

HyMARC: Hydrogen Carriers R&D Activities for Bulk Hydrogen Storage & Transport

Tom Autrey and Mark Bowden

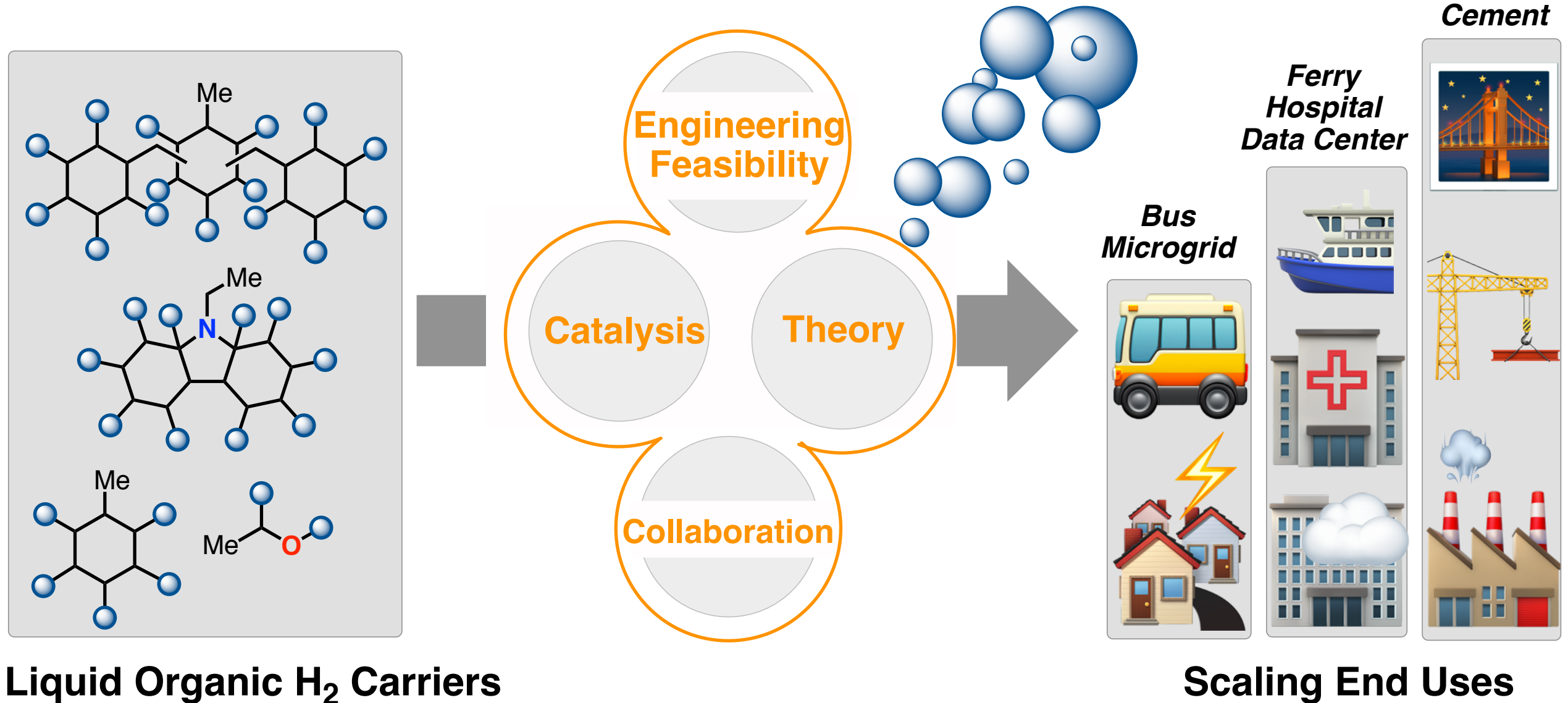
Project ID: ST204

Annual Merit Review May 21, 2020



What we do at PNNL

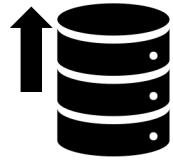
At PNNL, we use a top-down integrated approach driven by engineering feasibility and collaboration with HyMARC partners to explore the applications of LOHCs for end uses of varying scales



Far from perfect: Defining an ideal LOHC



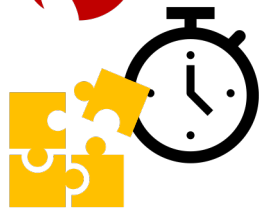
Low MP (<-30 °C). High BP (>300 °C): H₂ purification by simple condensation



High hydrogen storage capacity (>56 kg/m³ or >6 wt%)



Low heat of desorption (42–54 kJ/mol-H₂): low dehydrogenation temperature 1 bar P_{H_2} (e.g., <200 °C)



Long cycles of selective hydrogenation-dehydrogenation
(***This area needs a lot more development***)



Compatible with existing infrastructure for fuels

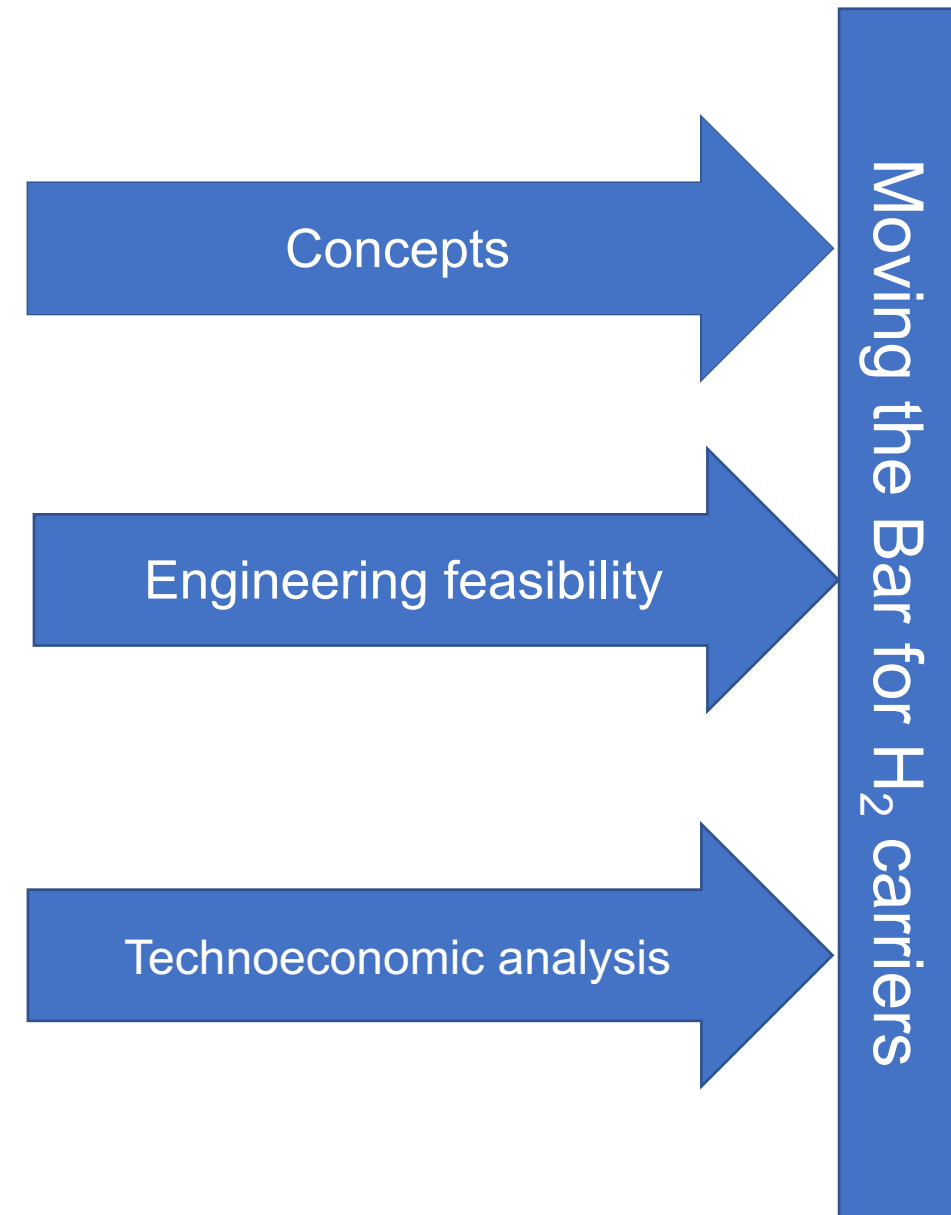


Low production costs and good technical availability

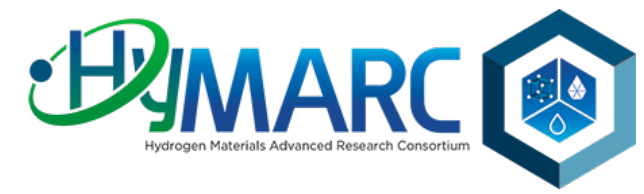


Toxicological and eco-toxicological safety during transportation and use

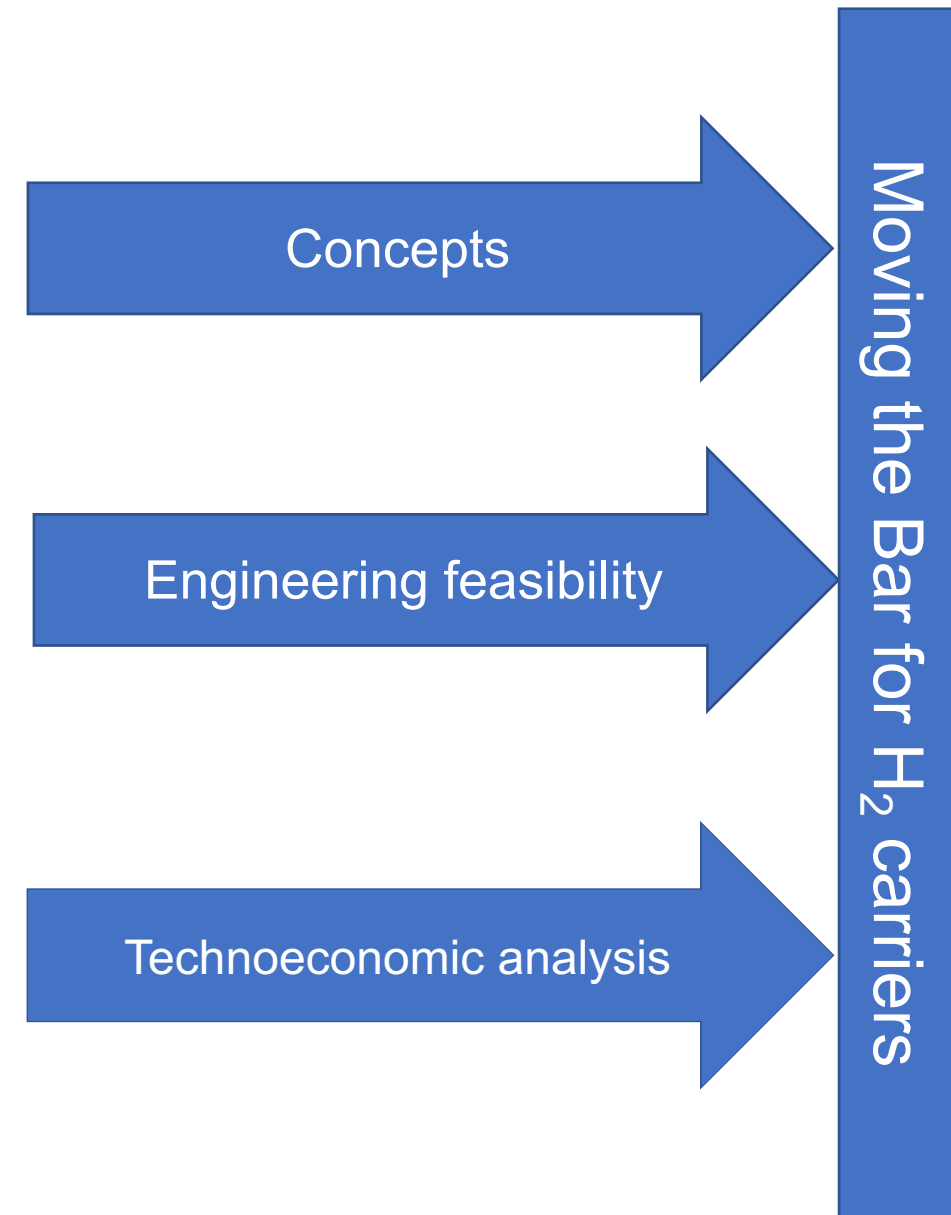
- HyMARC is working to identify off-board scenarios that will benefit from solid and liquid phase carriers of hydrogen.
- Our approach to move the bar forward is to address a defined set of questions for a series of applications
 - (i) what is a minimum footprint for each H₂ carrier
 - (ii) Are known catalysts capable of providing a sufficient rate of H₂ release;
 - (iii) is the power (W/l) and energy (Wh/l) for a given H₂ carrier sufficient to meet the demand.



HyMARC is working to identify off-board scenarios that will benefit from solid and liquid phase carriers of hydrogen



- Concepts
 - Identifying use case scenarios
 - ✓ Transport of H₂ from production facility to city gate
 - ✓ Transport of H₂ from city gate to refueling station
 - ✓ Backup power for data centers
 - ✓ Microgrid energy storage
 - ✓ Passenger ferry, train, bus
 - Identifying materials
 - Identifying approaches
 - ✓ One way carriers
 - ✓ Round trip carriers
 - ✓ H₂ carriers without generating hydrogen
- Engineering feasibility
 - minimum footprint for each H₂ carrier
- Technoeconomic analysis
 - Collaboration with LBL
 - Adapting, evolving



- **Identify promising *use cases*** (refueling station, city gate, emergency backup, ...)
 - Define power and duration requirements
 - Identify benefits and challenges to put *use case* into practice
- **Identify promising *carriers*** (formates, formic acid, ethanol)
 - Compare promising carriers to compressed hydrogen
 - Identify benefits and challenges to put *material* into practice
 - Use information from the literature when available, when not available
 - Use theory, experiment, modeling
- **Utilize Engineering analysis to provides methods of *comparison***
 - Energy: Compare round trip efficiency
 - Cost: Estimate operating costs
 - Size: “Kristone” Plots
 - Benefits: Chemical Compression
- **Utilize Technoeconomic Analysis**
 - Operating and capital costs
 - Insight into ancillary benefits
 - Insight into research areas to reduce cost

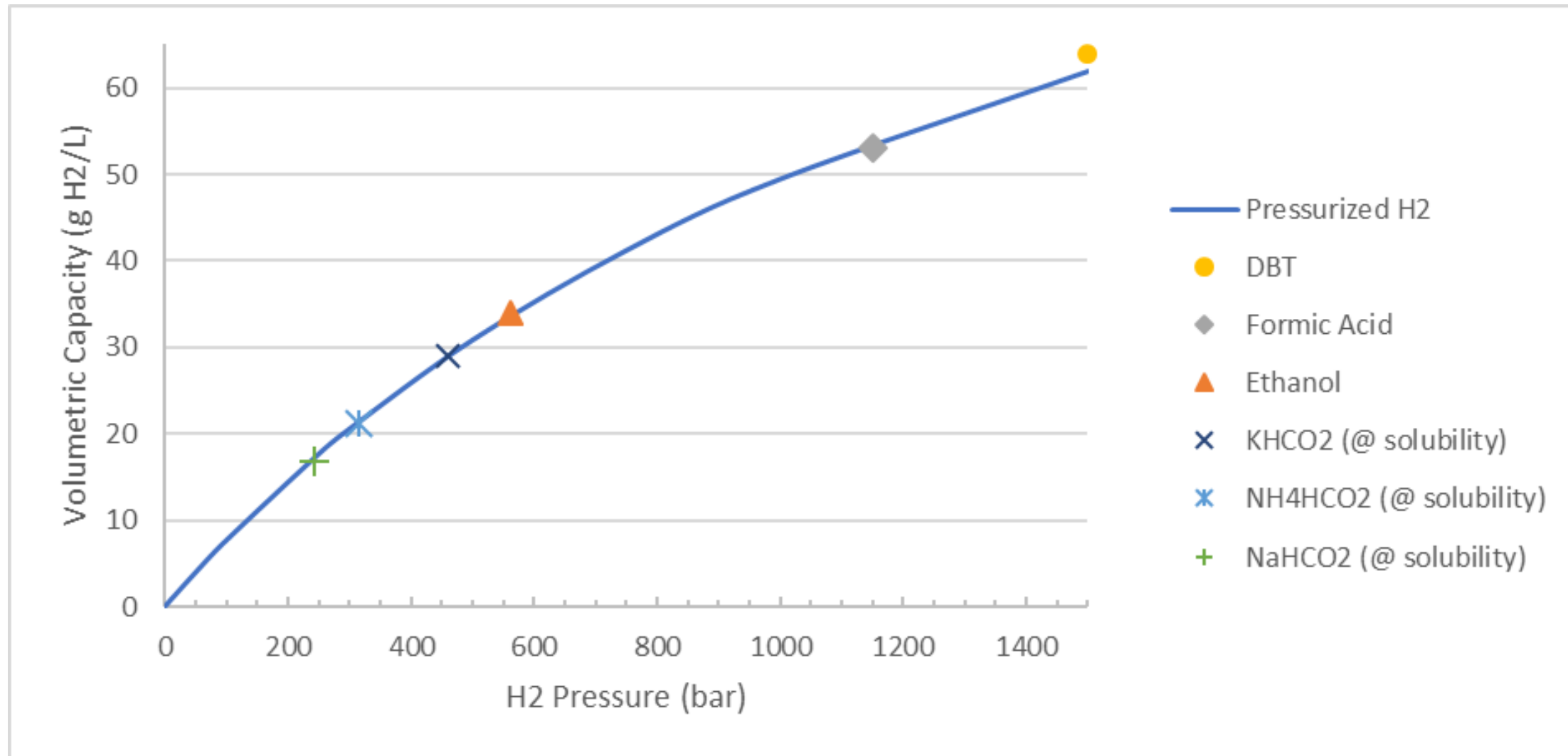
Bottom line – develop metrics for a set of achievable use cases

Relevance

H₂ carriers are scalable and have the potential to *store, transport* and produce *usable* hydrogen



equivalent volumetric density of H₂ carriers relative to comp H₂ gas



Bottom line – ethanol provides a storable H₂ density equivalent > 500 bar compressed H₂ gas

Approach

Identifying promising H₂ carriers (liquid phase)



Example: EtOH to EtOAc

35 g H₂/liter

Microgrid (5 MT H₂)

37 kJ/mol H₂

100 °C

7 kJ/mol H₂

-15 kJ/mol H₂

TBD

> 99%

0.98 cP, -114 C, 53 kPa

- Is the gravimetric/volumetric density greater than 250 bar H₂?
 - what is the volumetric footprint of the system
- What 'use case' are you targeting?
 - How much hydrogen carrier is needed?
- What is the enthalpy release on regen?
 - extra needs for heat management?
- What temperature is required to reach 1 bar H₂ ($T = \Delta H/\Delta S$)?
 - Minimum required energy input for release of H₂
- What is $\Delta G_{(350\text{ C, } 5\text{ bar})}$ H₂ release?
 - are extra compressors needed?
- What is $\Delta G_{(400\text{ C, } 200\text{ bar})}$ H₂ uptake?
 - Regeneration possible under moderate conditions?
- Are catalysts currently available to yield 1 kg H₂/minute?
 - How much catalyst is needed? What flow rate of carrier is needed?
- What is the selectivity for H₂ release?
 - How pure is the H₂? What separation processes are required?
- What is the viscosity, melting point, vapor pressure at the release temperature?
 - Are there special needs for pumping or separations?

Approach

Focus on high impact use cases



- Mobile Distributed (Refueling at City Gate, Transportation)
 - Benefits vs. Current Technology: Store stranded power, Environmental Concerns
 - Benefits vs. Gaseous H₂: Reduced volume and tankage cost
- Stationary Back-Up (Power Outage, Seasonal Storage)
 - Benefits vs. Current Technology: Store low cost electricity, Reliability vs. diesel, Size vs. batteries
 - Benefits vs. Gaseous H₂: Less hazardous and reduced volume

Categorize Applications to Reduce to Reasonable Number

Mobile Distributed Power									
use case	footprint	Duration hrs	Power MW	Energy MWh	MT [H2] /day	days	rate Kg H2/min	transport	ancillary considerations
city gate	large	25	4	100	50	365	35	miles to last mile	
ferry	medium	4.2	1.6	6.72	4.2	365	1.92		
long haul	small	20	0.24	0.84	0.06	365	0.73		
Stationary Back-Up									
use case	footprint	Duration hrs	Power MW	Energy MWh	MT [H2] /day	days	rate Kg H2/min	transport	ancillary considerations
steel mill	extreme	TBD	146		205	365	143	transport or on site	
data center	large	72	20	1440	28	3	19.6	on site generation	fraction of base line power
hospital	medium	168	0.586	99	0.83	7	0.57	on site generation	
microgrid	small	1000	0.065	65	0.112	180	0.078	transport or on site	sell product
Relion backup	smaller	TBD	0.0029	0.49	0.004	7	0.0028	on site generation	

Approach

Accelerating progress through collaboration

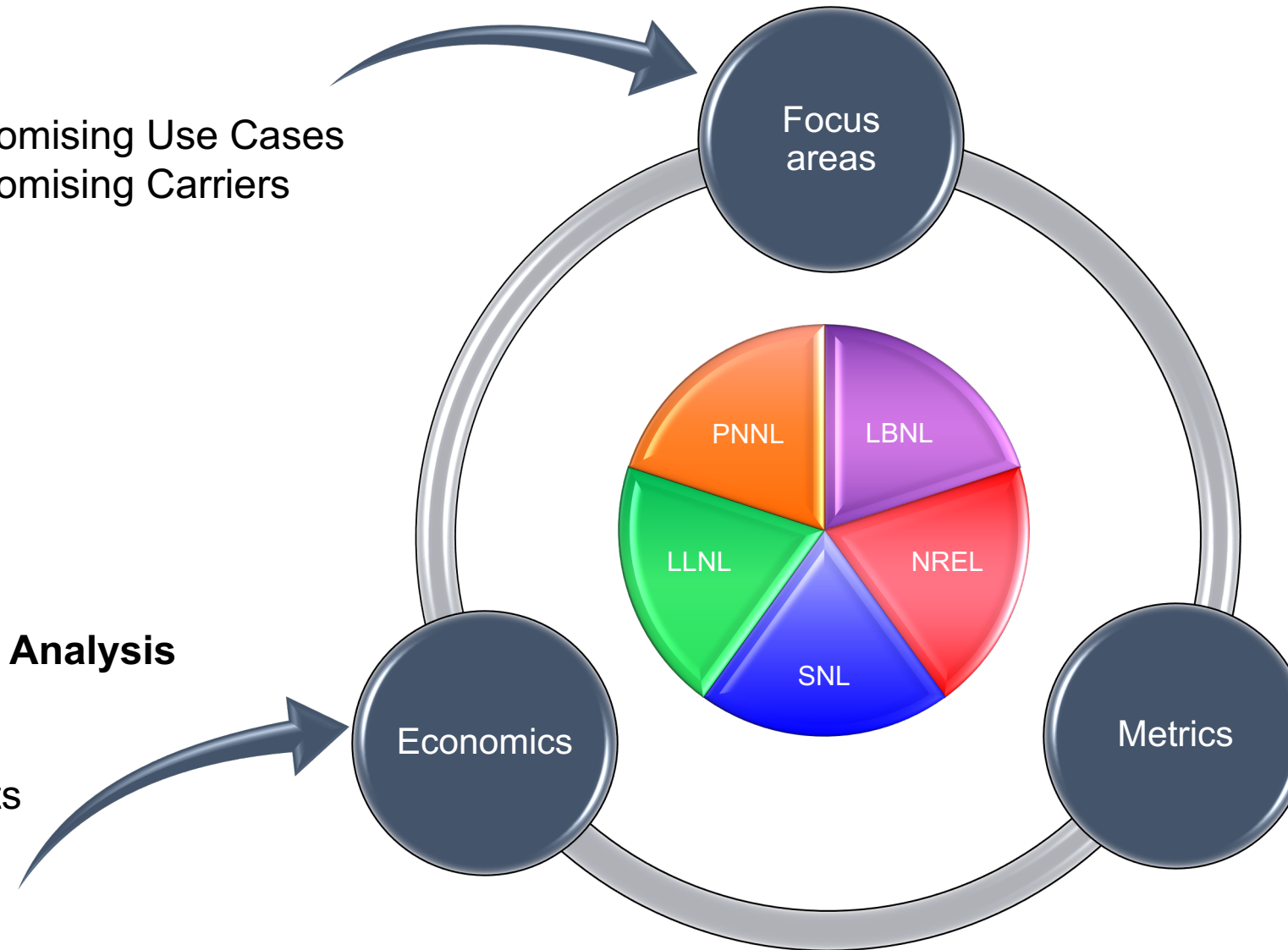


Concepts

- Identify Promising Use Cases
- Identify Promising Carriers

Technoeconomic Analysis

- Capital costs
- Operating costs
- Ancillary benefits

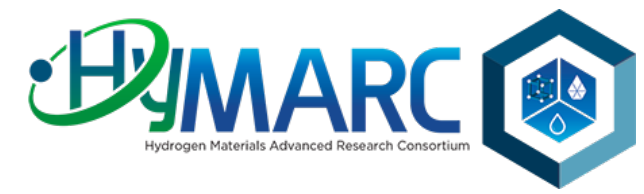


Engineering Feasibility

- System Design
- Round Trip Efficiency
- *Kristone* plots
- Chemical compression

Collaboration

Leverage and share broad experience through monthly conference calls with Hymarc partners and seedling projects

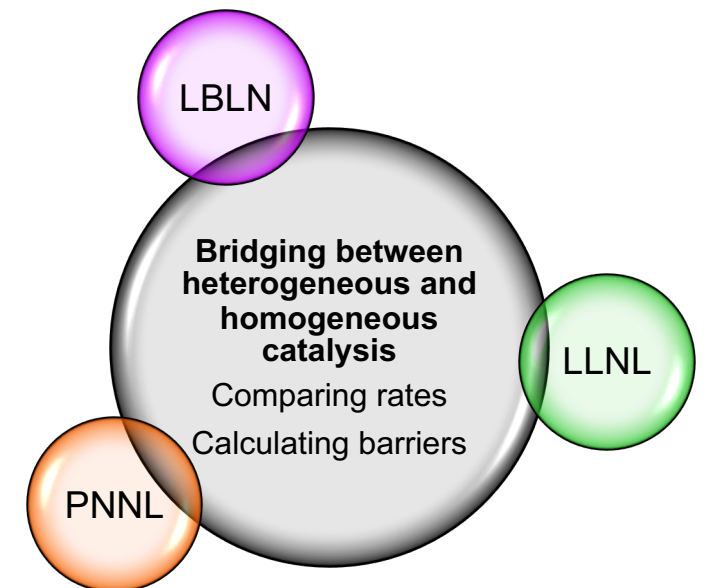
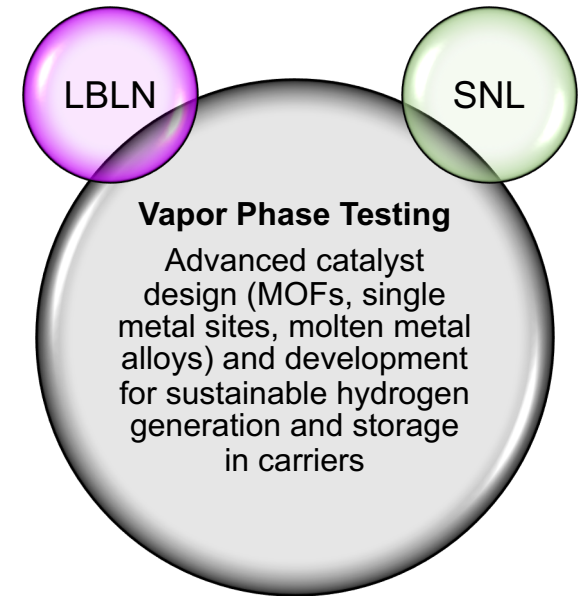
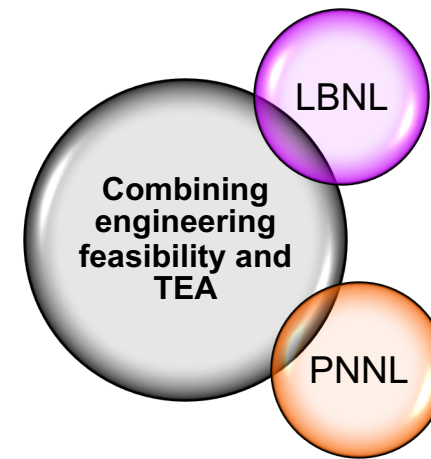
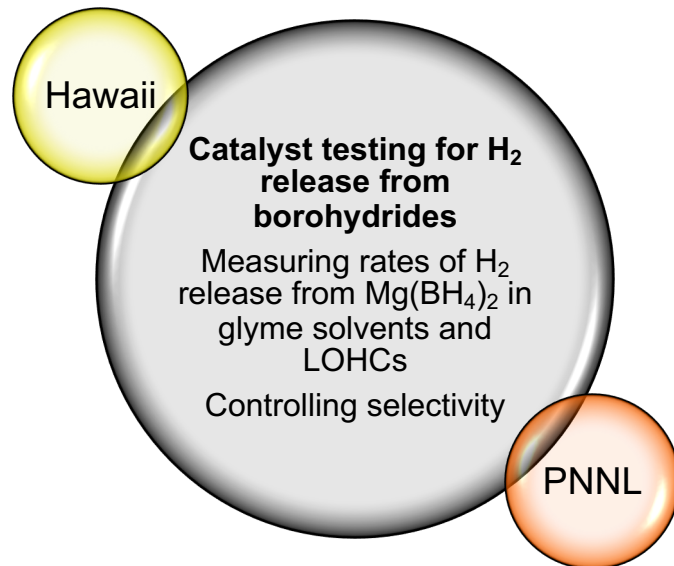
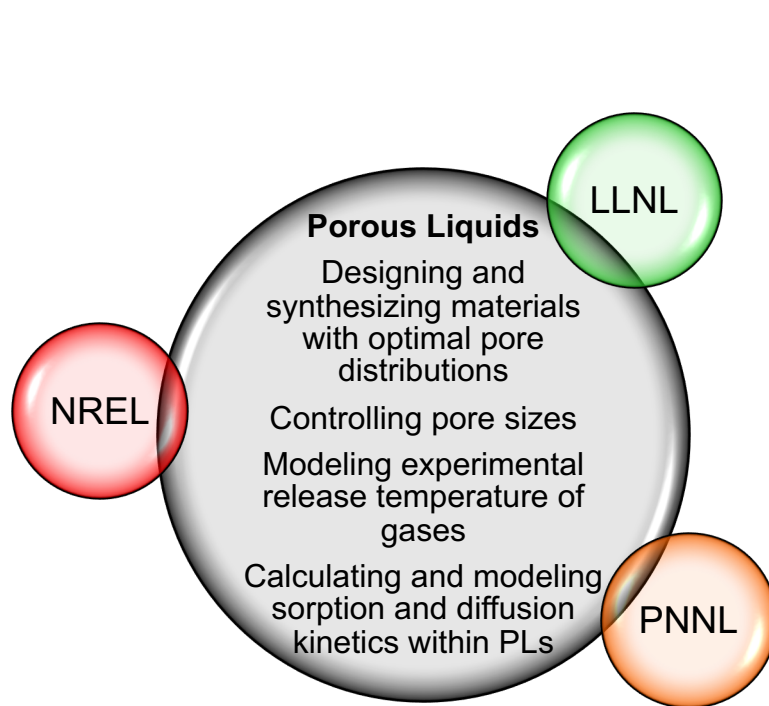


- DOE HyMARC
- WSU Hongfei, Tom, Kat
- USC Travis, Sam, Tom
- SNL Vitalie, Mark, John, Tom
- NREL Wade, Gennett, Tom, Abhi
- NREL Hawaii Gennett, Steve, Noemi, Jensen, Tom, Ba, Mark
- LBNL Hanna, Katarina, Kriston, Mark, Abhi, Ba
- LBNL Ji, Jinghua, Tom
- LLNL Brandon, Tom, Sam, Kat
- MSU, Nick, Abhi, Mark

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
Week 1	1	2	3 WSU H2 carriers 1-2 PM	4	5	6
Week 2	8	9 USC H2 carriers 1-2 PM	10 SNL H2 carriers 11-12 PM	11 NREL H2 carriers 11-12 PM	12 NREL/Hawaii 3-4 PM	13 LBNL TEA 11-12 PM
Week 3	15	16	17 LBNL 3-4 PM	18 LLNL Catalysis 11-12 PM	19	20
Week 4	22	23 MSU 1-2 PM	24	25	26 Hawaii H2 carriers 3-4 PM	27

Collaborations

multiply projects involving experts on focused concepts



Accomplishments

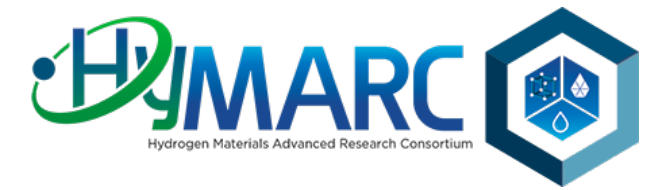
determining volumetric foot print and minimum rate required for H₂ release for targeted use cases



- A city gate will need to store 50,000 kg/H₂/day (equivalent to 800 MWh) requiring 1,000,000 liters (LOHC) ca. 1000 m³
 - To generate 50,000 kg H₂/day at a city gate requires a H₂ release rate of 35 kg H₂/minute (i.e., 1440 minutes/day) from a H₂ carrier
- A refueling station that requires 1,500 kg H₂/day needs to store 30,000 liters LOHC/day and release H₂ at an average rate of 1 kg H₂/min (i.e., 1440 minutes/day)
 - To generate 1,500 kg H₂/day a day from a H₂ carrier at a refueling station requires a H₂ release rate at an average rate of 1 kg H₂/min.

Bottom line – H₂ carriers are scalable – to accommodate a wide range of use cases

Accomplishments



Concept (defining storable, transportable, usable capacity):
Hydrogen Carrier Based on Formate/Bicarbonate Cycle



$\Delta_r H^0 = 20.4 \text{ kJ/mol}$, $\Delta_r G^0 = 1.4 \text{ kJ/mol}$, $\Delta_r S^0 = 59.9 \text{ J/mol K}$

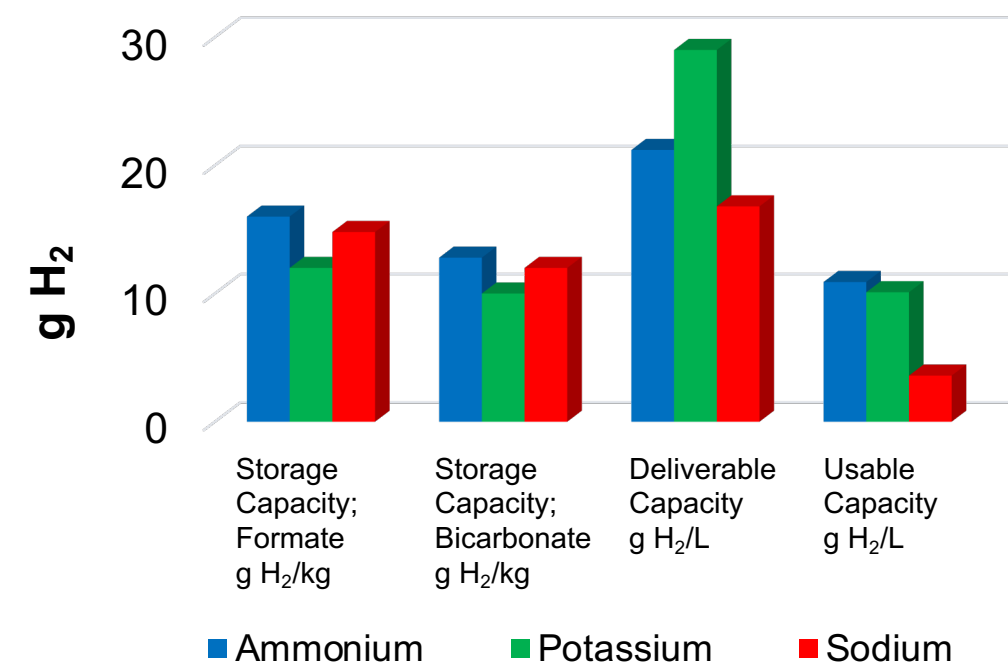
Advantages:

- High volumetric H₂ density
- Water provides 1/2 the H₂
- $\Delta G \sim 1$ for H₂ release and uptake
- Reversible at room temperature
- Low toxicity
- Provides >10 bar H₂ pressure

Limitations:

- Catalyst decomposition
- Slower reaction kinetics
- Dilution (due to low solubility of HCOO⁻/HCO₃⁻ in solvents)

H ₂ carrier	Volumetric density, g H ₂ /L in solution at max. solubility at 30 °C	Pure
H ₂ CO ₂	-	53.4
LiHCO ₂ .H ₂ O	31.4	41.7
NaHCO ₂	19.6	56.5
KHCO ₂	29.7	45.4
NH ₄ HCO ₂	21.4 ^a	40.3
CsHCO ₂	9.6	11.5

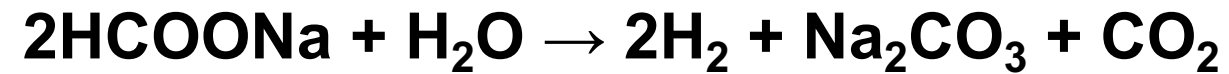


Bottom line – the formate / bicarbonate cycle operates at moderate temperature and pressure

Accomplishments



Concept (un-catalyzed release of H₂): Hydrogen Carrier Based on Formate Hydrothermal Decomposition



$$\Delta_r H^0 = 68.3 \text{ kJ/mol}, \Delta_r G^0 = 17.15 \text{ kJ/mol}, \\ \Delta_r S^0 = 164.8 \text{ J/mol K} \quad T_{1\text{bar}} = 412 \text{ K} (140 \text{ C})$$

Advantages:

- High volumetric H₂ density
- Water provides 1/2 the H₂
- Overcome challenges associated with limited solubility of formate/bicarbonate
- Provides >10 bar H₂ pressure

Limitations:

- CO₂ byproduct
- Higher temperature reaction

- Pressure sensitivity: Proposed system can deliver high P hydrogen (>50 bar at 350 °C (<30 min) compared to the conventional LOHC (eg. In PDBT systems, to shift eq. from 90% dehydrogenation to 90% hydrogenation, H₂ pressure has to be increased only by a factor of 2 or 3)
- Rehydrogenation: (a) Proposed system: 30-100 °C in the presence of a catalyst. (b) Conventional LOHCs: 100-300 °C in the presence of a catalyst.

Table 2 – Enthalpies of dehydrogenation and, where relevant, evaporation for the chemical hydrides.

Storage medium	Enthalpy of dehydrogenation [kWh/kg H ₂]	Typical temperatures for hydrogen release [C]	Boiling point of hydrogenated form [C]	Enthalpy of evaporation (if gas phase during dehydrogenation) [kWh/kg H ₂]	Total heat which must be provided [kWh/kg H ₂]
Methanol	2.3	250	64.7 (100 for water)	4.4 ^a (1.8 for water)	6.7
Ammonia	4.2	>425	33.3	2.1	6.3
Formic acid	4.3	<100	100.8	-	4.3
MCH	9.7	350	101	1.5	11.2
DNEC	7.6	220	>220	-	7.6
PDBT	9.0	300	390	-	9.0

^a For steam reforming of methanol, one must evaporate both methanol and water. In a real case, a stoichiometric excess of water of approximately 50% is typically used; this excess ratio is used to generate the value above [163].

Int. J. Hydrog. Energy, 2019, 44, 11901-11919

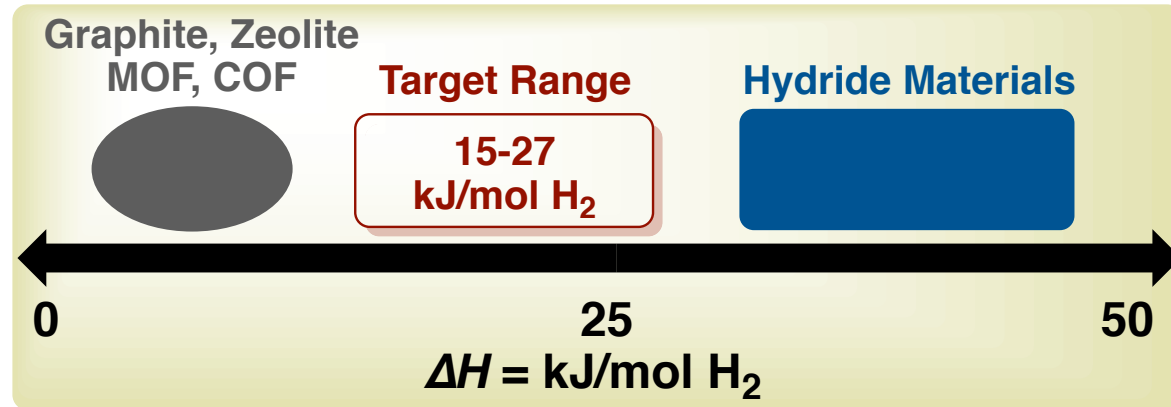
Energy Environ. Sci., 2017, 10, 1652–1659

Green Chem., 2010, 12, 2214–2224

Bottom line – non-catalytic hydrothermal formate decomposition temperature is comparable to the conventional LOHCs that use noble metal catalysts (Ru, Pt etc) to release H₂.

Accomplishments

Concept: Dehydrogenative coupling provides a means to modify thermodynamics. Molecular catalyst that enables both H₂ release and uptake can provide an approach for microgrid technology

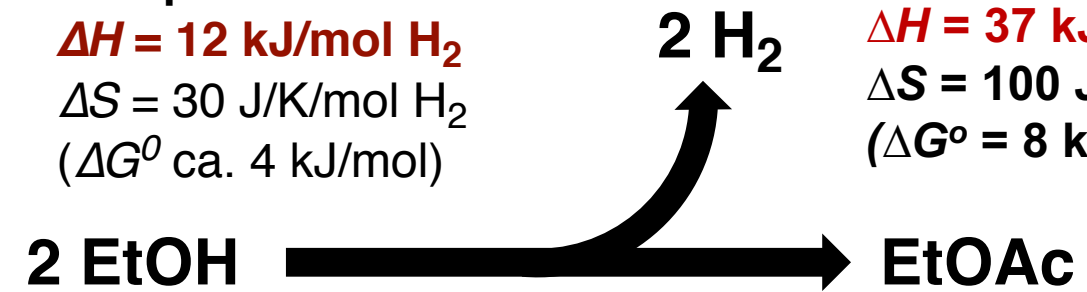


Gas-phase calculation

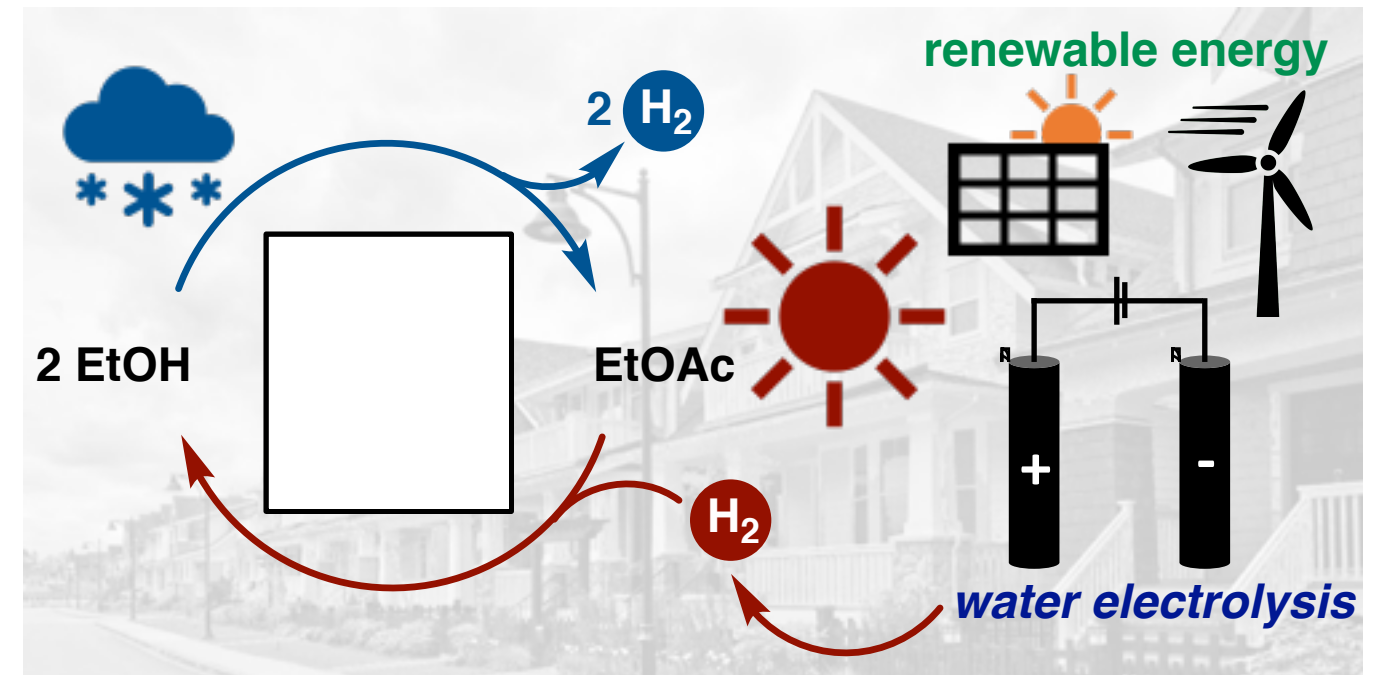
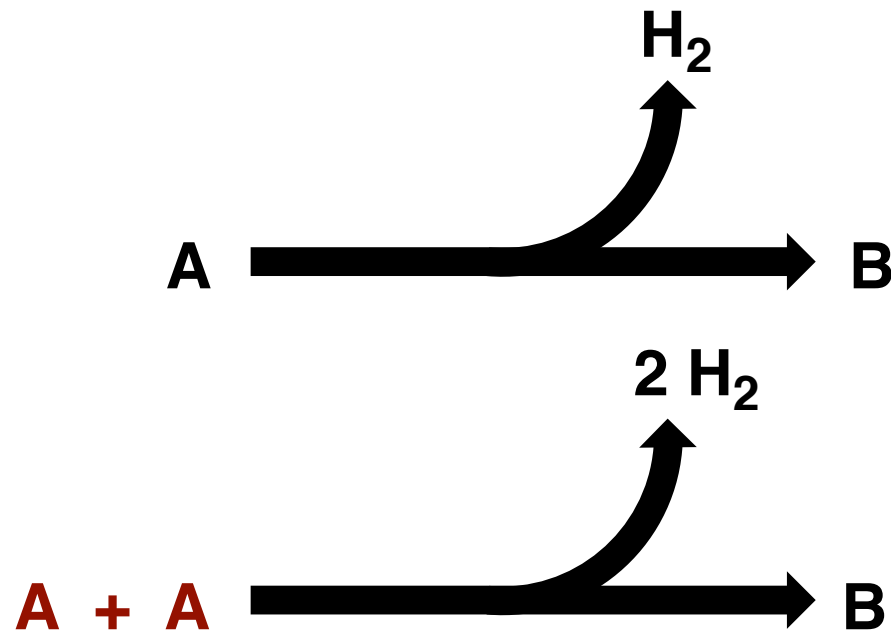
$$\Delta H = 12 \text{ kJ/mol H}_2$$
$$\Delta S = 30 \text{ J/K/mol H}_2$$
$$(\Delta G^\circ \text{ ca. } 4 \text{ kJ/mol})$$

Liquid phase calculation

$$\Delta H = 37 \text{ kJ/mol H}_2$$
$$\Delta S = 100 \text{ J/K/mol H}_2$$
$$(\Delta G^\circ = 8 \text{ kJ/mol H}_2)$$



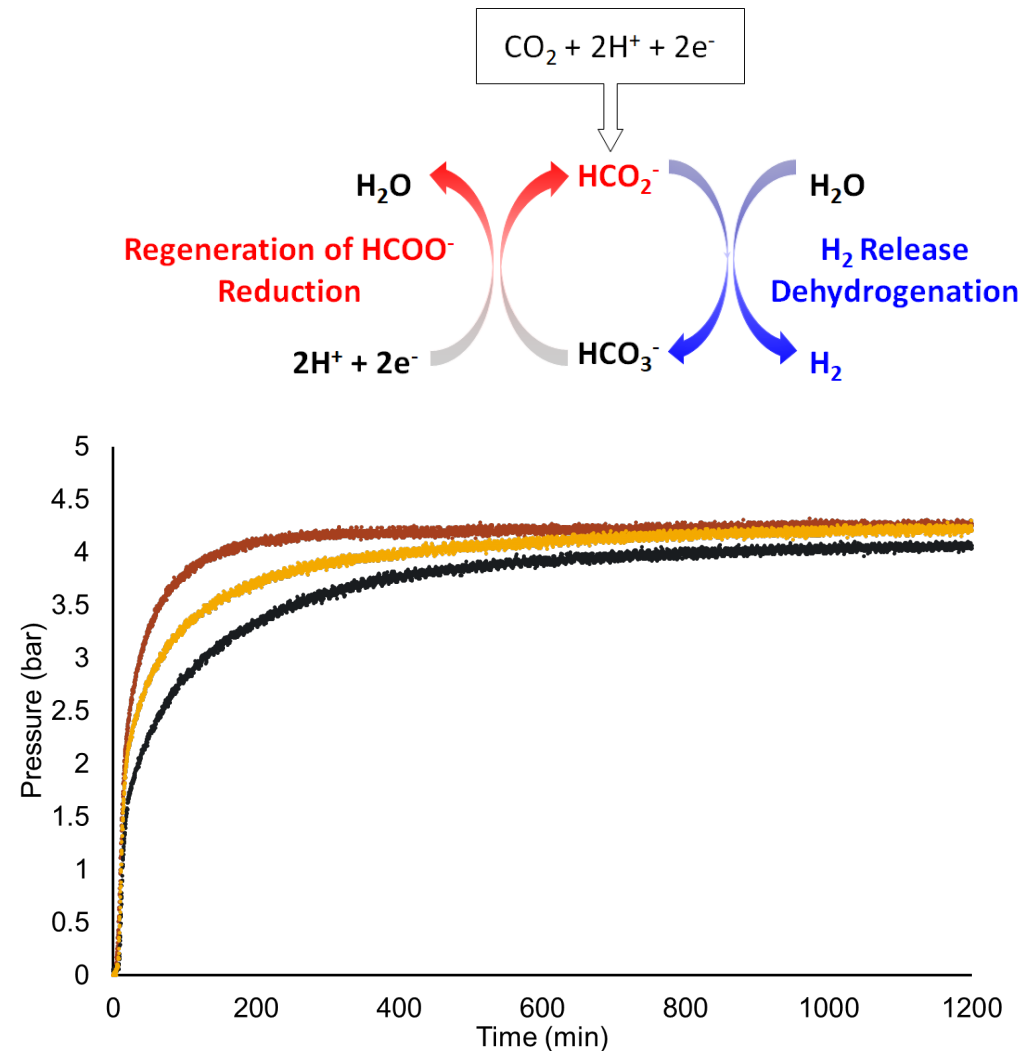
Modifying thermodynamics



Bottom line – the EtOH/ EtOAc cycle operates at moderate temperature and pressure

Accomplishments

Concepts: (i) Formation of H₂ carriers without H₂
(ii) Engineering approach to catalyst reactivation)



- Investigated potential for regeneration of H₂ carrier, formate, by electrochemical process
- Screened multiply Pd-supported catalysts (commercially available and from collaborators)
- Confirmed catalyst reactivation by washing with water
- Demonstrated ability to generate 3-4 bar H₂ backpressure (at the formate/bicarbonate equilibrium)

Bottom line – (i) The formate / bicarbonate cycle provides an opportunity to regenerate H₂ carriers without needing a discrete step to make H₂. (ii) Use double reactor to regenerate catalyst

Approach

Engineering feasibility: Developing Ragone plots of Energy vs Power for multiply H₂ carriers



A data center may need 10 MW Power for 100 hours (1GWh)

★ Interpolation from Ragone plot for liq. NH₃ PEM FC provides an estimate of the system 'foot print'

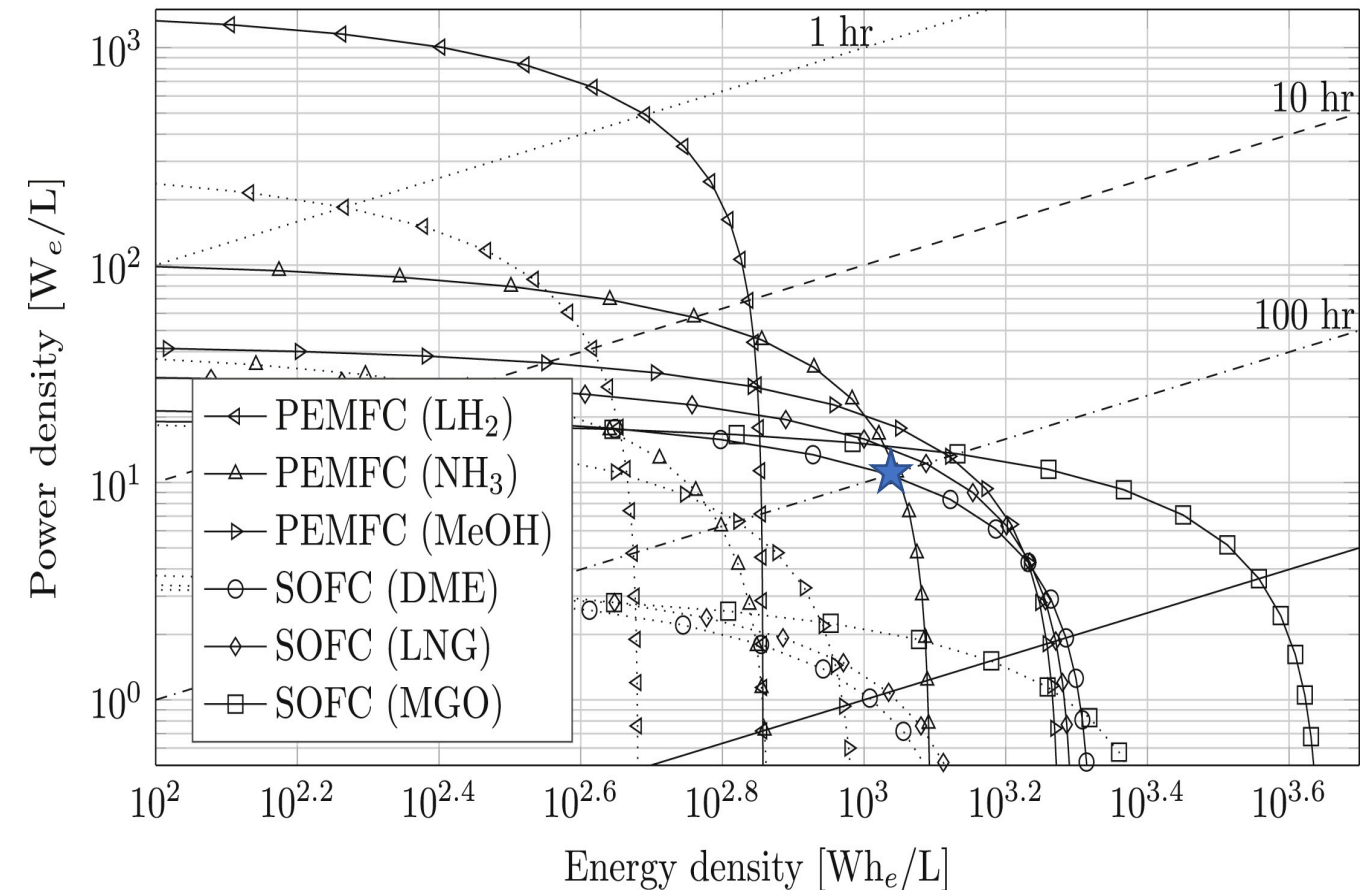
Power 10 W/liter (10 MW/10 W/liter = 1,000,000 liters)
Energy 1000 Wh/liter (1 GWh/1000 Wh/liter = 1,000,000 liters)

Liq NH₃ = 0.17 kg H₂/liter * 20 kWh/kg H₂ = 3.4 kWh/liter
(1 GWh/3400 Wh/liter NH₃ = 300,000 liters of liq NH₃)

Power ~ combination of volume of FC and BOP
Energy ~ volume of 'fuel' and tank

What does the footprint look like for a: passenger ferry, bus, train, city gate, refueling station, microgrid, ... using formic acid, formate salt, EtOH, methylcyclohexane, ...

Also need to consider a material and system capable of delivering 10 kg H₂/minute for the data center backup



(b) Volumetric density of fuel cell systems with various logistic fuels.

Figure 3 from A review of fuel cell systems for maritime applications. L. van Biert, M. Godjevac, K. Visser, P.V. Aravind. *Journal of Power Sources* 327 (2016) 345-364

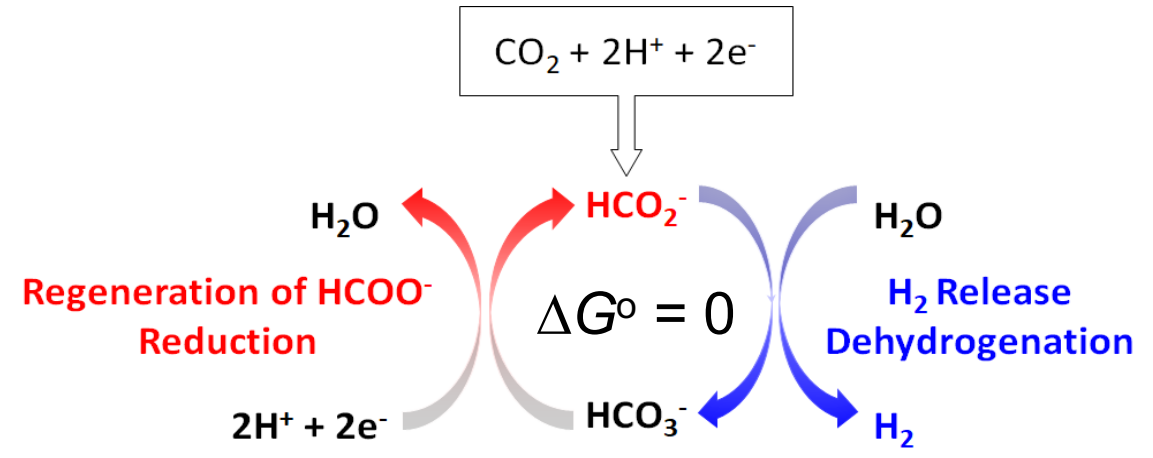
Bottom line – Ragone/Kristone plots provide a means to compare physical footprints for different H₂ carriers for different sets of use cases

Accomplishments

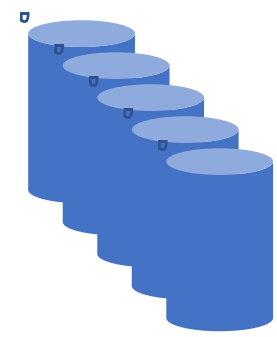
TEA of Formate regeneration from Bicarbonate suggests water removal most costly step



Electrochemistry enables regeneration of H₂ carrier 'without hydrogen'



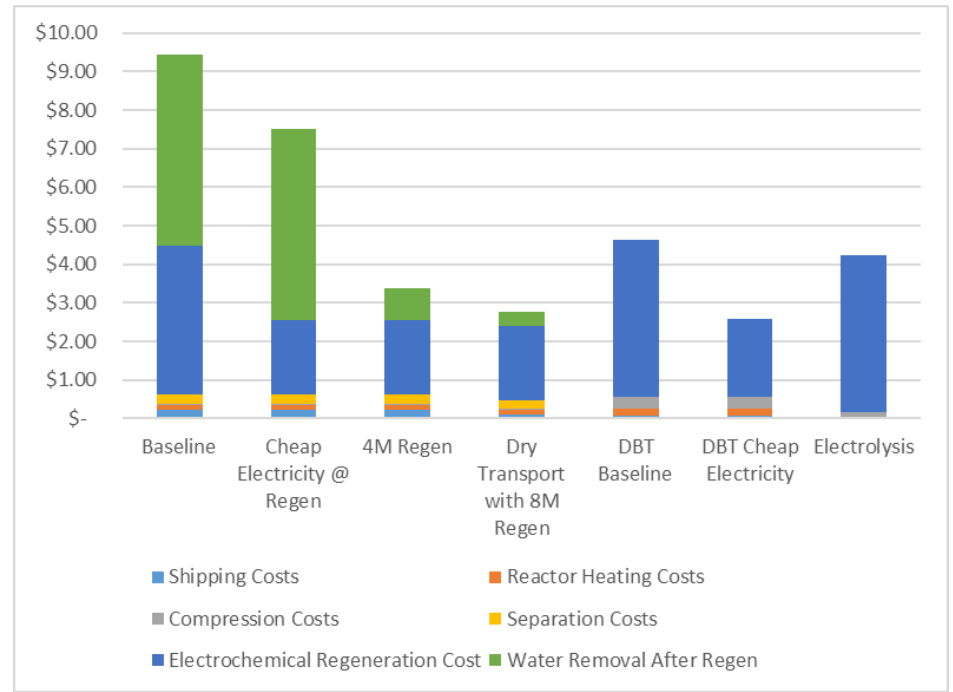
Microgrid
5 MT H₂ Annual Storage
 5 tanks **8 M NaHCO₂**
 300,000 L
 11' ID x 22' tall



Materials are inexpensive, non-flammable and non toxic (KHCO₃ is used as a de-icer)

Bottom line – initial EF and TEA suggests water removal is the expensive step. Need to think about special use case where heat is cheap (nuclear) or develop catalysts that work under more concentrated conditions

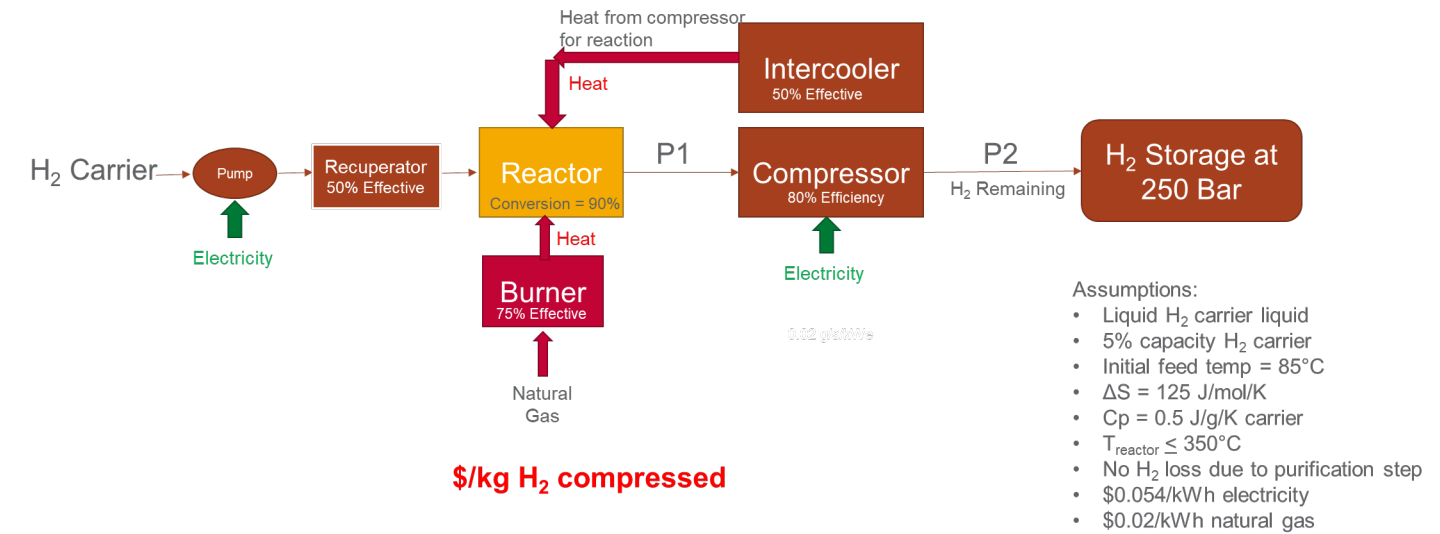
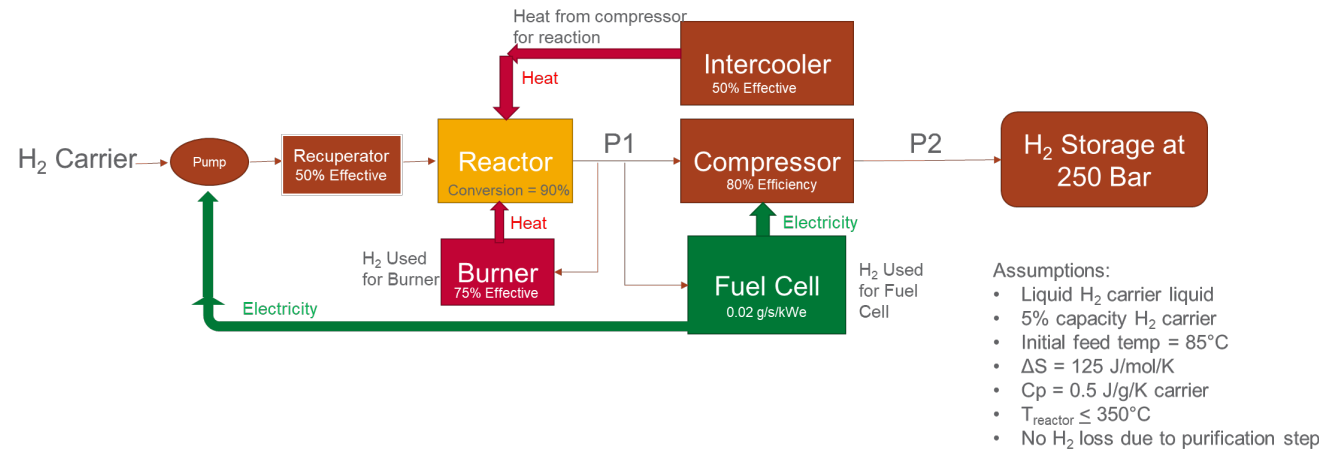
Preliminary TEA suggest water removal is great expense



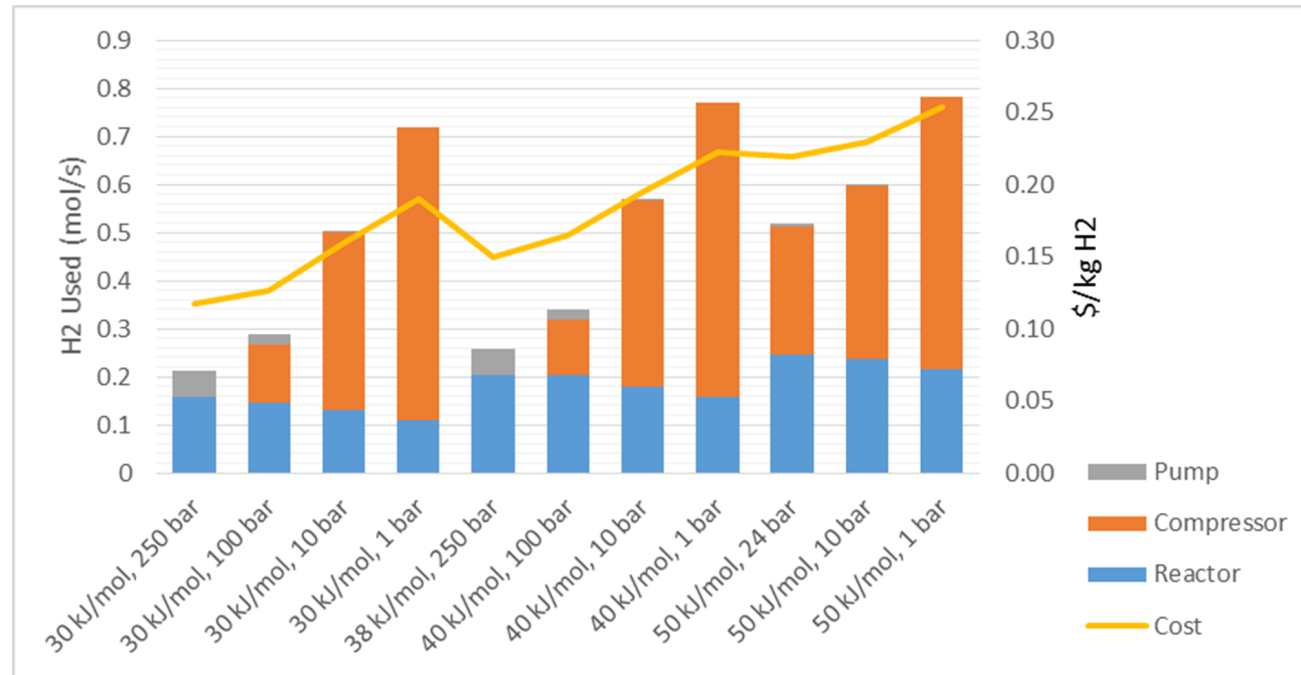
TEA analysis suggests efforts are needed to perform regeneration at higher concentrations or a use case with cheap source of heat, e.g., nuclear reactor

Accomplishments:

Engineering feasibility optimizing the temperature for H₂ release can provide initial stage of chemical compression



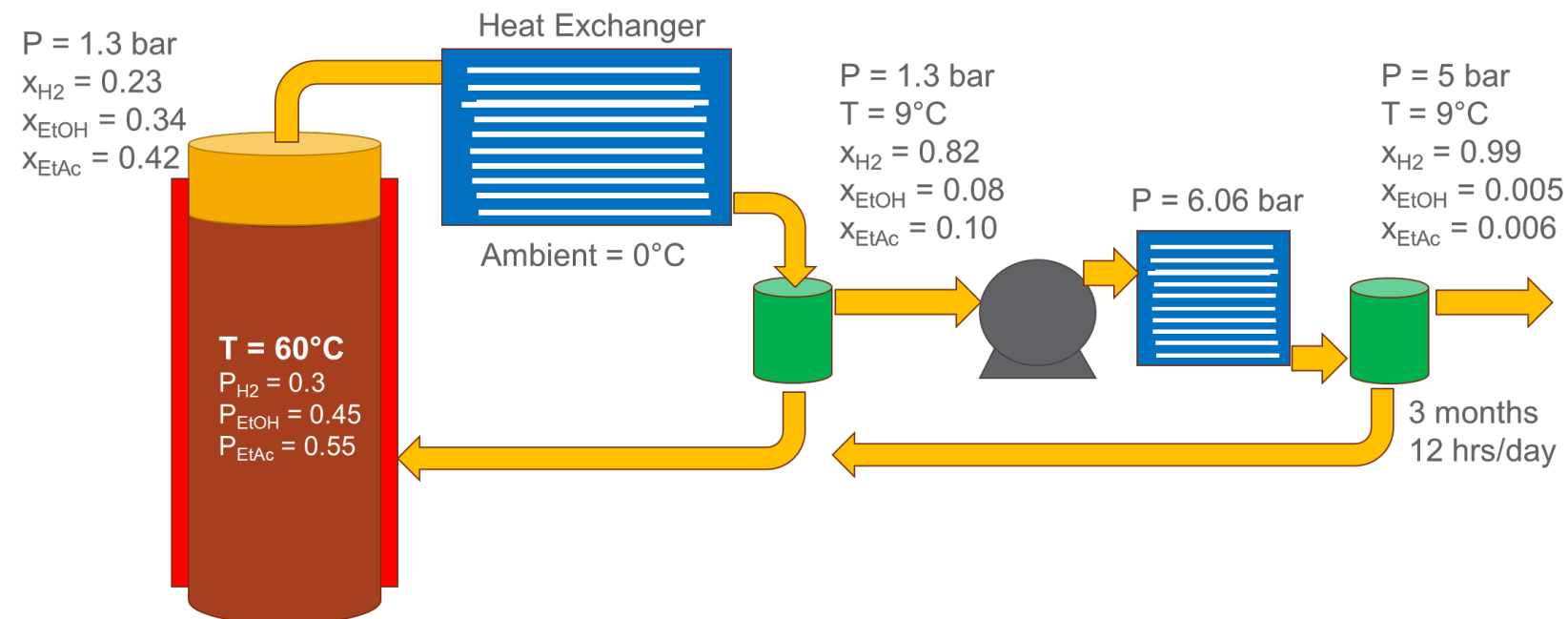
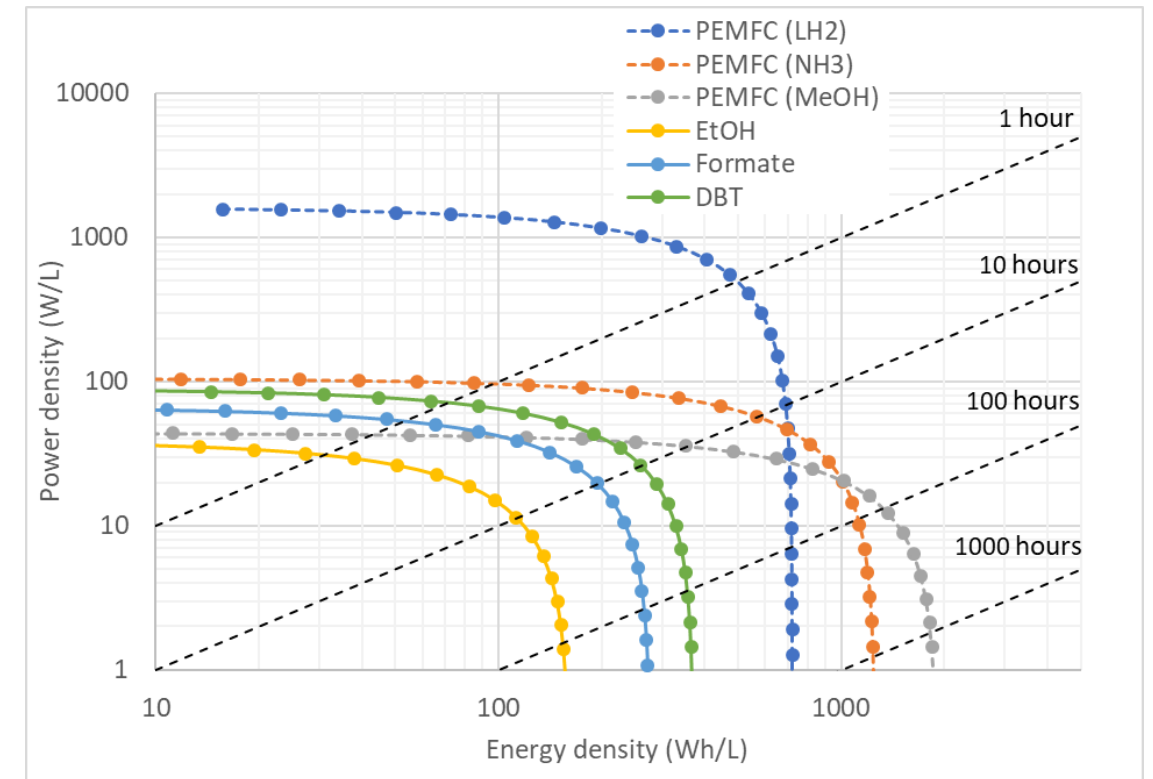
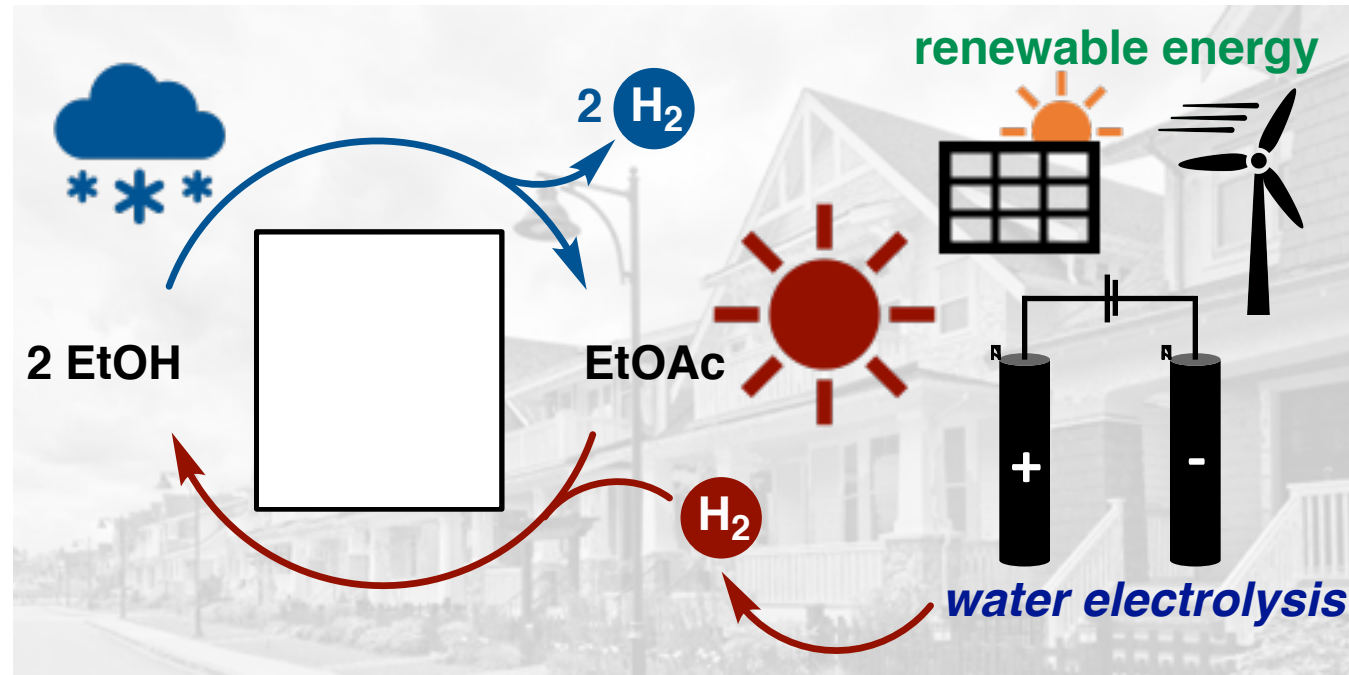
\$/kg H₂ compressed



Bottom line – chemical compression can reduce the needs of physical compression.

Accomplishment

Engineering Analysis using Kristone plot shows footprint of Ethanol/Ethyl Acetate Cycle



Bottom line – Ragone plots provide insight into the physical footprint for EtOH for multiply use cases ranging from seasonal storage, to data centers to a passenger ferry.

- **Concepts**

- Dehydrogenative coupling to alcohols (35 g H₂/liter)
 - ✓ modify ΔH and ΔS to obtain ΔG in range of 4-8 kJ/mol H₂.
 - ✓ One pot reversible release and uptake of H₂ with a molecular catalyst
 - ✓ condensed phase thermodynamics of alcohols are substantially different than gas phase thermodynamics
- Formate / bicarbonate cycle (30-50 g H₂/liter)
 - ✓ Synthesis of H₂ carriers without making H₂ in a discrete step – electrochemical regeneration
 - ✓ Regeneration of formate from bicarbonate under moderate conditions (5 bar H₂, 40 C)

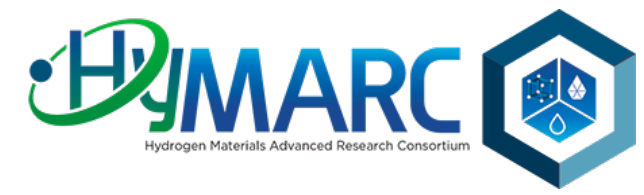
- **Engineering feasibility**

- Ragone plots to determine the volumetric footprint
 - ✓ EtOH for a microgrid (5 Mt H₂)
 - ✓ NH₃ and liq H₂ for a Data Center (1 GWh)
- Analysis of chemical compression to enable initial compression step
 - ✓ Formic acid (xxx bar H₂)
- Compiled list of existing catalysts that can provide >1 kg H₂/min
 - ✓ from formate xx kg Pd
 - ✓ formic acid xx kg Pd

- **Technoeconomic analysis**

- electrochemical regeneration of formate from bicarbonate
 - ✓ removal of water most costly step

Back up slides



Task 3.D.2. Porous liquids as hydrogen carriers

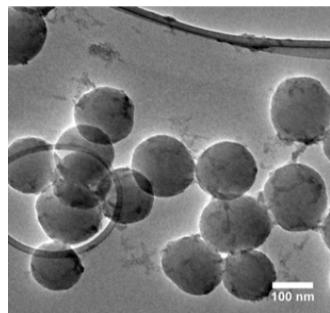
Relevant technical targets

- Volumetric - better sorbent packing
- Desorption Time – alleviate mass transport issues in monoliths
- Heats of Adsorption
 - **Decreasing** high Q_{ST} when coupled with illumination strategy
 - ‘Trapping’ gas from low Q_{ST} sites and **increasing** desorption temps.

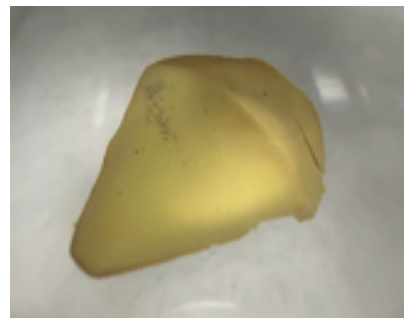
Project success

- ‘Fluid’ monolith with improved volumetric capacity and fast desorption times
- ‘On demand’ H₂ delivery when coupled with illumination strategies

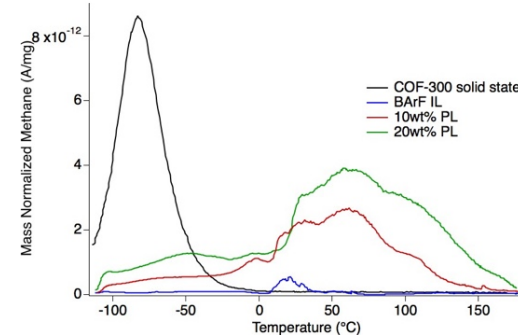
Well-defined
100 nm COF Colloids



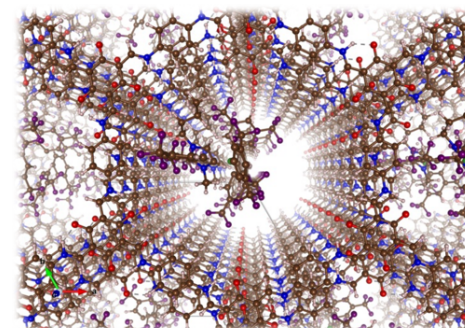
COF Monolith



Enhanced Gas Uptake &
Influence on Desorption Temp.

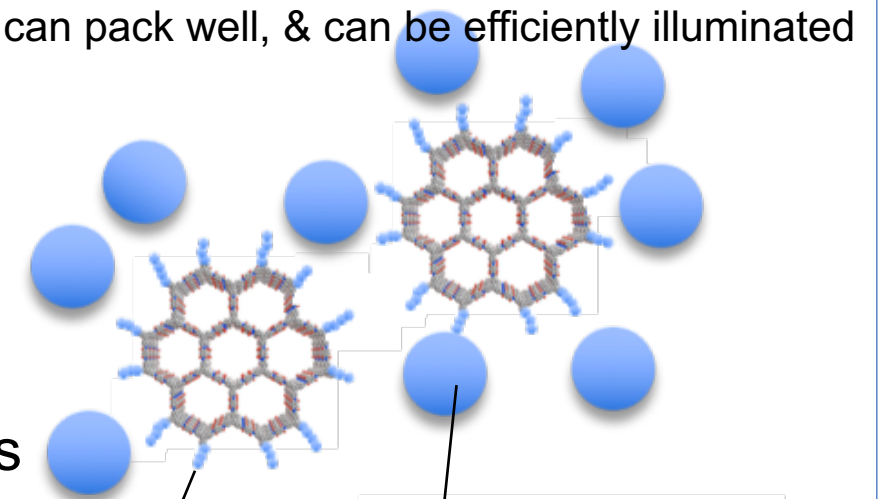


Modeling Porous
Liquid Dynamics



Approach:

Synthesize COF colloids so they stay suspended, can pack well, & can be efficiently illuminated



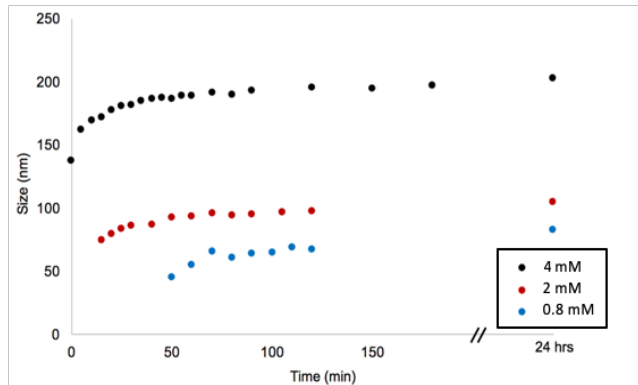
Use Size-excluded solvent w/ no vapor pressure for lubrication/fluidity

Tethered groups stabilize colloids against irreversible aggregation, enhance solubility

Task 3.D.2. Porous liquid Accomplishments

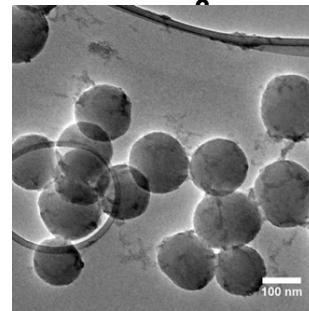
1. Control over COF Colloid Size & Surface Area

Dynamic Light Scattering

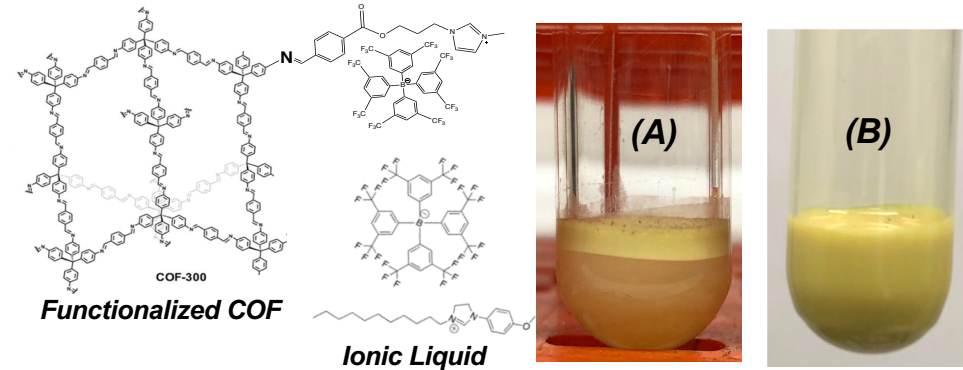


[M] < 6 mM in CH₃CN, r.t., 0.16 eq. Sc(Otf)₃ Catalyst

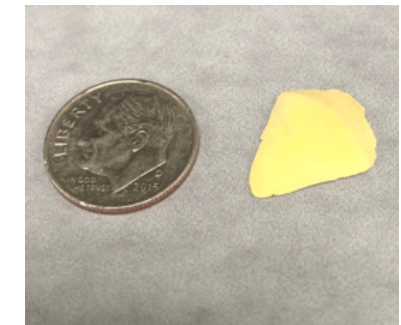
~100 nm particles



2. COF Functionalization for Indefinite Colloid Stability

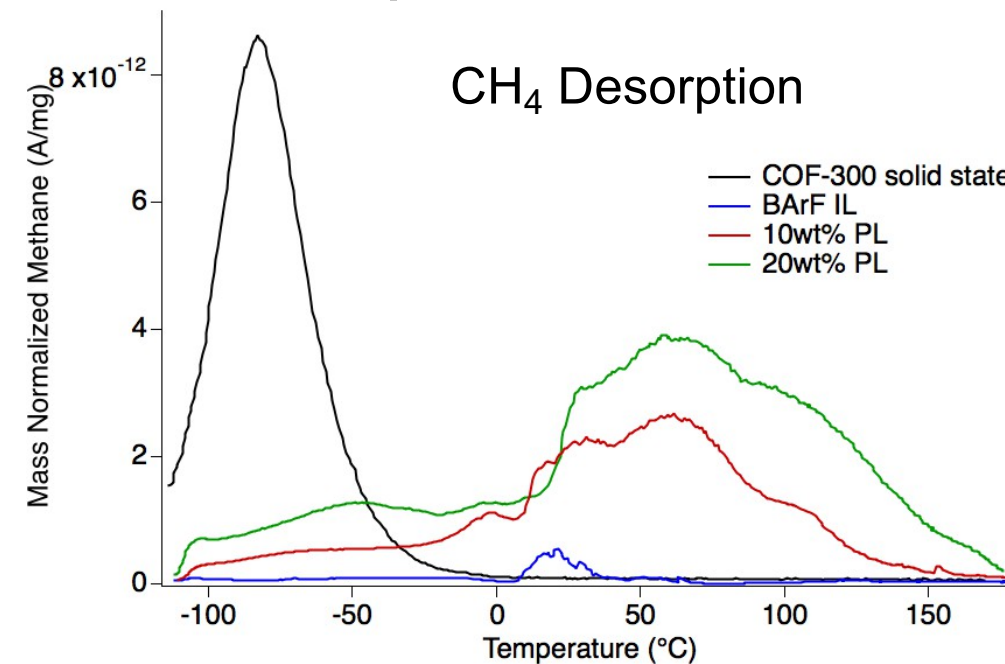
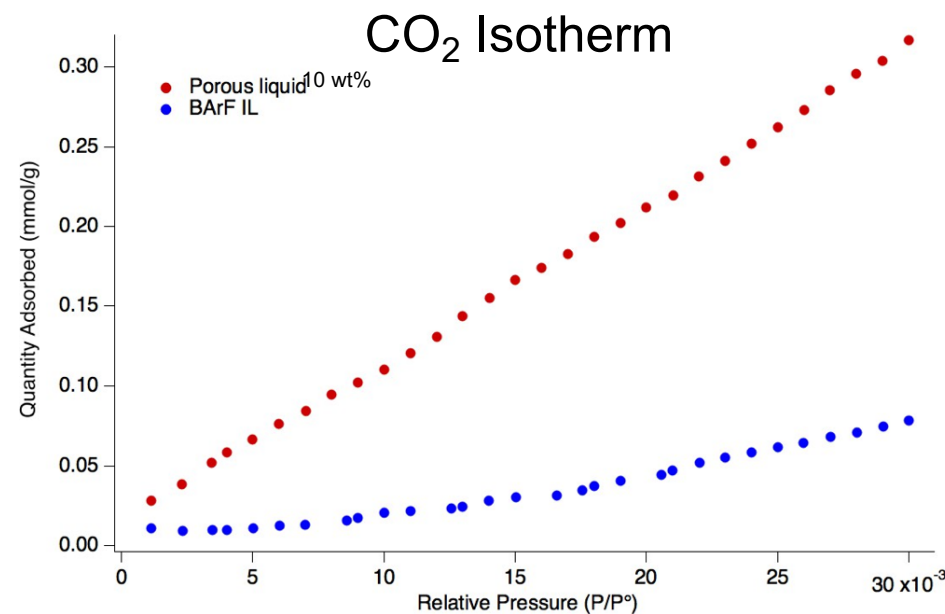


3. Colloids Used to Synthesize Monolith



400 m²/g, ~0.5 g/cm³

4. Enhanced Gas Uptake Demonstrated for Porous Liquid



CO₂ data indicates near 100% of theoretical pores remain open for gas binding

CH₄ data indicates dramatic uptake in gas relative to solvent (>20 fold increase), also dramatic effect on desorption temperature

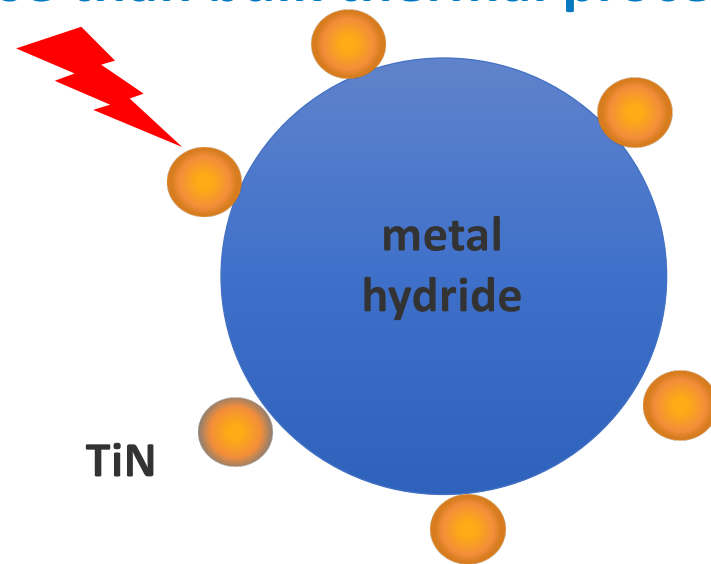
3f:9 Plasmon interactions for on-demand hydrogen release in hydrogen carriers

Approach:

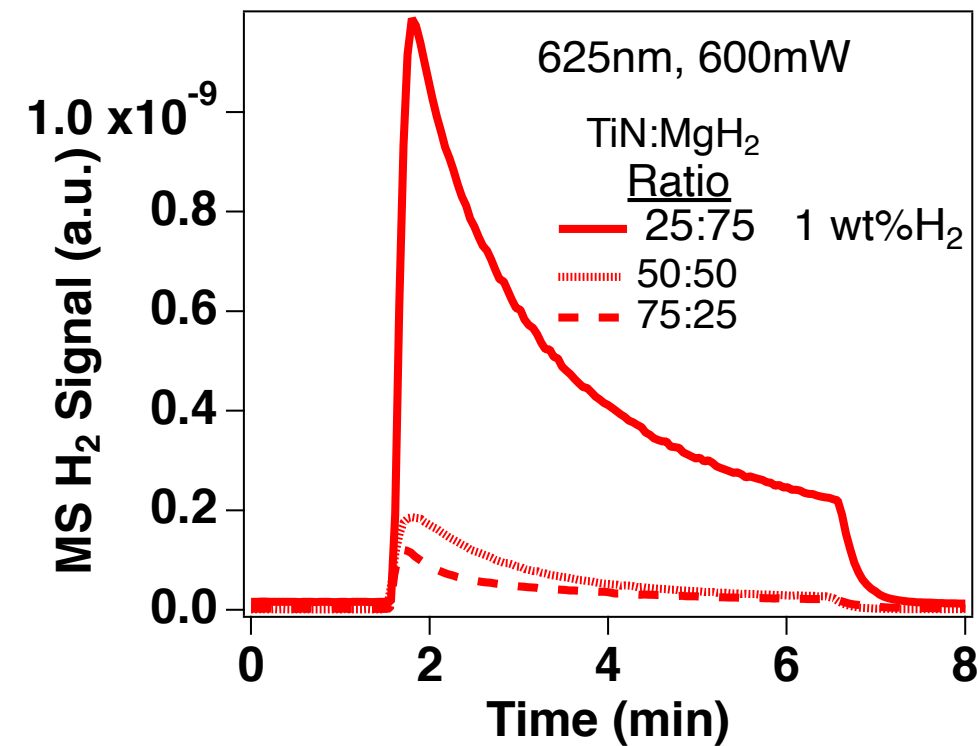
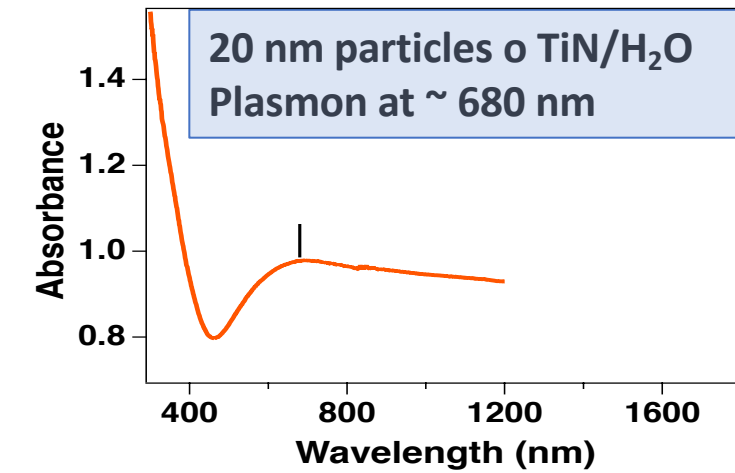
Reversibly release and store hydrogen at near-ambient conditions via an optically driven process.

Impact:

Deliver hydrogen using less energy and with a faster response than bulk thermal processes.

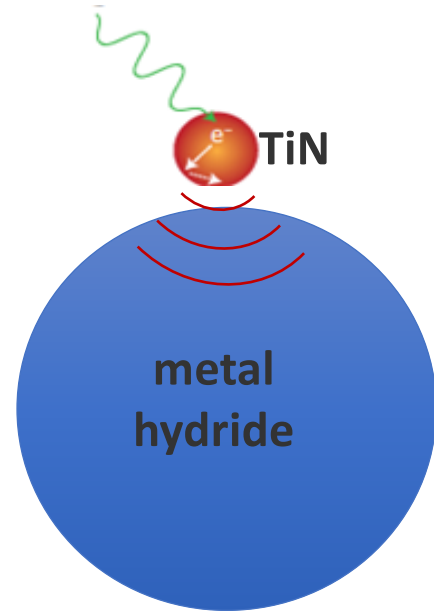


Photoexcite the TiN plasmon to drive rapid H₂ release

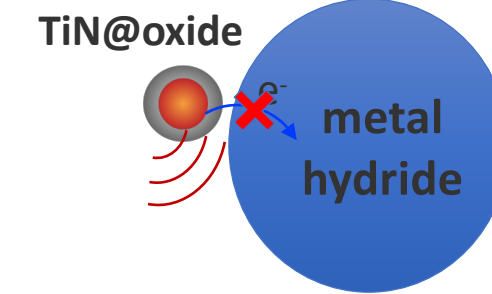
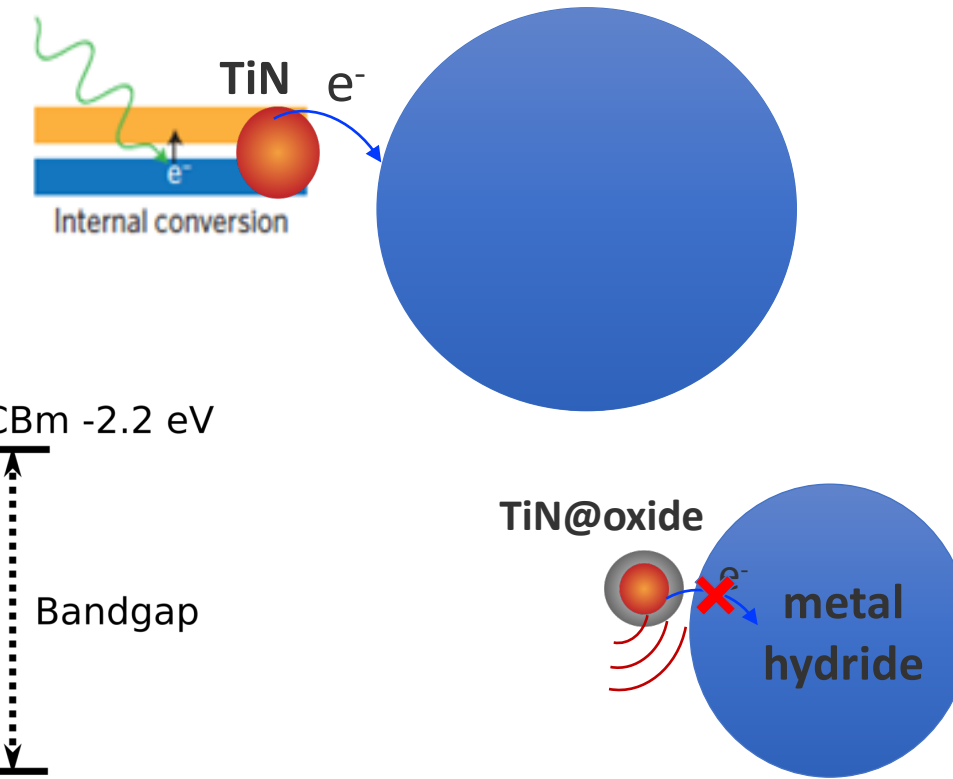
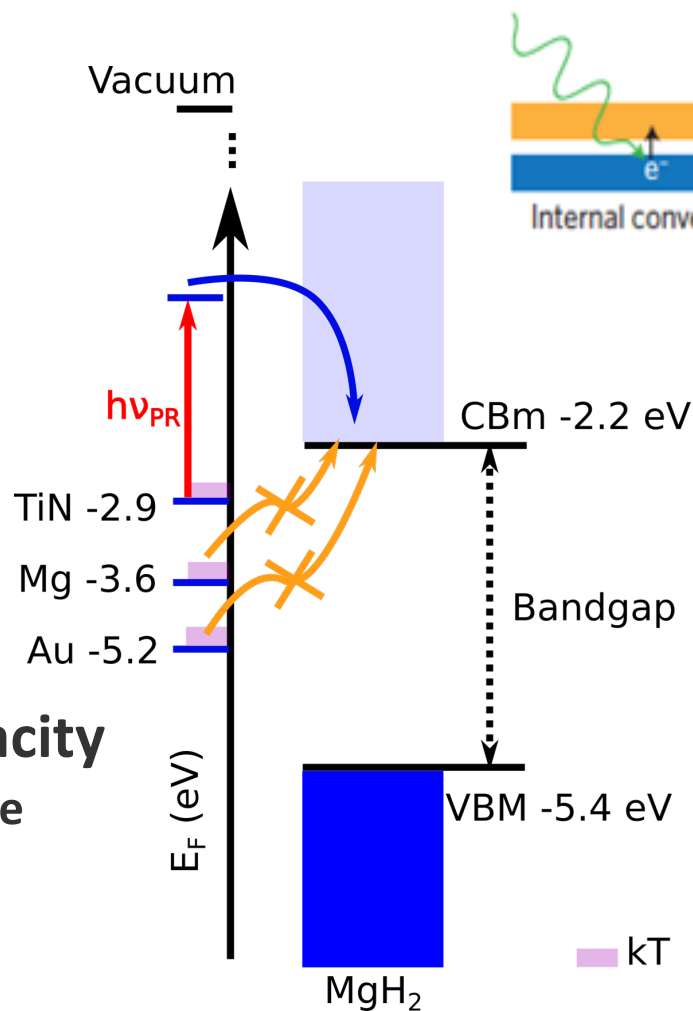


Result: 1 wt% H₂ in 5 min
TiN/MgH₂

Plasmonic heating



vs. Photo-excited electron transfer



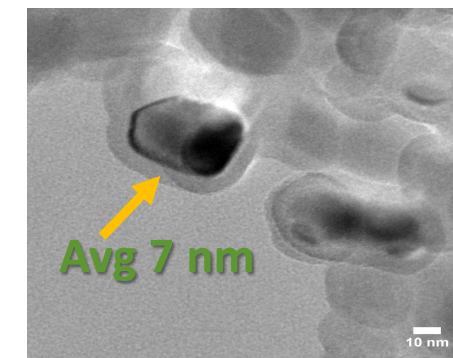
Path forward to increase capacity

- better interface TiN/metal hydride
- Confirm H_2 quantitative dehydrogenation by Sieverts measurements
- Resolve mechanism

Collaboration with:

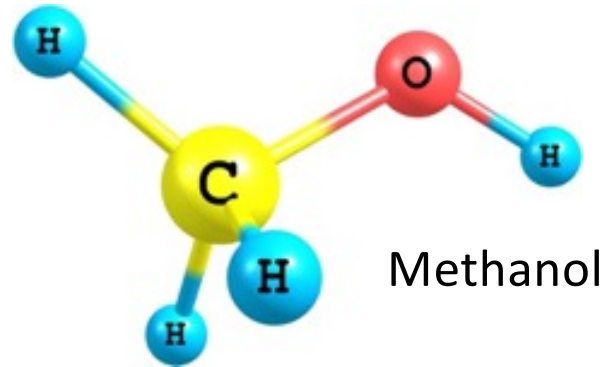
Prendergast, Sanz-Matias, Verma (LBNL)

- Charge transfer of photoexcited TiN electrons to the conduction band of MgH_2 is favorable
- charge transfer from Au, Mg or nonexcited TiN surfaces is thermodynamically disfavored.



TASK 3. TRANSITION METAL BASED CATALYSTS for Methanol dehydrogenation

Background



1. High gravimetric H₂ density. (~12%)
2. Low cost
3. Easy handleability and transportation
4. Being manufactured from a variety of renewable sources

Note:

1. Noble-metal-based catalysts: high activity, exorbitant price, low abundance.
2. Transition-metal-based catalysts: Lower price, low selectivity and low reactivity.

[1] Journal of Molecular Catalysis A: Chemical 152 2000. 157–165.

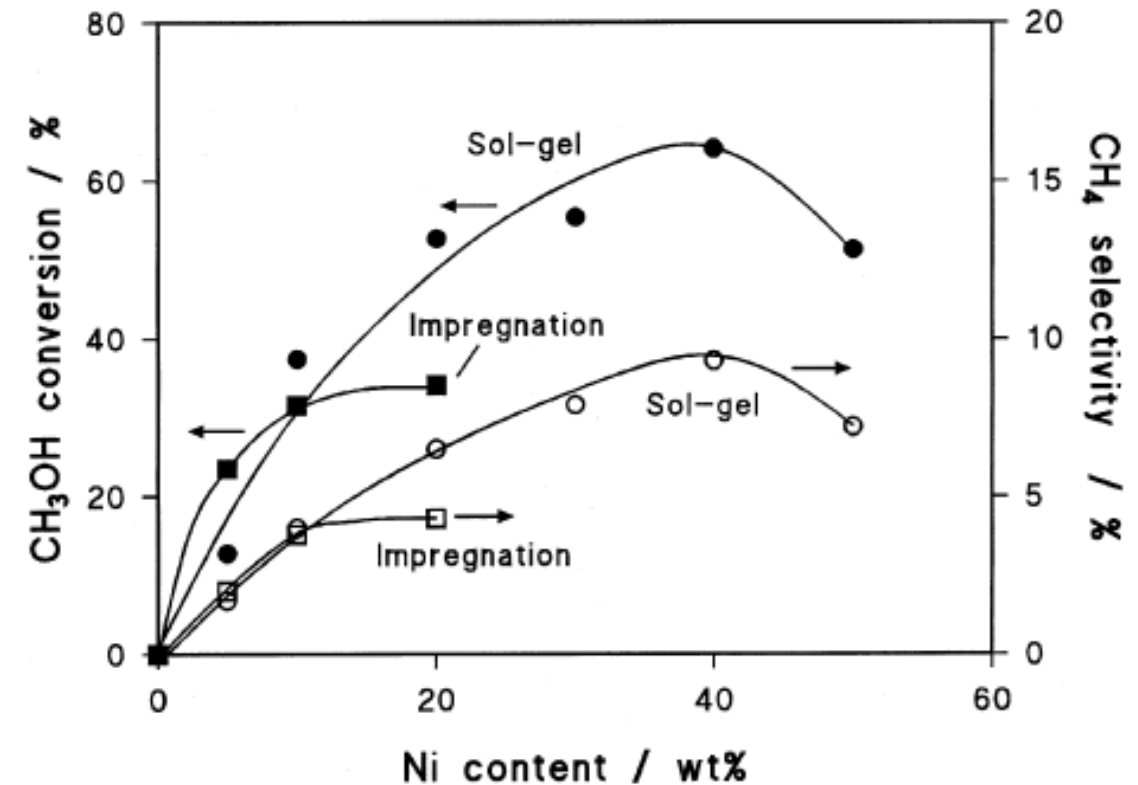


Figure. Methanol decomposition over nickel supported on silica at 250 °C. [1]

Modulation of Electronic Metal-Support Interaction for Catalysis

Ultrasmall Nickel Nanoclusters deposited on defective BN nanosheets as the Catalyst

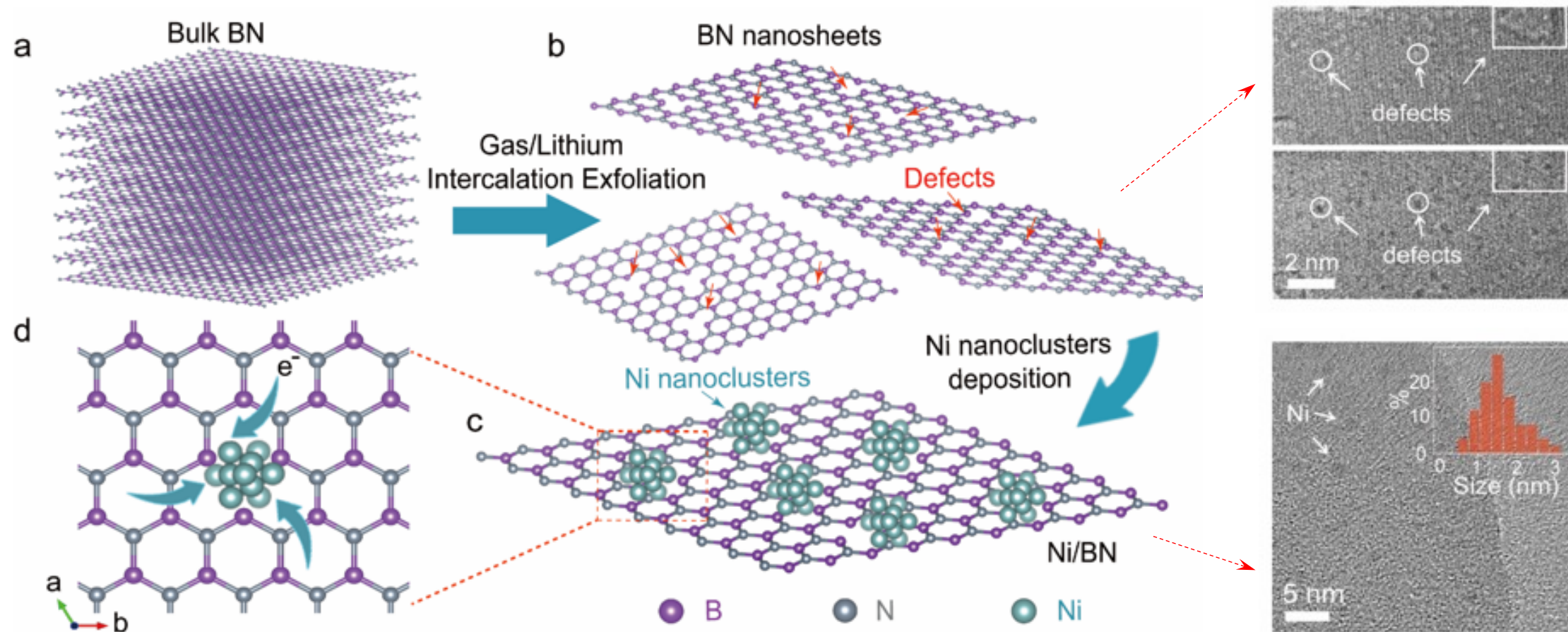
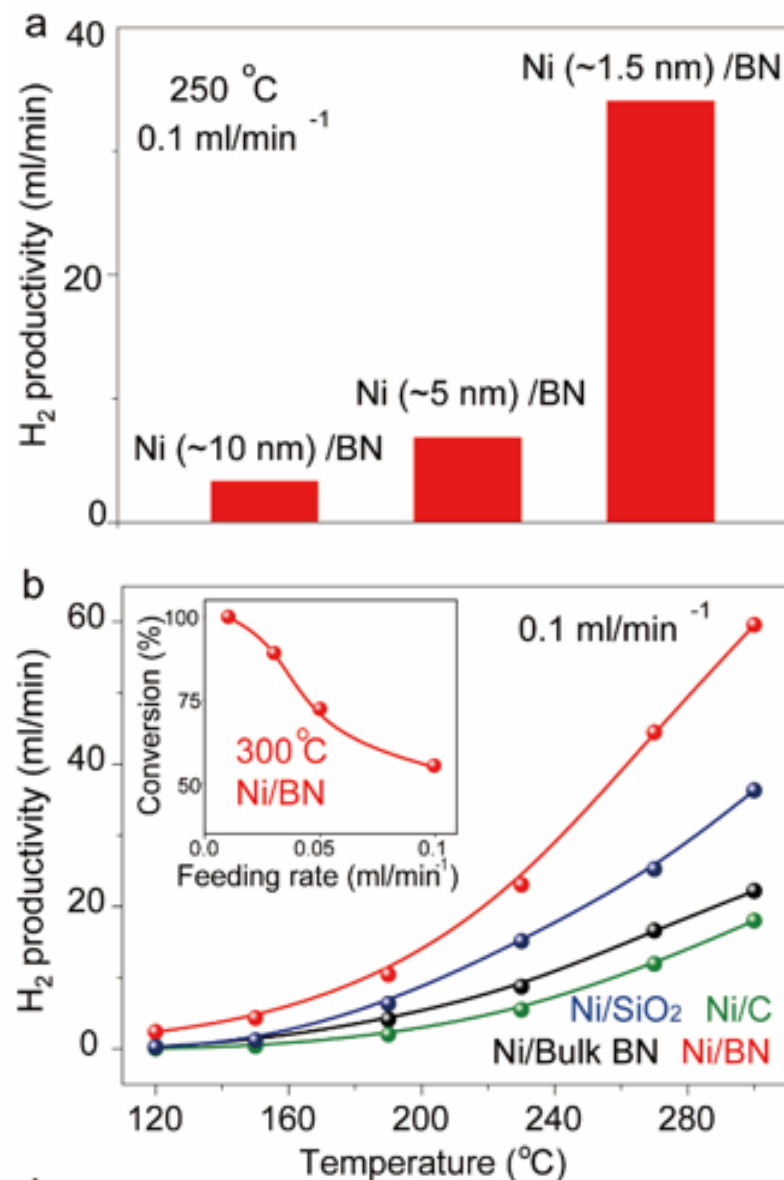


Figure. Schematic illustration of the formation of defective BN nanosheets and further deposition of Ni nanoclusters. The smaller nanoparticles (~1.5 nm) possess the capability of more localized electronic states for charge transfer. The defects help improve the binding energy of reactants at the surface of Ni nanoclusters, facilitating the catalytic reaction.

Zhuolei Zhang, Jeff Urban

Catalytic Performance



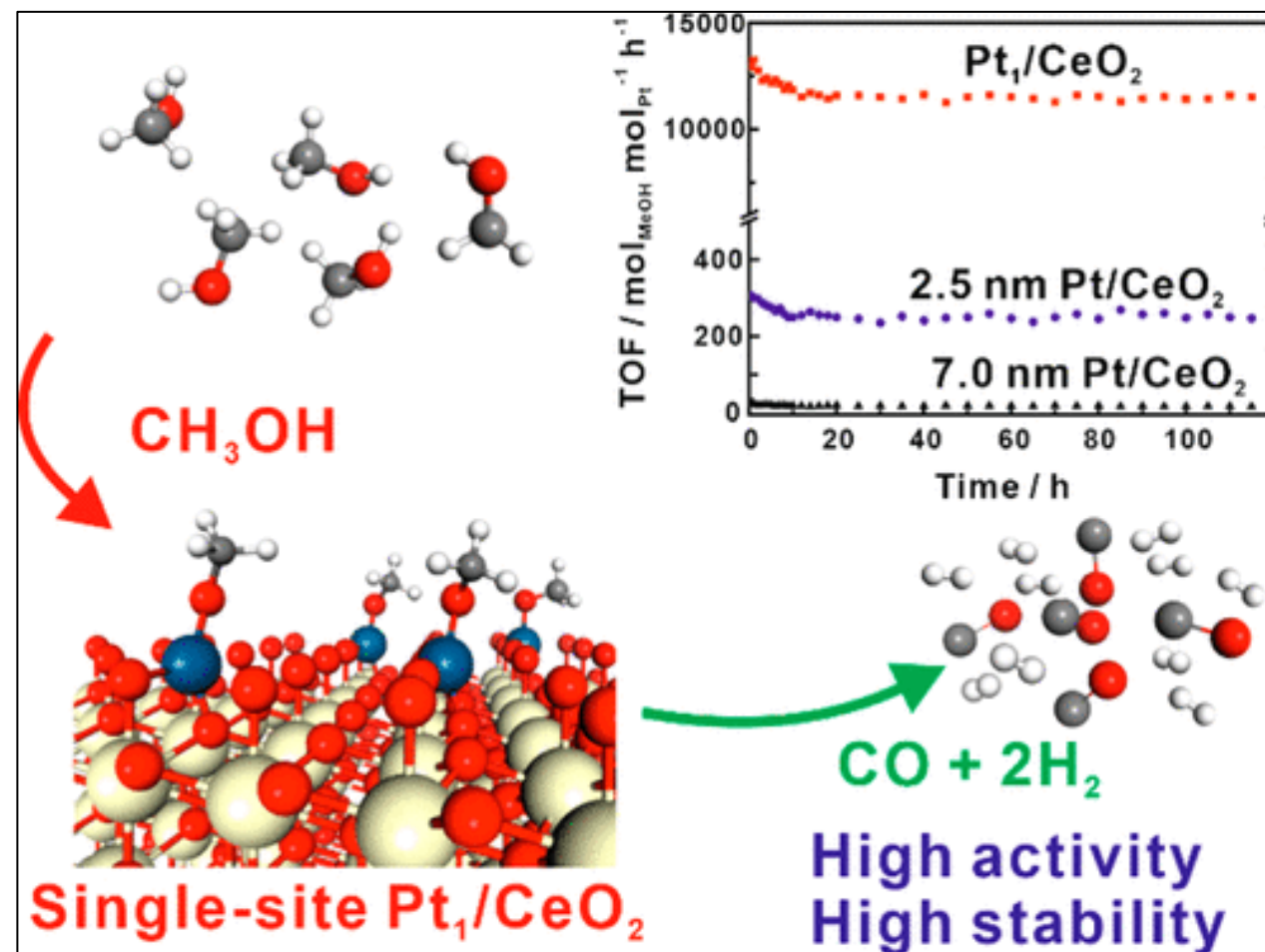
(c) Catalytic performance compared with that of some other catalysts.

Catalysts	WHSV (g CH ₃ OH g ⁻¹ catalysts h ⁻¹)	TOF (mol CH ₃ OH mol ⁻¹ metal h ⁻¹)
1.5 nm Ni/BN (This work)	23.8	237.6
Pt/CeO ₂ /Al ₂ O ₃	15.7	946.1
Pd/CeO ₂	1.0	123.4 (270 °C)
Rh/CeO ₂	1.0	95.3
Ni/UDD	1.3	31.9
Commercial Cu/Cr	2.1	9.5
Co/CeO ₂	1.5	13.8
Ni/N _{0.09} CF	15	73.4
Ni/N _{0.09} CF	45	131.1

Figure. (a) Hydrogen productivity of Ni/BN nanocomposite with various Ni nanocluster sizes. (b) Temperature-dependent hydrogen productivity of Ni nanoclusters on various substrates. (c) Catalytic performance compared with that of some other catalysts.

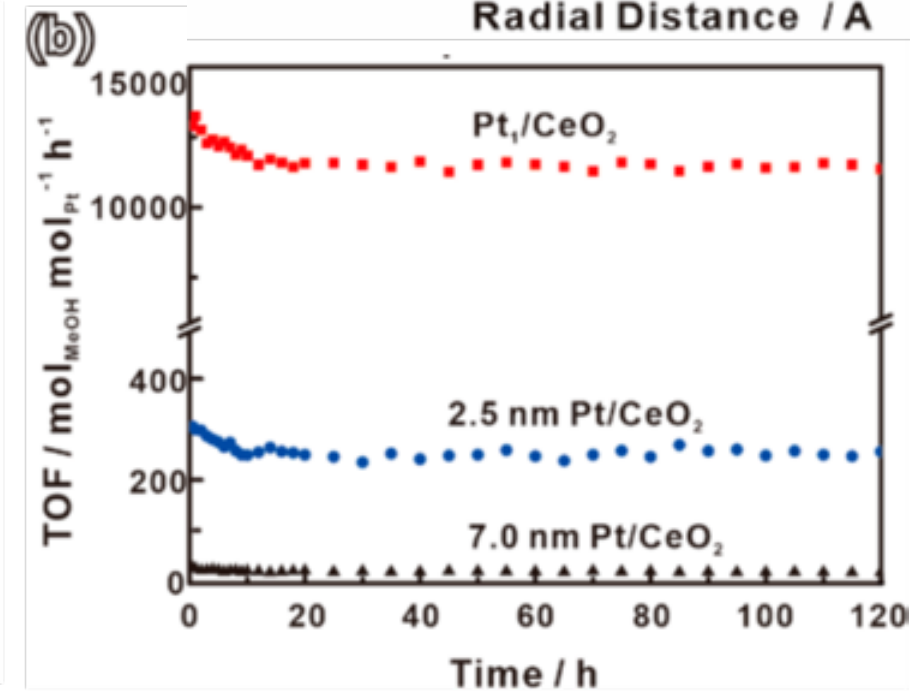
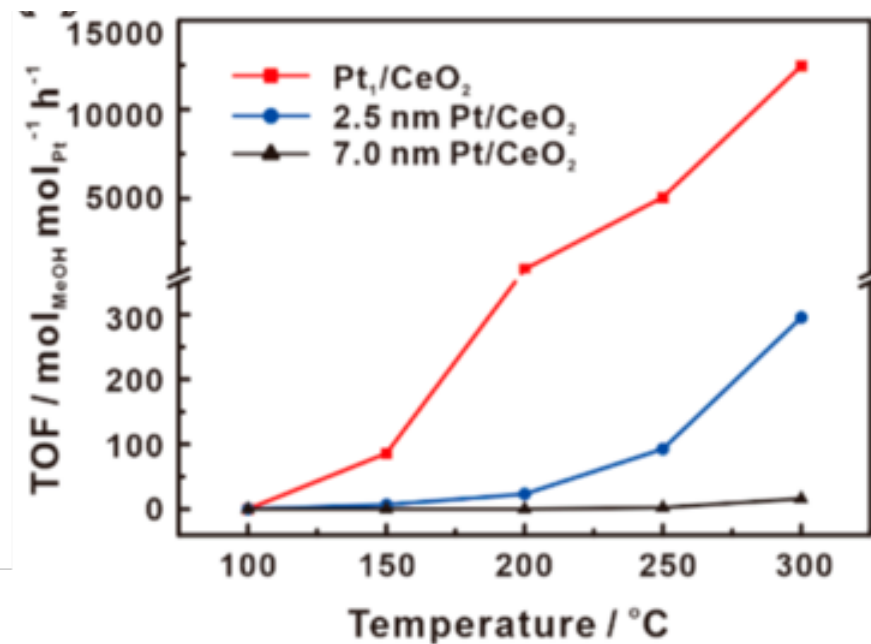
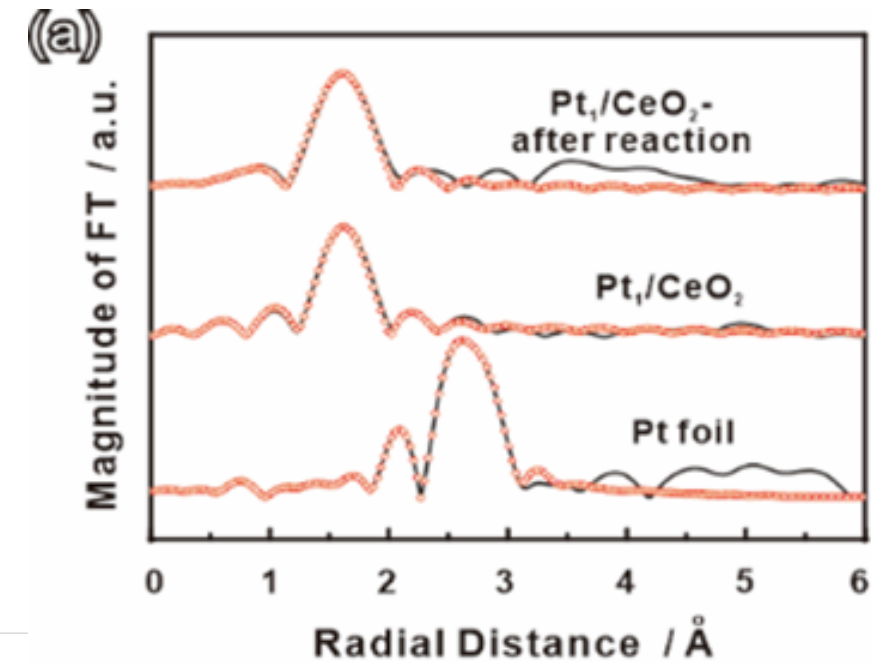
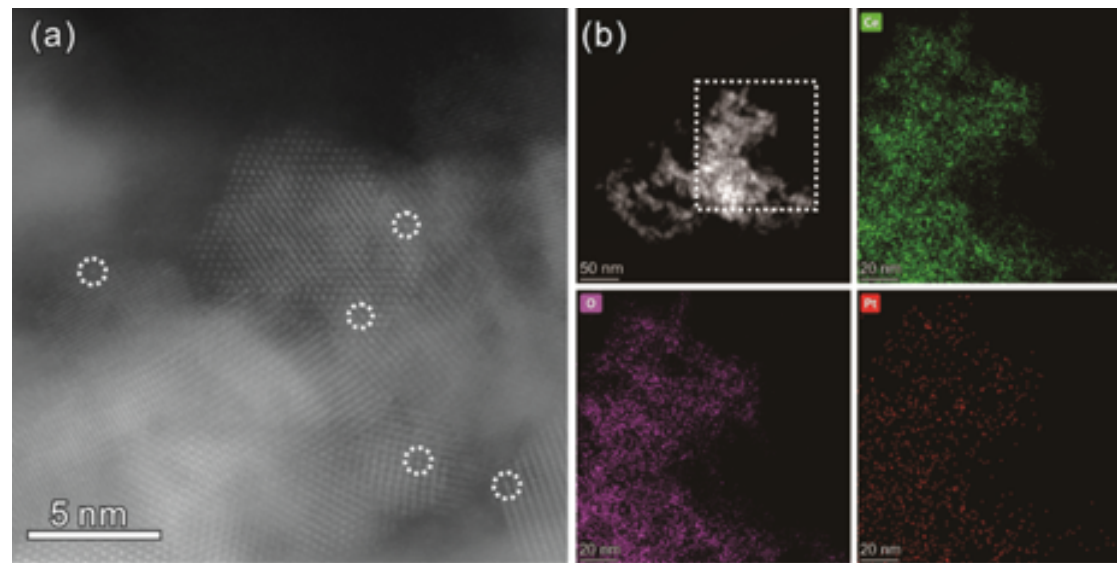
Task 3: Single-Site Catalyst for Efficient Hydrogen Generation with Alcohols

JACS 141, 17995 (2019)

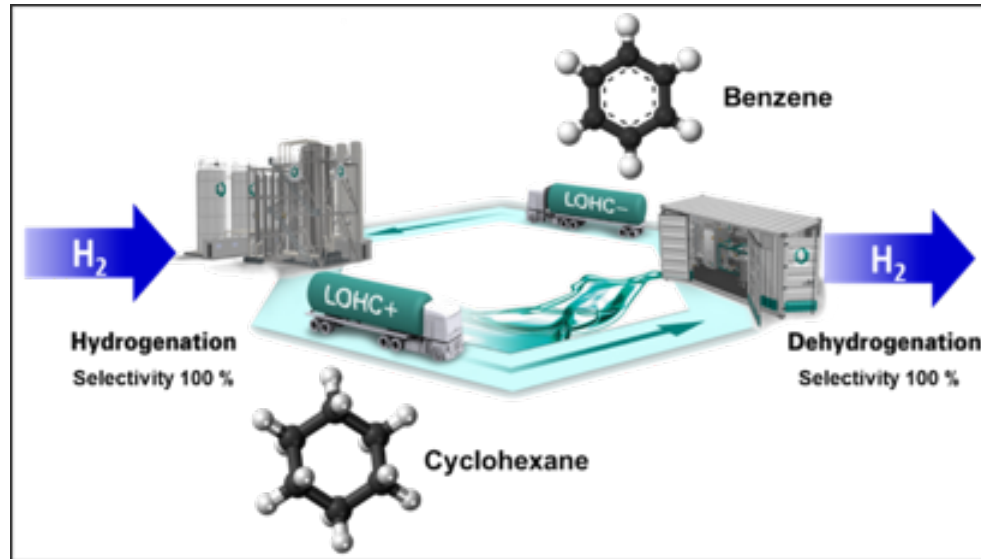


- In direct methanol dehydrogenation, the reaction rate of atomic Pt could reach **12000-14000 mol_{methanol}/mol_{pt}/hour**: **40 times** that of Pt nanoparticles of 2.5 nm diameter, and more than **800 times** that of 7nm Pt NPs.
- Furthermore, the atomic Pt catalyst has a high reaction stability (**120 hours**).

Single-Site Catalyst for Efficient Hydrogen Generation with Methanol



Reversible Hydrogen Generation/Storage Process Development: with Cyclohexane/Benzene and Single-Sites Catalyst (Pt_1/CeO_2)



- **Ji Su and Gabor Somorjai (MSD/LBNL):** Catalytic process development
- **Mark Allendorf and Vitalie Stavila (SNL):** Catalytic materials development
- **Yi-Sheng Liu and Jinghua Guo (ALS/LBNL):** XAS characterization
- **Pragya Verma, David Prendergast (TMF/LNBL):** DFT calculations
- **Tom Autrey (PNNL):** H_2 -carriers

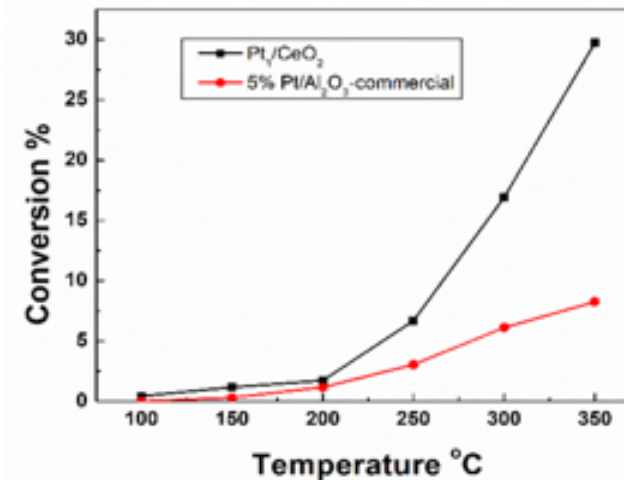
Single Pt sites catalyst VS Pt NPs

Reaction condition:

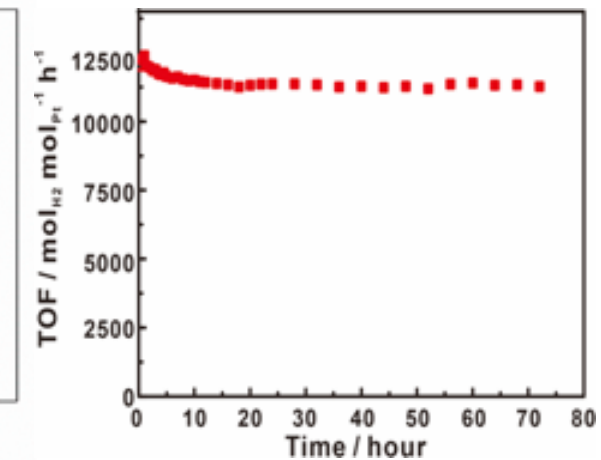
1 atm, 350°C, 100 mg catalysts;

Gas flow: N_2 30ml/min.

Cyclohexane Dehydrogenation



Single Site Catalyst Stability



Manuscript for Nature Catalysis

Target: produce 1 kg H₂/min from cyclohexane

Catalyst	Reaction conditions	Catalyst Required (for 1 kg H ₂ /min)	Pt loading
Pt ₁ /CeO ₂ (0.15 wt %)	Cyclohexane 0.05 ml/min Conversion: 29.7 %	121 kg	181.5 g
Pt ₁ /CeO ₂ (0.15 wt %)	Cyclohexane 0.02 ml/min Conversion: ~ 80 %	113 kg	169.5 g
Pt/Al ₂ O ₃	Cyclohexane 0.05 ml/min	434 kg	21700 g