# Designing new catalysts and processes for the sustainable production of fuels and chemicals

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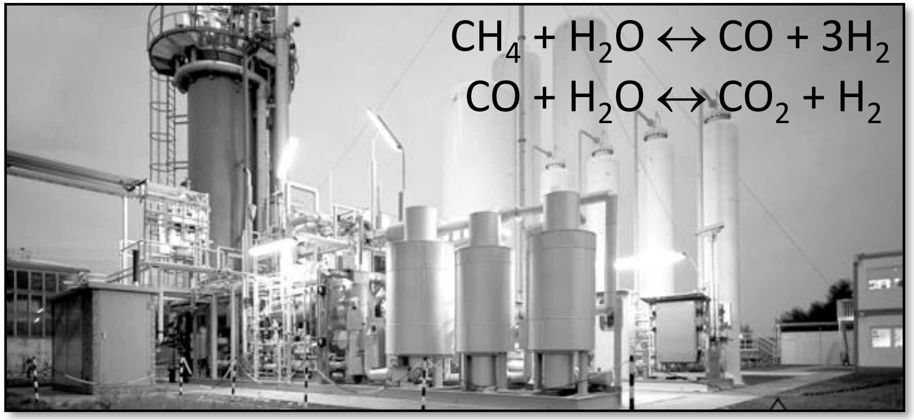
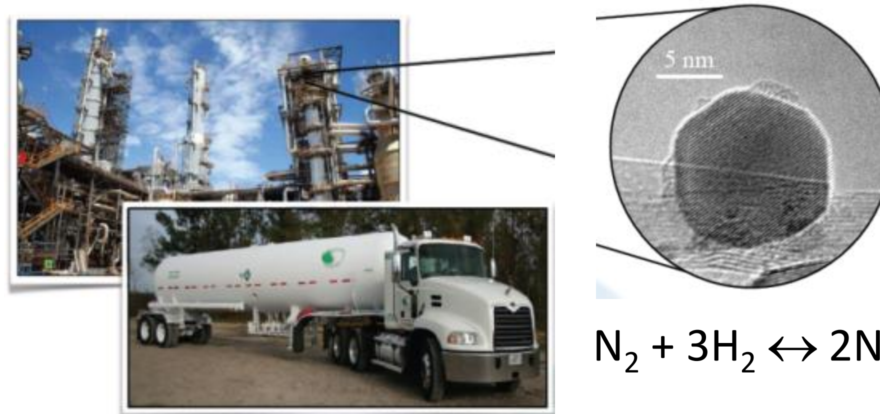
November 18, 2019

**Chemical Sciences Roundtable**
Advances, Challenges, and Long-Term Opportunities of Electrochemistry:
Addressing Societal Needs

National Academies of Sciences Building
Washington, D.C.

# The modern fuels and chemicals industry: A success story




$N_2 + 3H_2 \leftrightarrow 2NH_3$

***$H_2$ production by steam reforming***

*$H_2$*

***65 billion kg/yr***
*9 kg/person/yr*

***$NH_3$ production by Haber-Bosch***

*$NH_3$*

***180 billion kg/yr***
*>20 kg/person/yr*

***Petroleum refining***

***gasoline***

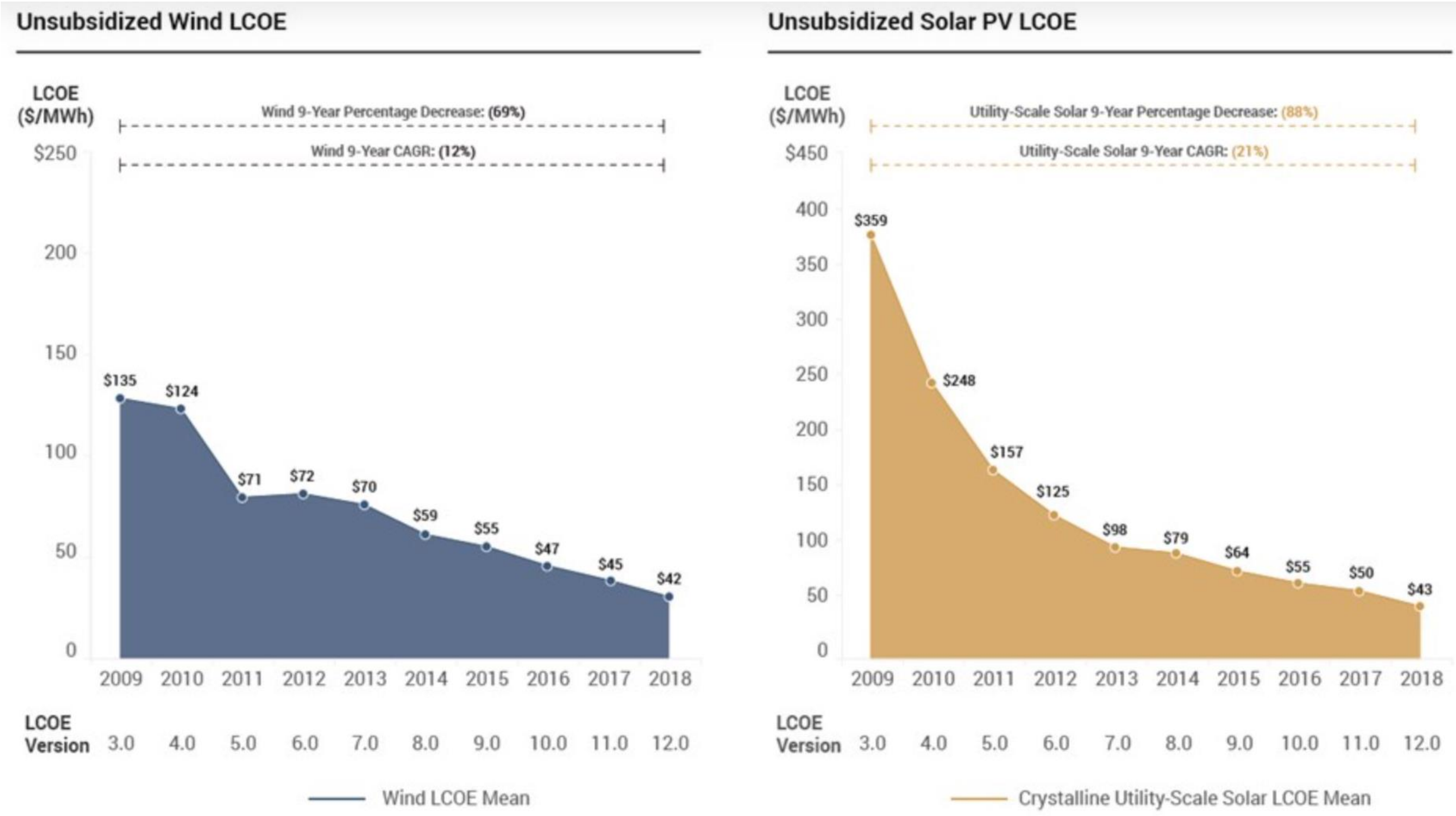
***1 trillion kg/yr***
*130 kg/person/yr*

***Plastics production***

***plastics***

***300 billion kg/yr***
*40 kg/person/yr*

# A game-changer: Dropping price of renewable electricity




https://www.lazard.com/perspective/levelized-cost-of-energy-and-levelized-cost-of-storage-2018/

# Electrolysis processes are already a scaled-up

**$Al_2O_3$ Electrolysis (aluminum electrorefining)**

**$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$**

- ~ 15 billion $kg_{Al}$/yr
- 27 GW
- 240 TWh/yr

*Kaiser Chalmette plant (1950's) Louisiana, USA*

https://www.amazon.com/Potroom-reduction-Aluminium-Chalmette-Louisiana/dp/B01685KYME

**Brine Electrolysis (chlor-alkali process)**

**$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$**

- ~ 60 billion $kg_{NaOH}$/yr
- 55 billion $kg_{Cl2}$/yr
- 11 GW
- 100 TWh/yr

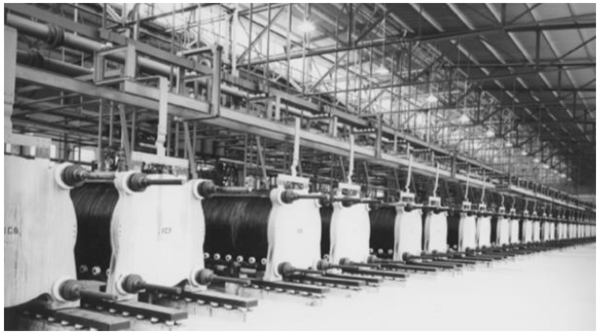
*Asahi Kasei plant (1970's)*

https://www.chemanager-online.com/en/topics/plant-engineering-components/asahi-kasei-lower-power-consumption-technology-chlor-alkali-indu

**Water Electrolysis (electrochemical $H_2$)**

**$2H_2O \rightarrow 2H_2 + O_2$**

- Mostly alkaline today and historically.
- PEM electrolysis is advancing fast.



*Norsk Hydro plant (1950's) Glomfjord, Norway*

https://nelhydrogen.com/assets/uploads/2017/01/Nel_Electrolyser_brochure.pdf

Ch. 17 (pp. 319-325) of *Fundamentals of Electrochemistry, Second Edition* (2006) By V. S. Bagotsky.

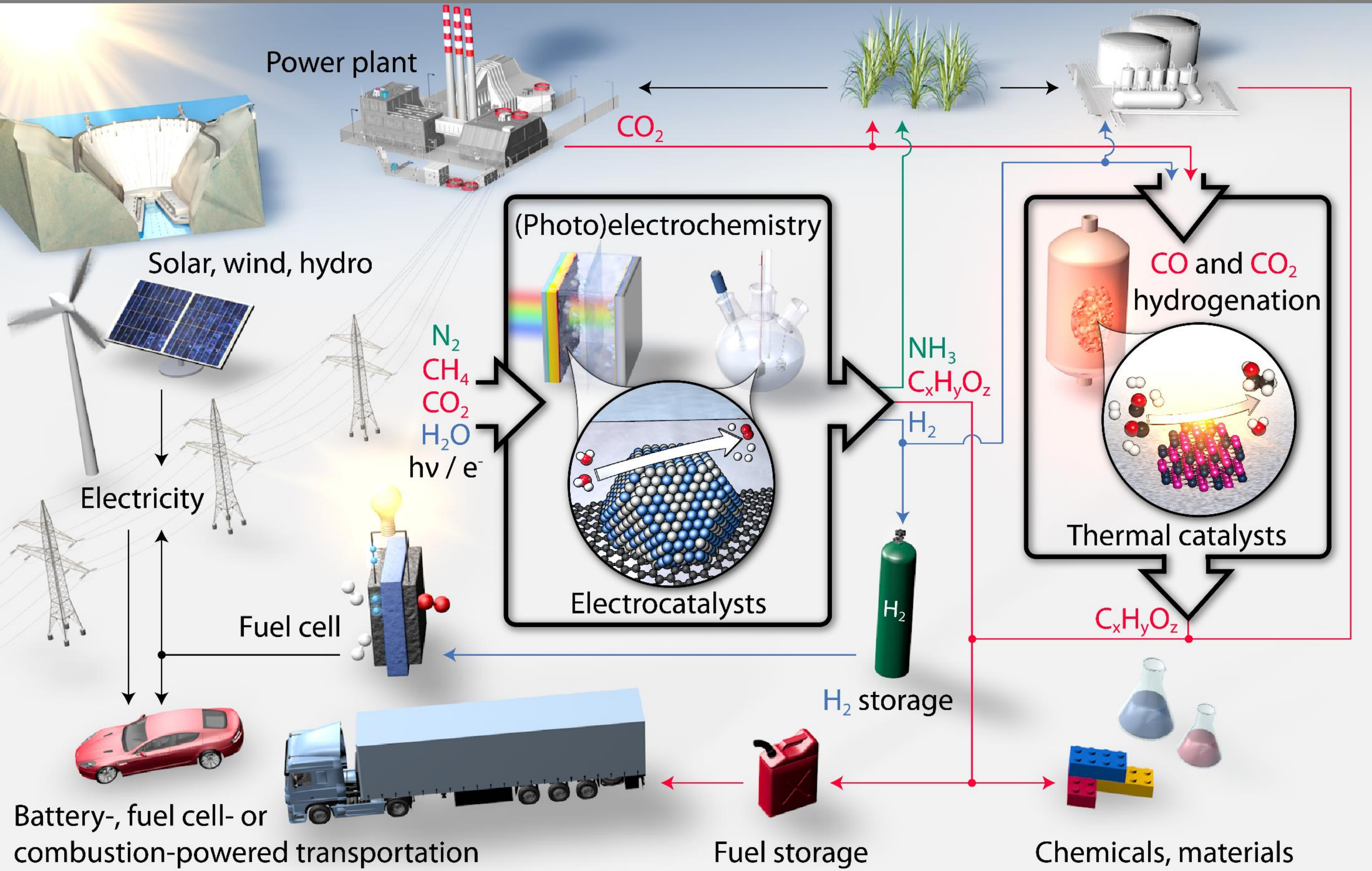
# How do we create a new paradigm?

**Production cost ($/kg) = CapEx ($/kg) + OpEx ($/kg)**

| Renewable electricity | Carbon capture |
| --- | --- |
| **1 ¢/kWh** | **$30/ton $CO_2$** |

| Energy storage | Electrolysis ($H_2O$, $CO_2$, $N_2$, etc.) |
| --- | --- |
| **$10/kWh** | **$0.20/kg product CapEx** |

# *Catalyzing a sustainable future*




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

$H_2$

$H_2O$
splitting

C-based products

$CO/CO_2$
reduction

$NH_3$

$N_2$
reduction

$H_2$

$H_2O$
splitting

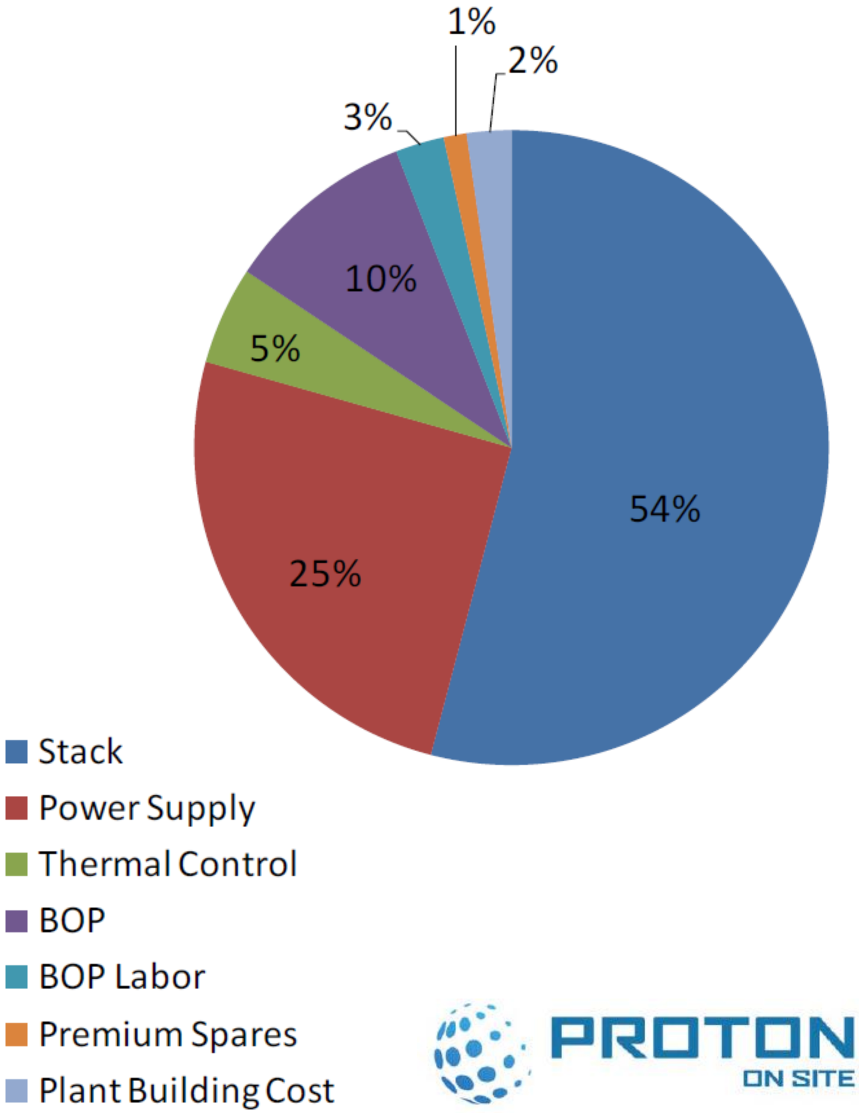
C-based
products

$CO/CO_2$
reduction

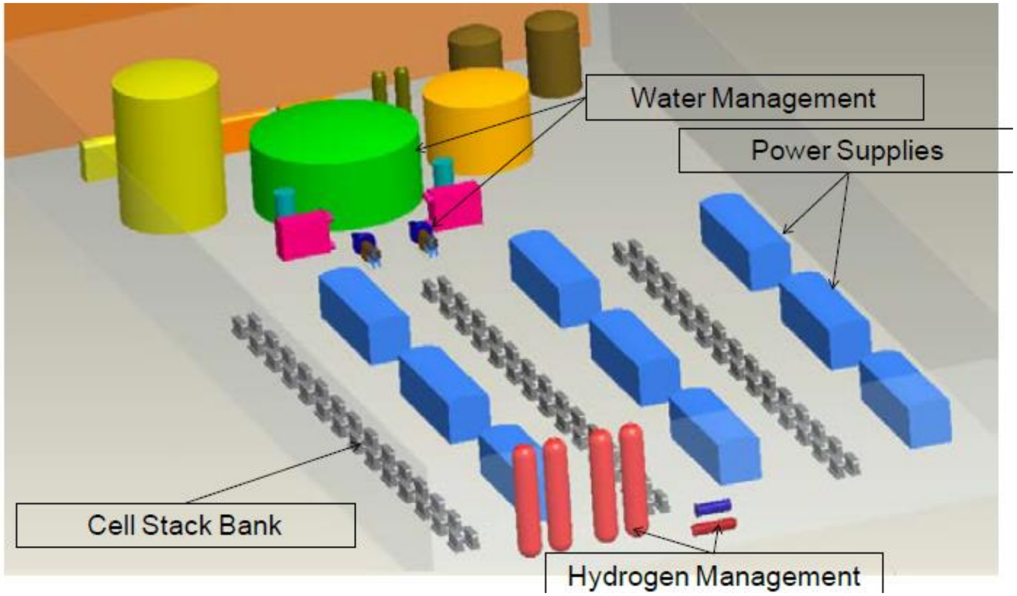
$NH_3$

$N_2$
reduction

# Large scale renewable $H_2$ production

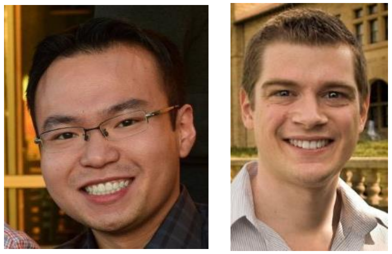



**Concept production plant**
50,000 kg/day production
Total capital cost ~ **\$0.50-\$0.60/kg $H_2$**
(less land)




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

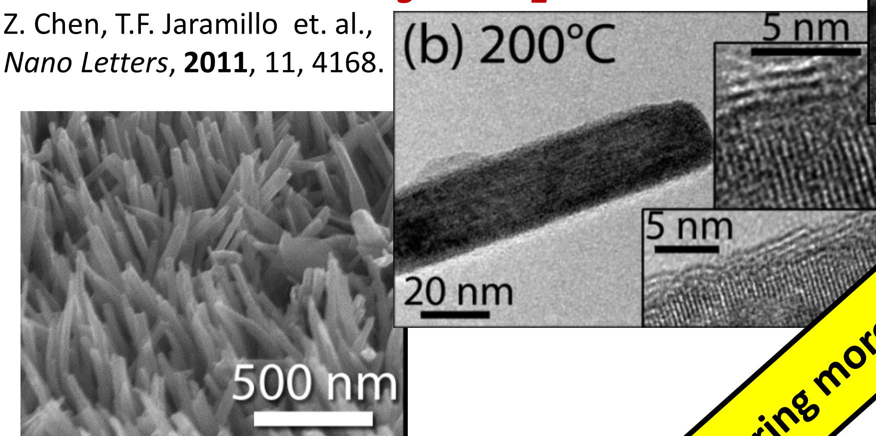
# Nano-structured $MoS_2$: Developing active, stable, earth abundant, scalable catalysts for hydrogen production



Zhebo Chen  Jakob Kibsgaard

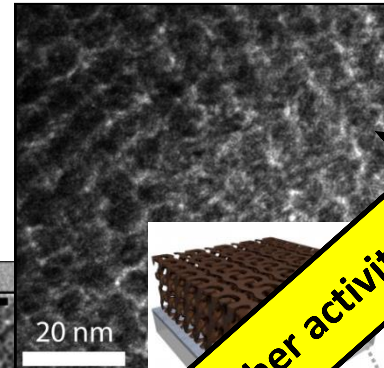
## 1. Core-shell $MoO_3$-$MoS_2$ nanowires

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



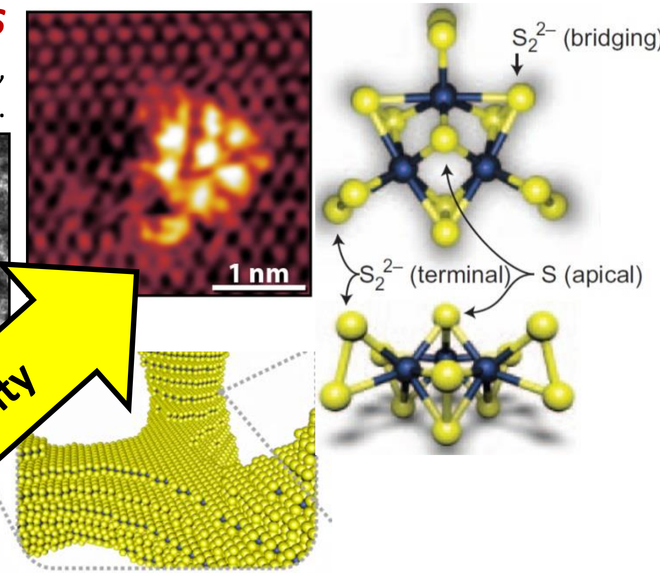

## 2. Mesoporous $MoS_2$

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



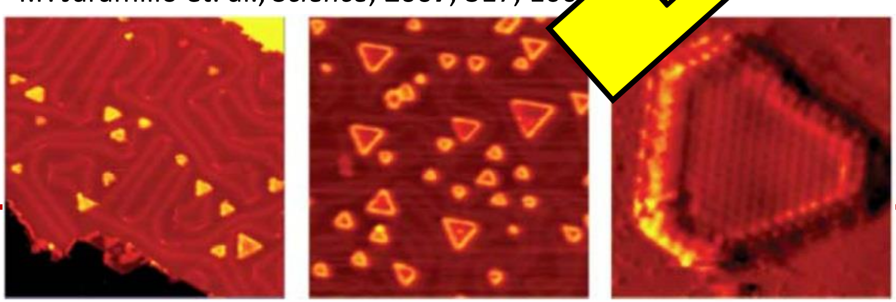

## 3. $[Mo_3S_{13}]^{2-}$ clusters

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

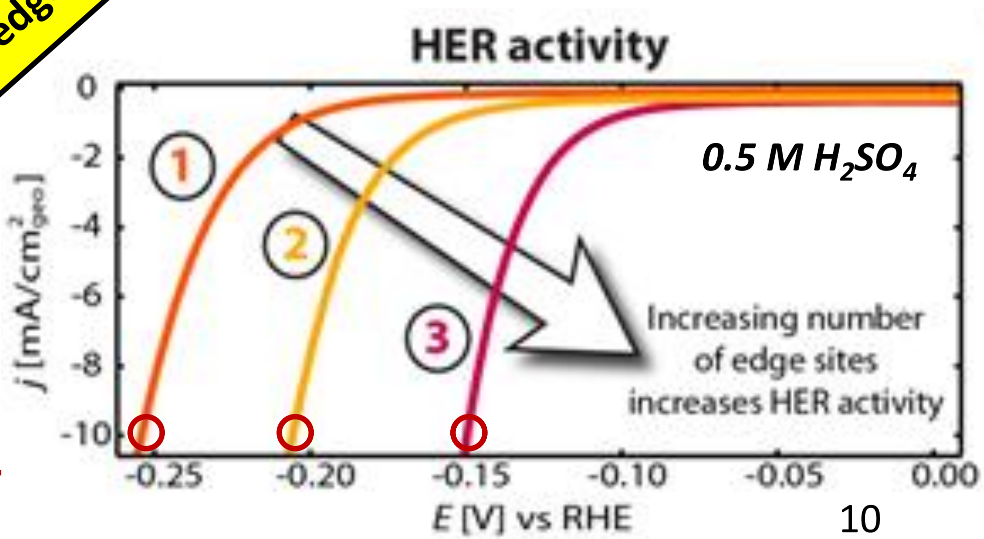



## $MoS_2$ nanoparticles

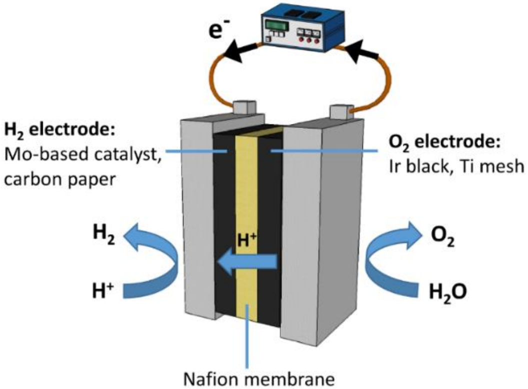
T.F. Jaramillo et. al., *Science*, **2007**, 317, 100

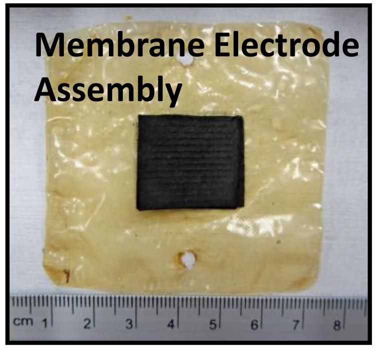


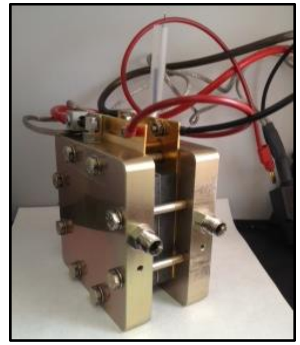
Engineering more edge sites= higher activity

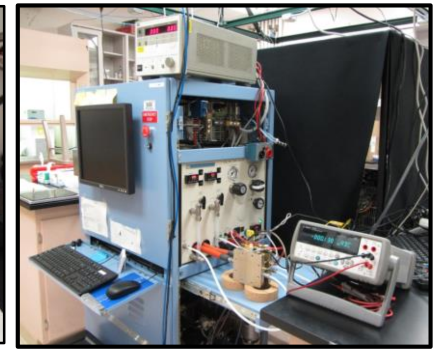


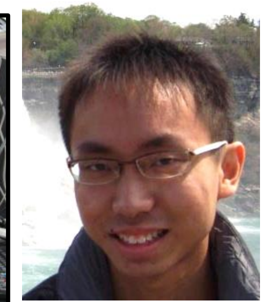
# Device Integration: PEM Electrolyzers



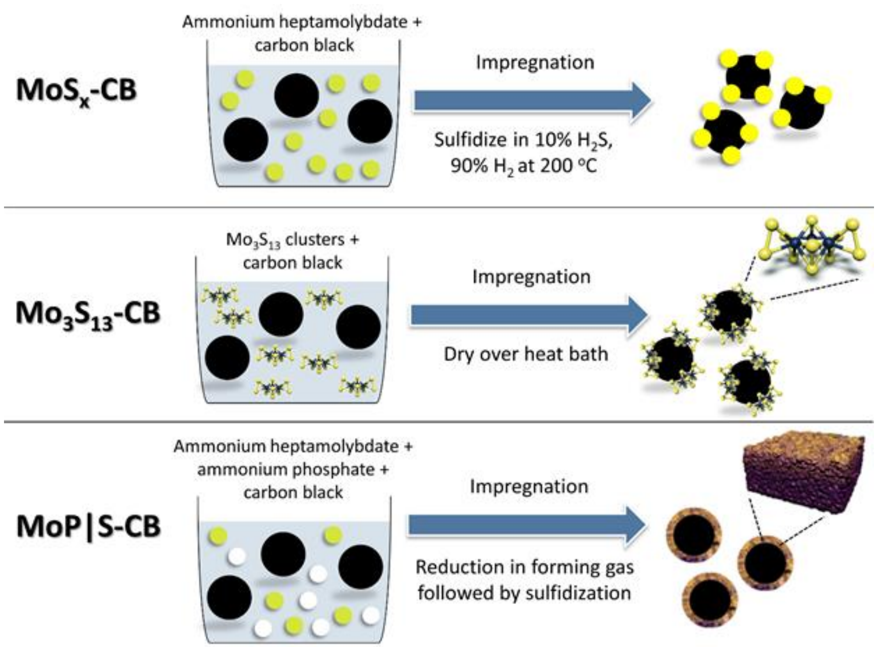



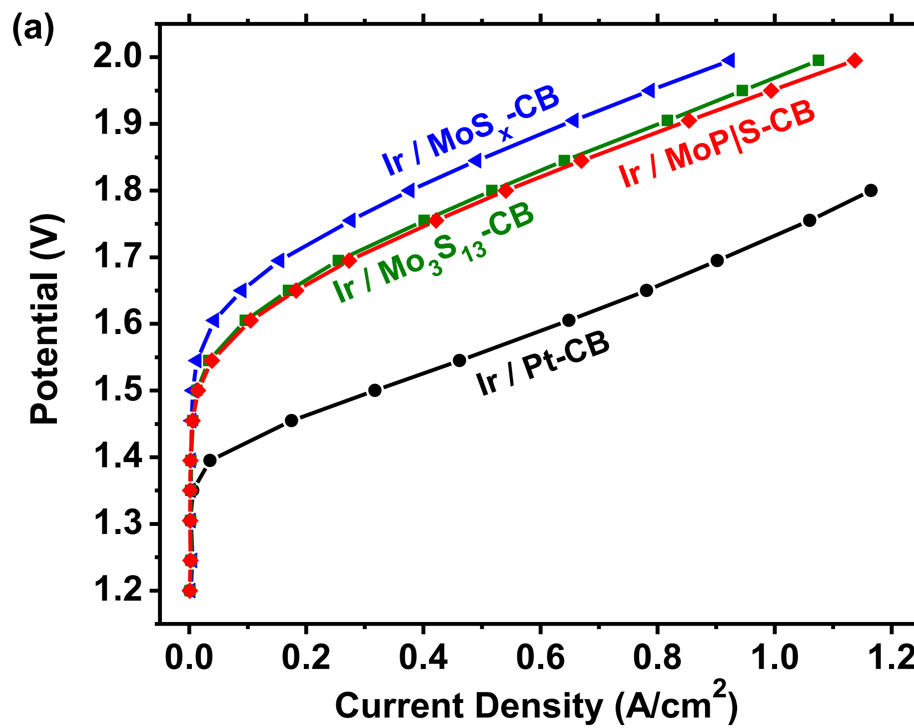







Desmond Ng



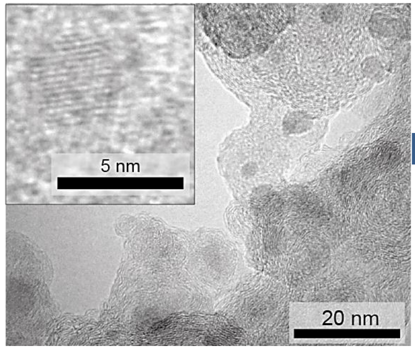




J.W.D. Ng, T.R. Hellstern, J. Kibsgaard, A.C. Hinckley, J.D. Benck, T.F. Jaramillo, *ChemSusChem*, **8** 3512-3519 (2015). 

# CoP in a commercial PEM water electrolyzer

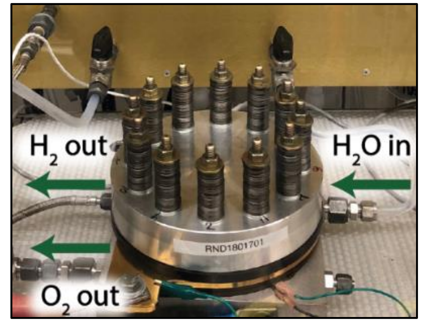
McKenzie Hubert

Laurie King

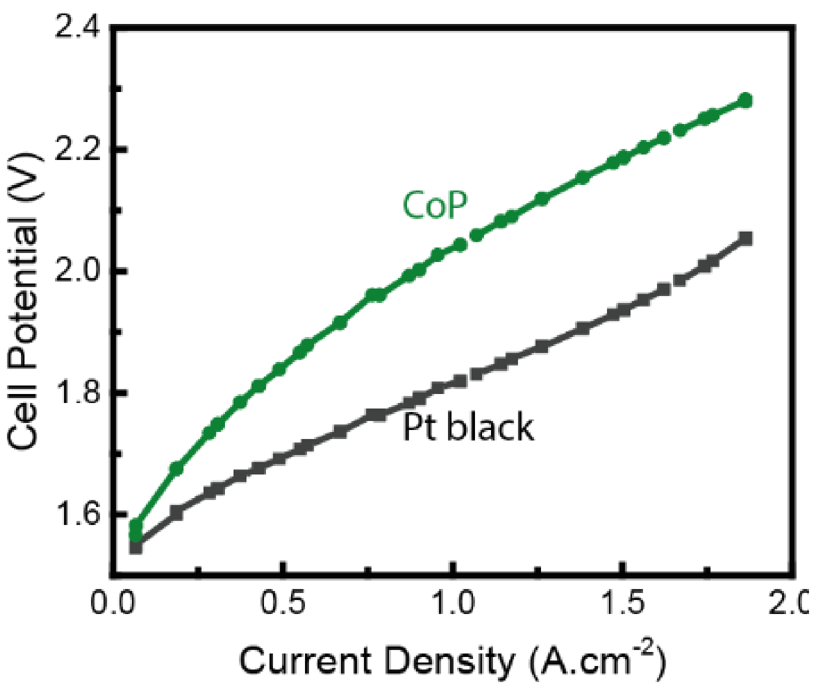


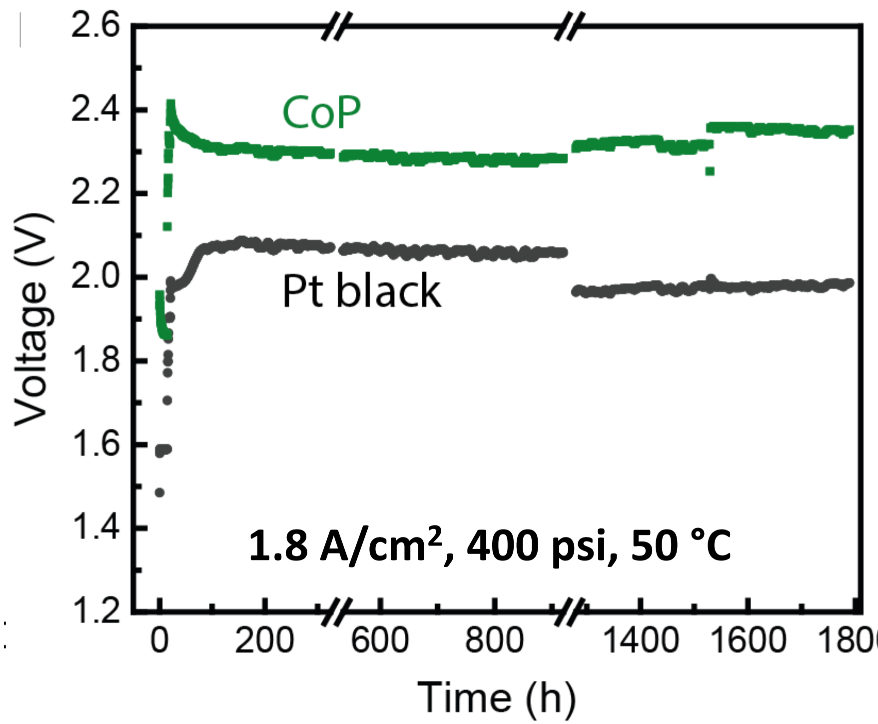

*CoP/C catalyst*

PROTON ON SITE | nel



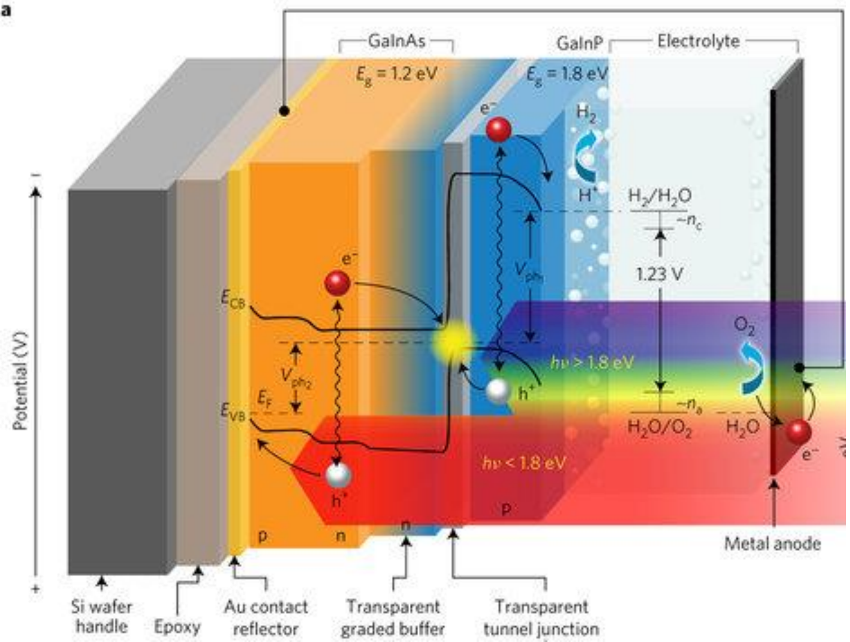

- 86 cm$^2$ MEA
- 1.5 mg cm$^{-2}$ CoP
- 400 psi, 50 °C
- 1.8 A/cm$^2$



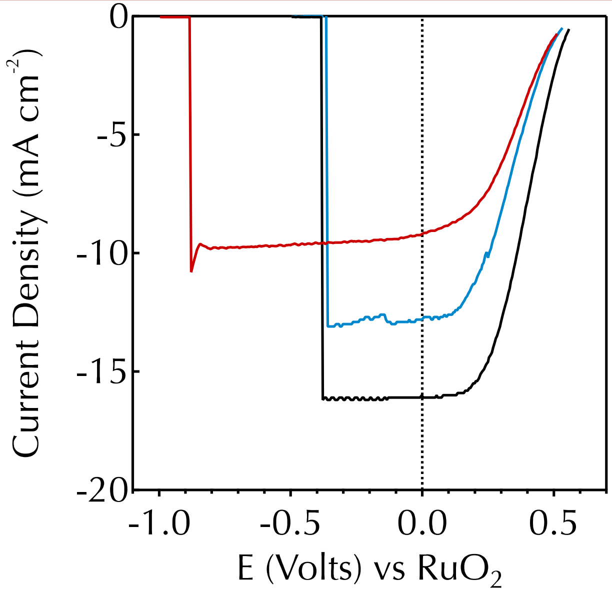

L. King, M. Hubert, C. Capuano, J. Manco, N. Danilovic, E. Valle, T. R. Hellstern, K. Ayers, T. F. Jaramillo, *Nature Nanotechnology*, accepted and in press (2019).

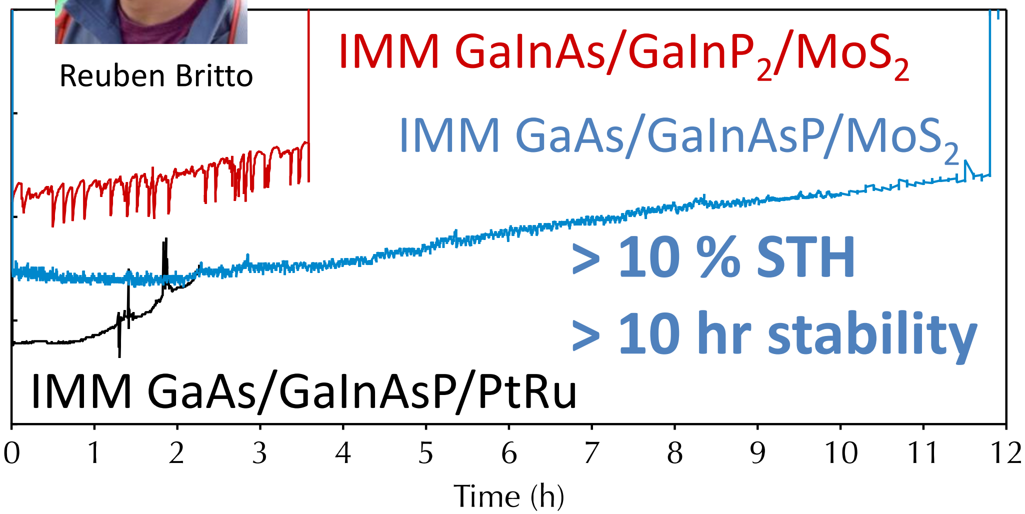
# Unassisted photoelectrochemical (PEC) water-splitting




James Young & Todd Deutsch
**NREL**

Reuben Britto



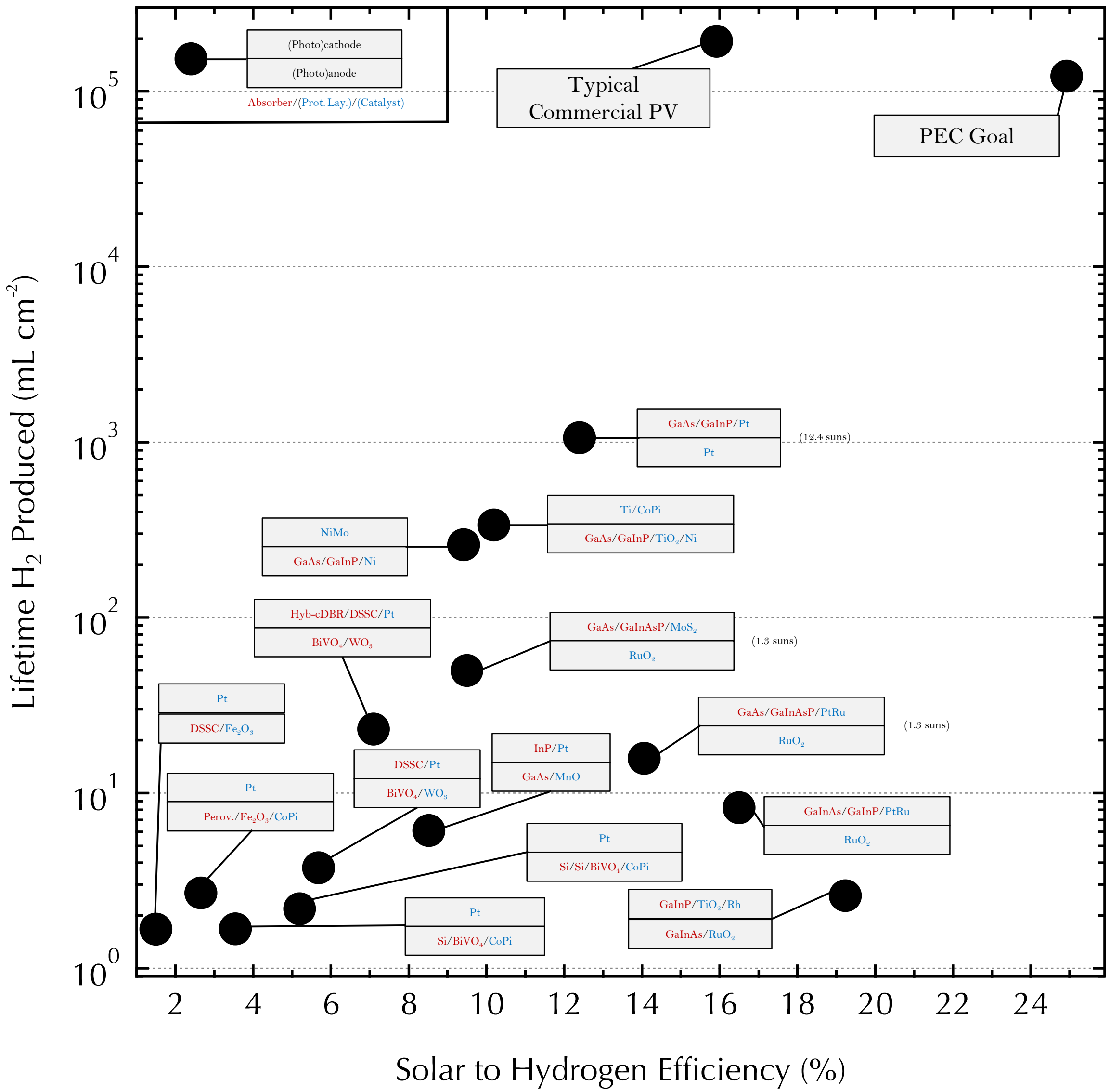




- 16.2% Solar-to-$H_2$ (STH) Efficiency.
- Uses Pt-Ru catalysts for $H_2$ evolution.
- Stable for only ~ 1 hour.

James L. Young, Myles A. Steiner, Henning Döscher, Ryan M. France, John A. Turner, Todd G. Deutsch. Nature Energy. 2, 17028 (2017)

R. Britto, J.L. Young, M.A. Steiner, D. Friedman, T.G. Deutsch, T.F. Jaramillo, *in preparation* (2019).

# Unassisted water-splitting: Durability is a major gap




Typical Commercial PV: 16% avg. eff. over 25 yr, CF: 16%, lifetime energy in equiv. $H_2$

PEC Goal: 25% STH over 10 yrs, CF: 16%

All data from 2 electrode spontaneous water splitting stability tests

R. Britto, J.L. Young, M.A. Steiner, D. Friedman, T.G. Deutsch, T.F. Jaramillo, *in preparation* (2019).

$H_2$

$H_2O$
splitting

C-based products

$CO/CO_2$
reduction

$NH_3$

$N_2$
reduction

# $CO_2$ electrocatalysis


Kendra Kuhl


Etosha Cave


David Abram


Toru Hatsukade


Jeremy Feaster


Stephanie Nitopi


Alan Landers


Daniel Corral


John Lin


Drew Higgins


Chris Hahn


Marat Orazov


Andrew Wong

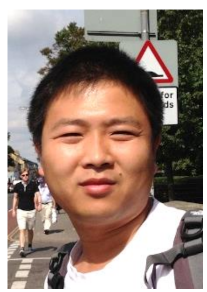

McKenzie Hubert


Yusaku Nishimura


Annelie Jongerius


Daniel Un


Carlos Morales Guío


Lei Wang

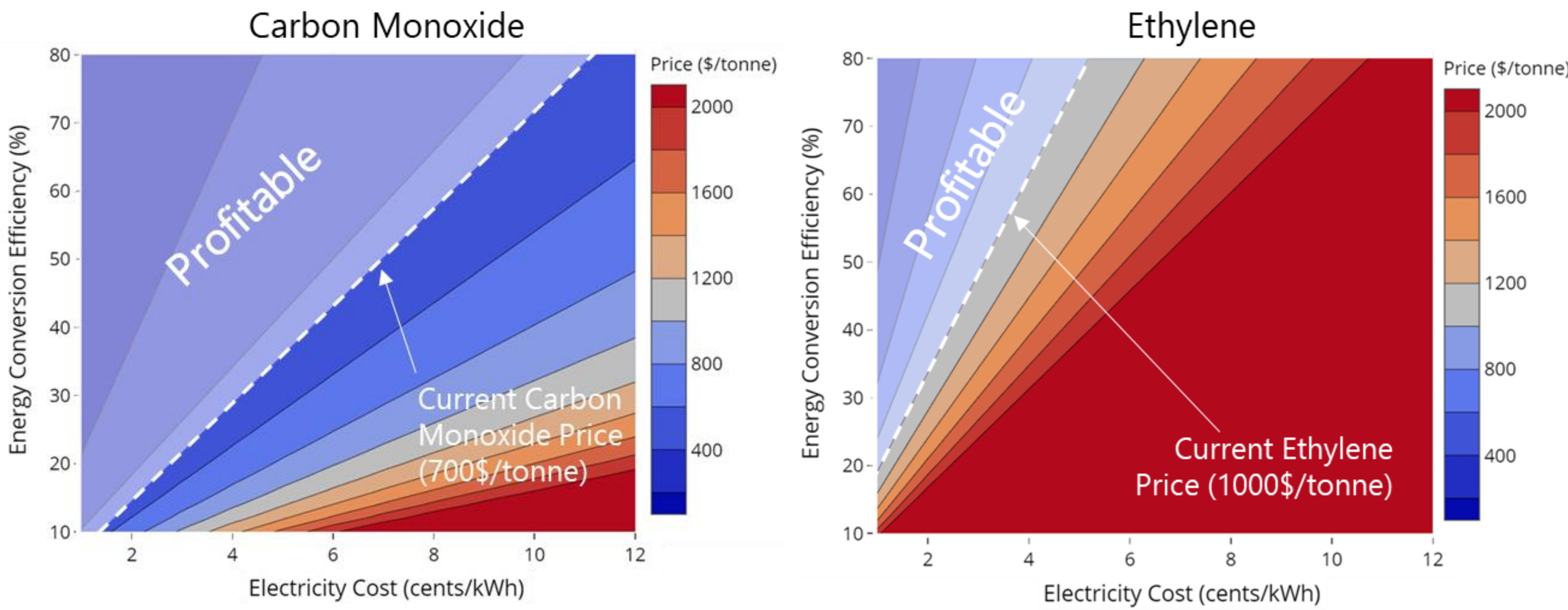

Kabir Abiose


Antaeres Antoniuk-Pablant


Jaime Aviles Acosta


David Koshy

# Can electrochemical technologies impact the fuels and chemicals industry?




The answer is yes. The cost of electricity is a strong driver for price; even short carbon-chain products require significant energy efficiency.

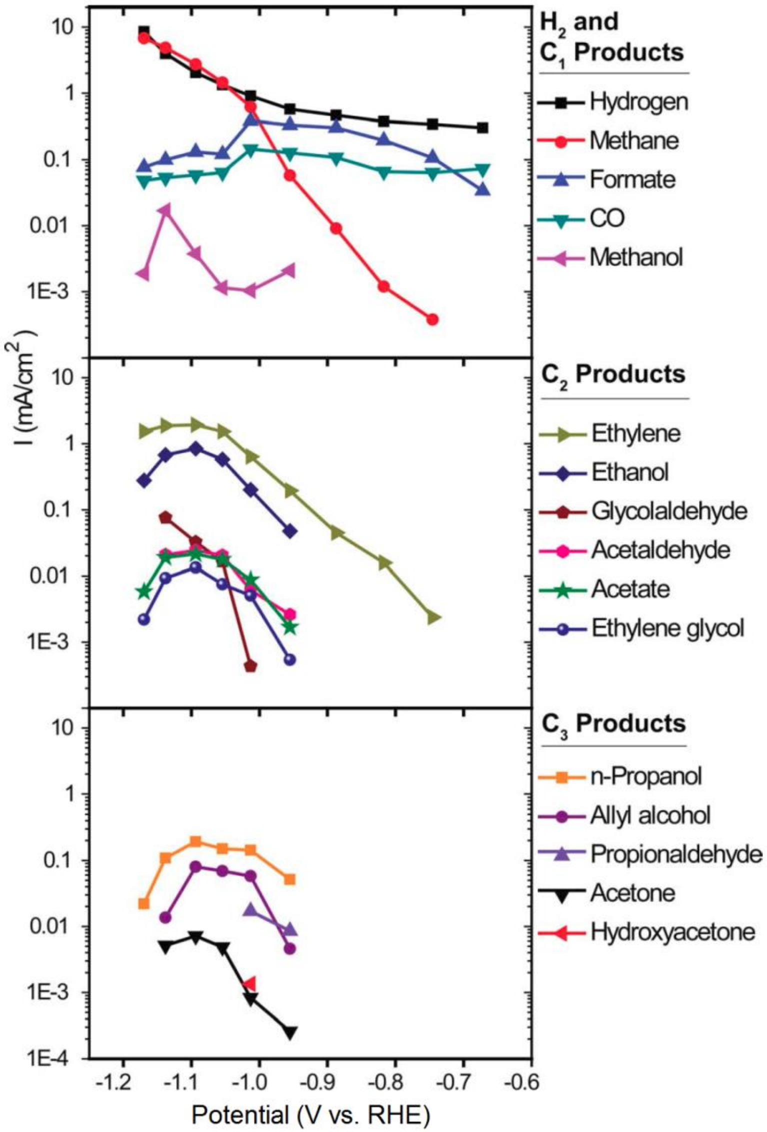
P. De Luna†, C. Hahn†, D.C. Higgins†, S. Jaffer, T.F. Jaramillo*, and E.H. Sargent*, *Science*, 2019, 364, eaav3506.

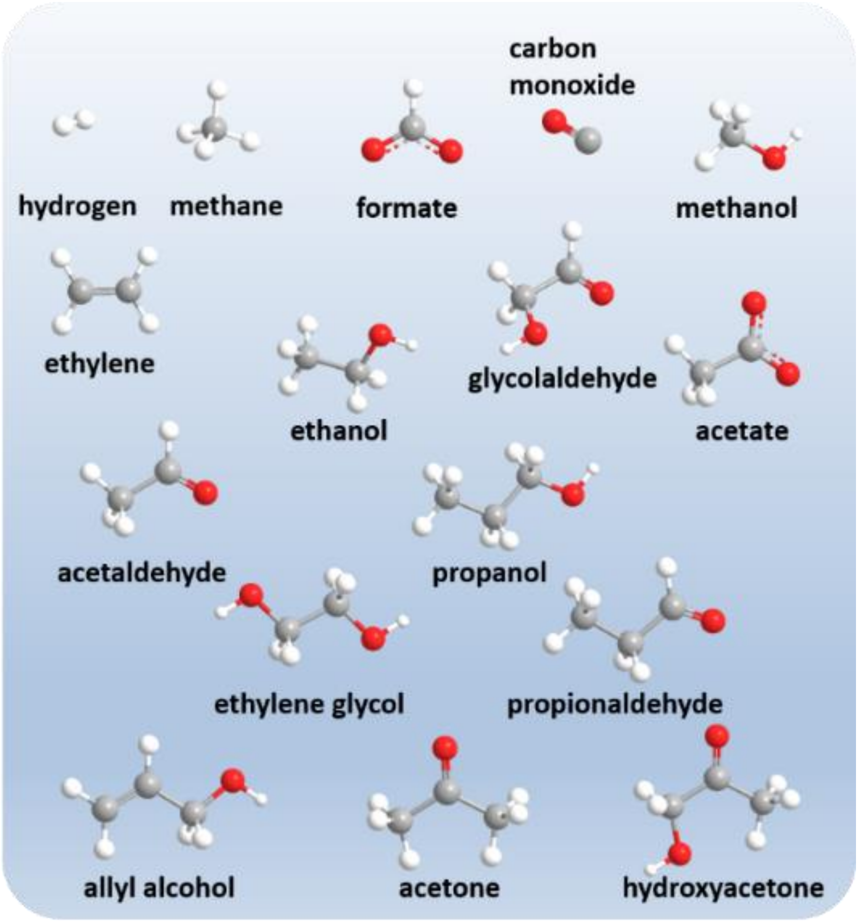
# 16 different reaction products from a Cu catalyst

Kendra Kuhl

Etosha Cave

David Abram

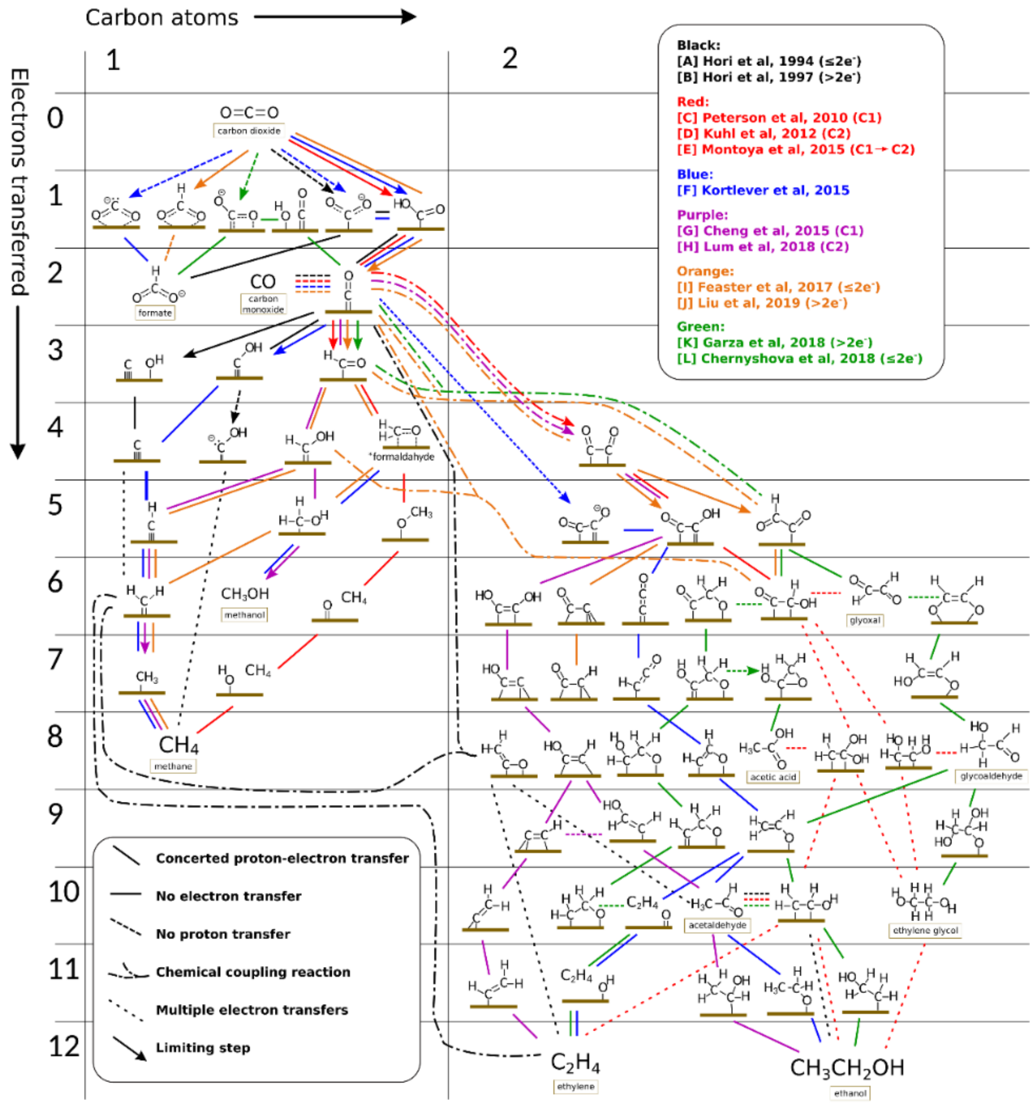



K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, *Energy Environ. Sci.*, 2012, 5, 7050-7059.

# Mechanistic aspects of $CO_2$ reduction on Cu

- Formate is a dead-end.
- CO is the key intermediate to further reduced (>2 $e^-$) products, e.g. $CH_4$, $C_{2+}$ compounds.
- **How can we suppress $H_2$ evolution?**



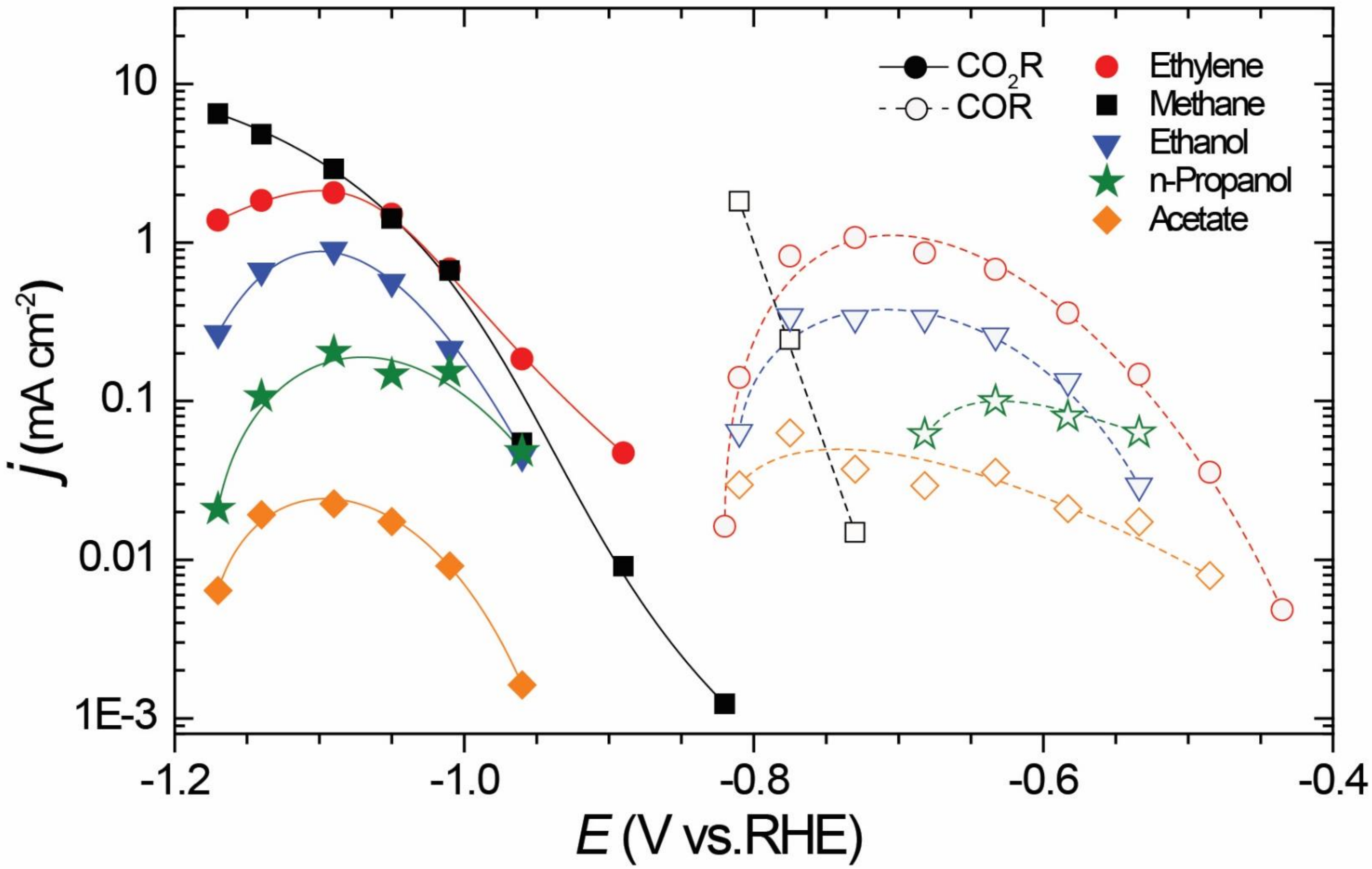

Stephanie Nitopi

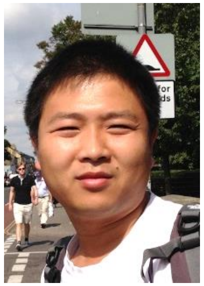
Chris Hahn

- **How can we favor $C_{2+}$ products over $C_1$ products ($CH_4$)?**
- **How can we favor $C_{2+}$ oxygenates over HC's?**
- **How can we selectively produce a single desired $C_{2+}$ oxygenate?**

S.A. Nitopi†, E. Bertheussen†, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E.L. Stephens, K. Chan, C. Hahn, J.K. Nørskov*, T.F. Jaramillo*, I. Chorkendorff*, *Chemical Reviews*, 2019.

# Comparing $CO_2R$ (pH neutral) and COR (alkaline) on pc-Cu



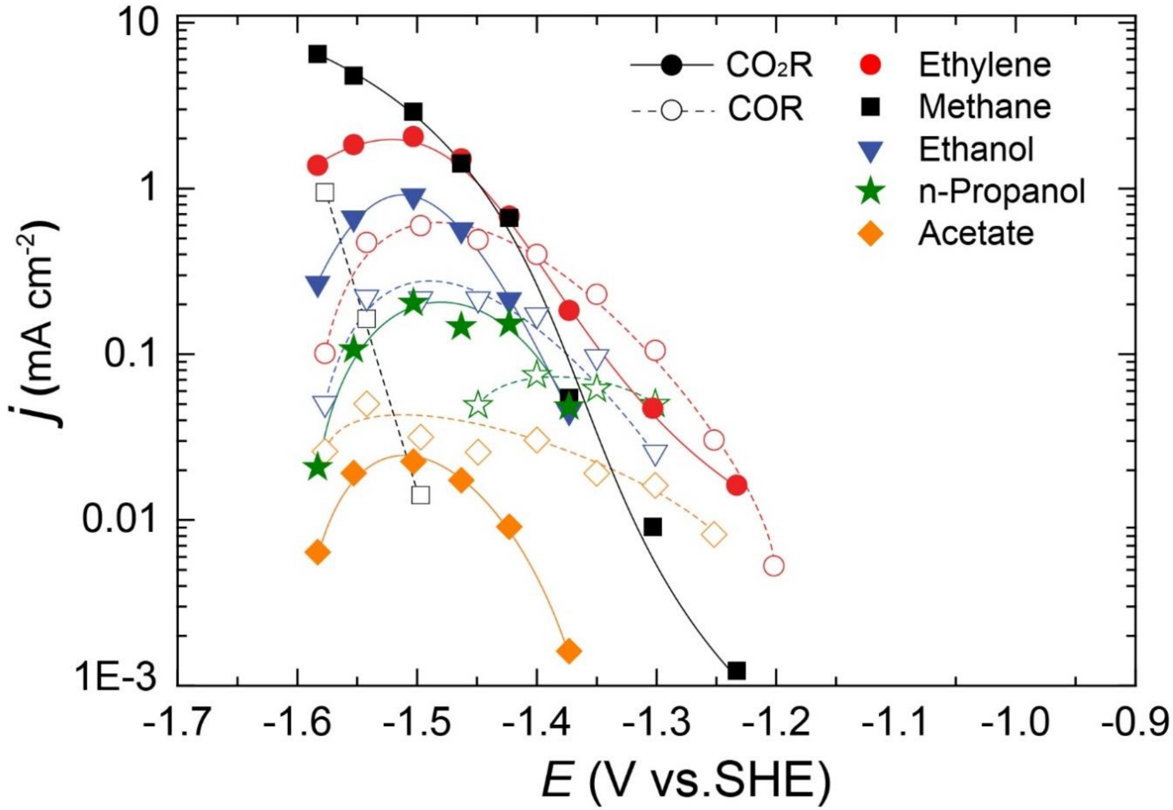
Lei Wang

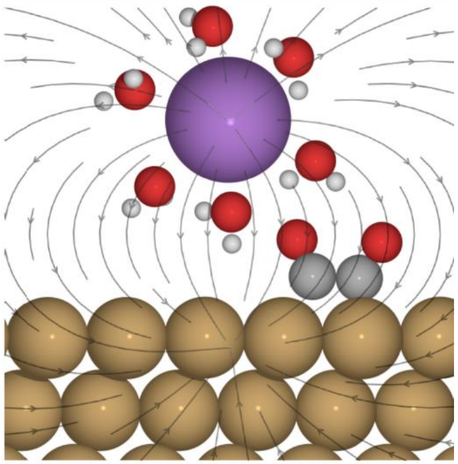
Chris Hahn

Product distribution for COR similar to that for $CO_2R$, however onset potentials for C2+ products are significantly more positive for COR.

L. Wang, S.A. Nitopi, E. Bertheussen, M. Orazov, C.G. Morales-Guio, X. Liu, D.C. Higgins, K. Chan, J.K. Nørskov, C. Hahn*, T.F. Jaramillo*, *ACS Catalysis*, 2018, 8, 7445-7454.

# pH Effects in $CO_2$ and CO Reduction



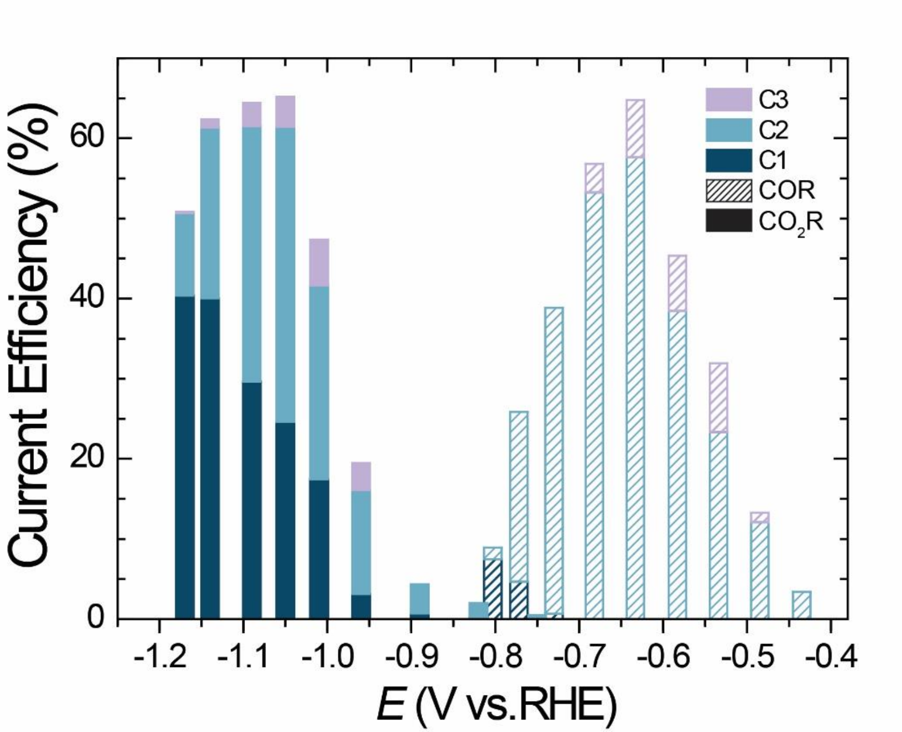
J. Resasco, L.D. Chen, E. Clark, C. Tsai, C. Hahn, T.F. Jaramillo, K. Chan, and A.T. Bell *J. Amer. Chem. Soc.*, 139, 11277–11287 (2017). DOI: 10.1021/jacs.7b06765

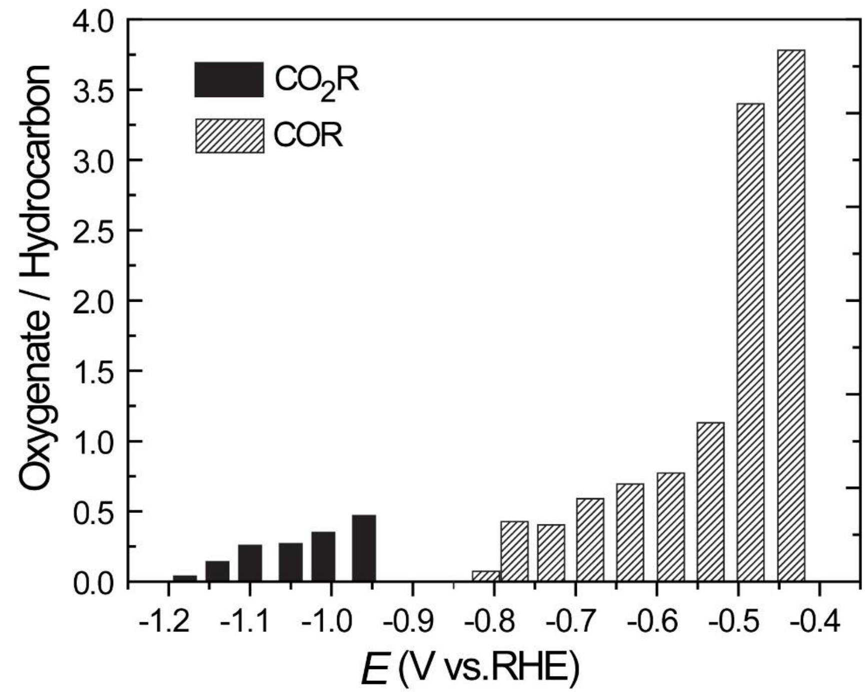
- The magnitude of the absolute electric field plays a crucial role in C-C coupling.
- A major effect involves the presence of cations at the interface.

X. Liu, P. Schlexer, J. Xiao, Y. Ji, L. Wang, R.B. Sandberg, M. Tang, K. Brown, H. Peng, S. Ringe, C. Hahn, T.F. Jaramillo, J.K. Nørskov, K. Chan, *Nature Communications*, 2019, 10, 32.

L. Wang, S.A. Nitopi, E. Bertheussen, M. Orazov, C.G. Morales-Guio, X. Liu, D.C. Higgins, K. Chan, J.K. Nørskov, C. Hahn*, T.F. Jaramillo*, *ACS Catalysis*, 2018, 8, 7445-7454.

# Selectivity of Cu for $CO_2R$ and COR



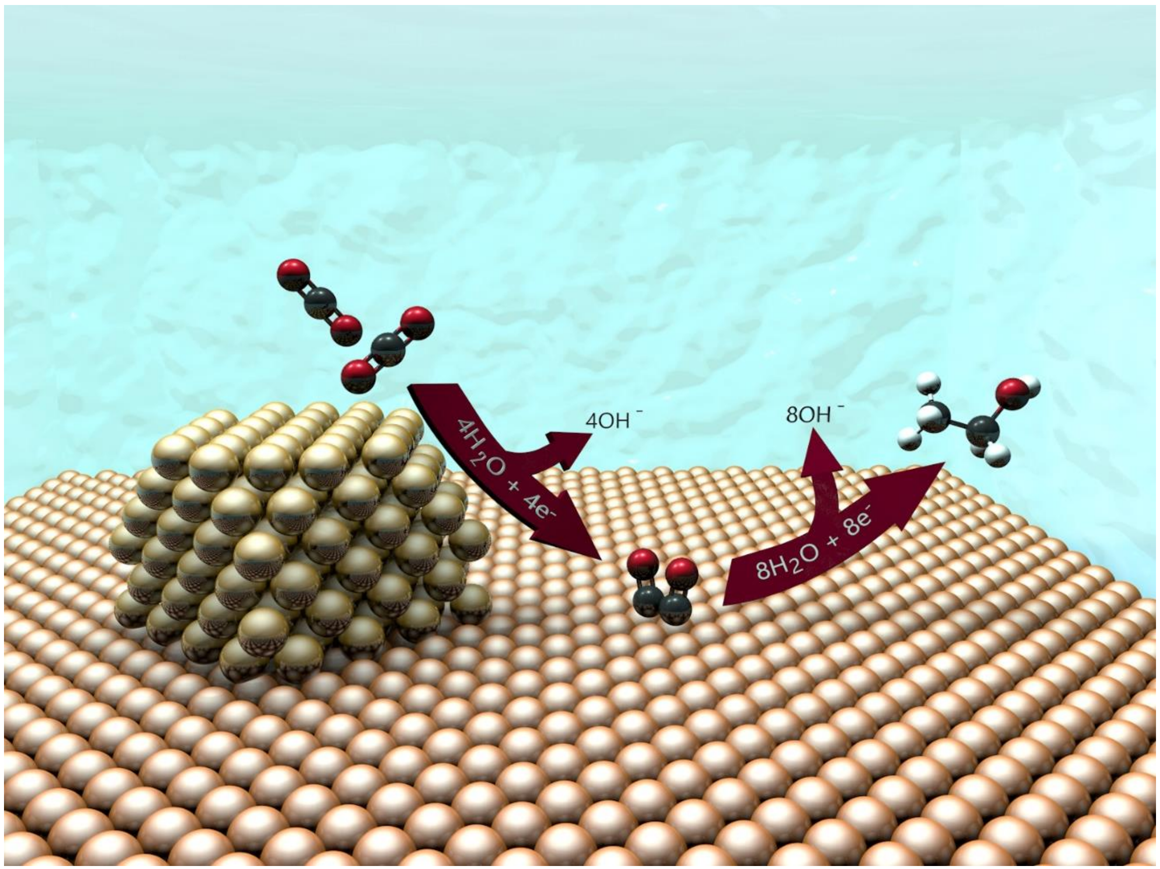




The applied potential may have a large role in guiding selectivity to C2+ oxygenates… Activity and selectivity are strongly coupled.

L. Wang, S.A. Nitopi, E. Bertheussen, M. Orazov, C.G. Morales-Guio, X. Liu, D.C. Higgins, K. Chan, J.K. Nørskov, C. Hahn*, T.F. Jaramillo*, *ACS Catalysis*, 2018, 8, 7445-7454.

# A scheme for improved $CO_2R$

*Tandem catalysis*
*at molecular length scales*




Carlos Morales Guío

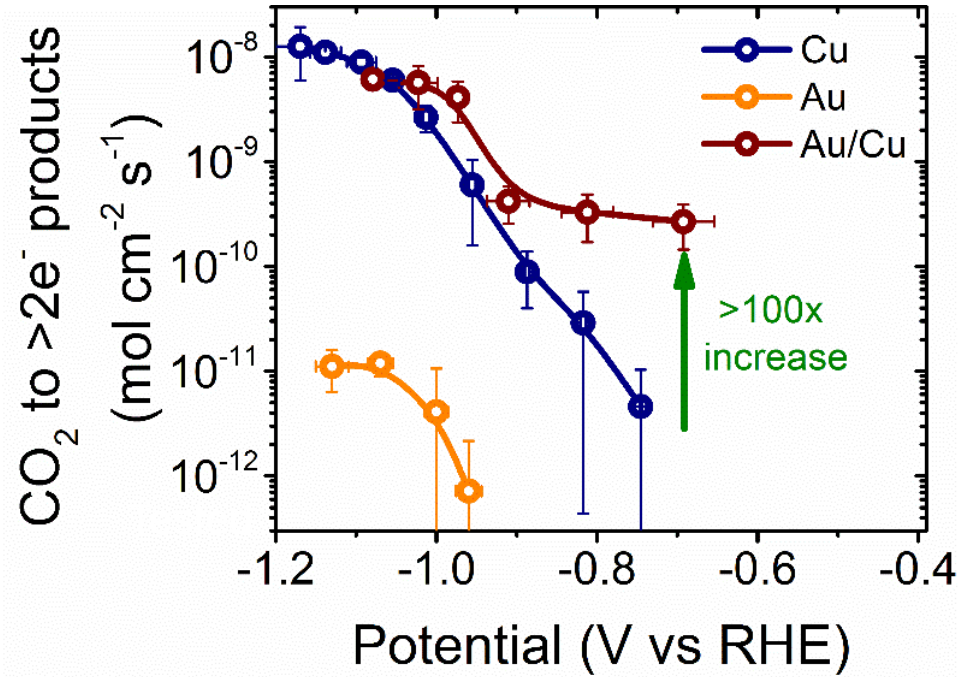
Etosha Cave

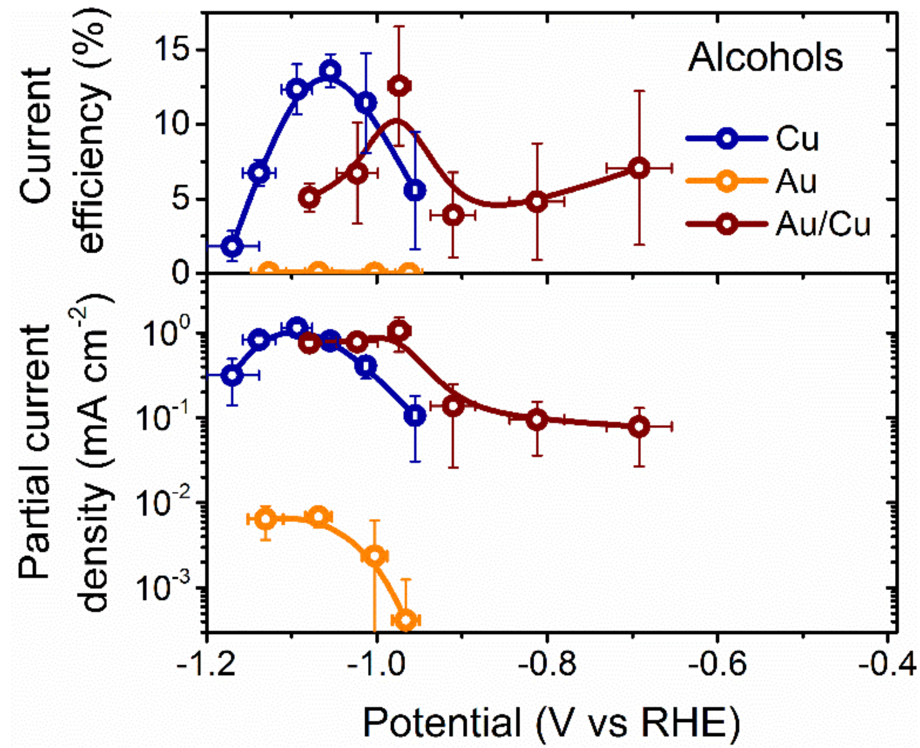
Chris Hahn

C.G. Morales-Guio†, E.R. Cave†, S.A. Nitopi, J.T. Feaster, L. Wang, K.P. Kuhl, A. Jackson, N.C. Johnson, D.N. Abram, T. Hatsukade, C. Hahn*, T.F. Jaramillo*, *Nature Catalysis*, 1, 764–771 (2018).

# Au Nanoparticles on pc-Cu (Au/Cu) Catalyst

***$CO_2$ reduction ($CO_2R$) in 0.1 M $KHCO_3$ (pH 7)***



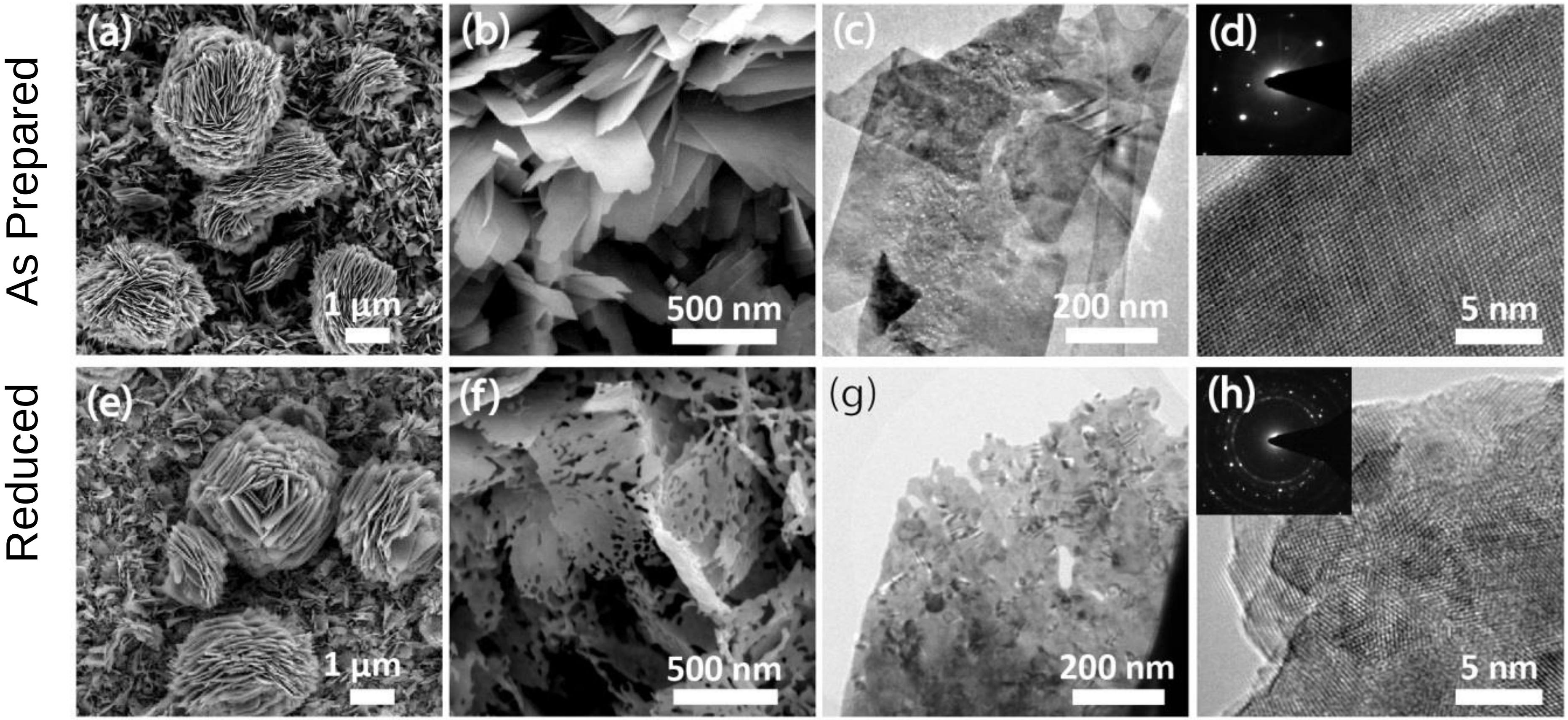




The Au/Cu catalyst has significantly enhanced activity to further reduced $CO_2R$ products than either pure Cu or pure Au.

C.G. Morales-Guio†, E.R. Cave†, S.A. Nitopi, J.T. Feaster, L. Wang, K.P. Kuhl, A. Jackson, N.C. Johnson, D.N. Abram, T. Hatsukade, C. Hahn*, T.F. Jaramillo*, *Nature Catalysis*, 1, 764–771 (2018).

***Electrodes surface area can impact selectivity.***

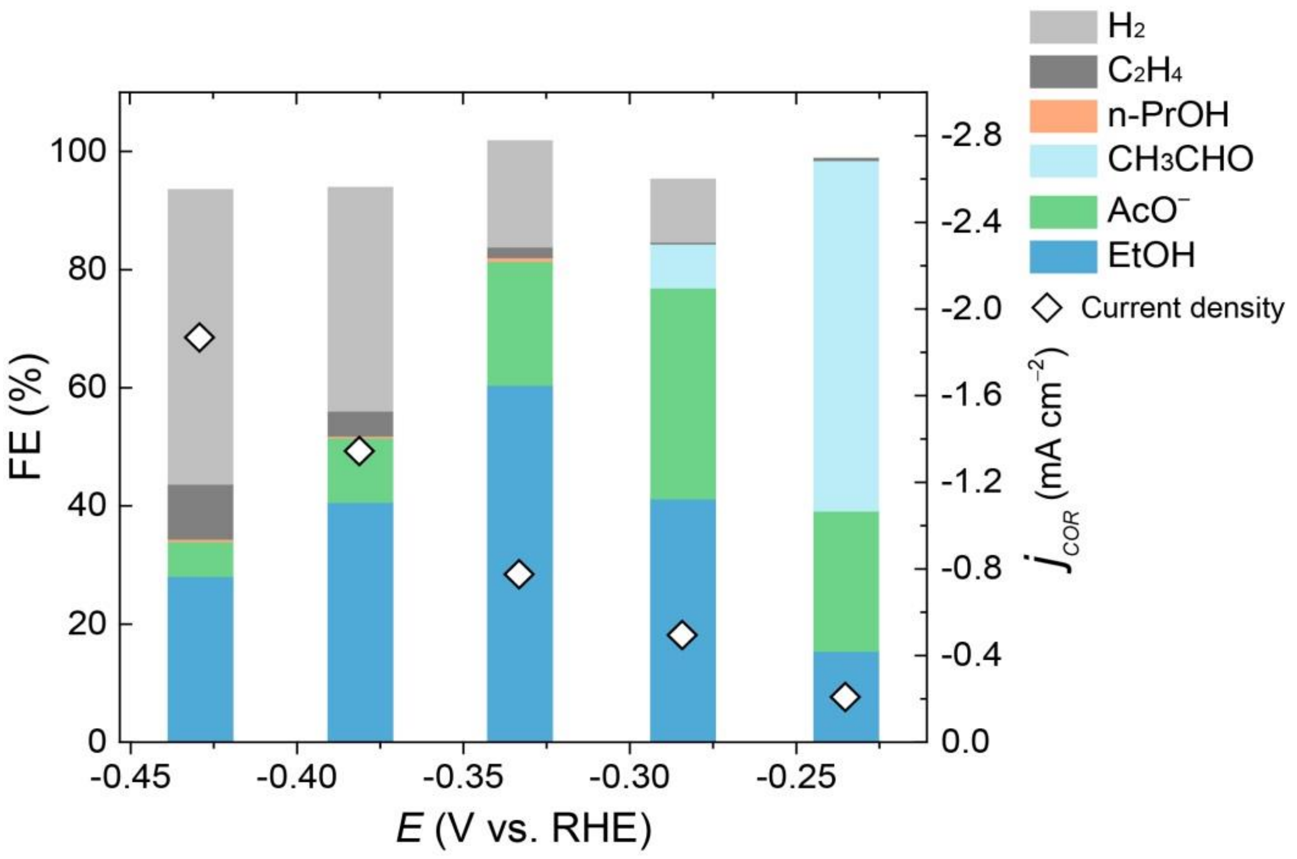
# High surface area catalyst morphologies – Cu nano-flowers

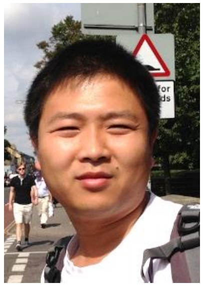



A high surface area Cu nano-flower catalyst was synthesized by developing a chemical CuO growth and electrochemical reduction procedure.

L. Wang, S. Nitopi, A.B. Wong, J. L. Snider, A.C. Nielander, C.G. Morales-Guio, M. Orazov, D.C. Higgins, C. Hahn, T.F. Jaramillo, *Nature Catalysis* (2019).

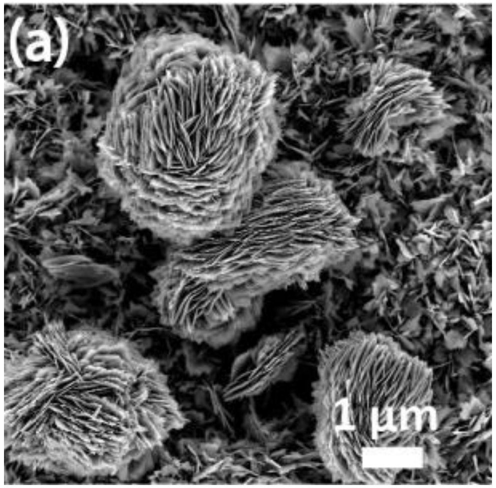
# COR on high surface area Cu nanoflowers



Lei Wang

Chris Hahn




- Nearly 100% selectivity is observed for C2+ oxygenates at only -0.23 V.
- This catalyst system exhibits the highest selectivity to oxygenated products known to date.

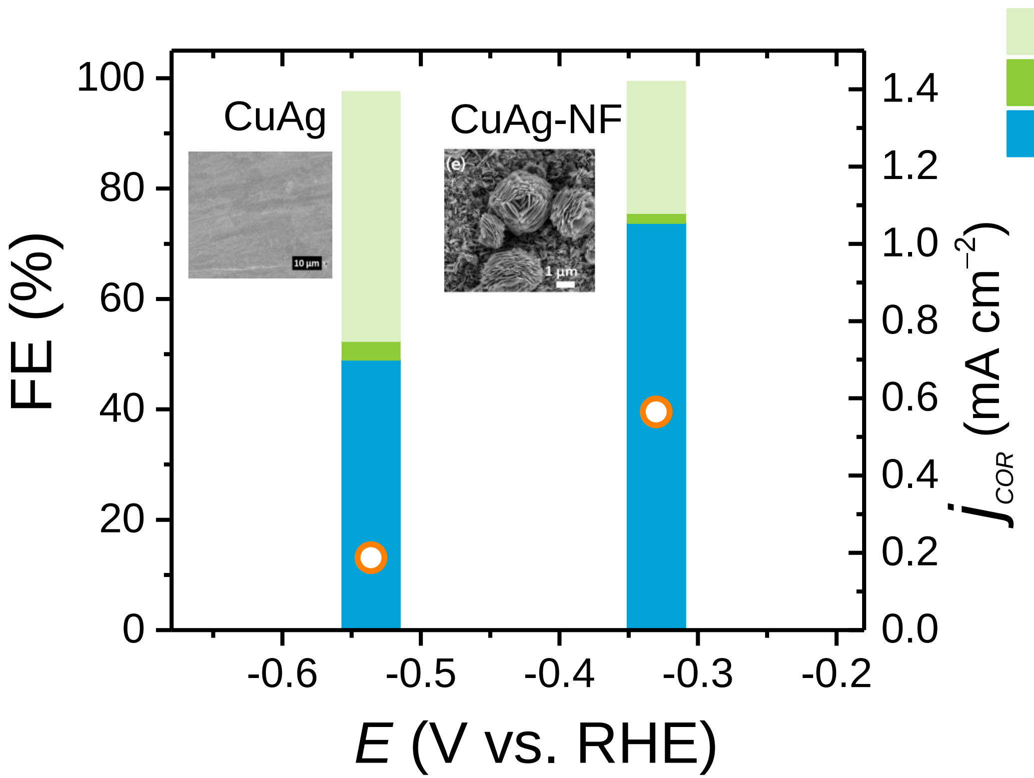

L. Wang, S. Nitopi, A.B. Wong, J. L. Snider, A.C. Nielander, C.G. Morales-Guio, M. Orazov, D.C. Higgins, C. Hahn, T.F. Jaramillo, *Nature Catalysis* (2019).

***Further impacting selectivity by tuning the binding energy of *O-bound intermediates:***

***Cu-Ag surface alloys***

# CuAg catalysts for COR: Acetaldehyde production

*CuAg electrodes were prepared by Ag galvanic exchange on Cu.*




Lei Wang

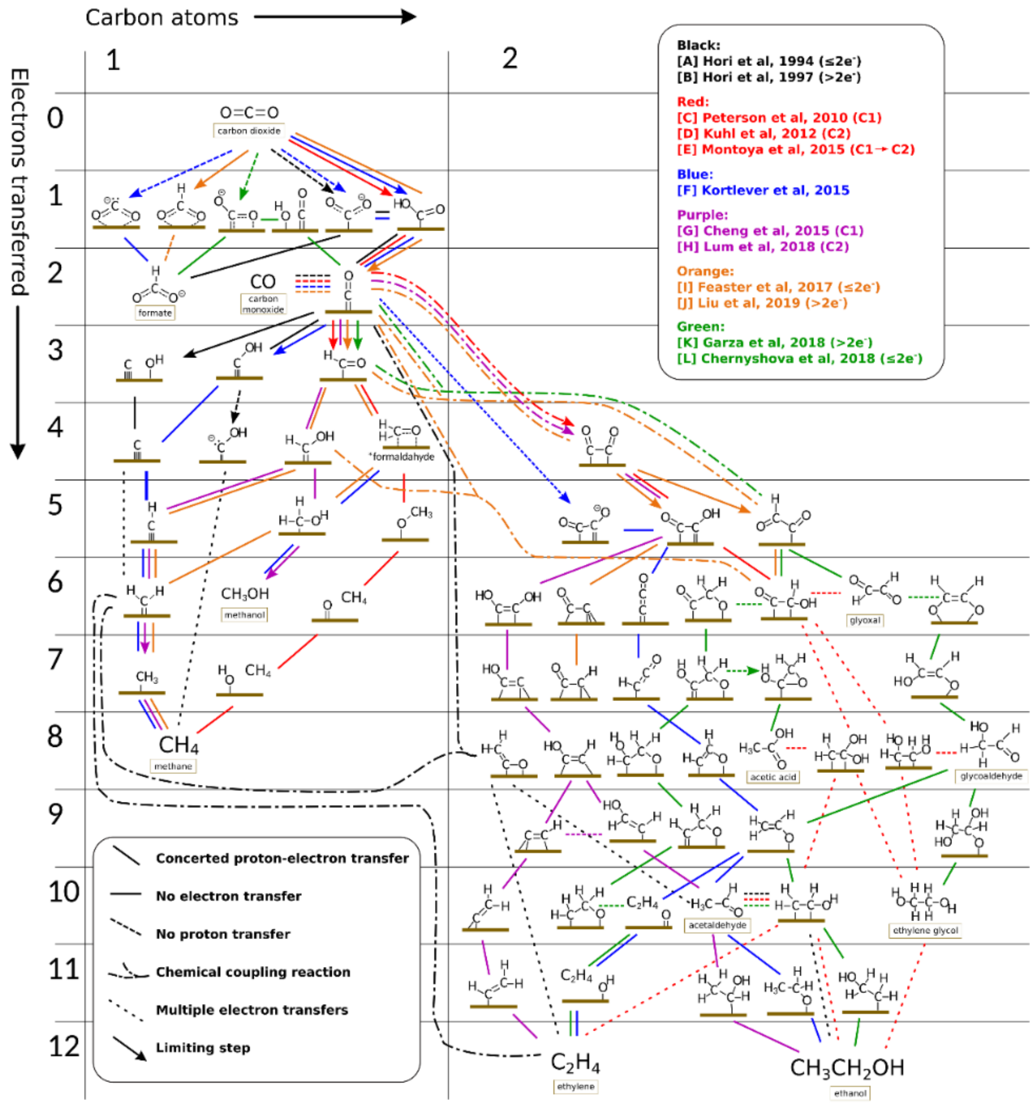
Chris Hahn

- ❑ *High surface area CuAg-NF electrodes improve selectivity by suppressing the HER while increasing COR reaction rates, particularly to acetaldehyde.*

Wang, L., Higgins, D.C., Ji, Y., Morales-Guio, C.G., Chan, K., Hahn, C.*, Jaramillo, T.F.*, Submitted, 2019.

# Mechanistic aspects of $CO_2$ reduction on Cu

- Formate is a dead-end.
- CO is the key intermediate to further reduced (>2 e$^-$) products, e.g. $CH_4$, $C_{2+}$ compounds.
- **How can we suppress $H_2$ evolution?**





Stephanie Nitopi


Chris Hahn

- **How can we favor $C_{2+}$ products over $C_1$ products ($CH_4$)?**
- **How can we favor $C_{2+}$ oxygenates over HC's?**
- **How can we selectively produce a single desired $C_{2+}$ oxygenate?**

S.A. Nitopi†, E. Bertheussen†, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E.L. Stephens, K. Chan, C. Hahn, J.K. Nørskov*, T.F. Jaramillo*, I. Chorkendorff*, *Chemical Reviews*, 2019.

$H_2$

$H_2O$ splitting

C-based products

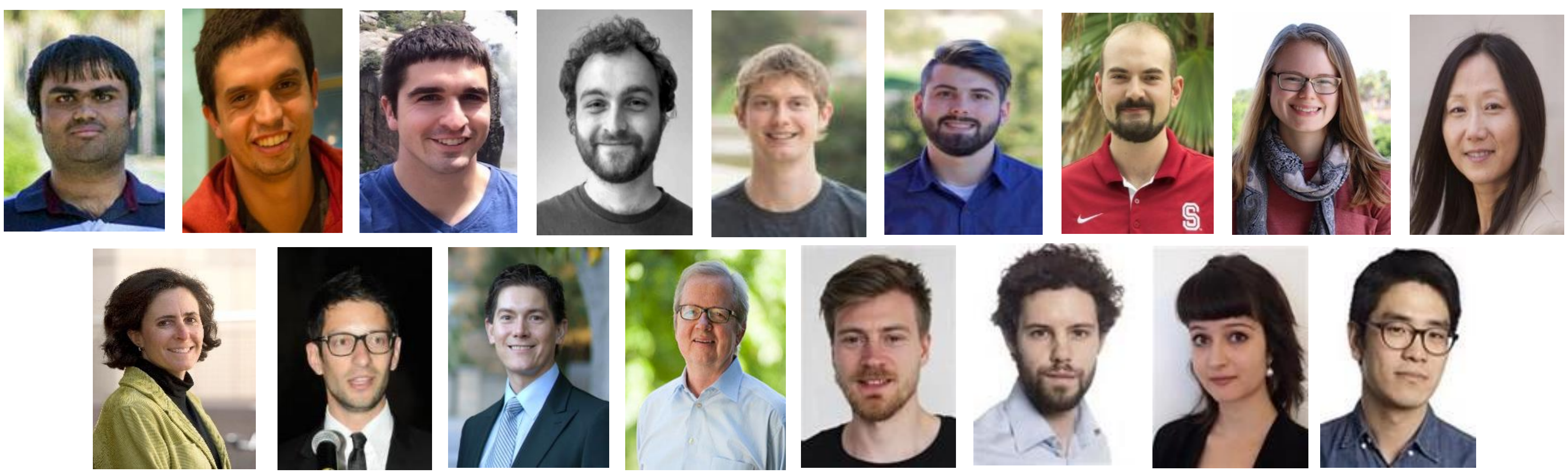
$CO/CO_2$ reduction

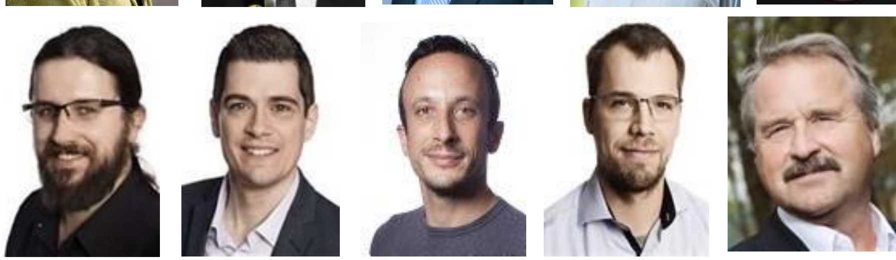
$NH_3$

$N_2$ reduction

# V-Sustain $NH_3$ Team

- Aayush R. Singh
- Adam Nielander
- Joshua M. McEnaney
- Jay A. Schwalbe
- Brian Rohr
- Michael Statt
- Jon Grant Baker
- Sarah Blair
- Zhenan Bao
- Stacey F. Bent
- Matteo Cargnello
- Thomas F. Jaramillo
- Jens K. Nørskov
- Kasper Enemark-Rasmussen
- Stefano Mezzavilla
- Suzanne Z. Andersen
- Sungeun Yang
- Viktor Čolić
- Jakob Kibsgaard
- Ifan E. L. Stephens
- Peter C. K. Vesborg
- Ib Chorkendorff



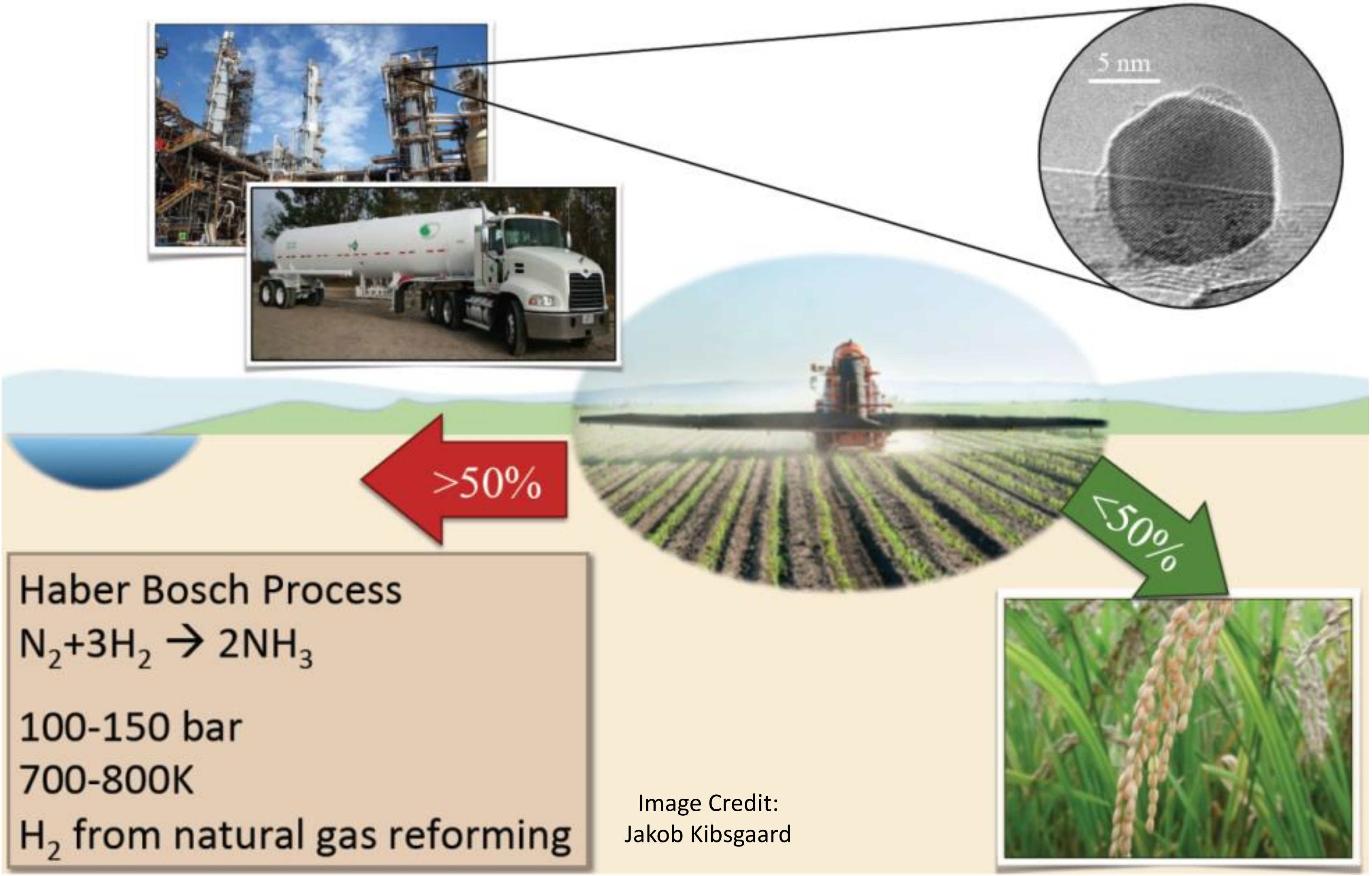


VILLUM FONDEN

SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

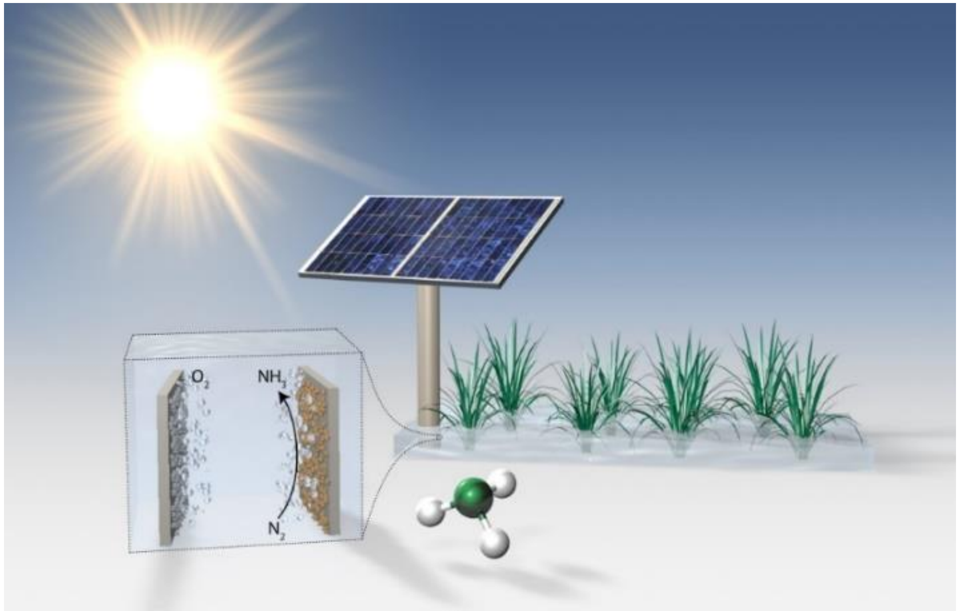
SURFCAT
Surface Physics and Catalysis

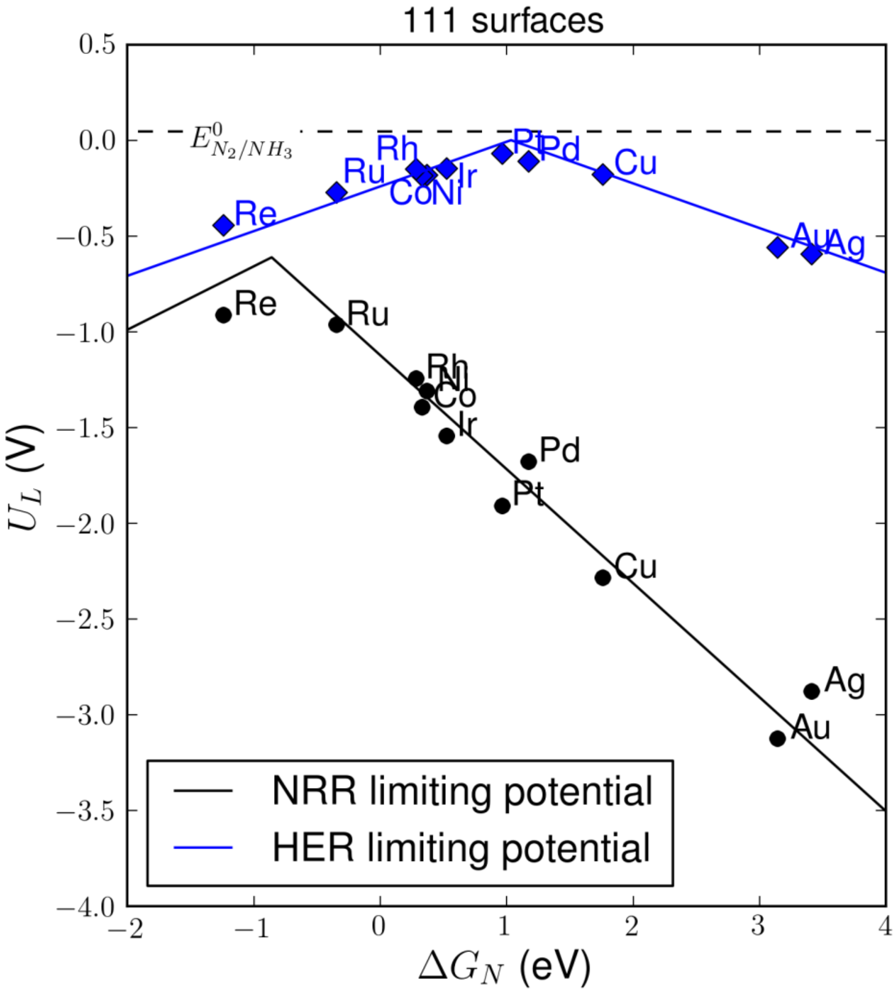
# The Haber Bosch Process – Industrial Ammonia Synthesis




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

# Electrocatalysis on metals




Competition with the $H_2$ evolution is a significant challenge

Can we control the kinetics of protons at the active site?


Montoya, J. H.; Tsai, C.; Vojvodic, A.; Nørskov, J. K. *ChemSusChem* **2015**, *8*, 2180.

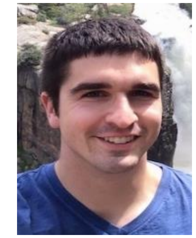
# Alternative Strategy:
# Stepwise cycling process to circumvent $H_2$ evolution

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

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

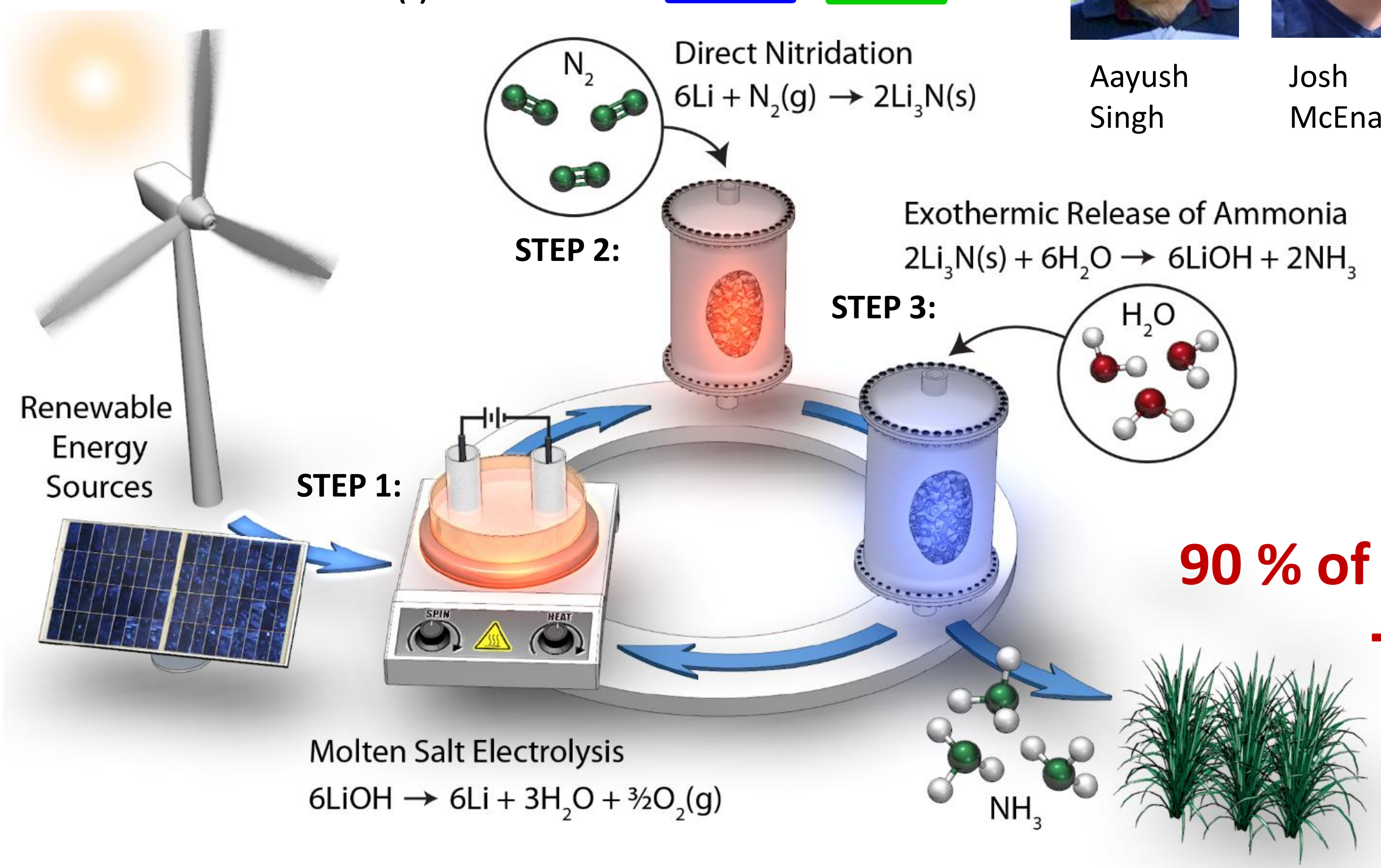
**STEP 3:** $2Li_3N_{(s)} + 6H_2O \longrightarrow 6LiOH + 2NH_3$

Aayush Singh



Josh McEnaney

Jay Schwalbe




**90 % of electrons → $NH_3$**

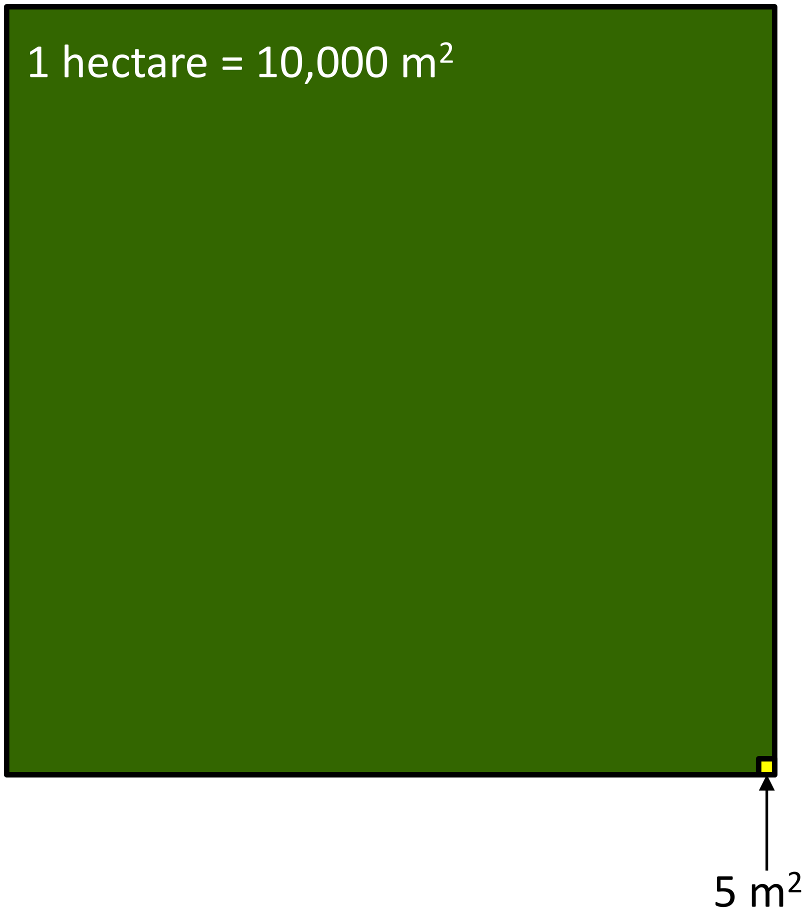
J. M. McEnaney, A. R. Singh, J. A. Schwalbe, J. Kibsgaard, J. C. Lin, M. Cargnello, T. F. Jaramillo, J. K. Nørskov
*Energy Environ. Sci.* **10** 1621 (2017).

# Solar-driven $NH_3$ feasibility: Land Area

Typical agricultural field requires:

100 kg $NH_3$/hectare/yr

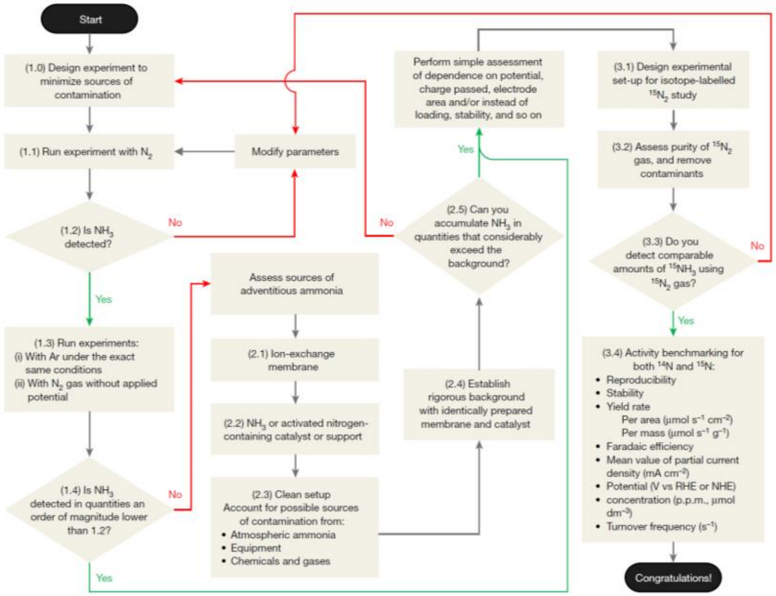
For a 90% Faradaic Efficiency process:
Only 5 $m^2$ of solar cells needed!



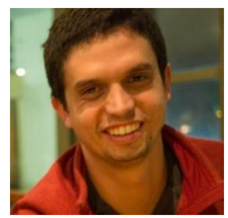

Sawyer, J.; Nafziger, E.; Randall, G.; Bundy, L.; Rehm, G.; Joern, B. Concepts and Rationale for Regional Nitrogen Rate Guidelines for Corn; Iowa State University-University Extension PM: Ames, IA, 2015.

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.

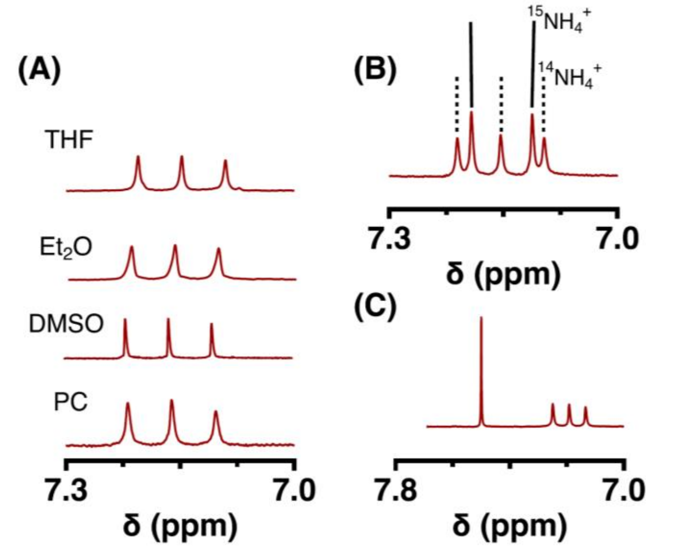
# Protocols for electrochemical $NH_3$ production




Suzanne Andersen



Adam Nielander




**"A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements"**

Suzanne Z. Andersen, Viktor Čolić, Sungeun Yang, Jay A. Schwalbe, Adam C. Nielander, Joshua M. McEnaney, Kasper Enemark-Rasmussen, Jon G. Baker, Aayush R. Singh, Brian A. Rohr, Michael J. Statt, Sarah J. Blair, Stefano Mezzavilla, Jakob Kibsgaard, Peter C. K. Vesborg, Matteo Cargnello, Stacey F. Bent, Thomas F. Jaramillo, Ifan E. L. Stephens, Jens K. Nørskov & Ib Chorkendorff

*Nature* 570 (2019) 504–508.

**"A Versatile Method for Ammonia Detection in a Range of Relevant Electrolytes via Direct Nuclear Magnetic Resonance Techniques"**

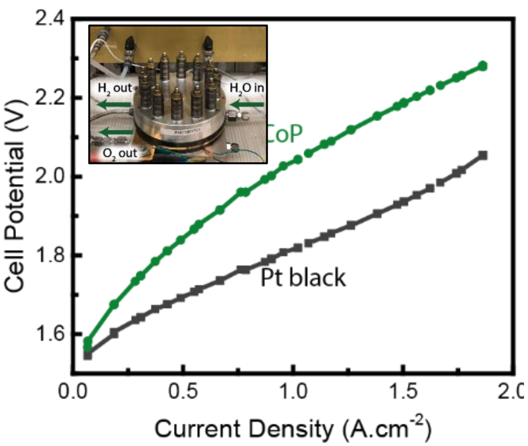
Adam C. Nielander, Joshua M. McEnaney, Jay A. Schwalbe, Jon G. Baker, Sarah J. Blair, Lei Wang, Jeffrey G. Pelton, Suzanne Z. Andersen, Kasper Enemark-Rasmussen, Viktor Čolić, Sungeun Yang, Stacey F. Bent, Matteo Cargnello, Jakob Kibsgaard, Peter C. K. Vesborg, Ib Chorkendorff, Thomas F. Jaramillo

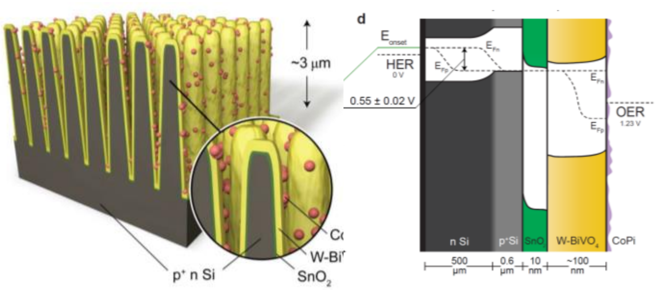
*ACS Catalysis* 9 (2019) 5797-5802

# Summary & Conclusions

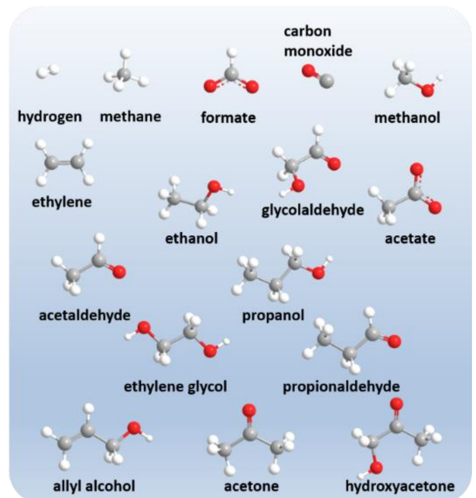
**Electrochemical pathways to fuels and chemicals are promising, enabled by efforts in catalyst design and development.**

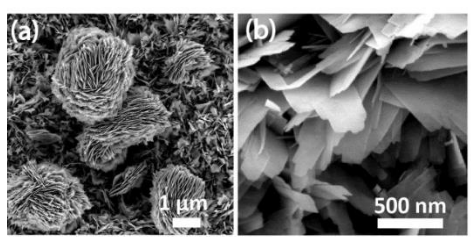
**$H_2$ production by water electrolysis and PEC water-splitting.**



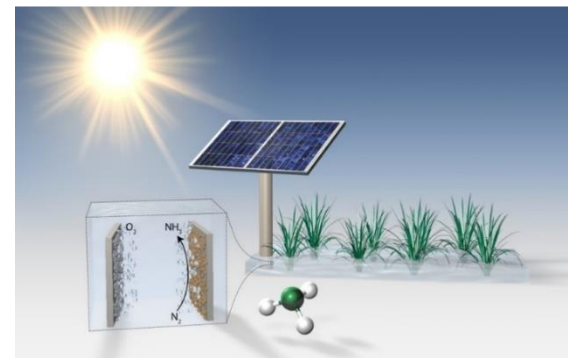



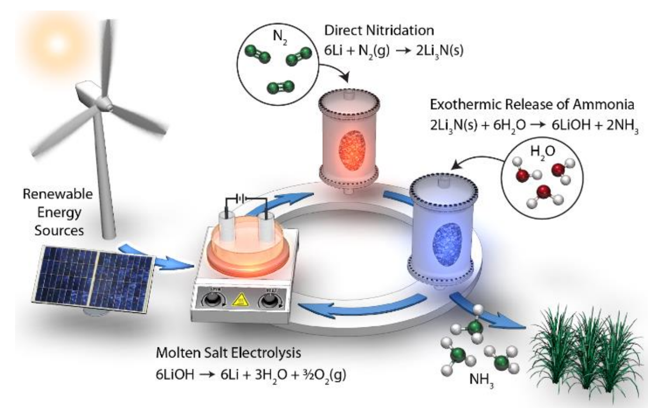

**$CO_2$ electrolysis for the production of carbon-based fuels and chemicals.**




**$N_2$ reduction for ammonia ($NH_3$) production powered by renewable electricity.**





# Jaramillo Laboratory

**PhD Students**
- Michael Boyd
- Alan Landers
- John Lin
- Joel Sánchez
- Eduardo Valle
- David Palm
- Micha Ben-Naim
- McKenzie Hubert
- Melissa Kreider
- David Koshy
- Samuel Dull
- Sarah Blair
- Jaime Acosta-Aviles
- Kabir Abiose
- Daniel Corral
- José Zamora Zeledon

**Undergrad & M.S.**
Alexandra Young
Alvaro Simán
Sela Berenblum
Kristin Abels
Jackelyn Rodríguez

**Post-doctroral Researchers**
- Dr. Michaela Burke-Stevens
- Dr. Dong Un (Daniel) Lee
- Dr. Josh McEnaney
- Dr. Adam Nielander
- Dr. Lei Wang
- Dr. Andrew Wong

**SLAC Research Associate**
Dr. Alessandro Gallo

**Staff Scientists**
Dr. Christopher Hahn

**Collaborators**
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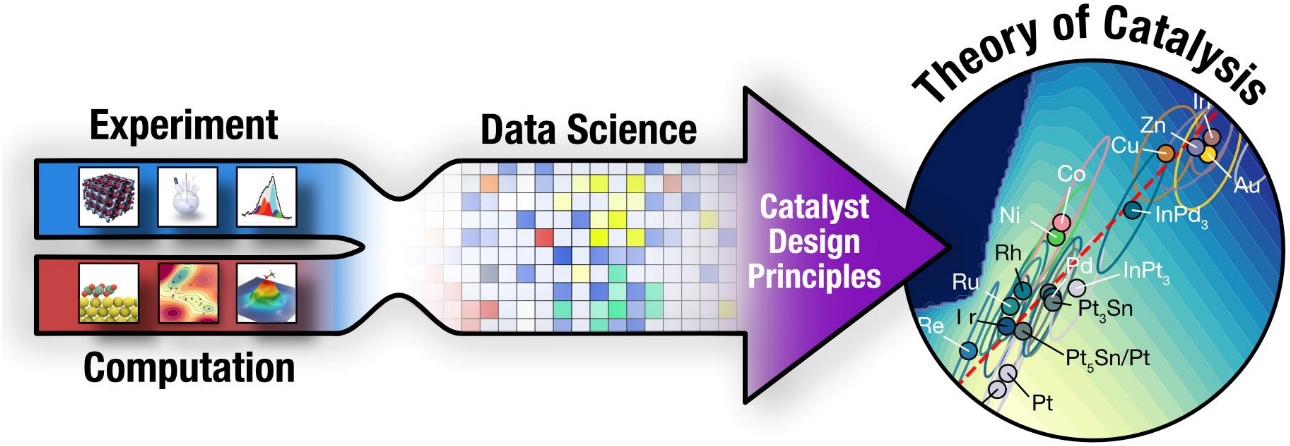
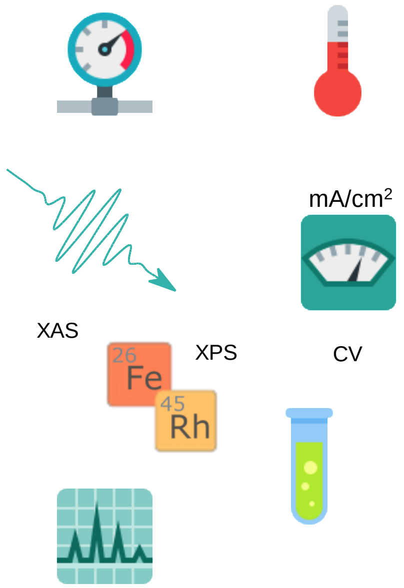
Prof. Ib Chorkendorff, Prof. J. Kibsgaard
Prof. I.E.L. Stephens, Prof. P.C.K. Vesborg
Prof. S.F. Bent, Prof. Z. Bao
Prof. M. Cargnello, Prof. A. Nilsson
Dr. K. Ayers, Dr. C. Capuano, Prof. J. Harris
Dr. T. Deutsch, Dr. J. Young
Dr. M. Steiner, Dr. D. Friedman
Dr. P. De Luna, Dr. S. Jaffer, Prof. E.H. Sargent
Dr. E. Clark, Dr. J. Resasco, Prof. A.T. Bell
Dr. Y.-G. Kim, Dr. J. Baricuatro, Prof. Manny Soriaga


NSF
GCEP
Global Climate & Energy Project
STANFORD UNIVERSITY
SBIR STTR
HydroGEN
Advanced Water Splitting Materials
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
U.S. DEPARTMENT OF ENERGY | Office of Science
JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS
Stanford Natural Gas Initiative

# Integrating experiments into data science efforts to advance catalysis theory



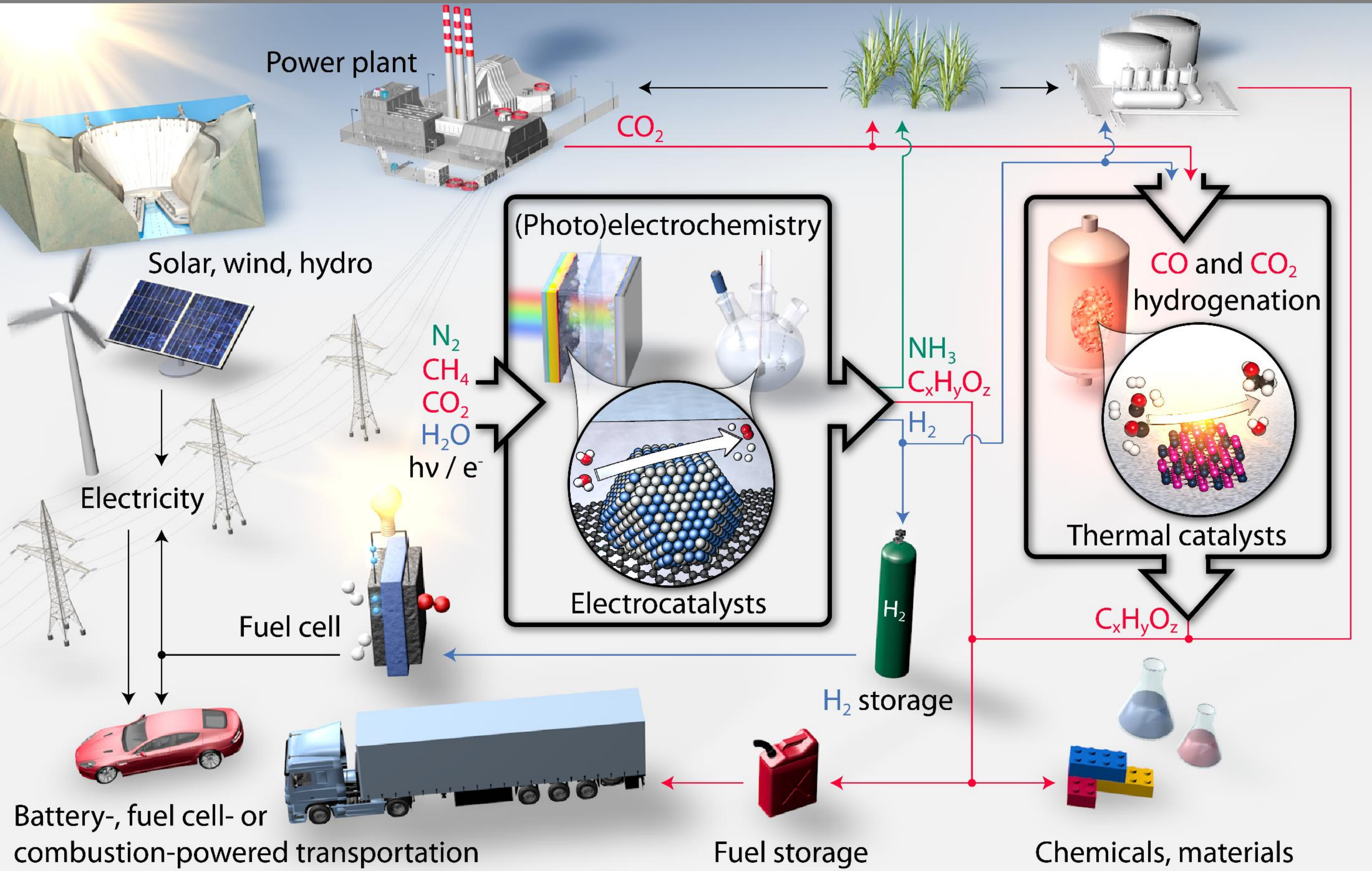

**Question:**
Is it possible to identify a small, manageable # of experimental parameters for the community to keep track of in a uniform manner?




<u>Synthesis/Characterization</u>
- Synthesis parameters
- Measured catalyst composition
- Particle size
- Crystal structure
- Support material
- …

<u>Catalyst performance:</u>
- Reaction studied
- Reaction conditions
  (feed, T, P, electrolyte, voltage, etc.)
- Reaction rate per cm$^2$
- Reaction rate per gram
- Selectivity
- …

# *Catalyzing a Sustainable Future*




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