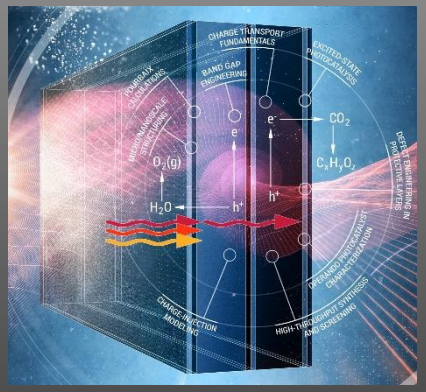
Artificial Photosynthesis—The Selective CO_2 Reduction Challenge



Harry Atwater

Joint Center for Artificial Photosynthesis
ISF-2

July 8th 2017

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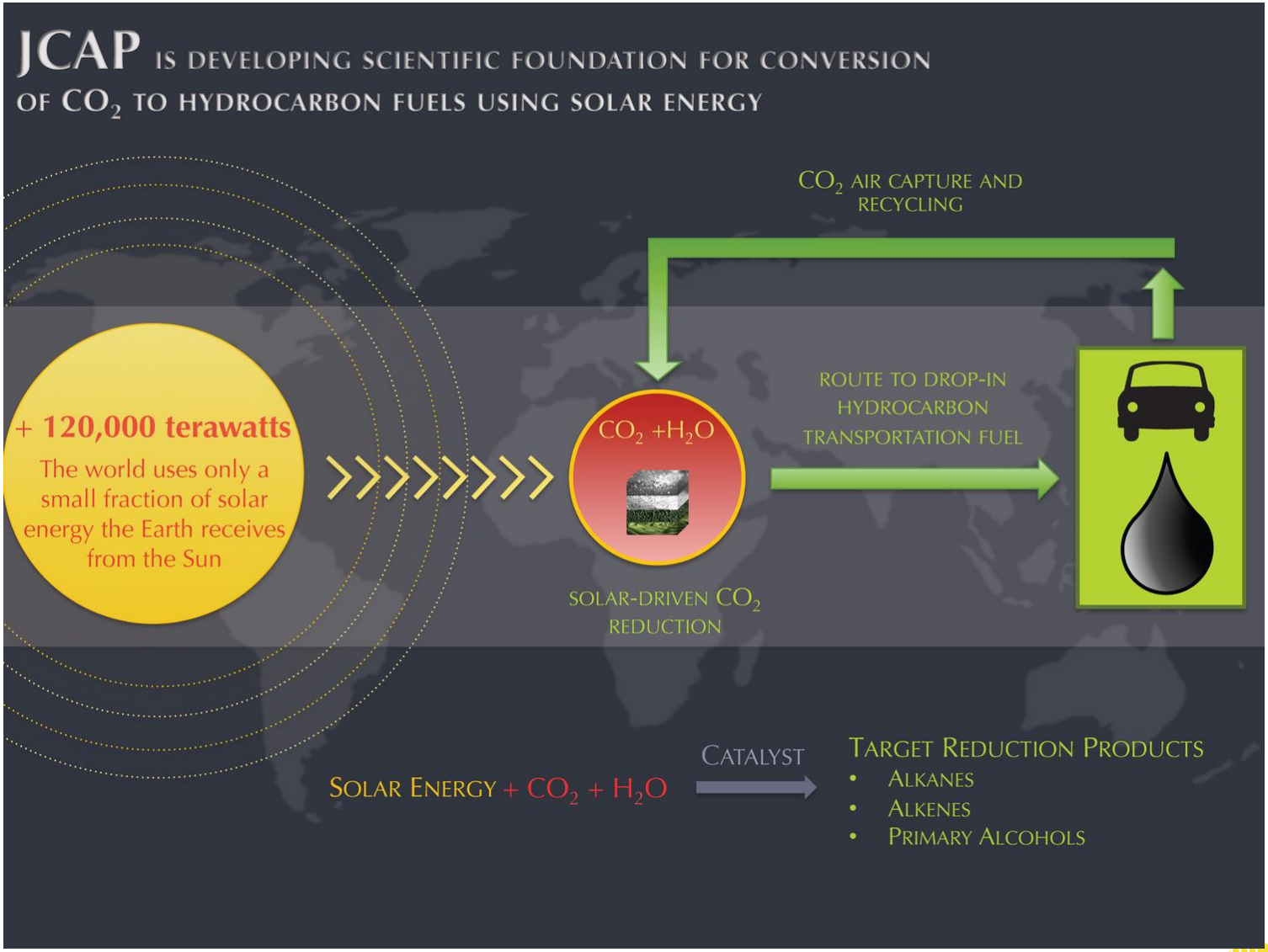
JCAP MISSION



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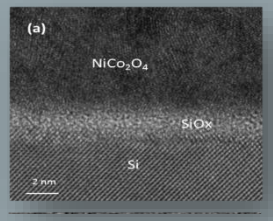
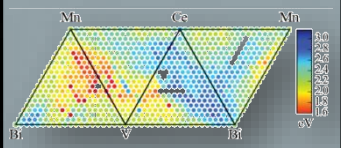
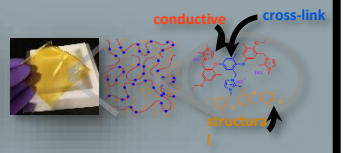
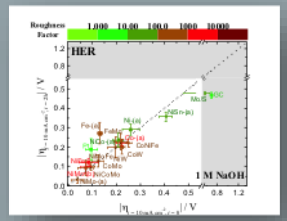
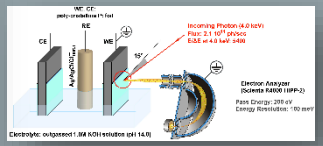
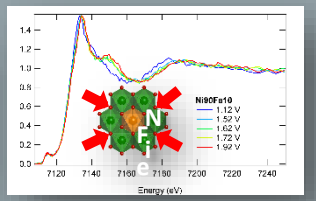
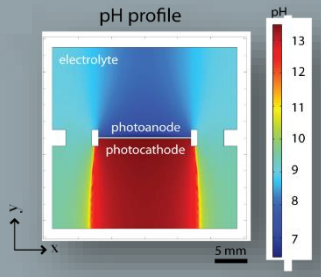
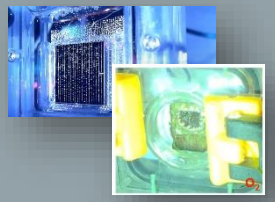
JCAP's first phase: solar fuels for water-splitting

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

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JCAP: Solar Fuels Generators

Hydrogen evolution reaction (HER)

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

Oxygen evolution reaction (OER)

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

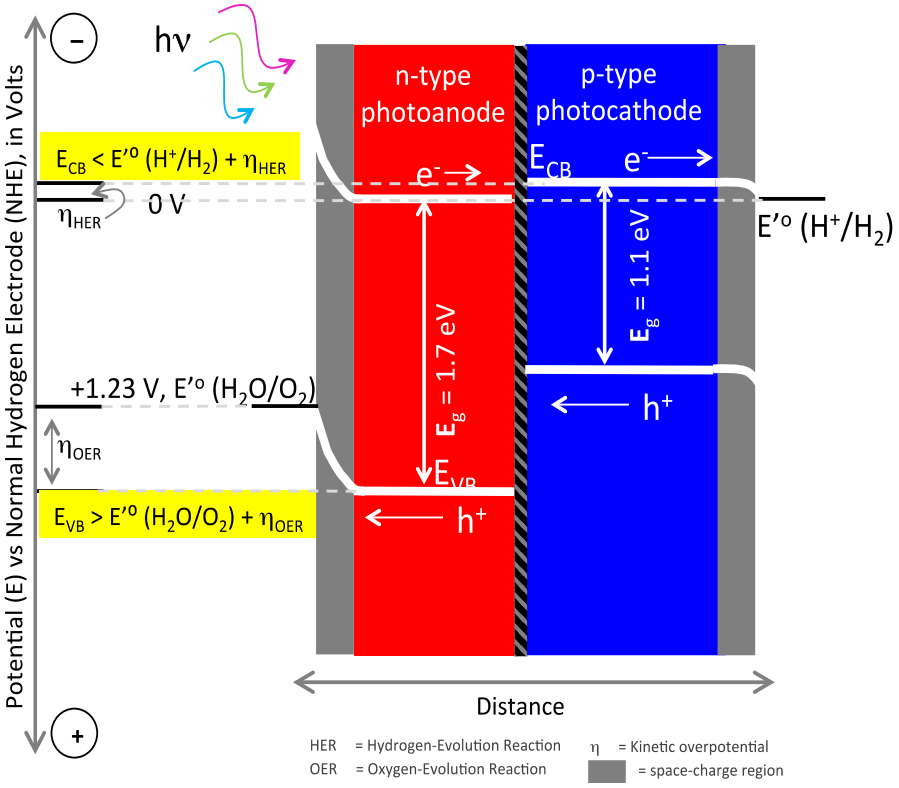
CO_2 reduction reaction (CO_2RR)

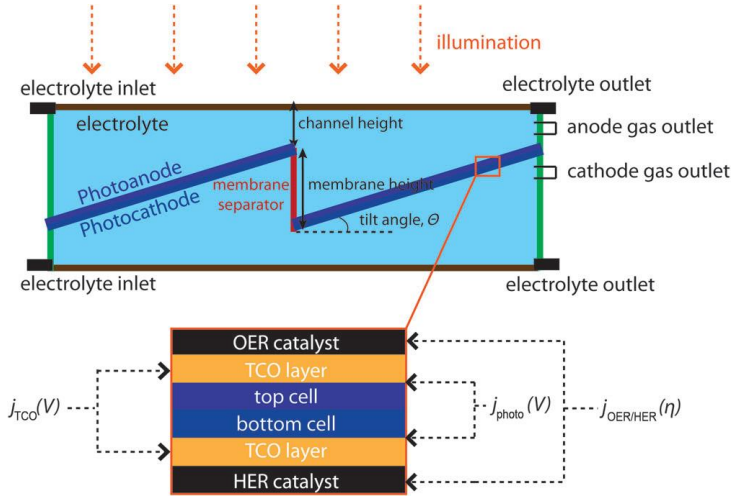
$CO_2 + H_2O \longrightarrow HCOOH + \frac{1}{2}O_2$

$CO_2 + H_2O \longrightarrow HCHO + O_2$

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

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





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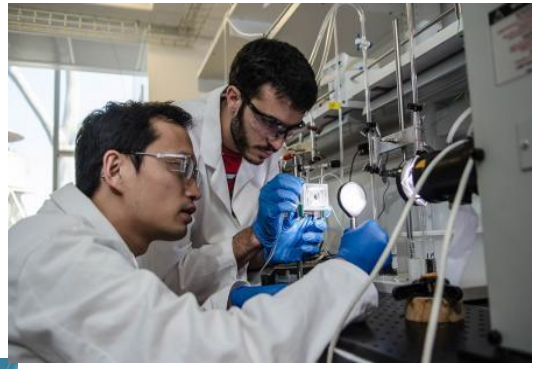
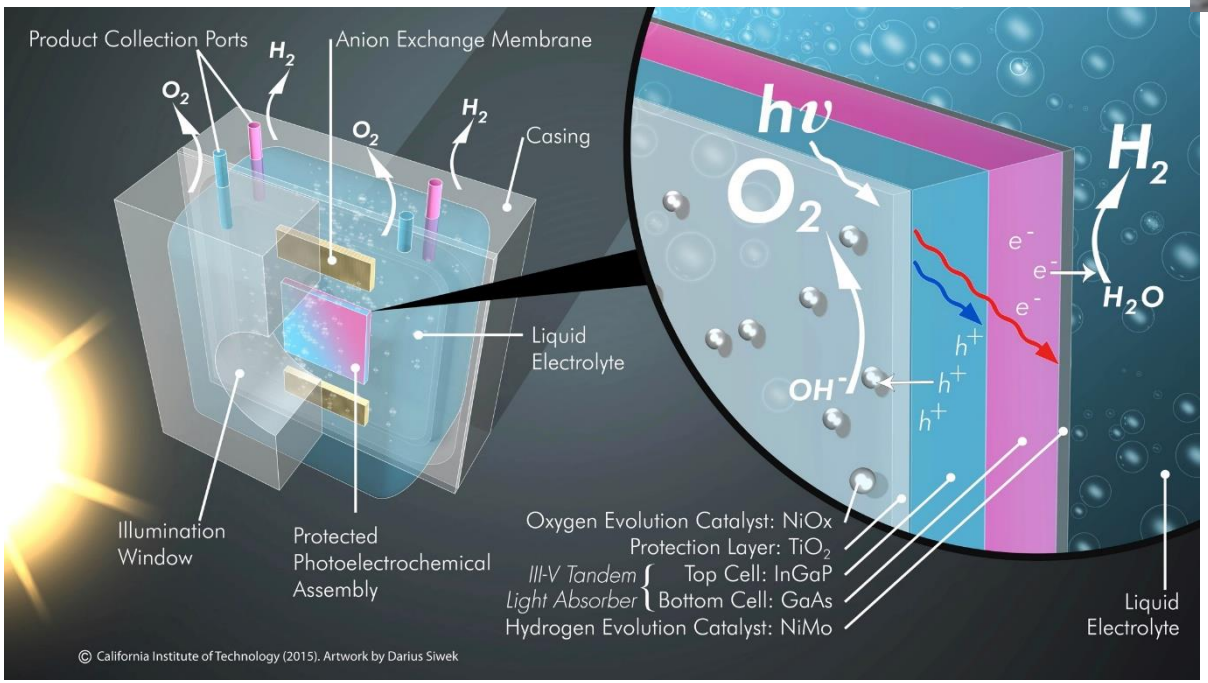
JCAP'S FIRST PHASE: SOLAR FUELS FOR WATER-SPLITTING

Oxide-Protected Photoanode Device:

A >10% efficient, stable, unassisted solar-driven water-splitting in a monolithic photoelectrochemical system integrating

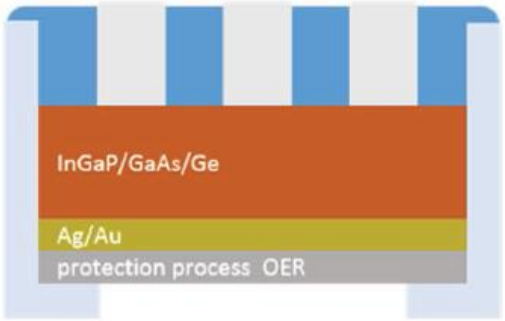
- protected tandem junction photoabsorbers,
- earth-abundant electrocatalysts, and
- anion exchange membranes.





CX Xiang and Erik Verlage assemble a monolithically integrated III-V device, protected by a TiO_2 stabilization layer, which performs unassisted solar water splitting with hydrogen fuel and oxygen

Catalytic Grid Photocathode Device:



E. Verlage, S. Hu, R. Liu, R. J. R. Jones, K. Sun, C. Xiang, N. S. Lewis, Harry A. Atwater, *Energy Environ. Sci.*, 2015.
K.A. Walczak, G.Segev, D.M. Larson, J.W. Beeman, F.A. Houle, and I.D. Sharp, *Adv. Energy Mater.*, 2017.

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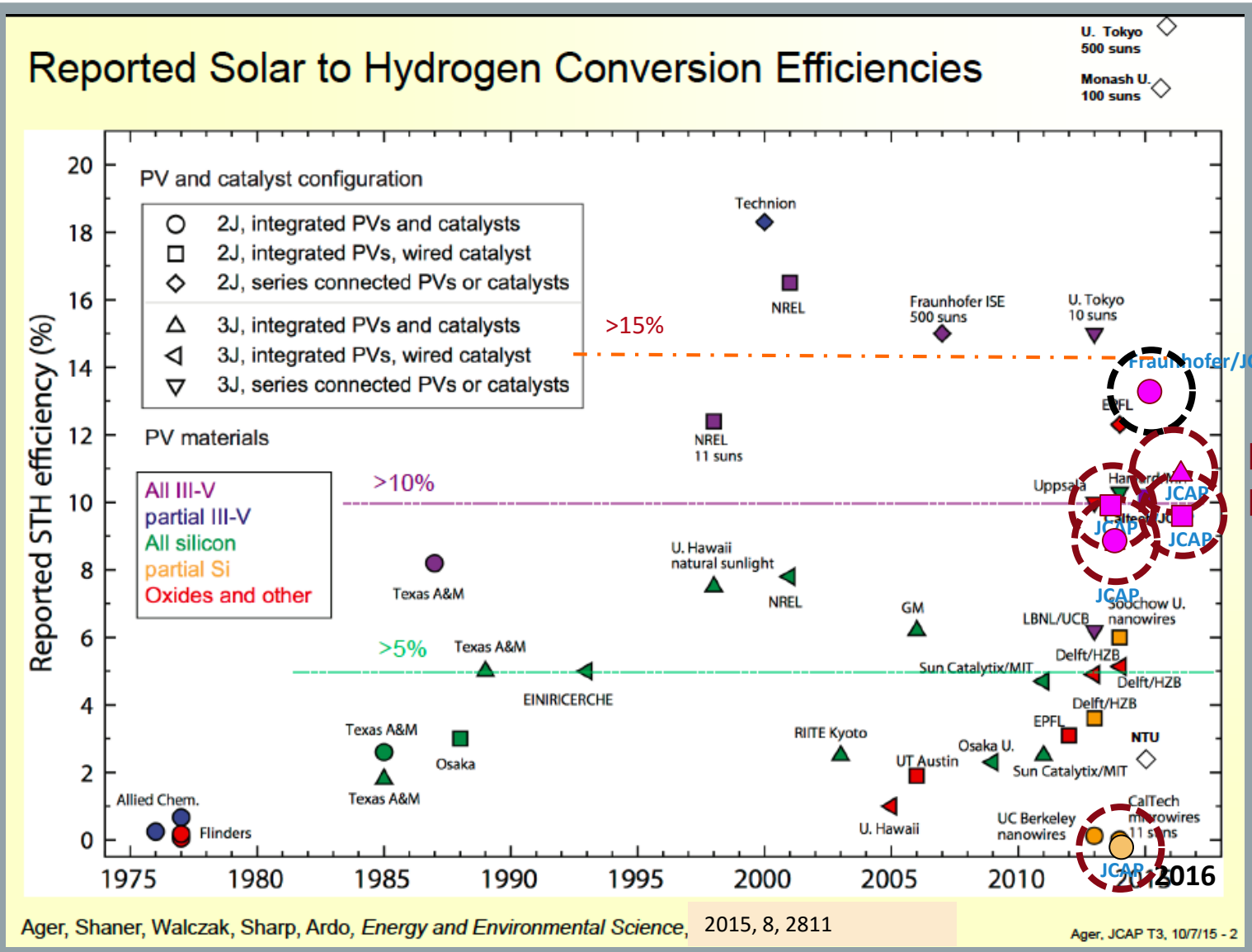
STATE OF THE ART FOR PEC HYDROGEN GENERATION – 2015



With membranes

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

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PEC HYDROGEN GENERATION PERFORMANCE LIMITS

$$V_{PEC}(j) = \sum_i V_{PV_i}(j) - V_{cat,a}(j) - V_{cat,c}(j) - V_{series}(j) \geq E_{rxn}$$

PV Voltage: $V_{PV}(j) = \frac{n_d k_B T}{q} \ln\left(\frac{j}{j_0} + 1\right)$

Catalyst Voltage: $V_{cat}(j) = \frac{RT}{\alpha n_e F} \sinh^{-1}\left(\frac{j}{2 j_{0,cat}}\right)$

Device operating point: $V_{op}(j_{op}) = E_{rxn}$

Water splitting PEC efficiency: $\eta_{PEC} = \frac{j_{op} E_{rxn} f_{FE}}{P_{in}}$

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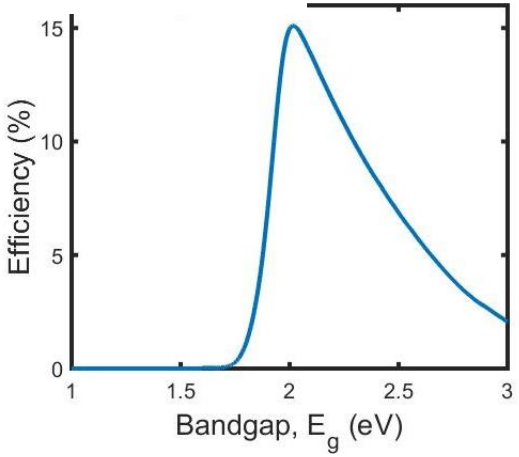
REALISTIC PERFORMANCE LIMITS FOR PEC HYDROGEN GENERATION

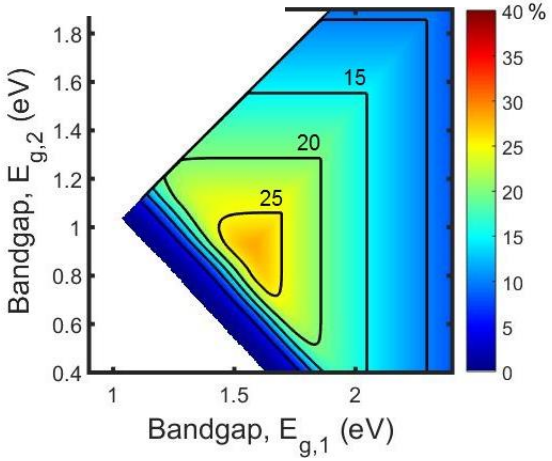
- Absorption of 90% of incident photons above the bandgap of the semiconductor
- An external radiative efficiency (ERE) of 3% (typical III-V)
- Catalytic exchange current densities of 1 $mA \cdot cm^{-2}$ (HER)and 10^{-3} $mA \cdot cm^{-2}$ (OER); consistent with the best reported values for Pt and IrO_2
- Diode ideality factor, n_d, of 1.
- The electrochemical potential for water-splitting at standard conditions, E_{rxn}=1.23 V.
- Unity Faradaic efficiency.

Single Junction:



η=15.1%, E_g=2.05eV

Dual Junction:



η=28.3%, E_g=1.59, 0.92eV

Fountaine, Lewerenz, Atwater Nature Communications (2016)

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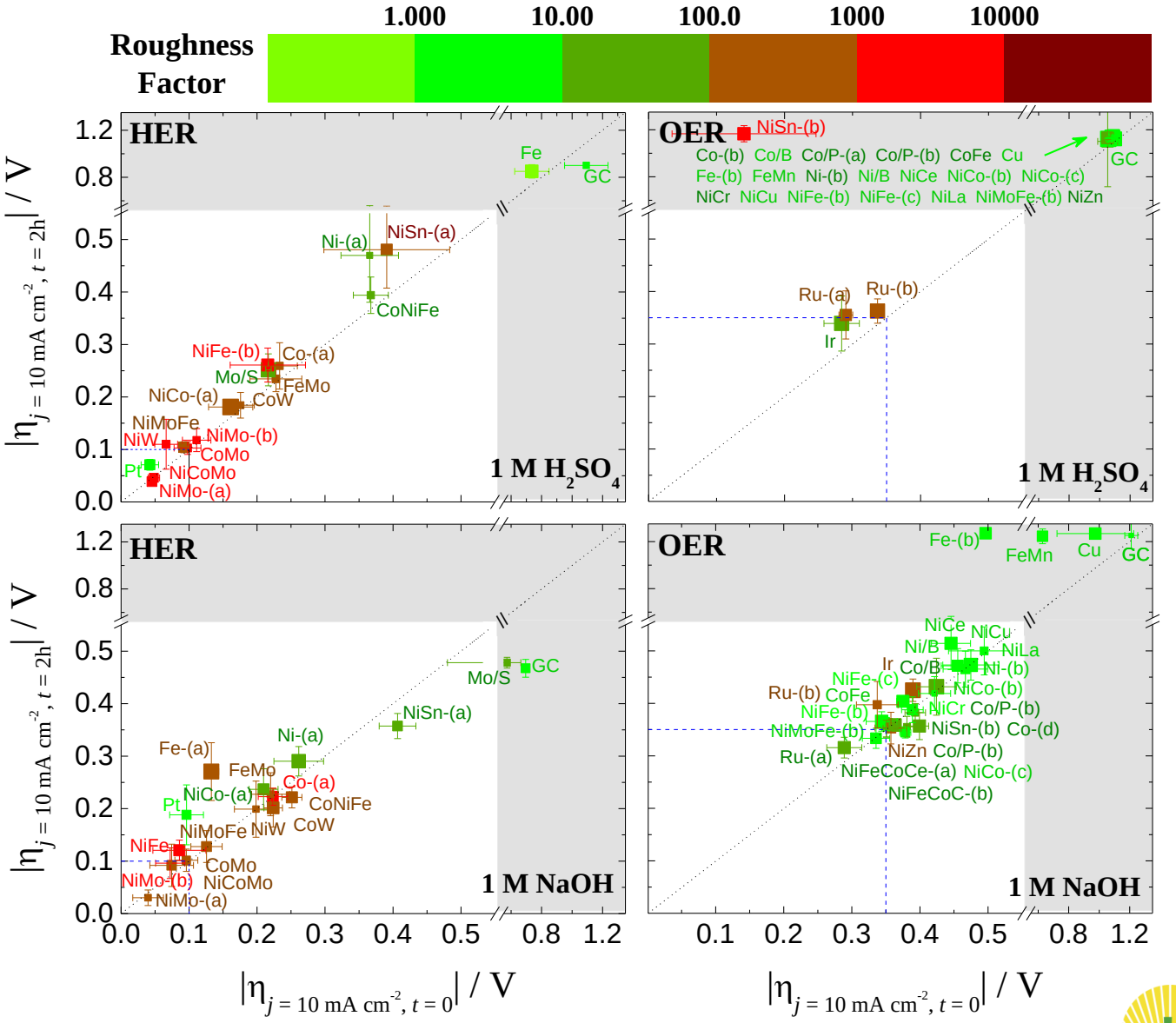
MATERIALS SELECTION: CATALYST BENCHMARKING



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

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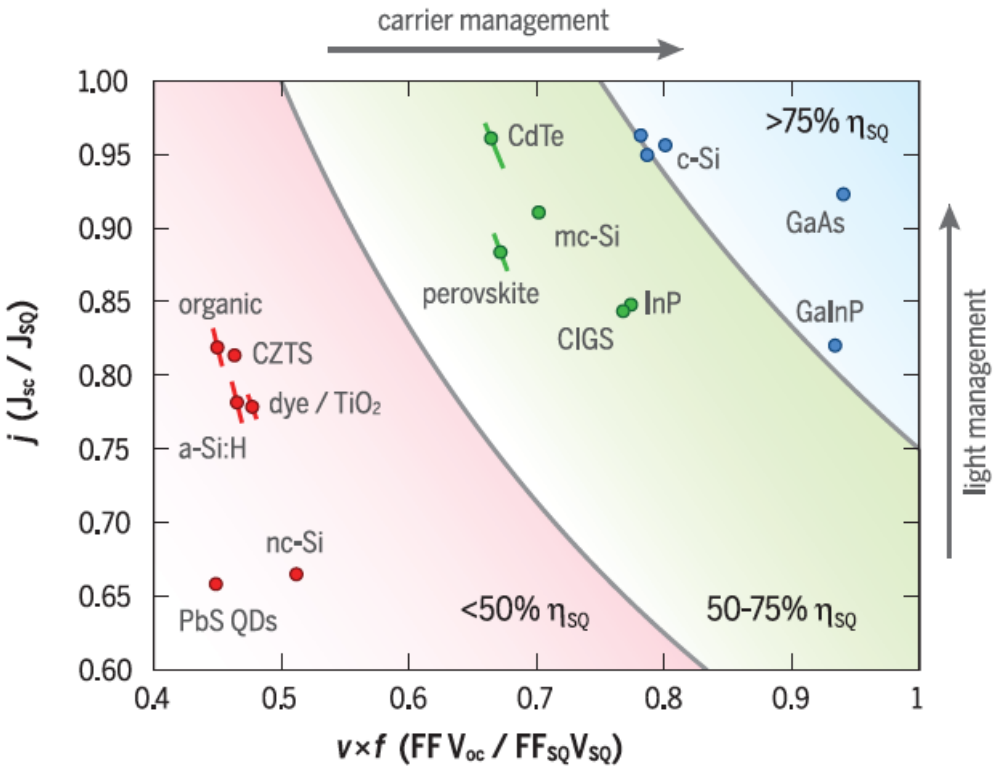
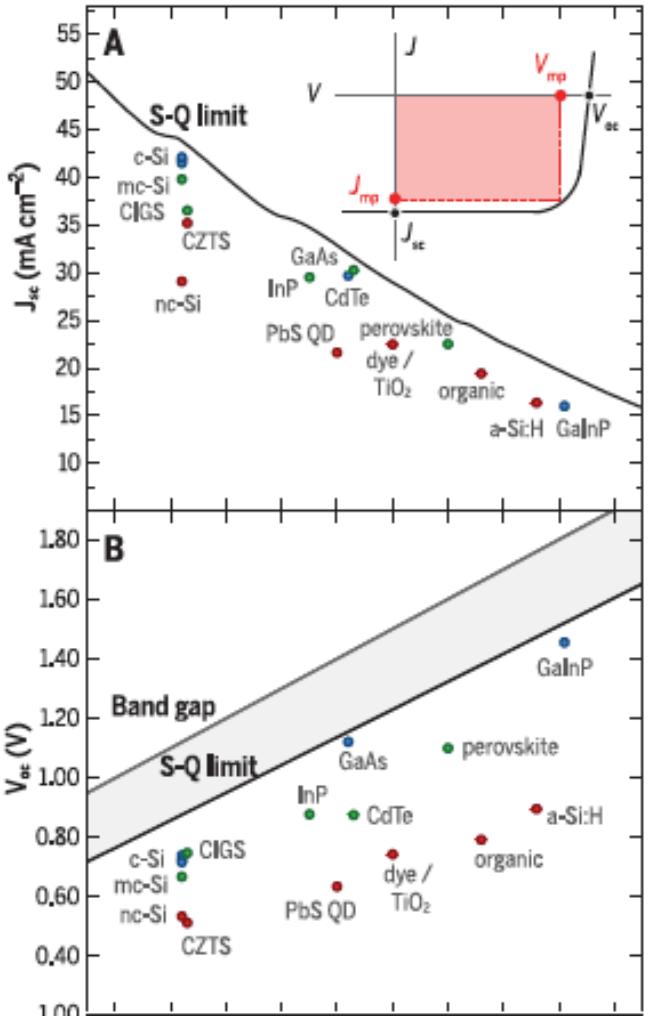
MATERIALS SELECTION: PHOTOELECTRODES





A.Polman, M. Knight, E.C. Garnett, B. Erhler and W.C. Sinke, Science (2016)

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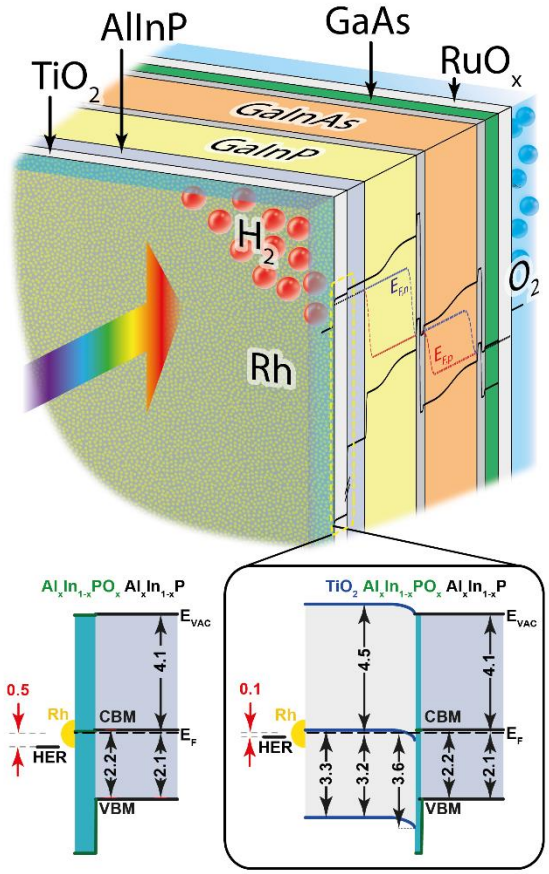
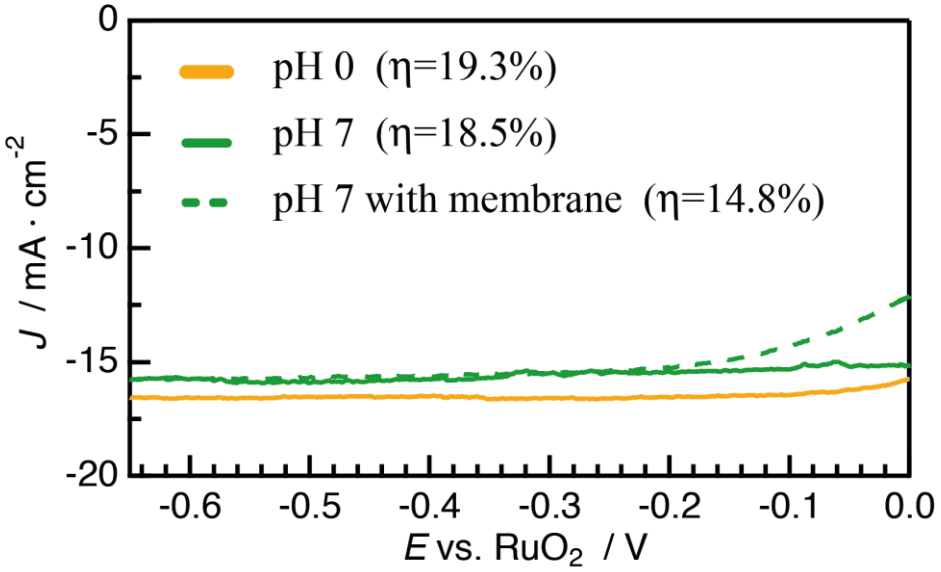
19.3% STH EFFICIENCY INTEGRATED PEC DEVICE



GaInP with E_g = 1.78 eV; GaInAs with E_g = 1.26 eV



W.H. Cheng, M.H Richter, M.M May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H.A. Atwater, and H.J. Lewerenz, *ArXiv 2017*

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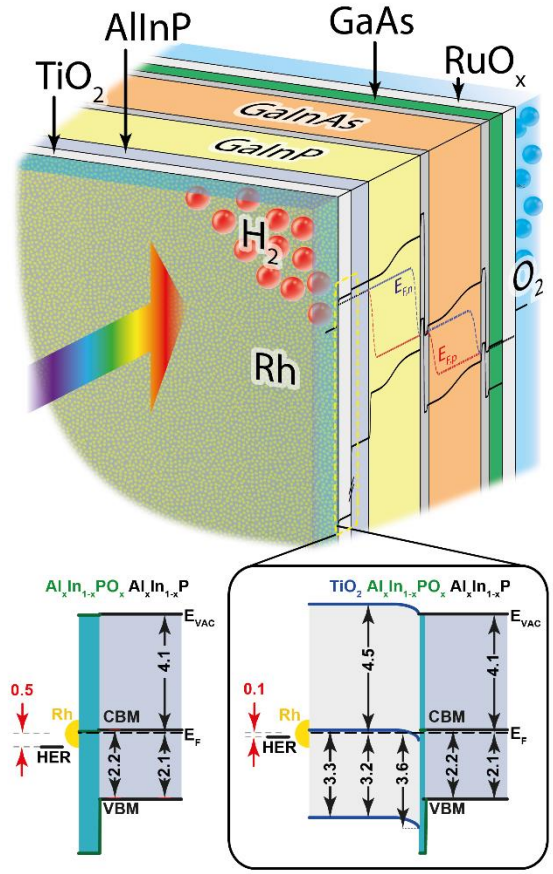
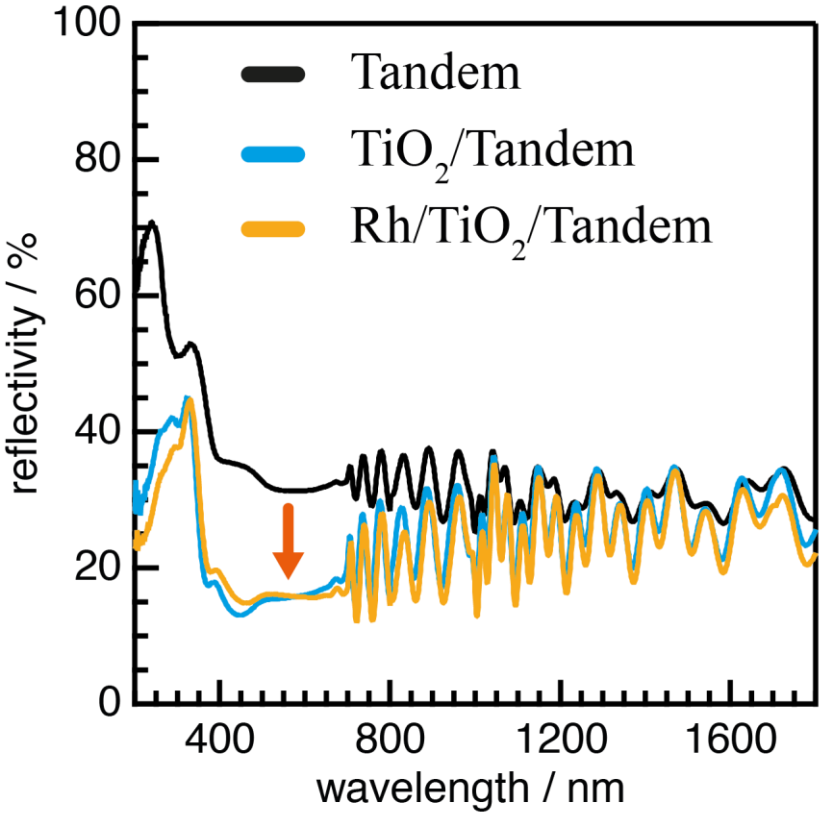
19.3% STH EFFICIENCY INTEGRATED PEC DEVICE





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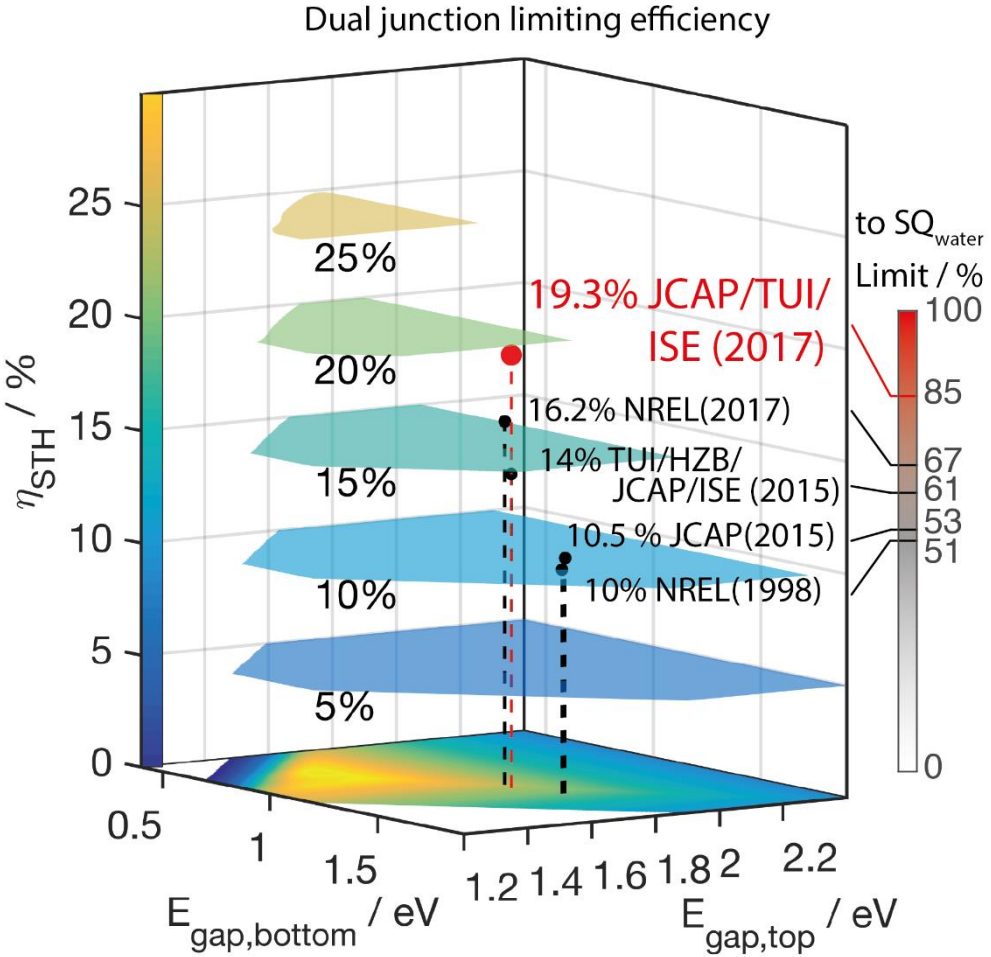
RAPID ADVANCES IN EFFICIENCY OF INTEGRATED STH PECS



W.H. Cheng, M.H Richter, M.M May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H.A. Atwater, and H.J. Lewerenz, *ArXiv 2017*

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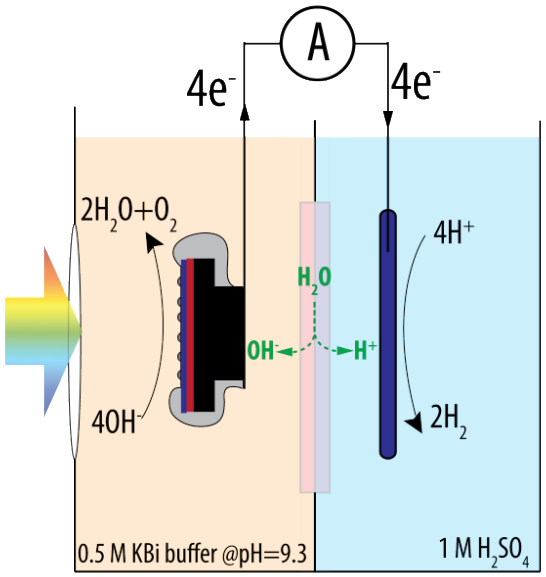
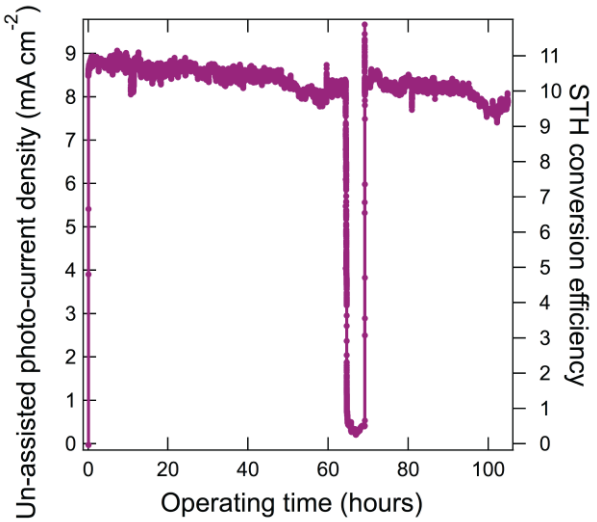
UNASSISTED WATER SPLITTING WITH BIPOLAR MEMBRANE AT 10% ENERGY CONVERSION EFFICIENCY

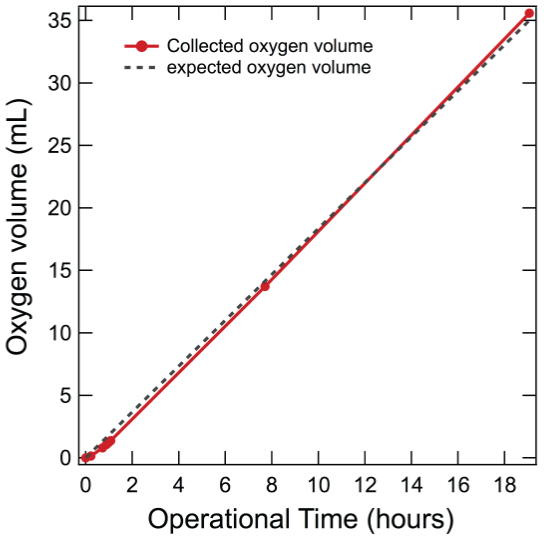
Schematic illustration of a bipolar membrane device



Un-assisted solar-driven water-splitting performance



Product gas collection performance



All earth-abundant electrocatalysts: NiO_x for OER in the KBi buffer and CoP_x for HER in 1.0 M H_2SO_4.

- > 1.0 cm^2, > 10% STH conversion efficiency, >100 hour stability was achieved using a tandem photoabsorber in a cell configuration that incorporates a bipolar membrane.
- The acid stable electrocatalyst, CoP, was successfully integrated into the cell.

Bipolar membrane:

- near-unity transference numbers for proton and hydroxide transport at relatively high operational current densities
- ~400-500 mV voltage loss due to ohmic resistance, water dissociation and water transport processes, further improvements can be made by incorporating water dissociation catalysts at the interface.

K. Sun, R. Liu, E. Verlage, N. S. Lewis, C. Xiang, E&ES (2016)

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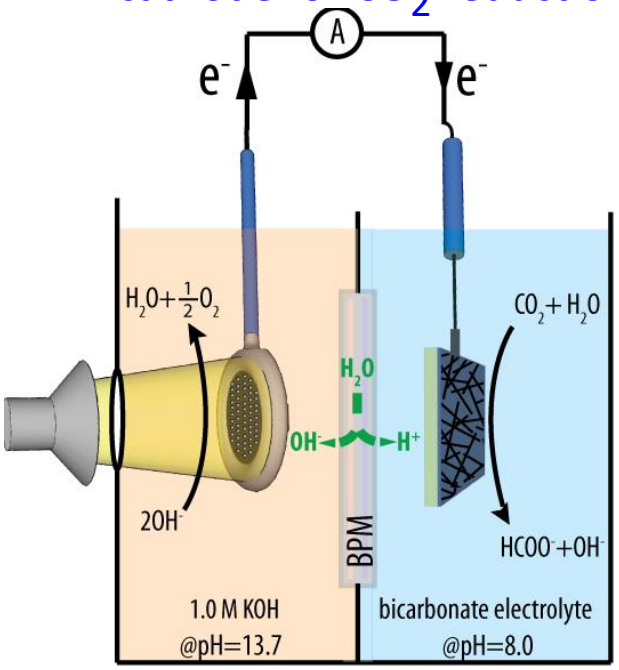
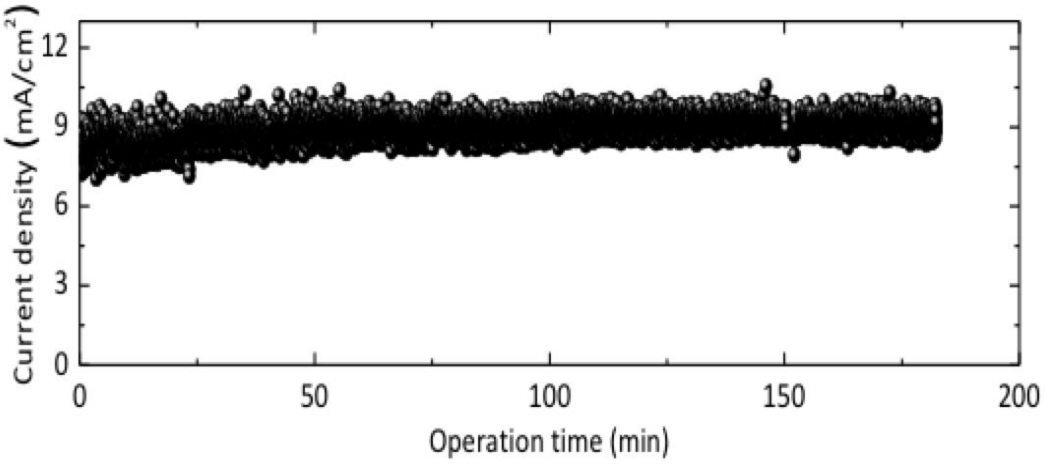
SOLAR-DRIVEN REDUCTION OF CO_2 TO FORMATE AT 10% ENERGY CONVERSION EFFICIENCY

Schematic illustration of the series connected photoanode and dark cathode for CO_2 reduction to formate



Best combination of catholyte and anolyte to achieve the lowest total overpotential for the device

Un-assisted solar to formate conversion efficiency at 10% under 1.0 Sun illumination



Minimal product crossovers even at high formate concentration

- **Photoanode: InGaP/GaAs/TiO_2/NiO_x at pH=14 electrolyte previously used for solar water-splitting.**
- **Dark cathode: Pd/C nanoparticles on Ti mesh in pH=8 bicarbonate solution achieved ≤ 100 mV overpotential and >94% Faradaic efficiency at 10 mA cm^{-2}.**
- **Bipolar membrane sustained the steady-state pH differential and minimized the product crossovers.**

CX Xiang, et.al. ACS Energy Lett., 2016, 1, pp 764–770

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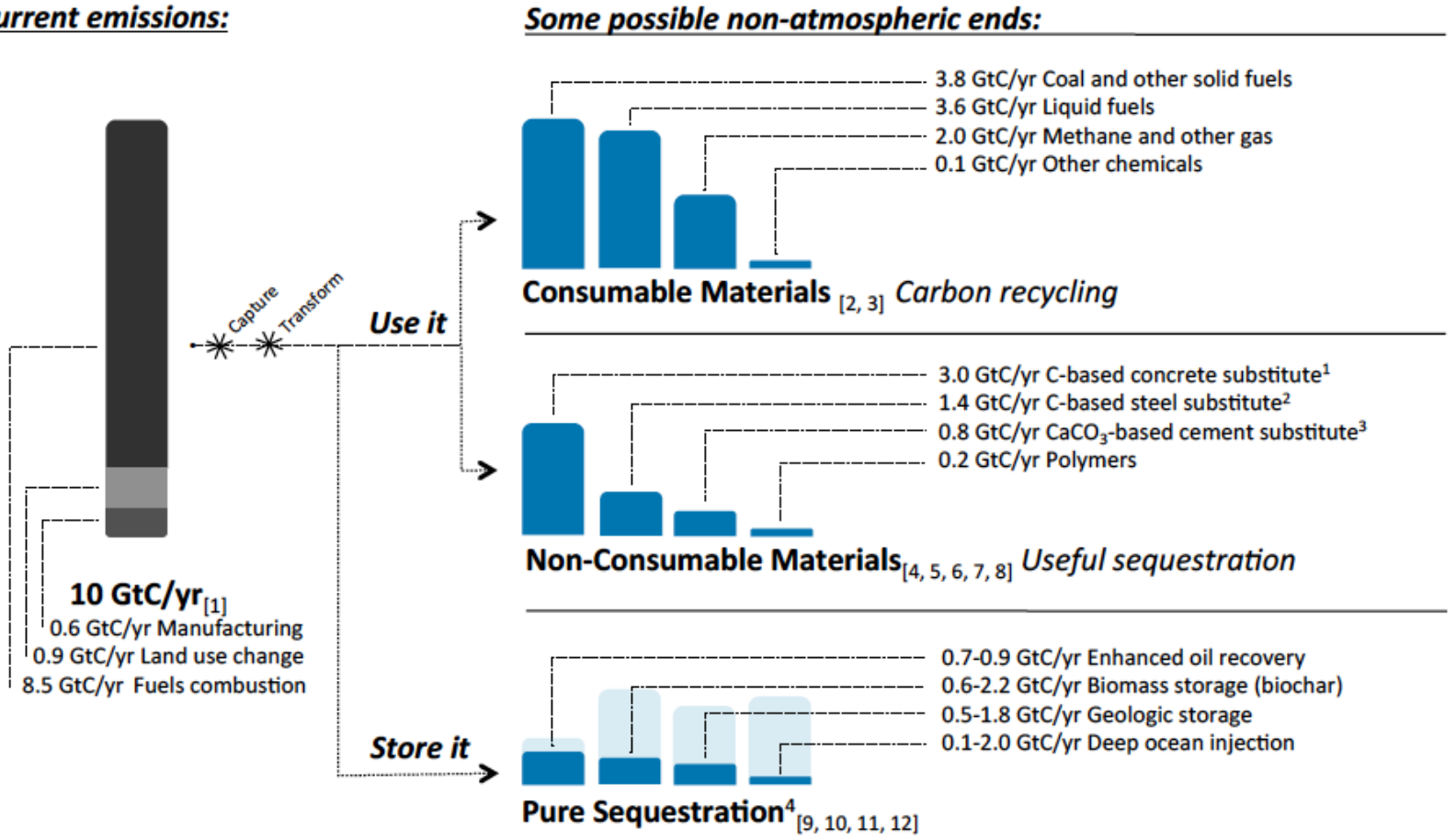
RELATIVE SCALE OF EMISSIONS AND POTENTIAL USES FOR CO_2



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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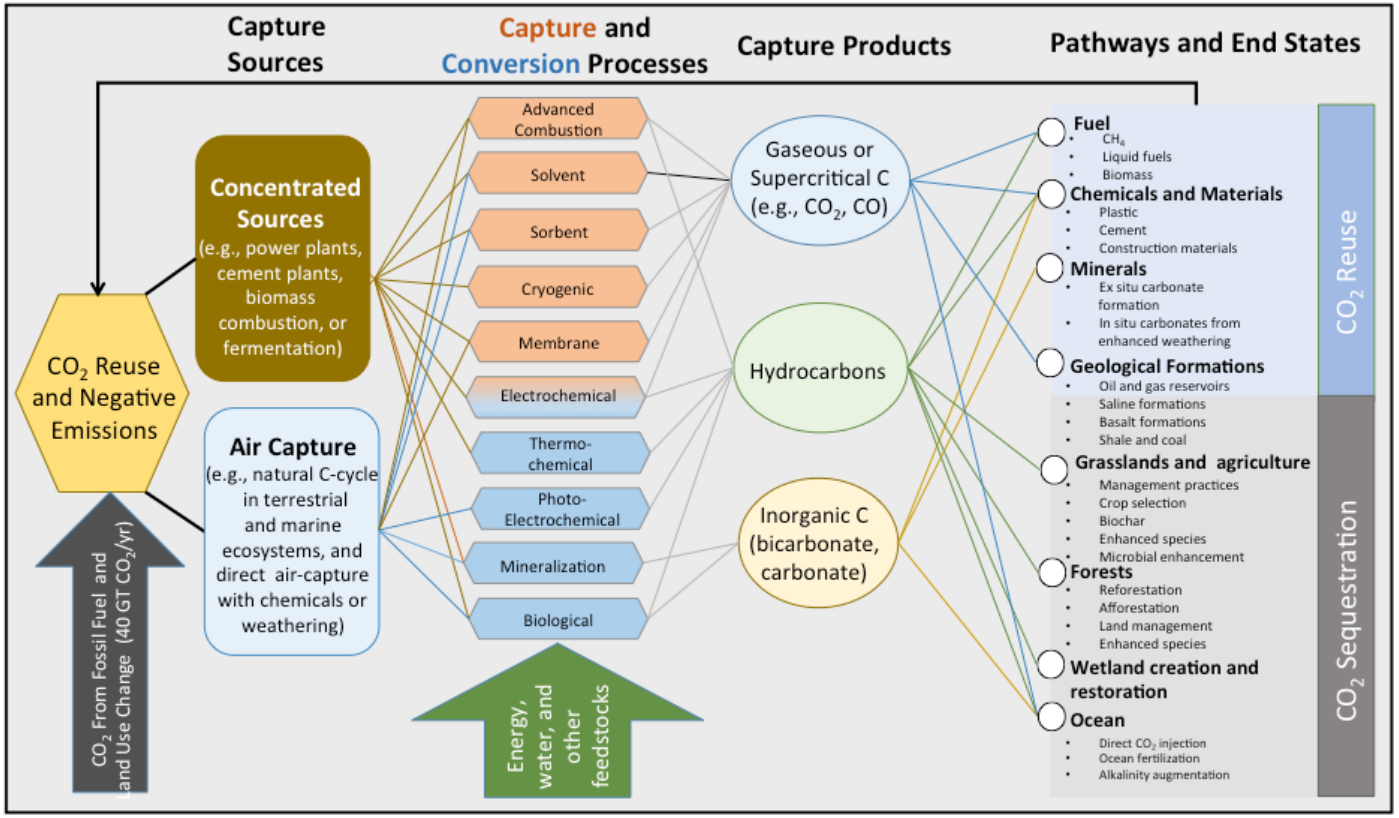
THE CO_2 UTILIZATION LANDSCAPE

- Focus on processes able to capture, reduce or sequester 1 $GtCO_2$/yr scale
- 1 of the top 5 Priorities: Synthetic Transformations of CO_2
- Recommendations:
  - Reduce the cost of carbon-free/neutral energy in the form of heat/electricity
  - Focus on fundamentals of electrocatalysis and photoelectrocatalysis
  - Identify catalysts made of abundant elements that reduce the overpotentials for CO2RR and OER at high reaction rates.



Secretary of Energy Advisory Board Report, 12/13/2016

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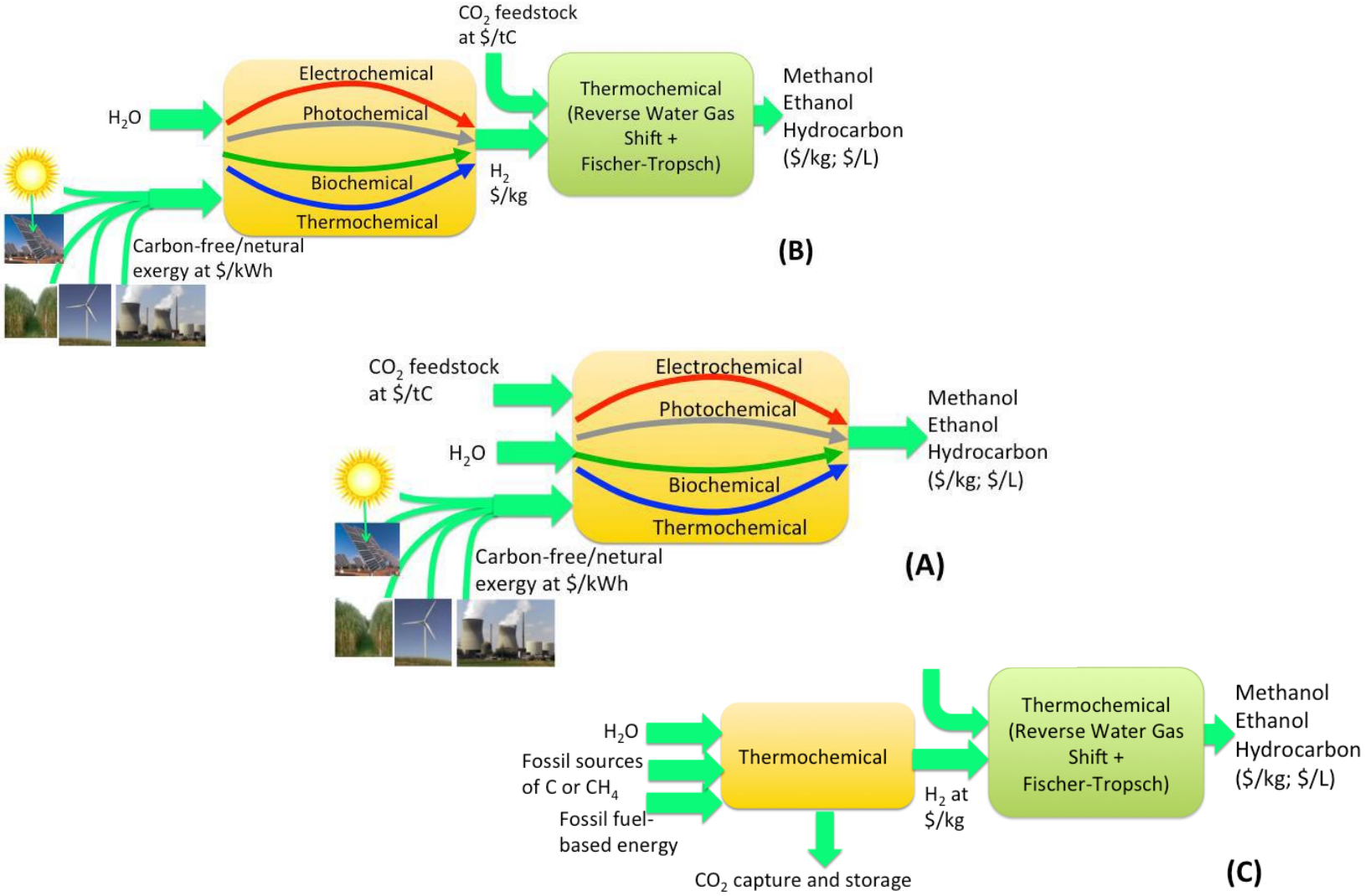
THE CO_2 UTILIZATION LANDSCAPE



Secretary of Energy Advisory Board Report, 12/13/2016

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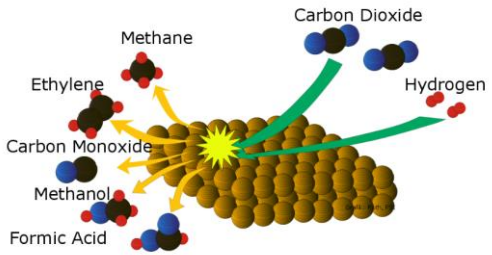
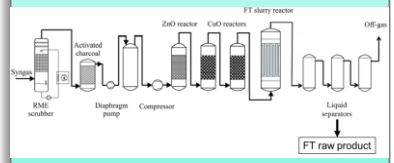
ROUTES TO FUELS FROM CO_2: COMPARING APPROACHES

Approaches to reduction of CO_2 to fuels:



Thermocatalysis



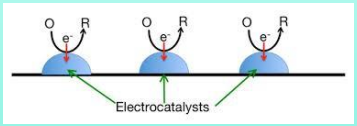
Advantages:

Mature technology; heat only required as energy input

Disadvantages:

High capital cost and intrinsically large-scale for plant; efficiency < 100%

Electrocatalysis



Room temperature operation, high FE and throughput for certain products (e.g., CO, $HCOO^-$)

Limited throughput, low selectivity and STF efficiency for alkane and alcohol fuels

Photocatalysis

Low capital cost, scalable, uses sunlight as direct energy input

Low efficiency and selectivity, product separation

Biocatalysis

Low capital cost; near room temperature; near neutral pH operation

Limited durability (bacteria die after 30 days); limited pH range, low throughput

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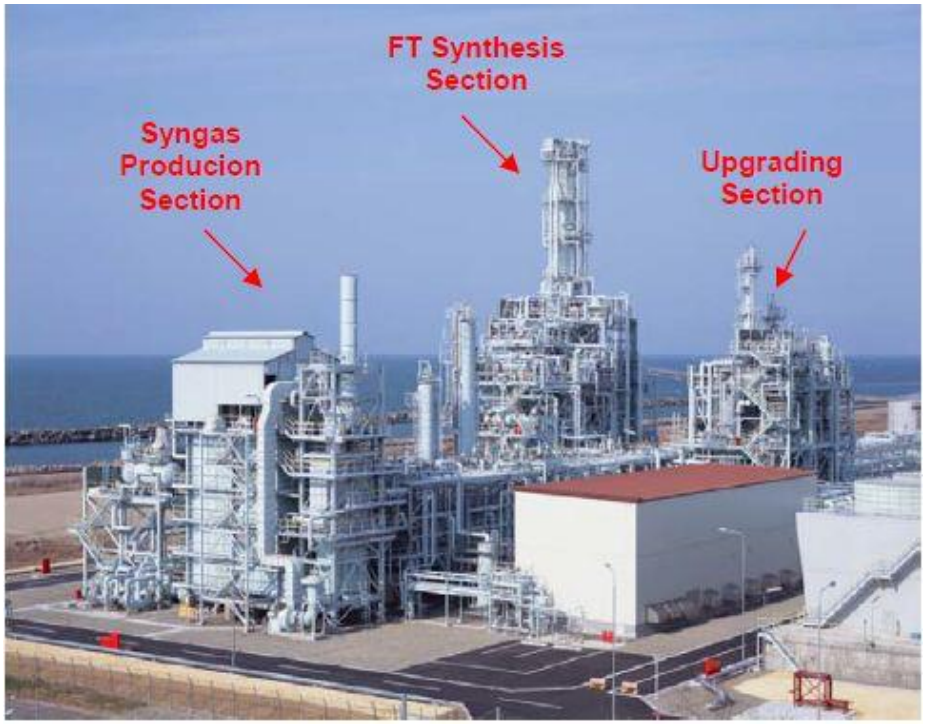
WHY NOT JUST MAKE CO AND H_2 AND USE THERMOCHEMISTRY TO DO THE REST?

- High capital cost for thermochemical plant
- Fischer-Tropsch thermal conversion efficiency 50-60%
- Requires source of hydrogen using process other than steam reforming (PEC water splitting technology development ongoing)



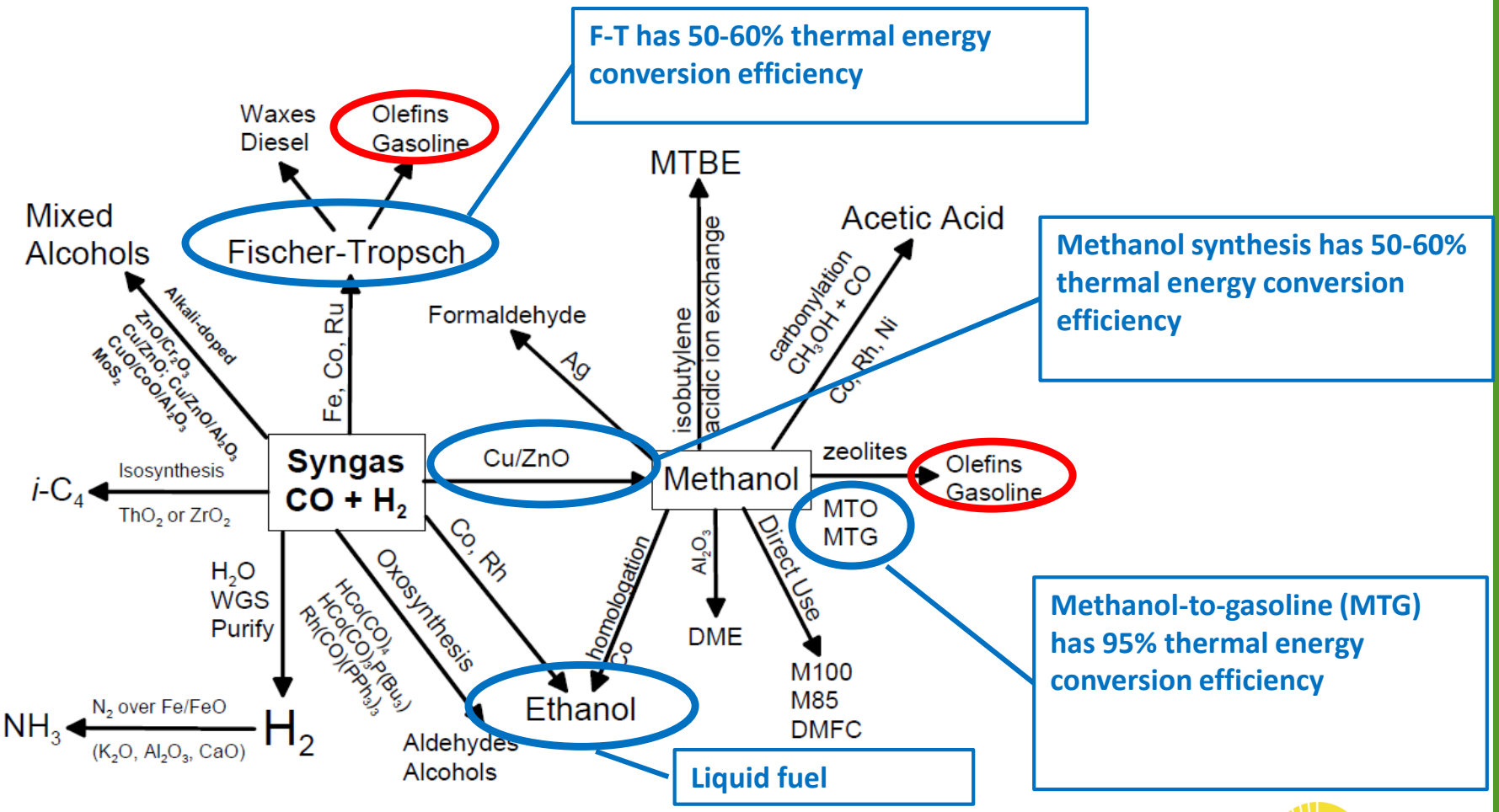
Japanese Gas to Liquids Pilot Plant, Niigata City, Japan

Production scale: 500 barrels/day

JCAP aims for direct, selective CO_2R catalysis strategies under mild P & T conditions that have potential for scalable production of fuels from sunlight with low capital cost.

CHEMICAL SYNTHESES FROM SYNGAS AND METHANOL

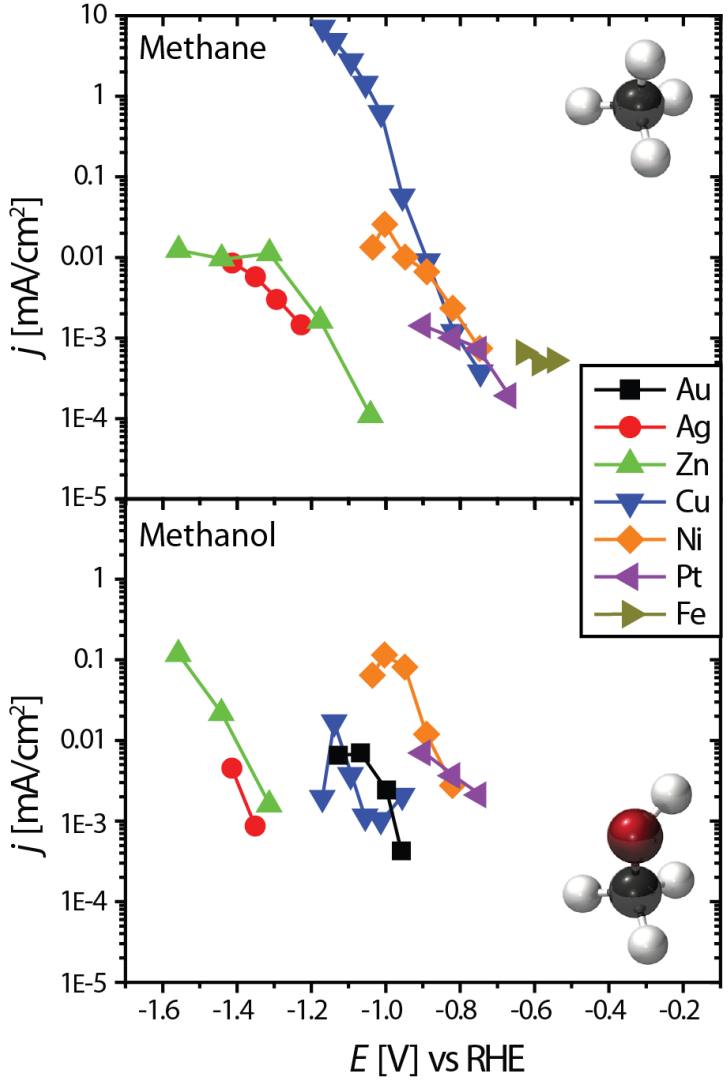
- Many chemical conversions from syngas to products, including gasoline via Fischer-Tropsch
- Many chemical conversions from methanol to products, including gasoline
- Methanol is an achievable product from CO_2R PEC



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.

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

CU IS THE BEST ELEMENTAL CATALYST – SO FAR



Selectivity is a major issue:
Competition with HER

Kuhl, Cave, Abram, Jaramillo
Energy Environ. Sci. 5, 7050 (2012).

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

POSSIBLE PATHWAYS FOR CO_2 REDUCTION CATALYSIS ON COPPER

C_1 Products: CO_2 Adsorption

$CO_2 \rightarrow$ HCOO-

$CO_2 \rightarrow$ CO, CH_4

$CO_2 \rightarrow$ CH_3OH

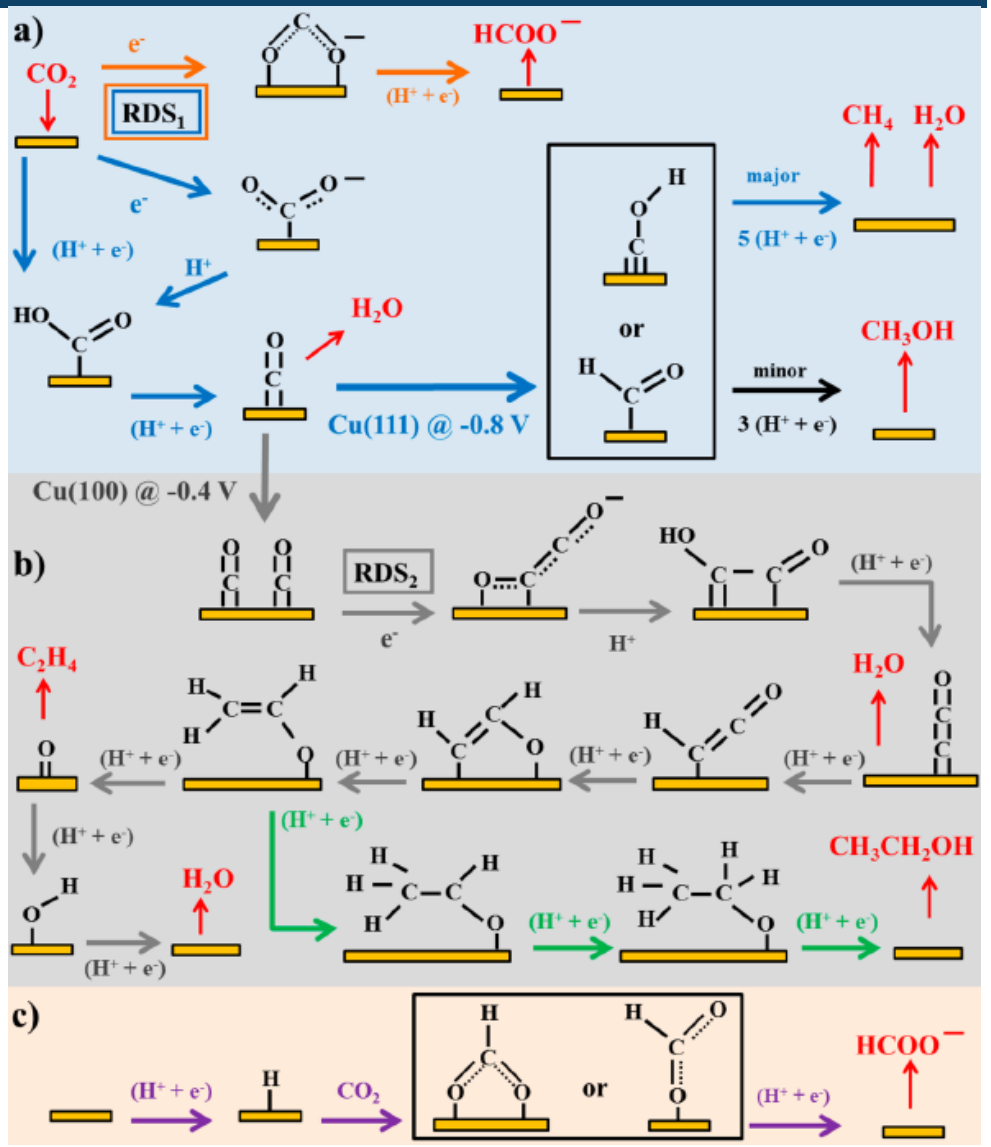
C_2 Products: CO Dimerization

$CO_2 \rightarrow$ C_2H_4

$CO_2 \rightarrow$ CH_3CH_2OH

C_1 Products: CO_2 Insertion

$CO_2 \rightarrow$ 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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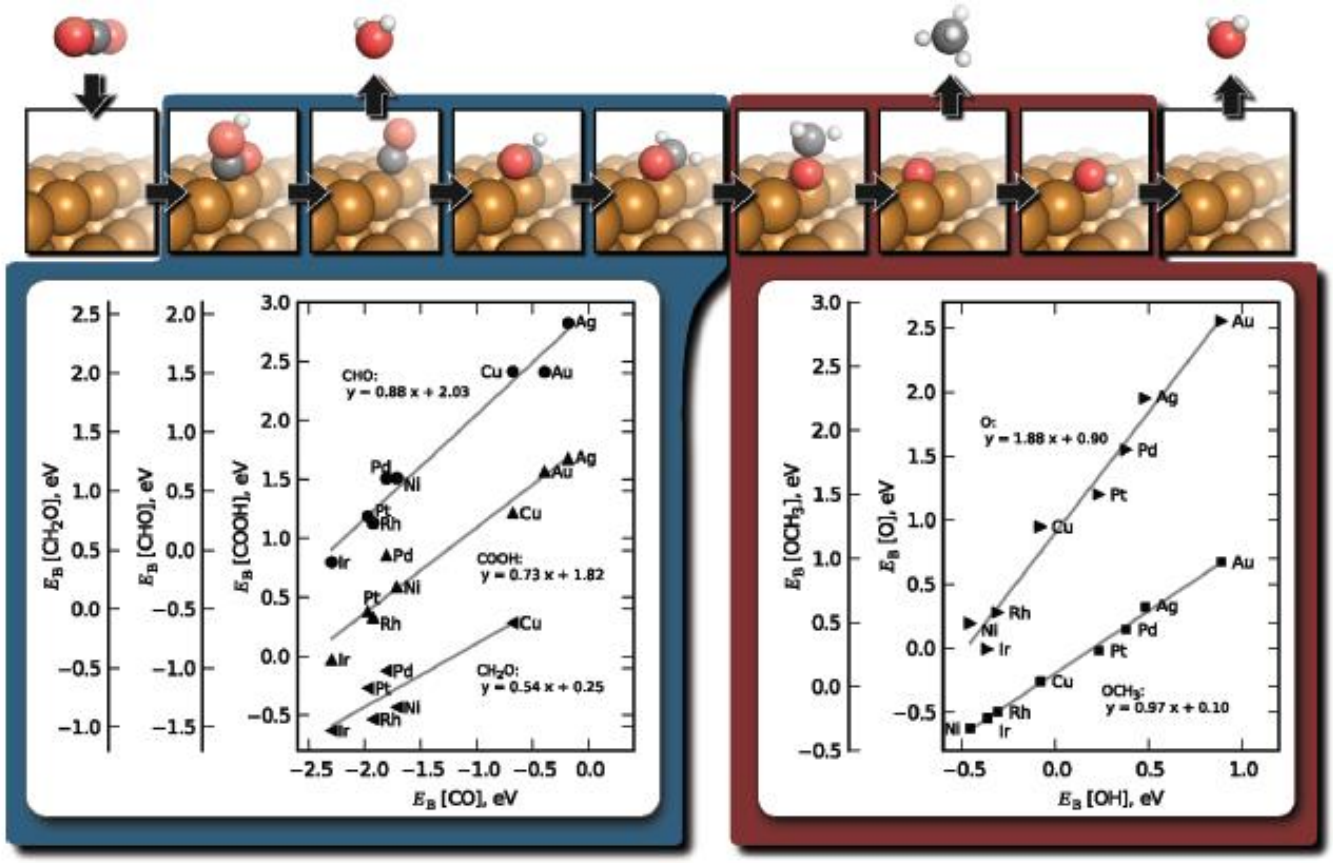
SCALING RELATIONSHIPS FOR CO_2 INTERMEDIATES ON CU



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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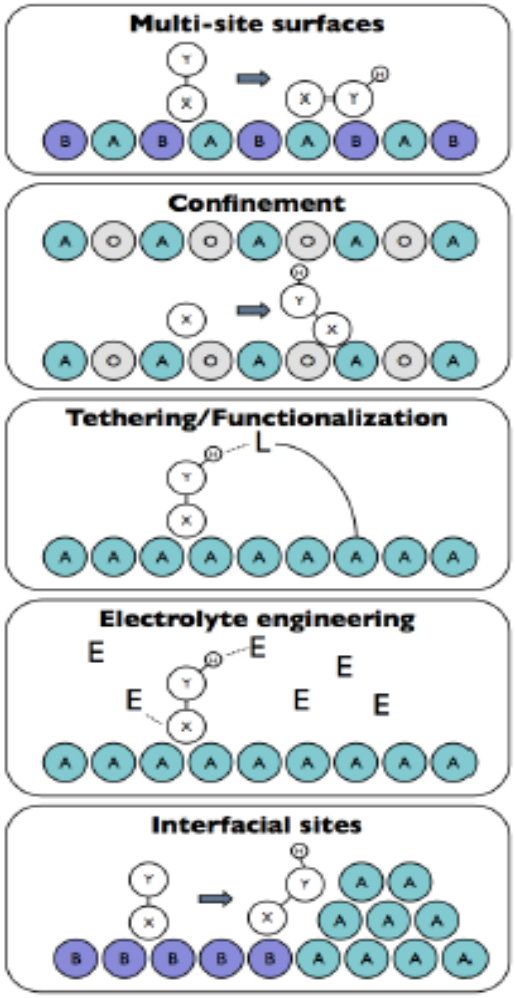
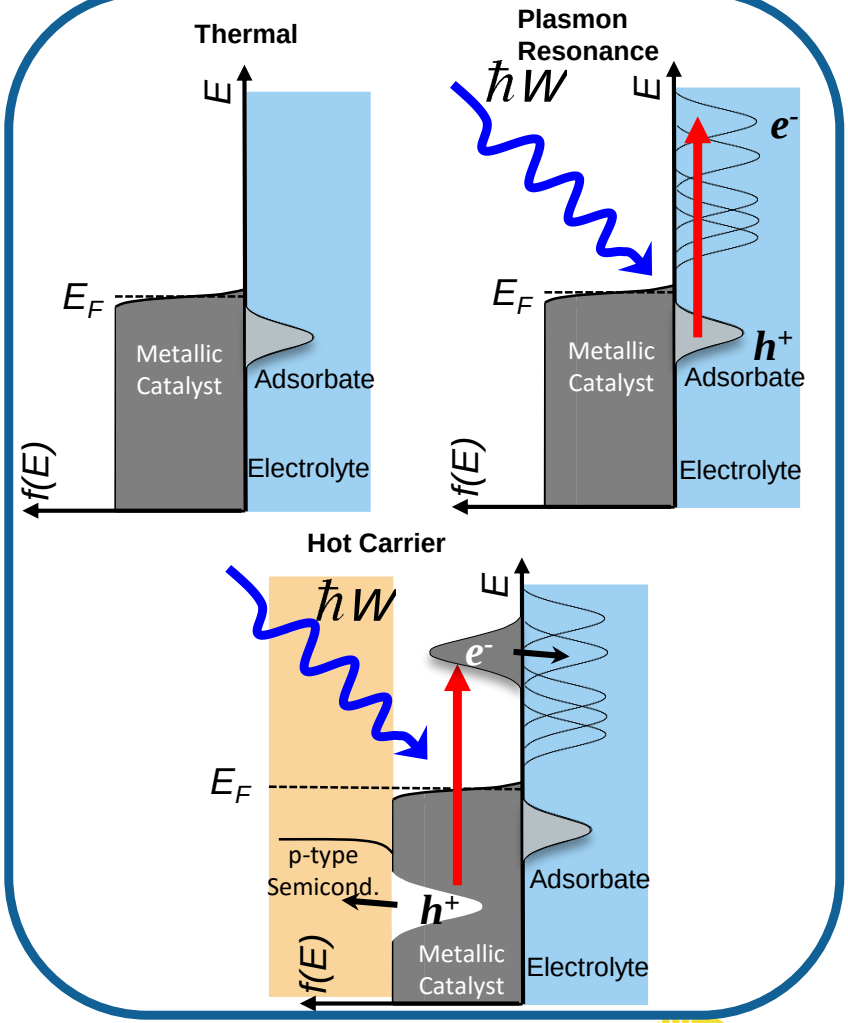
OVERCOMING SCALING RELATIONSHIPS FOR CO_2 REDUCTION

Electrocatalysis Strategies



Photocatalysis Strategies



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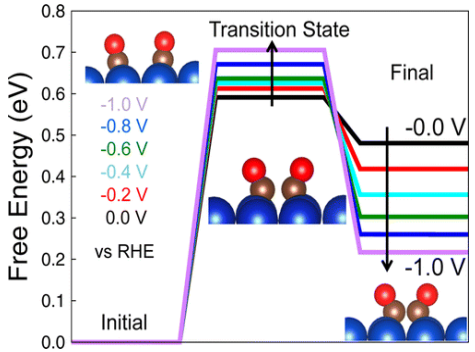
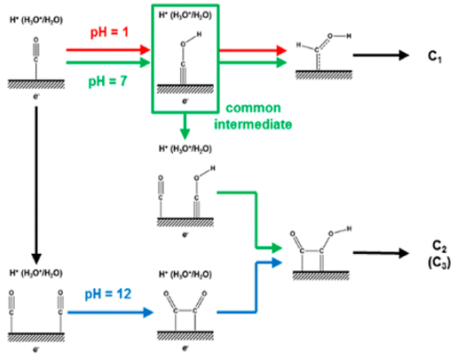
Theory Developments

Kinetics and Mechanisms

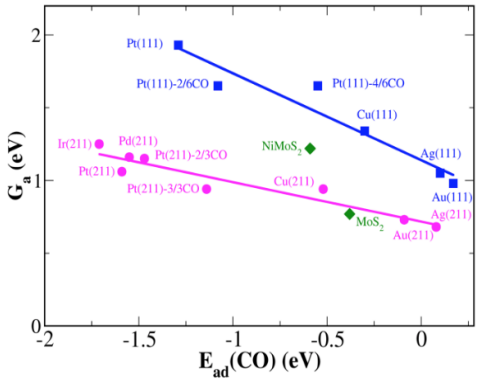


J.D. Goodpaster, A.T. Bell, and M. Head-Gordon, *J. Phys. Chem. Lett.*, **2016**, 7, 1471-1477.



W.A. Goddard *et al.*, *JACS*, **2016**, 138, 483-486.
W.A. Goddard *et al. J. Phys. Chem. Lett.*, **2015**, 6, 4767-4773.

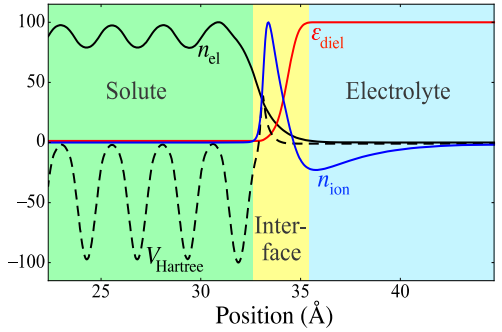
Catalyst Screening



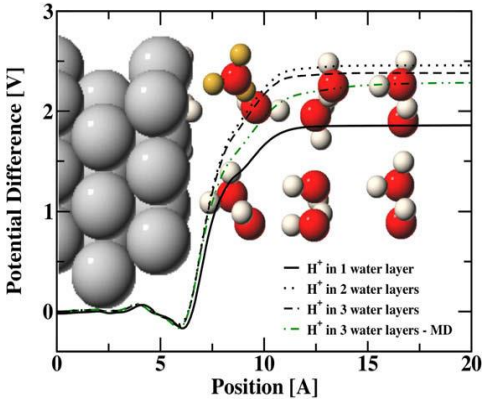
J. Xiao, X. Liu, K. Chan, and J.K. Nørskov, **2016**.
J.K. Nørskov *et al.*, *ACS Catalysis*, **2016**, 6, 4428-4437.

Z.W. Ulissi, M.T. Tang, K. Chan, and J.K. Nørskov, **2016**.

Electrochemical Interface and Higher Order Methods



K. Mathew and R.G. Hennig, **2016**, https://arxiv.org/abs/1601.03346



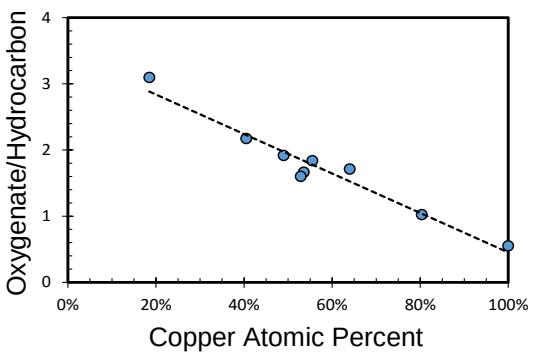
J.K. Nørskov *et al.*, *Chem. Phys. Lett.*, **2008**, 466, 68-71.

Selective CO_2 Reduction

JCAP Joint Center for Artificial Photosynthesis

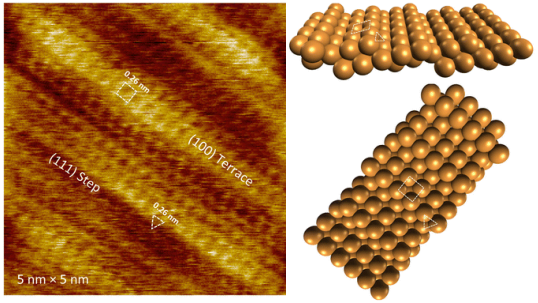
Experimental Developments

Catalyst Composition



E.L. Clark and A.T. Bell *et al.*, **2016**.

Catalyst Surface Structure

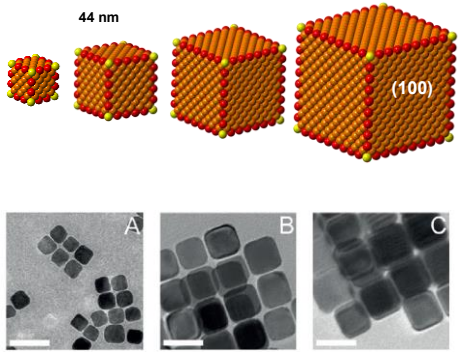


OECSTM Image
Post-ORC Cu(pc)-[Cu(100)]

Surface Lattice Model
Cu(S)-[3(100)x(111)] or Cu(511)

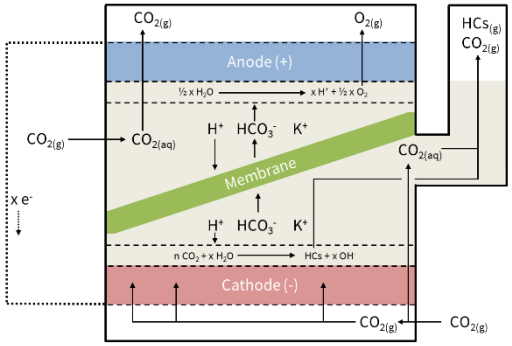
Y.G. Kim, A. Javier, J.H. Baricuatro, and M.P. Soriaga, *Electrocatal.*, **2016**, 7, 391-399.

Catalyst Morphology



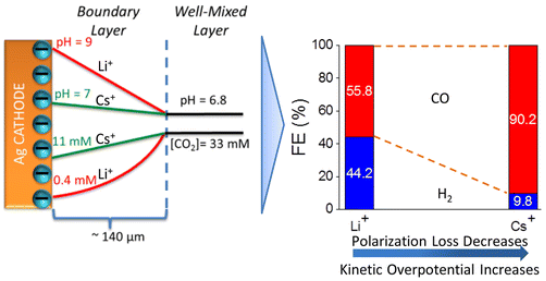
A. Loiudice, P. Lobaccaro, J.W. Ager, and R. Buonsanti, *Angew. Chem.*, **2016**, 55, 5789-5792.

Reactor Design



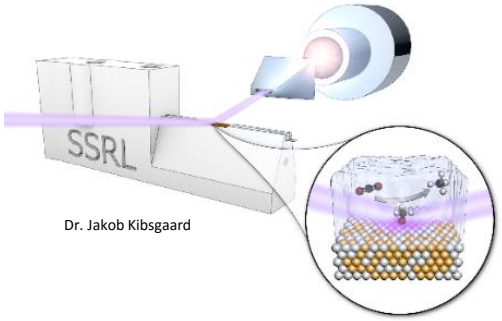
J.T. Feaster, C. Hahn, and T.F. Jaramillo *et al.*, **2016**.

Electrolyte Composition and Ionomer-Catalyst Interactions



M.R. Singh, Y. Kwon, Y. Lum, J.W. Ager, and A.T. Bell, *J. Am. Chem. Soc.*, **2016**, 138, 13006-13012.

Catalyst and Reaction Intermediate Characterization



Dr. Jakob Kibsgaard

J.T. Feaster, J. Yano, T.F. Jaramillo, and W.S. Drisdell *et al.*, **2016**.

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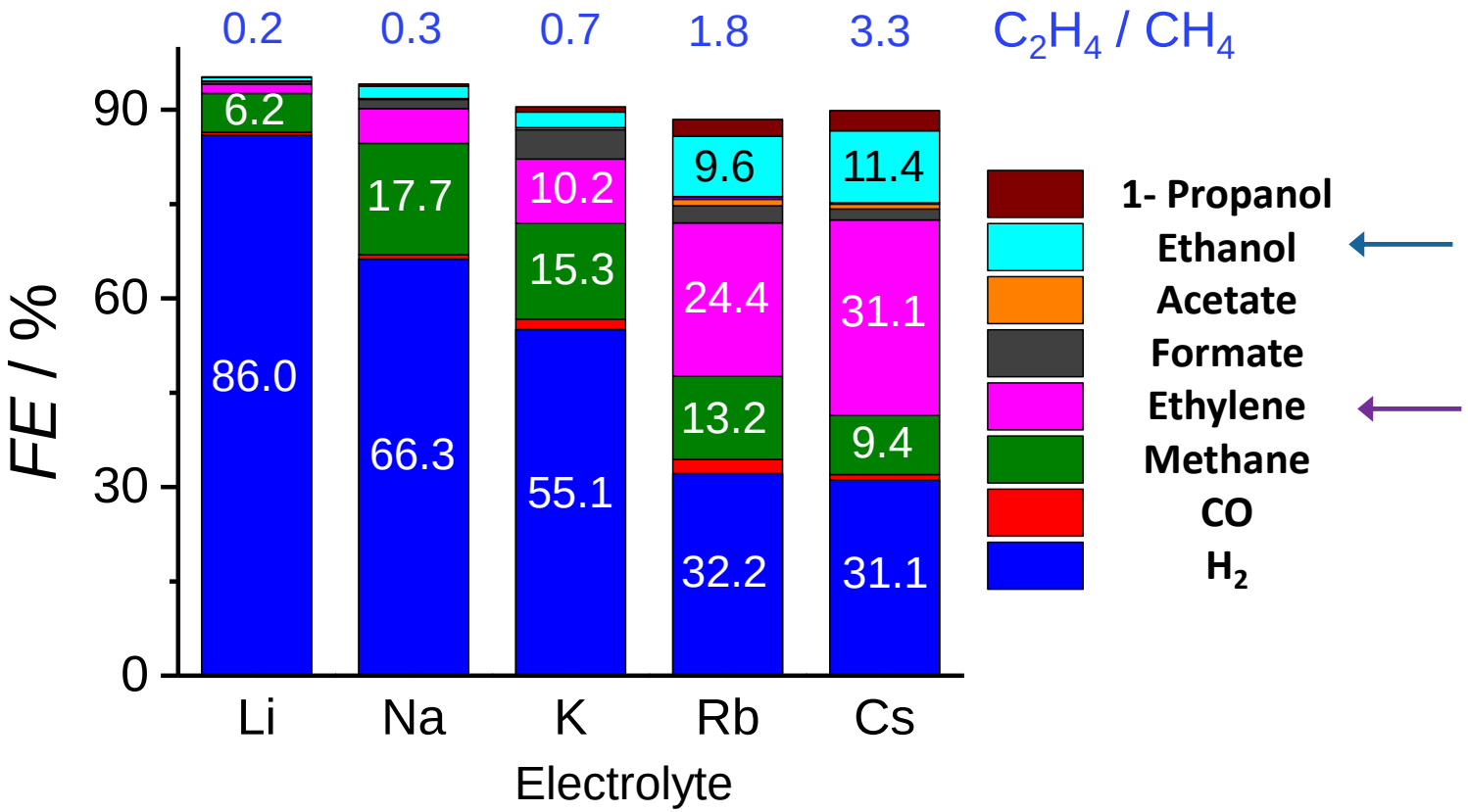
ELECTROLYTE SELECTION: CHOICE OF CATION

Use of $CsHCO_3$ buffer increases FE to C_{2+} products (ethanol, ethylene) on Cu foil



−1.0 V vs RHE in CO_2-saturated 0.1 M $MHCO_3$

Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T.
J. Am. Chem. Soc. **2016**, 138, 13006–13012.
Also: Murata, A.; Hori, Y. *Bull. Chem. Soc. Jpn*. **1991**, 64, 123–127.

IDENTIFICATION OF ELECTROCATALYSTS FOR CO_2RR TO H_2COO

Scientific Achievement

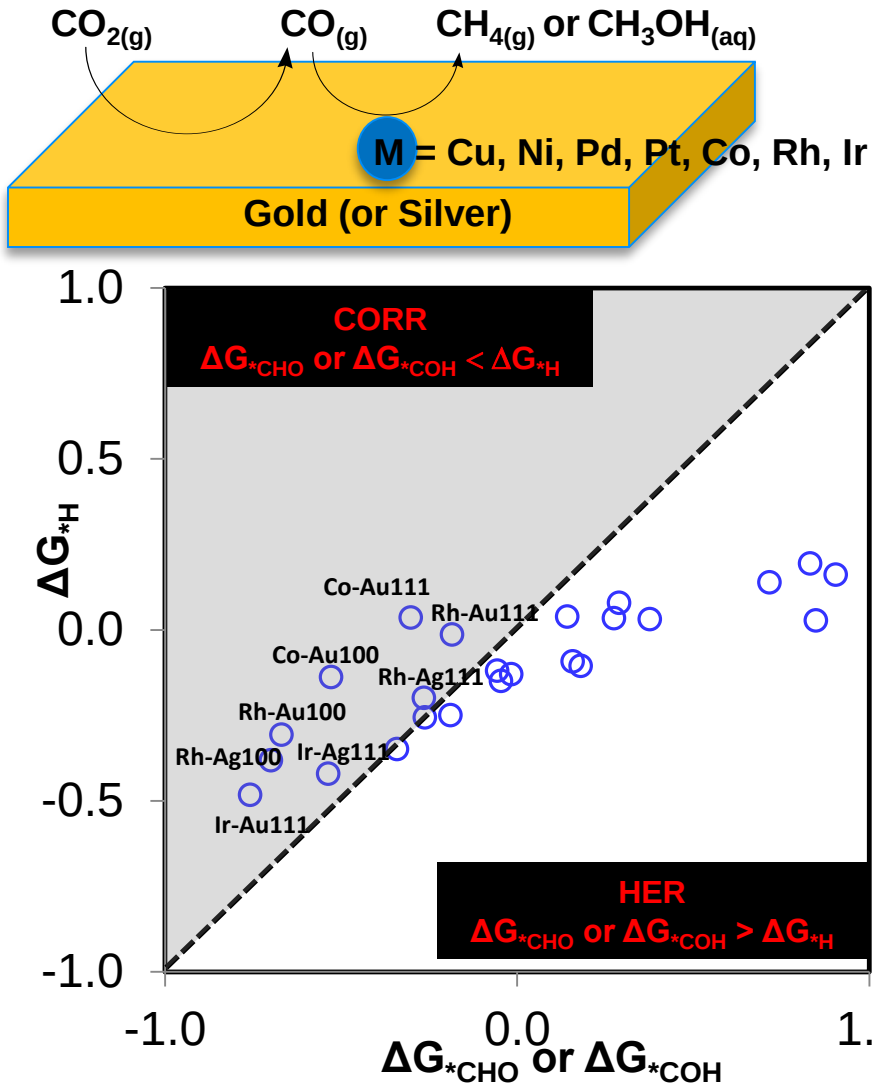
Identified tandem, bimetallic catalysts for the preferential formation of H_2COO over H_2.

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, ACS Catal. 6, 7769−7777 (2016)

ELECTROCHEMICAL REDUCTION OF CO_2 SELECTIVELY TO METHANOL

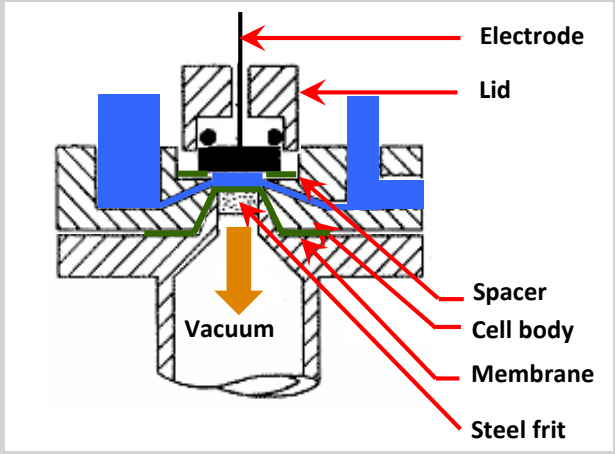
Near-Surface Alloy for Selective Reduction of CO_2 to CH_3OH

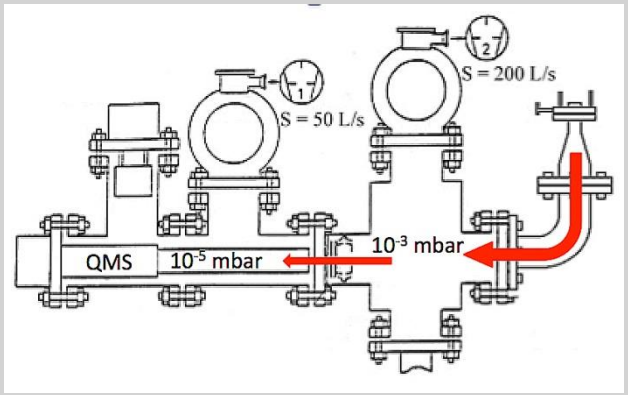
A theoretical prediction: a near-surface alloy (NSA) of a monolayer of Au on bulk W was empirically found to generate CH_3OH to the *exclusion* of other hydrocarbons and alcohols.

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.

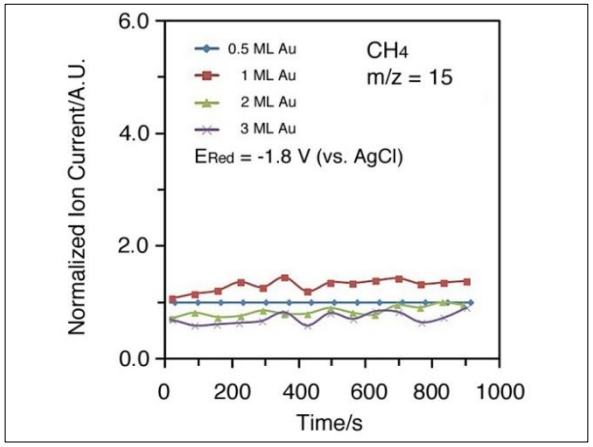


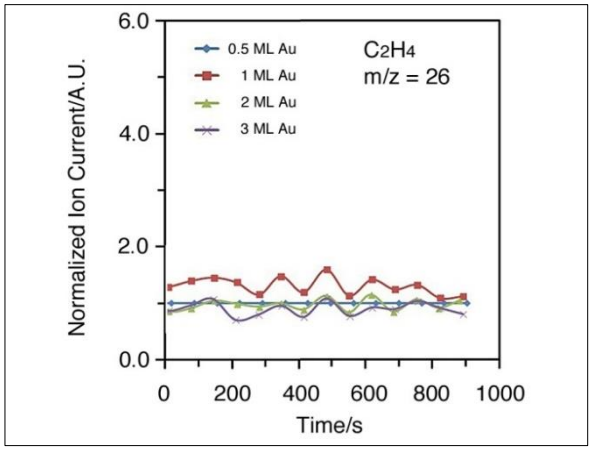


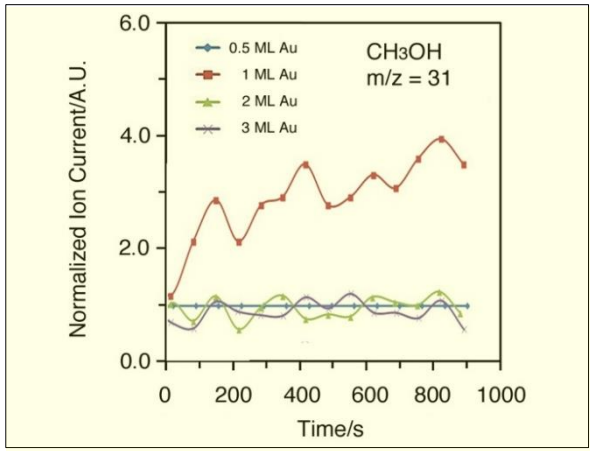
Products from CO_2 reduction at -1.2 V(RHE) in 0.1 M $KHCO_3$ were analyzed by Differential Electrochemical Mass Spectrometry (DEMS). Only CH_3OH was found.

ELECTROCHEMICAL REDUCTION OF CO_2 SELECTIVELY TO METHANOL

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







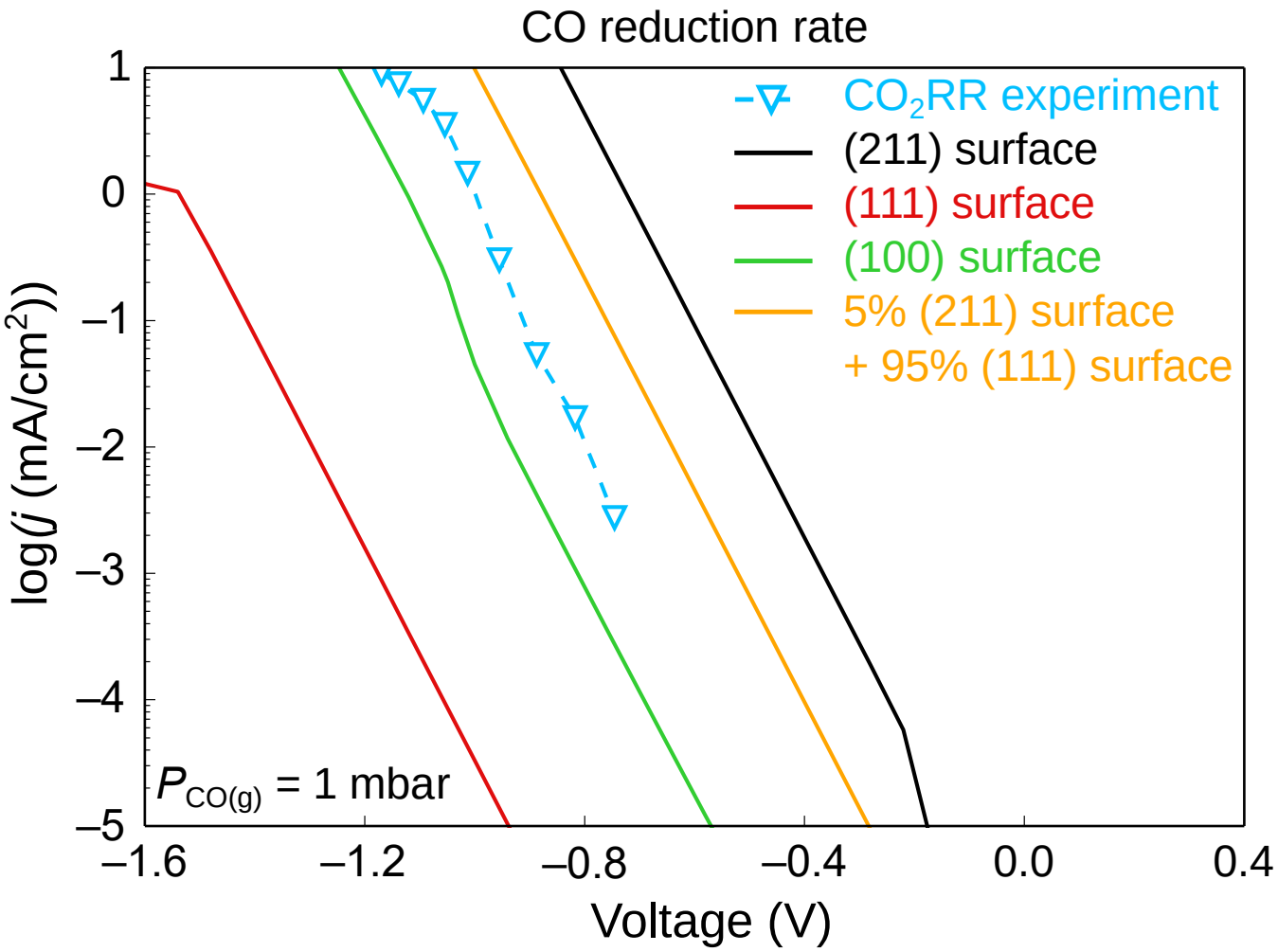
Theoretical Prognosis	*Experimental Result*
CH_3OH-Selective	**CH_3OH-Selective**
High Activity	**Not yet optimized**
Low Overvoltage	**Not yet optimized**
HER Suppression	**Not yet optimized**

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*, **6** 495. (2015).

POLARIZATION CURVES, CU – THEORY VS EXPERIMENT



Liu, Xiao, Peng, Hong, Chan, Nørskov, Nature Comm. (2017)

Exp.: Kuhl, *et al. JACS* doi:10.1021/ja505791r (2014).
Kuhl, Cave, Abram, Jaramillo,
Energy & Environmental Science 5, 7050 (2012).

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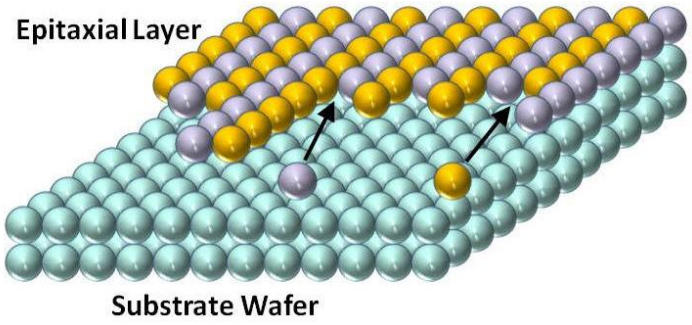
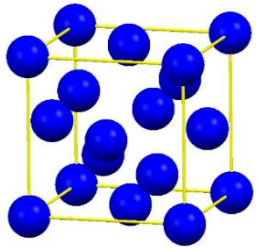
Epitaxial Growth Using Physical Vapor Deposition

Directing growth orientation utilizing interfacial energy

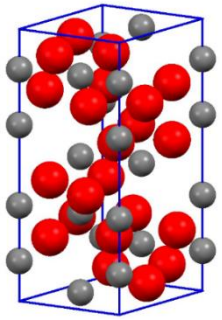


Si



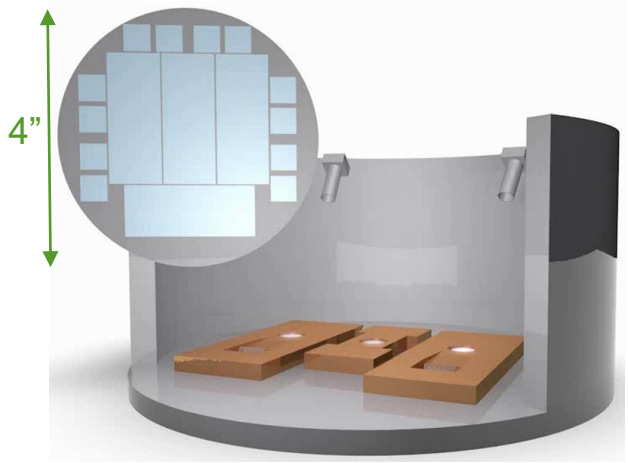
(100), (111)

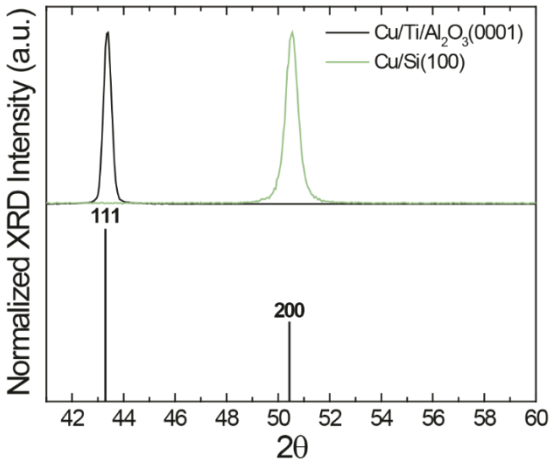
Al_2O_3



(0001)

E-beam Evaporation





D. B. Knorr and T.-M. Lu, *Textures and Microstructures*, **1991**, 13, 155-164.

B. G. Demczyk, R. Naik, G. Auner, C. Kota and U. Rao, *Journal of Applied Physics*, **1994**, 75, 1956-1961.

I. Hashim, B. Park, and H.A. Atwater, *Applied Physics Letters*, **1993**, 63, 2833-2835.

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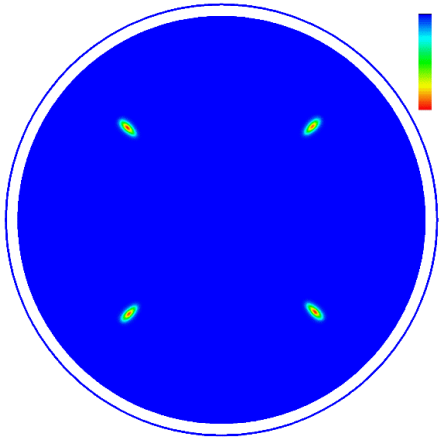
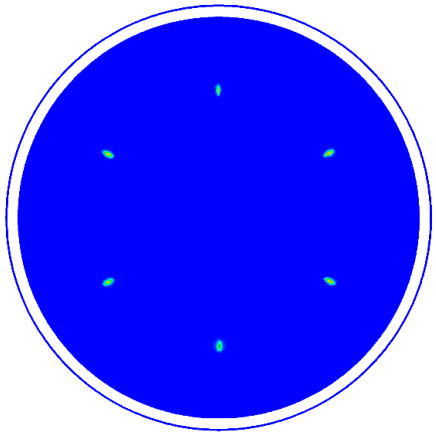
TEXTURE OF CU THIN FILMS

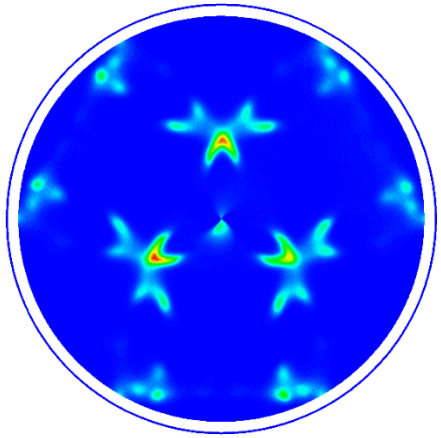
Cu(100)/Si(100)



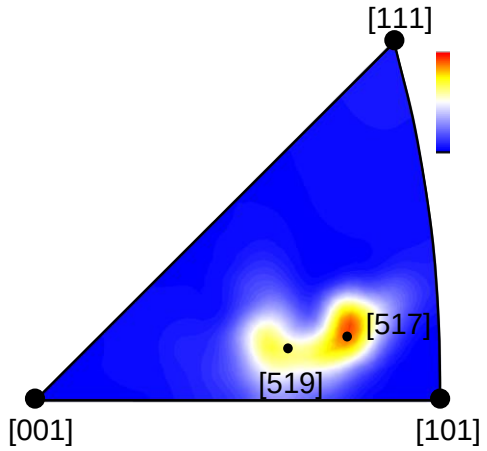
Cu(111)/Al_2O_3(0001)



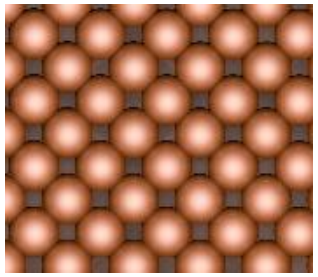
Cu(751)/Si(111)



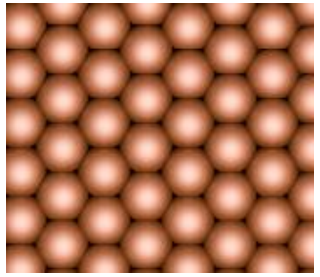
Inverse Pole Figure



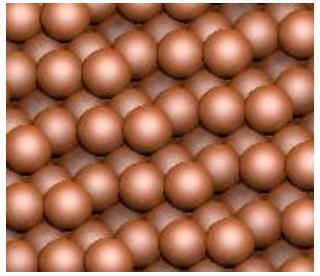
Cu(100)



Cu(111)

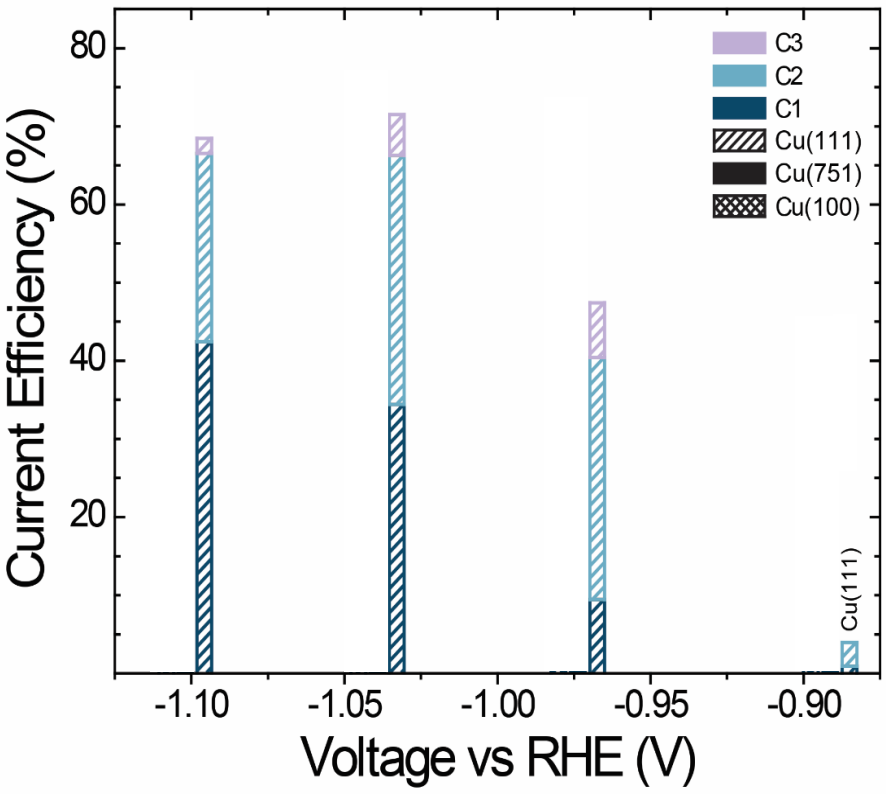


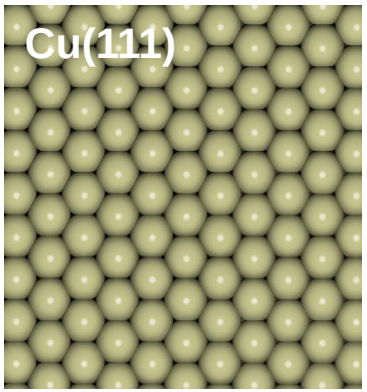
Cu(751)

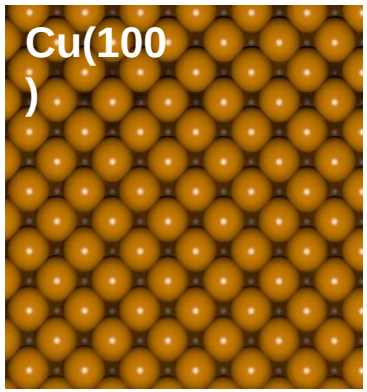


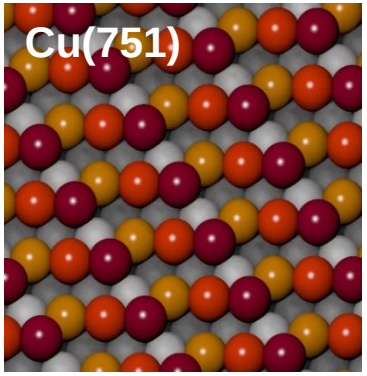
C. Hahn, T. Hatsukade, Y.G. Kim, A. Vallionis, J.H. Baricuatro, D.C. Higgins, S. Nitopi, M.P. Soriaga and T.F. Jaramillo, PNAS, **2017**.

Effects of Surface Structure on C-C Coupling Selectivity





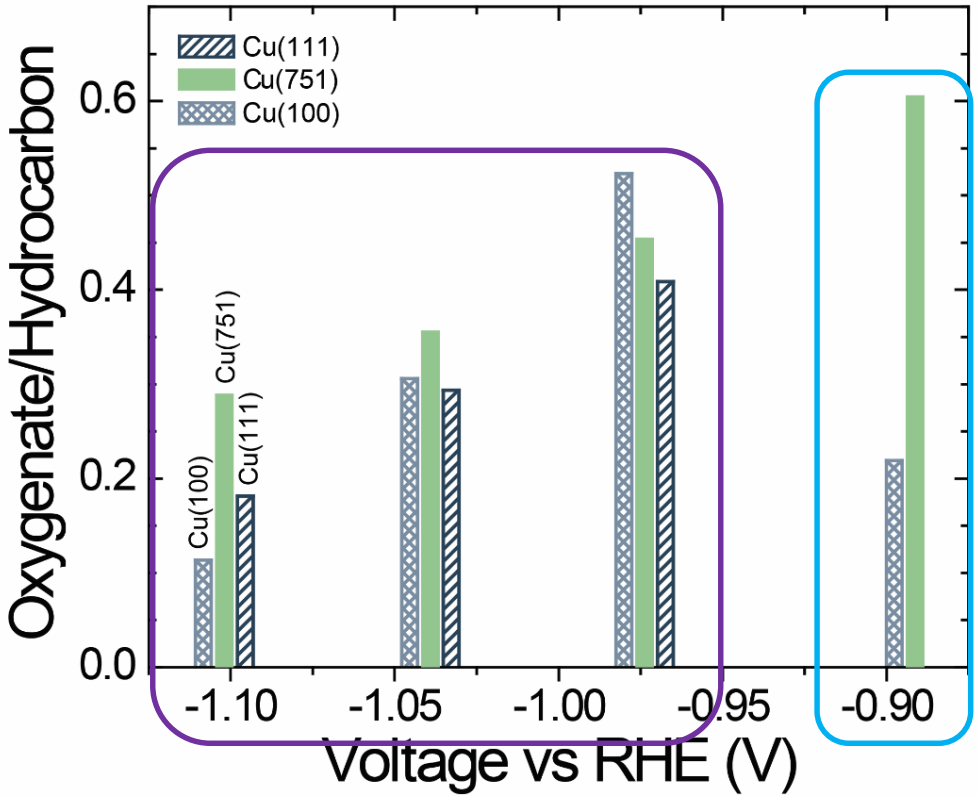




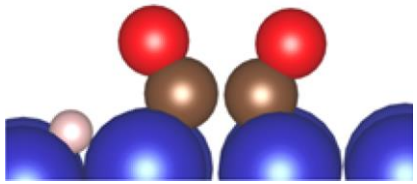
C-C coupling is favored on under-coordinated sites.
Epitaxial Cu thin films are single-crystal analogous for C-C coupling selectivity.

C. Hahn, T. Hatsukade, Y.G. Kim, A. Vallionis, J.H. Baricuatro, D.C. Higgins, S. Nitopi, M.P. Soriaga and T.F. Jaramillo, PNAS, **2017**.

JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

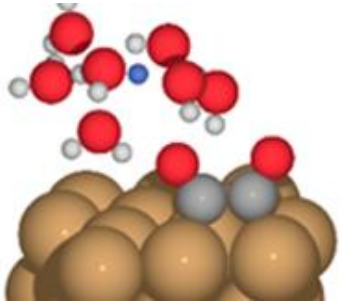


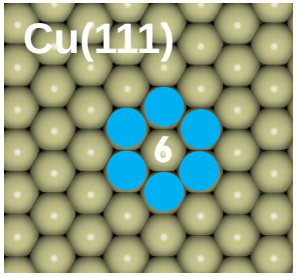
Hydride Transfer

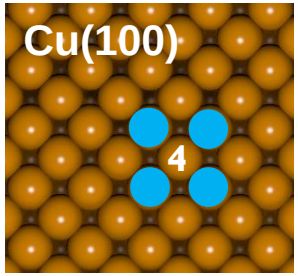


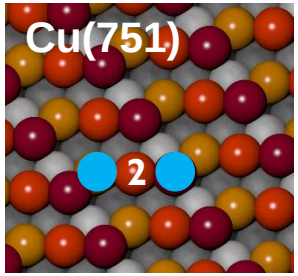
J.D. Goodpaster, A.T. Bell, M. Head-Gordon, *JCPL*, **2016**, 7, 1471-1477.

Proton-coupled Electron Transfer









Cu(751) has the lowest number of nearest neighbors, and is the least likely to have adsorbed H* adjacent to C2 intermediates.
PCET instead of hydride transfer leads to less structure sensitivity.

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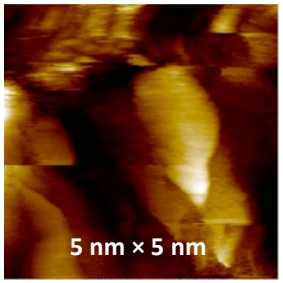
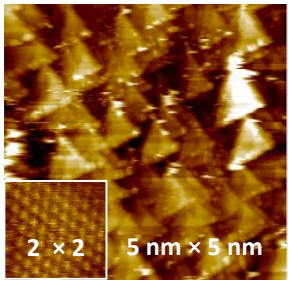
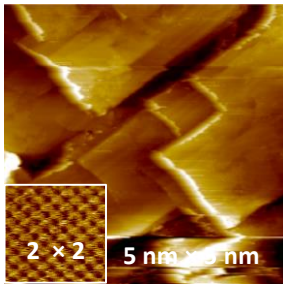
OECSTM: Cu Reconstruction at CO_2R Conditions (-0.9 V/0.1 *M* KOH)



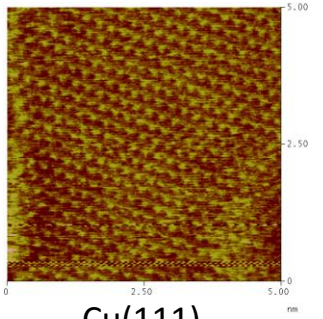
Cu(pc)
t = 0 m



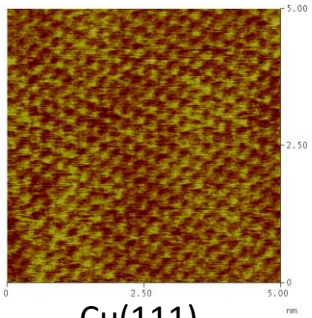
Cu(pc) → Cu(111)
t = 30 m



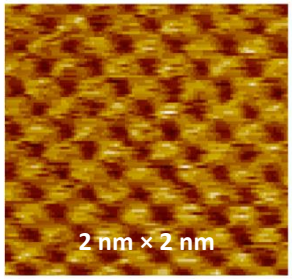
Cu(pc) → Cu(111) → Cu(100)
t = 60 m



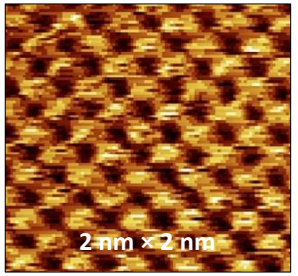
Cu(111)
t = 0 m



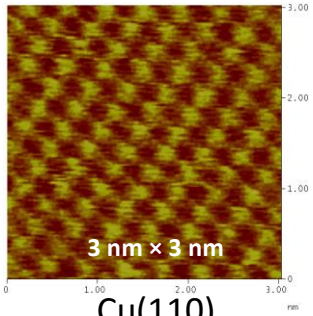
Cu(111)
t = 60 m



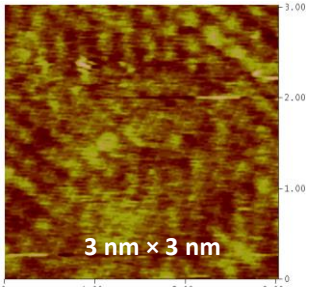
Cu(100)
t = 0 m



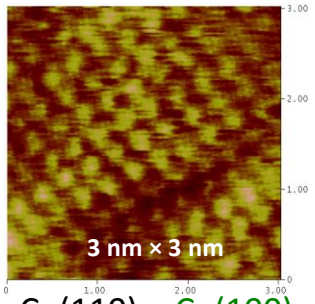
Cu(100)
t = 60 m



Cu(110)
t = 0 m



Cu(110) → Disordered Cu(111)
t = 30 m

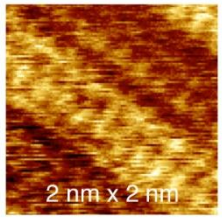


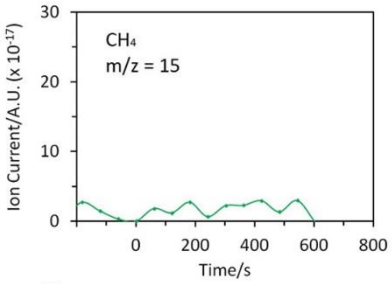
Cu(110) → Cu(100)
t = 60 m

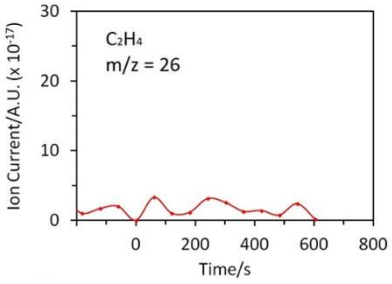
Y.-G. Kim, J. H. Baricuatro, A. Javier and M. P. Soriaga, J.Electroanal. Chem. **780** pp 290-295 (2106)

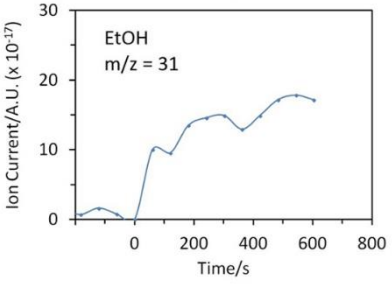
Regulating CO-Reduction Selectivity by Control of Surface Structure

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

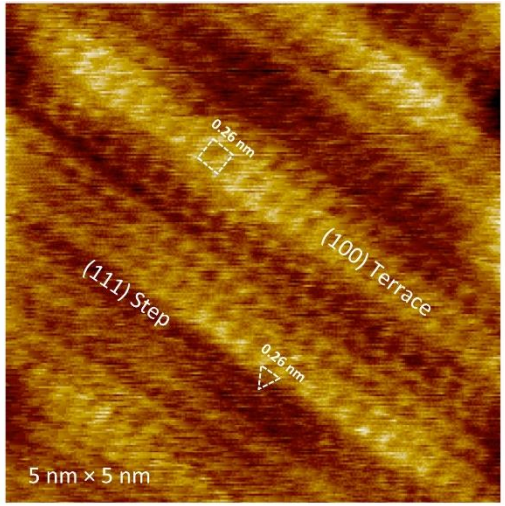


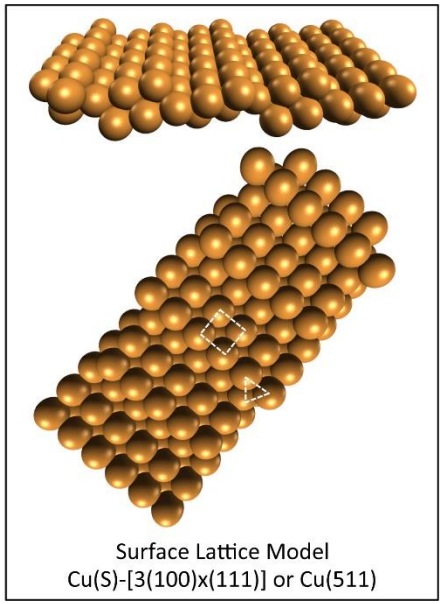


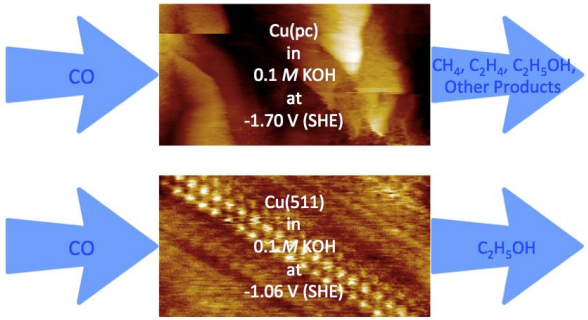




CO-to-C_2H_5OH on Cu(511)

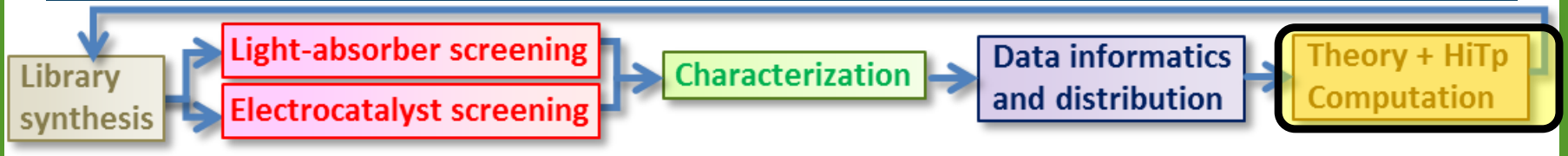






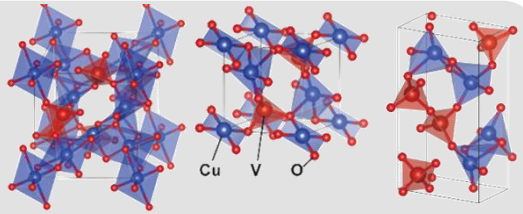
Y.-G. Kim, J. H. Baricuatro, A. Javier and M. P. Soriaga, J.Electroanal. Chem. **780** pp 290-295 (2106)

High throughput Discovery of Photoanodes



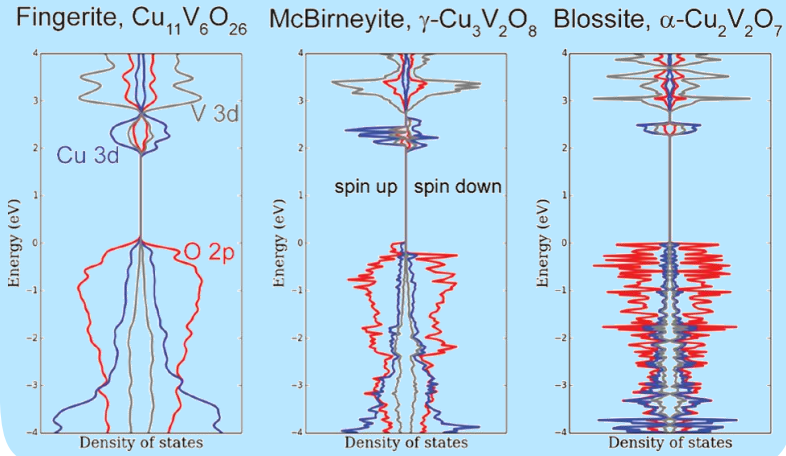
Design Materials & Interface with MP Database

Joint project with the Materials Project to design photoanodes and identify candidate materials.



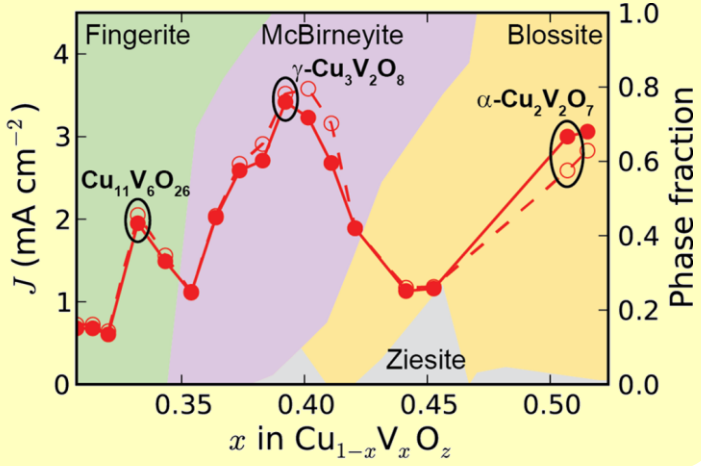
High Throughput Computation

Judicious choice of functional to rapidly evaluate the electronic structure and Pourbaix stability of hundreds of materials



High Throughput Experimentation

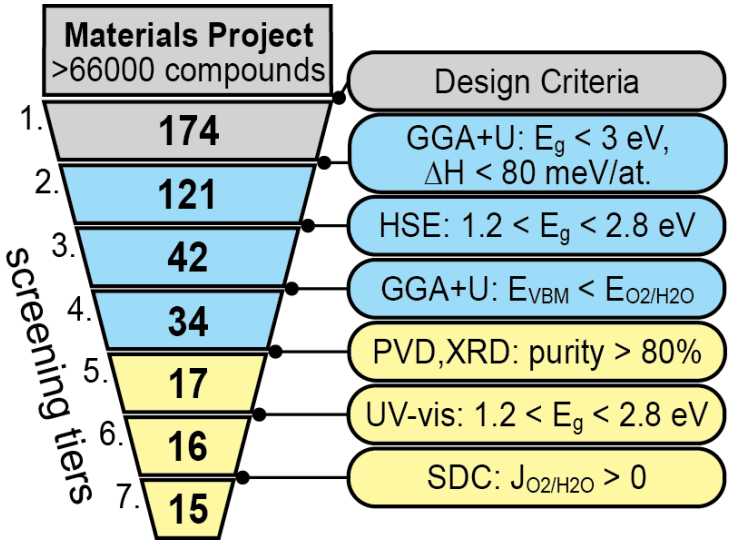
Identify synthesis conditions, generate composition maps of optical and photoelectrochemical properties.



L. Zhou, Q. Yan, A. Shinde, D. Guevarra, P. F. Newhouse, N. Becerra-Stasiewicz, J. B. Neaton, J. M. Gregoire, Adv. Energy Mater. 5, 1500968 (2015).

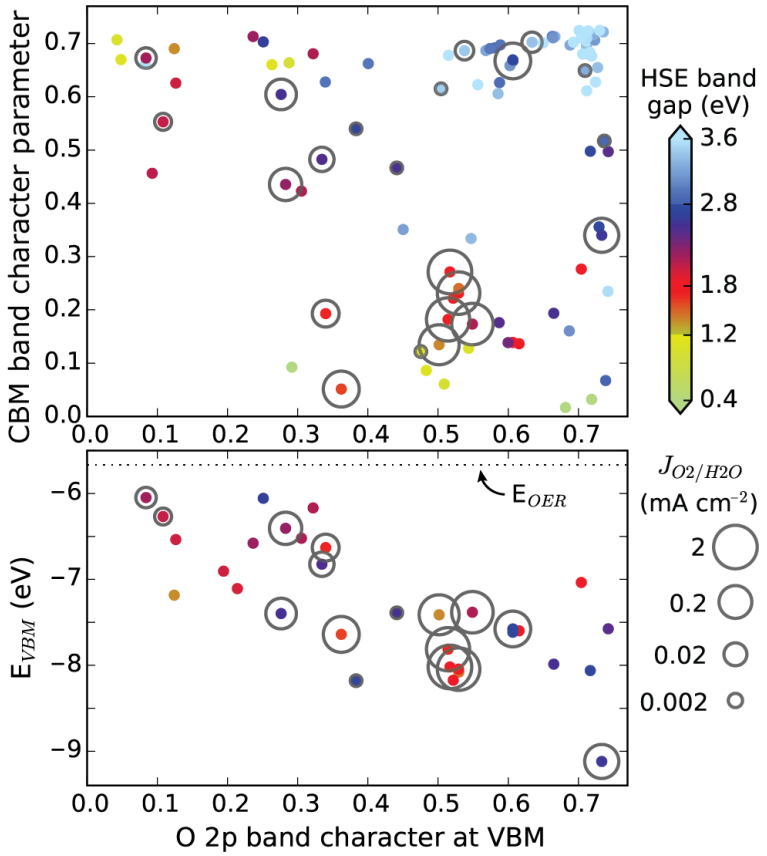
HIGH THROUGHPUT DISCOVERY OF PHOTOANODES: INTEGRATED THEORY-EXPERIMENT PIPELINE

Stitching complementary techniques together accelerates hypothesis-based discoveries



Pipeline execution summary:

- Out of the 15 hits there are 12 discoveries (3 of 15 were already reported)
- The 88% hit rate upon successful synthesis provides credence to the design criteria and the computational workflow
- These experimentally-verified predictions foundationally demonstrate that high throughput computation can accelerate experimental discovery of functional materials.



- Varying the electronic band character in complex oxides enables tuning of the band gap energy and band positions.

Q. Yan, et.al. (Persson, Gregoire, Neaton) *PNAS*, 114 3040-3043 (2017).

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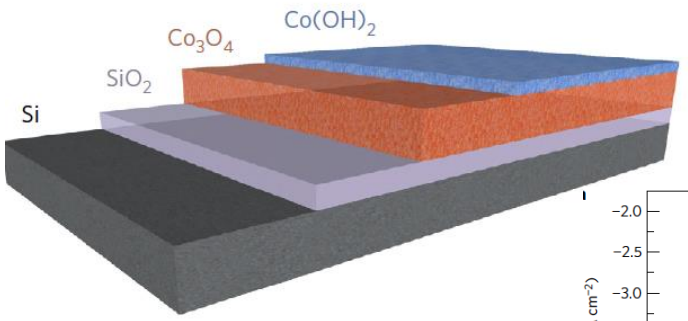
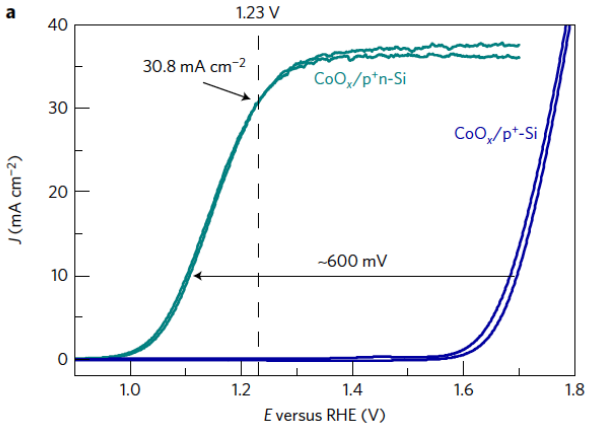
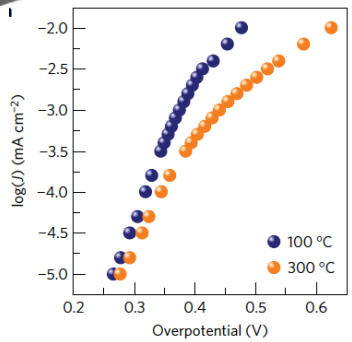
BIPHASIC OER CATALYST INTEGRATED ON SI



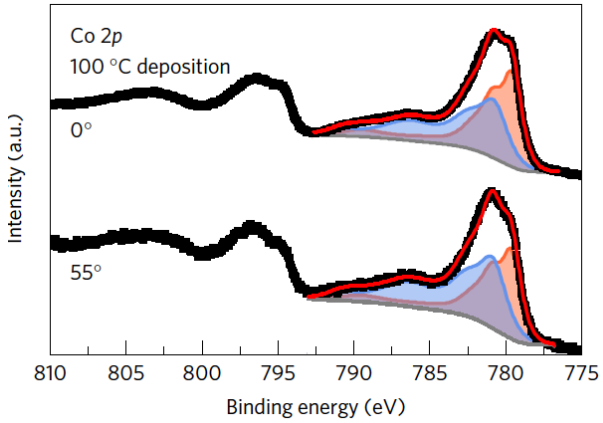
Onset potential for water oxidation of <1V versus RHE and a saturation current density of 37.5 mA/cm^2:

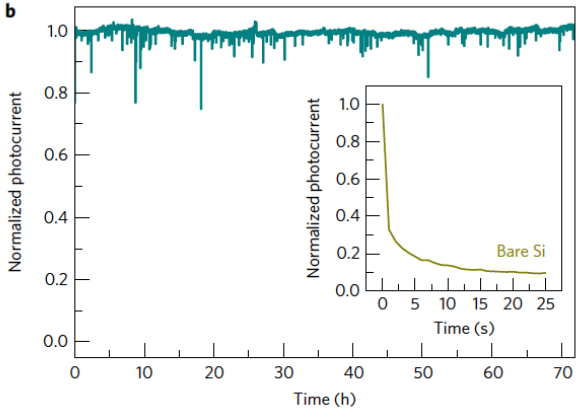


Tafel slope:
~50mV/decade:



More $Co(OH)_2$ component increases with increasing photoelectron take-off angle → surface layer:





No detectable transfer of Co from the film into solution after 72 hr.

J. Yang, et.al. (Toma, Yano, Sharp) *Nature Materials*, 114 3040-3043 (2017).

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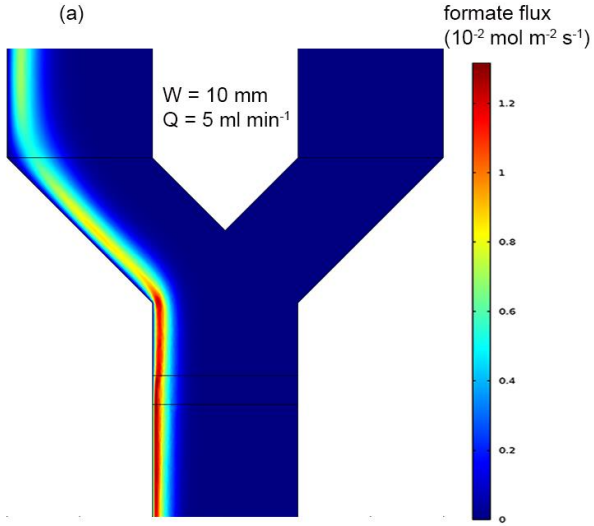
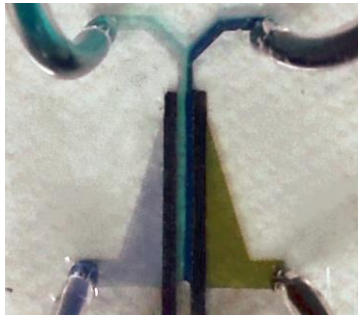
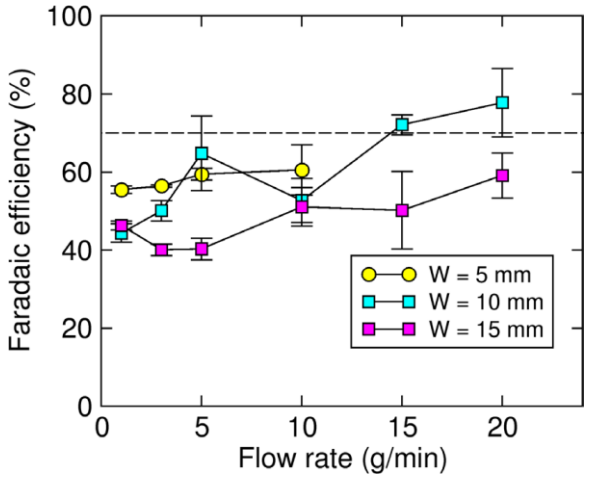
MEMBRANELESS FLOW CELL PROTOTYPE FOR SEPARATIONS







A new electrochemical CO_2 test bed implements isolates the fuel-containing electrolyte produced at the cathode from the anode and produces a stream of liquid products.

Cell design validated with 2-D Multiphysics modeling and experimentally implemented.

Separation efficiency as high as 90% demonstrated.

Overall Faradaic efficiency (sum of both channels) for formate production with 01 M $KHCO_3$ electrolyte saturated in CO_2 and Sn cathode at 5 mA/cm^2.

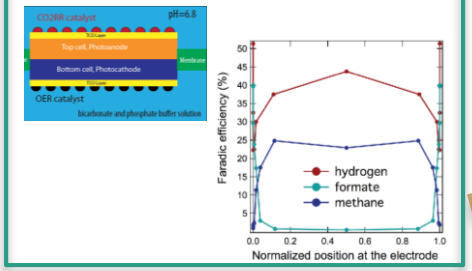
Goulet, M.A.; Kjeang, E. *J. of Power Sources*. 2014, *260*, 186-196.
Ismagilov, R.F.; Stroock, A.D.; Kenis, P.J.A.; et al. *Appl. Phys. Letters.* 2000, *76,* 2376-2378.

Monroe, M. M.; Lobaccaro, P.; Lum, Y.; Ager, J. W., *J. Phys. D. Appl. Phys. 50*, 154006 (2017).

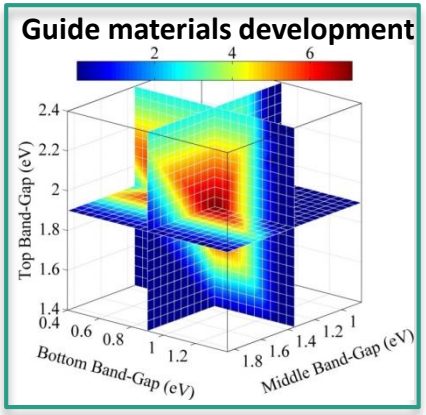
MULTIPHYSICS MODELING: VIRTUAL INTEGRATOR AND TESTING PLATFORM

Theory

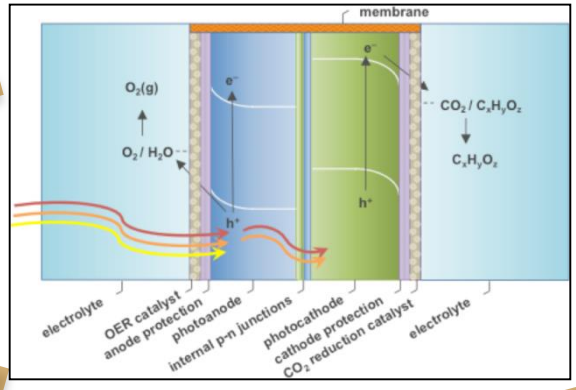
Optimize geometries of prototype designs



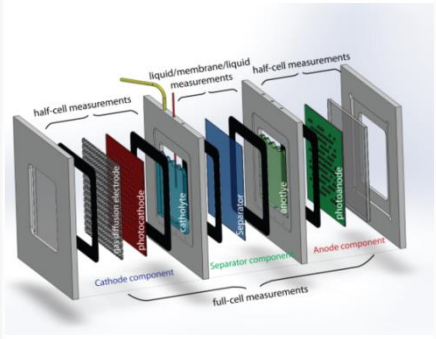
Guide materials development



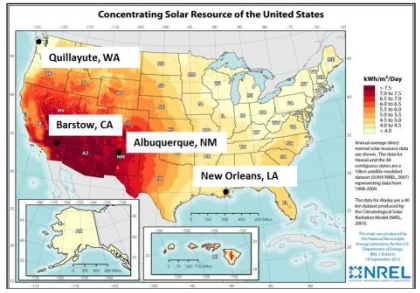
Multiscale model



Evaluate viability of new design concepts

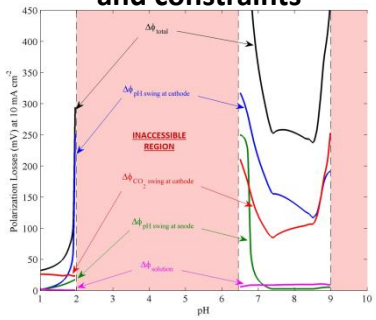


Understand cell performance in real-life environment



	Barstow	Albuquerque	New Orleans	Quillayute
Weighted Average Annual η_{STH} [%]	11.2	11.0	10.0	9.1
Annual kg of H2 Produced per [sq. m] of Aperture	8.80	7.98	4.85	2.91

Define operational conditions and constraints



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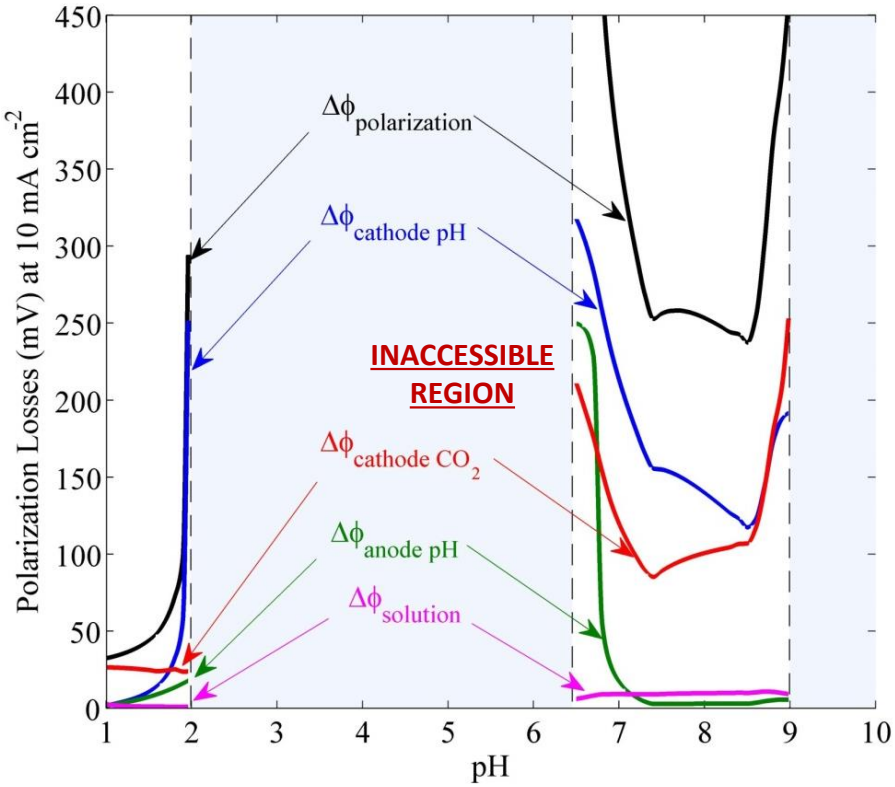
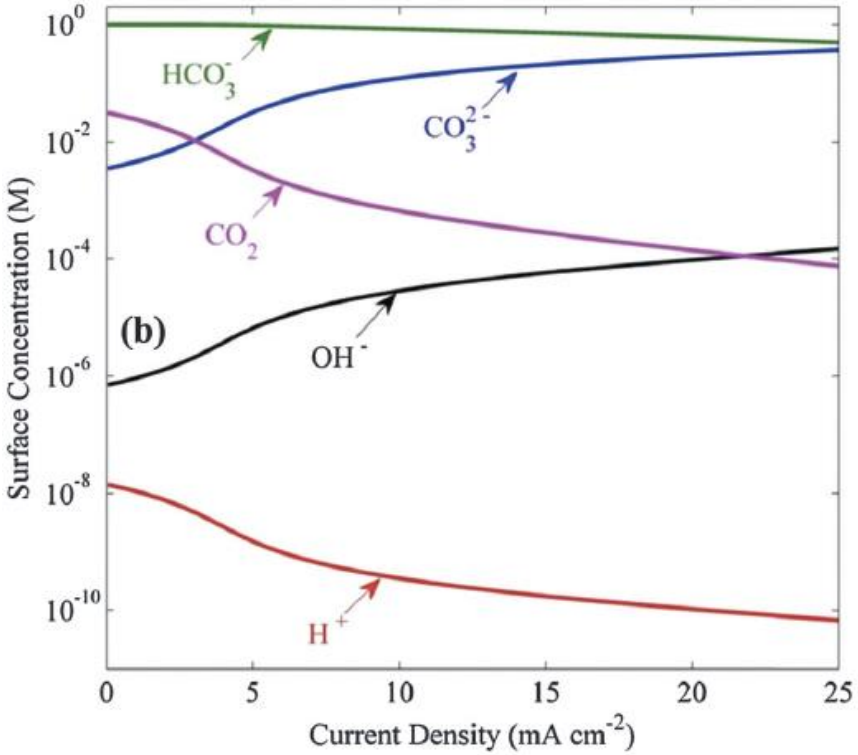
EXPLORING DEVICE-LEVEL LIMITATIONS





- 20 mA/cm^2 is feasible with 1 atm CO_2 or equivalent high concentration locally
- For aqueous: pH 7.5 to 8.5 shows lowest total losses while maintaining selectivity towards CO_2 reduction

Key is local CO_2 concentration

M. R. Singh, E.L. Clark, A.T. Bell, doi: 10.1039/C5CP03283K

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SUMMARY

- A strategy for selective EC-CO_2 reduction: multifunctional cathode that combines multiple active sites, functional coatings, nanoscale confining volumes
- Mechanism discovery: initial focus predominantly on Cu and Cu alloys
- Materials discovery:
  - bimetallic alloy candidates screened and synthesized
  - oxide photoanode theory/experimental effort achieves high predictive yield
- Integration - focus on OER (– biphasic cobalt oxide)
- Prototyping: device architectures for EC and PEC CO2RR

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