Developing New Pathways for the Production of Fuels and Chemicals in a Sustainable Manner

Thomas F. Jaramillo

Dept. of Chemical Engineering, Stanford University
Deputy Director, SUNCAT Center for Interfacial Science & Catalysis

November 2, 2017

5th Arab-American Frontiers of Science, Engineering, and Medicine Symposium
Rabat, Morocco

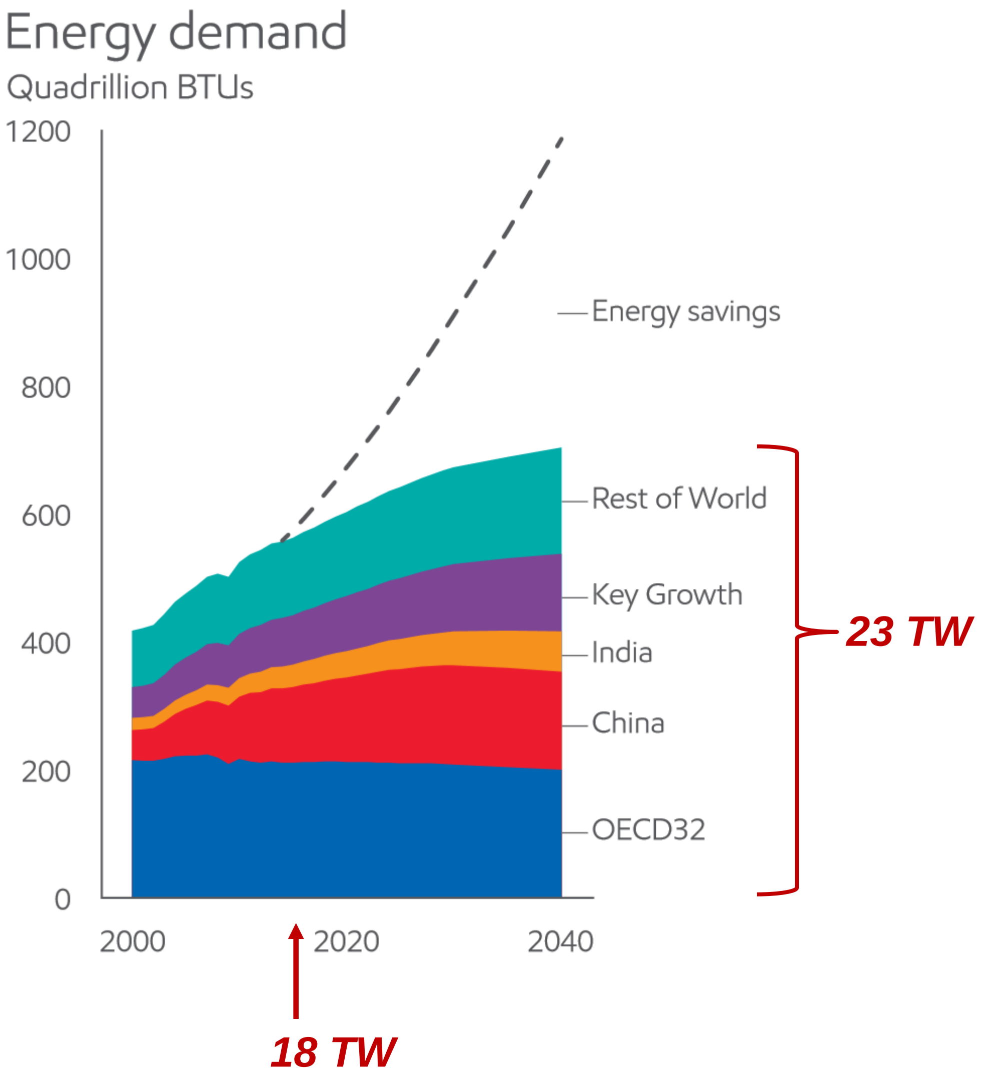
Fossil fuels: An amazing resource

- Consider petroleum
  - Massive world-wide resource, extremely abundant
    - Provides ~ 5 TW of power across the globe (out of 18 TW total)
  - Huge energy density
    - Can drive a car 500 miles on one tank of gas, or fly a commercial jet half-way around the earth.
    - A full tank of gasoline in a car is approximately equivalent to:
      - The potential energy of 1 million gallons of water at 200 ft elevation
      - The electrical energy stored in 80,000 iPhone 6 batteries
  - High power density
    - Can power anything… automobiles, trucks, shipping vessels, commercial and military aircraft….
    - The power transfer in filling up your car at the pump is approximately 5 MW.
  - Yet very chemically stable
    - When you drive your car, do you worry about it exploding?
  - Easy to store and to transport
    - Approx. 100,000 miles of gasoline pipeline in the USA.
    - As a liquid fuel it can fit into any size and shape of container with ease.
  - Cost
    - How do the gas prices of today (~ $2-3/gallon) compare with other consumer goods? Bottled water? Milk? Orange juice?
  - Convenience
    - Have you ever timed yourself at the gas pump? How long does it take to fill the tank?

Any future energy technology would need to compete with these attributes!

Global Projections

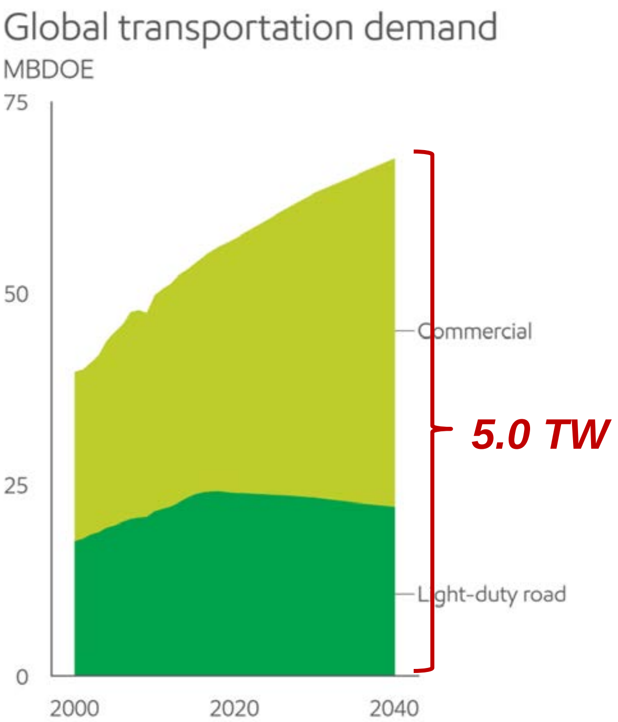
Global energy demand increases by 25% between 2014-2040



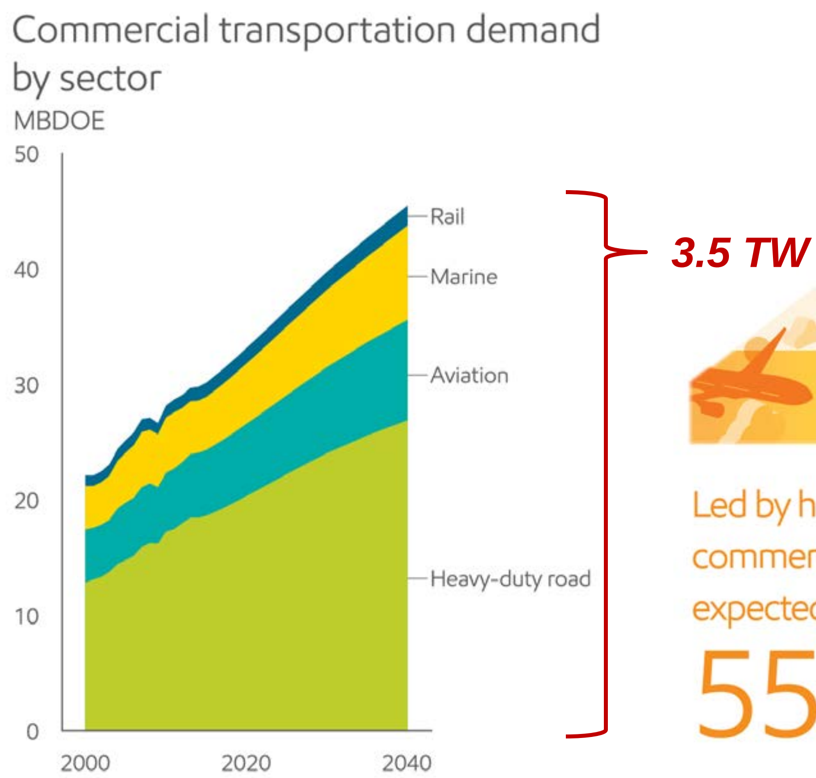
"The Outlook for Energy: A View to 2040" by ExxonMobil (2016).

The future of transportation

Global energy demand for transportation to rise by about 30 % from 2014-2040



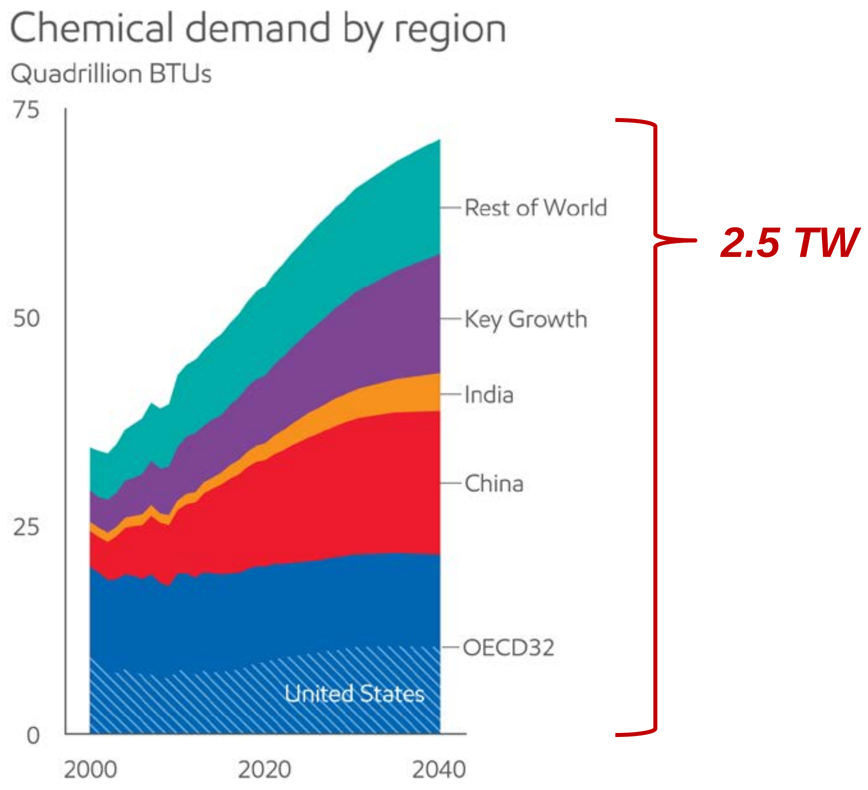
Trade, economic growth spur close to 55 % increase in commercial transport needs



For the bulk of transportation in 2040, chemical fuels will be needed.

The future of the chemical industry

Chemicals is one of the fastest-growing energy-demand sectors



The chemical industry will demand ~ 2.5 TW.
More efficient, sustainable processes are needed.

"The Outlook for Energy: A View to 2040" by ExxonMobil (2016).

Fuels and chemical production needs for these two sectors in 2040:

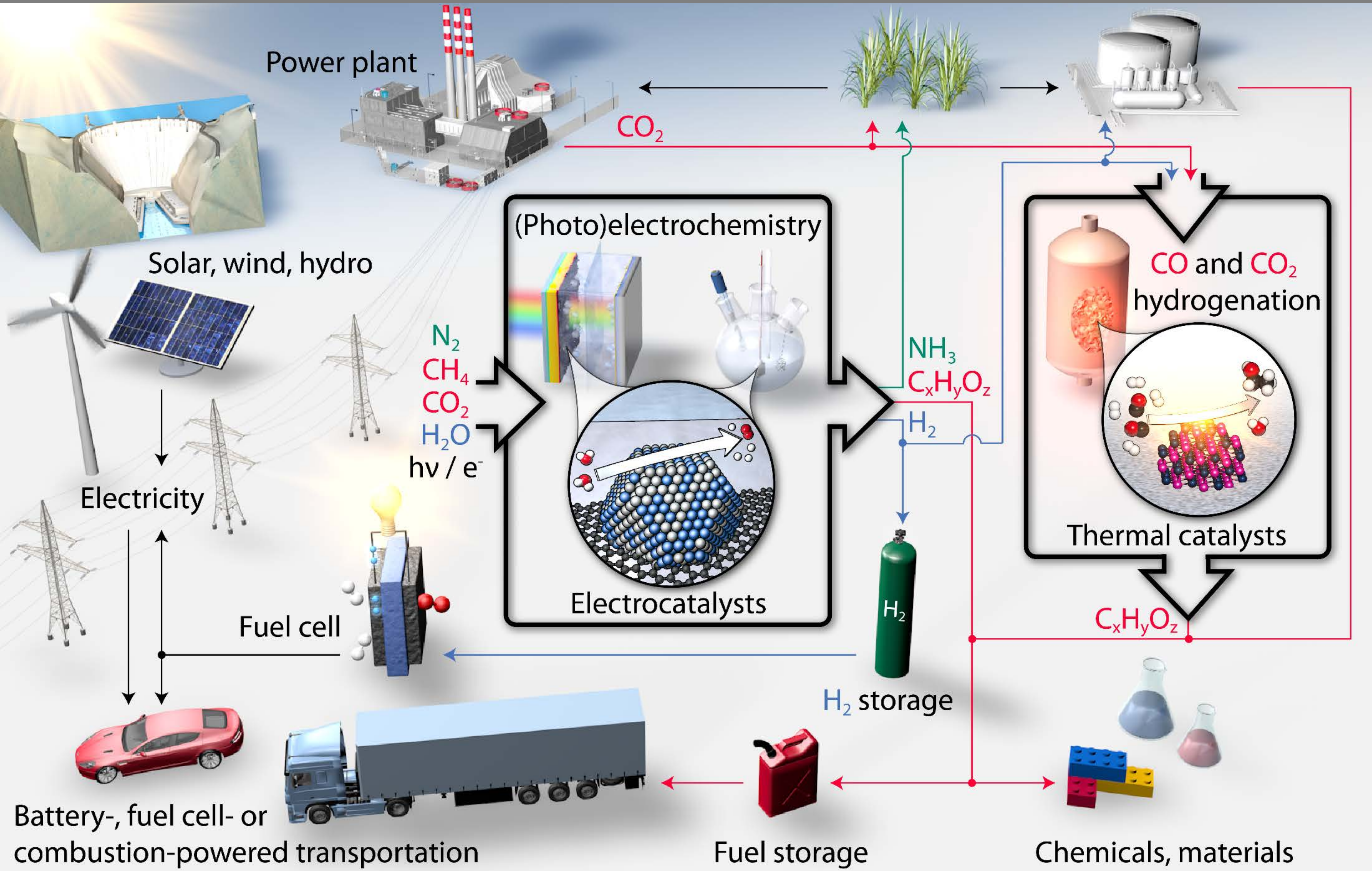
- Heavy-duty transportation 3.5 TW
- Chemical industry <u>2.5 TW</u>

6.0 TW

Can we produce fuels and chemicals in a more sustainable manner than we do today?

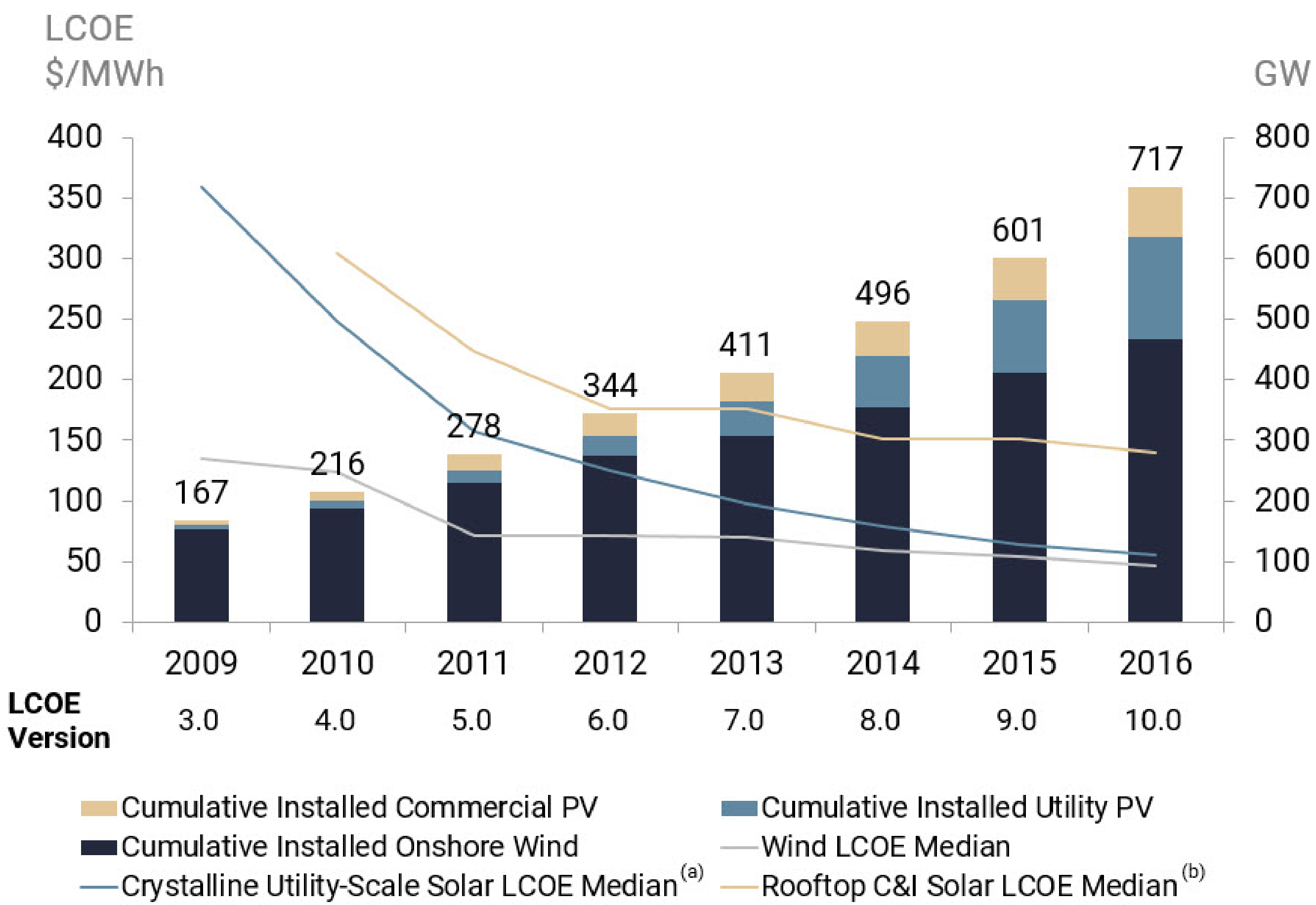
A vision for the future:
A more sustainable approach to fuels and chemicals

Catalyzing a Sustainable Future



Z. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T. F. Jaramillo, *Science*, **355** 6321 (2017)

Dropping costs of renewable electricity



Source: Lazard estimates and BNEF.
Note: LCOE medians represent average between low end and high end of LCOE range for each technology.
(a) Low end represents crystalline utility-scale solar with single-axis tracking in high insolation jurisdictions (e.g., Southwest U.S.), while high end represents crystalline utility-scale solar with fixed-tilt design.
(b) Lazard's LCOE initiated reporting of rooftop C&I solar in 2010.

https://www.lazard.com/perspective/levelized-cost-of-energy-analysis-100/

Developing catalysts, processes, and devices

Electrocatalysis

Fuel Production

$2H^+ + 2e^- \Leftrightarrow H_2$

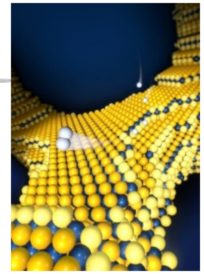
$CO_2 + nH^+ + ne^- \Leftrightarrow C_xH_y + C_aH_bO_cH + mH_2O$

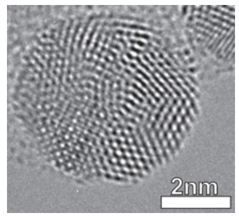
$2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^-$

$O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O_2$

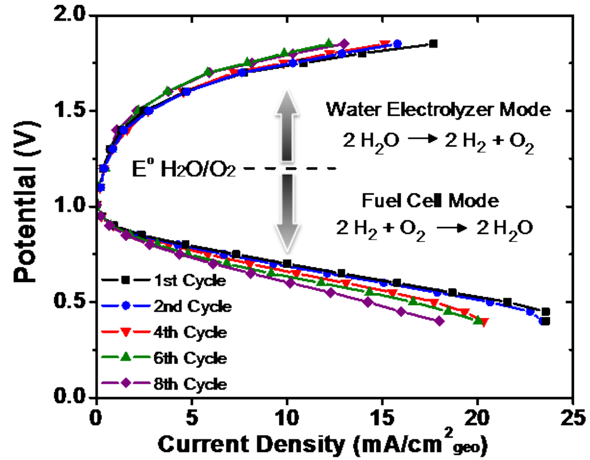
$N_2 + 6H^+ + 6e^- \Leftrightarrow 2NH_3$

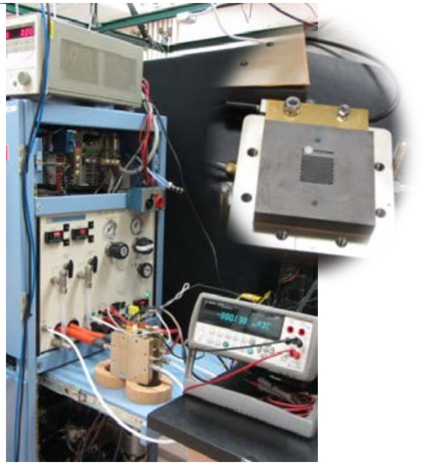
Fuel Consumption



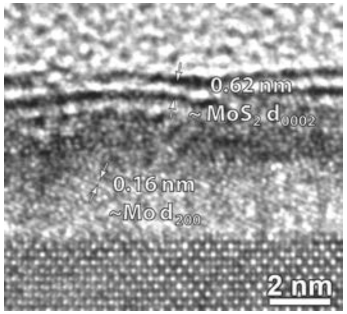


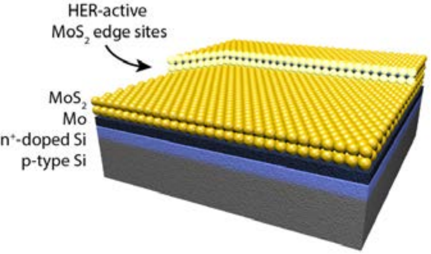
Integrated Devices

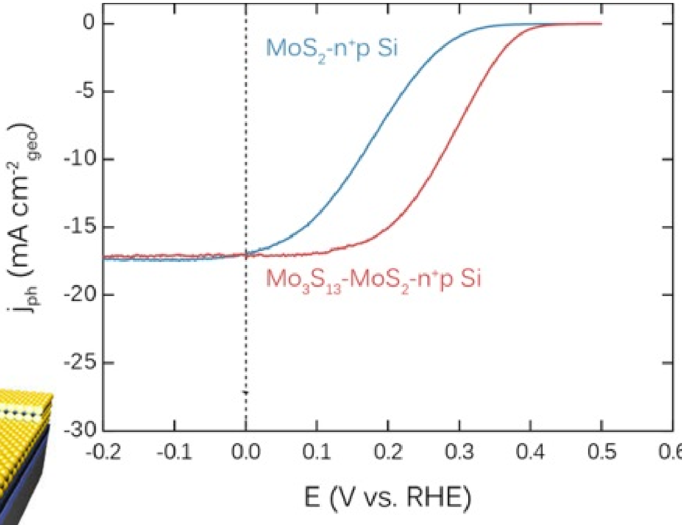




Solar Photoelectrochemistry



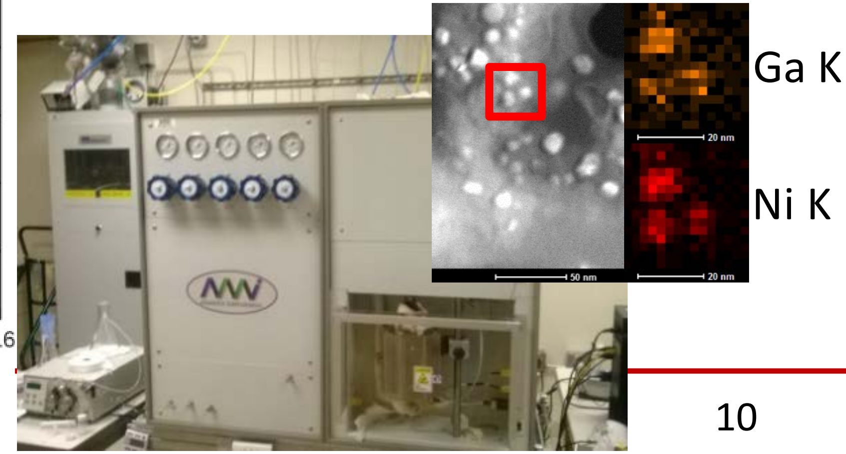




Thermal catalysis

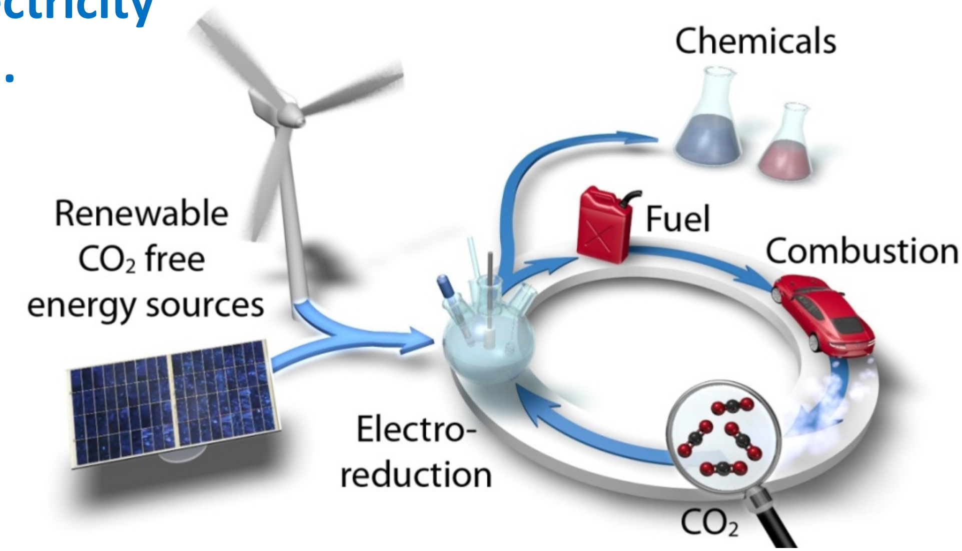
$2CO + 4\ H_2 \rightarrow C_2H_5OH + H_2O$

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

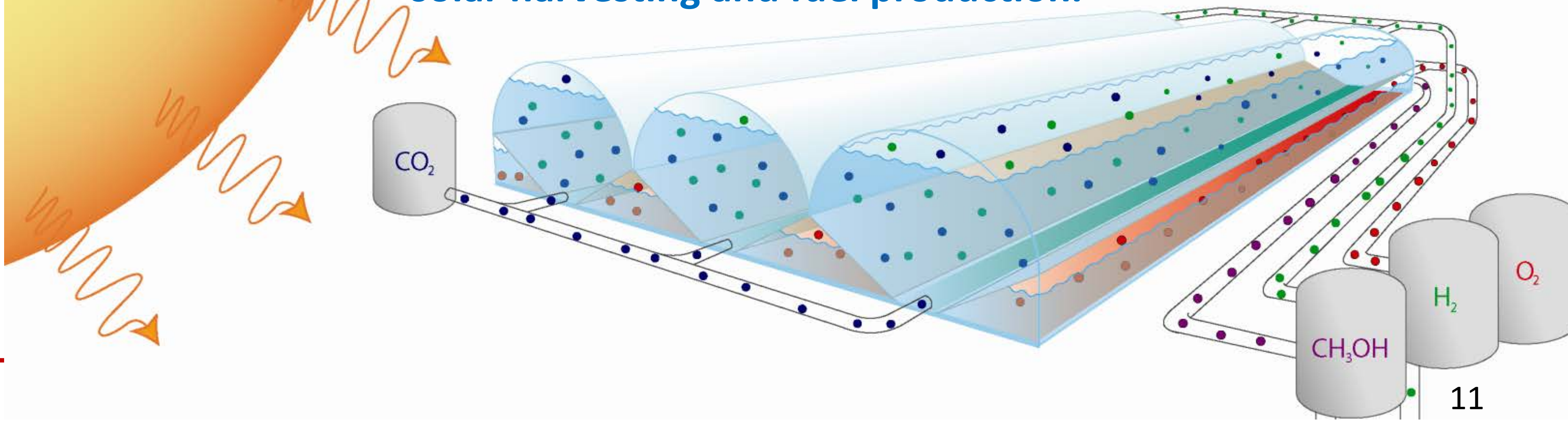


Electrochemical & Photoelectrochemical Pathways

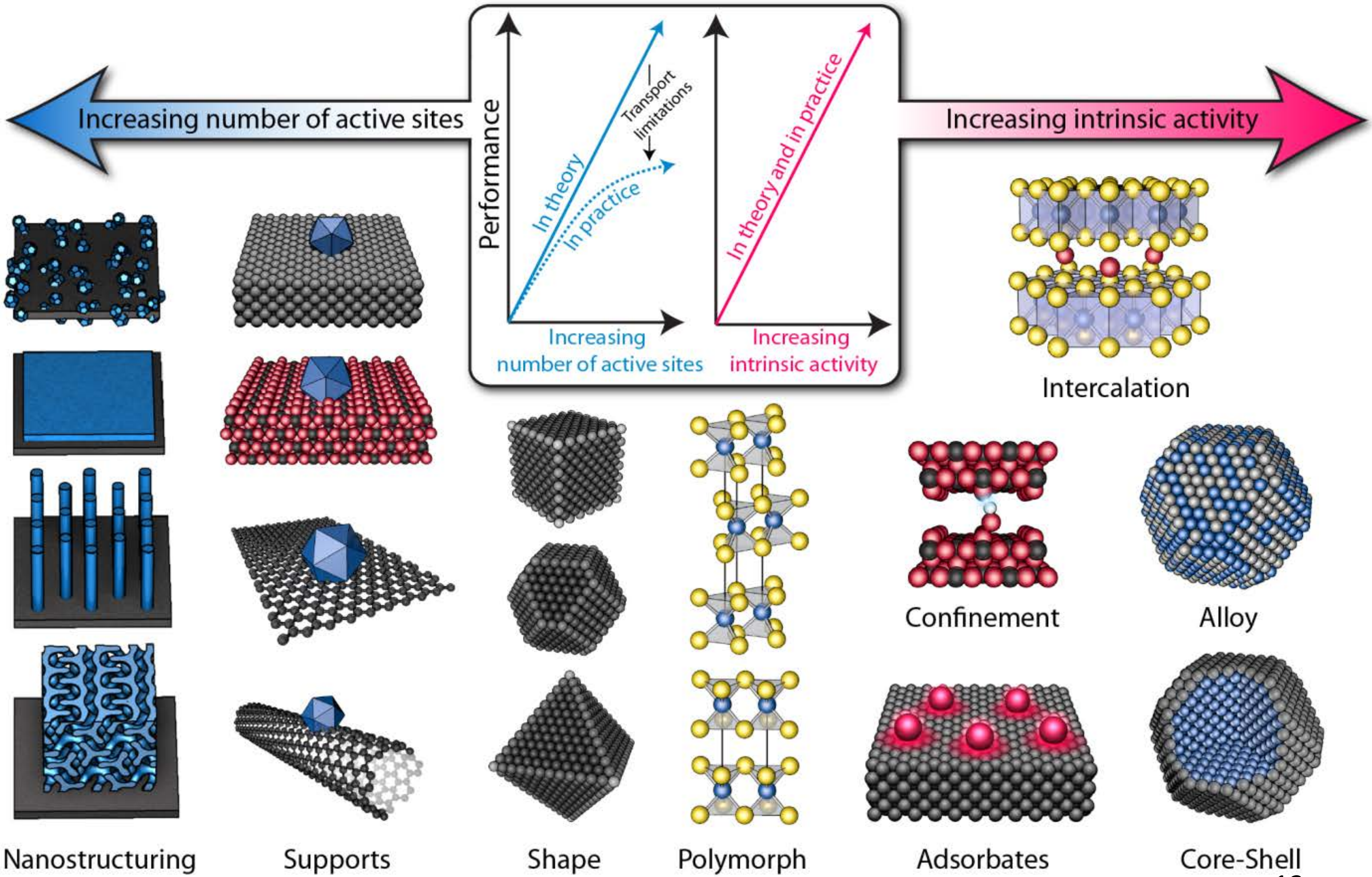
Scheme 1: Separate devices for electricity generation and for fuel production.



Scheme 2: One integrated device for solar harvesting and fuel production.



Catalyst development strategies



Z.-W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T.F. Jaramillo, *Science* **355** 6321 (2017).

Hydrogen (H_2)

Carbon-based fuels and chemicals

Ammonia (NH_3)

Hydrogen (H_2)

Carbon-based fuels and chemicals

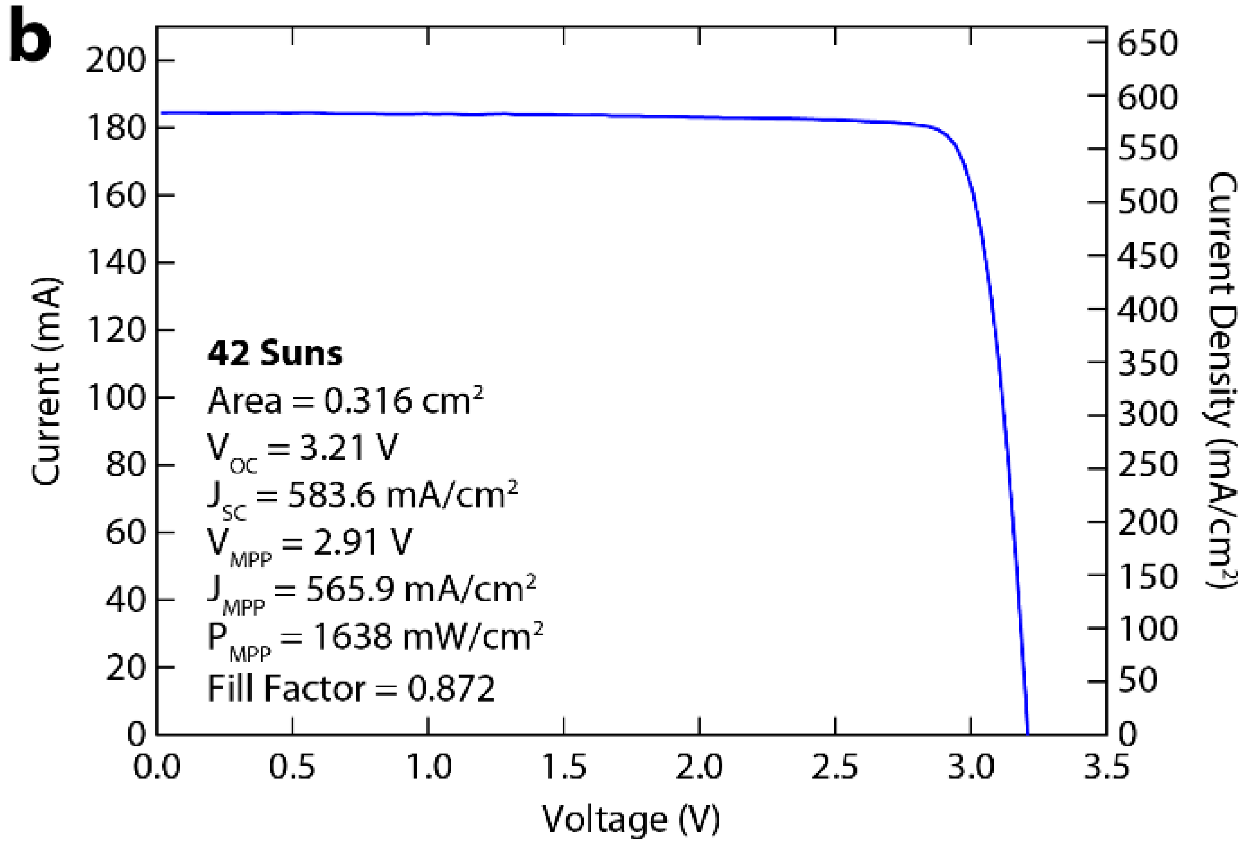
Ammonia (NH_3)

PV-electrolysis with a 3j III-V PV

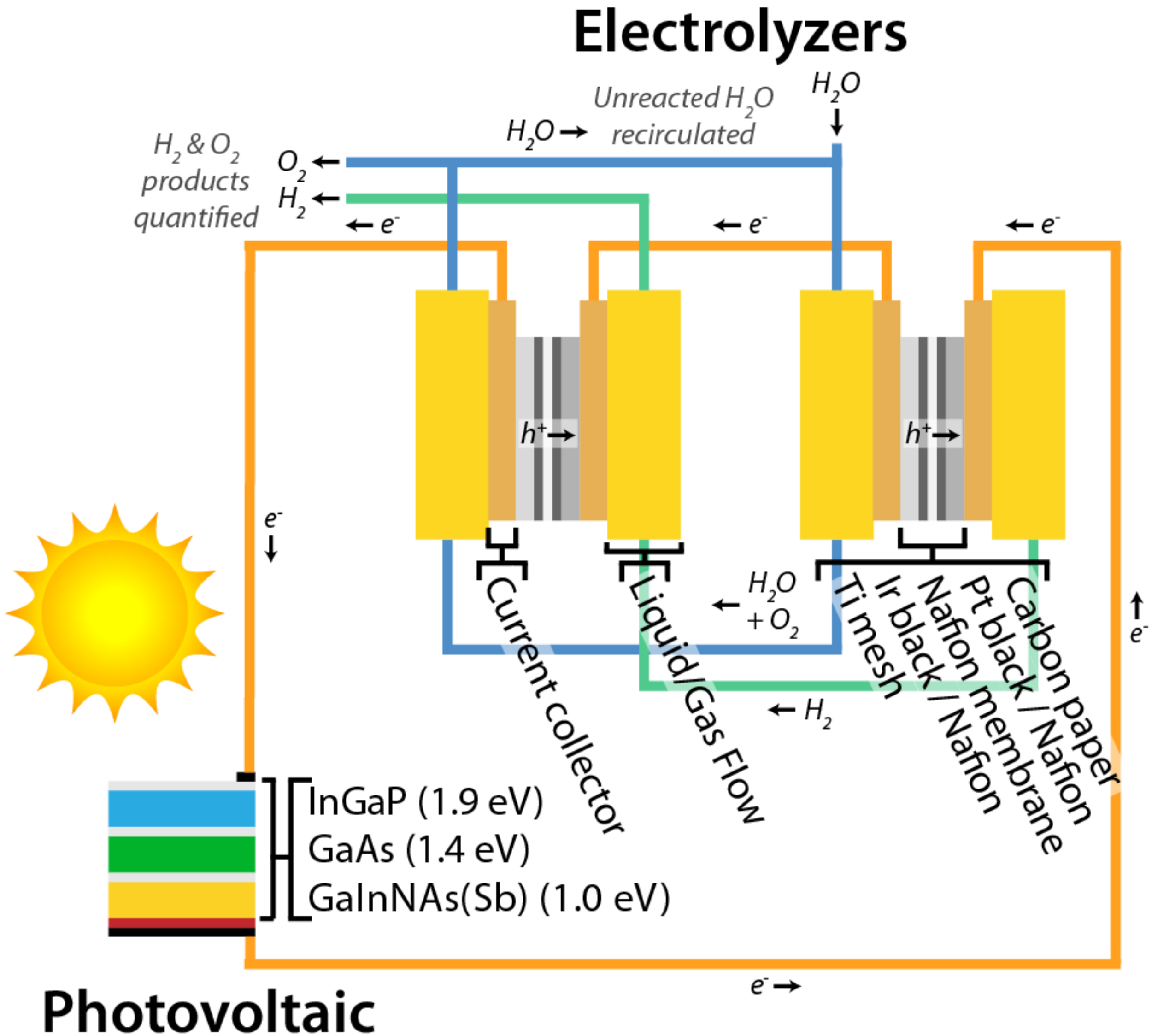
InGaP ($E_g = 1.895\ eV$)
GaAs ($E_g = 1.414\ eV$)
GaInNAs(Sb) ($E_g = 0.965\ eV$)

PV efficiency = 39 %

Fabricated by
Solar Junction

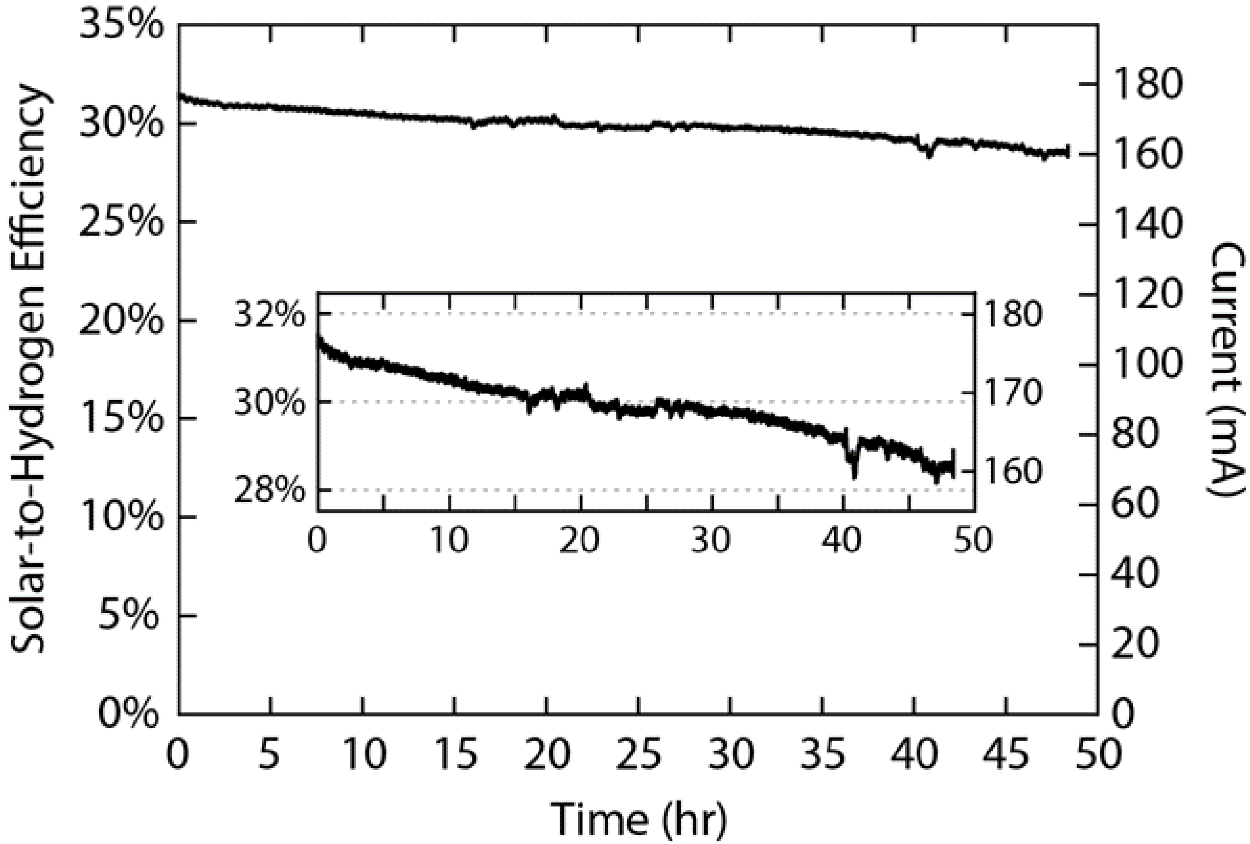


A dual electrolyzer setup



J. Jia, L.C. Seitz, J.D. Benck, Y. Huo, Y. Chen, J.W.D. Ng, T. Bilir, J.S. Harris, T.F. Jaramillo, *Nature Communications,* 7, 13237, **2016**.

Solar-to-Hydrogen (STH) Efficiency = 30%



$$STH = \frac{P_{out}}{P_{in}} = \frac{2 \times 1.18\text{V} \times 175.6mA}{42 \times 100mW/cm^2 \times 0.316cm^2} = \frac{414.3mW}{1328mW} = 31.2\%$$

Average STH over 48 hour experiment = 30.0%

J. Jia, L.C. Seitz, J.D. Benck, Y. Huo, Y. Chen, J.W.D. Ng, T. Bilir, J.S. Harris, T.F. Jaramillo, *Nature Communications,* 7, 13237, **2016**.

Hydrogen evolution reaction (HER) mechanisms

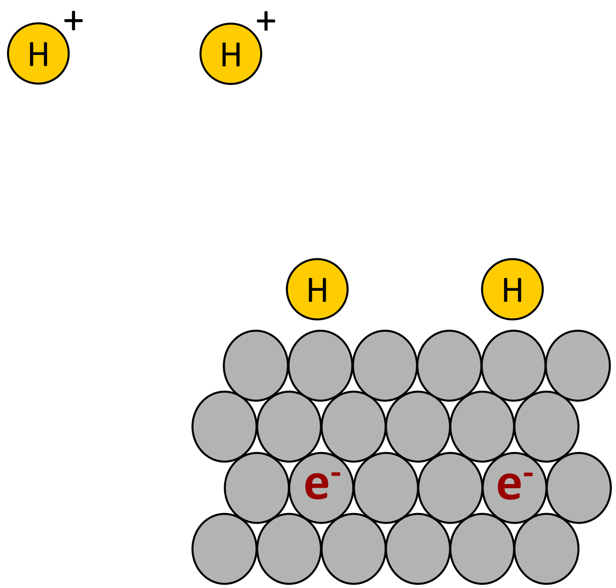
Overall Rxn: $2H^+ + 2e^- \rightarrow H_2$

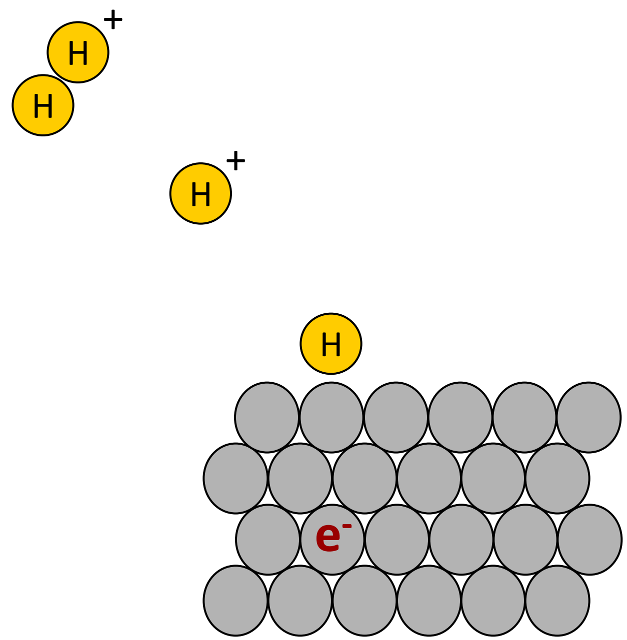
Volmer-Tafel
<u>(i.e. Langmuir-Hinshelwood)</u>

[**Volmer**] $\{H^+ + e^- \rightarrow H^*\} \times 2$
[**Tafel**] $2H^* \rightarrow H_2$

Volmer-Heyrovsky
<u>(i.e. to Eley-Rideal)</u>

[**Volmer**] $H^+ + e^- \rightarrow H^*$
[**Heyrovsky**] $H^+ + H^* + e^- \rightarrow H_2$



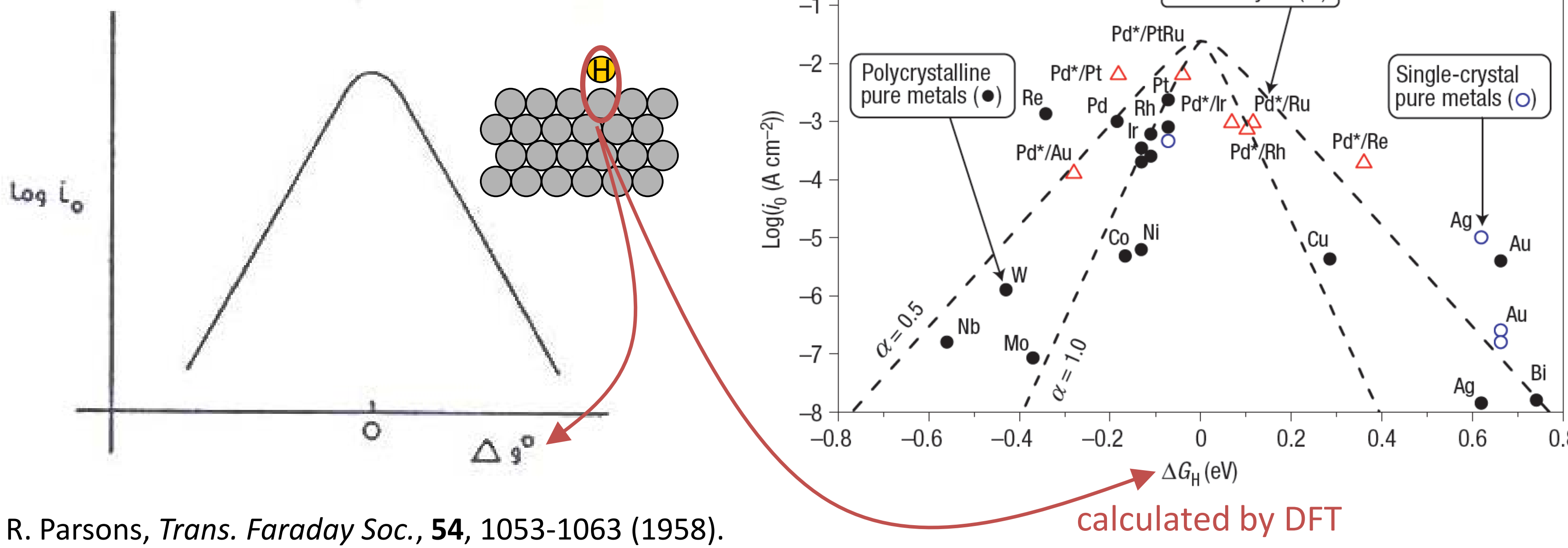


Design principles for H_2 evolution catalysts

mid-20th Century → early-21st Century

THE RATE OF ELECTROLYTIC HYDROGEN EVOLUTION
AND THE HEAT OF ADSORPTION OF HYDROGEN

By Roger Parsons
Dept. of Physical and Inorganic Chemistry, The University, Bristol 8
Received 10th December, 1957



R. Parsons, *Trans. Faraday Soc.*, **54**, 1053-1063 (1958).

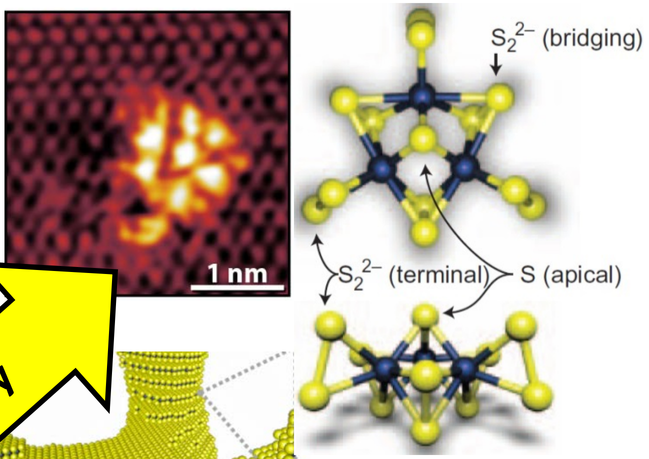
"Once this relation is established the complete current-voltage curve can be calculated for a metal, given the standard free energy of adsorption of hydrogen upon it."

J. Greeley, T.F. Jaramillo, J. Bonde, I. Chorkendorff, J.K. Nørskov, *Nature Materials*, **5**, 909-913 (2006).

Nano-structured MoS_2: Developing active, stable, earth abundant, scalable catalysts for hydrogen production

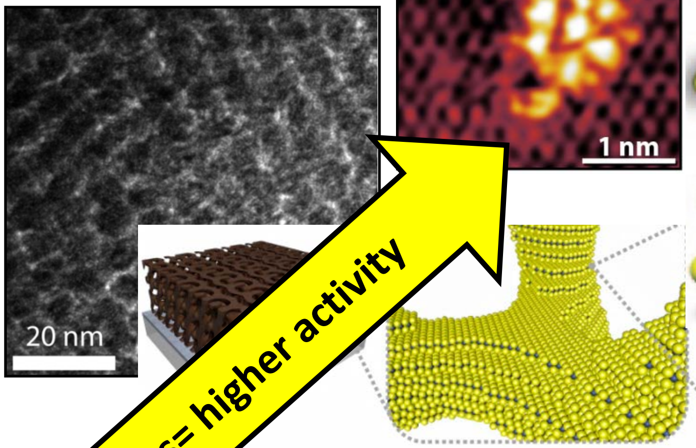
3. $[Mo_3S_{13}]^{2-}$ clusters

J. Kibsgaard, T.F. Jaramillo et. al., *Nature Chemistry,* **2014**, 6, 248.



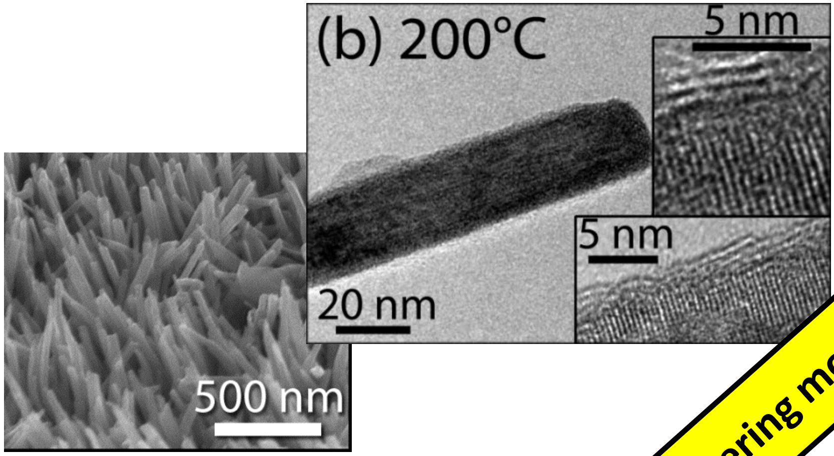
2. Mesoporous MoS_2 thin films

J. Kibsgaard, T.F. Jaramillo et. al., *Nature Materials,* **2012**, 11, 963.



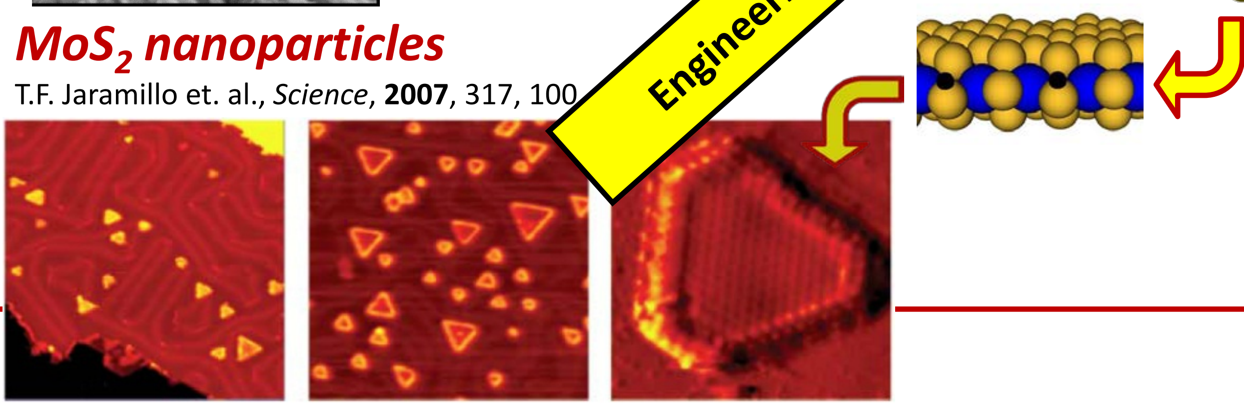
1. Core-shell MoO_3-MoS_2 nanowires

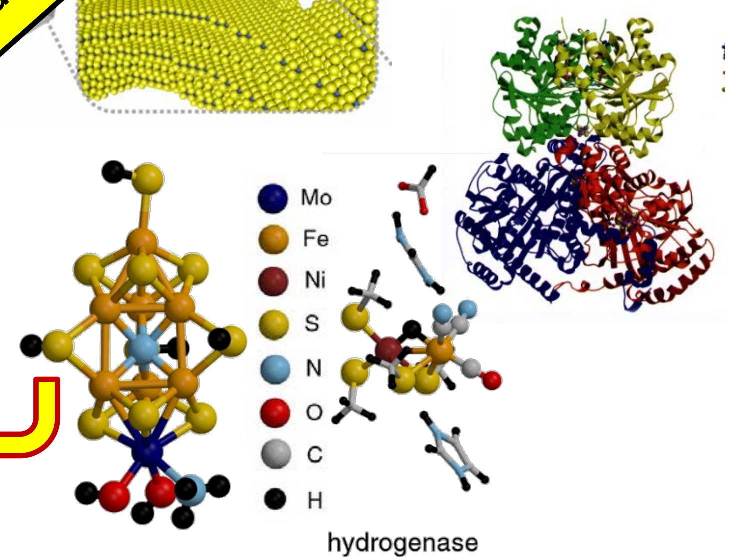
Z. Chen, T.F. Jaramillo et. al., *Nano Letters*, **2011**, 11, 4168.



MoS_2 nanoparticles

T.F. Jaramillo et. al., *Science*, **2007**, 317, 100

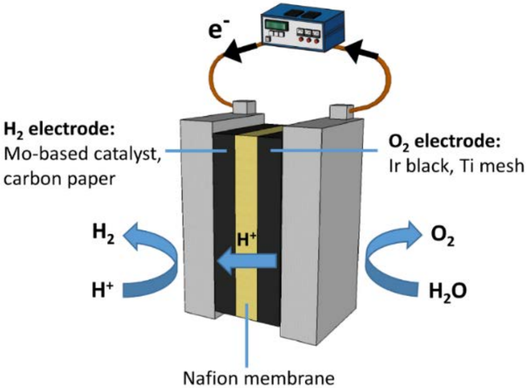


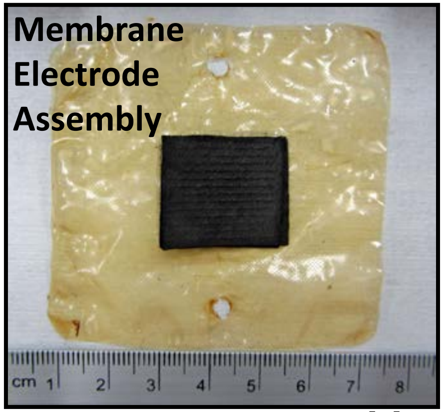


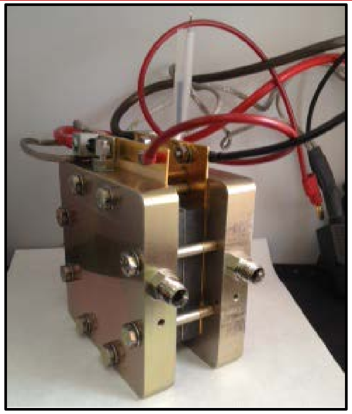
ΔG_H= -0.07 eV ΔG_H= -0.06 eV

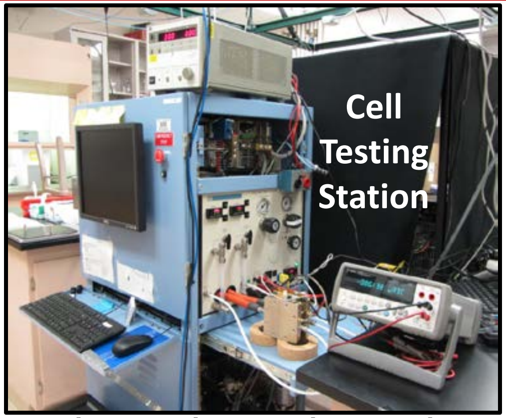
B. Hinnemann and J.K Nørskov,
J. Am. Chem. Soc. **2004**, 126, 3920.

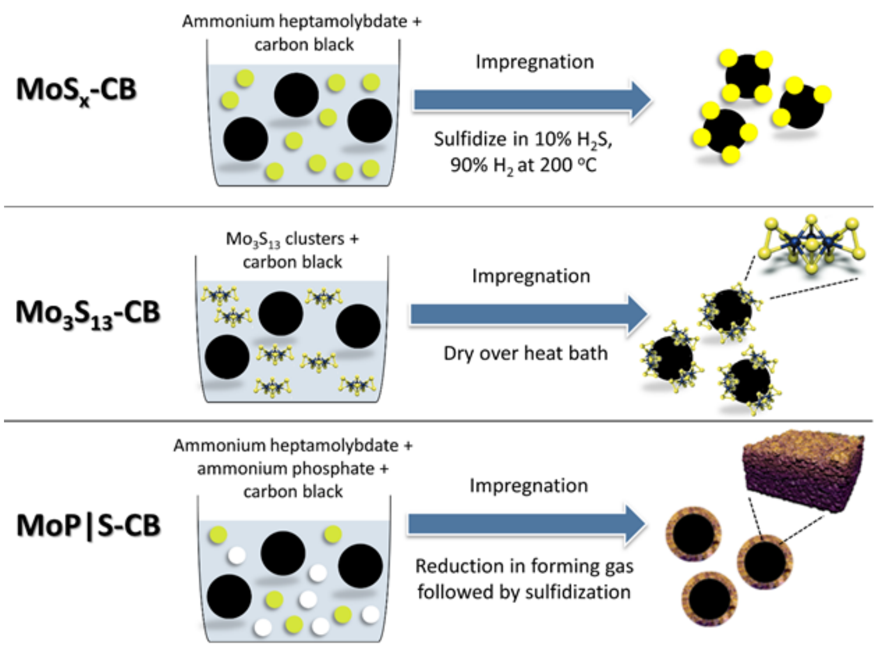
Device Integration: PEM Electrolyzers

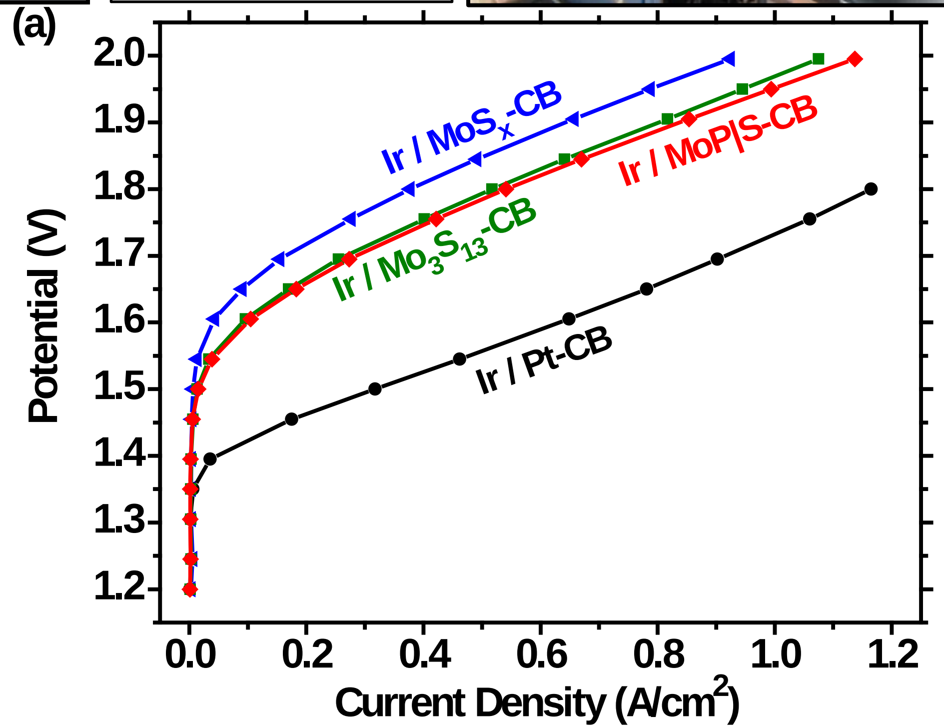






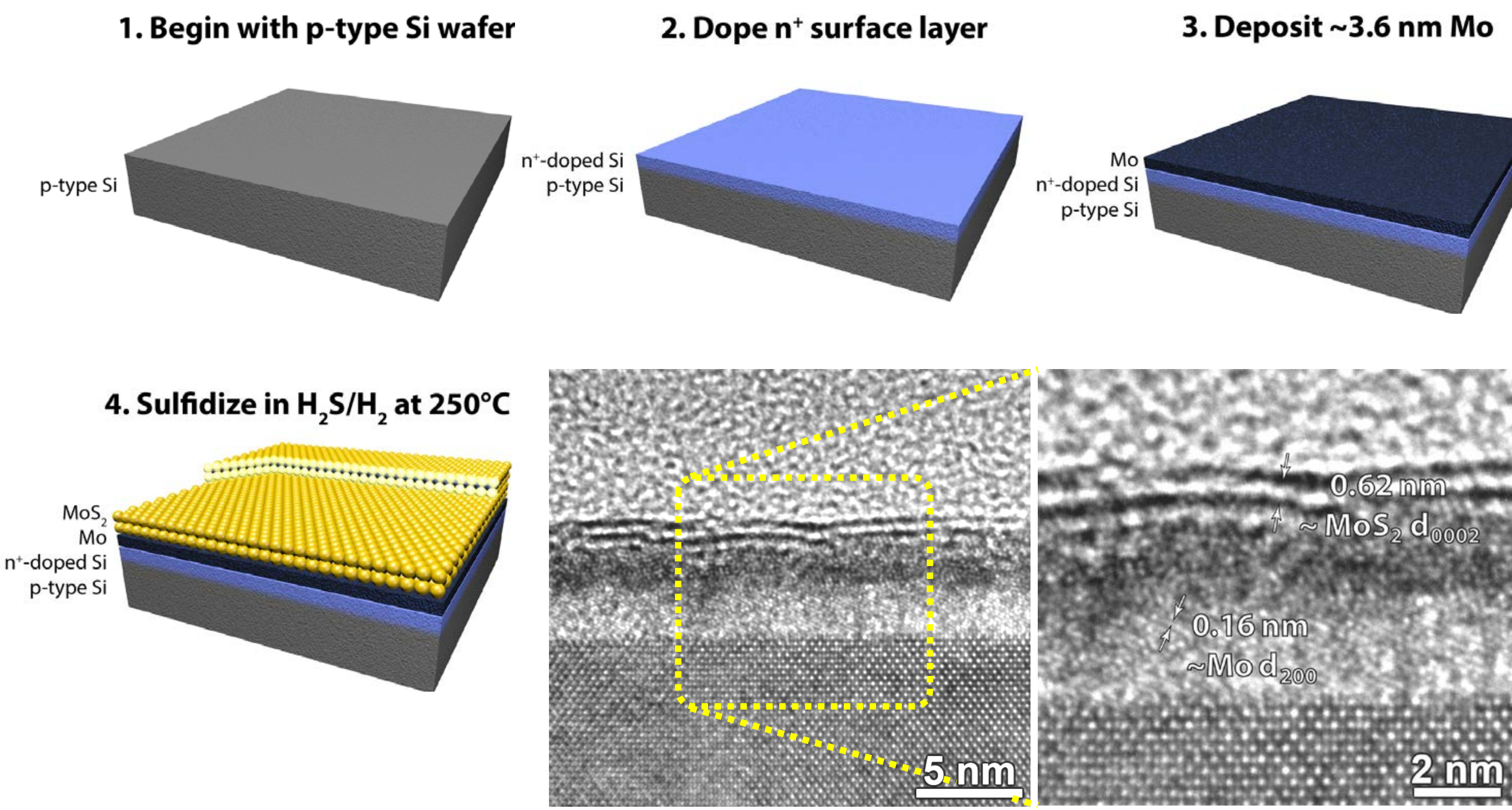






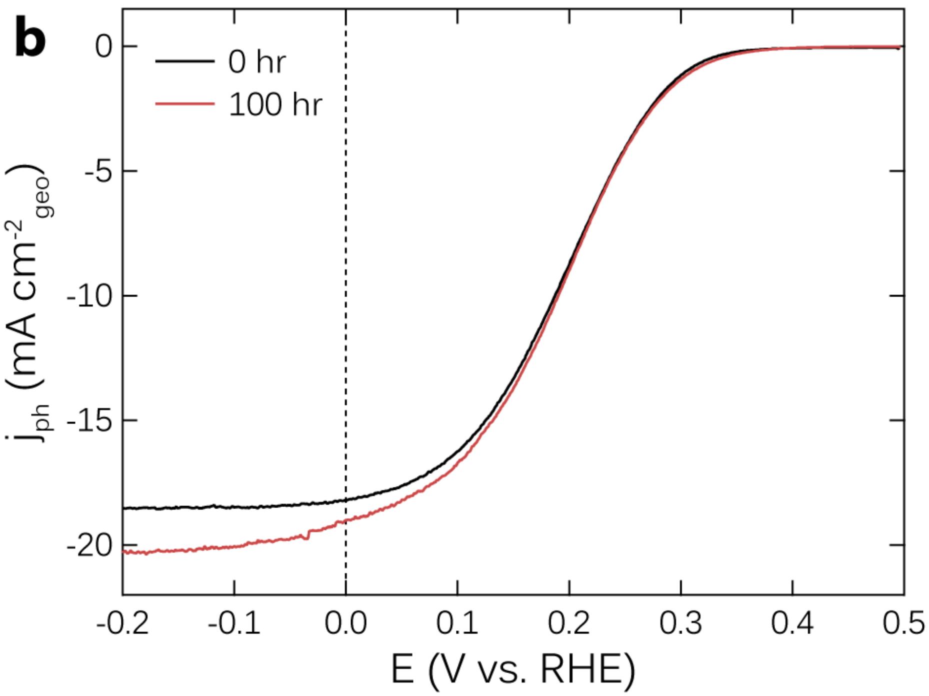
J.W.D. Ng, T.R. Hellstern, J. Kibsgaard, A.C. Hinckley, J.D. Benck, T.F. Jaramillo, *ChemSusChem*, **8** 3512-3519 (2015).

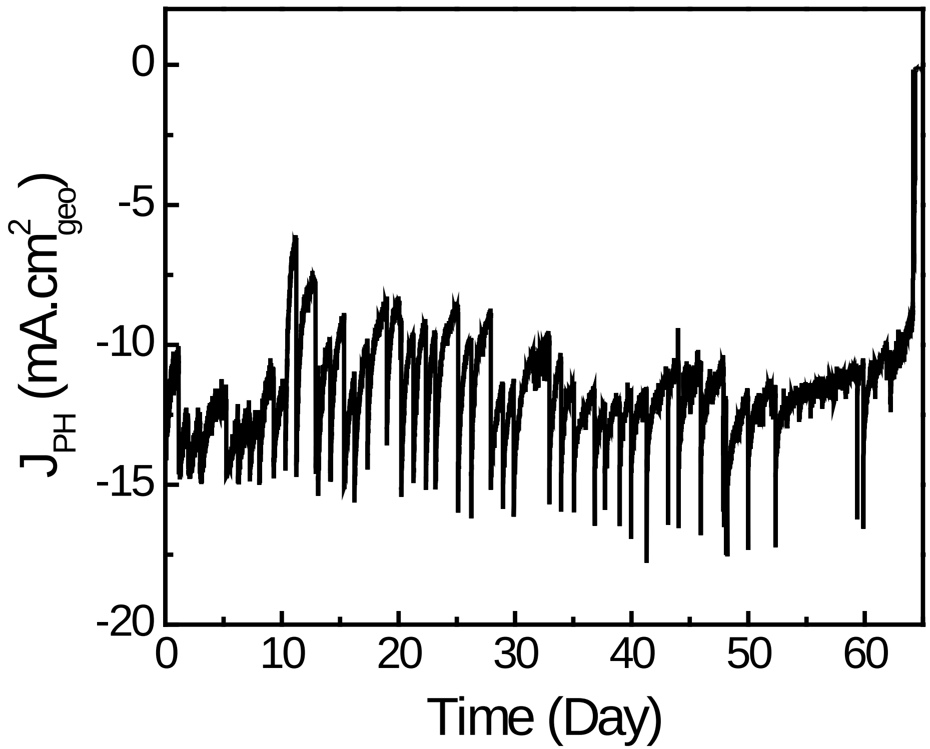
MoS_2-Si Photocathode Fabrication



J.D. Benck, S.-C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, and T.F. Jaramillo, *Advanced Energy Materials*, 4, 1400739, **2014**.

MoS_2-Si Stability & Activity





Stable over
> 100 hour experiment

Stable over
> 1500 hour experiment

J.D. Benck, S.-C. Lee, K.D. Fong, J. Kibsgaard, R. Sinclair, and T.F. Jaramillo, *Advanced Energy Materials*, 4, 1400739, **2014**.

L.A. King, T.R. Hellstern, J. Park, R. Sinclair, T.F. Jaramillo, *ACS Applied Materials & Interfaces* (accepted and in press, **2017**)

Hydrogen (H_2)

Carbon-based fuels and chemicals

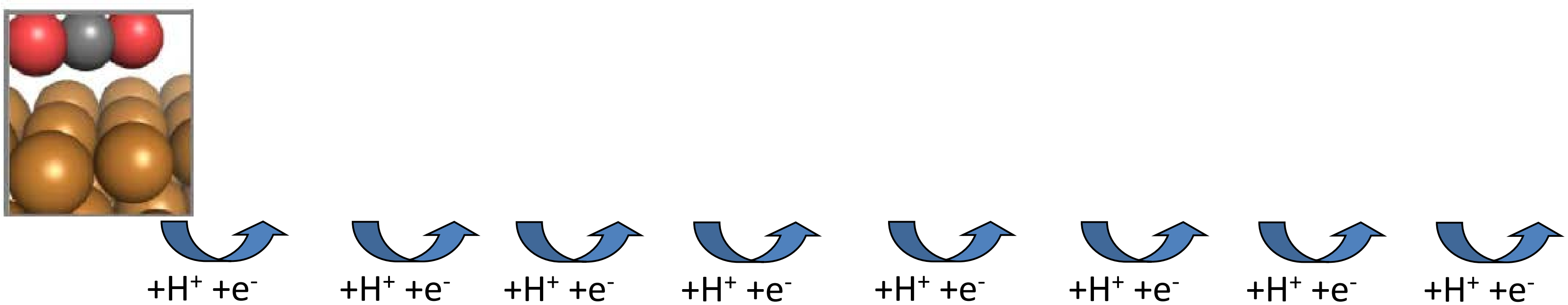
Ammonia (NH_3)

Thermodynamic & Kinetic Considerations

Y. Hori, "Electrochemical CO_2 reduction on metal electrodes" within *Modern Aspects of Electrochemistry*, Number 42, Edited by C. Vayenas et. al., Springer, New York, 2008.

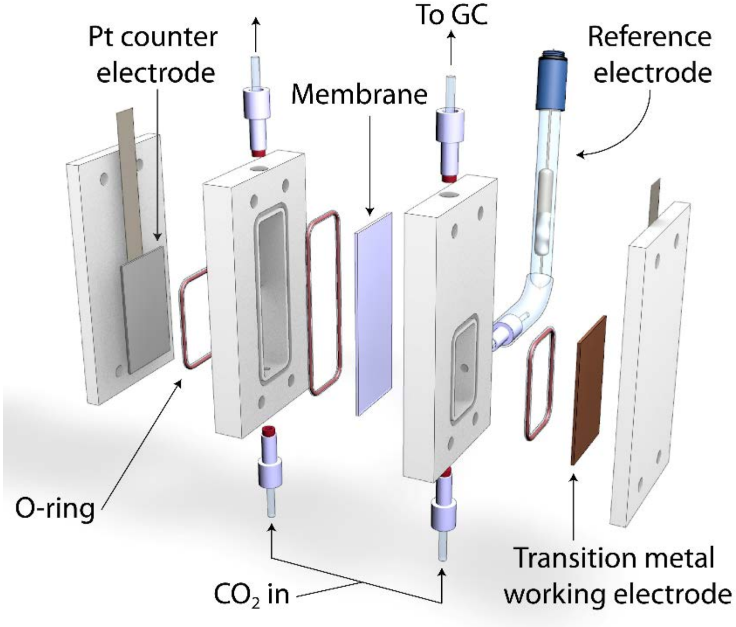
Reaction			E^0 vs. RHE
$2H^+ + 2e^-$	←→	H_2	0.00 V
$CO_2 + 2H^+ + 2e^-$	←→	$CO + H_2O$	- 0.11 V
$CO_2 + 8H^+ + 8e^-$	←→	$CH_4 + 2H_2O$	+ 0.16 V
$2CO_2 + 12H^+ + 12e^-$	←→	$C_2H_4 + 4H_2O$	+ 0.07 V
$2CO_2 + 12H^+ + 12e^-$	←→	$C_2H_5OH + 3H_2O$	+ 0.08 V
$3CO_2 + 18H^+ + 18e^-$	←→	$C_3H_7OH + 5H_2O$	+ 0.09 V

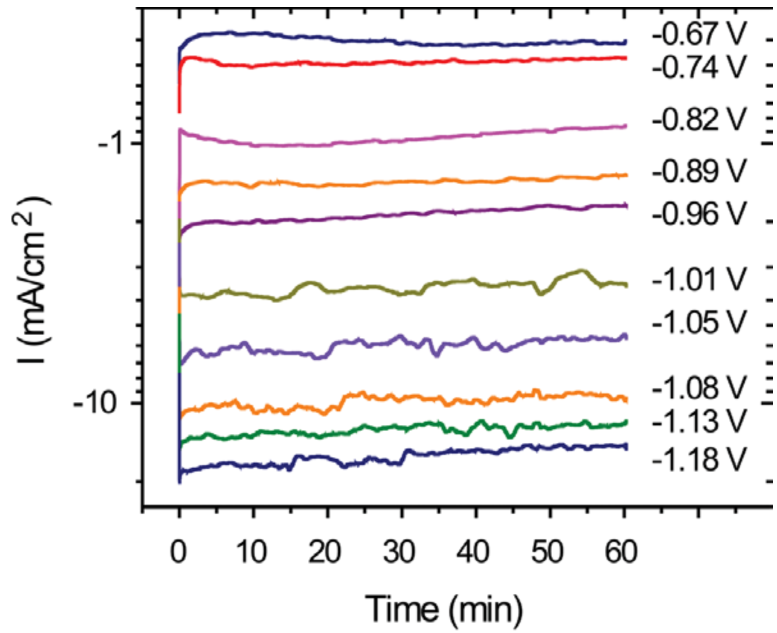
All values are close to the H_2 evolution potential (0.00 V).



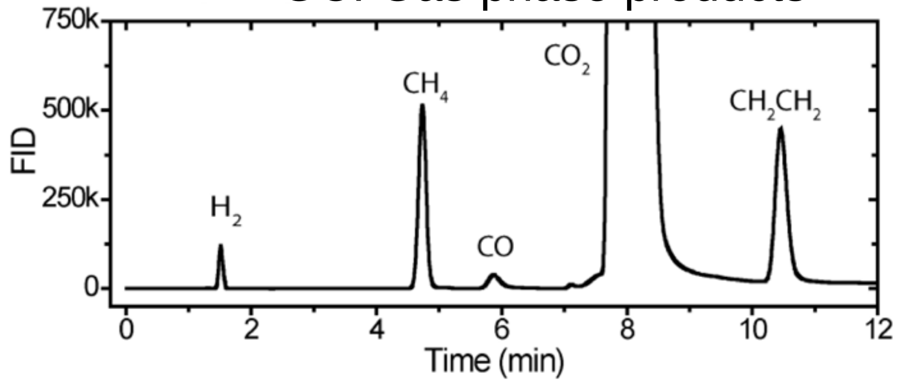
A. Peterson, F. Abild-Pederson, F. Studt, J. Rossmeisl, J.K. Nørskov, *Energy& Environmental Science* v3 (**2010**) 1311-1315.

CO_2 reactor design and development

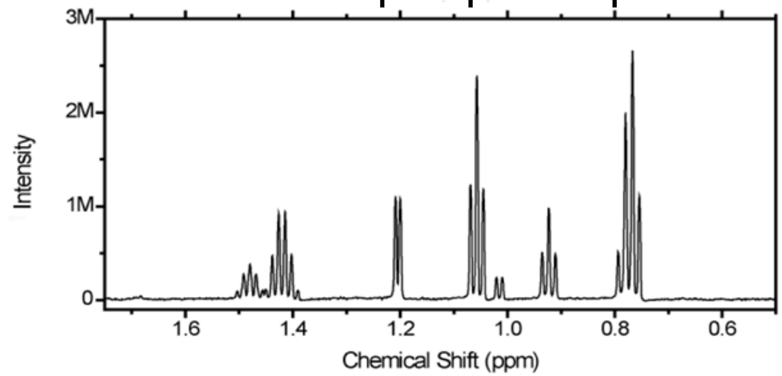




GC: Gas phase products

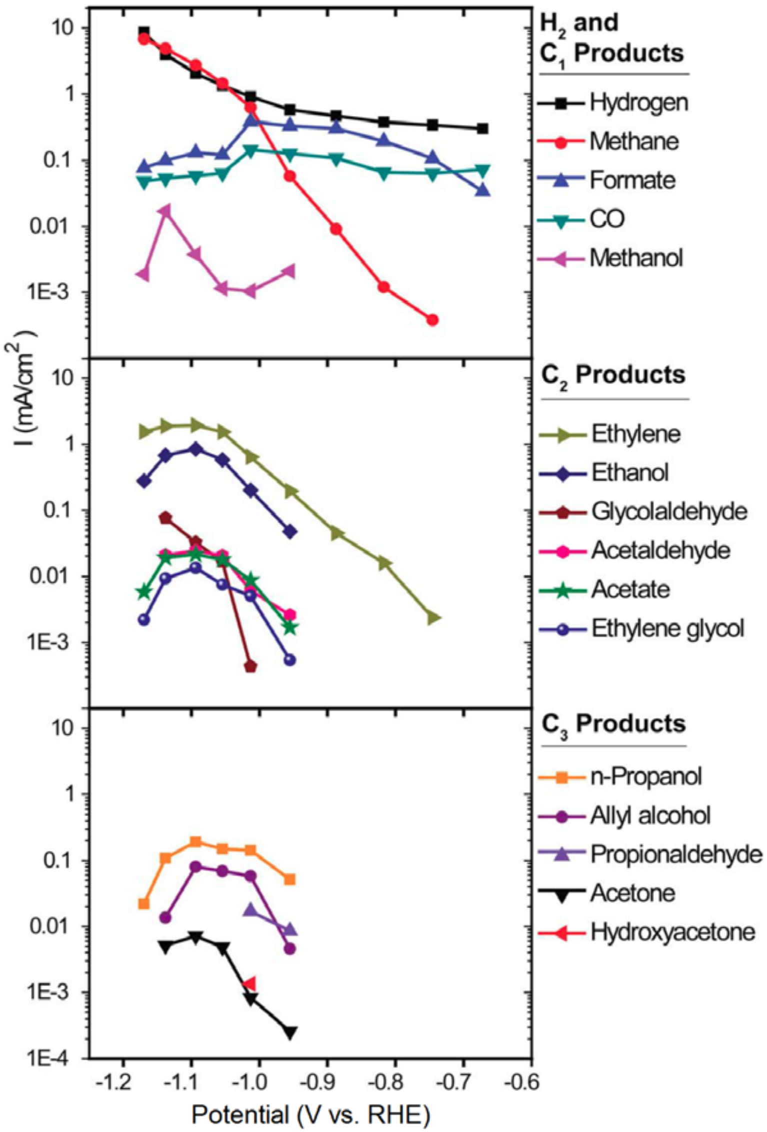


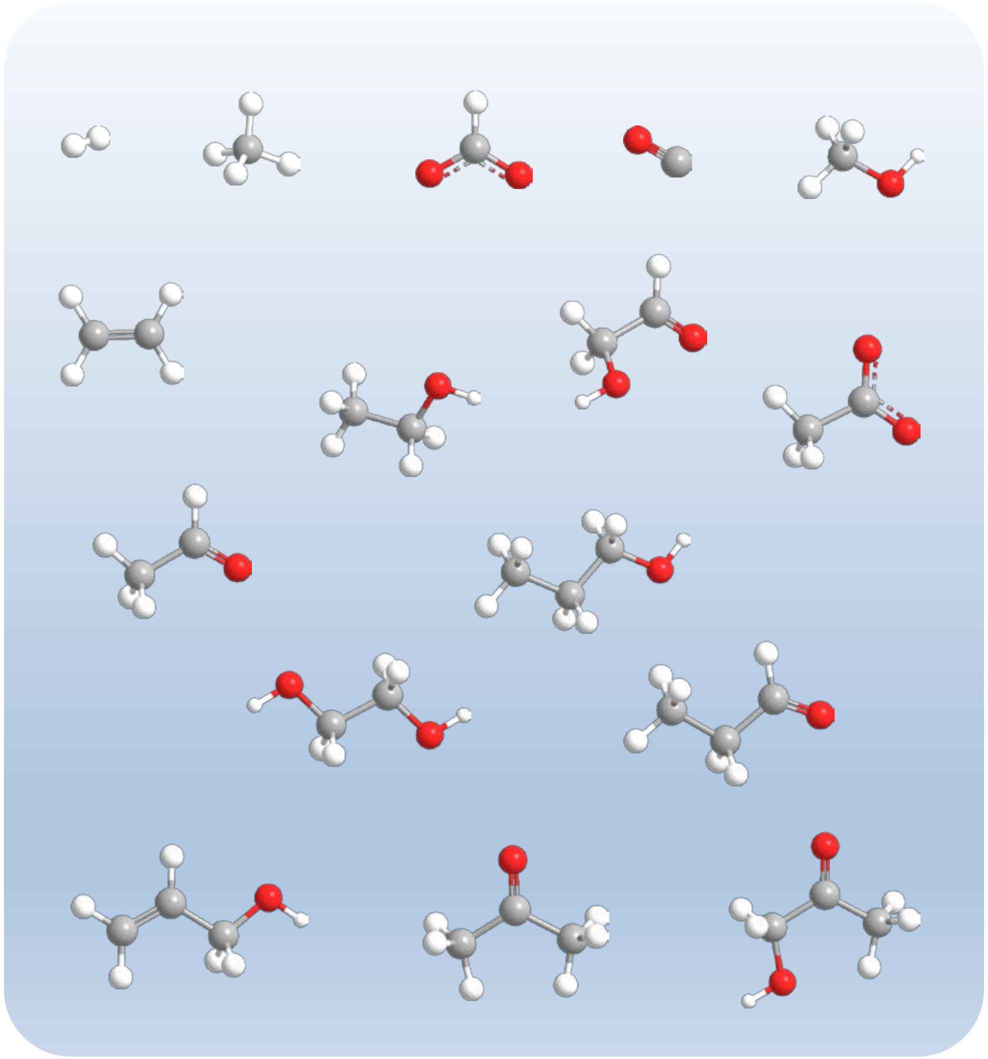
NMR: Liquid phase products



K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *Energy Environ. Sci.*, 2012, 5, 7050-7059.
T. Hatsukade, K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *PCCP*, 2014, 16, 13814.

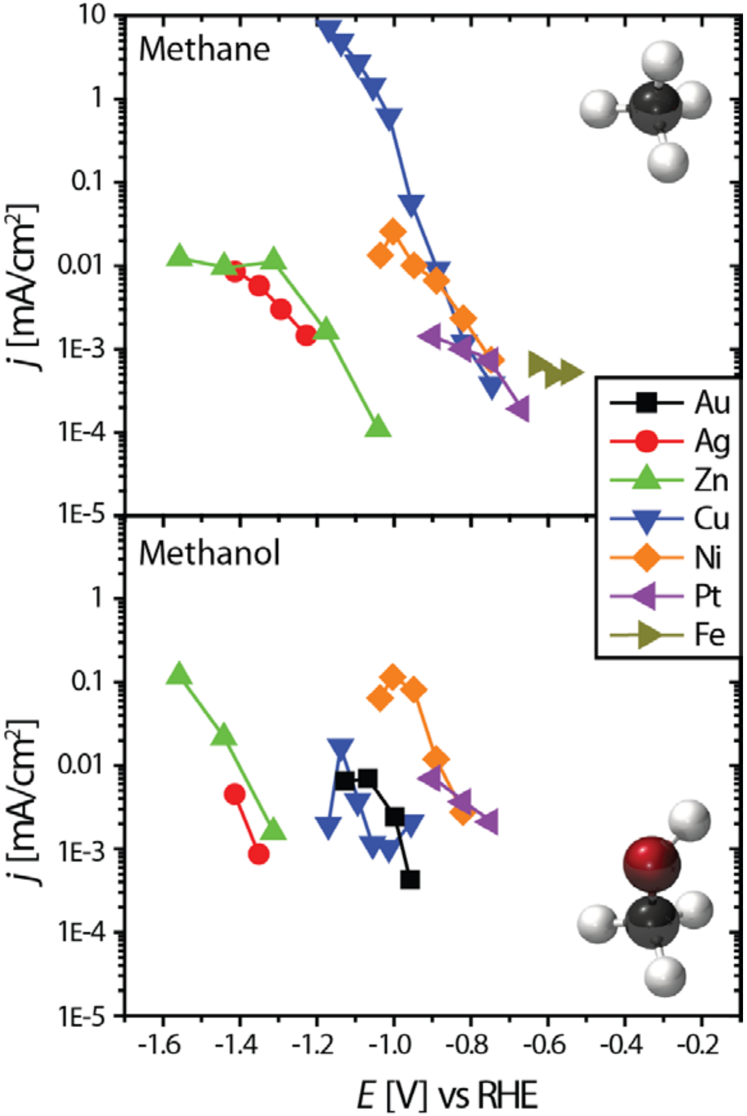
16 different reaction products from a Cu catalyst

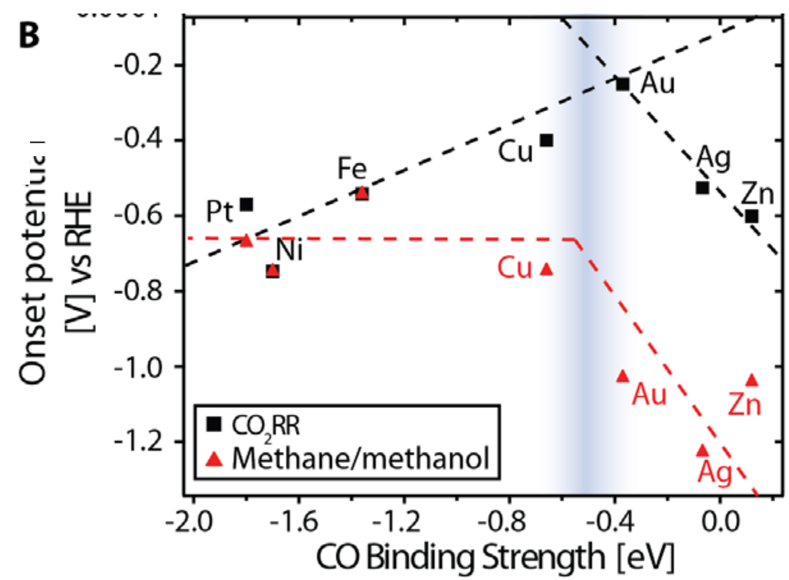


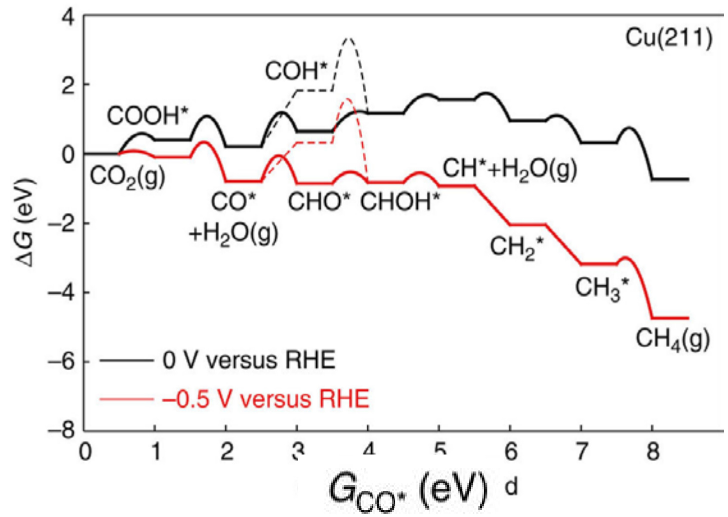


K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *Energy Environ. Sci.*, 2012, 5, 7050-7059.

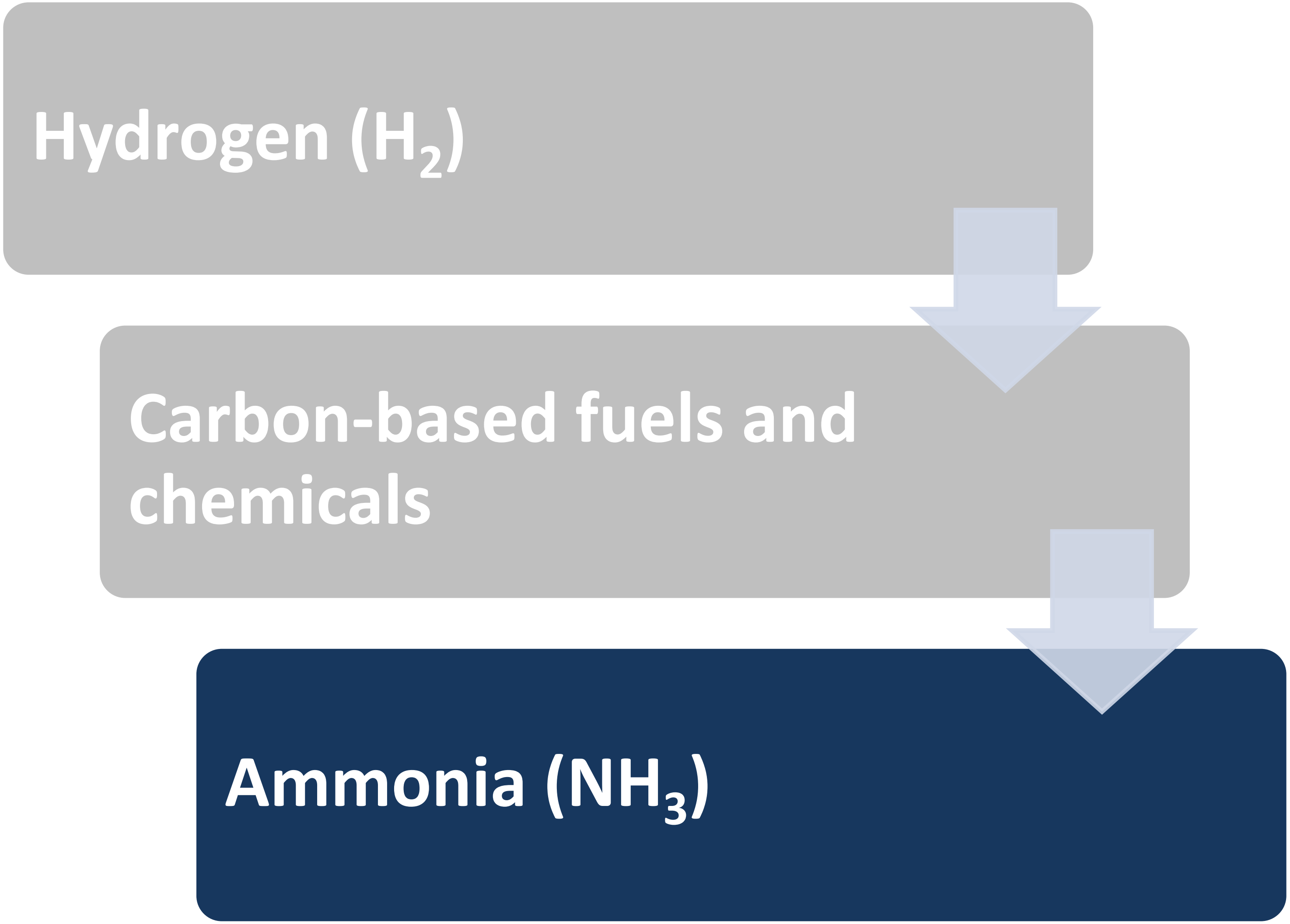
Understanding pathways to C_1 products across different transition metal catalysts



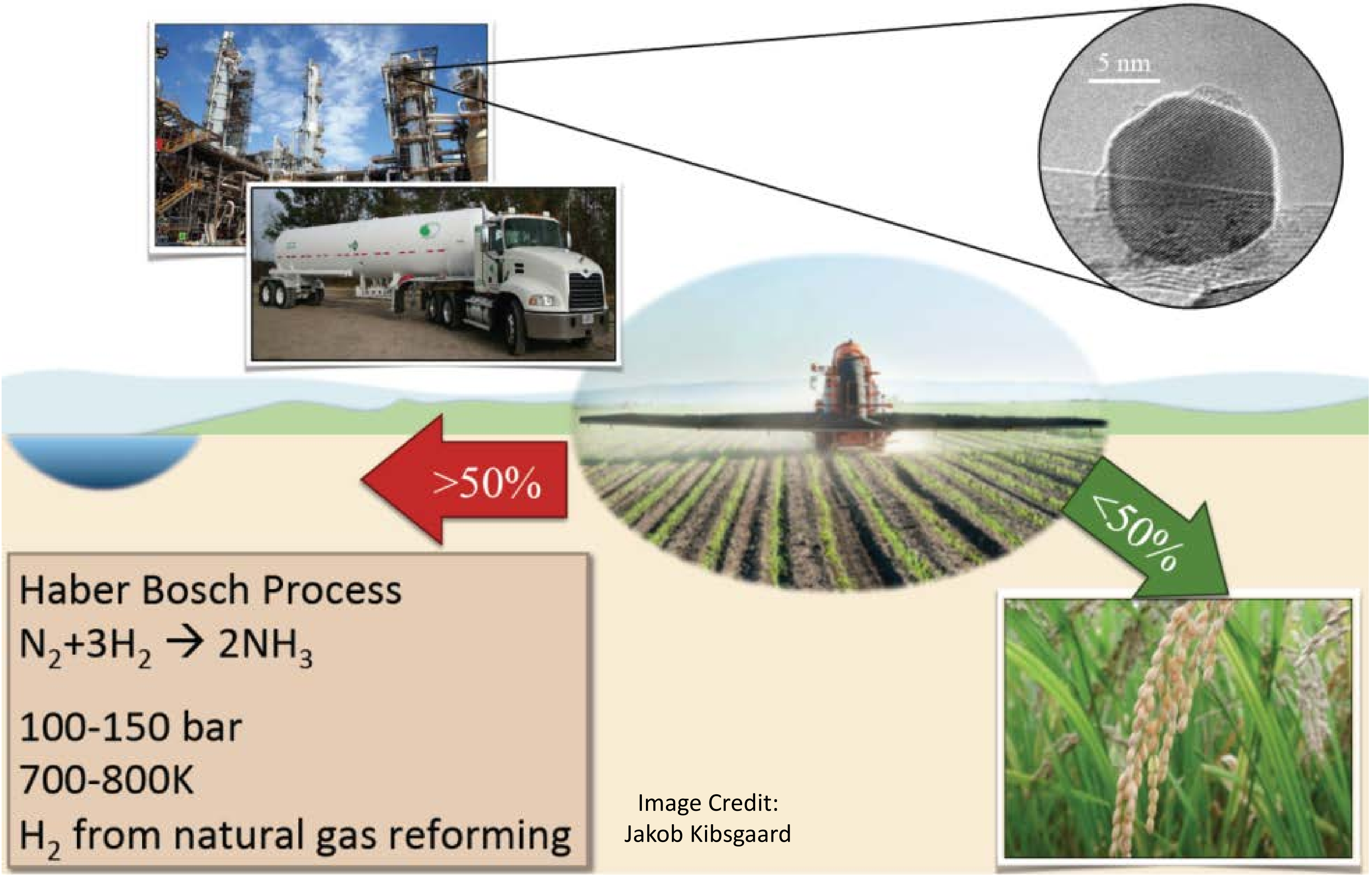




K.P. Kuhl, T. Hatsukade, E.R. Cave, D.N. Abram, J. Kibsgaard, and T.F. Jaramillo, *J. Am. Chem. Soc.*, 2014, 136, 14107-14113.
X. Liu*, J. Xiao*, H. Peng, X. Hong, K. Chan, and J.K. Nørskov, *Nat. Comm.*, 2017, 8, 15438.

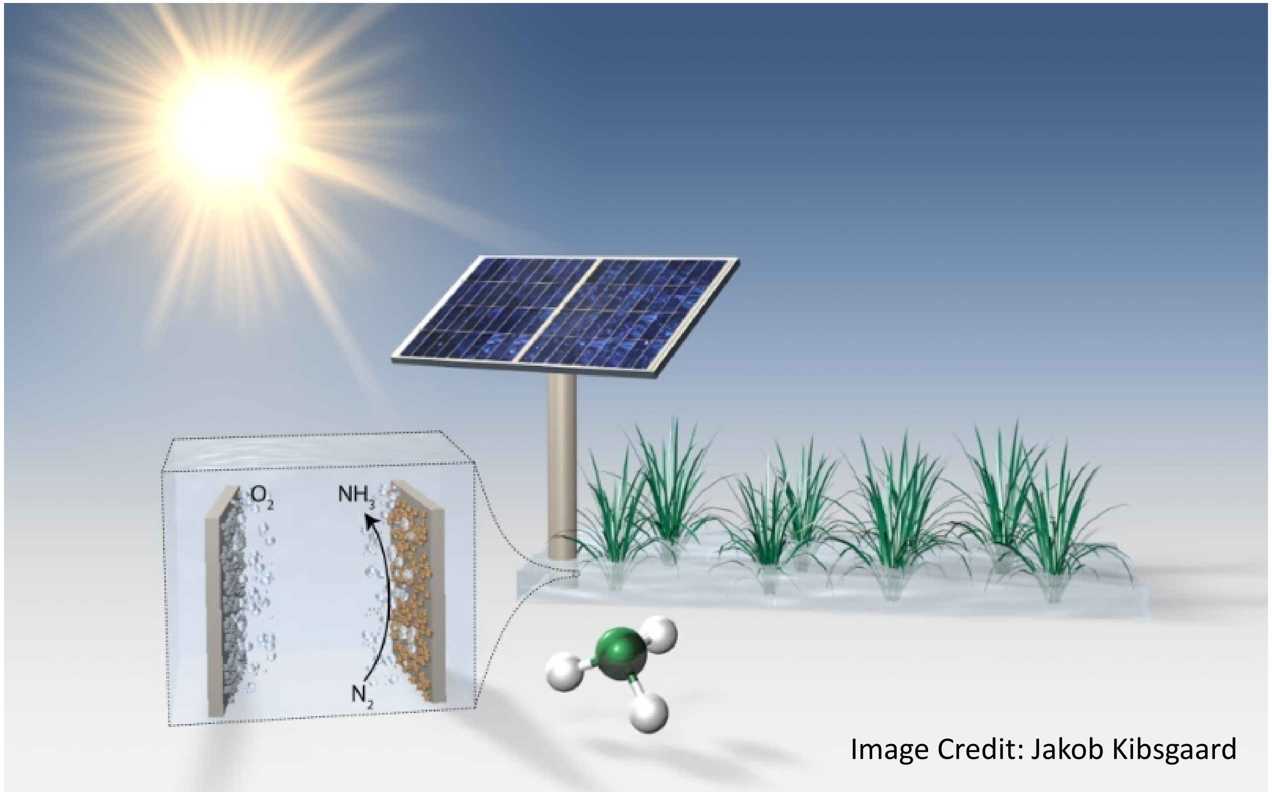

Hydrogen (H_2)
Carbon-based fuels and chemicals
Ammonia (NH_3)

The Haber Bosch Process – Industrial Ammonia Synthesis



Appl, M. *Ullmann's Encyclopedia of Industrial Chemistry* (2000).
Ammonia, <http://ietd.iipnetwork.org/content/ammonia> (2014).

Sustainable ammonia production



Key Goal: Aqueous electrochemical NH_3 production

- Directly from N_2 and H_2O
- Decentralized fertilizer production, produced as-needed
- Renewably powered (wind/solar)

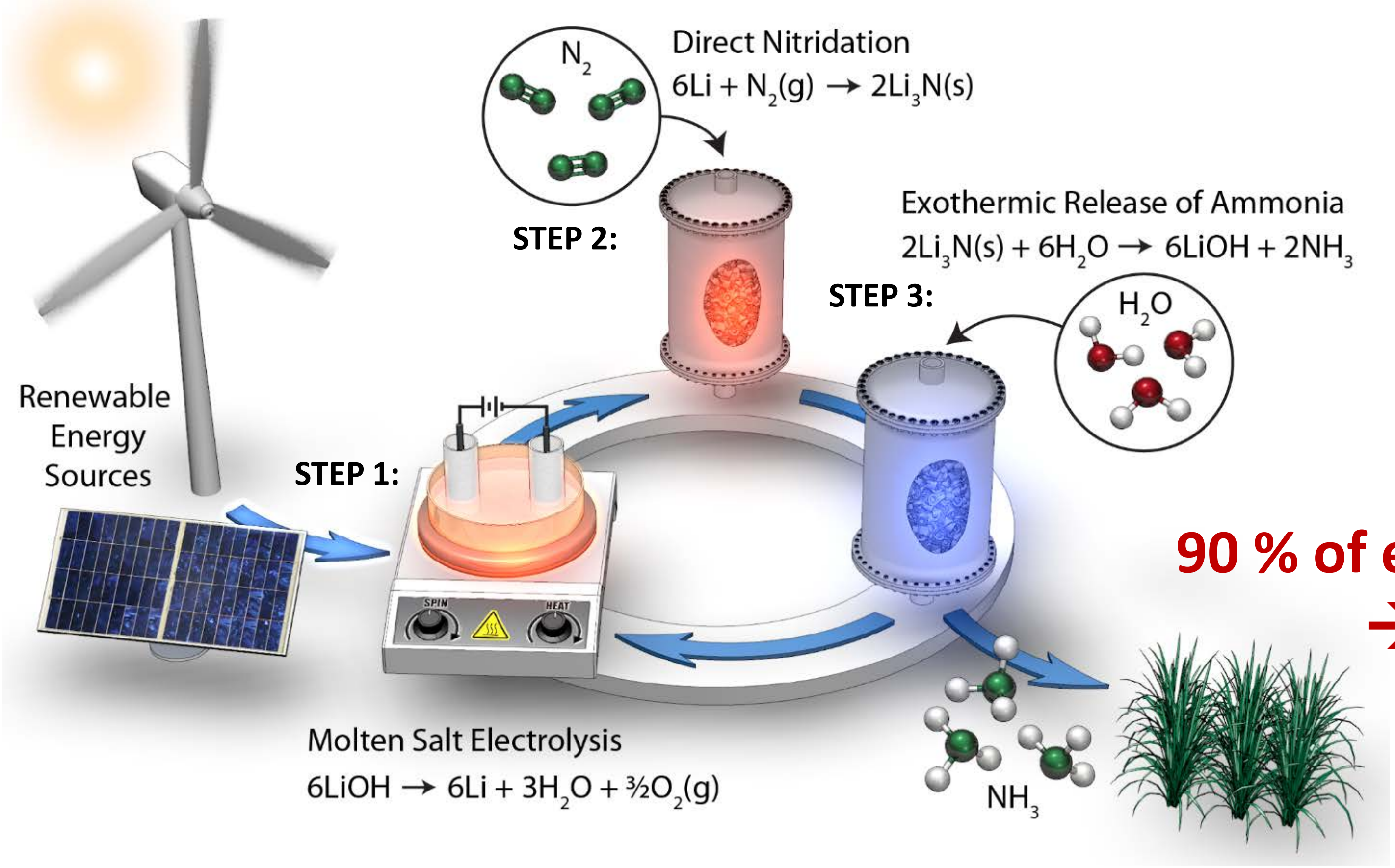
Many challenges and opportunities for catalyst development!

Stepwise cycling process to circumvent H_2 evolution

STEP 1: $6LiOH \longrightarrow 6Li + 3H_2O + 3/2O_{2(g)}$

STEP 2: $6Li + N_{2(g)} \longrightarrow 2Li_3N_{(s)}$

STEP 3: $2Li_3N_{(s)} + 6H_2O \longrightarrow 6LiOH + 2NH_3$

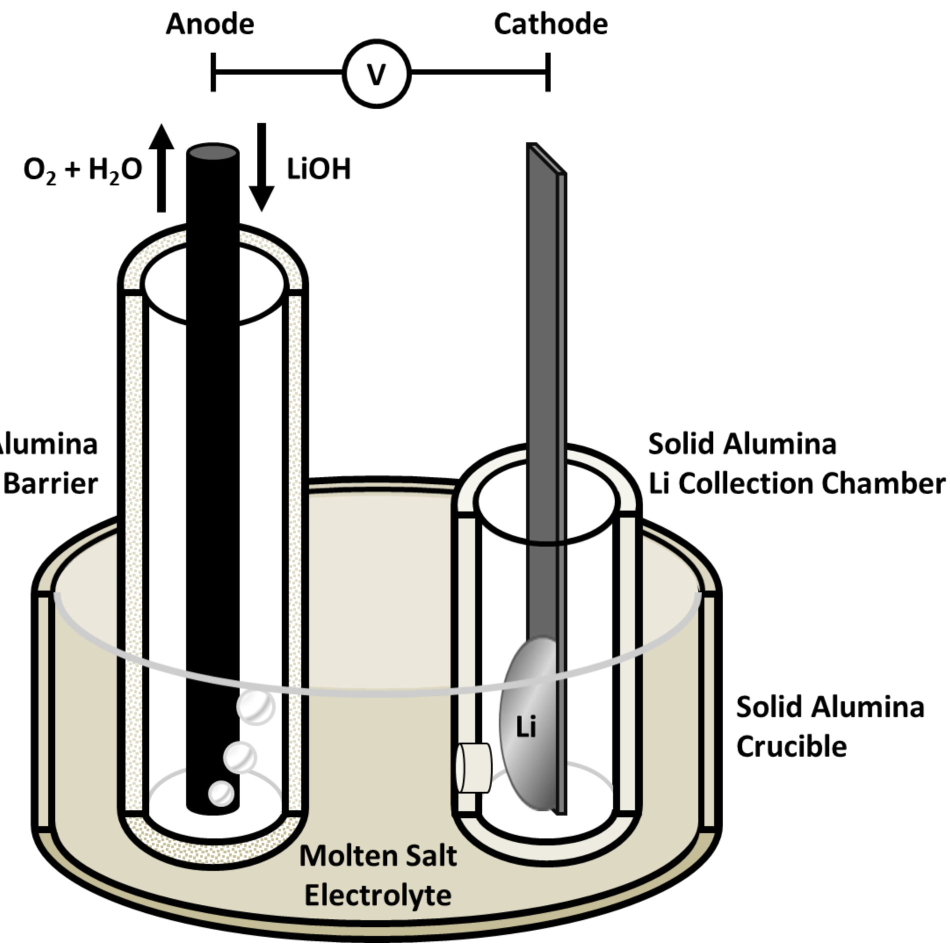


90 % of electrons → NH_3

J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, T. F. Jaramillo, J. K. Nørskov *Energy Environ. Sci.* **10** 1621 (2017).

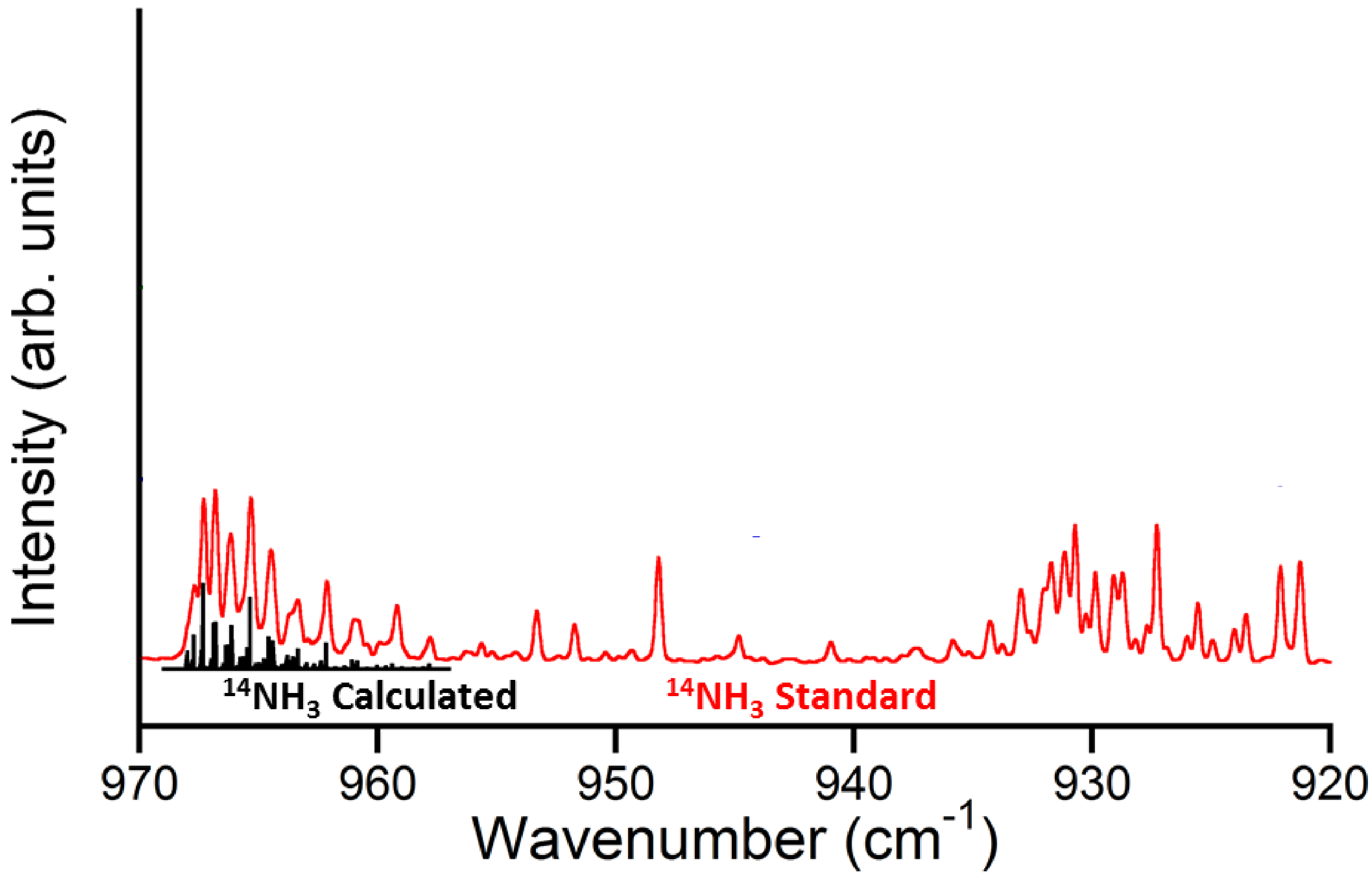
LiOH Electrolysis – Electrochemical Cell Design

- LiOH-LiCl melt at anode
- LiCl-KCl melt in main chamber and at cathode
- 350-450 ℃ operating temperature
- Performed in glove box- O_2 and H_2O evolution detected
- Diffusion barrier improves yield substantially due to prevention of adverse reactions at the cathode



J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, T. F. Jaramillo, J. K. Nørskov
Energy Environ. Sci. **10** 1621 (2017).

Ammonia Detection Methods: Gas Phase FTIR and Isotopic Labeling



- Specific signal for verification of ammonia production
- Isotopic studies prove that ammonia was produced from N_2

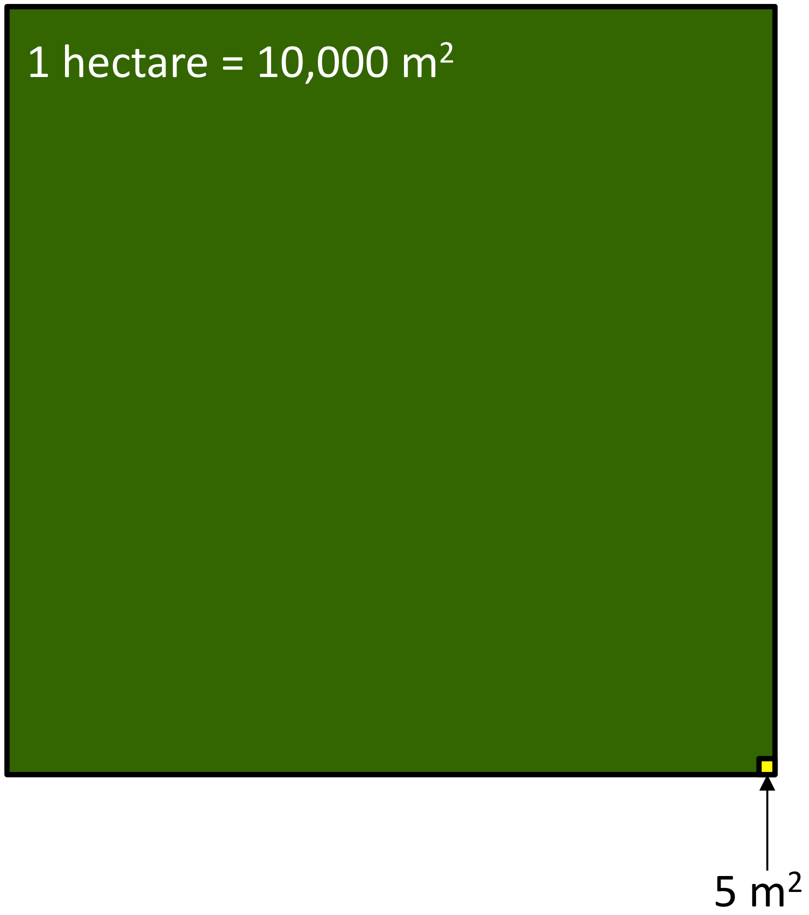
J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, T. F. Jaramillo, J. K. Nørskov *Energy Environ. Sci.* **10** 1621 (2017).

Solar-driven NH_3 feasibility: Land Area

Typical agricultural field requires:

100 kg NH_3/hectare/yr

For a 100% Faradaic Efficiency process:
Only 5 m^2 of solar cells needed!

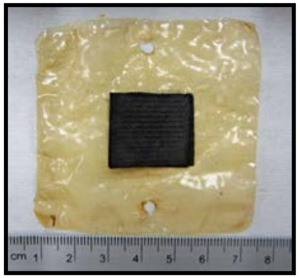


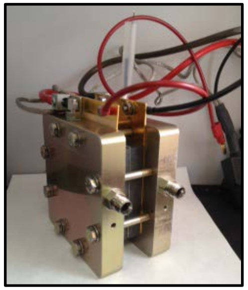
Sawyer, J.; Nafziger, E.; Randall, G.; Bundy, L.; Rehm, G.; Joern, B. Concepts and Rationale for Regional Nitrogen Rate Guidelines for Corn; Iowa State University-University Extension PM: Ames, IA, 2015.

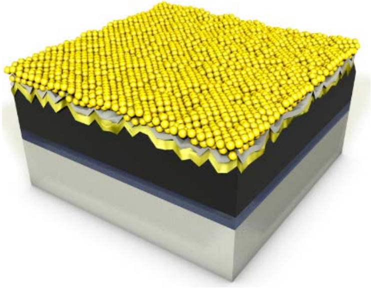
Singh, A. R.; Rohr, B. A.; Schwalbe, J. A.; Cargnello, M.; Chan, K.; Jaramillo, T. F.; Chorkendorff, I.; Nørskov, J. K. *ACS Catalysis* **2016**, *7*, 706.

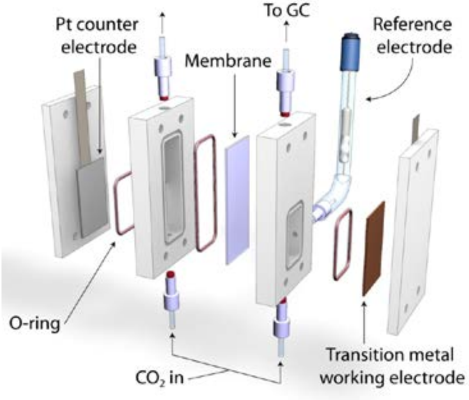
Summary & Conclusions

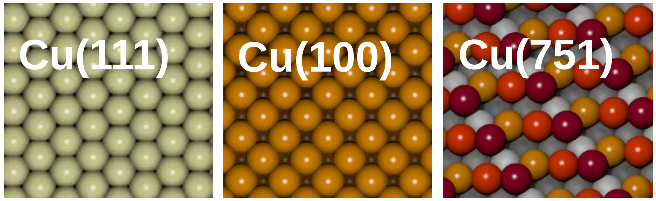
- **Sustainable pathways to fuels and chemicals are promising.**
- **Development of catalysts and new approaches involving zero or low-content precious metals**
- **Integration of non-precious H_2 catalysts into electrolyzers & photocathodes**
- **Catalyst and process development for CO_2/CO reduction and for N_2 electrochemistry.**

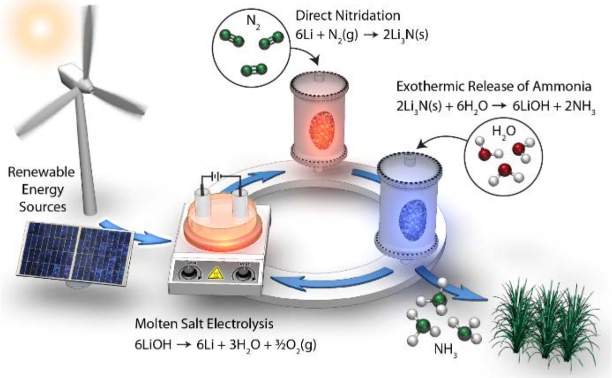


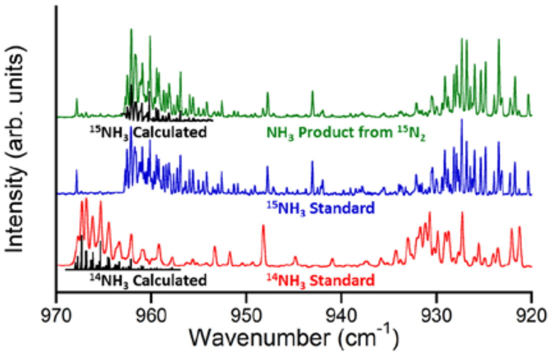












Jaramillo Laboratory

PhD Students
- Jeremy Feaster
- Jon Snider
- Alaina Strickler
- Reuben Britto
- Brenna Gibbons
- Zhihua (Bill) Chen
- Michael Boyd
- Stephanie Nitopi
- Alan Landers
- John Lin
- Joel Sánchez
- Eduardo Valle
- David Palm
- Micha Ben-Naim
- McKenzie Hubert
- Melissa Kreider

Post-doctroral Researchers
- Dr. Antaeres Antoniuk Pablant
- Dr. Michaela Burke-Stevens
- Dr. Ches Upham
- Dr. Dong Un (Daniel) Lee
- Dr. Josh McEnaney
- Dr. Drew Higgins
- Dr. Amber Janda
- Dr. Carlos Morales-Guio
- Dr. Adam Nielander
- Dr. Lei Wang
- Dr. Marat Orazov
- Dr. Andrew Wong

SLAC Research Associate
Dr. Alessandro Gallo

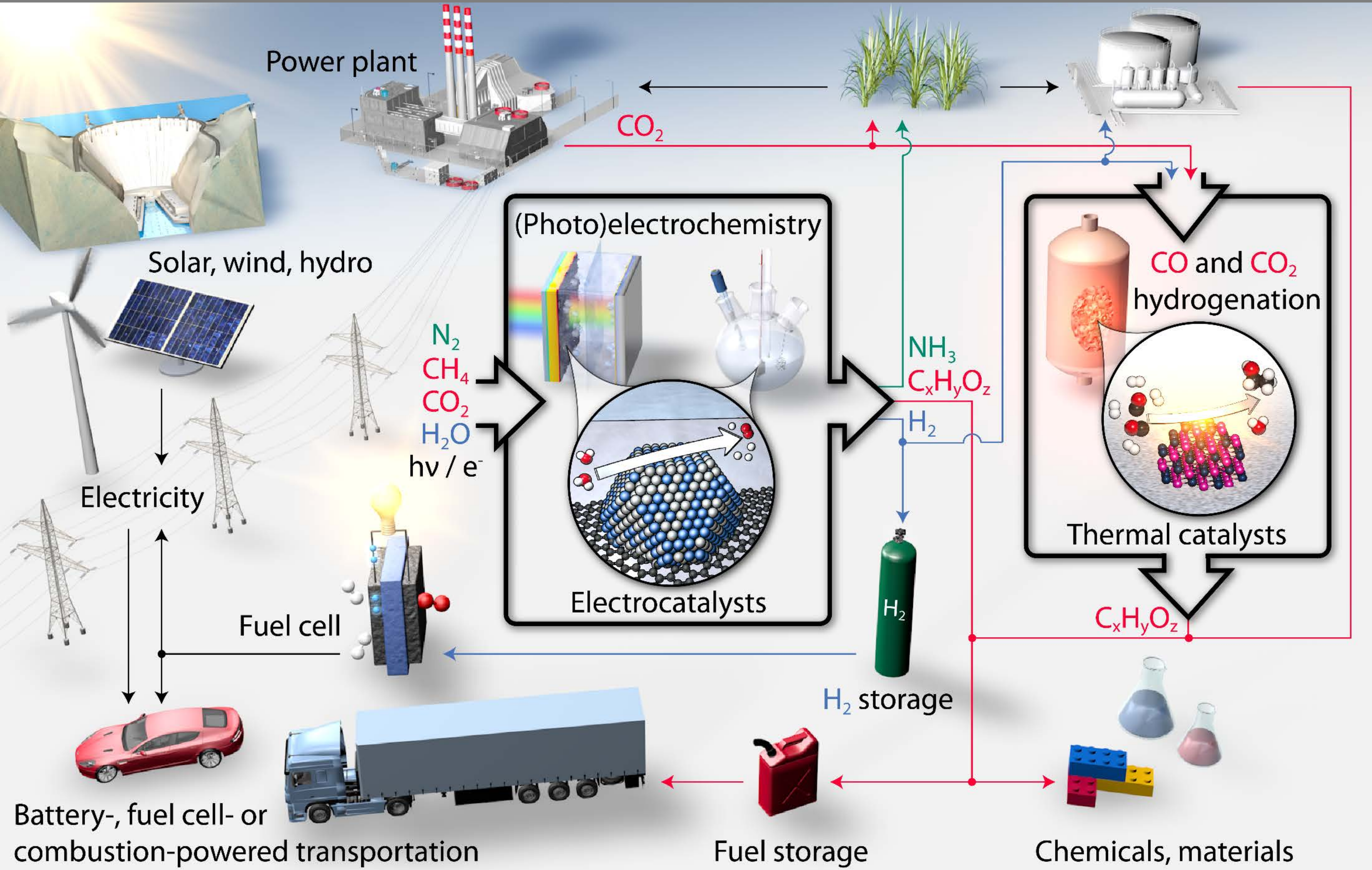
Staff Scientists
Dr. Christopher Hahn
Dr. Melis Duyar
Dr. Drew Higgins
Dr. Laurie King

Visiting Scholars
Yusaku Nishimura

Undergraduate Researchers
Alex Young
Alvaro Simán

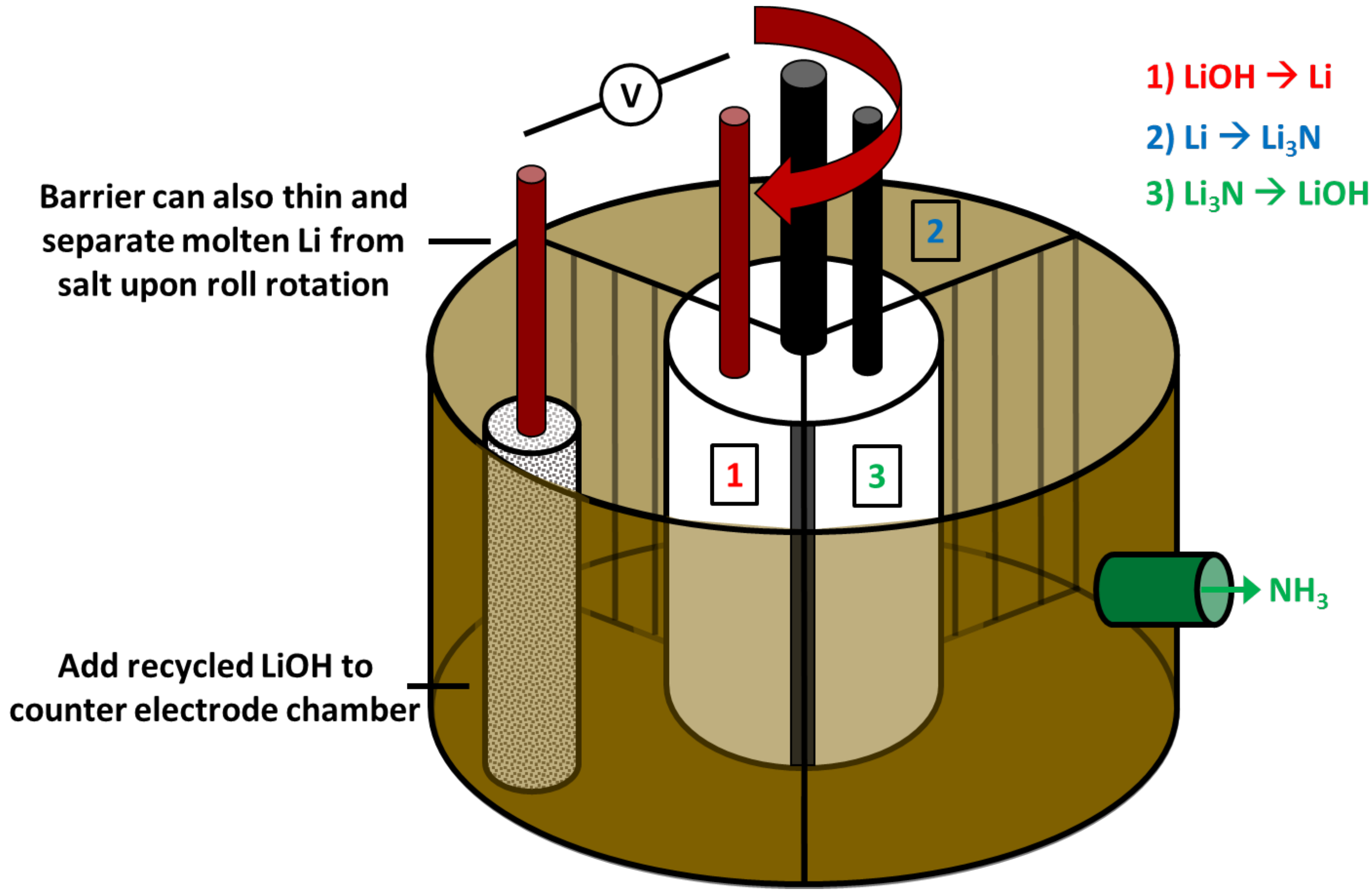
U.S. DEPARTMENT OF ENERGY
JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS
NSF
GCEP Global Climate & Energy Project STANFORD UNIVERSITY
SUNCAT CENTER FOR INTERFACE SCIENCE AND CATALYSIS
SLAC NATIONAL ACCELERATOR LABORATORY

Catalyzing a Sustainable Future



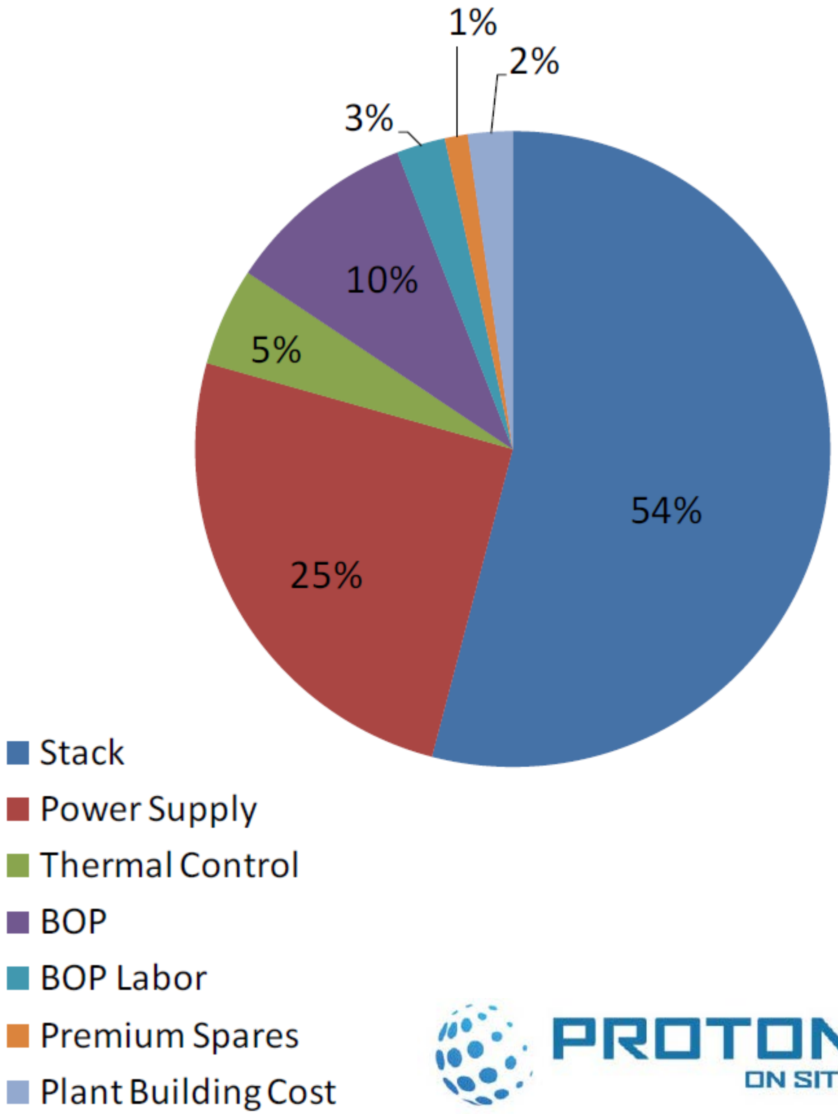
Z. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T. F. Jaramillo, *Science*, **355** 6321 (2017)

Continuous Device Concept



J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, T. F. Jaramillo, J. K. Nørskov
Energy Environ. Sci. **10** 1621 (2017).

Large scale renewable H_2 production

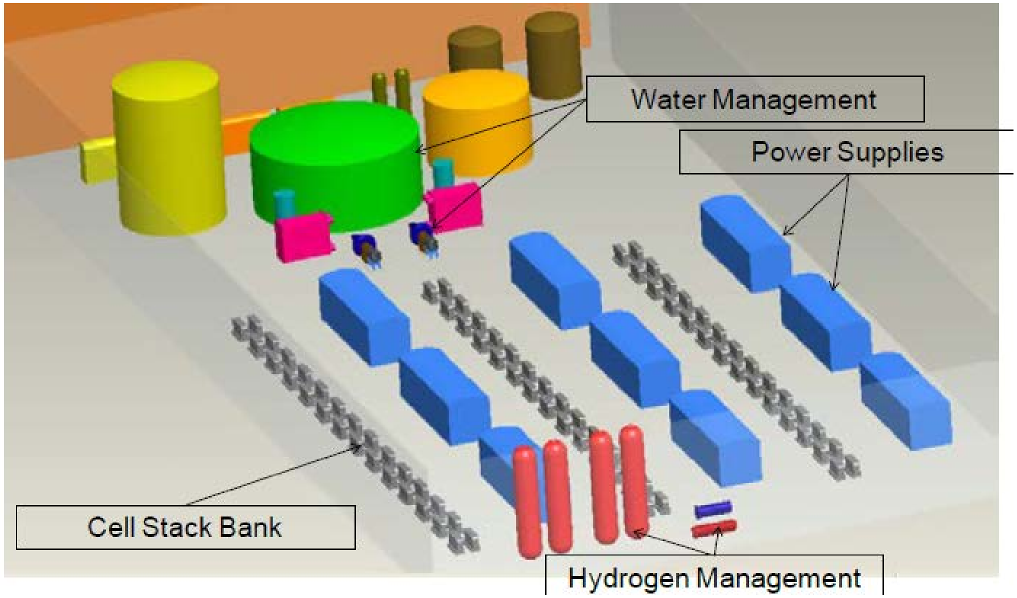


Concept production plant

50,000 kg/day production

Total capital cost ~ **\$0.50-\$0.60/kg H_2**

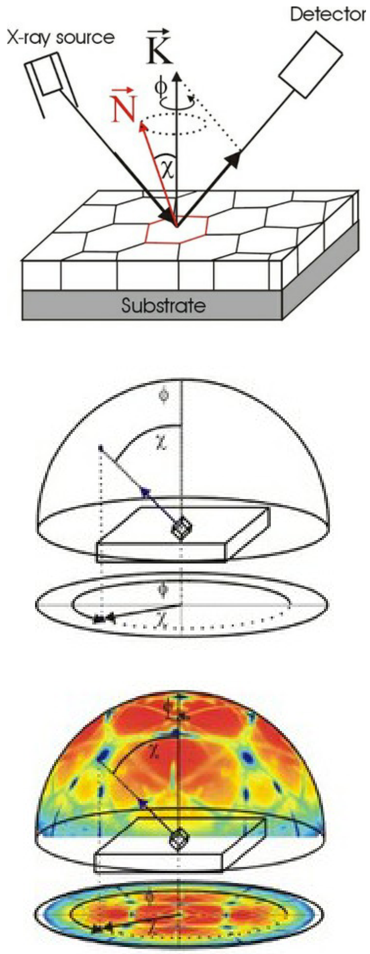
(less land)



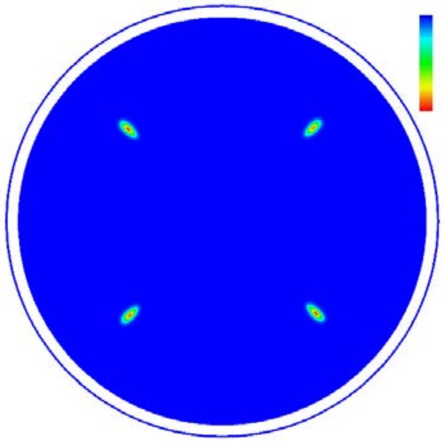
Kathy Ayers, Proton Onsite, DOE EERE Annual Merit Review (2013).

Development of large format, oriented surfaces

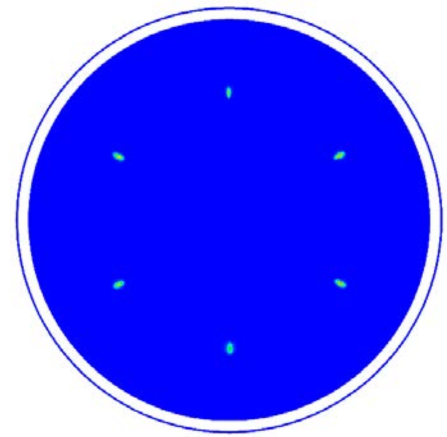
X-ray Pole Figures



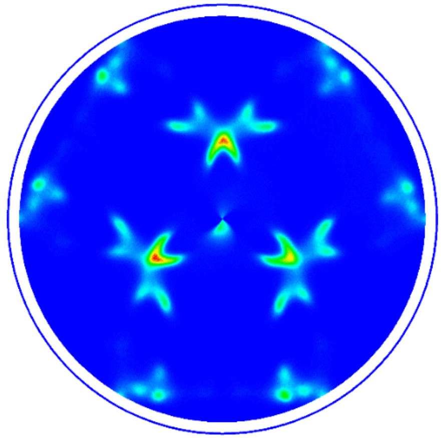
Cu(100)/Si(100)



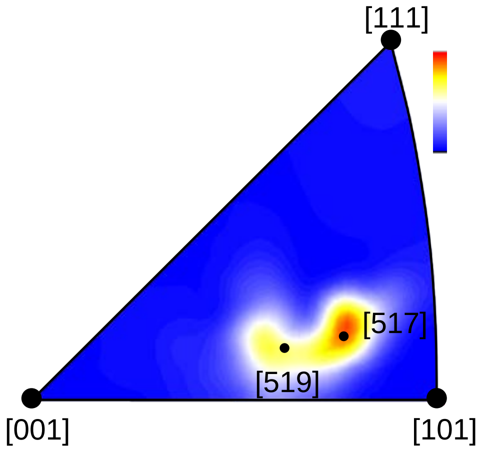
Cu(111)/Al_2O_3(0001)



Cu(751)/Si(111)



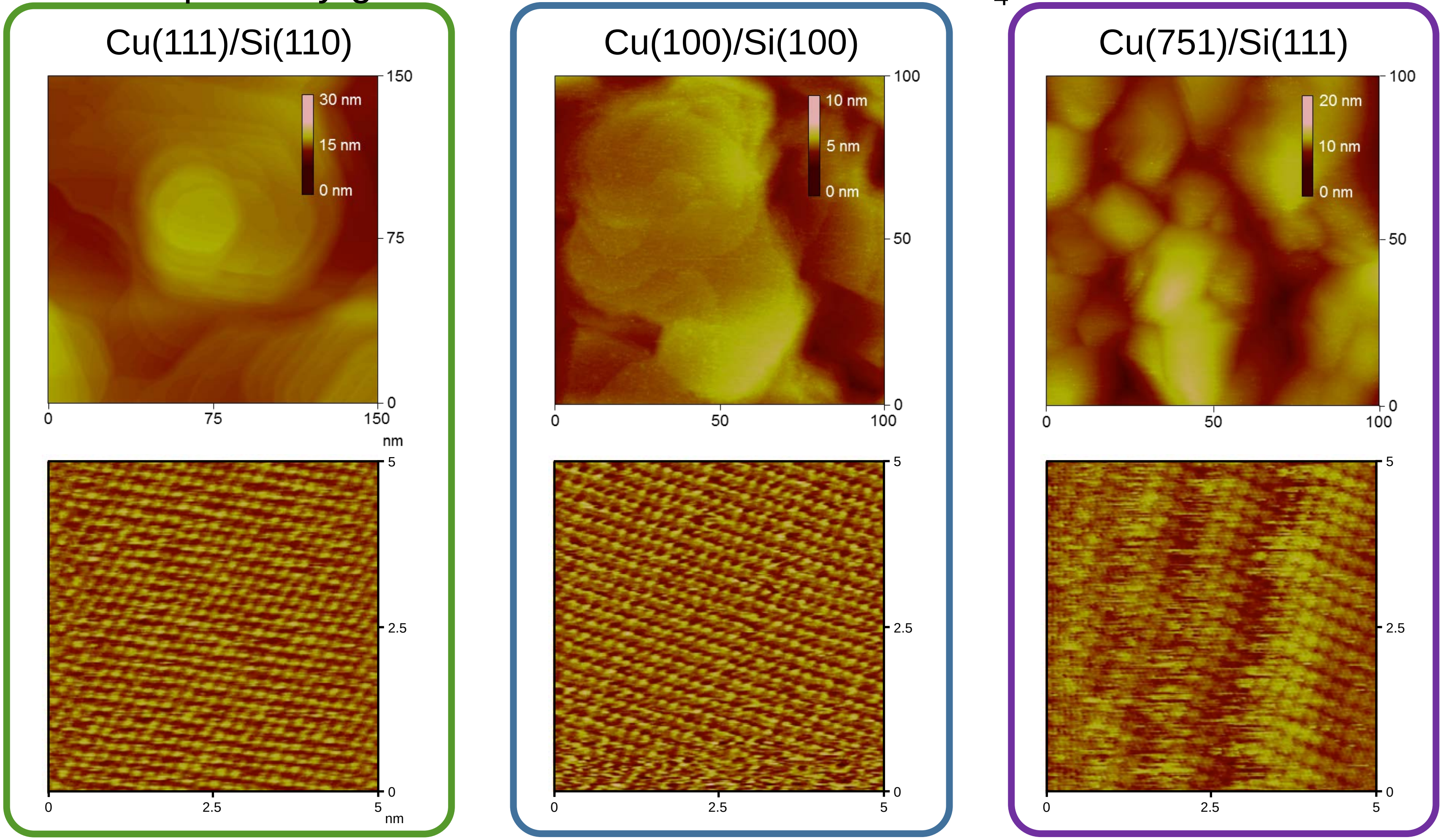
Inverse Pole Figure



https://fys.kuleuven.be/iks/nvsf/experimental-facilities/x-ray-diffraction-2013-bruker-d8-discover
C. Hahn*, T. Hatsukade*, Y-G. Kim, A. Vailionis, M.P. Soriaga, and T.F. Jaramillo *et al. PNAS,* 2017.

In-situ electrochemical scanning tunneling microscopy (EC-STM)

Cu epitaxially grown on Si: ECSTM in 0.1 *M* $HClO_4$ at -0.24 V vs RHE

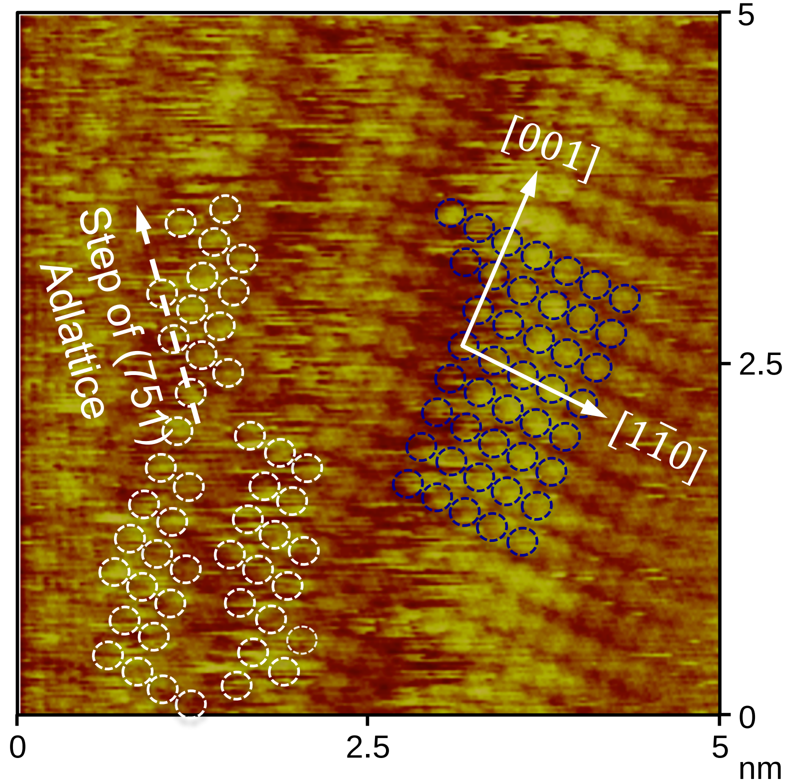


Surface structures match expectations based on the bulk structure.

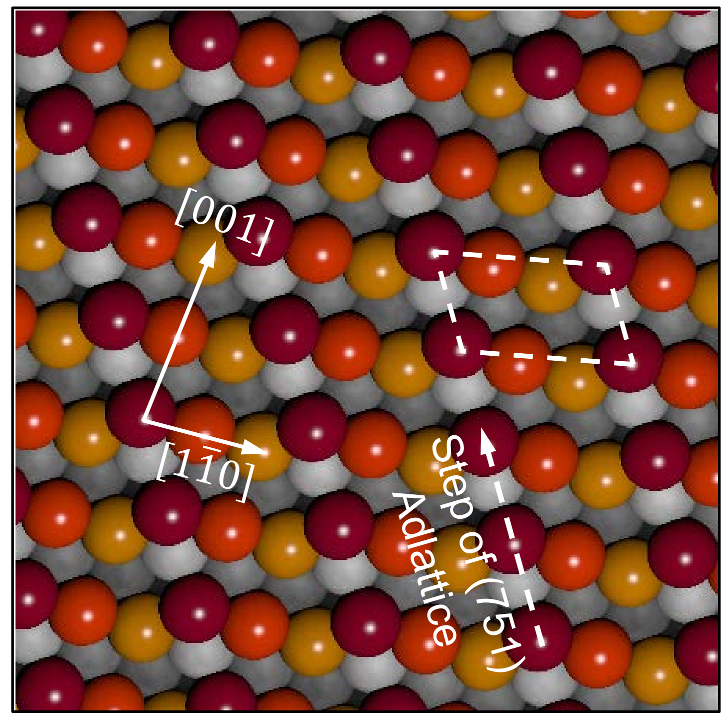
C. Hahn, T. Hatsukade, Y.-G. Kim, A. Vailionis, J.H. Baricuatro, D.C. Higgins, S.A. Nitopi, M.P. Soriaga, and T.F. Jaramillo. Proc. Nat. Acad. Sci., 114, 5918–5923 (2017).

Many steps sites observed on Cu(751)

Cu(S) – [*n*(110)-(100)]/Si(111)
n = 2, 3, 4, 5, 6, 7: Cu(210), (320), (430), (540), (650), (760)

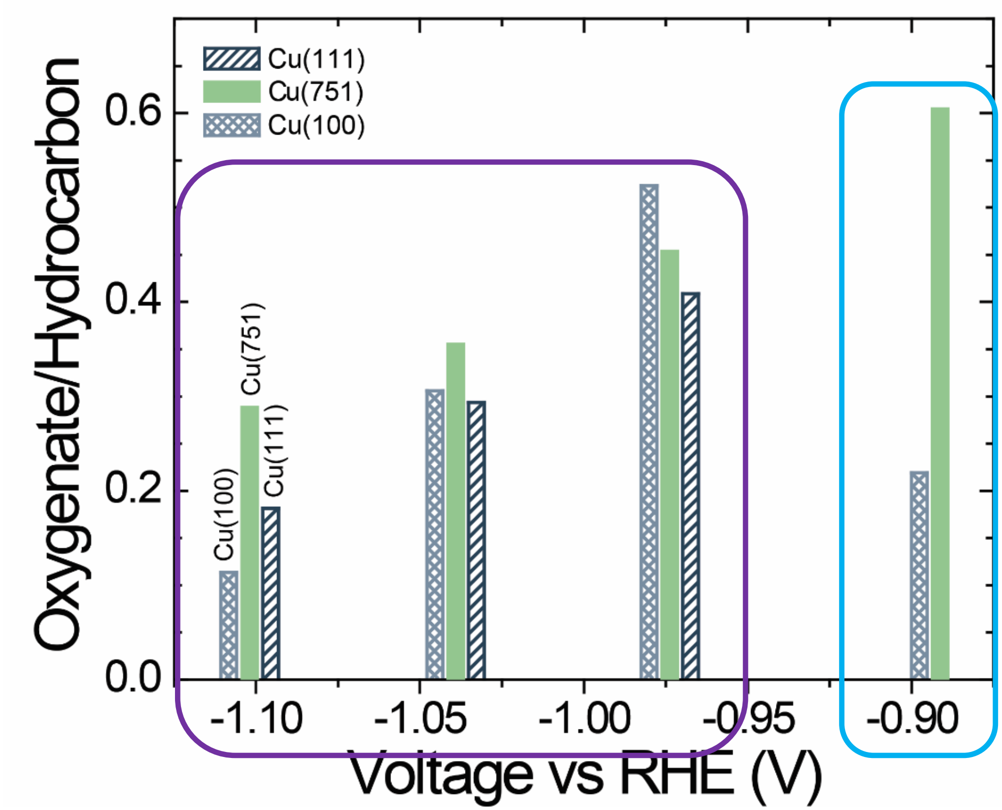


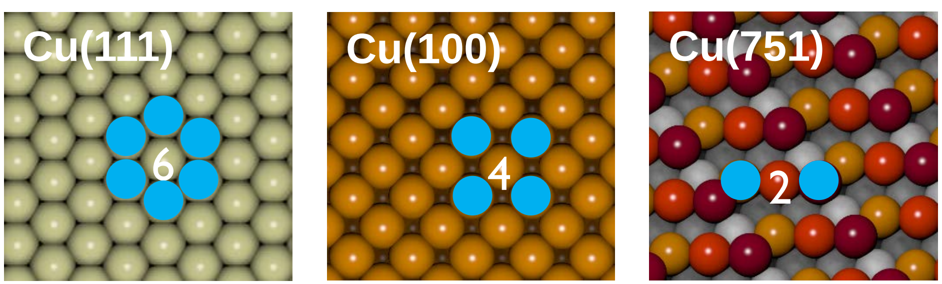
Cu(751) Model Surface



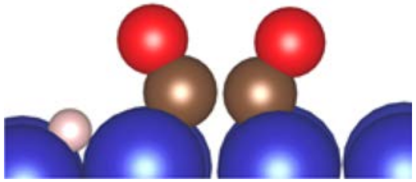
C. Hahn, T. Hatsukade, Y.-G. Kim, A. Vailionis, J.H. Baricuatro, D.C. Higgins, S.A. Nitopi, M.P. Soriaga, and T.F. Jaramillo. Proc. Nat. Acad. Sci., 114, 5918–5923 (2017).

Undercoordinated surface sites steer catalyst selectivity towards oxygenates vs. hydrocarbons



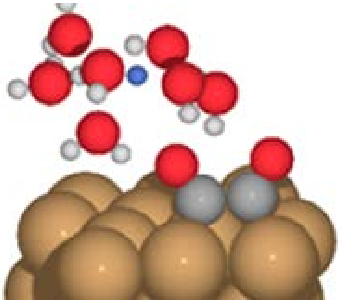


Hydride Transfer



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

Proton-coupled Electron Transfer



C. Hahn, T. Hatsukade, Y.-G. Kim, A. Vailionis, J.H. Baricuatro, D.C. Higgins, S.A. Nitopi, M.P. Soriaga, and T.F. Jaramillo. Proc. Nat. Acad. Sci., 114, 5918–5923 (2017).