A Novel Modular Coal-to-Methanol Reactor Using Electroactive Membranes

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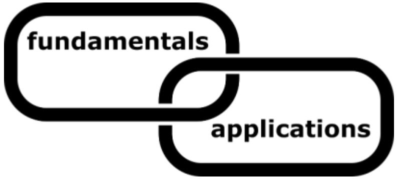
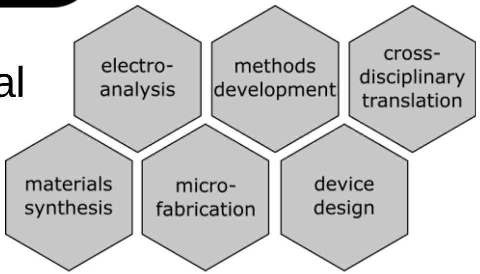
McKone Group: The Pitt Redox Lab

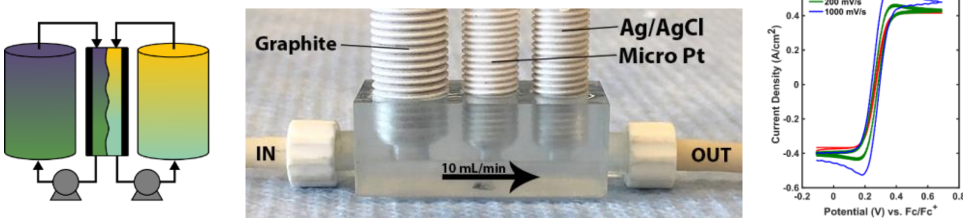


use-inspired
basic research

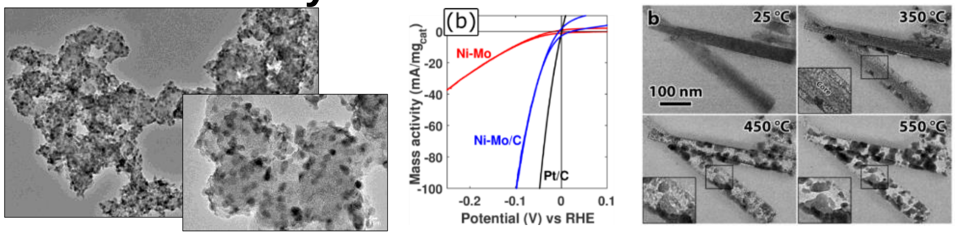
electrochemical science and technology



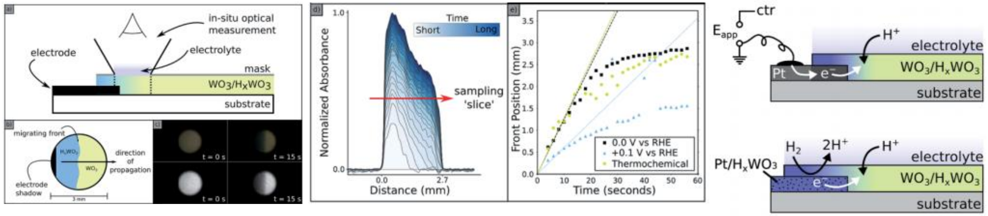
Redox Flow Batteries



Alkaline electrolysis and fuel cells

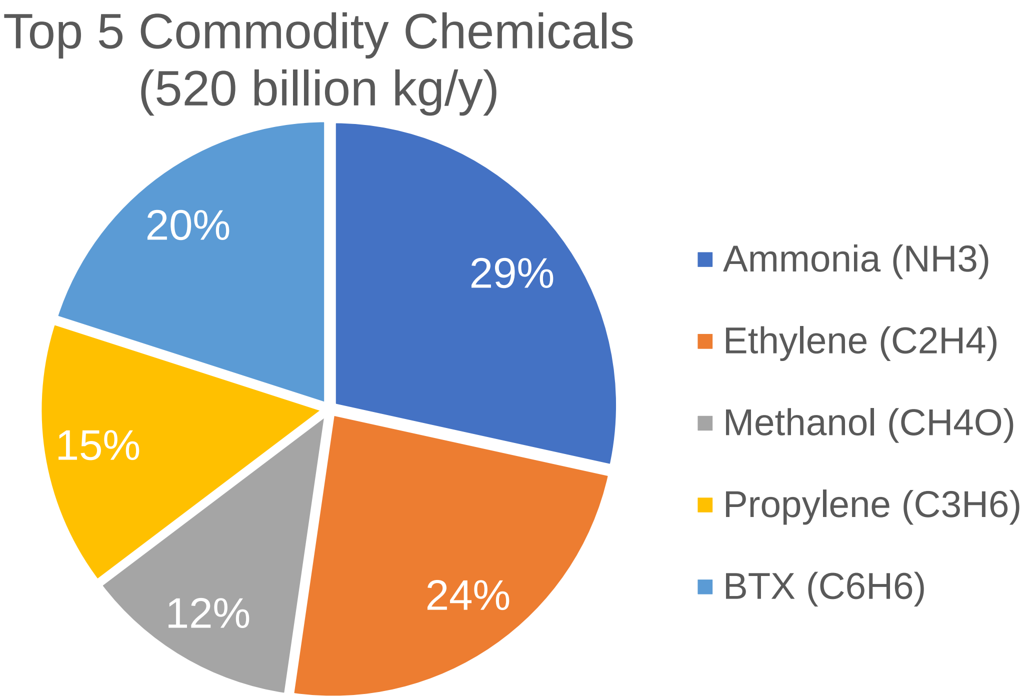


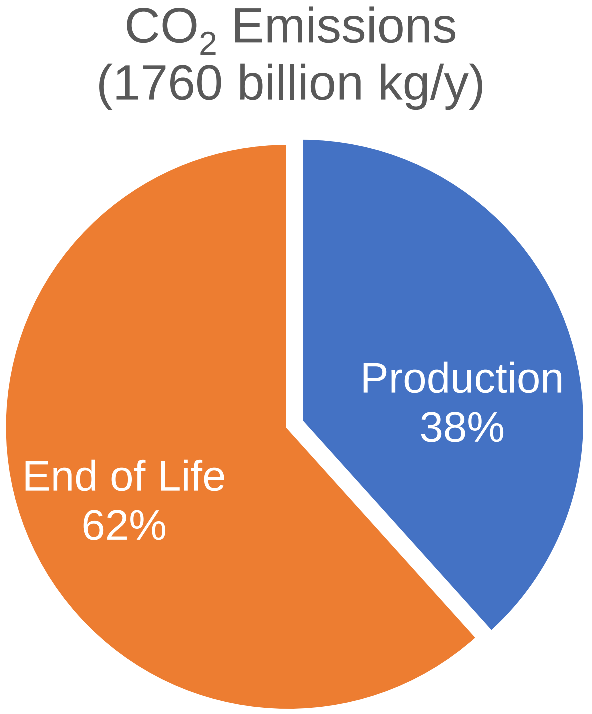
Thermo-electrochemical catalysis



Reducing the C-intensity of chemical manufacturing

still requires a lot of carbon and hydrogen…

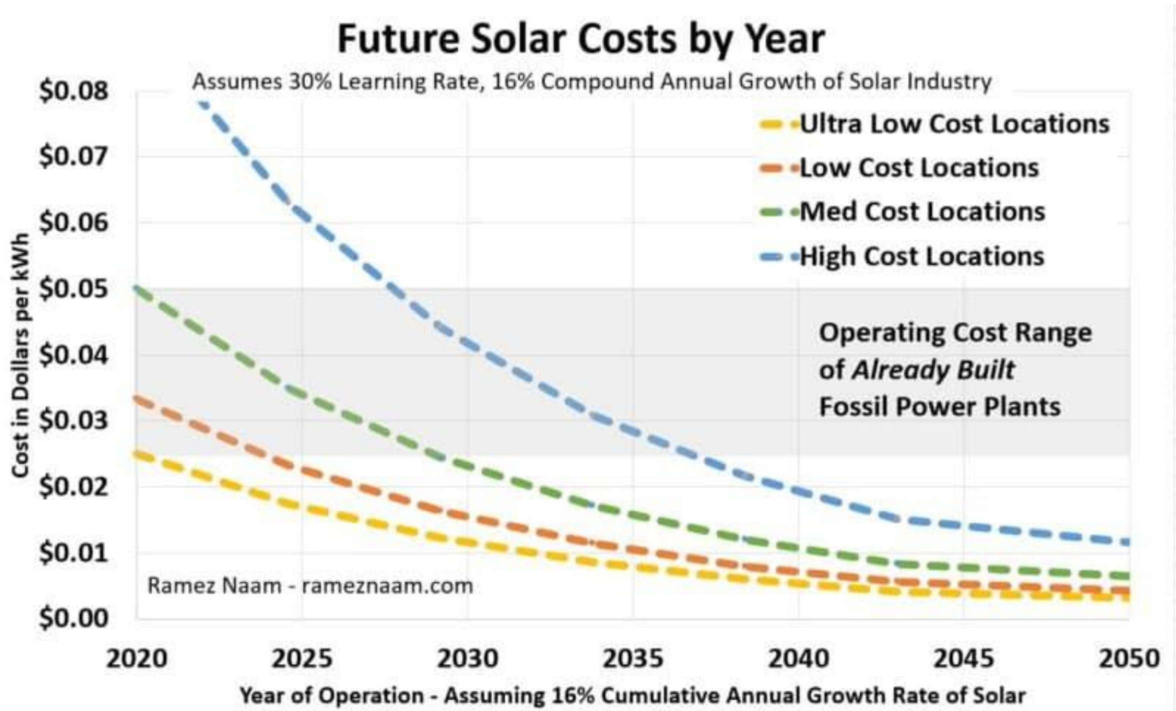




Data from Schiffer and Manthiram *Joule* **2017**, *1* (1), 10-14.

Opportunities from renewable (over)supply

Cheap electrons from renewables provide an opportunity to use carbon-rich feedstocks and sequestered CO_2 for value-added chemical production



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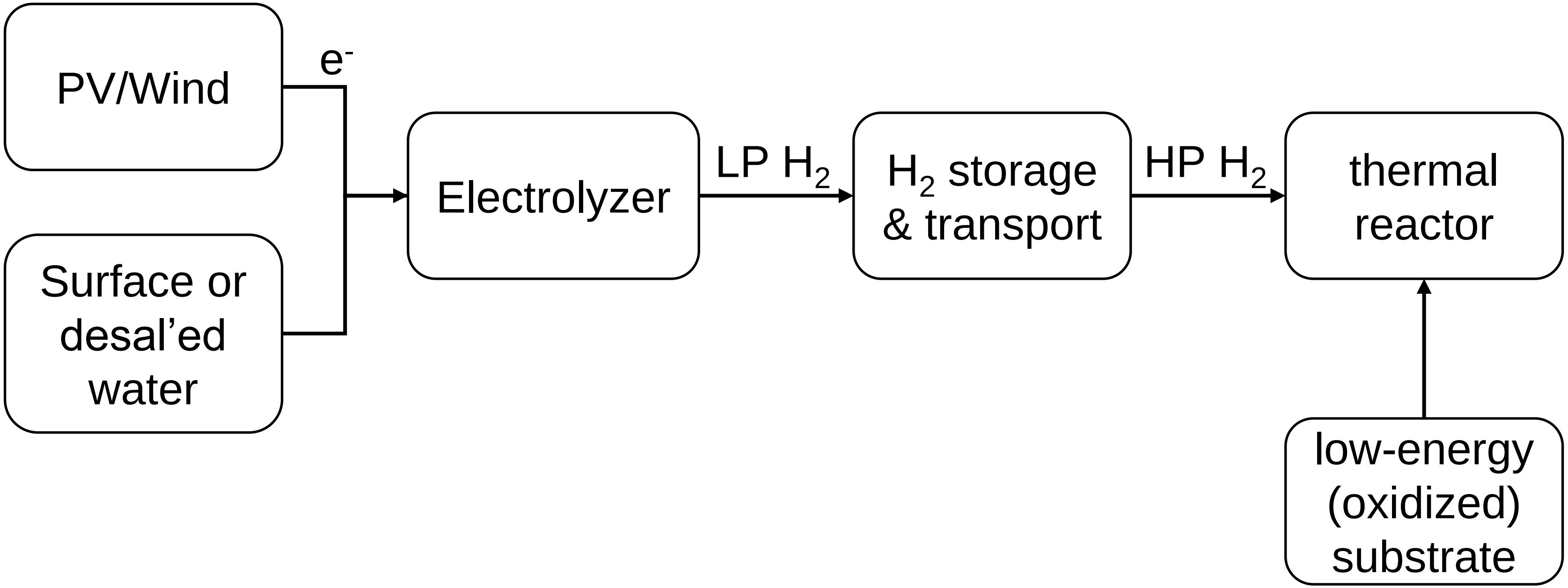
Hedging our bets…

Electrolytic hydrogen is an attractive alternative to fossil-derived hydrogen



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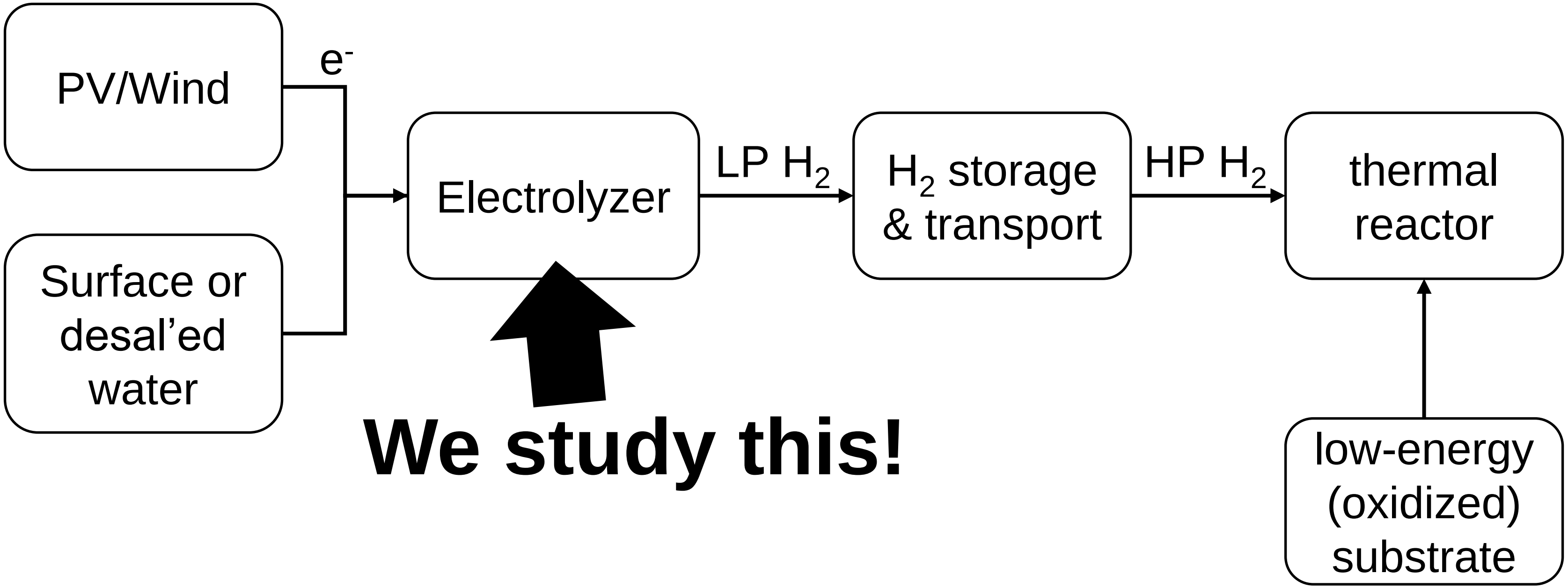
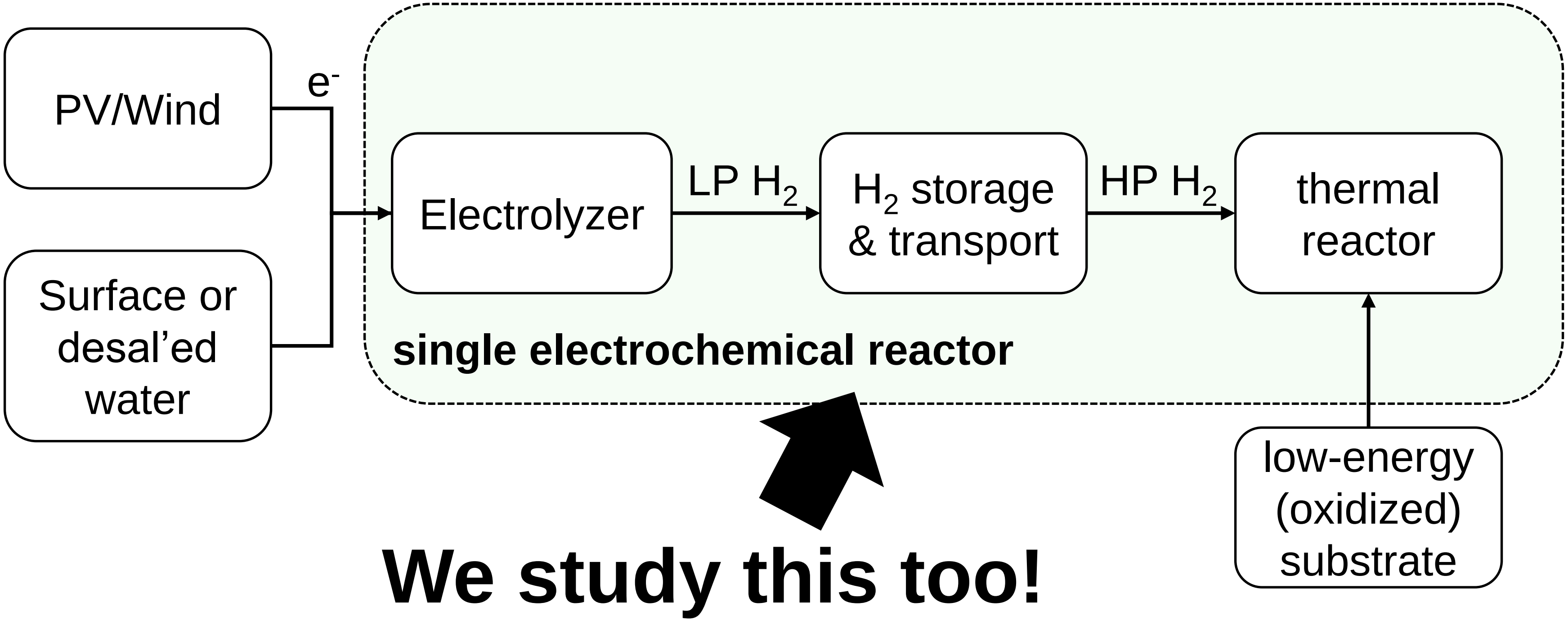


Hedging our bets…

Process intensification: radical decrease in process complexity, cost, and/or footprint by replacing several individual process units with one electrochemical reactor



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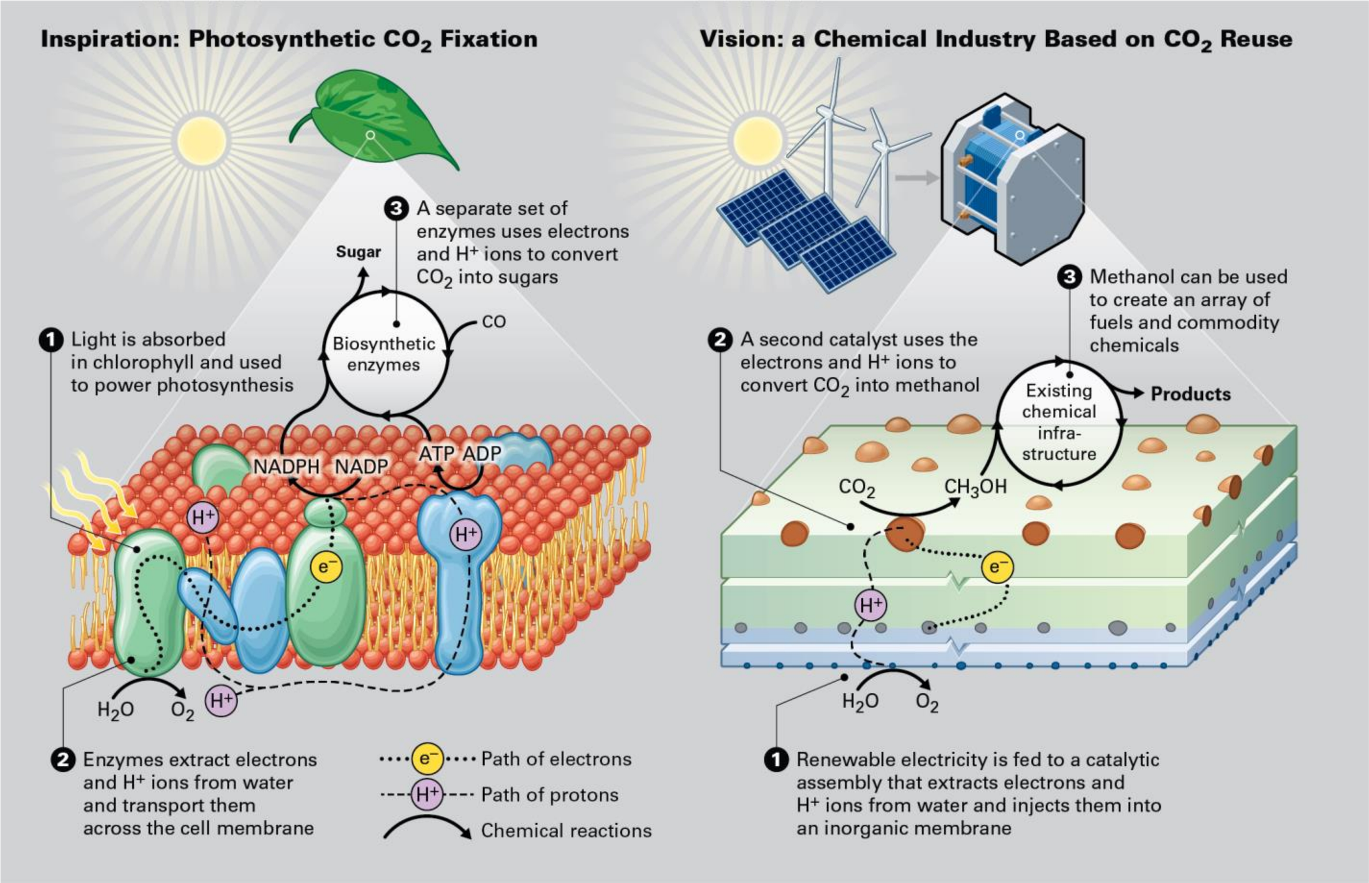
Electrochemically Pumped Membrane Reactor

Linking thermal & electrochemical steps across a charge-conducting membrane



Also see work by Surendranath, Berlinguette, CoorsTek, and others

image credit: J. McKone & Rick Henkel

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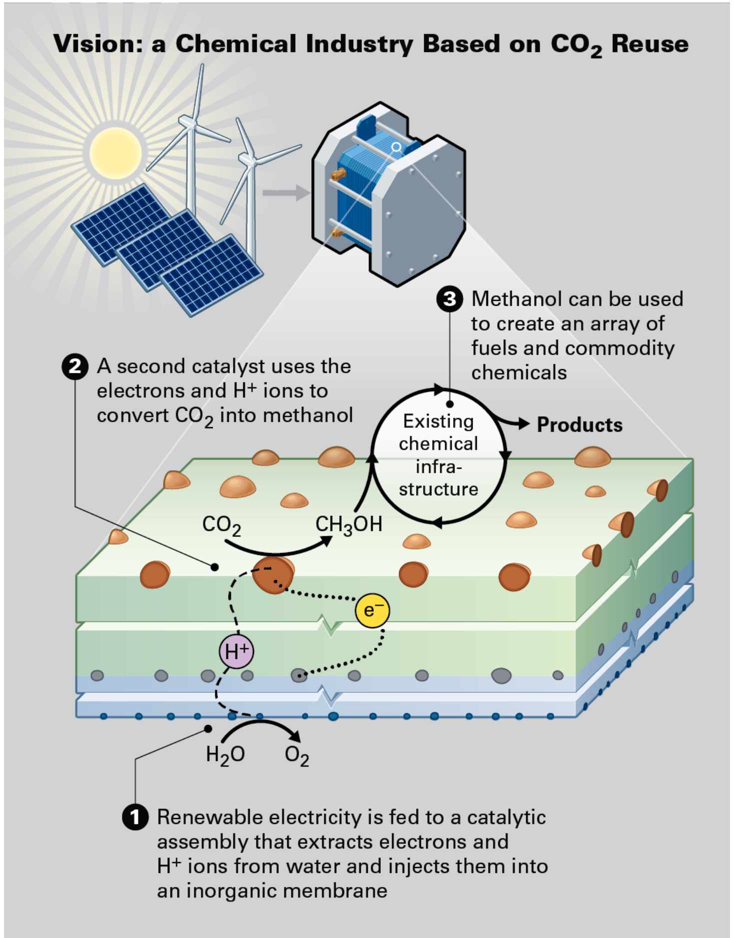

Wish list:

1. Inorganic proton-electron conductor, stable under reducing conditions and elevated T
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5. Ability to tune reactivity of hydrogen within oxide phase to match reactant

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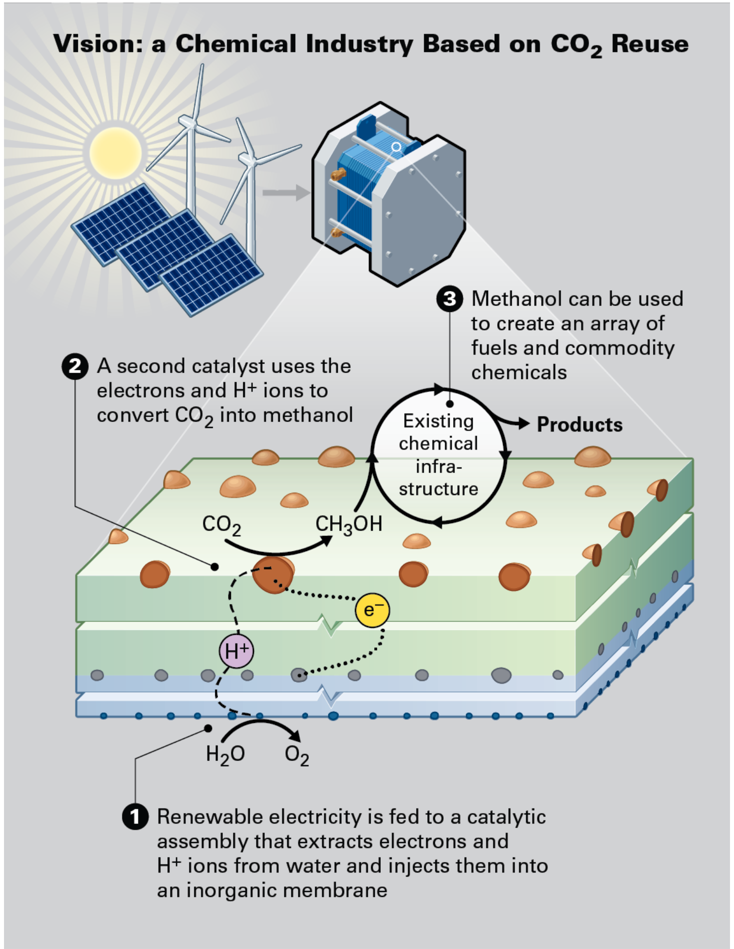

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Transition metal hydrogen bronzes

$$H_xMO_Y$$

(M = Ti, V, Mo, etc.)

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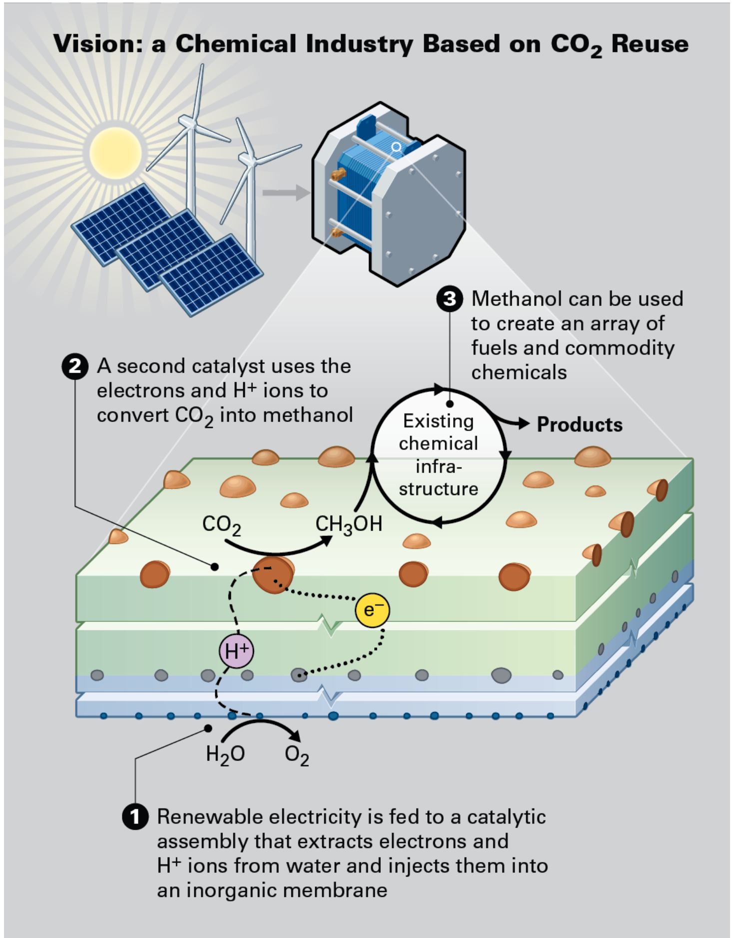

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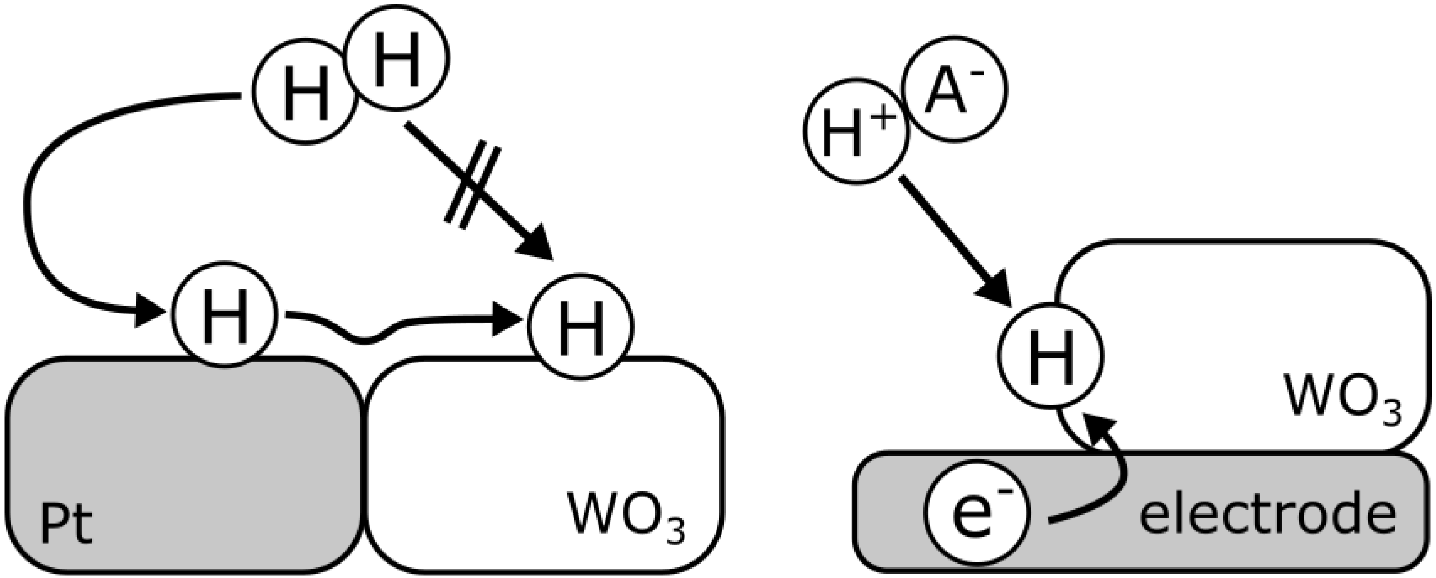
H-spillover and H-intercalation

classical pictures imply different pathways



Adapted from: Conner, W. C.; Falconer, J. L. *Chem. Rev.* **1995**, *95* (3), 759–788.

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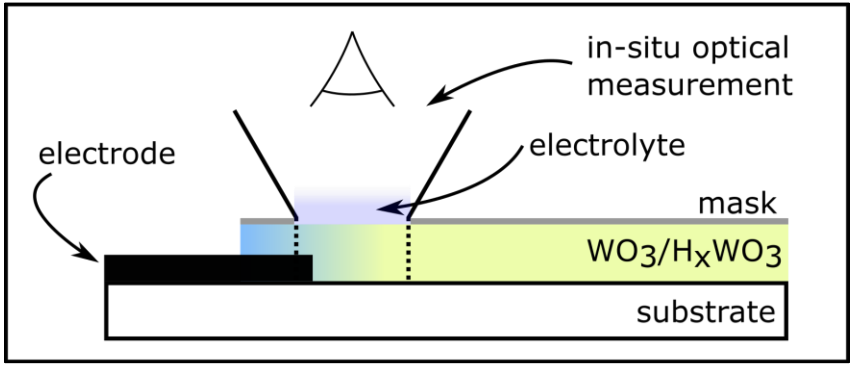
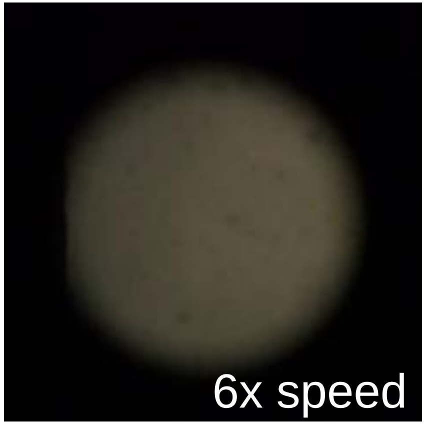
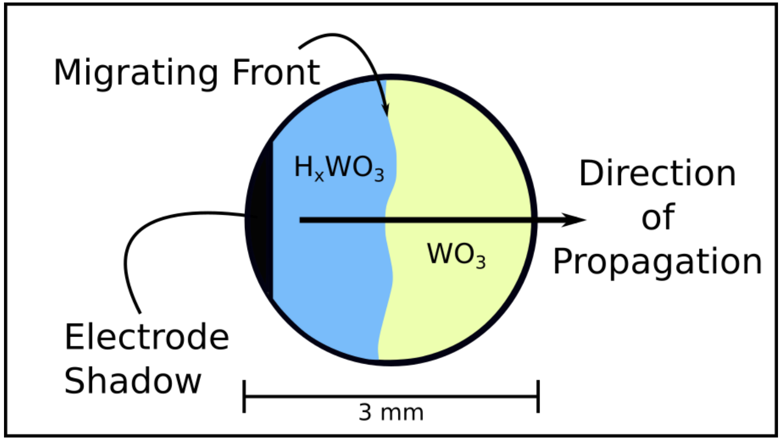
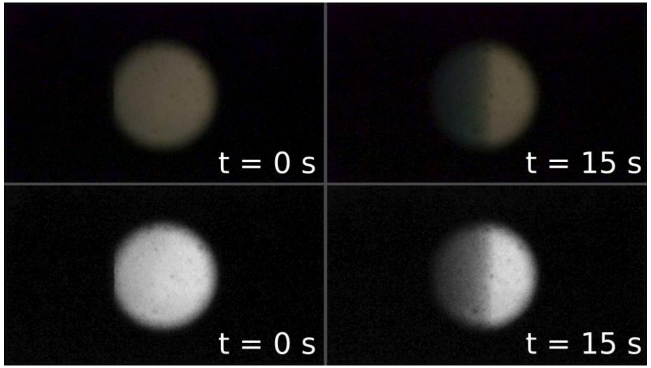
Dynamics of hydrogen uptake and diffusion

Imaging lateral H migration via H_xWO_3 “fronts”









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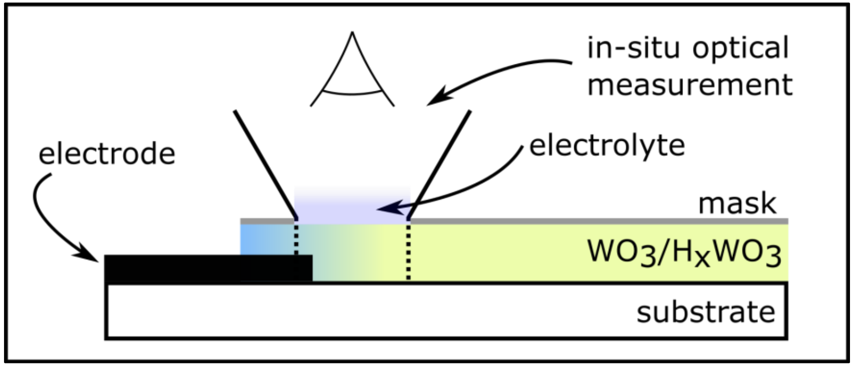

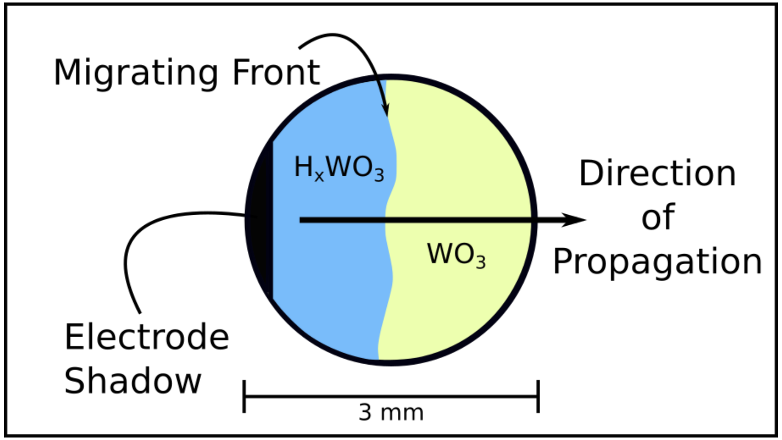

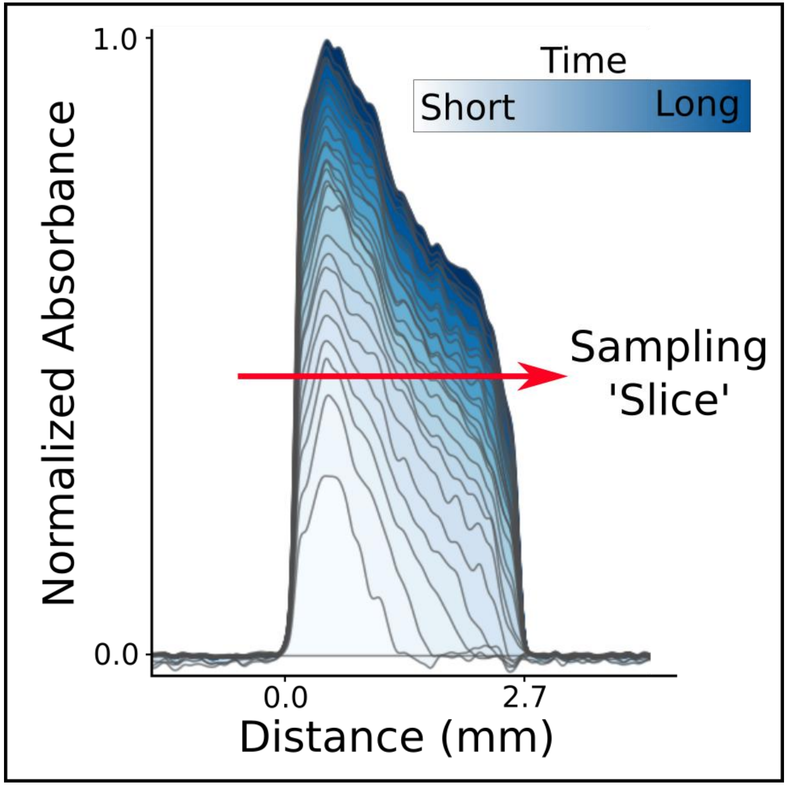

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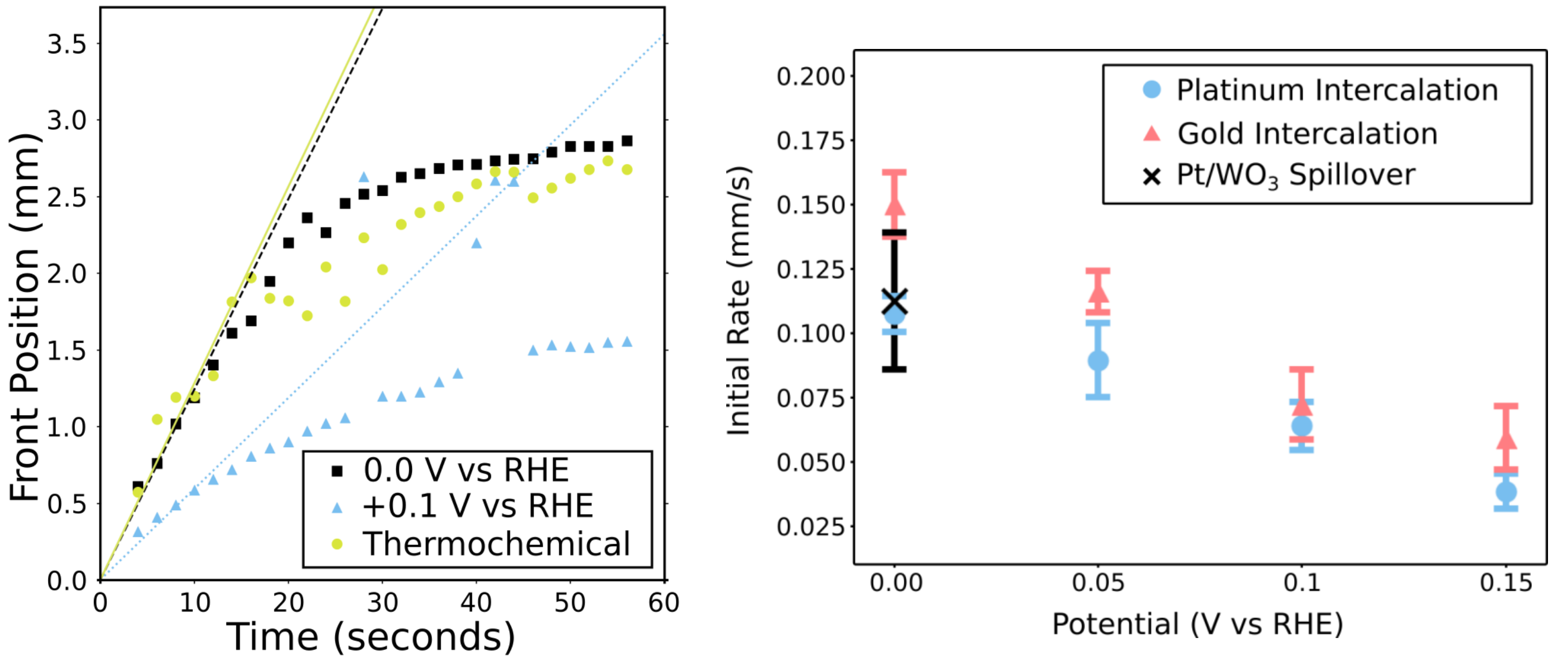
Dynamics of hydrogen uptake and diffusion

H-front migration rates imply single mechanism



Initial migration rate is constant and ***way too fast*** to be gated by H^+ (or H atom) diffusion!

Dynamics of hydrogen uptake and diffusion

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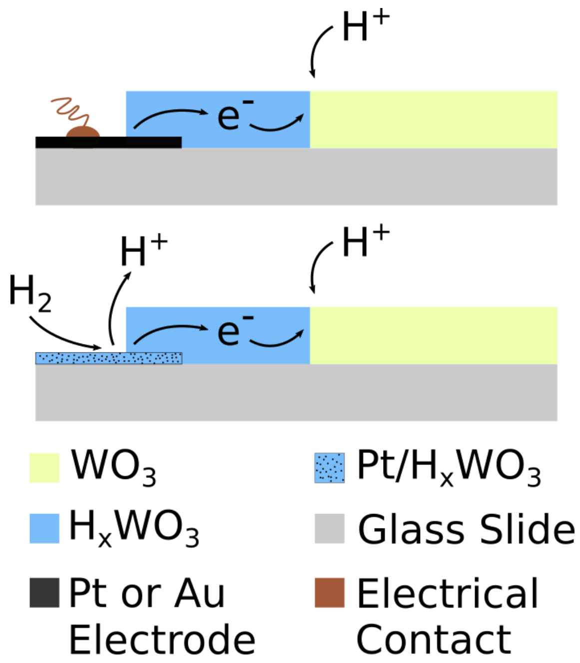

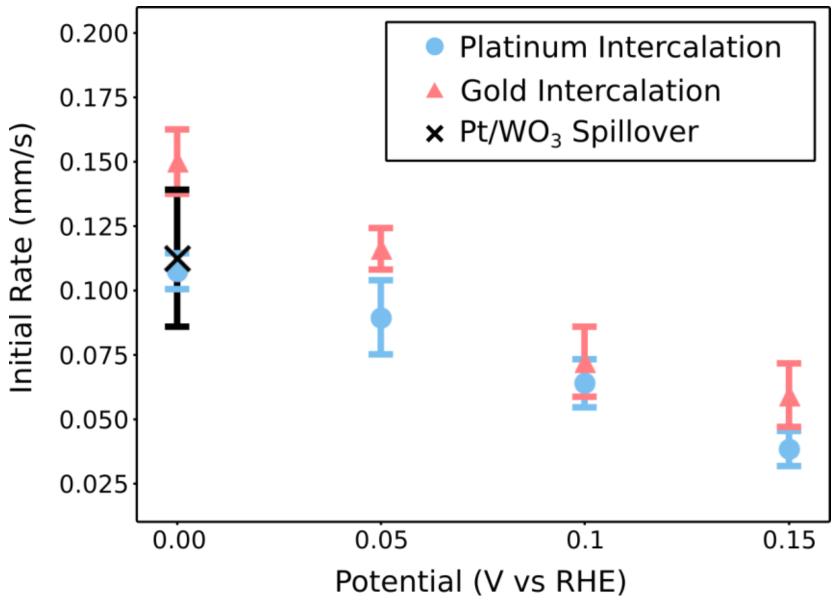

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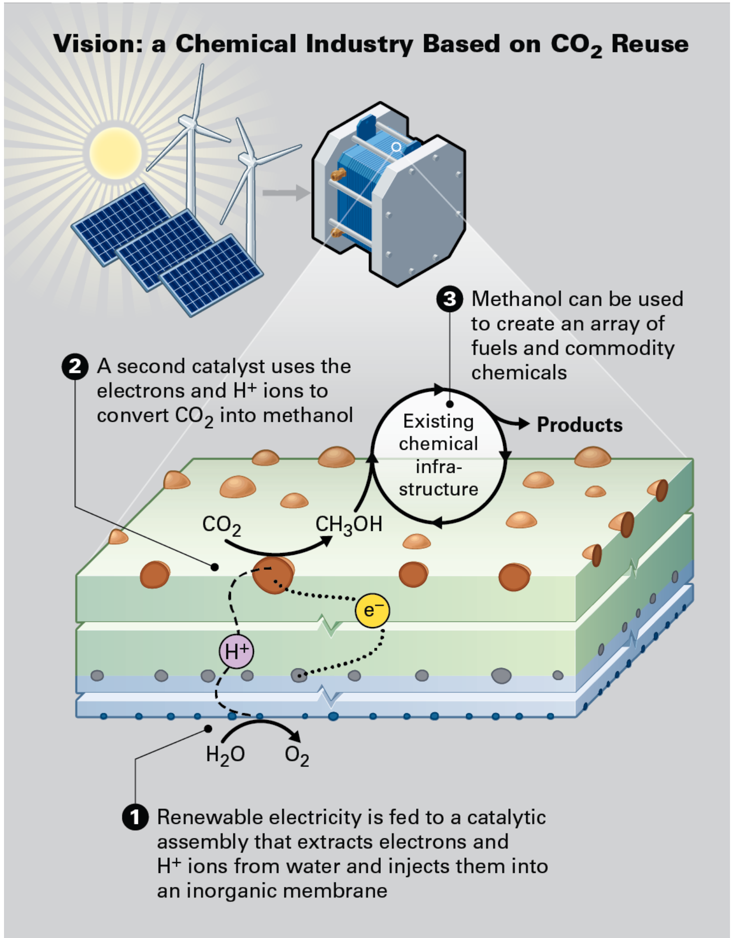

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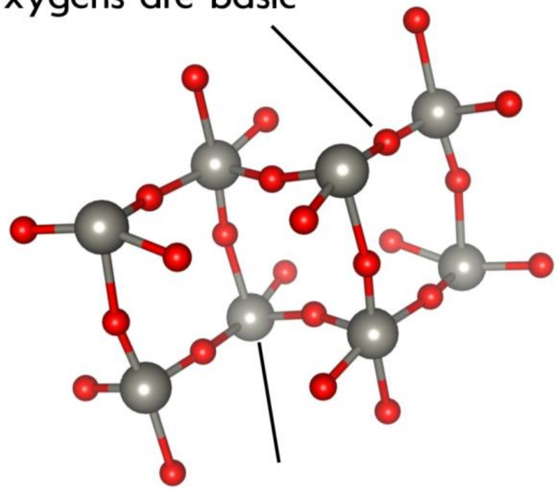
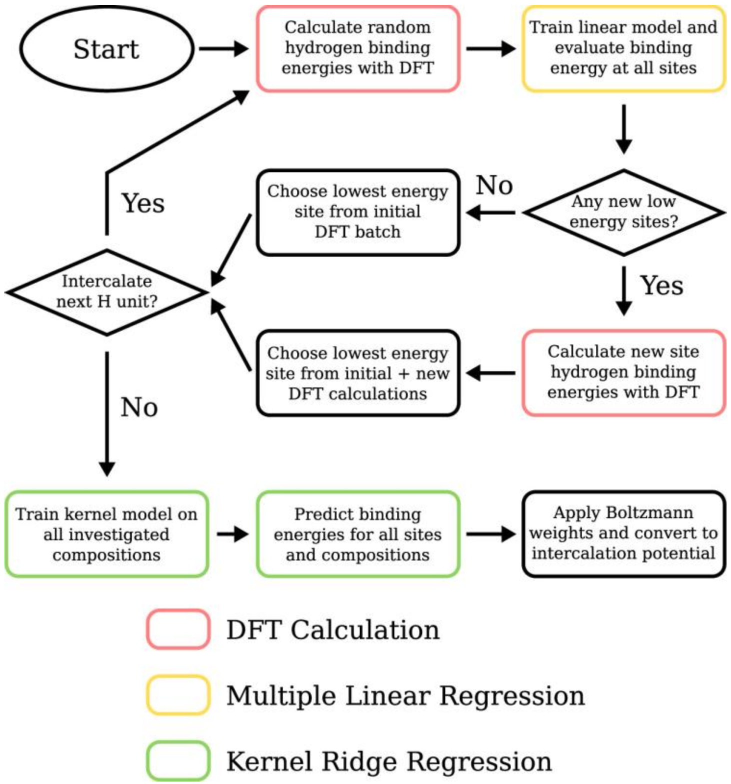
Using quantum chemistry
to predict bronze PCET thermochemistry

Collab w/ G. Mpourmpakis





Regression models: trained on DFT-predicted acid/base properties on subset of H-locations in H_xWO_3

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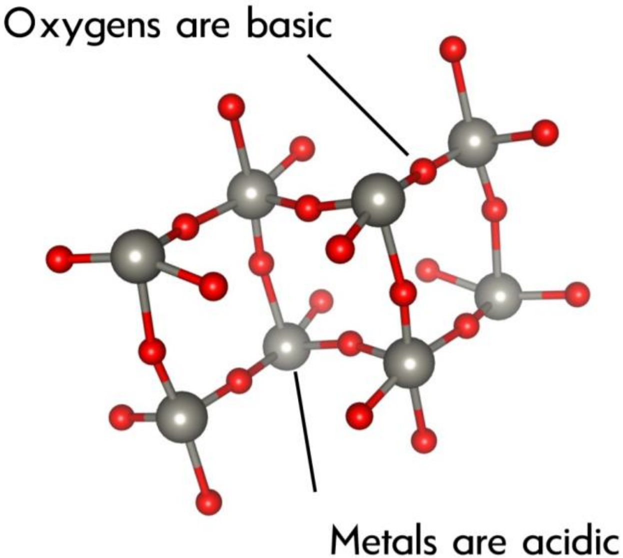

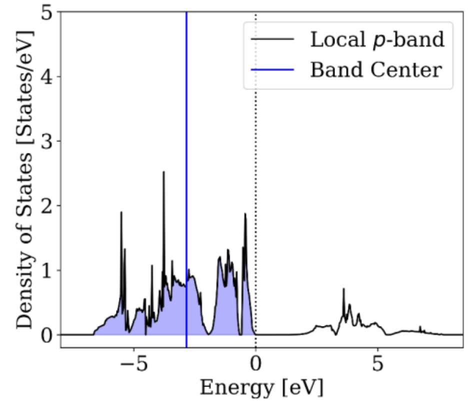

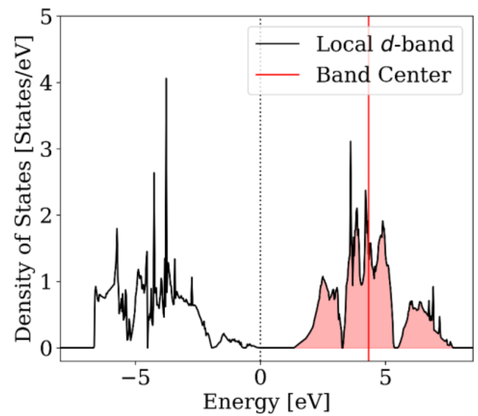

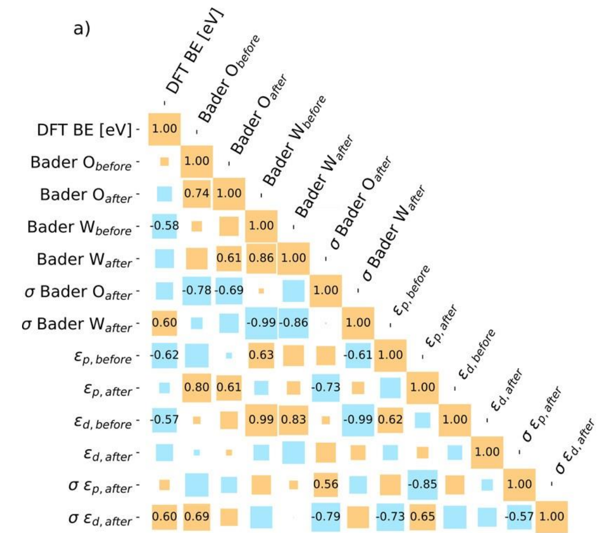

Regression models: trained on DFT-predicted acid/base properties on subset of H-locations in H_xWO_3

Correlation coefficients for DFT-predicted energy (related to E°) vs DFT-predicted acid/base properties

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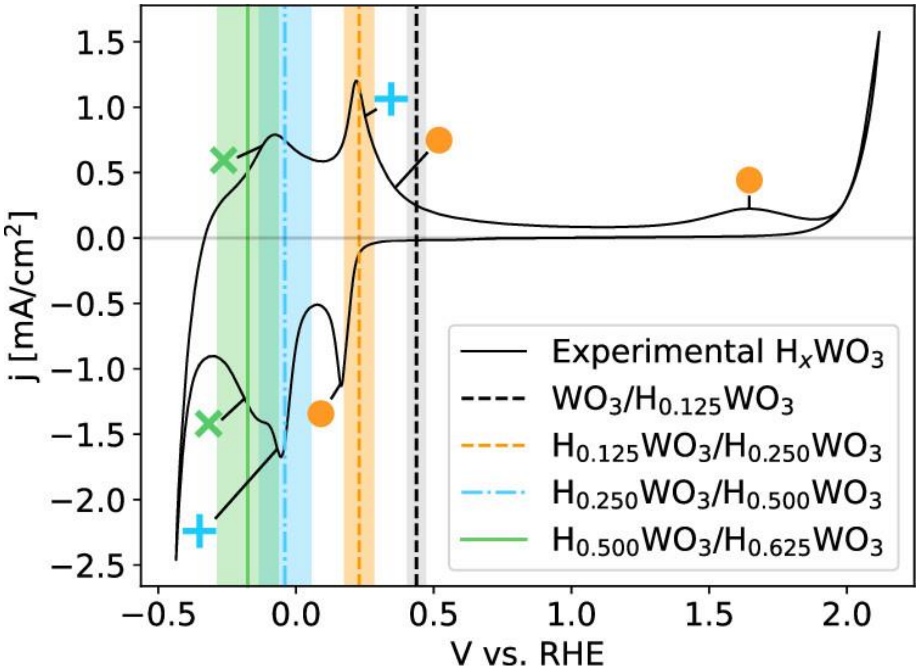
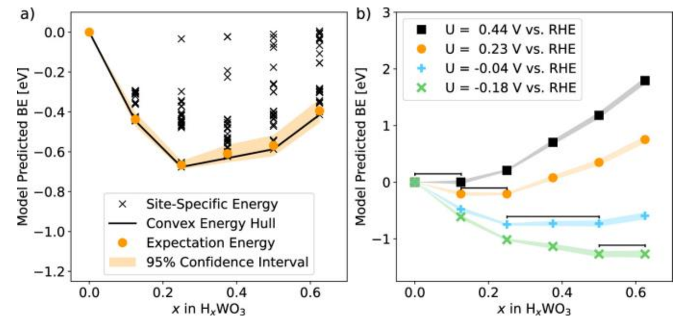
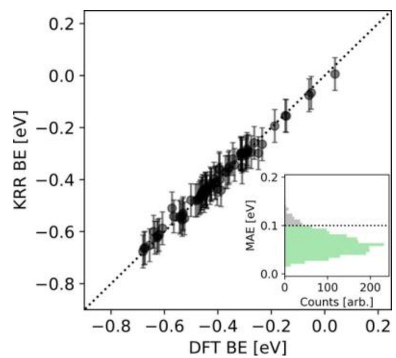
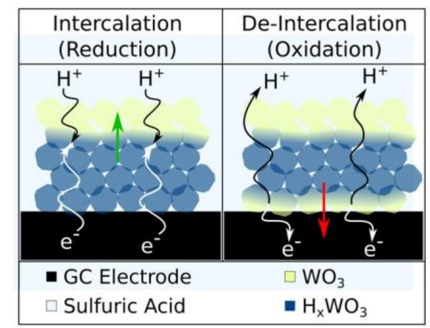






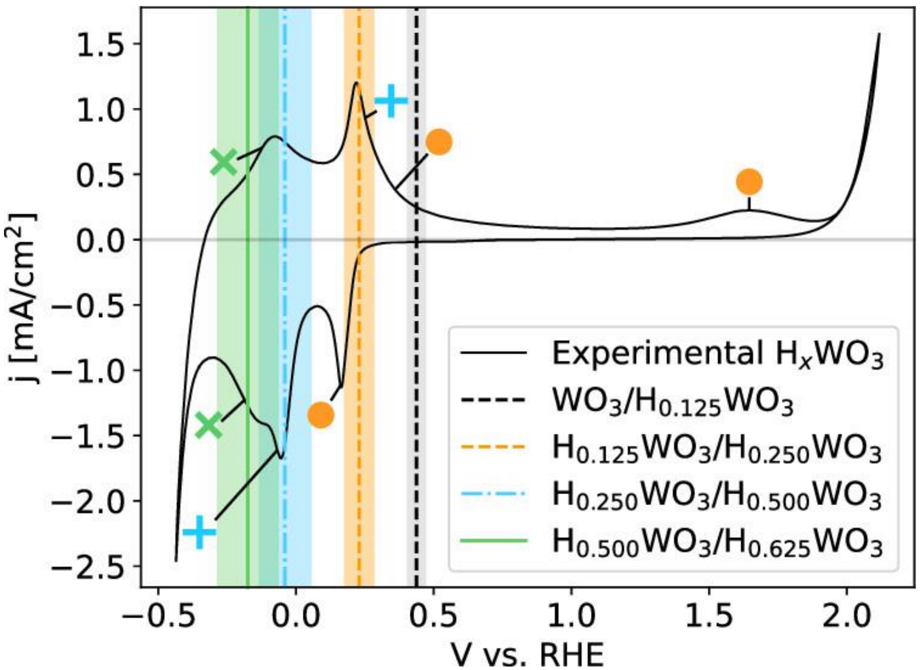


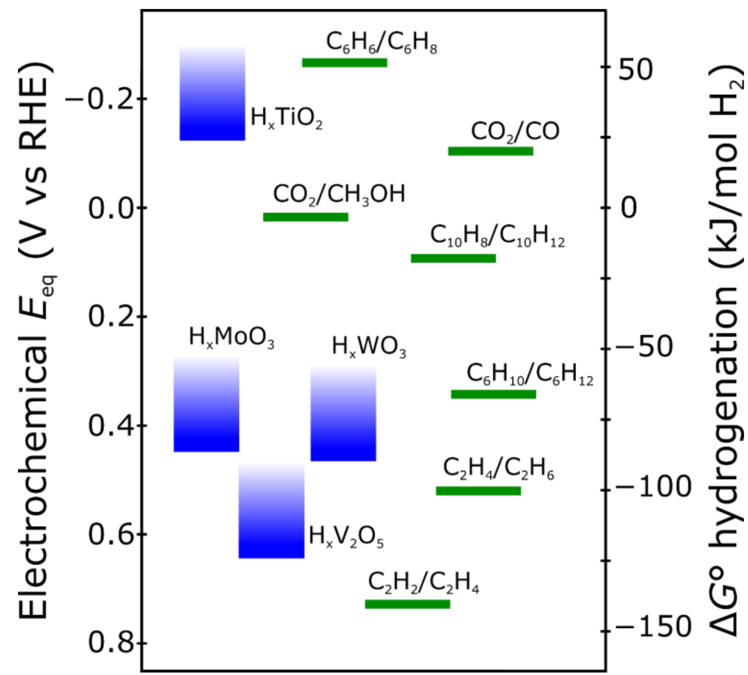
DFT + regression models: greatly decrease computational cost for convex hull calculations

Important feature of H_xWO_3: fast reduction but severely inhibited oxidation

Using quantum chemistry
to predict bronze PCET thermochemistry

With G. Mpourmpakis



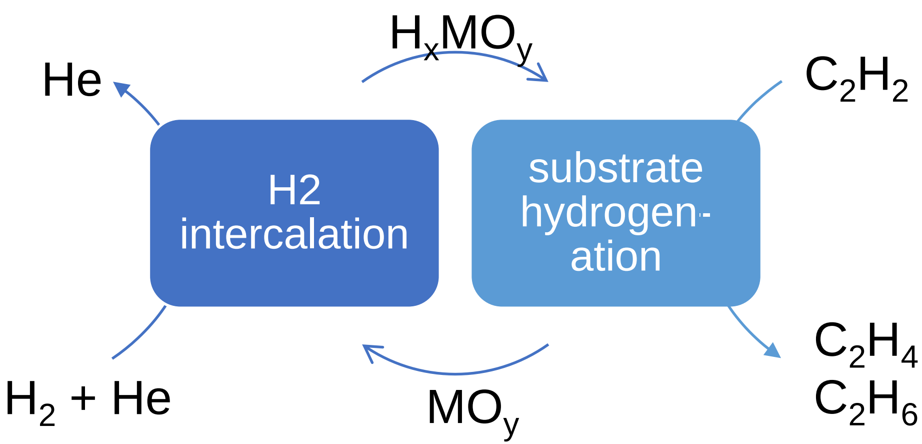


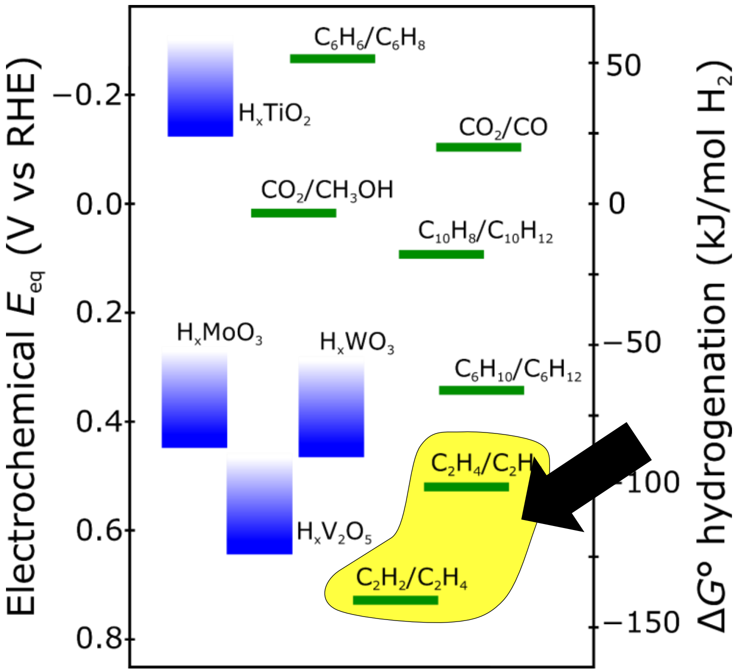
Model is highly extensible: input requires only reactant oxide crystal structure

Chemical Looping Hydrogenation

Electrochemical properties of H_xWO_3 allow us to predict how it will behave in a looping configuration

With G. Veser





Model reaction: acetylene hydrogenation

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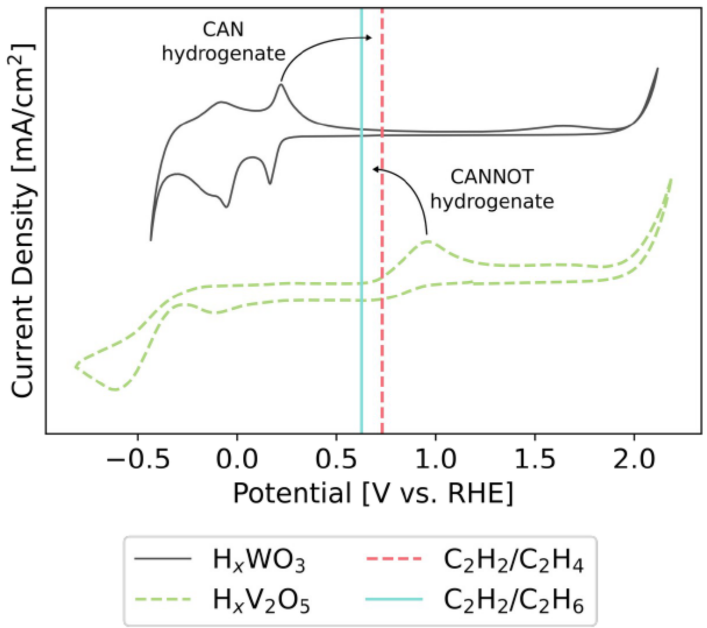
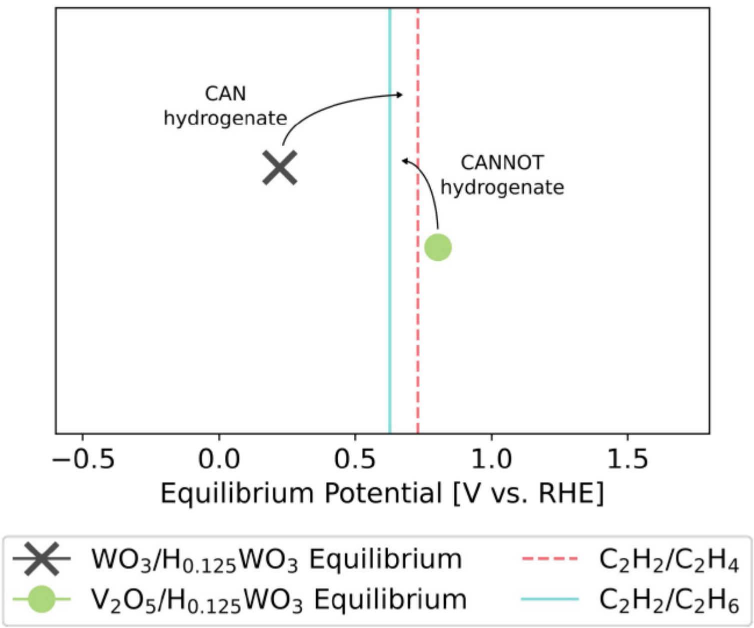
Cyclic voltammogram



DFT calculations



Both results suggest that H_xWO_3 will hydrogenate C_2H_2 and $H_xV_2O_5$ will not

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Chemical Looping Hydrogenation

Predictions validated: HxWO3 hydrogenates acetylene and HxV2O5 does not

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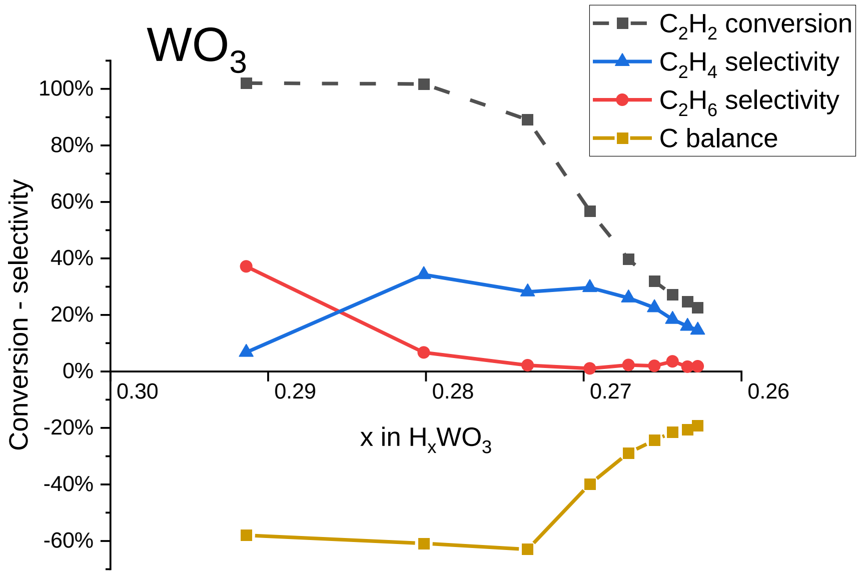

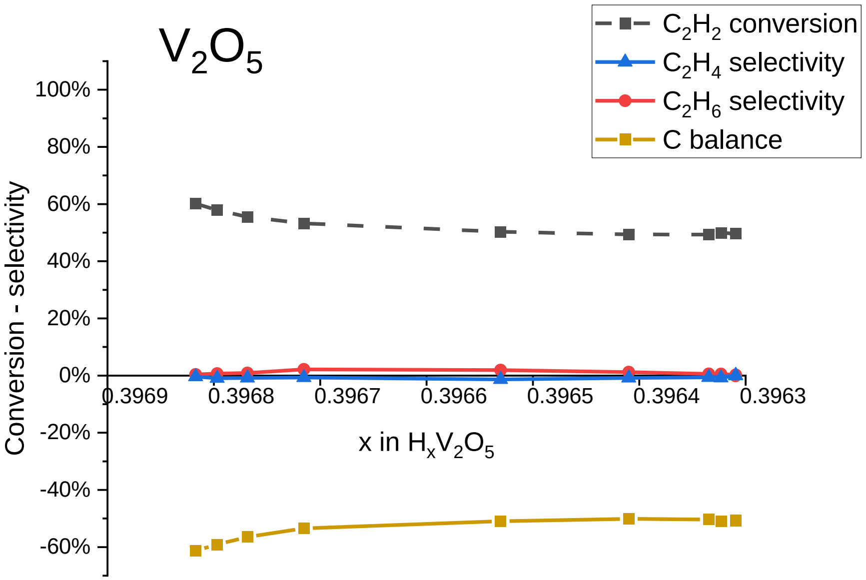

ALSO: note product distribution – ethylene is primary C2 product

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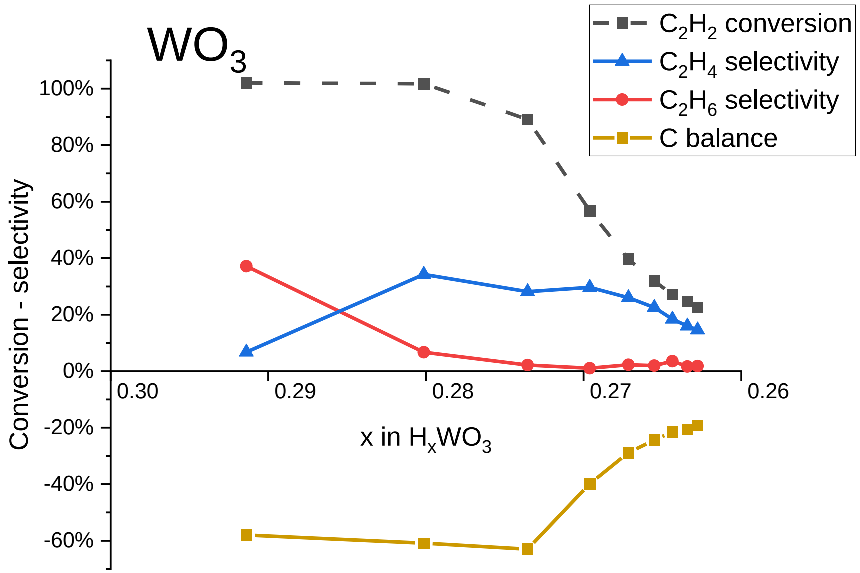

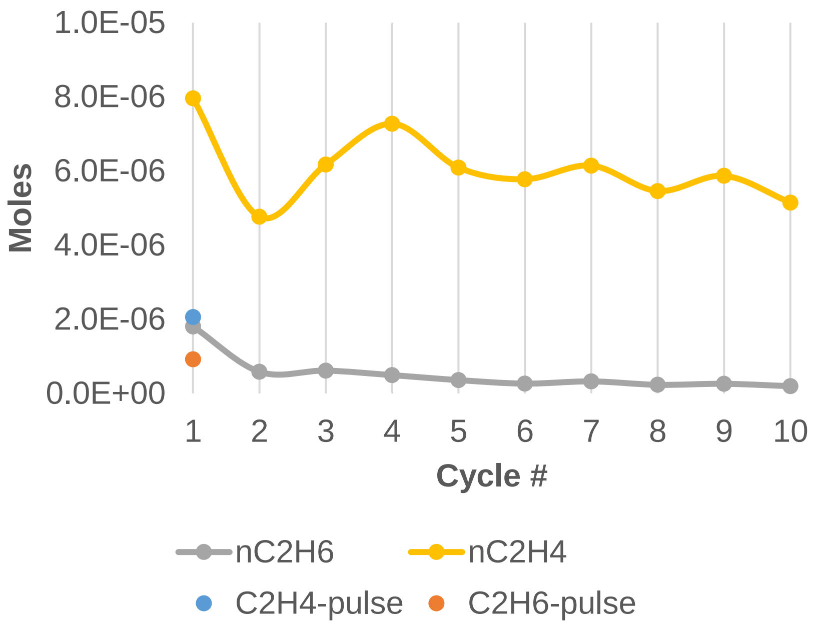

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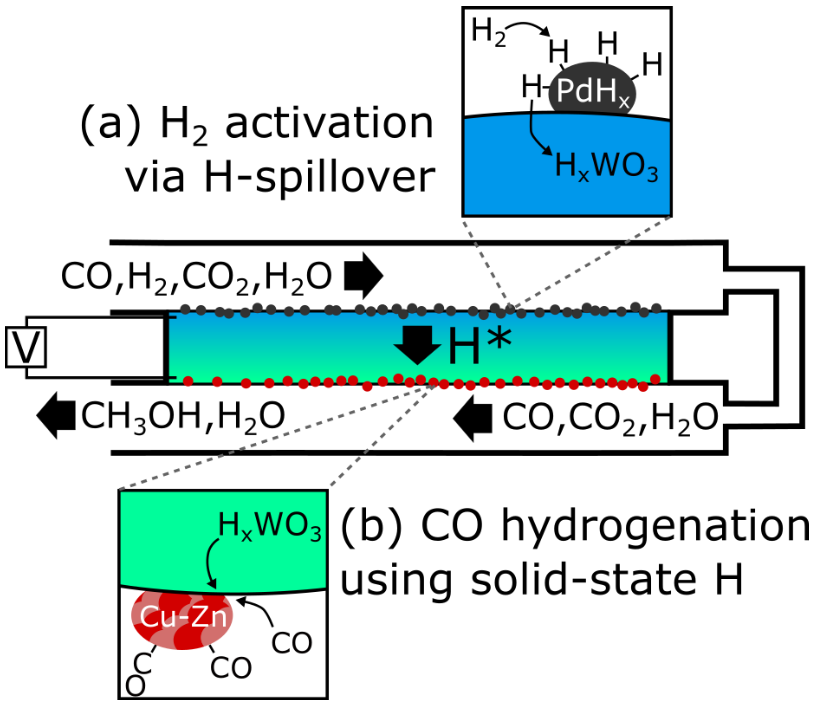
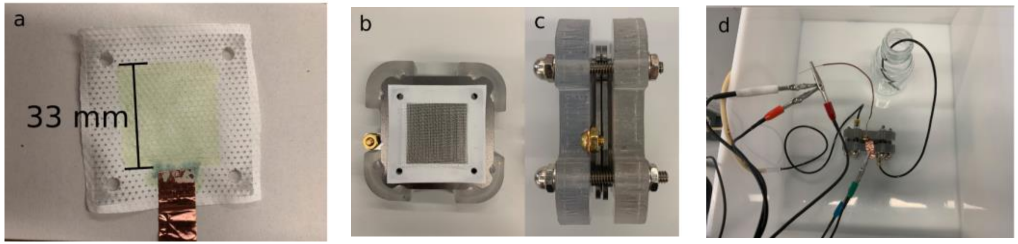
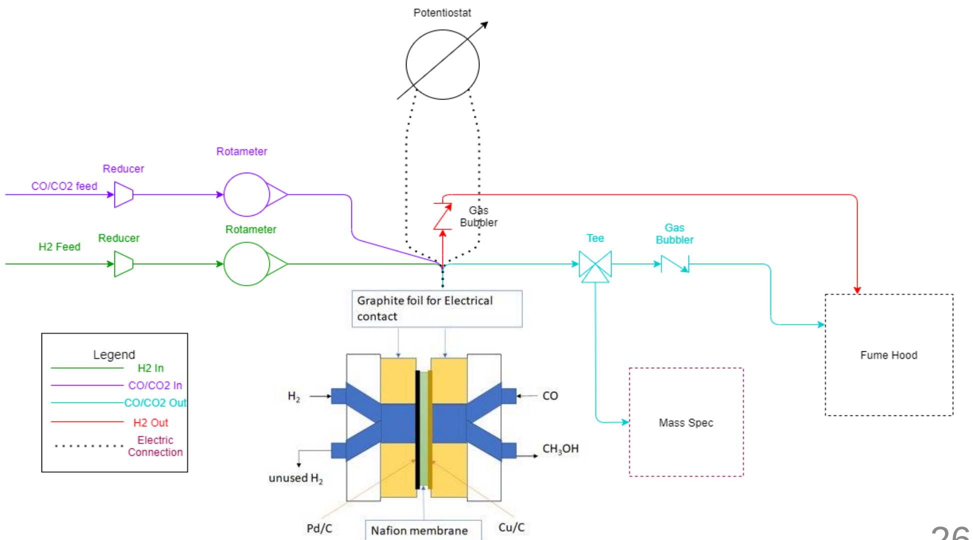
Electrochemically pumped syngas-methanol

Applied voltage to increase chemical potential of hydrogen







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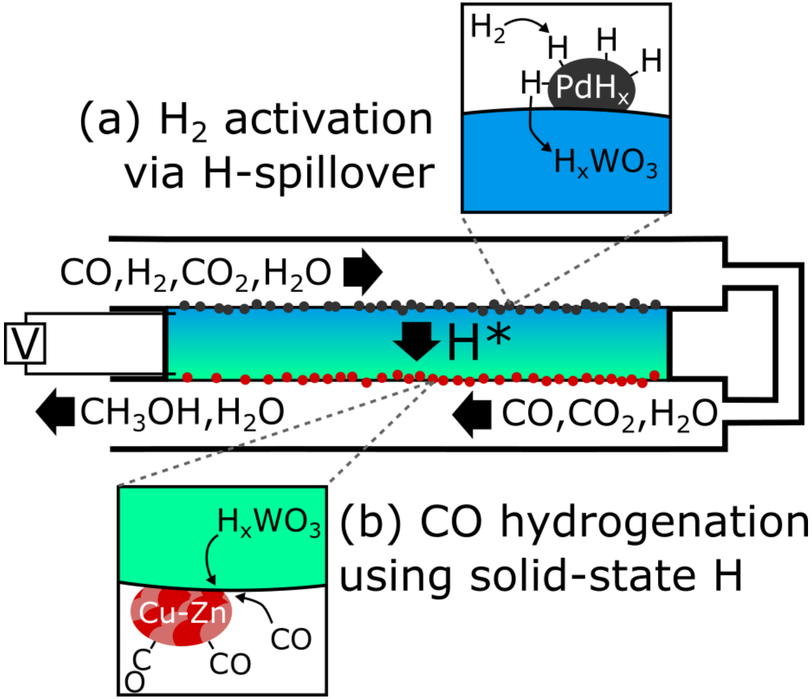

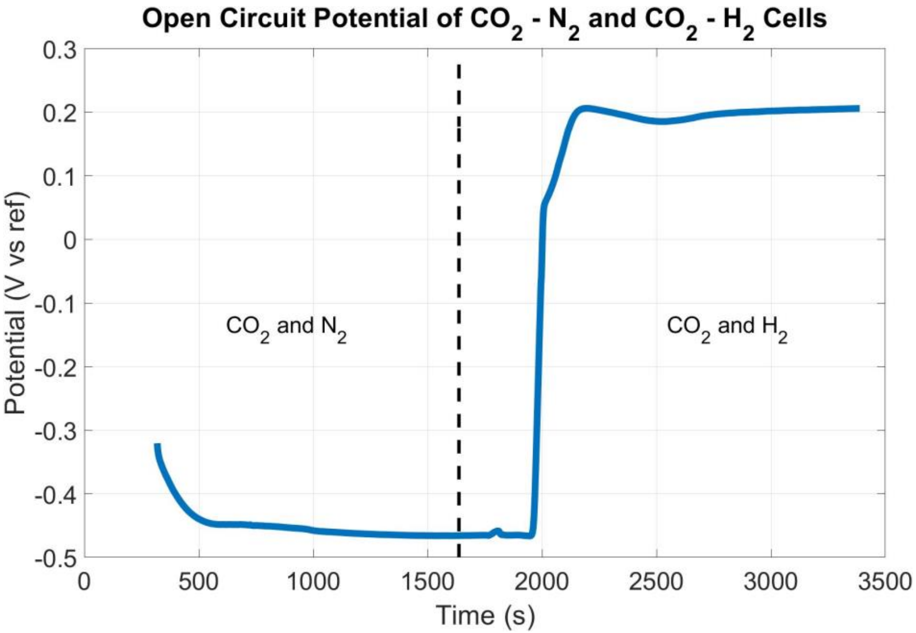

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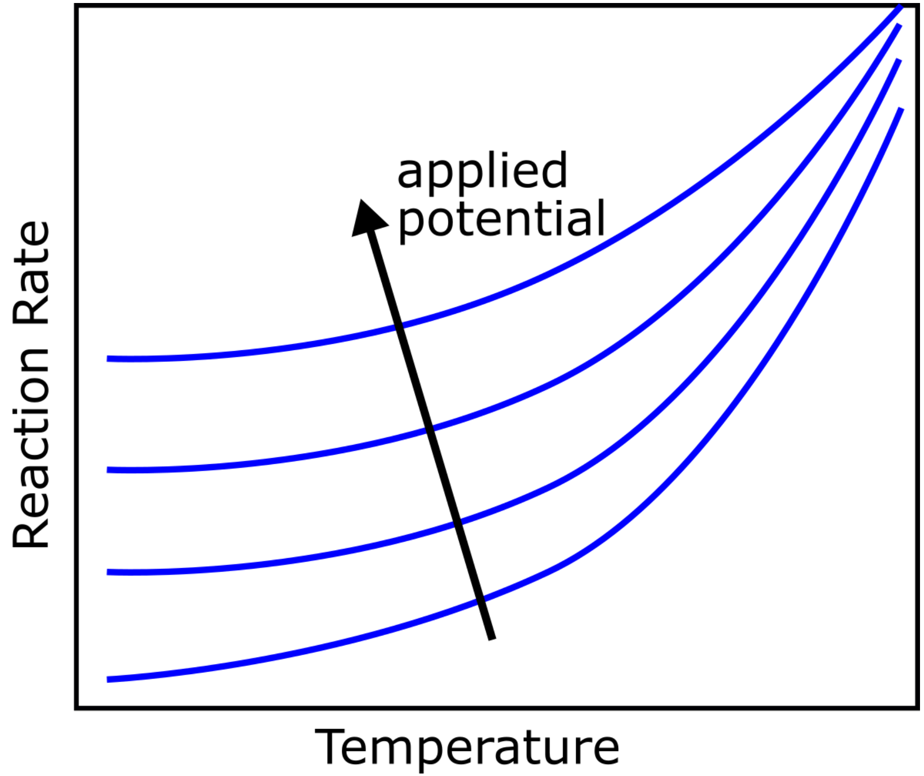
Final thought: electrochemical intensification

Are there circumstances under which heat and electricity together can enhance catalytic reactivity more than either can individually?



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Shawnee Sparrow
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Emily Siegel
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Carissa Yim
Ryan Earle
Natalie Britton
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Judy Yang (Pitt)
Stephen House (Pitt)
Susan Fullerton (Pitt)
Venkat Viswanathan (CMU)
Ellen Matson (UR)
Tim Cook (UB)

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