investigator
Full Management Authority – Research and Resource Allocation
80% Annual Time Commitment

JCAP Deputy Directors

Program and Research Management
Strategic Planning, Budget and Schedule Formulations
Performance assessments
Communications
Fostering Beneficial Collaborations
Program Representation
Site-specific management and operational responsibilities
75-95% Annual Time Commitment

Research Thrust Coordinators

Coordination of Research Effort
10-100 % Annual Time Commitment

DOE User Facilities Group

works with JCAP researchers and coordinates work at the user facilities

Governance Board

provides oversight in the matters of budgets, research strategies, personnel, new partnering arrangements, and infrastructure

Scientific and Strategic Advisory Boards

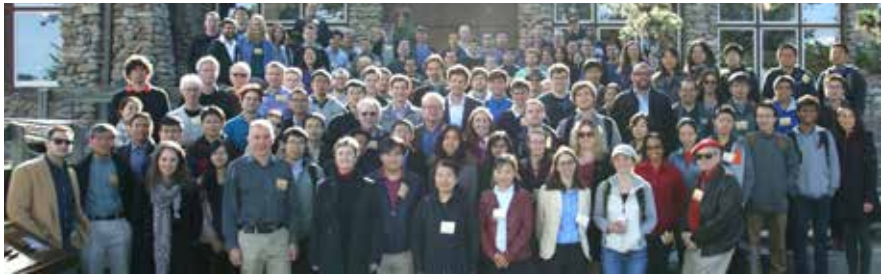
provide the Hub with broad perspective on JCAP's R&D program accomplishments, direction, and strategy
advise on engagement with other research organizations and industrial partners

Director's Advisory Committee

helps the Director in making significant strategic decisions impacting operations of the Hub

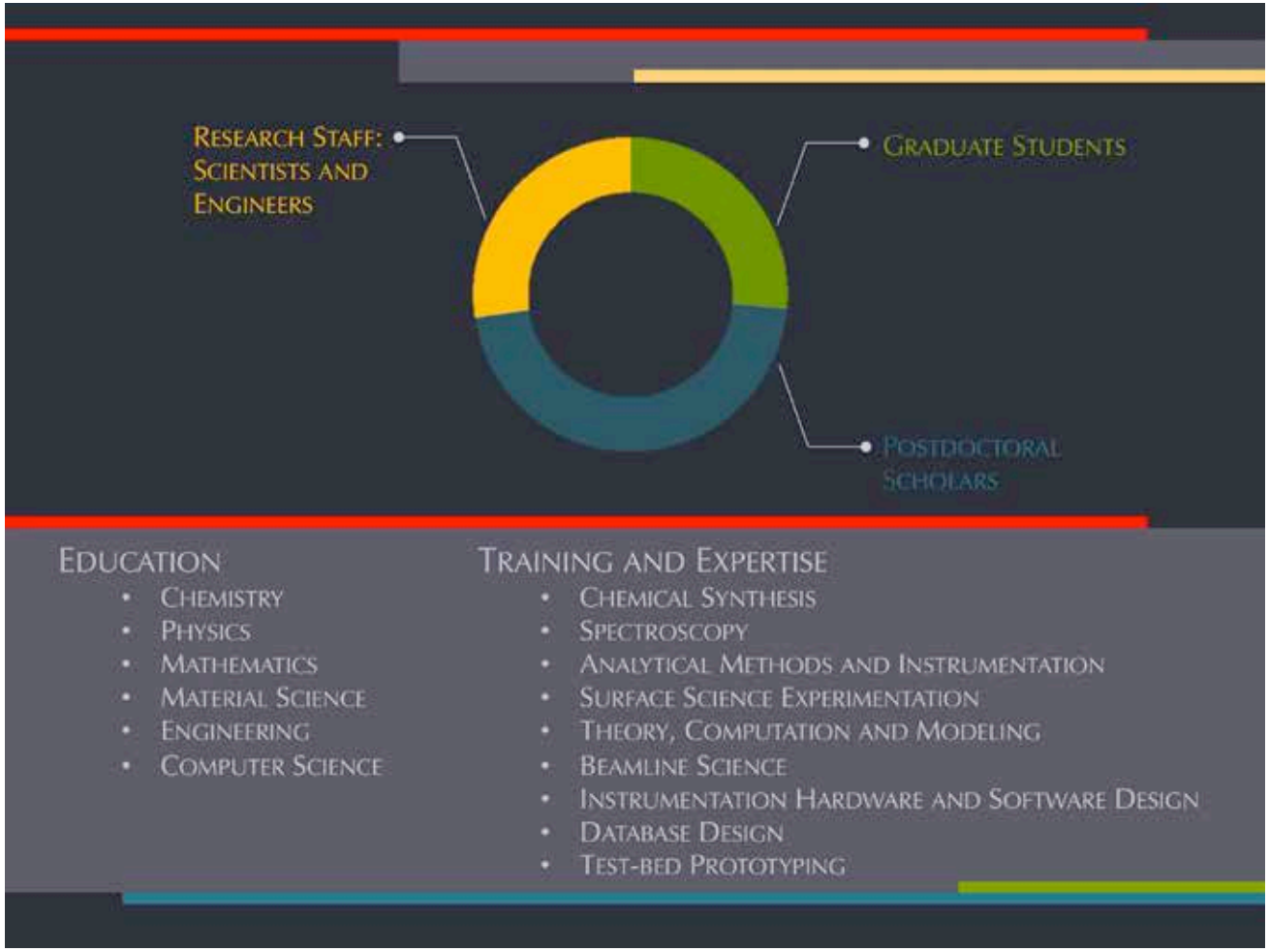
PI Council

is charged with advising the Director on research scope and scientific strategies, and assisting with integration of JCAP's research with other R&D programs



JCAP
Joint Center for Artificial Photosynthesis

JCAP RESEARCH TEAM



32 Faculty and Senior Scientist Principal Investigators
Multi-Institutional GB

1 Nobel Laureate

12 National Academies of Science and Engineering Members

1 National Medal of Science Recipient

8 American Academy of Arts and Sciences Members

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JCAP MAJOR RESEARCH FACILITY INVESTMENTS

Jorgensen Laboratory @Caltech

Support: DOE/Caltech/Resnick Institute

Chu Hall @ LBNL

Support: CPUC, Foundations, State of CA

JCAP
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JCAP PARTNERSHIPS AND CAPABILITIES

ACADEMIC/LAB/EFRC PARTNERSHIPS

Virginia Tech
School of Mines Colorado 1874
The University of Texas at Austin
Rensselaer Polytechnic Institute 1824
National Taiwan University
Technische Universität Ilmenau
lmi
Fraunhofer ISE
HZB Helmholtz Zentrum Berlin

INDUSTRIAL INTERACTIONS

SIEMENS
Google
Panasonic
Sempra Energy
HRI Honda Research Institute
TOYOTA CENTRAL R&D LABS., INC.

ENABLING CAPABLITIES AND PARTNERSHIPS

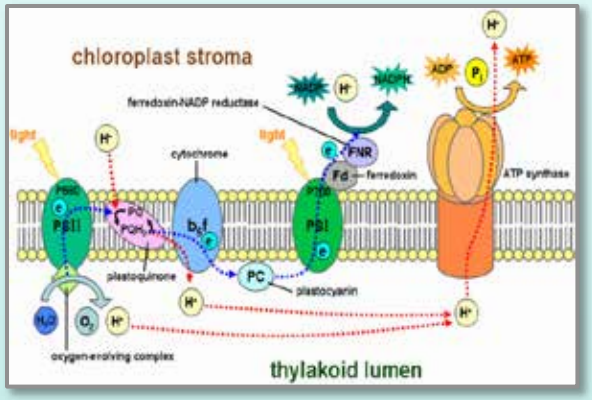
NERSC
MOLECULAR FOUNDRY
MATERIALS PROJECT
ALS ADVANCED LIGHT SOURCE
SSRL

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

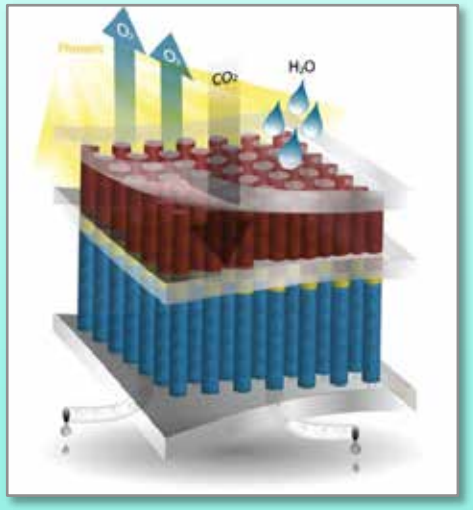
FOCUS IN FIRST PHASE OF JCAP 2010-2015

JCAP's Mission is to demonstrate a scalably manufacturable solar-fuels generator using Earth-abundant elements that, with no wires, robustly produces fuel from the Sun ten times more efficiently than (current) crops.

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)

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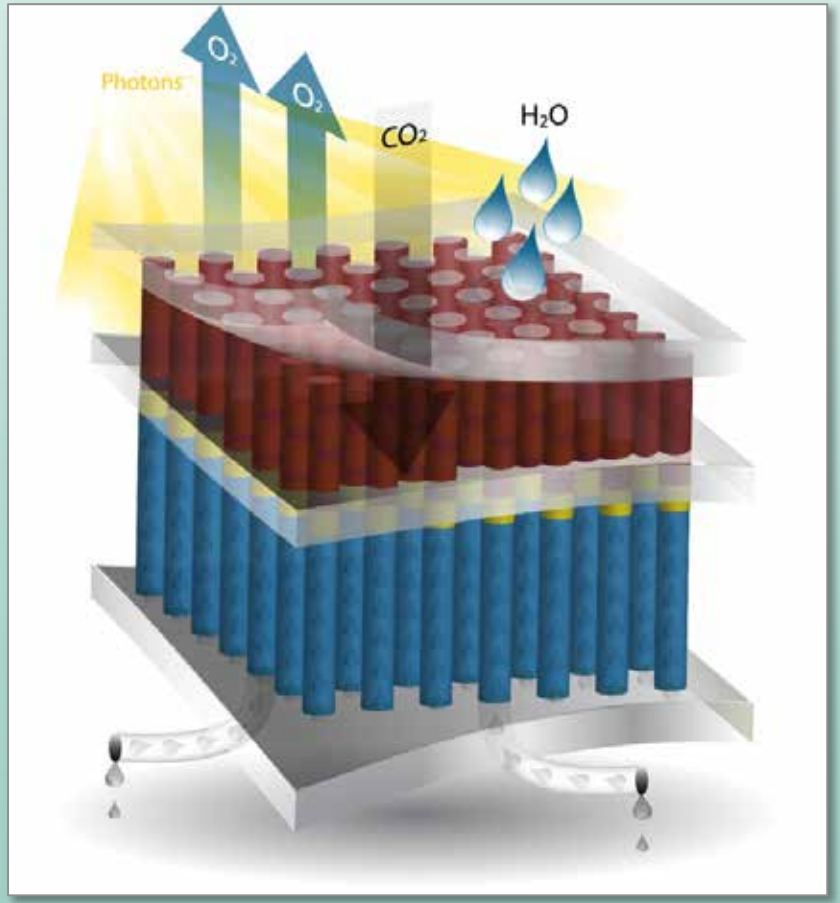
An Integrated Approach to Artificial Photosynthesis

JCAP System Concept



Oxygen Forming Reaction

Oxygen evolution reaction (OER)

$$H_2O \longrightarrow \tfrac{1}{2}O_2\,(g) + 2H^+ + 2e^-$$

Fuel Forming Reactions

Hydrogen evolution reaction (HER)

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

CO_2 reduction reaction (CO2RR)

$$CO_2 + H_2O \longrightarrow HCOOH + \tfrac{1}{2}O_2$$

$$CO_2 + H_2O \longrightarrow HCHO + O_2$$

$$CO_2 + 2H_2O \longrightarrow CH_3OH + 3/2\ O_2$$

$$CO_2 + 2H_2O \longrightarrow CH_4 + 2O_2$$

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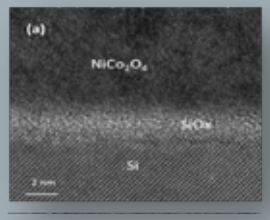
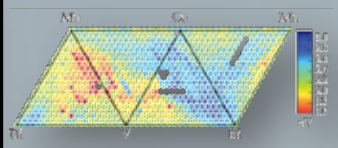
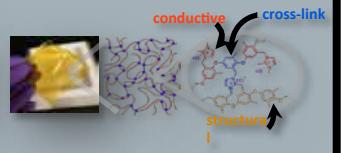
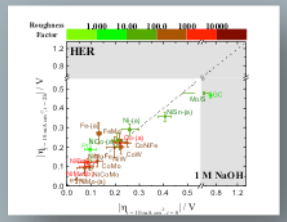
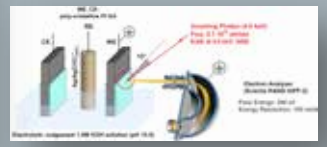
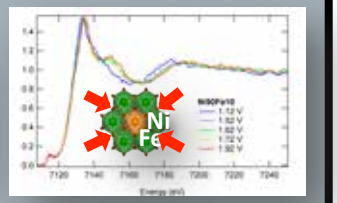
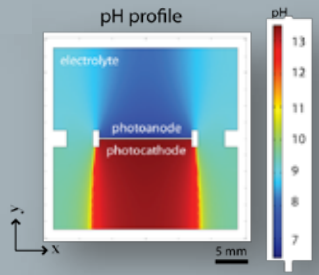
JCAP Project 2010-2015

JCAP's Contributions and Accomplishments in Years 1-5 (+6)

Materials	*Discovery*	 Photoelectrode materials and corrosion protection	 High throughput experimentation	 Membrane separators
	Measurement and mechanisms	 Catalyst benchmarking	 in situ and operando studies	 Catalytic structures and mechanisms
Devices	*Integration and demonstration*	 Multiphysics modeling	 Prototype designs	 Demonstrations of robust >10% efficient water splitting

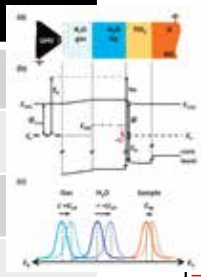
JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

PROTECTION SCHEMES FOR OPERATION AT EXTREME pH

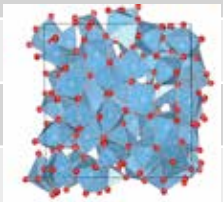
Passive corrosion protection, catalytically active surface protection:

-- Optimized potentials and long lifetimes

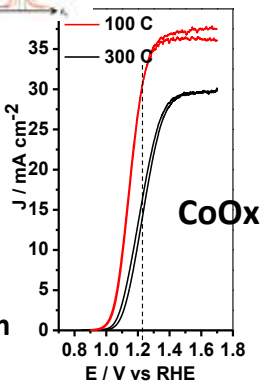
Photoanodes	Photocathodes
n-Si(111) and np$^+$-Si(100) | NiO_x	InP | TiO_2
a:Si-H | NiO_x	
n- and np+ Si microwires | TiO_2 |$NiCrO_x$	
n- and np+ Si | CoO_x	
p+- and np+ Si | p-type $NiCo_2O_4$	
$BiVO_4$ | TiO_2 | Ni	
n-CdTe | TiO_2 | Ni	
n-CdTe | NiO_x	
p+n-InP | NiO_x	

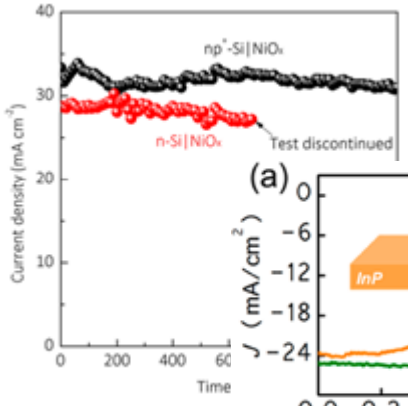


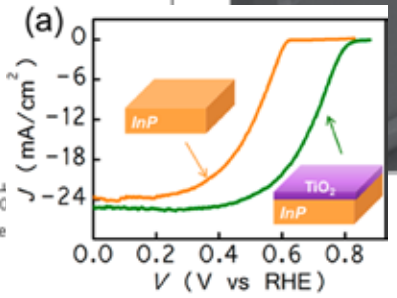
Operando studies of interface energetics

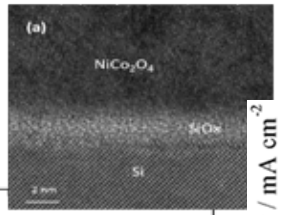


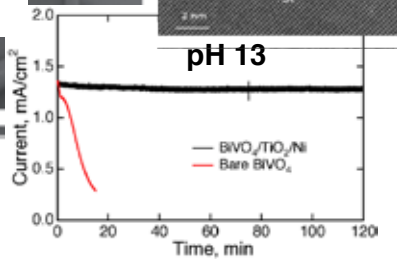
Theory: O vacancy mechanism for h+ transport in leaky TiO_2

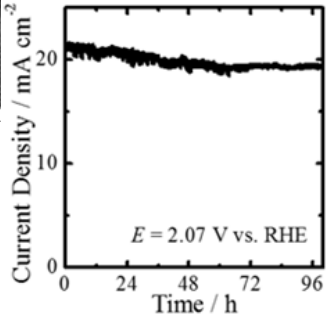


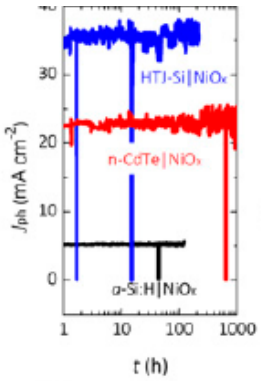












Review: Hu et al, J Phys Chem C 119 (2015) 24201

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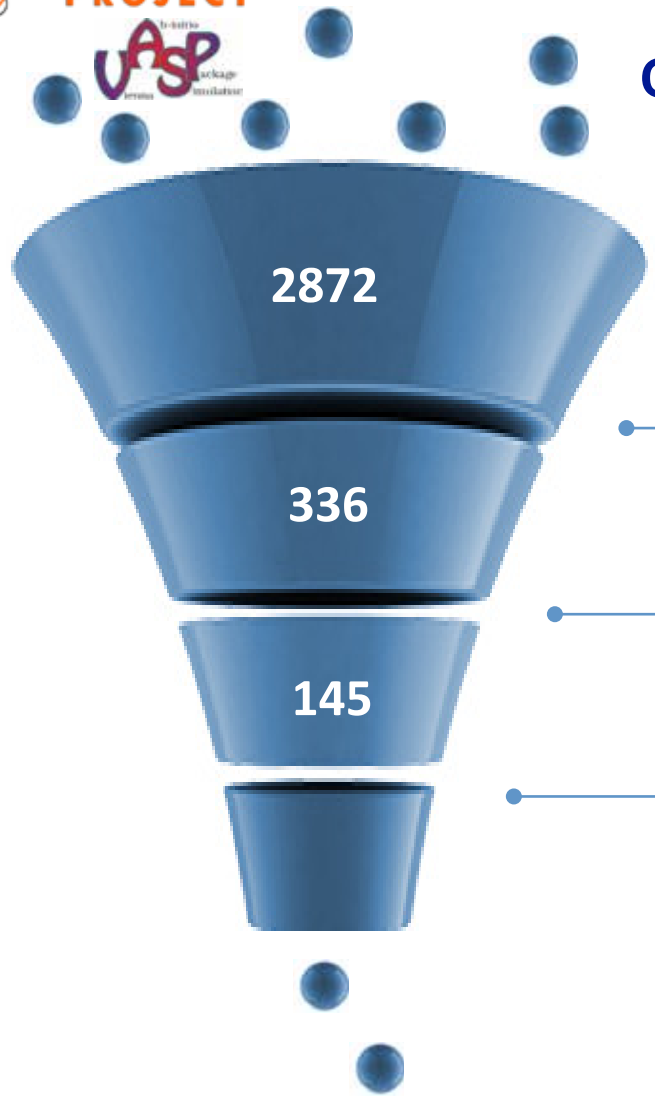
STABLE OXIDE-BASED PHOTOANODES

MATERIALS PROJECT



Cr, Mn, Cu and V based ternary oxides

Phase stability

PBE+U band gap

$\Delta H < 50$ meV/atom

$0.2 \text{ eV} < E_g < 3.5 \text{ eV}$

Semi-empirical U's
Wang et al,
Phys. Rev. B 73, 195107 (2006)

HSE band gap

$1.2 \text{ eV} < E_g < 3.2 \text{ eV}$

Band edge energies

Stability in water

Pourbaix diagrams
Persson et al,
Phys. Rev. B 85, 235438 (2012)

MP database

HSE, bulk

PBE+U, surface

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

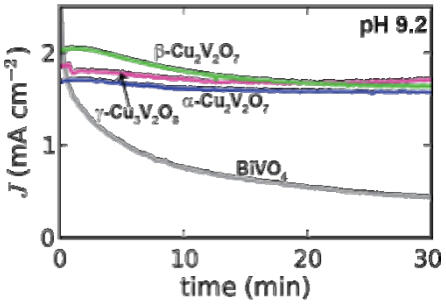
STABLE OXIDE-BASED PHOTOANODES

Scientific Achievement

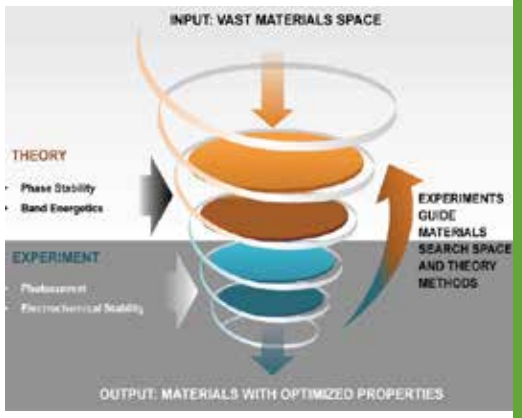
Computation, synthesis, and spectroscopy are used to identify and study the earth-abundant Cu and Mn vanadates as a highly promising light absorbers for photocatalytic water splitting.

Significance and Impact

The detailed understanding of β-$Mn_2V_2O_7$ reveals that it is a unique metal oxide semiconductor due to its desirable band gap and near-perfect band alignment to the standard potentials for water splitting. The additional discovery of 4 CuO-V_2O_5 phases with band gap below 2 eV marks a vast expansion of the known photoelectrocatalyst for efficient solar fuel generation.



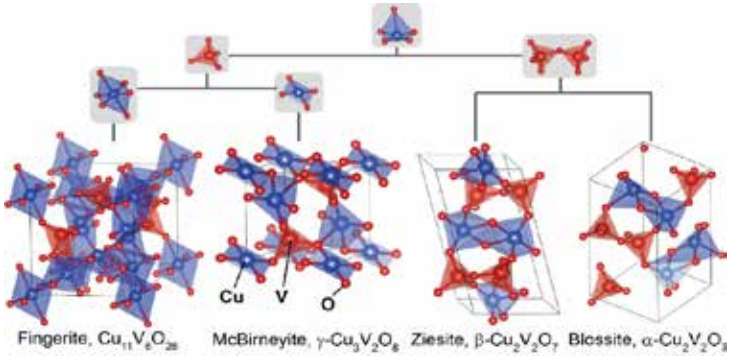
Stability of Copper Vanadates [2]



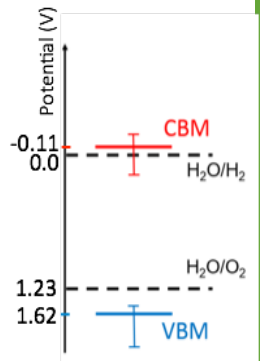
Theory-Experiment feedback loop

Research Details

- A density functional theory (DFT) was used to understand the structural, electronic, and magnetic properties of Mn and Cu vanadates.
- The optical and photoelectrochemical properties of these phases were mapped using combinatorial chemistry and high throughput experimentation.
- Photoelectrochemical characterization revealed excellent stability and opportunities for improving the photoelectrocatalytic activity to enable efficient photo-driven water splitting.



Structural motifs and electronic structure of CuO-V_2O_5 phases[2]



Band Energetics of β-$Mn_2V_2O_7$ [1]

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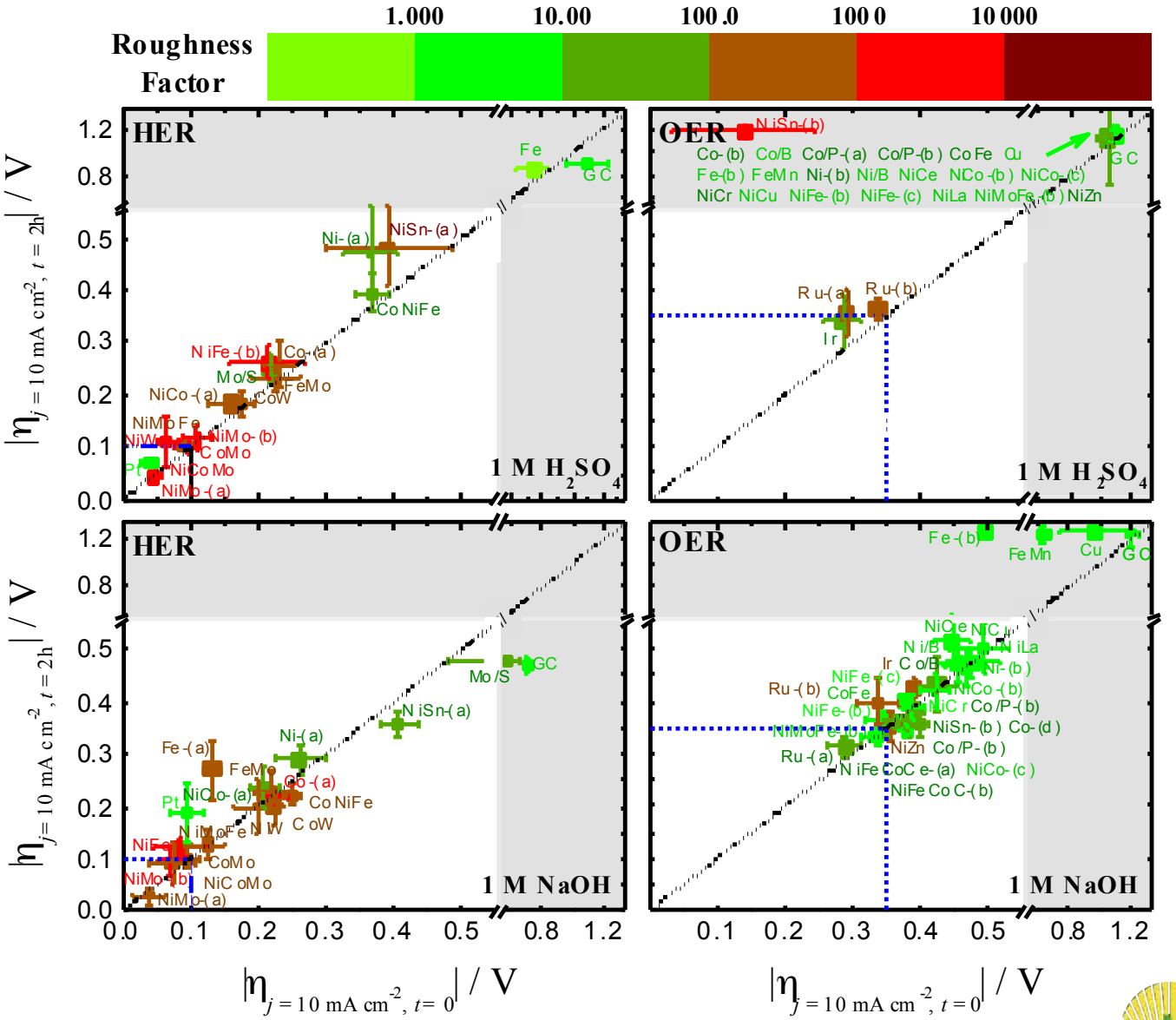
COMPREHENSIVE CATALYST BENCHMARKING



McCrory et al, JACS 137 (2015) 4347; *ibid* 135 (2013) 16977

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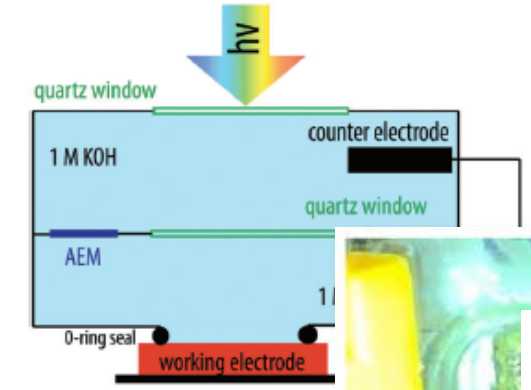
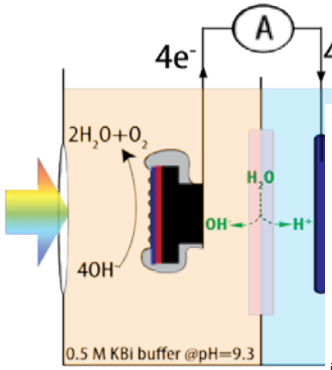
A PORTFOLIO OF STABLE HIGH EFFICIENCY WATER-SPLITTING PROTOTYPES

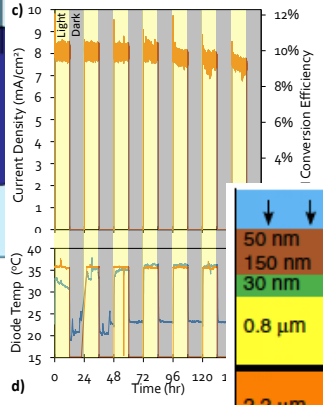
Demonstrations of efficient water splitting devices using III-V semiconductor stacks and membranes for full product separation



8.6% STH, photoanode in base

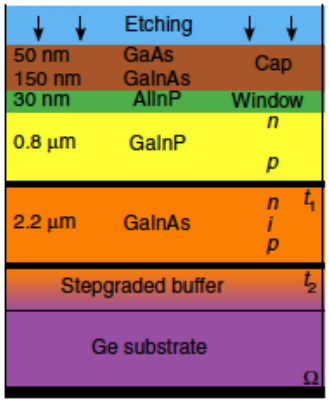
10% STH, photoanode in base





10% STH, photocathode in acid

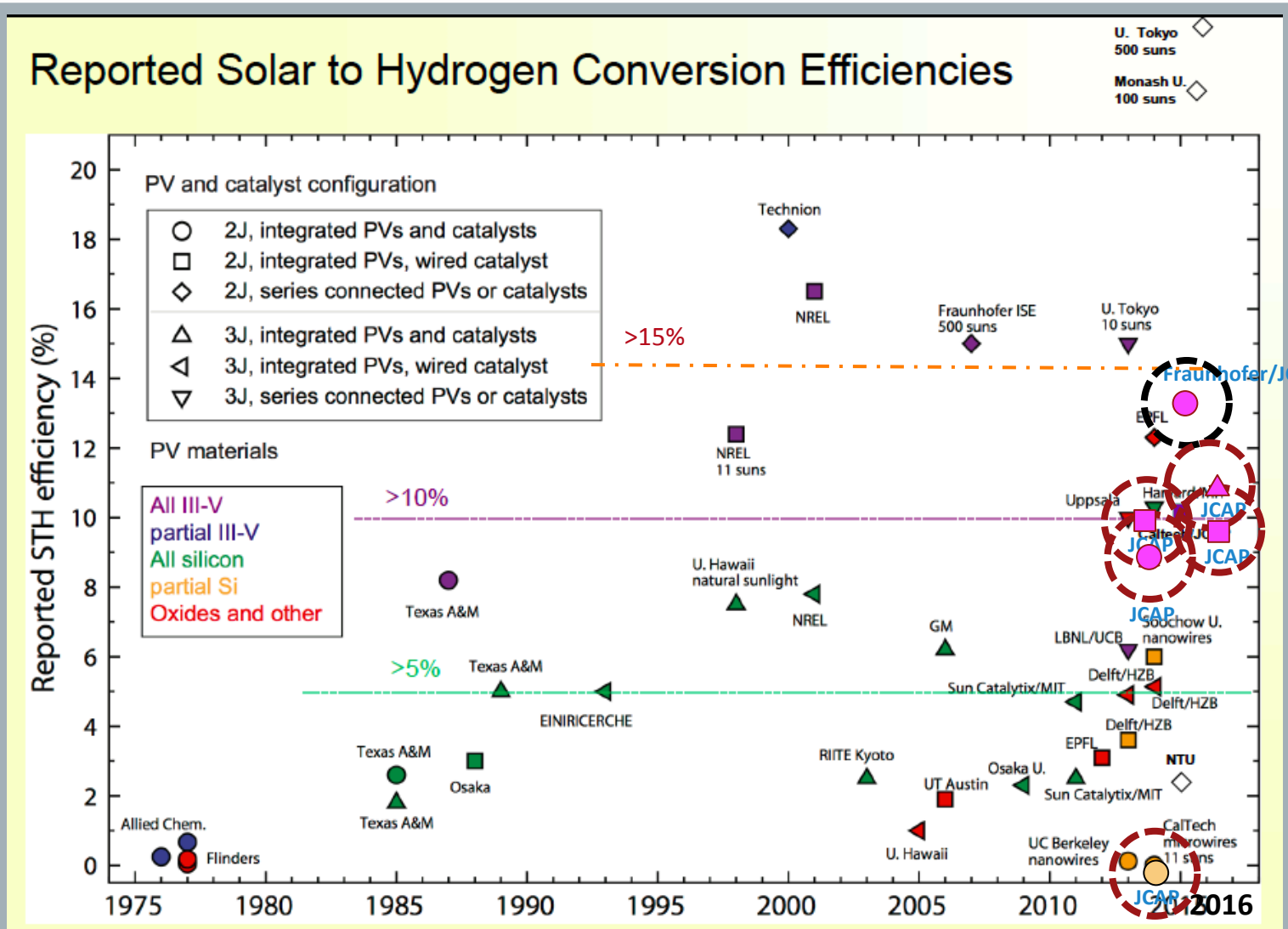
10% STH, photoanode, bipolar membrane



14% STH, photocathode in acid, no membrane

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

STATE OF THE ART FOR PEC HYDROGEN GENERATION



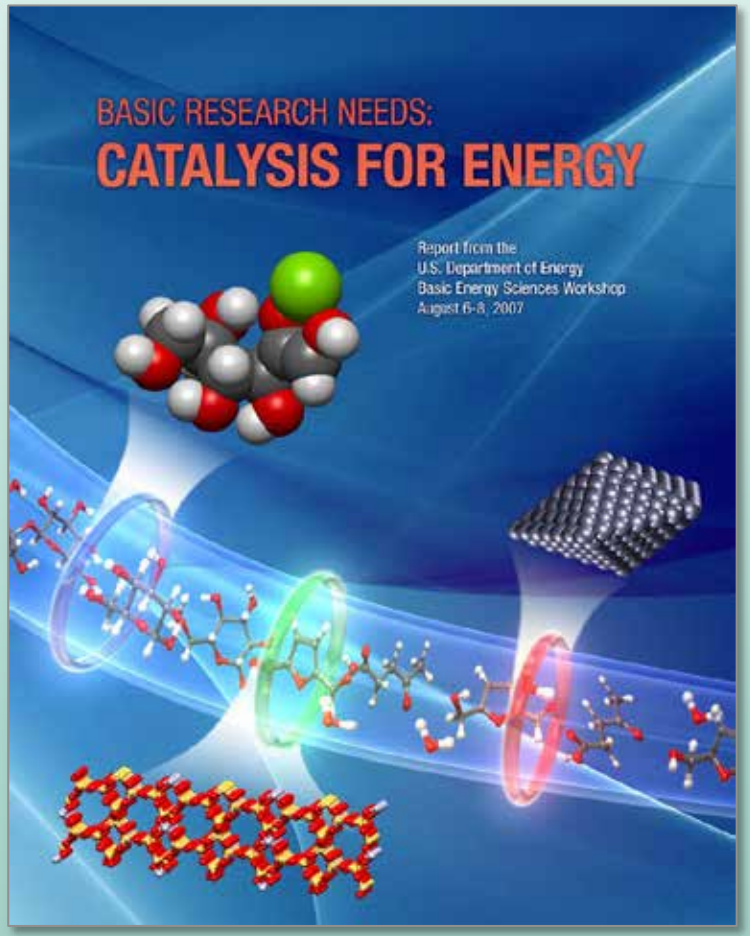
Ager, Shaner, Walczak, Sharp, Ardo, *Energy and Environmental Science*, 2015, 8, 2811

Ager, JCAP T3, 10/7/15 - 2

With membranes

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

FUELS FROM SUNLIGHT: A GRAND CHALLENGE FOR CATALYSIS



"Currently, no commercially available processes exist for the conversion of carbon dioxide to fuels and chemicals."

"The major obstacle preventing efficient conversion of carbon dioxide into energy-bearing products is the lack of catalysts that can readily couple an abundant energy source (e.g., electricity from solar or direct solar radiation) with inexpensive reducing agents (e.g., hydrogen derived from water or methane) to achieve rapid and selective cleavage of C–O bonds in carbon dioxide and formation of C–H bonds in the product."

"All known electrocatalysts or photocatalysts showing activity for carbon dioxide conversion to simple energy-storage products, such as carbon monoxide or formic acid, are inefficient and/or require use of sacrificial reducing agents."

"Opportunities exist for discovering and developing such catalysts with the goal of achieving higher selectivity and efficiency. At present, only laboratory-scale proof-of-concept systems produce carbon monoxide and formic acid with reasonable electron conversion efficiencies, but still at high overpotentials (greater than 0.6V)."

JCAP RENEWAL PROJECT

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

JCAP'S MISSION IN RENEWAL

There is no currently known catalyst, whether electrochemical or photoelectrochemical, that can reduce carbon dioxide with high efficiency and selectivity. Controlled catalysis is the grand challenge at the heart of solar-fuels generation from carbon dioxide.

In its five-year renewal project, JCAP will create the scientific foundation for a scalable technology that converts carbon dioxide into renewable transportation fuels, under mild conditions, with only solar added energy.

JCAP Renewal 5 Year Goals: Level One Milestones

Catalytic Mechanisms, Materials Discovery and Testbed Development

- *Discovery and understanding of highly selective catalytic mechanisms for carbon dioxide reduction and oxygen evolution under mild conditions of temperature and pressure, and with input partial pressures of carbon dioxide in air between ambient atmospheric levels of 400 ppm and 1 atm. These advances will inform the design of overall solar-energy-to-fuels components for key processes including light capture, energy transfer, electron transport and charge separation.*

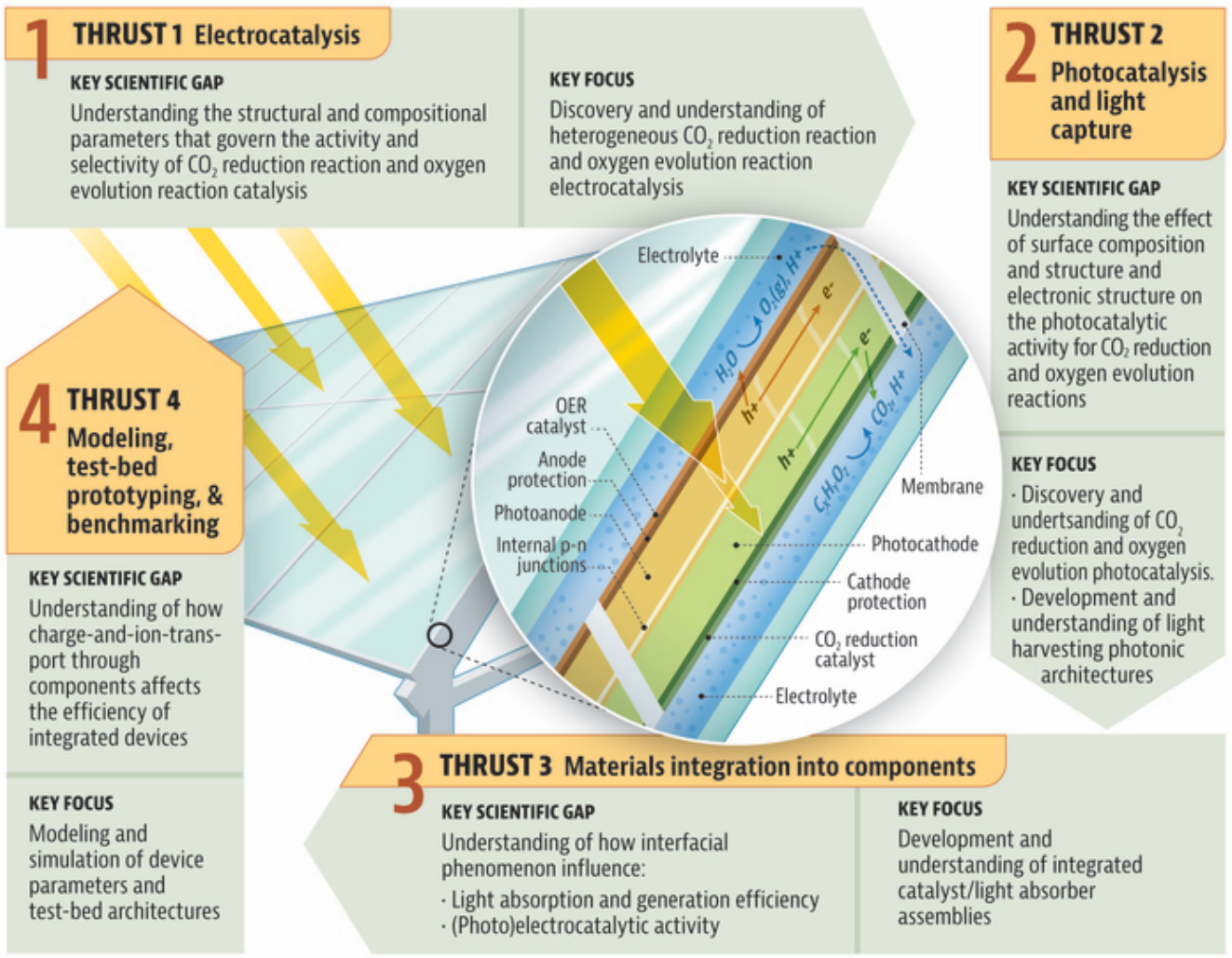
- *Accelerated discovery of electrocatalytic and photocatalytic materials and useful light-absorber photoelectrodes, followed by integration. This is required to design and construct components for test-bed prototypes that demonstrate selective, efficient CO_2 reduction into hydrocarbon fuels at full solar flux.*

- *Demonstration, in JCAP test-bed prototypes, of artificial photosynthetic carbon dioxide reduction components and oxygen evolution components that exceed natural photosynthesis in efficiency and rival it in selectivity. Results of these demonstrations will be used to determine the practicality of prototype solar-fuels systems.*

JCAP RENEWAL PROJECT

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

JCAP'S RESEARCH THRUSTS

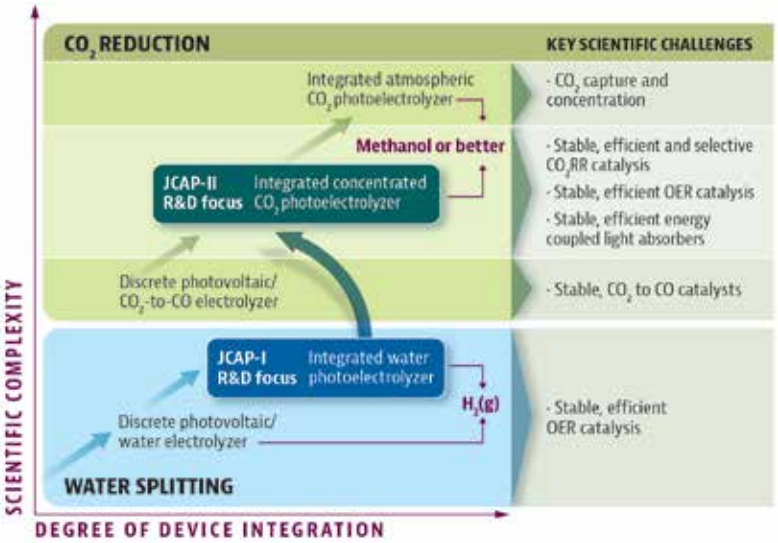


JCAP RENEWAL PROJECT

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

STRATEGY FOR OPERATING THE HUB

Accelerate discovery in a high-risk, high-reward R&D program



1. Year 1: H_2 PEC
   - Capitalize on JCAP-1 advances in photoelectrode & catalyst development, integration and modeling to realize high efficiency water splitting prototypes incorporating these advances

2. Years 1 and 2: Selective CO_2R Components

   Divergent:
   - Broadly-based discovery-oriented research effort
   - Significantly increased role of theory

3. Years 3-5: Selective CO_2R Components

   Convergent:
   - Integration of JCAP-discovered materials into photoelectrodes
   - Evaluation of photoelectrodes in testbeds

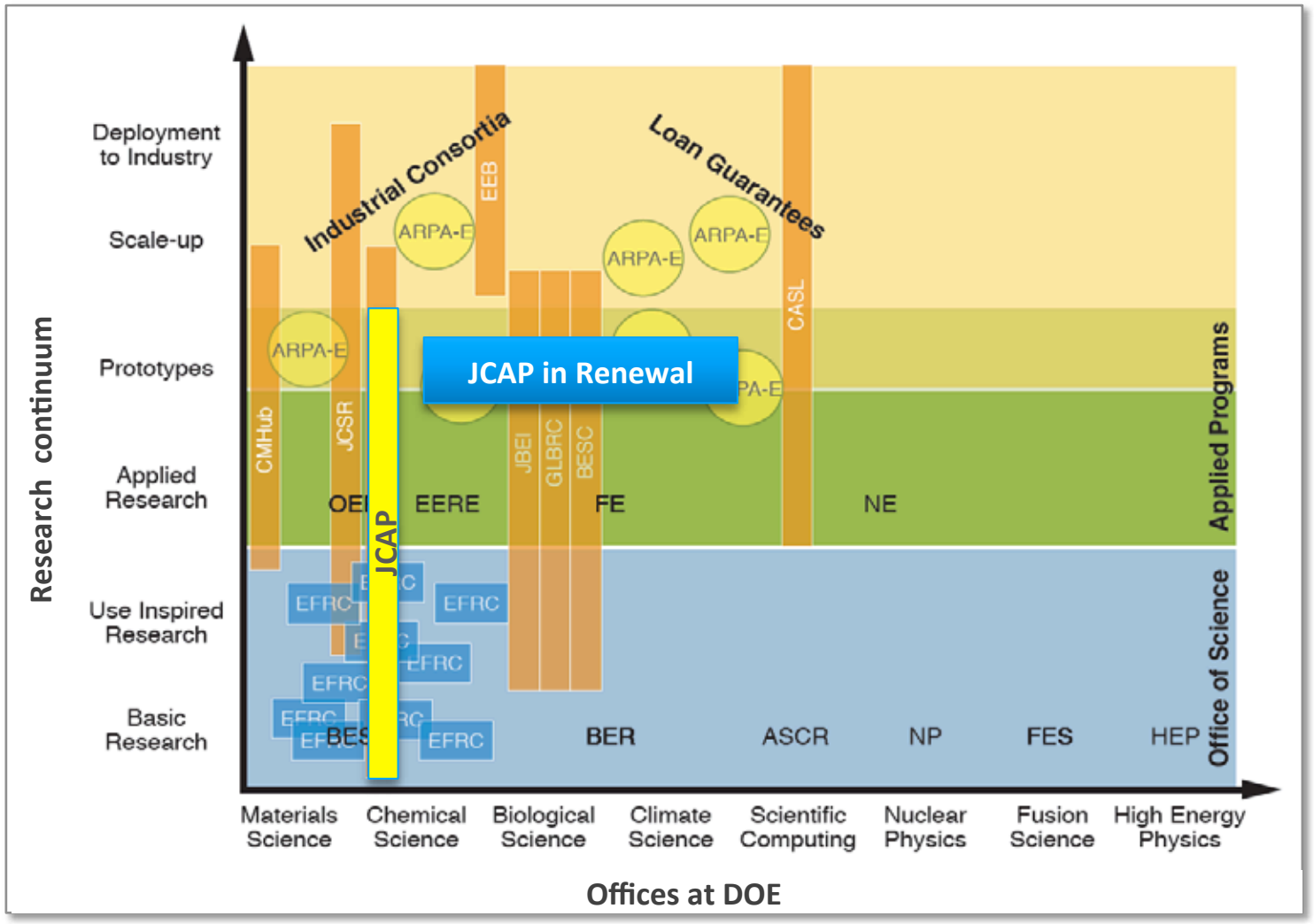
   Divergent:
   - Feedback from integration and testbeds to next phase of discovery science effort

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

2010-2015 JCAP ACCOMPLISHMENTS CREATE LEVERAGE FOR RENEWAL PROJECT

JCAP Accomplishment/Capability Developed in 1st 5-Year Project	Relevance to CO_2 Reduction	Renewal Project R&D Thrust
• **Protective coatings for photoelectrodes**	Ability to protect/stabilize semiconductor photoanodes enables efficient solar-driven production of protons and electrons required to produce fuels from CO_2	2 and 3
• **High-throughput materials discovery**	Distinctive integrated theory/ experimental capability to discover, synthesize and screen new electrocatalysts, photocatalysts and photoelectrode materials	1 and 2
• **New electrocatalysts with benchmarked performance**	Discovered water oxidation and CO_2 reduction catalysts; quantitatively benchmarked these for activity, selectivity and stability	1 and 2
• **Operando and *in situ* characterization of materials and related theory**	Connection of performance data to underlying physical and chemical mechanisms leading to knowledge that informs new materials design	1, 2 and 3
• **Separator membrane synthesis and properties**	Materials and design principles for membrane separators in water-splitting also applicable to CO_2 reduction	4
• **Multiphysics modeling and simulation tools**	Modeling capablities and tools allow system-level requirements for solar-driven CO_2 reduction to be determined, leading to development of credible prototypes	4
• **Robust prototype designs and fabrication experience**	Experience gained from building and testing water-splitting prototypes facilitates development of testbed prototypes for CO_2 reduction	4
• **Fully integrated prototype with unassisted water splitting**	Ability to integrate discovered semiconductors, catalysts, and membranes into functional architectures necessary for full CO_2 reduction prototypes	1, 2, 3 and 4

JCAP'S LOCATION ON THE R&D LANDSCAPE



Secretary of Energy Advisory Board Task Force Report to Support the Evaluation of New Funding Constructs for Energy R&D in the DOE, March 28, 2014

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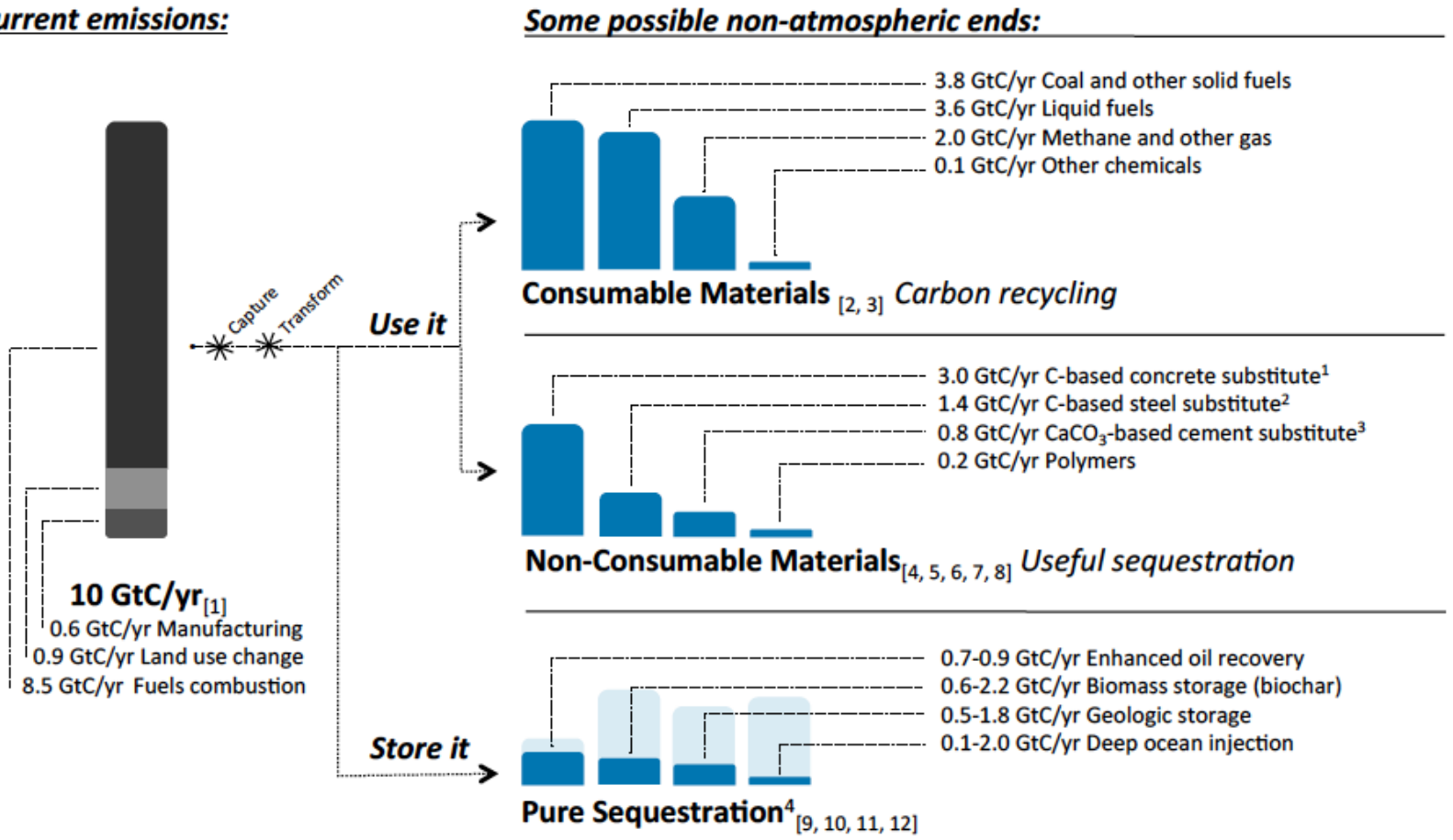
RELATIVE SCALE OF EMISSIONS AND POTENTIAL USES FOR CO_2



GtC = 1 billion metric tons of carbon equivalent, i.e. 1Gt MeOH = 12.01/(12.01+16.00+4*1.01) Gt = 0.37 GtC.
[1] Assuming cement is composed of CaCO3, and the aggregate is composed of 50% CaCO3 by mass • [2] Assuming a steel substitute that is similar in composition to carbon fiber, i.e. 90% C by mass.
[3] Assuming cement is composed of CaCO3 • [4] Estimated feasible scale-up rates by 2050, excluding geoengineering approaches. Shaded bars indicate the upper range of estimates.

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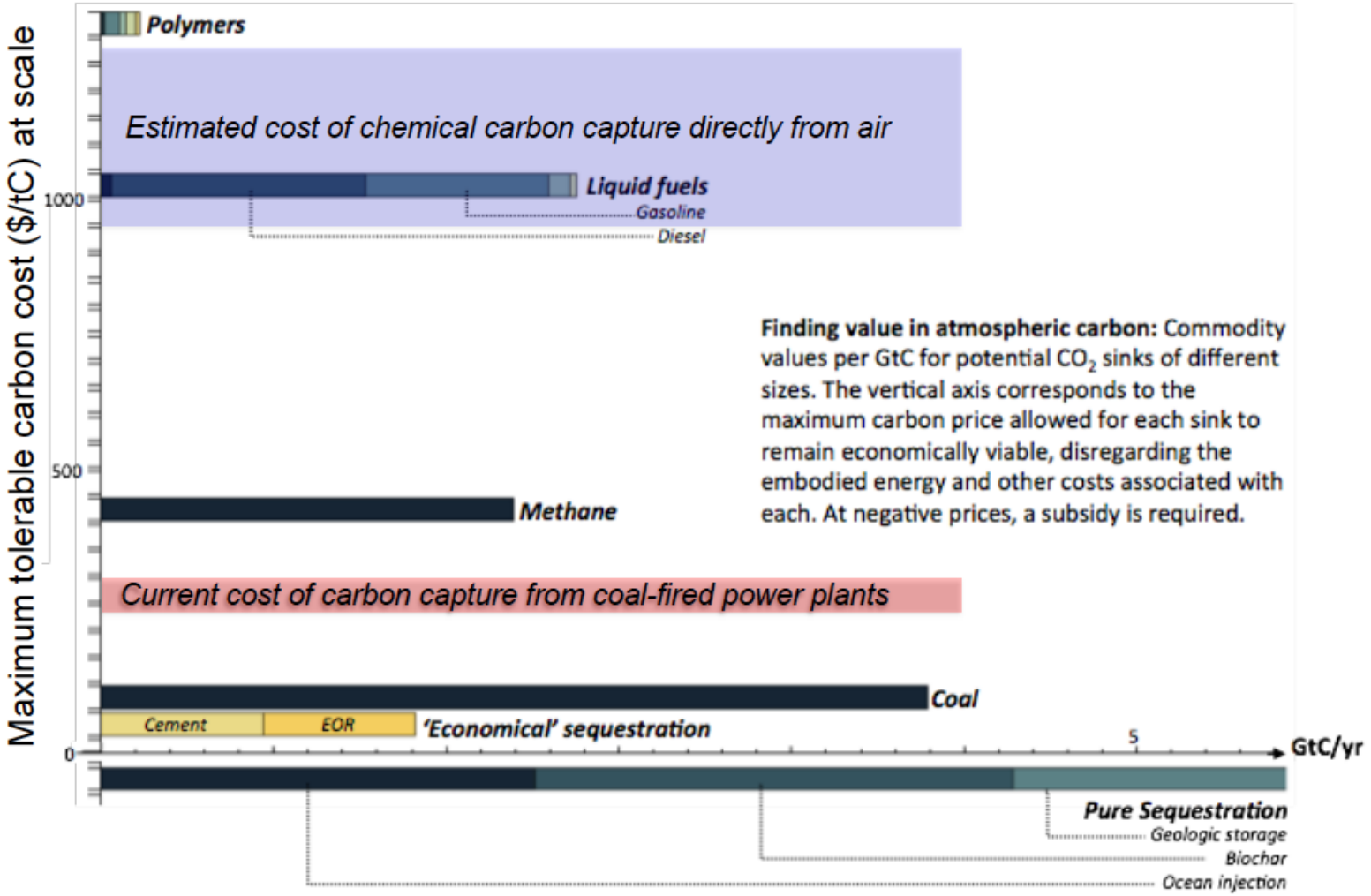
COSTS OF CARBON IN DIFFERENT FORMS



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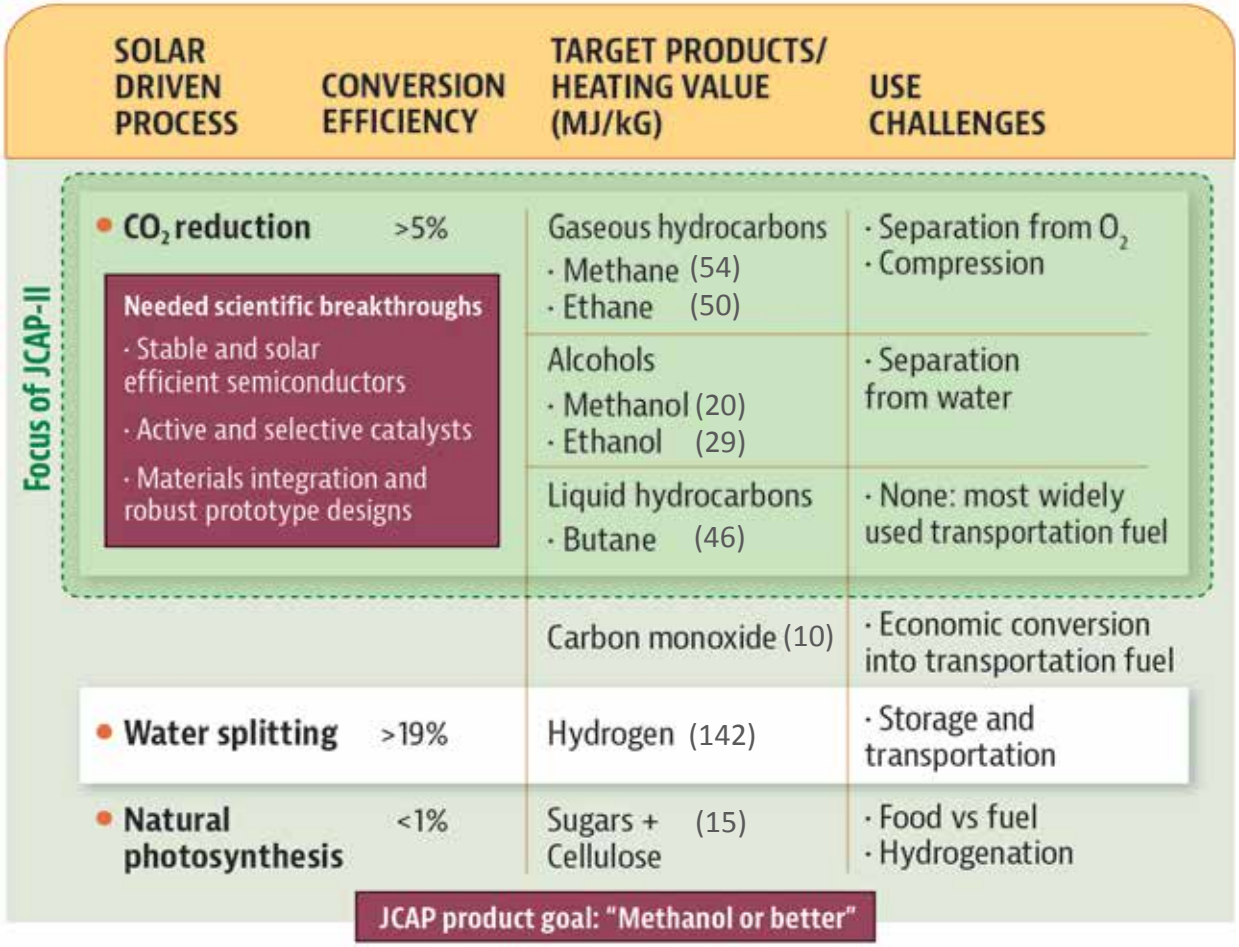
JCAP FUEL TARGETS BEYOND WATER SPLITTING

JCAP's desired fuel products are liquid or gaseous hydrocarbons or alcohols, defined by a heating value exceeding that for carbon monoxide



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ROUTES TO FUELS FROM CO_2: COMPARING E-CHEM TO THERMOCHEMICAL PATHWAYS

Two principal routes to reduce CO_2 to fuels:

1. Direct reduction of CO_2 to fuel or chemicals (eg. CH_4, CH_3OH, $H_2C{=}CH_2$, etc.)
2. Thermochemical synthesis of fuel from intermediate reduced species (H_2 or CO).
   Three possible reactions (illustrated for methanol synthesis) :

(1) $3H_2$ (g) + CO_2 (g) → CH_3OH (l) + H_2O (l)
(2) $2H_2$ (g) + CO (g) → CH_3OH (l)
(3) 3CO (g) + $2H_2O$ (l) → CH_3OH (l) + $2CO_2$ (g)

These reactant mixtures are equivalent, because:

H_2 and CO are equivalent as energy carriers

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad \Delta H^0_{298} = 286 \text{ kJ/mol.}$$

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad \Delta H^0_{298} = 283 \text{ kJ/mol.}$$

- *No energetic advantage to producing CO instead of H_2 for subsequent conversion to liquid fuel.*
- *Chemical reaction and toxicity reasons to prefer H_2 over CO generation.*

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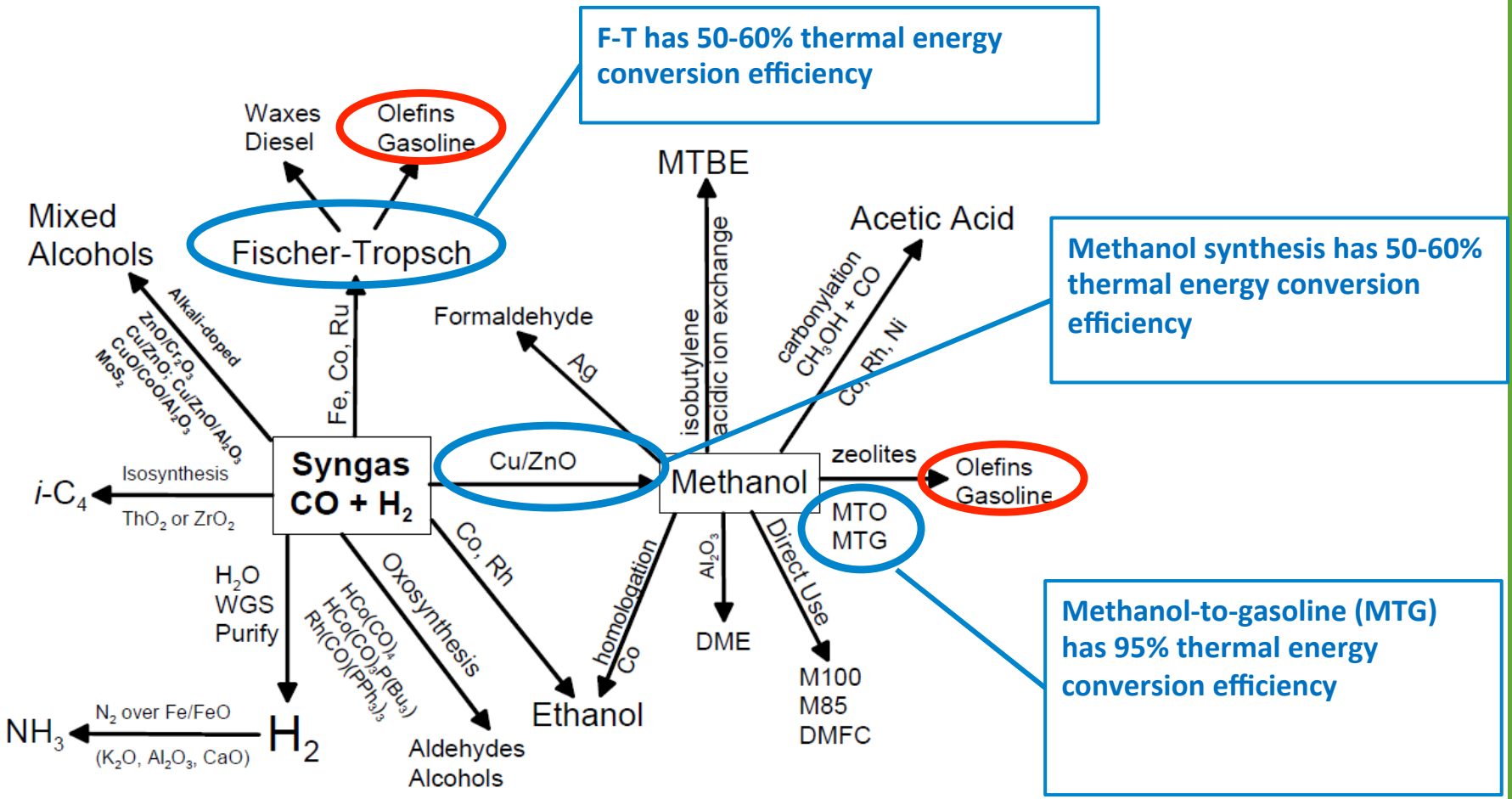
CHEMICAL SYNTHESES FROM SYNGAS AND METHANOL

- Many chemical conversions from syngas to products, including gasoline via Fishcer-Tropsch
- Many chemical conversions from methanol to products, including gasoline
- Methanol is an achievable product from CO_2R PEC



Source: P.L. Spath and D.C. Dayton, Preliminary screening—technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomas-derived syngas, National Renewable Energy Laboratory, NREL/TP-510-34929, December, 2003.

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SOLAR-TO-FUEL ENERGY COMPARISON

- **Conversion of PEC-H_2 (or CO) to a liquid fuel requires additional steps, reducing the Solar Energy to Fuel Energy conversion efficiency.**
- **A CO_2R PEC-CH_3OH generator will produce equivalent fuel energy operating at only 60% of the efficiency of a PEC-H_2 generator that requires an additional conversion step to produce CH_3OH.**

Fuel	PEC-H_2 efficiency	Conversion efficiency	Solar to fuel efficiency
H_2 (g)	10%	NA	10%
CH_3OH (from H_2 + CO_2)		60%	6%
Gasoline from CH_3OH (MTG)		95%	5.7%
Low Temp F-T (from H_2 + CO_2)		60%	6%

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POSSIBLE PATHWAYS FOR CO_2 REDUCTION CATALYSIS

C_1 Products: CO_2 Adsorption

CO_2 → HCOO-

CO_2 → CO, CH_4

CO_2 → CH_3OH

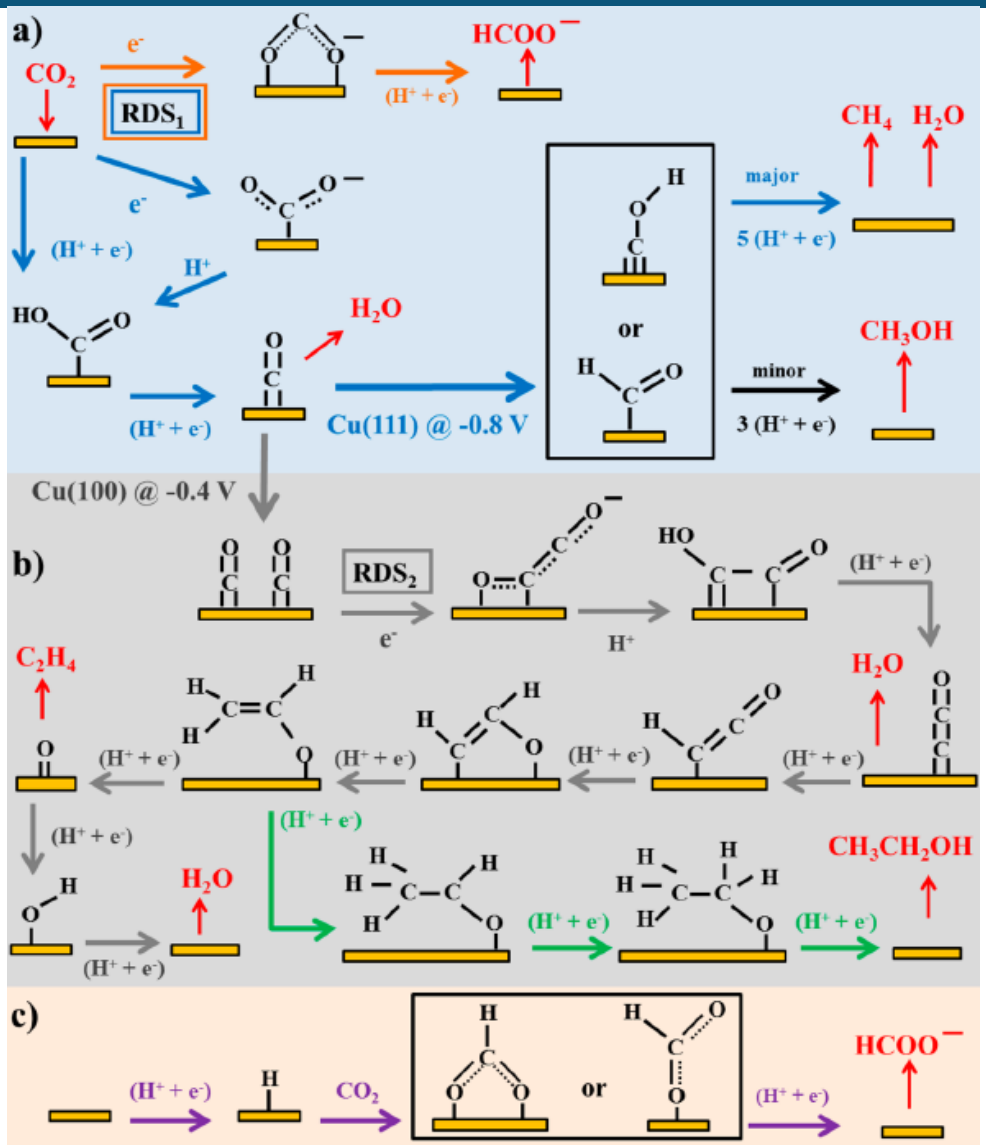
C_2 Products: CO Dimerization

CO_2 → C_2H_4

CO_2 → CH_3CH_2OH

C_1 Products: CO_2 Insertion

CO_2 → HCOO-



R. Kortlever, J. Shen, K-J P. Schouten, F. Calle-Vallejo, and M.T. M. Koper, J Phys Chem Lett., 6, 4073−4082 (2015).

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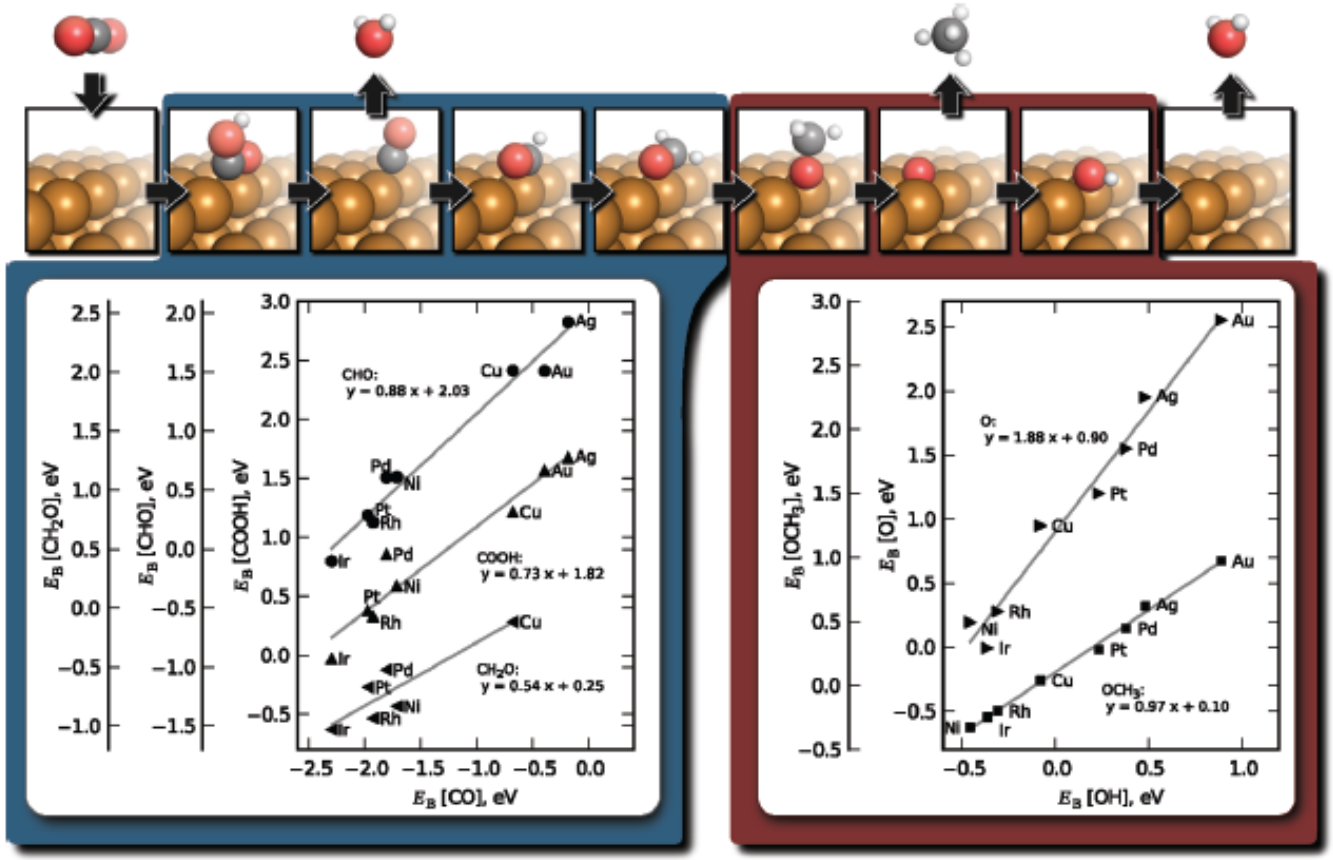
SCALING RELATIONSHIPS FOR CO_2 INTERMEDIATES ON CU



Adsorption energies of the key bound intermediates on fcc Cu (211)

Adsorption energies of adsorbates binding through oxygen

Peterson and Nørskov, J Phys Chem Lett., 3, 251−25 (2012).

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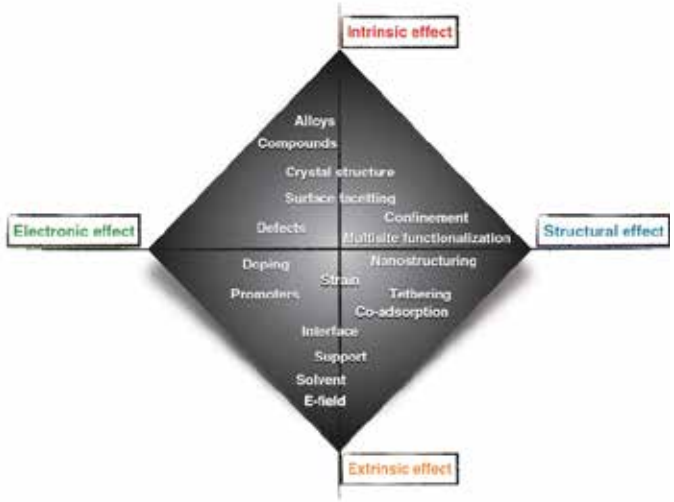
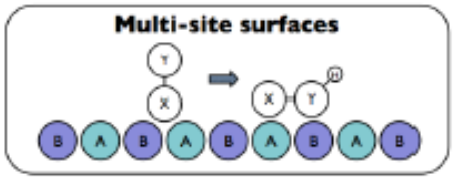
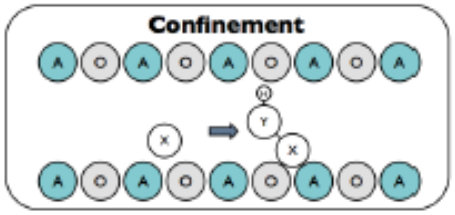
Overcoming scaling relationships for CO_2 intermediates on Cu

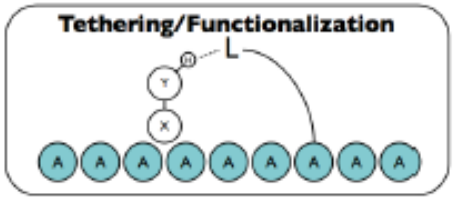




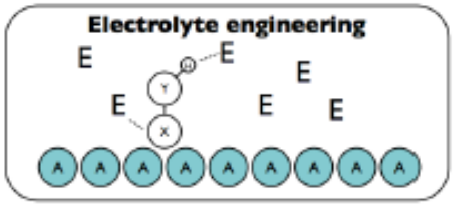
A.T. Bell; N.S. Lewis; M.F. Soriaga



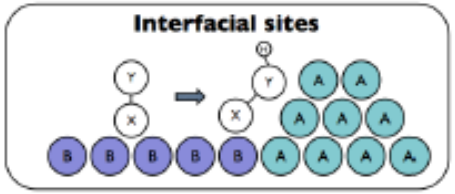
D. Toste, F. Toma



Agapie and Peters; Grubbs



A.T. Bell



T.F. Jaramillo; M.F. Soriaga

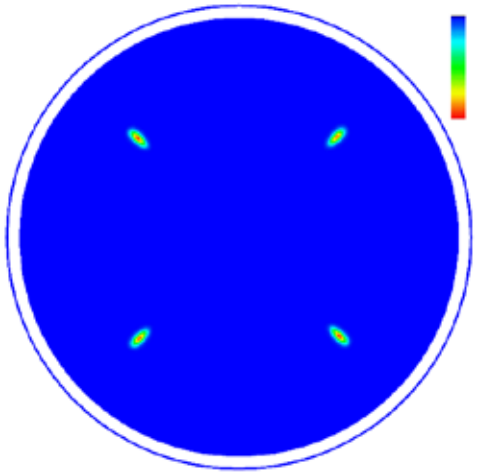
A. Vojvodic and J.K. Nørskov, National Science Review 00: 1–4doi: 10.1093/nsr/nwv023 (2015)

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

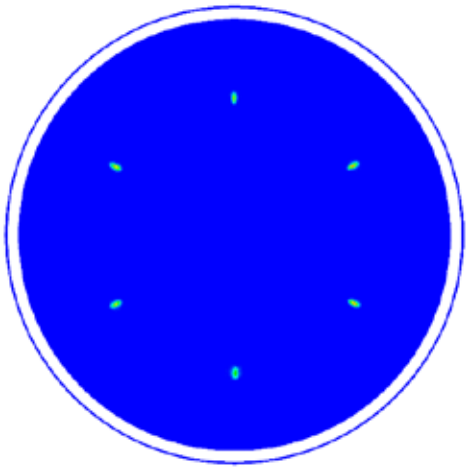
JCAP MISSION AND STRATEGY

EPITAXIALLY ORIENTED CU SURFACES

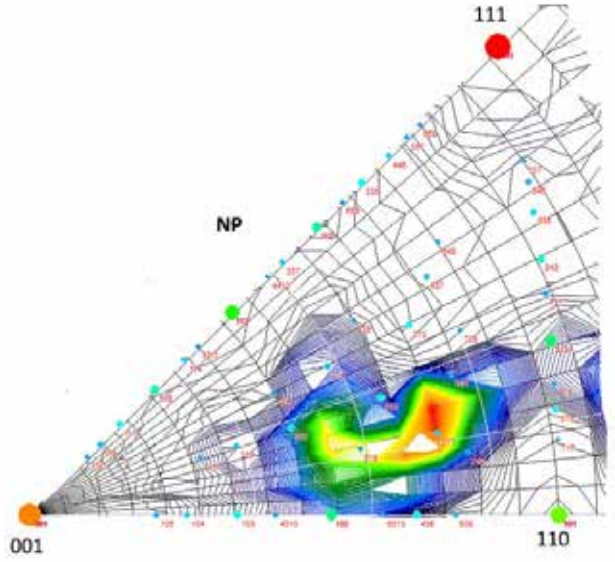
Cu(100)/Si(100)



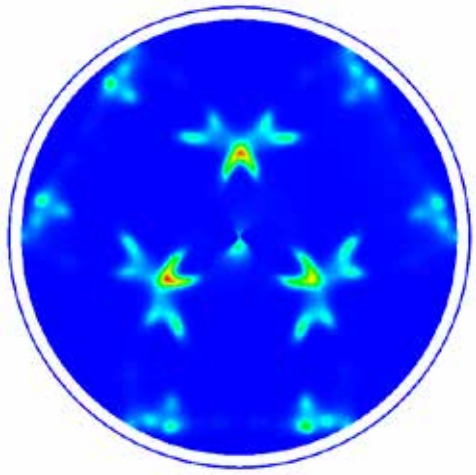
Cu(111)/Al_2O_3(0001)



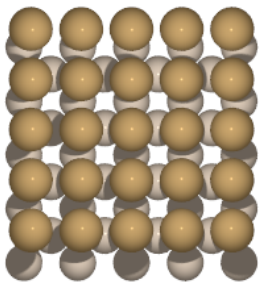
Inverse Pole Figure



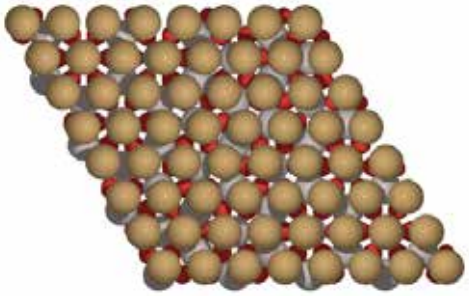
Cu(751)/Si(111)



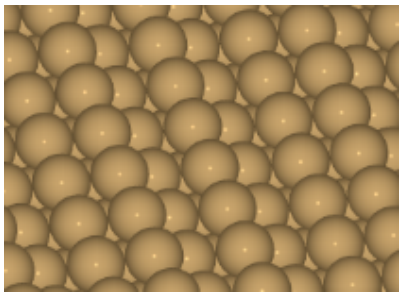
Cu(100)



Cu(111)

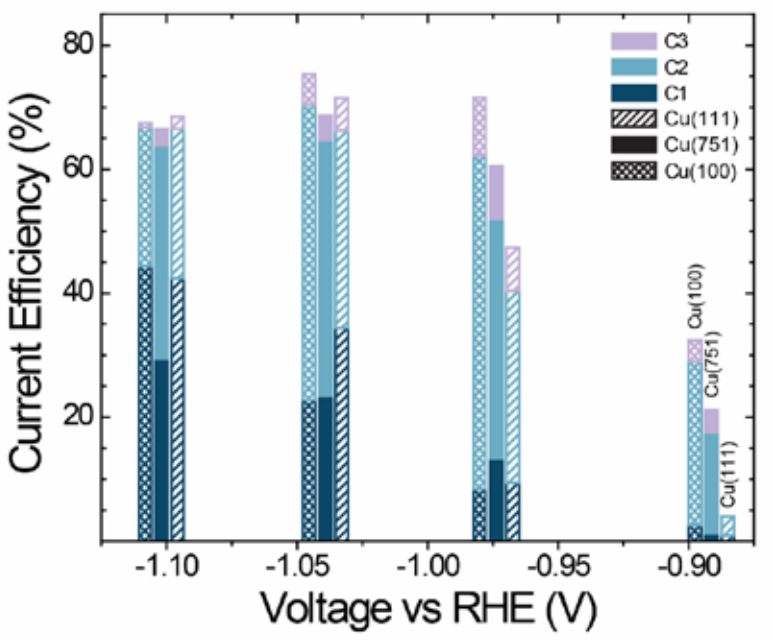


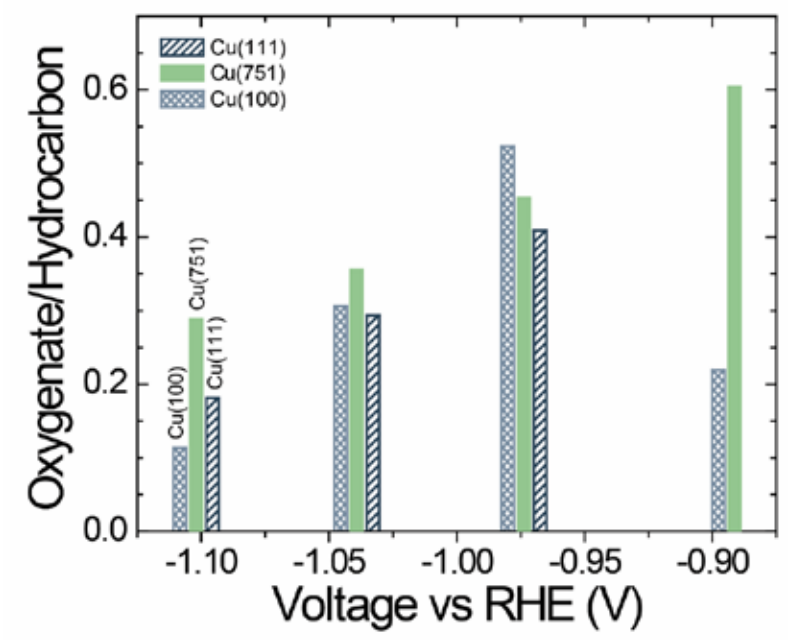
Cu(751)



Images by Dr. Karen Chan

SELECTIVITY OF EPITAXIALLY ORIENTED CU SURFACES

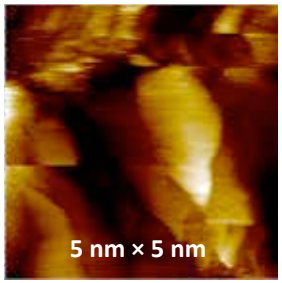




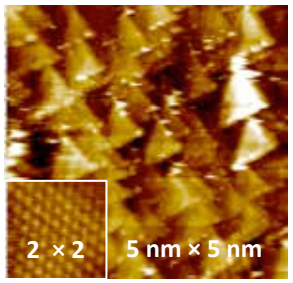
Cu(100) surfaces and step sites favor C-C coupling selectivity

Step sites guide selectivity towards more oxygenates

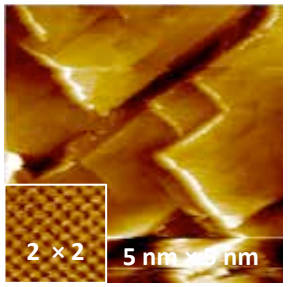
OECSTM: CU RECONSTRUCTION AT CO_2R CONDITIONS (-0.9 V/0.1 *M* KOH)



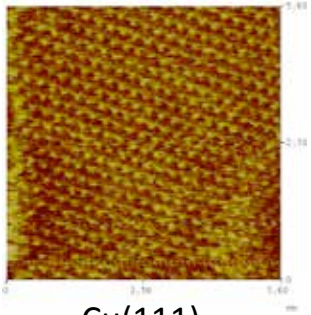
Cu(pc)
t = 0 m



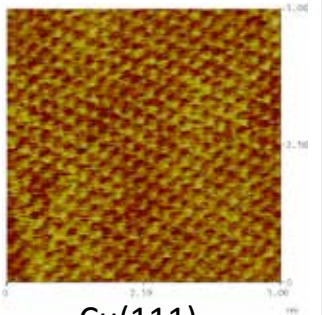
Cu(pc) → Cu(111)
t = 30 m



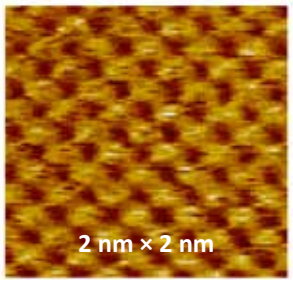
Cu(pc) → Cu(111) → Cu(100)
t = 60 m



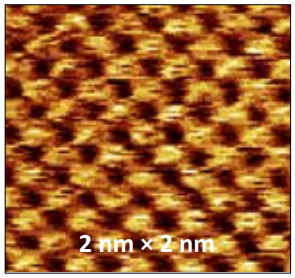
Cu(111)
t = 0 m



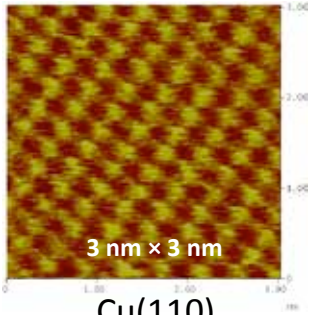
Cu(111)
t = 60 m



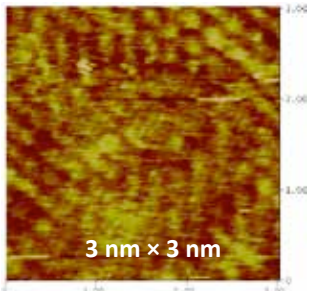
Cu(100)
t = 0 m



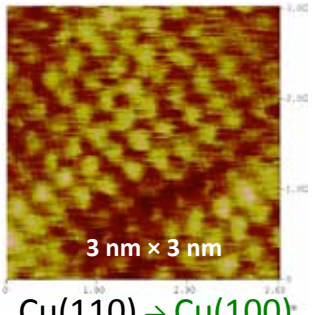
Cu(100)
t = 60 m



Cu(110)
t = 0 m



Cu(110) → Disordered Cu(111)
t = 30 m

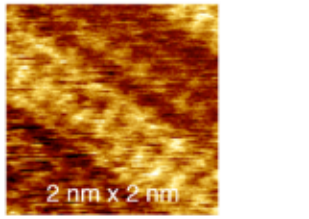


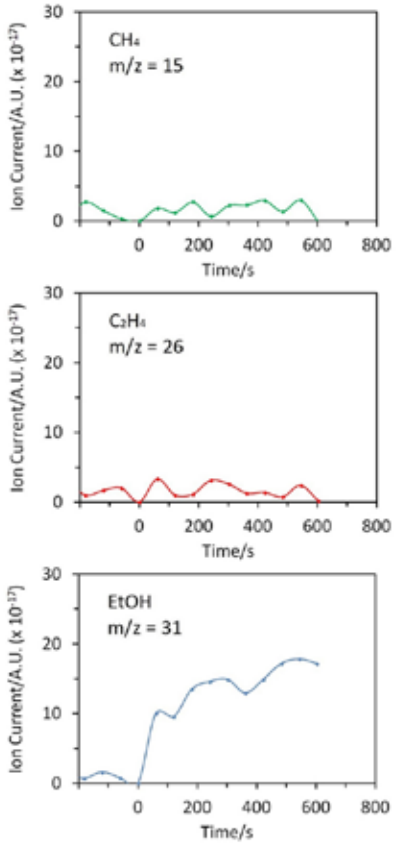
Cu(110) → Cu(100)
t = 60 m

Y.-G. KIM, J. H. BARICUATRO, A. JAVIER AND M. P. SORIAGA

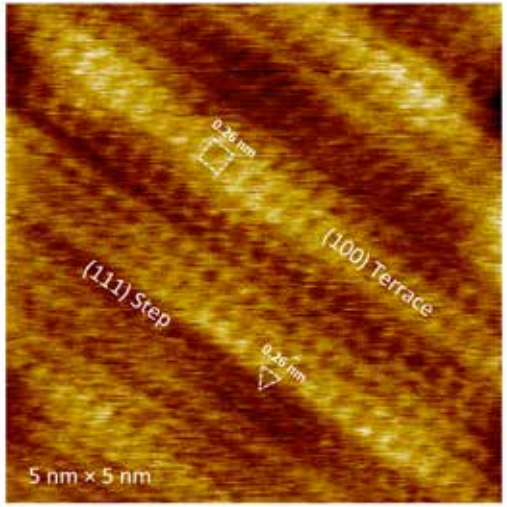
REGULATING CO-REDUCTION SELECTIVITY BY CONTROL OF SURFACE STRUCTURE

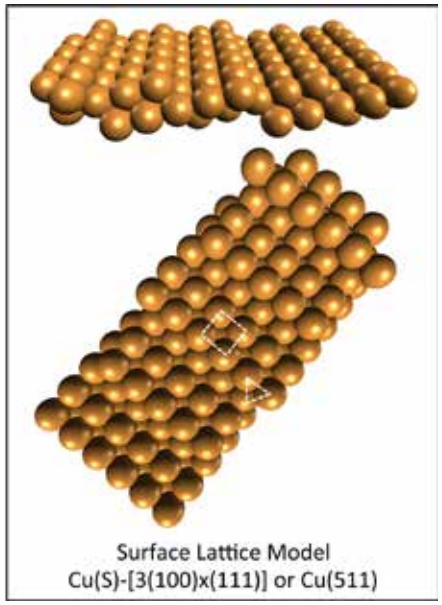
Ethanol-product Selectivity of Post-ORC Cu(pc)-[Cu(100)] at -1.0 V in 0.1 M KOH

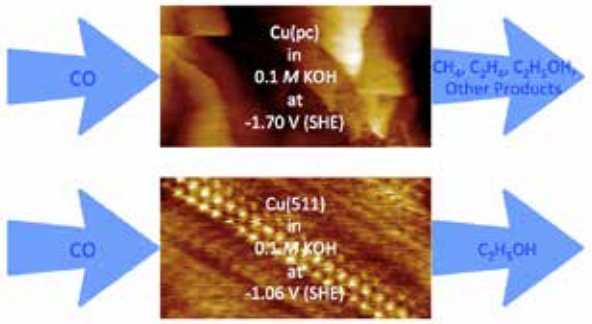




CO-to-C_2H_5OH on Cu(511)







Y.-G. KIM, J. H. BARICUATRO, A. JAVIER AND M. P. SORIAGA

SIMULATION OF C-C BOND FORMATION DURING CO_2R OVER CU

Scientific Achievement

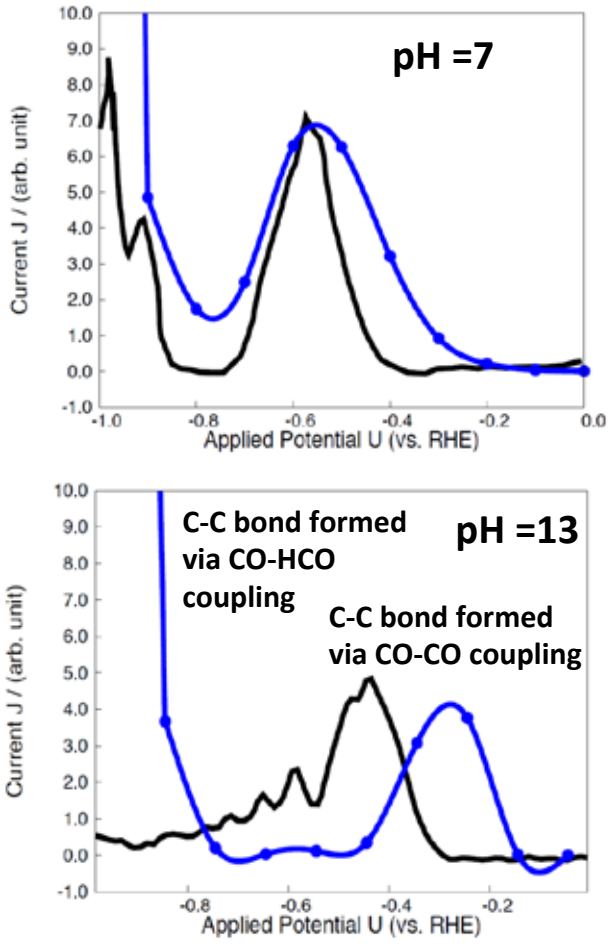
Simulated the effects of applied potential on the rate of C-C bond formation during the electrochemical reduction of CO_2.

Significance and Impact

Developed a theoretical model for predicting the rate coefficients involved in the reduction of CO_2, which takes into account the effects of the electrolyte and the applied field. The model can be used to simulate the effects of catalyst composition, electrolyte composition, and applied field on the kinetics of CO_2 reduction.

Research Details

DFT/RPBE/APW was used to calculate the free energy of activation for all elementary steps. The space charge field was determined by solving the linearized Poisson-Boltzmann equation. Rate coefficients determined theoretically were used in a microkinetic model to determine the rate of C-C bond formation vs potential



Predicted (blue) and measured rate of C_2H_4 formation for pH = 7 and pH = 13

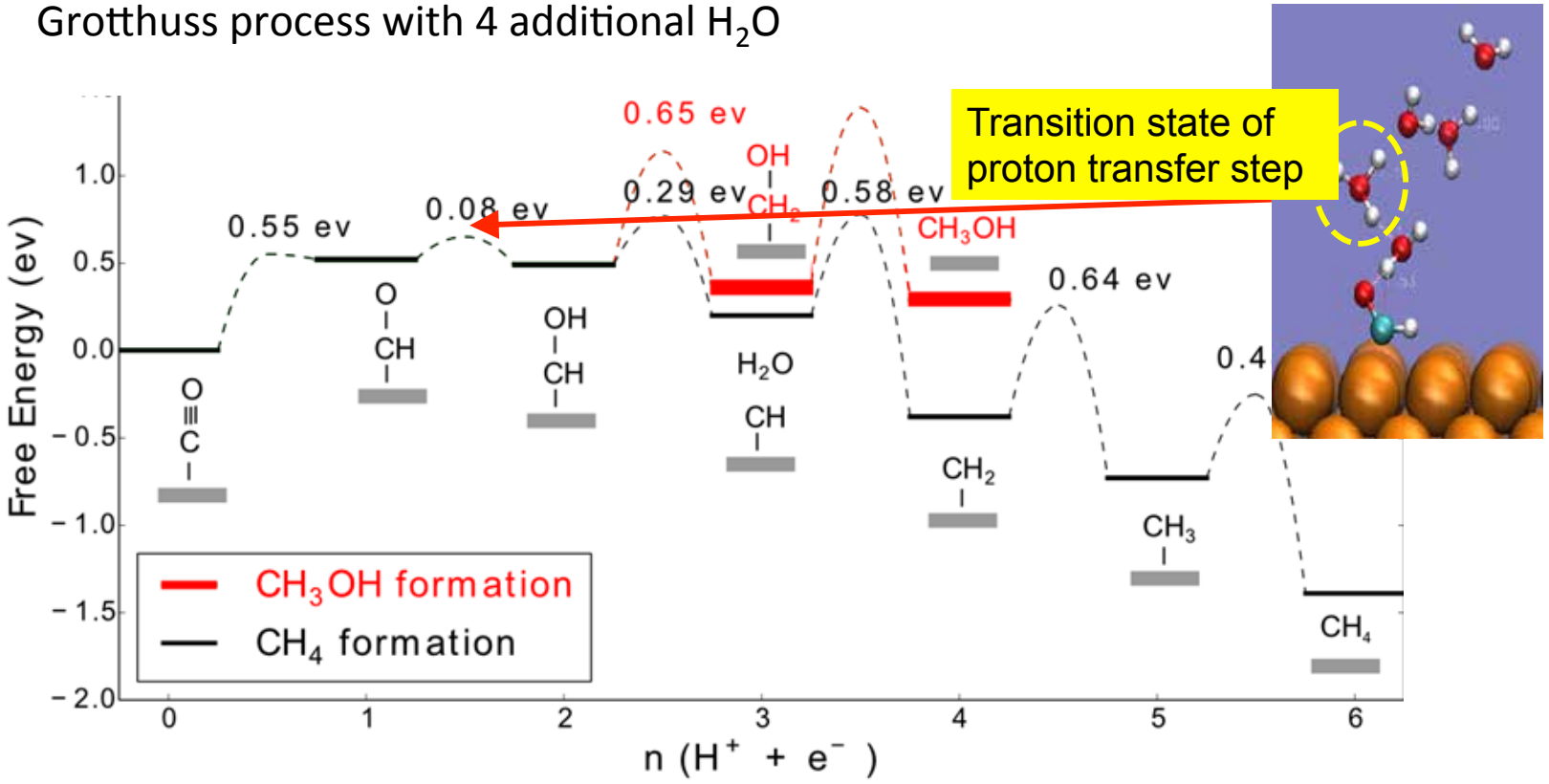
J. Goodpaster, M. Head-Gordon, and A. T. Bell, J. Phys. Chem. Lett. , 7, 1471-1477, 2016.

BARRIERS FOR REDUCTION OF CO/CU(100), WITH EXPLICIT SOLVENT AT PH 0

Scientific Achievement: Explicit solvent QM Metadynamics simulation of electrochemical process. Predict potential for CH_4 product 0.55 eV: exp't = 0.56 eV.

- Can use QM to calculate accurate free energy barrier at operating temperature. Thus can use theory to predict accurate barriers for new electrocatalyst.

Significance and Impact : explicit solvent proton transfer transition state: Grotthuss process with 4 additional H_2O



Cheng, Xiao, Goddard; J Phys. Chem. Lett.vol 6 pp4767-4773 (Dec. 15, 2015)

IDENTIFICATION OF ELECTROCATALYSTS FOR CO_2RR TO H_2COO

Scientific Achievement

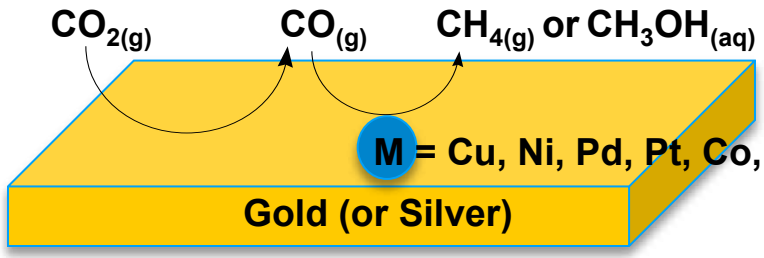
Identified tandem, bimetallic catalysts for the preferential formation of H_2COO over H_2.

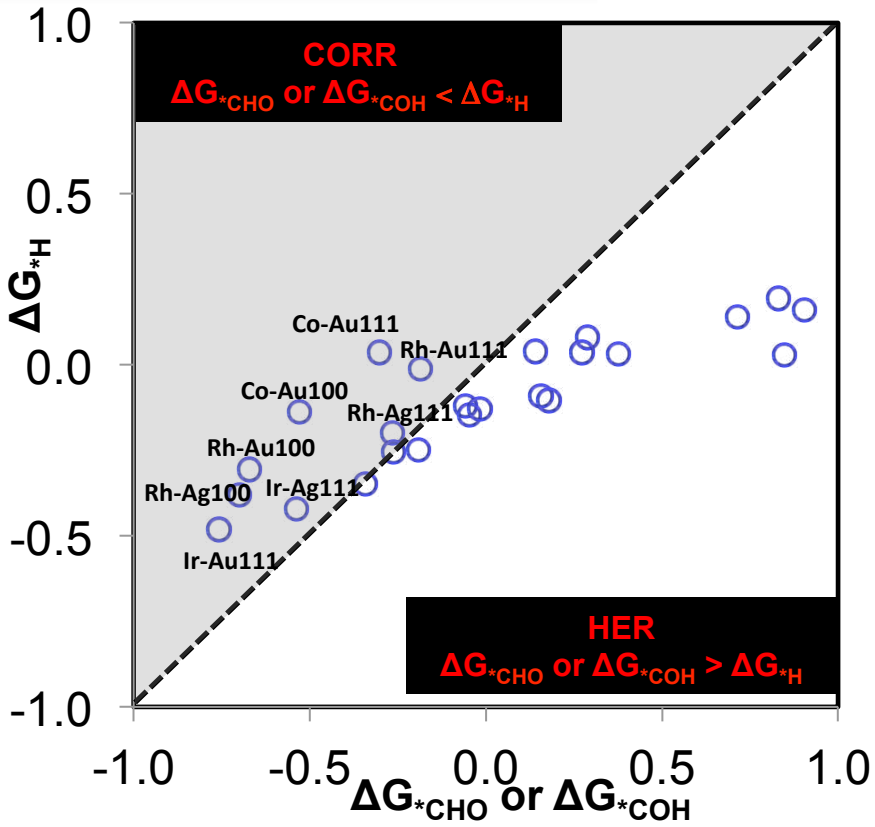
Significance and Impact

Selective reduction of CO_2 to H_2COO can be achieved by embedding metal atoms that favor CORR over HER in a host metal that favors CO_2 reduction to CO. The CORR catalyst must bind *CHO (or *COH) more tightly than *H

Research Details

DFT/RPBE/APW was used to calculate the free energy of activation for all elementary steps in CO2 reduction to CO on Au(111) or Ag(111) surfaces and the reduction of CO to H2CO vs H2 on Cu, Ni, Pd, Pt , Co, Rh, and Ir atoms embedded in the host metal surface.





M.-J. Cheng, A.T. Bell, and M. Head-Gordon, J. Phys. Chem. C, in preparation.

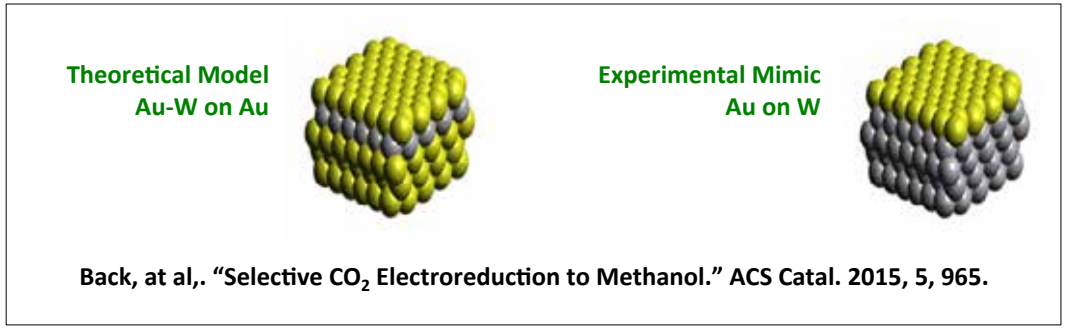
ELECTROCHEMICAL REDUCTION OF CO_2 SELECTIVELY TO METHANOL

Discovery of Near-Surface Alloy for the Reduction of CO_2 *Exclusively* to CH_3OH

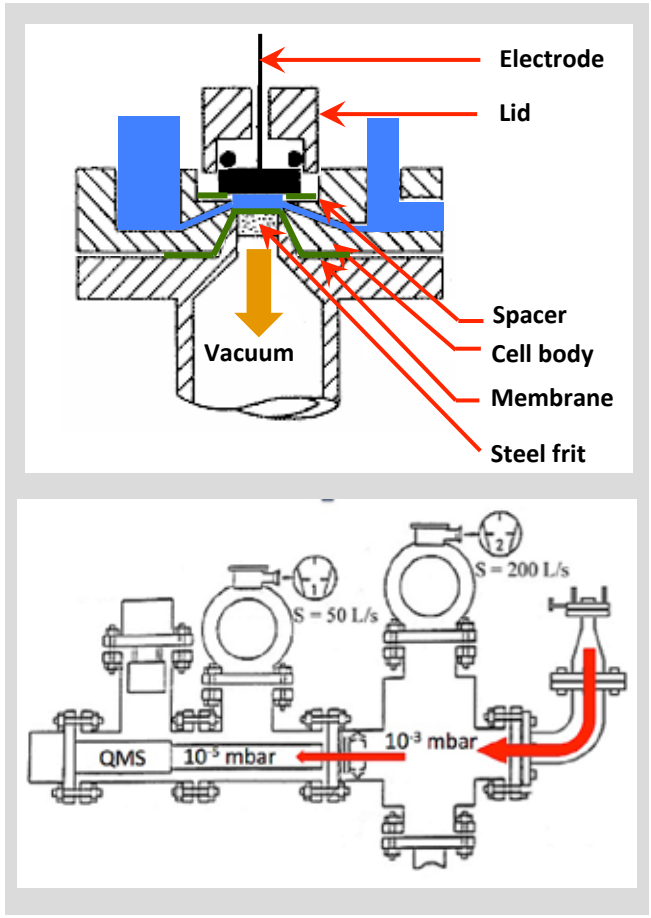
A theoretical prediction: a near-surface alloy (NSA) of a monolayer of Au on bulk W was empirically found to generate CH_3OH to the *exclusion* of other hydrocarbons and alcohols.

Approach

- Combined density-functional theory and adsorption-energy descriptors ΔG°_{CO}, ΔG°_{H} and ΔG°_{OH} predicted a Au-W-Au NSA that would be CH_3OH-product-selective.
- Overlayer NSA films of (0.5 to 3 ML) Au on W were prepared by controlled galvanostatic deposition.



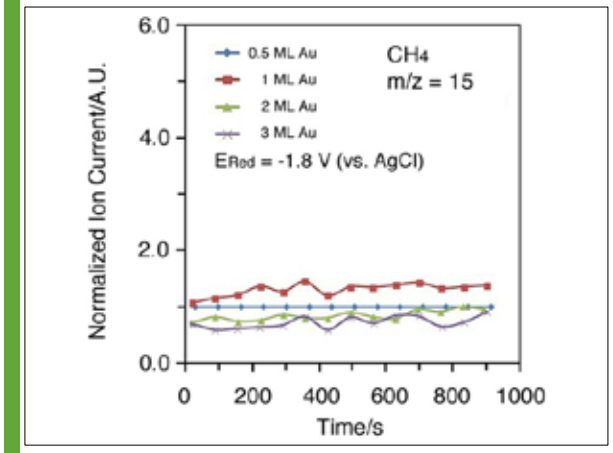
Back, at al,. "Selective CO_2 Electroreduction to Methanol." ACS Catal. 2015, 5, 965.

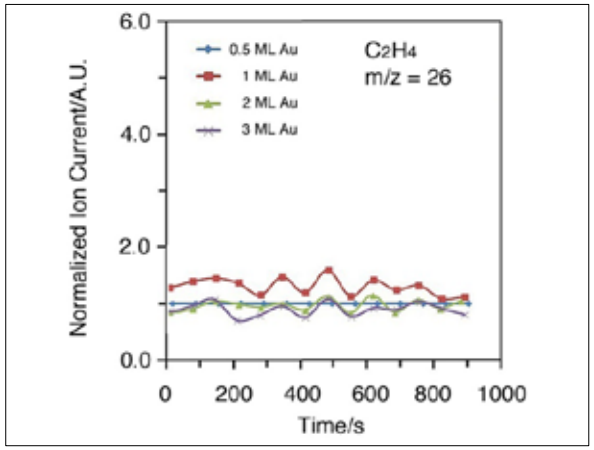


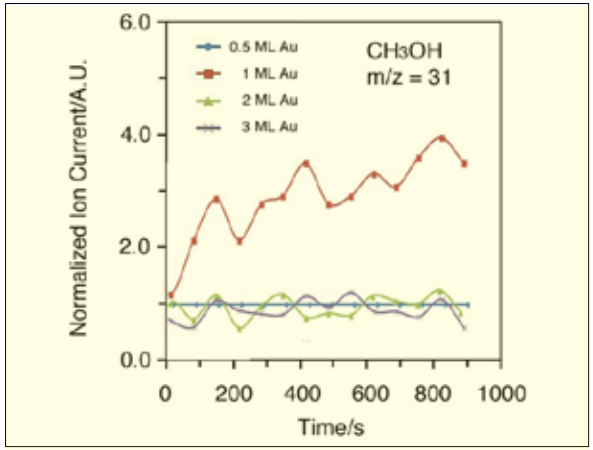
Products from CO_2 reduction at -1.2 V(RHE) in 0.1 M $KHCO_3$ were analyzed by Differential Electrochemical Mass Spectrometry (DEMS). Only CH_3OH was found.

ELECTROCHEMICAL REDUCTION OF CO_2 SELECTIVELY TO METHANOL

Constant-potential DEMS of CO_2 Reduction on Au-W Near-Surface Alloy







Theoretical Prognosis	*Experimental Result*
CH_3OH-Selective	**CH_3OH-Selective**
High Activity	**Not yet optimized**
Low Overvoltage	**Not yet optimized**
HER Suppression	**Not yet optimized**

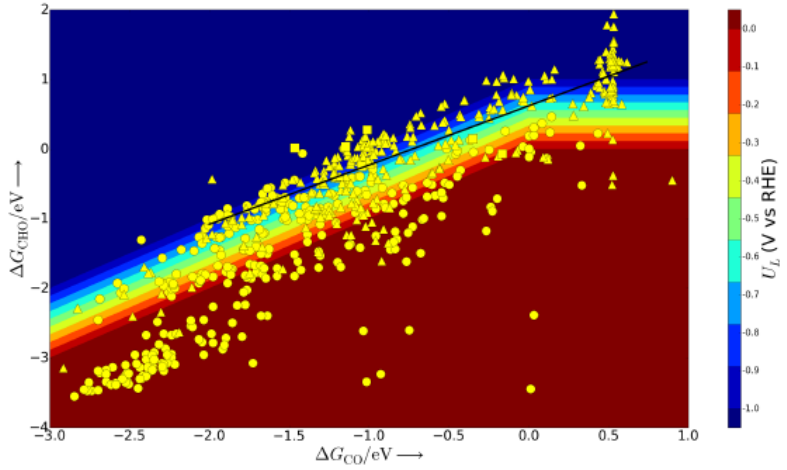
Future Work:

Prepare NSA as prescribed by theory
Try different substrates with the same NSA
Obtain complete and quantitative product analysis
Have theory scrutinized by other theory groups

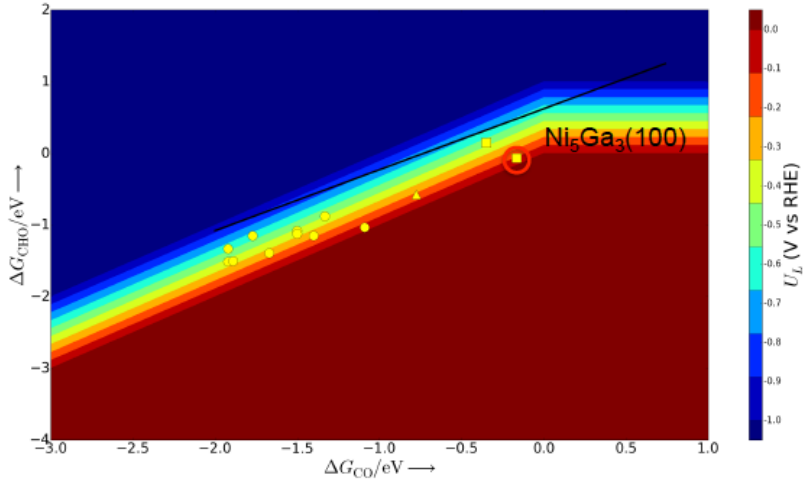
A. Javier, J. H. Baricuatro, Y.-G. Kim and M. P. Soriaga*. "Au-on-W Near-Surface Alloy as a CH_3OH-Product-Selective Electrocatalyst for CO_2 Reduction: Empirical (DEMS) Confirmation of a Computational (DFT) Prediction." *Electrocatalysis*. In press. (2015).

BREAKING SCALING RELATIONSHIPS WITH BIFUNCTIONAL CATALYSTS

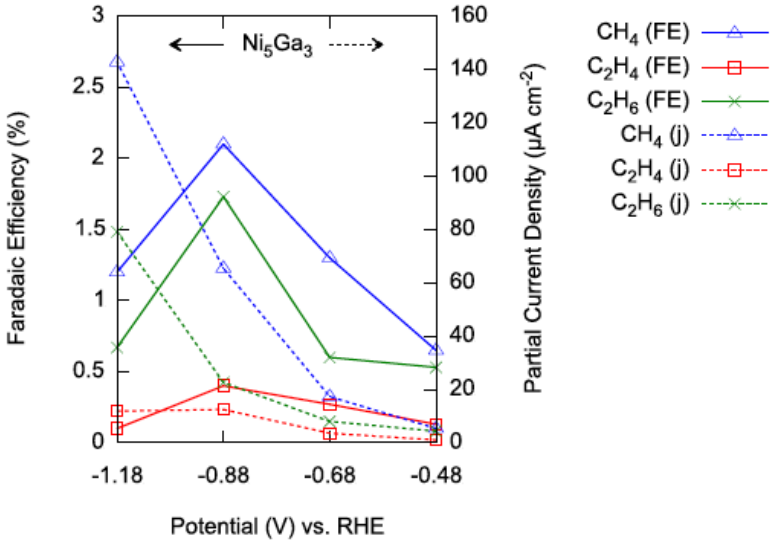
Screening many alloy candidates:



Include only stable configurations:



Hansen, Shi, Lausche, Peterson, Nørskov , Phys. Chem Chem Phys. (2016)



Torelli, Francis, Crompton, Javier, Thompson, Brunschwig, Soriaga, Lewis, ACS Catal., DOI: 10.1021/ acscatal.5b02888

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

CO_2 REDUCTION: SELECTED ACHIEVEMENTS TO DATE

SUMMARY

- A strategy for selective CO_2 reduction: multifunctional cathode that combines multiple active sites, functional coatings, nanoscale confining volumes
- Cu nanoscale surface observation reveals role of facetting in selectivity
- Experimental catalysts exhibiting elements of selectivity: Au/W and NiGa
- Approaches for breaking scale between CO binding and other intermediates
- Theoretical methods for DFT at applied potential: barriers → microkinetic models
- Theoretical methods that incorporate explicit water
- Experimental investigation of electrolyte effects on solvation and selectivity

SCIENTIFIC OUTPUTS AND DELIVERABLES

Deliverables for JCAP milestones include:

SCIENTIFIC PEER-REVIEWED PUBLICATIONS OF JCAP WORK ON DISCOVERY OF MATERIALS, MECHANISMS, AND UNDERSTANDING OF INTERFACES AND TEST-BEDS

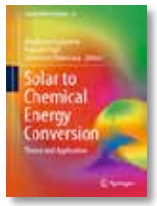
300+ cumulative publications (total): 113 publications in 2015
~10 papers/month (2016 calendar year)
31% in journals with impact factor > 10

IP DISCLOSURES

38 provisional applications
18 nonprovisional applications
9 PCT applications

CONFERENCE PROCEEDINGS, TECHNICAL REPORTS, CONFERENCE PRESENTATIONS

ACS, MRS, ECS, GC, etc.
~ 30 presentations and invited talks/quarter



BOOK CHAPTERS AND REVIEW ARTICLES

14 review articles
5 book chapters

DEVELOPED CAPABILITIES (E.G., HARDWARE, SOFTWARE, FABRICATION PROCESSES)

high throughput experimentation and data
electrochemical cells
test-bed modules and testing

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

Workforce Development and Training: Academia and National Labs

JCAP has more than 20 alumni who are tenure track faculty in the US, Asian, and European Universities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UC Santa Cruz


J. Velazquez
UC Davis


J. Goodpaster
U. Minnesota


J. Panetier
Binghamton U.


M.-J. Cheng
Tsinghua U.


R. Sundararaman
RPI


J. Yang
UC Irvine


C. McCrory
U. Michigan

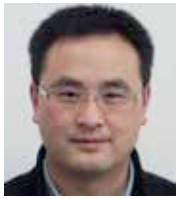

M. McDowell
Georg. Tech.


S. Hu
Yale


R. Buonsanti
EPFL


J. Mendoza-Cortes
Fl. State U.


O. Luca
U. Colorado


S. Chen
E. Ch. Normal U.


S. Haussener
EPFL

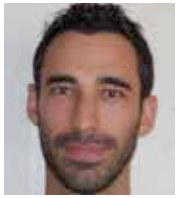

M. H. Lee
Kyung Hee U.


Y. Li
Shanghai J. T. U.


N. Lynd
U. Texas, Austin


K. Perrine
Michigan Tech.


J. Sanabria
U. Costa Rica


G. Sudre
U. Claude Bernard

Many JCAP Ph.D. alumni continue with postdoctoral appointments at leading national and international universities and research staff appointments at the National Labs.

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