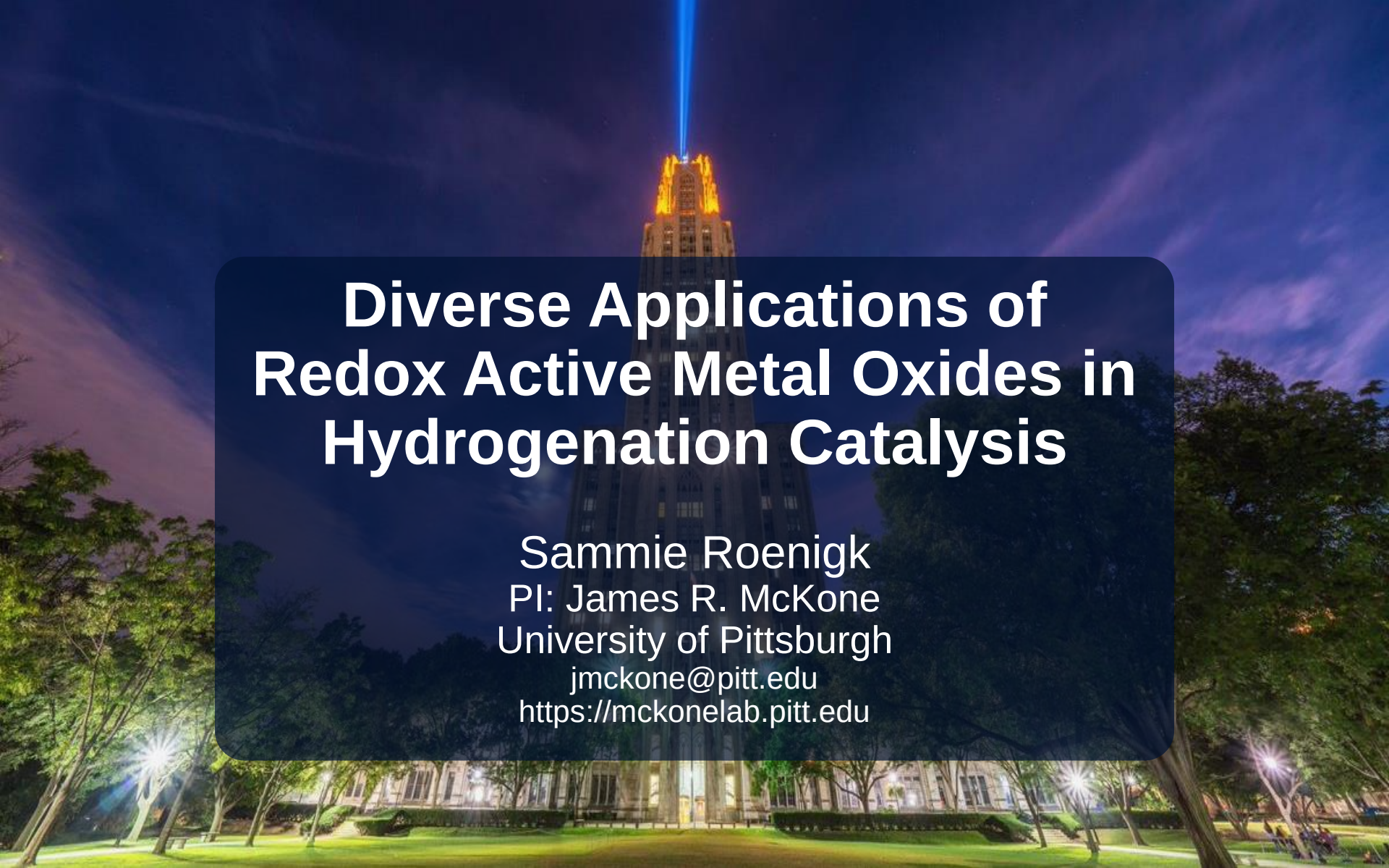

Diverse Applications of Redox Active Metal Oxides in Hydrogenation Catalysis

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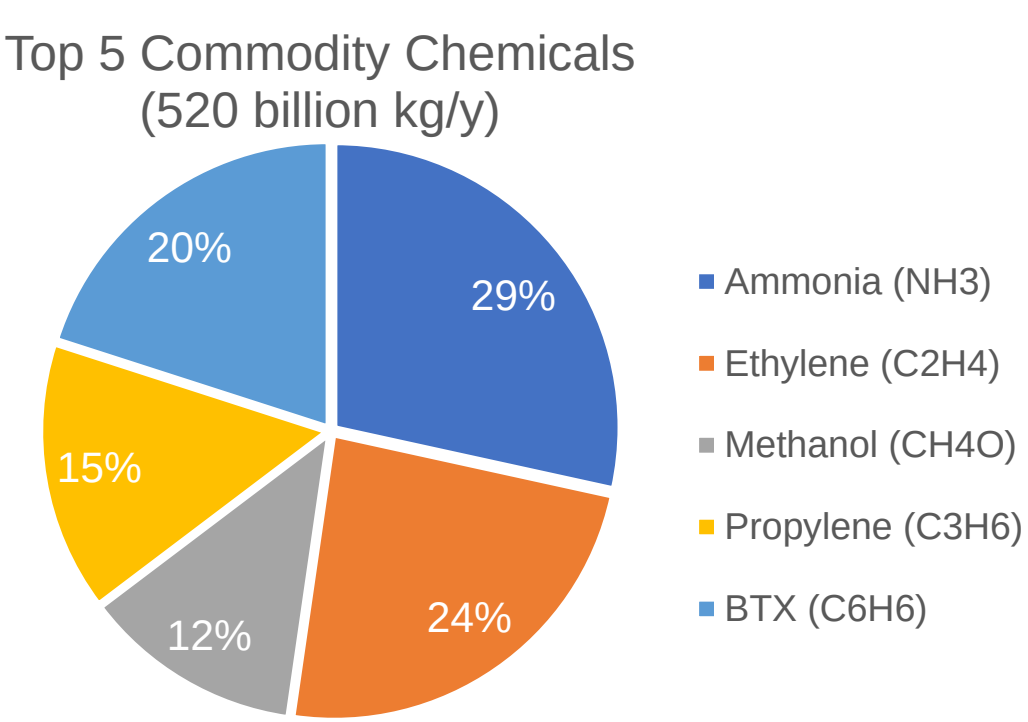
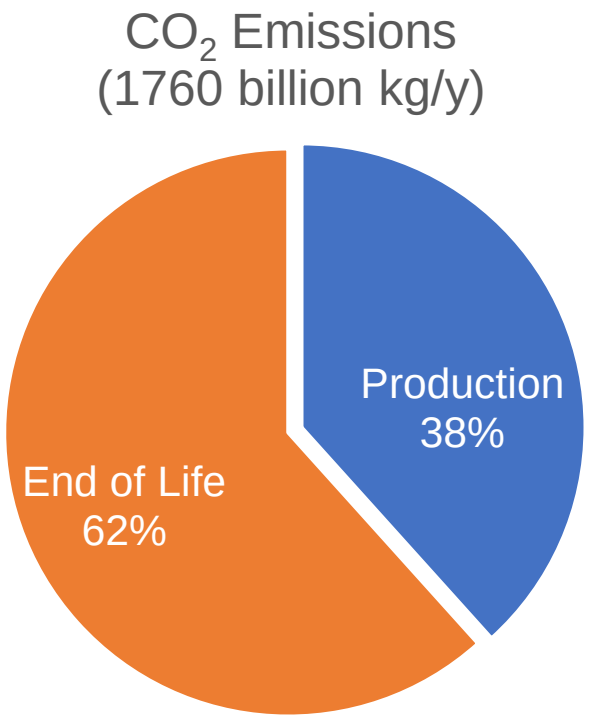
Reducing the C-intensity of chemical manufacturing

still requires a lot of carbon and hydrogen…

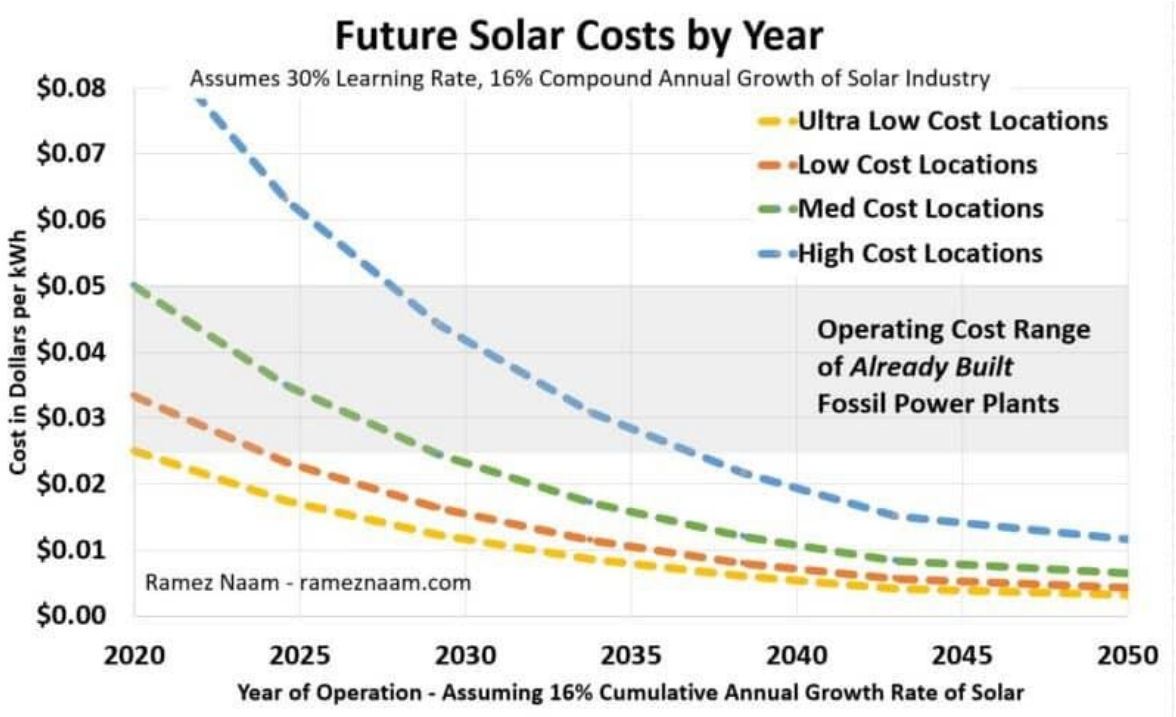




Data from Schiffer and Manthiram *Joule* **2017**, *1* (1), 10-14.

Opportunities from renewable (over)supply

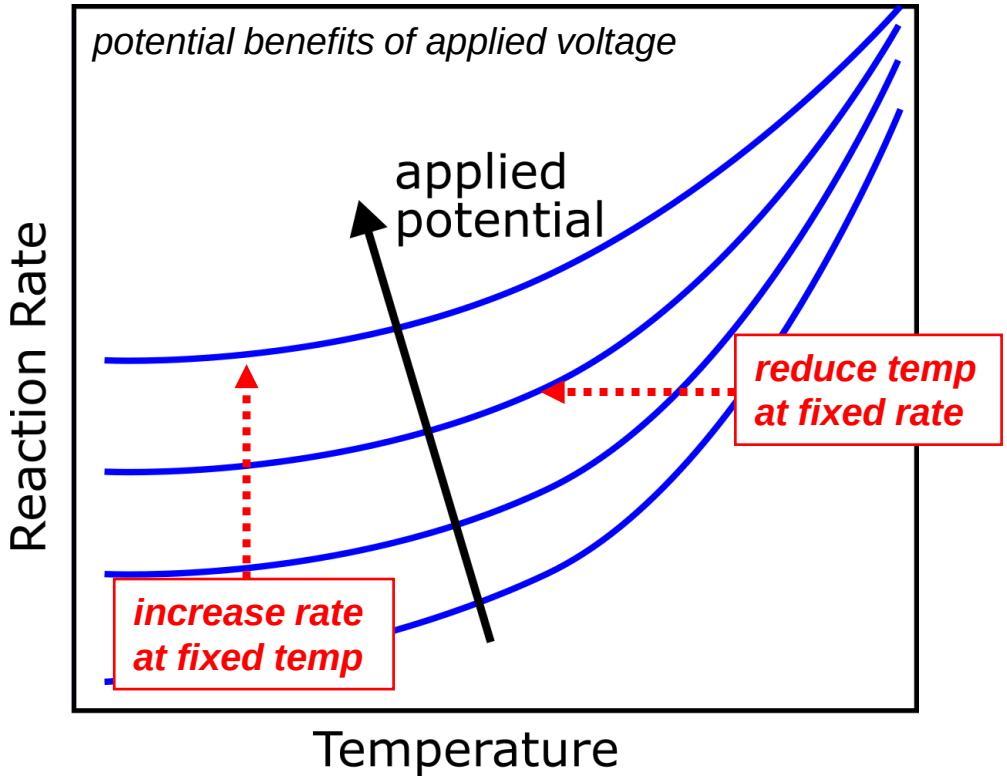
Cheap electrons from renewables provide an opportunity to use carbon-rich feedstocks and sequestered CO_2 for value-added chemical production



https://rameznaam.com/2020/05/14/solars-future-is-insanely-cheap-2020/

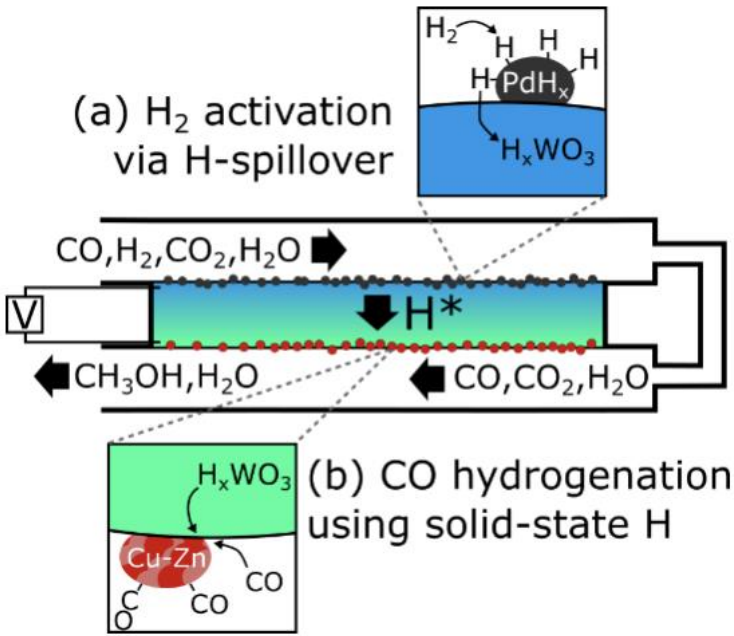
Electrochemical intensification

Research question: are there circumstances under which heat and electricity together can enhance catalytic reactivity more than either can individually?

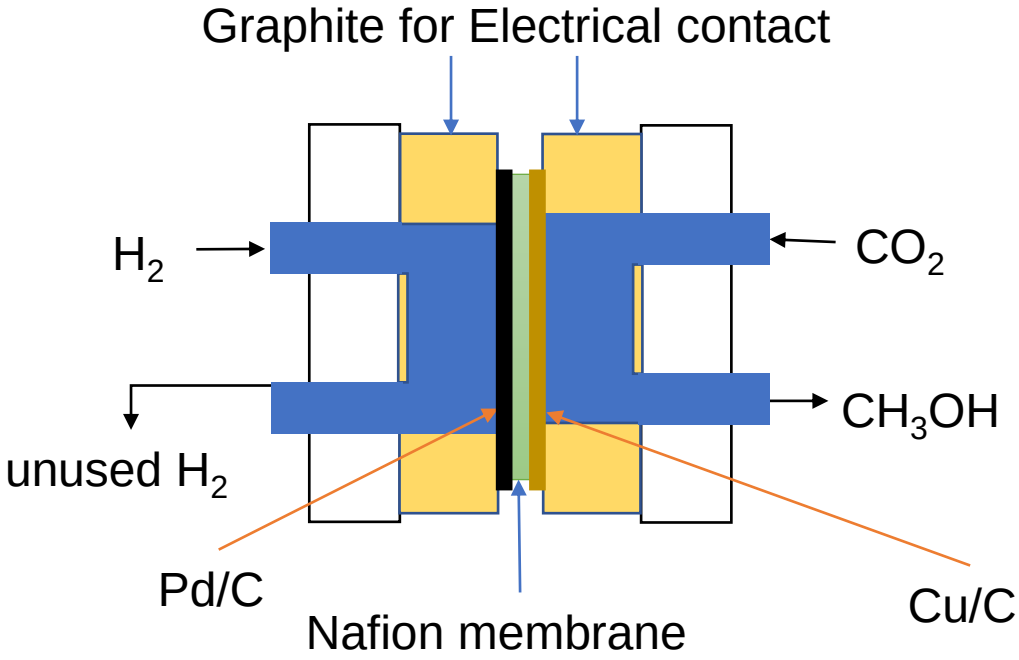


Electrochemically pumped syngas-methanol

Building a library of reactor materials for intensified chemical production



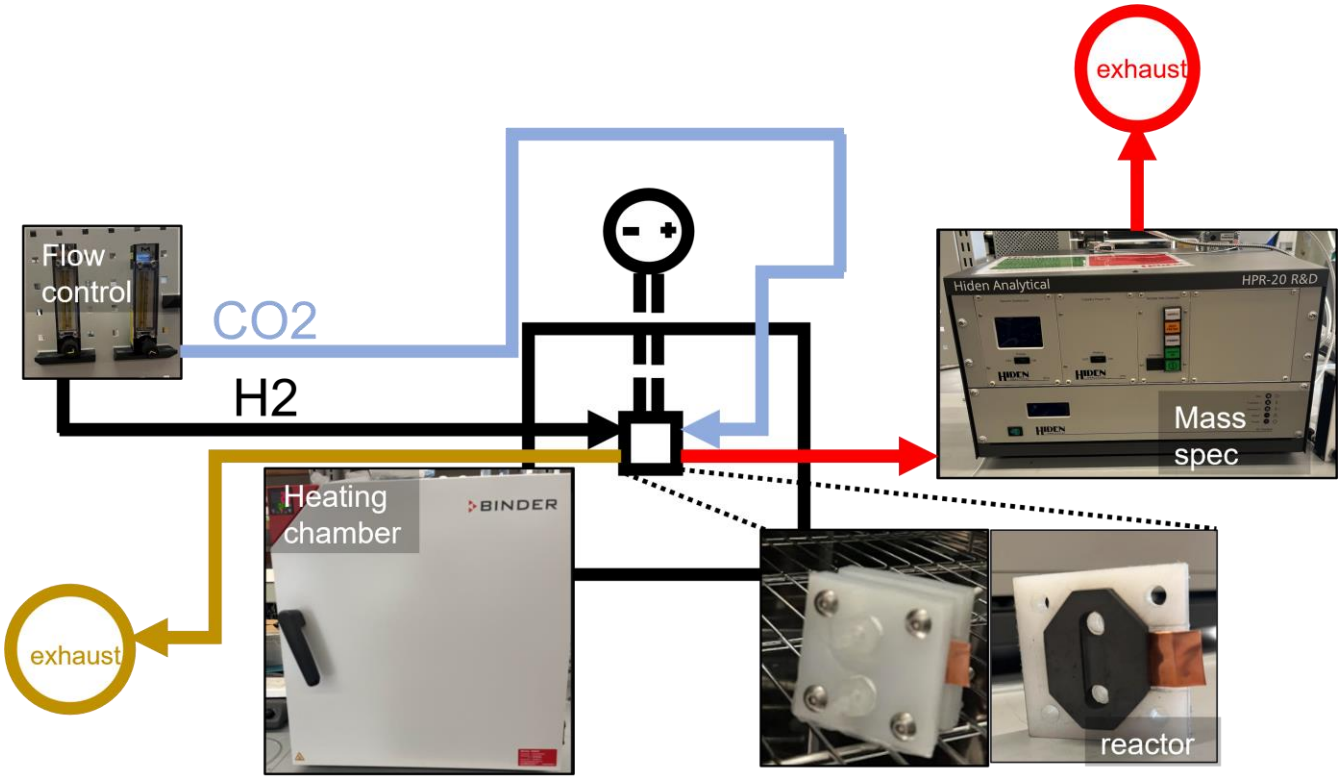
proposed reactor architecture



current iteration: proof of concept

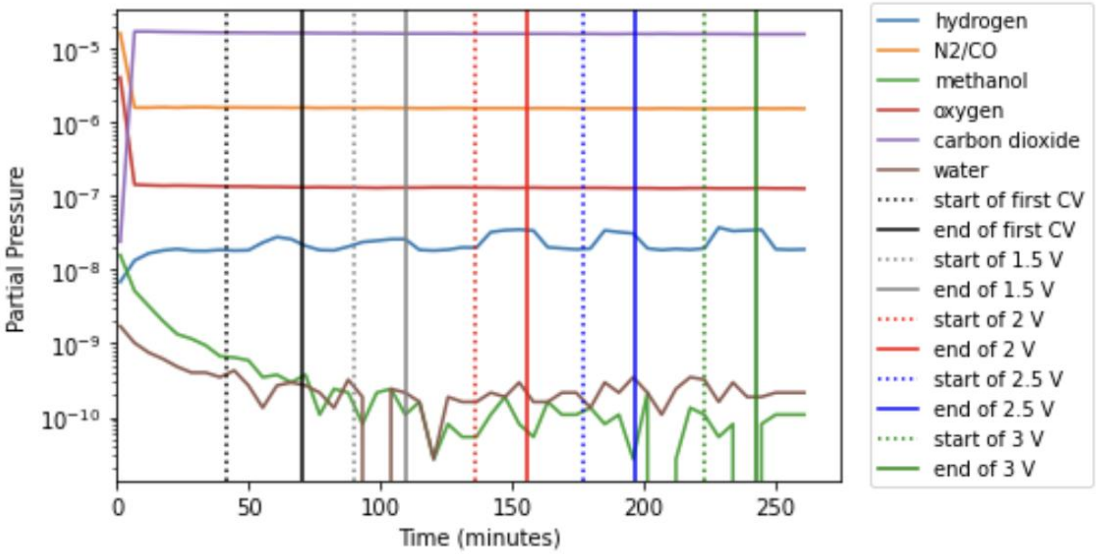
Electrochemically pumped syngas-methanol

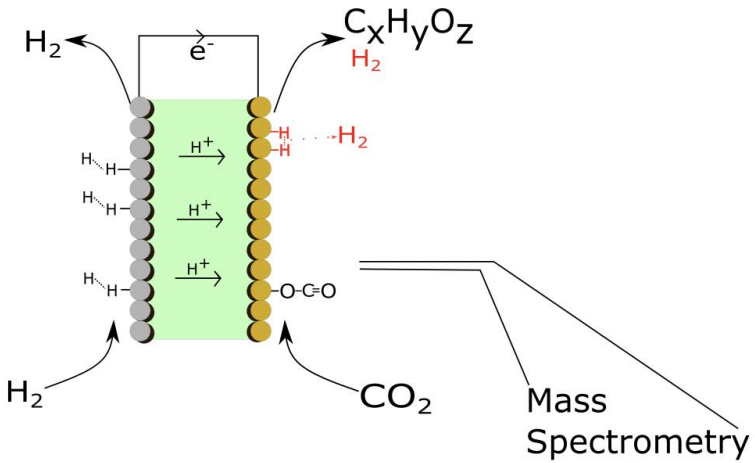
experimental configuration: based on modified fuel cell design



Electrochemically Pumped Membrane Reactor

Preliminary results: Pd/C anode and Cu/C cathode

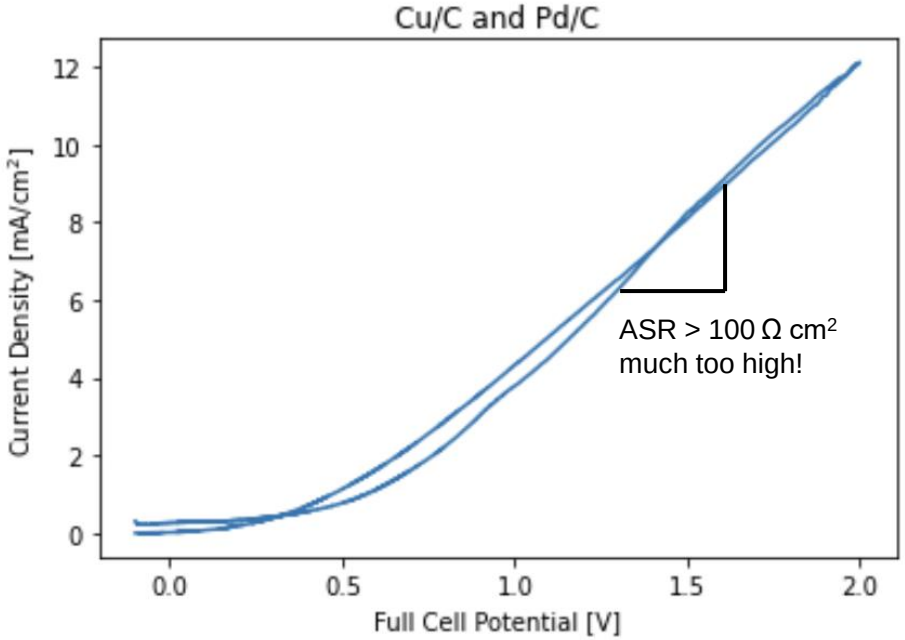


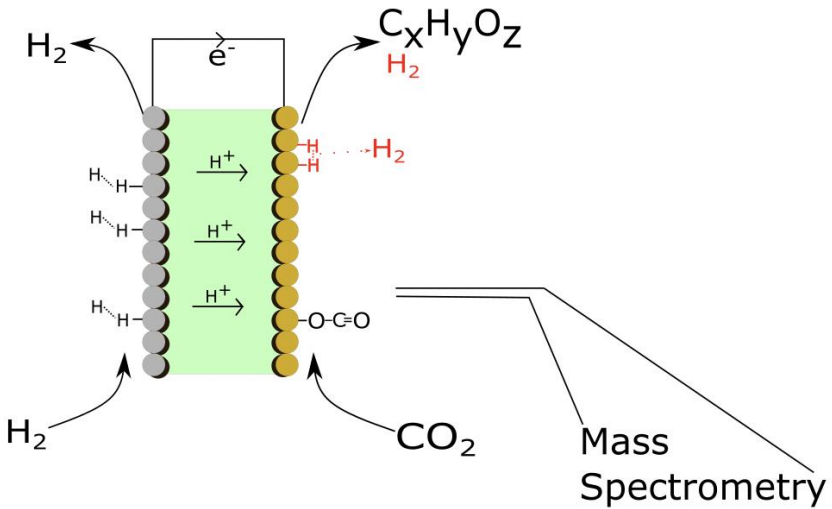


- ✓ Pumps H atoms from anode to cathode
- ❑ H intermediates hydrogenate CO_2 feedstock

Electrochemically Pumped Membrane Reactor

Preliminary results: Pd/C anode and Cu/C cathode

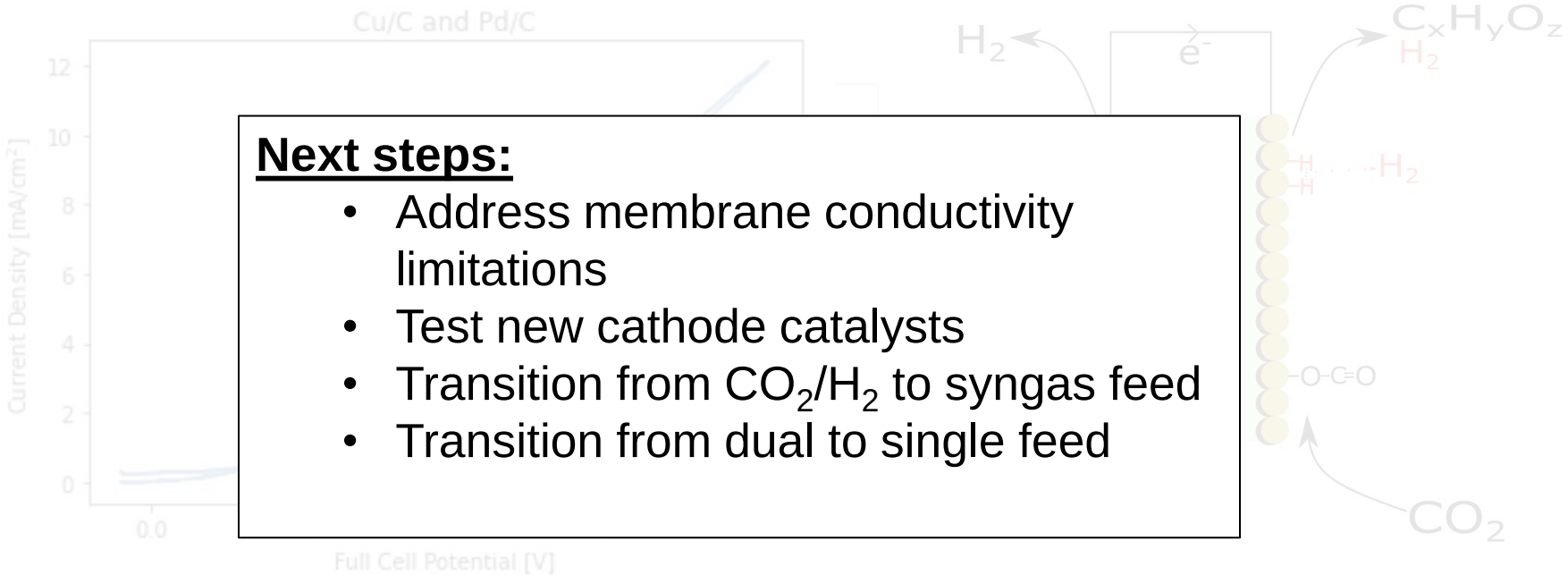




Nafion membrane exhibits low H^+ conductivity

Electrochemically Pumped Membrane Reactor

Preliminary results: Pd/C anode and Cu/C cathode



Next steps:

- Address membrane conductivity limitations
- Test new cathode catalysts
- Transition from CO_2/H_2 to syngas feed
- Transition from dual to single feed

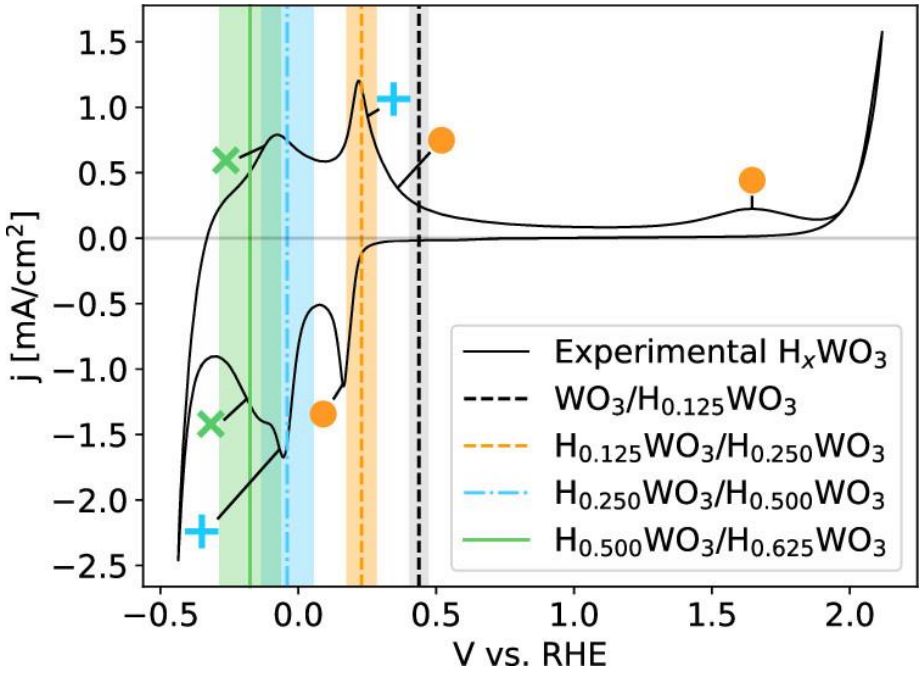
✓ Pumps H atoms from anode to cathode

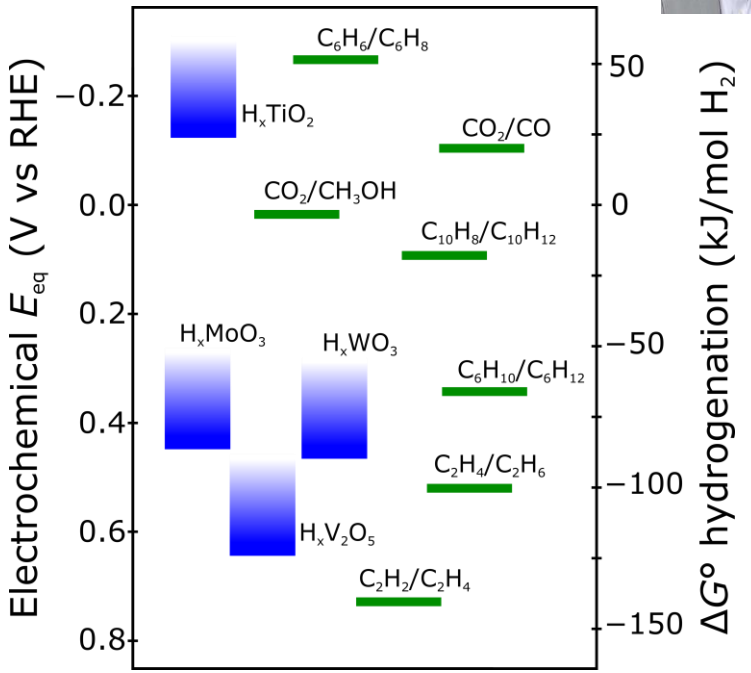
❑ H intermediates hydrogenate CO_2 feedstock

Electrochemically Pumped Membrane Reactor

Metal oxide bronzes are interesting candidates for cathode catalysts

With G. Mpourmpakis



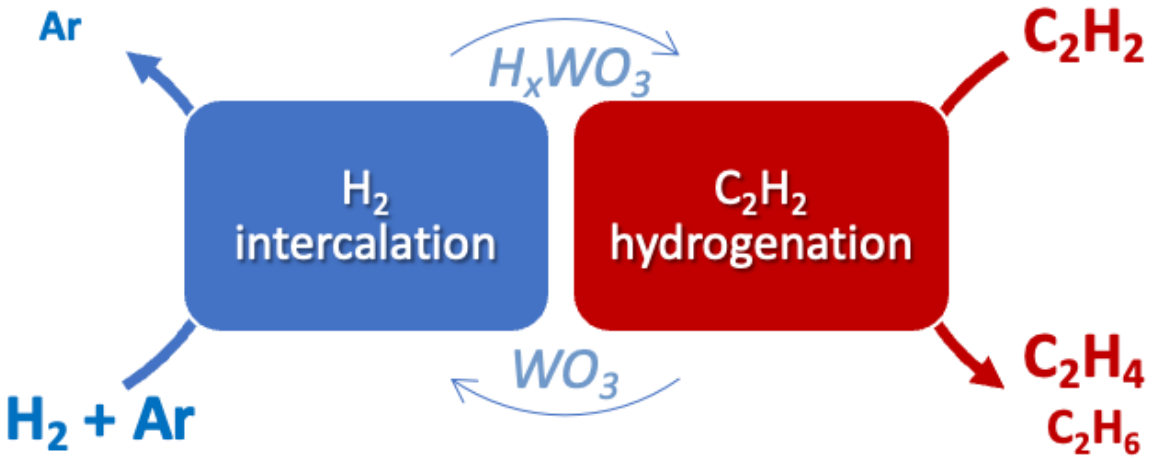


Electrochemistry and quantum chemistry can be used to predict the reactivity of H atoms inserted in H_xMO_y

Miu, E. V.; Mpourmpakis, G.; McKone, J. R. *ACS Appl. Mater. Interfaces* **2020**, *12* (40), 44658–44670.

Another promising application

Metal oxide bronzes as H carriers for *chemical looping hydrogenation*

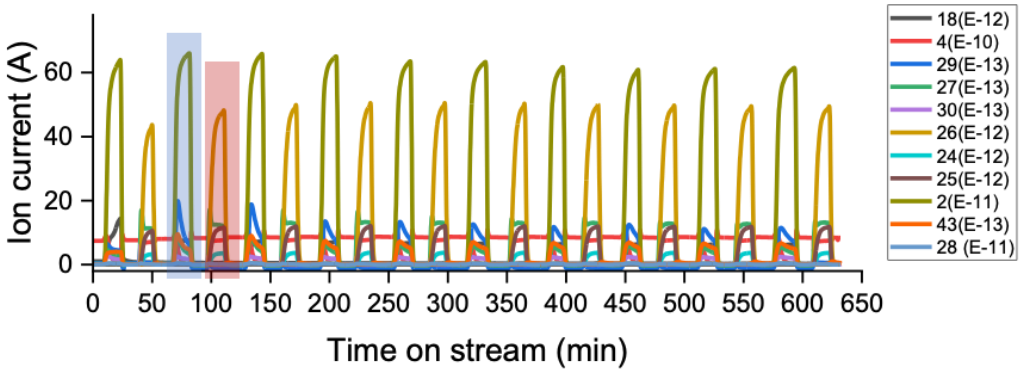


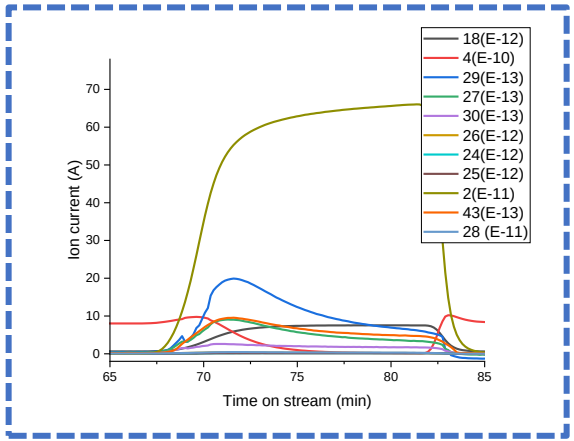
(manuscript in prep)

Chemical Looping Hydrogenation

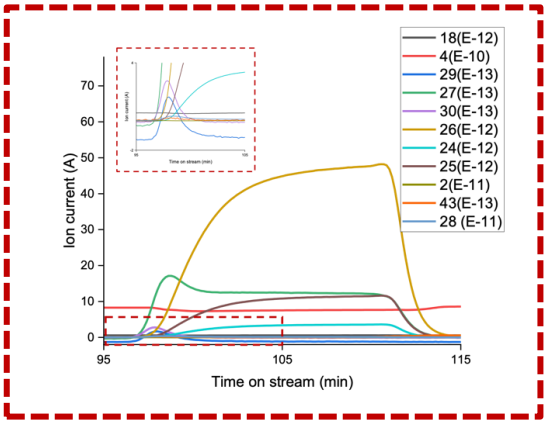
H_xWO_3 hydrogenates acetylene via sequential H uptake/delivery

With
G. Veser





H_2 is inserted into WO_3, followed by H_2 breakthrough



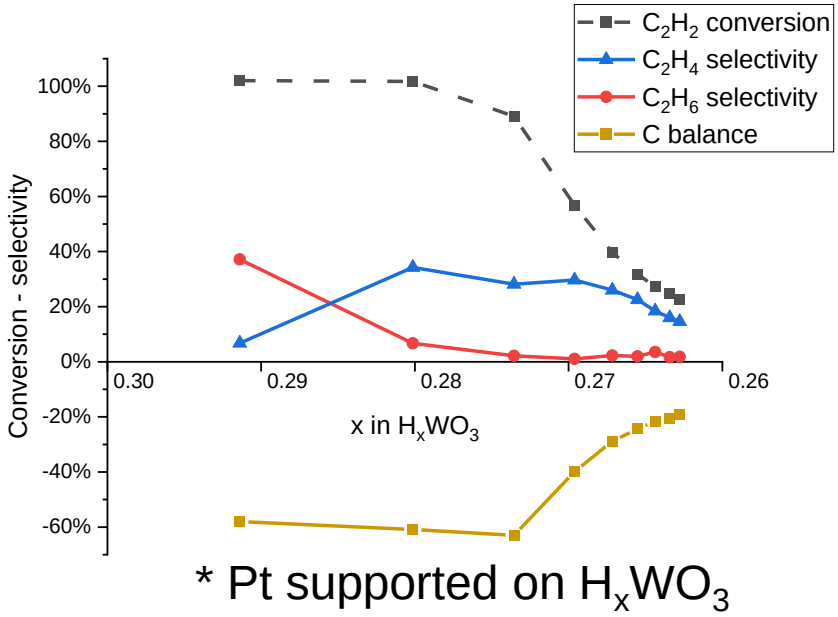
As C_2H_2 breaks through, hydrogenated products are produced, which could be observed from mass spec signal increase in m/z = 27 and m/z 29, 30

(manuscript in prep)

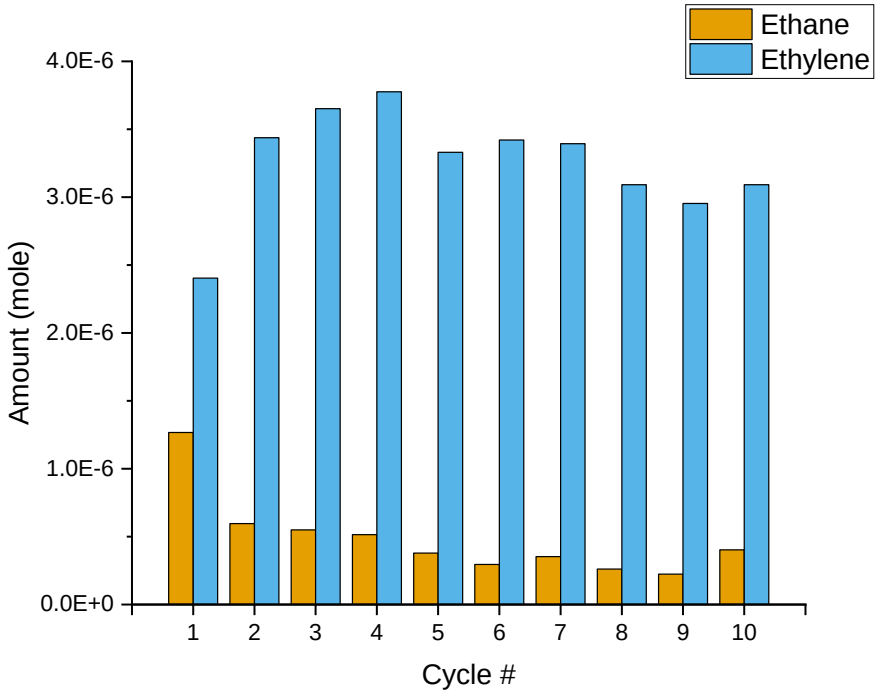
Chemical Looping Hydrogenation

Very small H-atom capacity utilized in ~$H_{0.25}WO_3$
BUT ethylene is the predominant product!

With G. Veser



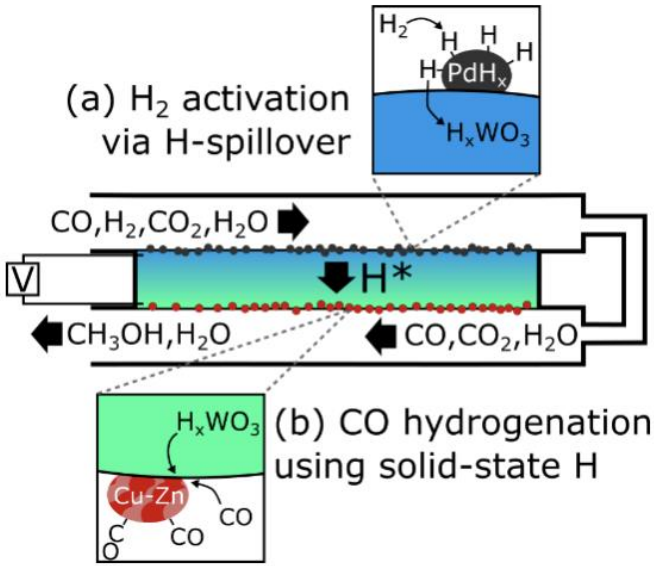
* Pt supported on H_xWO_3

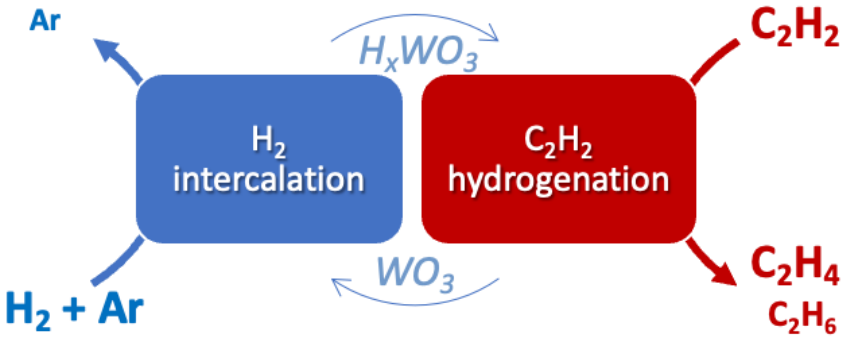


(manuscript in prep)

University of Pittsburgh

Summary





- Two promising modes of reactivity involving redox-active metal oxides
- Each benefits from understanding solid state proton-electron transfer
- Both present opportunities to integrate electrochemical and thermochemical reactivity for enhanced syngas utilization

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