HyMARC—PNNL Activities

P.I. – Tom Autrey

DOE Project award #68196

DOE Hydrogen Program

Annual Merit Review and Peer Evaluation Meeting

June 6-8, 2022

Project ID ST-204

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Goal

- What:
  - Accelerate the use of carriers for hydrogen storage & transport
- How:
  - Matching use cases to materials
  - Modelling engineering solutions
  - Developing materials and catalysts
- Why:
  - To enable carbon neutral carbon technologies, meeting national priorities for environmentally clean energy independence

Overview

Timeline and Budget

- Project Start Date: 10/1/2018
- FY21 DOE Funding: $1.25 M
- FY22 Planned DOE Funding: $0.65 M
- Total DOE Funds Received to Date: $5.75 M

Barriers

- System Weight and Volume
- Efficiency

Partners

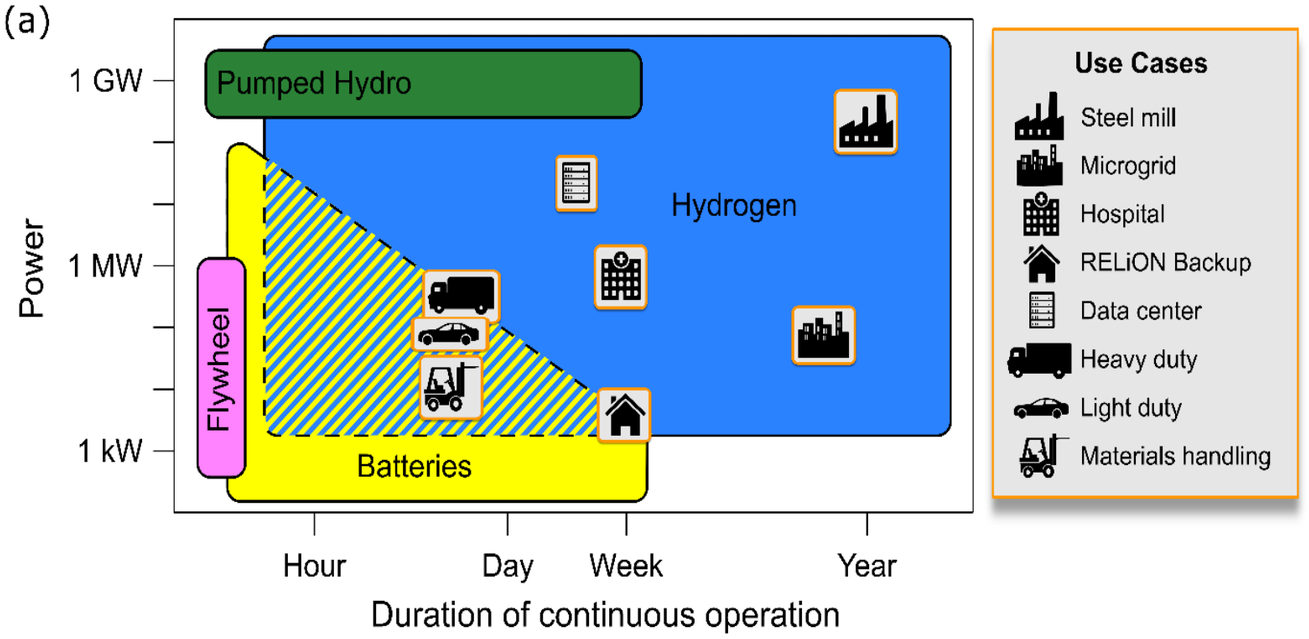
- National Renewable Energy Laboratory
- Sandia National Laboratory
- Lawrence Berkeley National Laboratory
- Lawrence Livermore National Laboratory
- University of Hawaii
- HyMARC Seedlings (U. Southern California, Montana State U., Washington State U.)
- Korean Institute of Science and Technology
- University of Geneva

Relevance

H_2 carriers are <u>scalable (MW to GW)</u> and have the potential to *store*, *transport* and *produce* usable hydrogen for applications beyond onboard storage

PNNL is working with DOE to address barriers and define properties that impede the widespread use of hydrogen as an energy carrier

- What use cases will benefit from solid and liquid carriers?
- What physiochemical properties of carriers are needed to fulfill applications?
- What is the footprint of the carrier system, and are known catalysts capable of providing a sufficient rate of H_2 release?



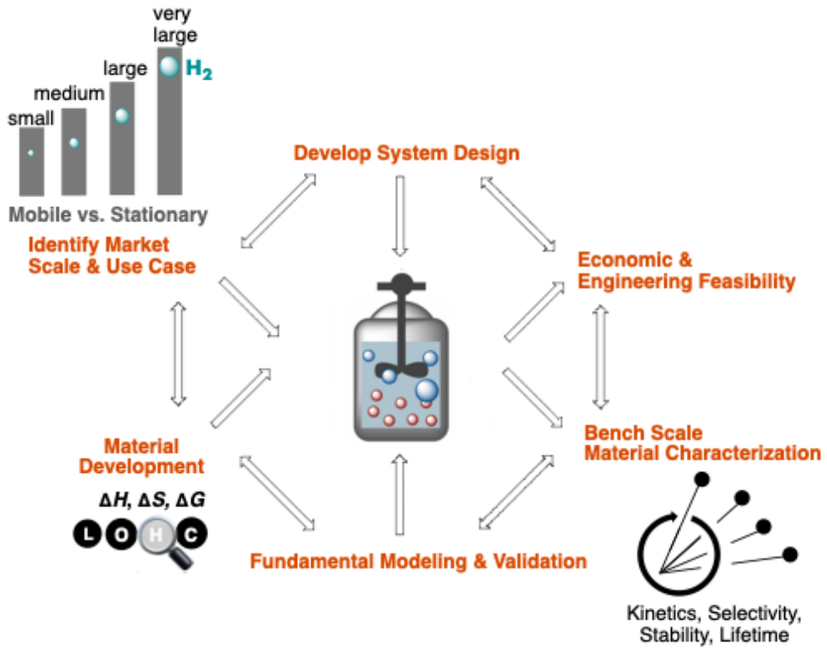
Hydrogen carriers provide versatile energy storage suited to large scales and long durations

Approach: meeting in the middle

To develop and understand carrier systems, we must consider:

- The properties of known materials
  - Thermodynamics
  - Kinetics
  - Physical properties
- The requirements for identified use cases
  - Power
  - Energy
  - Duration

This allows us to estimate system size, weight, and cost, and compare with incumbent technologies.



Milestones

- Demonstrate >10 cycles of hydrogen release and uptake from the formate/bicarbonate couple using a molecular catalyst
  - release 1.5 bar T < 80 C)
  - regeneration <35 bar < 50 C

Build a flow-through reactor to test performance and robustness of hydrogen carrier materials and catalysts. Demonstrate hydrogen release from a 5 M aqueous potassium formate solution in a continuous flow mode showing release of hydrogen (>95% pure) at temperatures < 80 °C for a period of at least 12 hours

Successful development requires consideration of materials properties, use cases, efficiency, and cost

Approach to evaluating materials and developing targets

- Forward Engineering Approach
  - Start with Material Properties
  - Stage-Gate Approach to Continued Evaluation
  - Base Acceptability of Chosen Material on Other Materials
  - Design System Based on Use Case
  - Compare to Incumbent Technology and 250 bar H_2 for developing targets
- Reverse Engineering Approach
  - Start with Use Case
  - Obtain Characteristics of Incumbent Technology and 250 bar H_2
  - Design System with Generic Material that falls within the range
  - Develop a range of acceptable material properties for developing targets

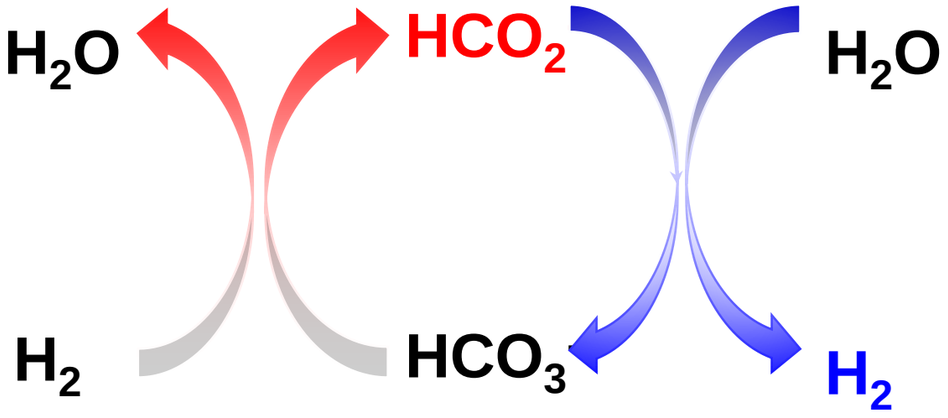
Two approaches should overlap and provide self consistency

Milestones

- Demonstrate >10 cycles of hydrogen release and uptake from the formate/bicarbonate couple using a molecular catalyst
  - release 1.5 bar T < 80 C)
  - regeneration <35 bar < 50 C

- Build a flow-through reactor to test performance and robustness of hydrogen carrier materials and catalysts.
- Demonstrate hydrogen release from a 5 M aqueous potassium formate solution in a continuous flow mode showing release of hydrogen for a period of at least 12 hours
  - >95% purity
  - Temperature < 80 °C

The formate/bicarbonate cycle for use as a hydrogen carrier

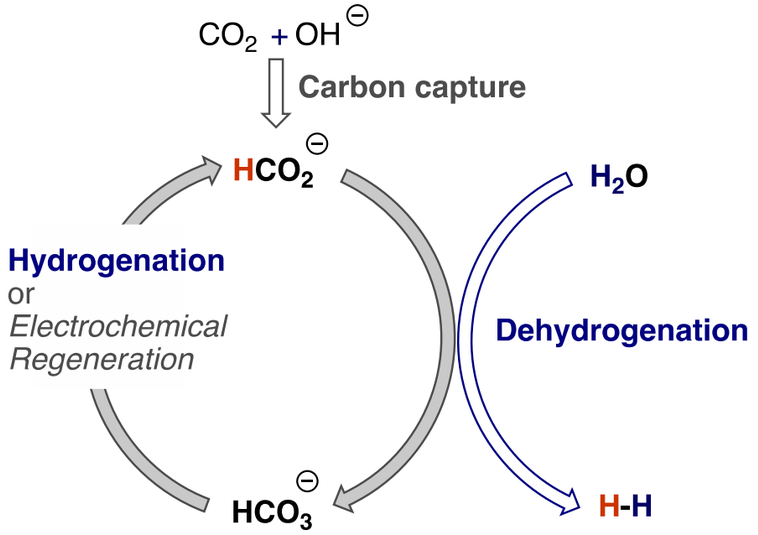


Current status is 70% toward completion of these milestones

Accomplishment: Multiple cycles of formate/bicarbonate

Catalysis Milestones Achieved

- H_2 release under isobaric, isochoric at T < 80 ºC
- H_2 uptake at < 35 bar H_2 and T < 50 ºC
- 10+ cycles of H_2 dehydrogenation, hydrogenation



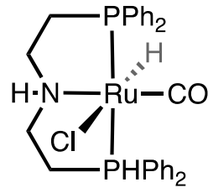
Formate-Bicarbonate Cycle

single molecular catalyst

Ru-MACHO

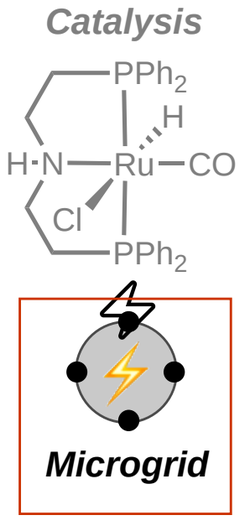
$KHCO_2 + H_2O \rightleftharpoons KHCO_3 + H_2$

Catalysis

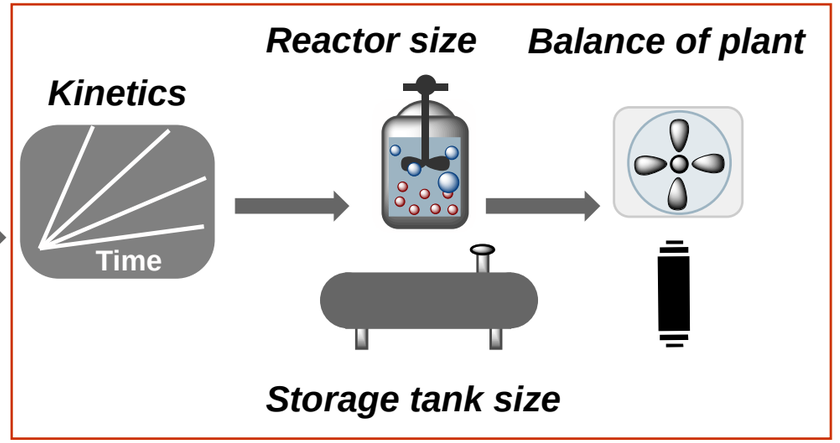


Ru-MACHO

Catalysis



Future Focus



Next Steps

- Measured variable-temperature dehydrogenation kinetic data for process modeling of reactor, storage tanks size, and infrastructure cost of $KHCO_2$/$KHCO_3$ as H_2 carrier system
- Explore end use scenarios for employing batch vs flow reactor for hydrogenation
- Use theory and experimental data to identify mechanism, reaction order, and catalyst deactivation

Homogeneous catalyst mixed with carrier simplifies engineering

Accomplishment: Improved performance with catalyst control

Hydrogenation of $KHCO_3$

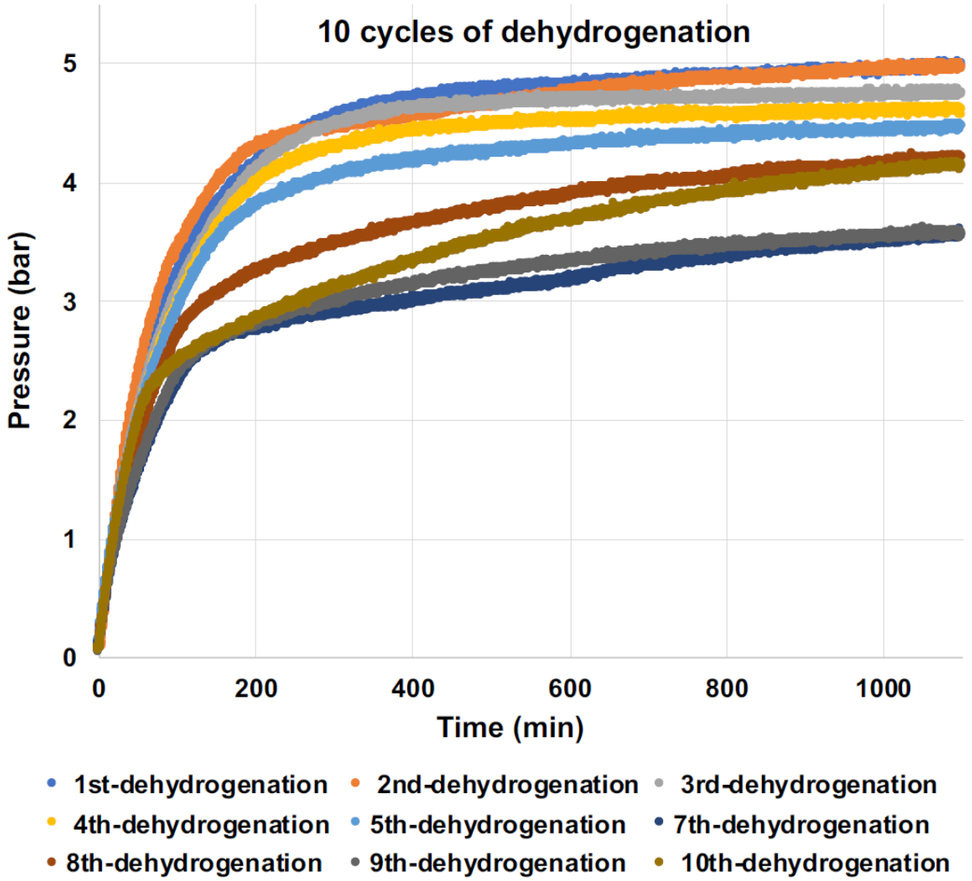
Entry	Rxn mix	Conditions	Formate Yield (%)
1	2.5 mL 6M $KHCO_3$ + 0.5 g dioxane	25°C, 42 bar	0.4
2	2.5 mL 6M $KHCO_3$ + 0.5 g dioxane	50°C, 42 bar	6.6
3	2.5 mL 6M $KHCO_3$ + 0.5 g dioxane	70°C, 42 bar	41.0
4	2.5 mL 6M $KHCO_3$ + 2 g dioxane	50°C, 42 bar	90.6
5	2.5 mL 6M $KHCO_3$ + 2 g toluene	50°C, 42 bar	6.8
6	2.5 mL 6M $KHCO_3$ + 0.5 g dioxane + 30 mg PTC	50°C, 42 bar	41.6
7	2.5 mL 6M $KHCO_3$ + 2 g toluene + 30 mg PTC	50°C, 42 bar	84.0

PTC = phase transfer catalyst

Dehydrogenation of $KHCO_2$

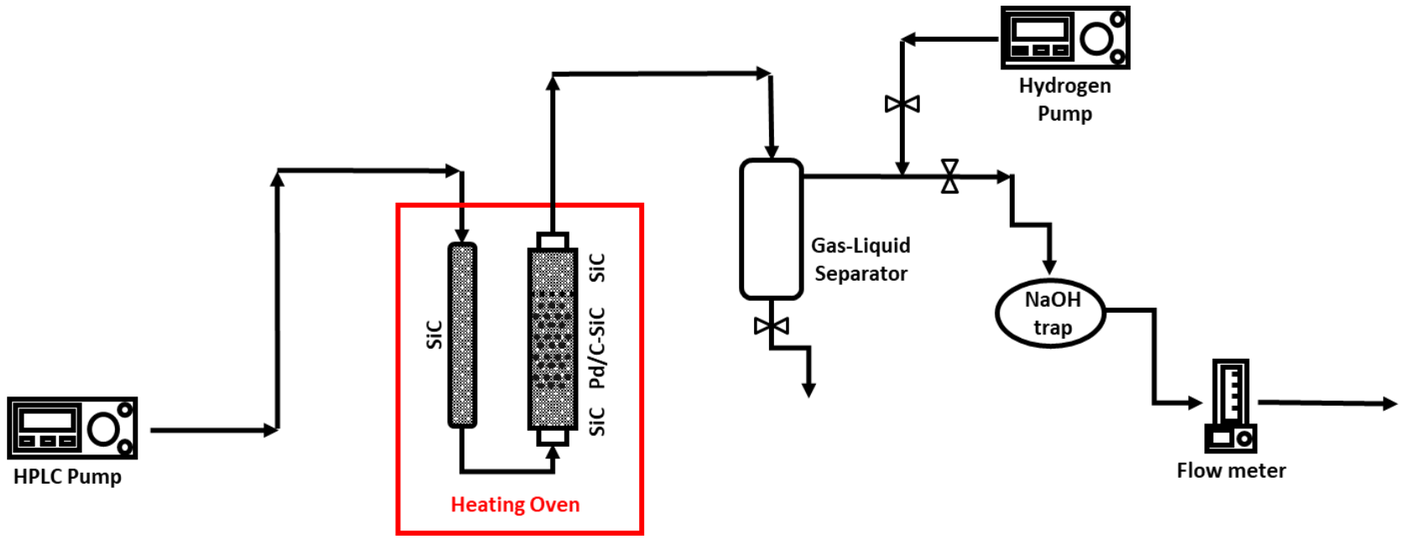
Entry	Rxn mix	Conditions	Bicarbonate Yield (%)	CO_2 (%)
1	2.5 mL 6M $KHCO_2$ + 0.5 g dioxane	70°C, isochoric	1.5	-
2	2.5 mL 6M $KHCO_2$ + 2 g dioxane	70°C, isochoric	62.7	3.5
3	2.5 mL 6 M $KHCO_2$ (5:1 H_2O: dioxane)	70°C, 24 h isobaric	99%	-

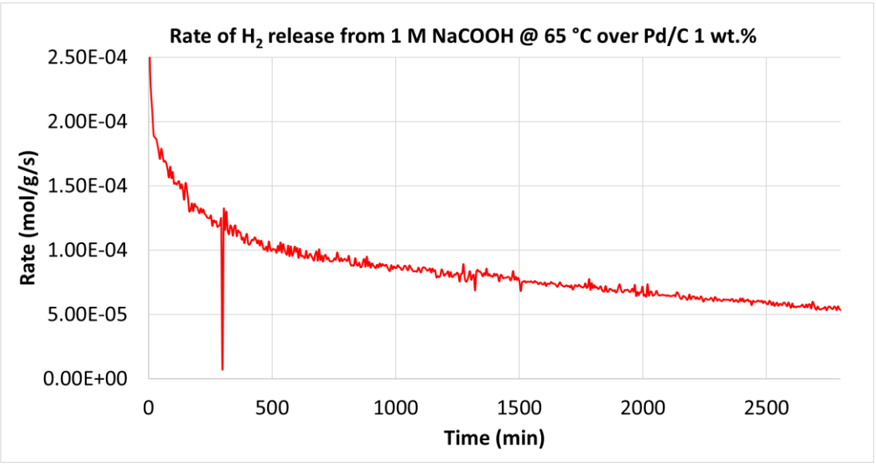
- After 4+ cycles, the dehydrogenation rate started to decrease.
- Addition of a phase transfer catalyst (PTC) improved the rate of hydrogenation and dehydrogenation.



Demonstrated 10+ cycles of H_2 release and uptake from $KHCO_2$/$KHCO_3$

Accomplishments: Construction of a Flow-Through Reactor

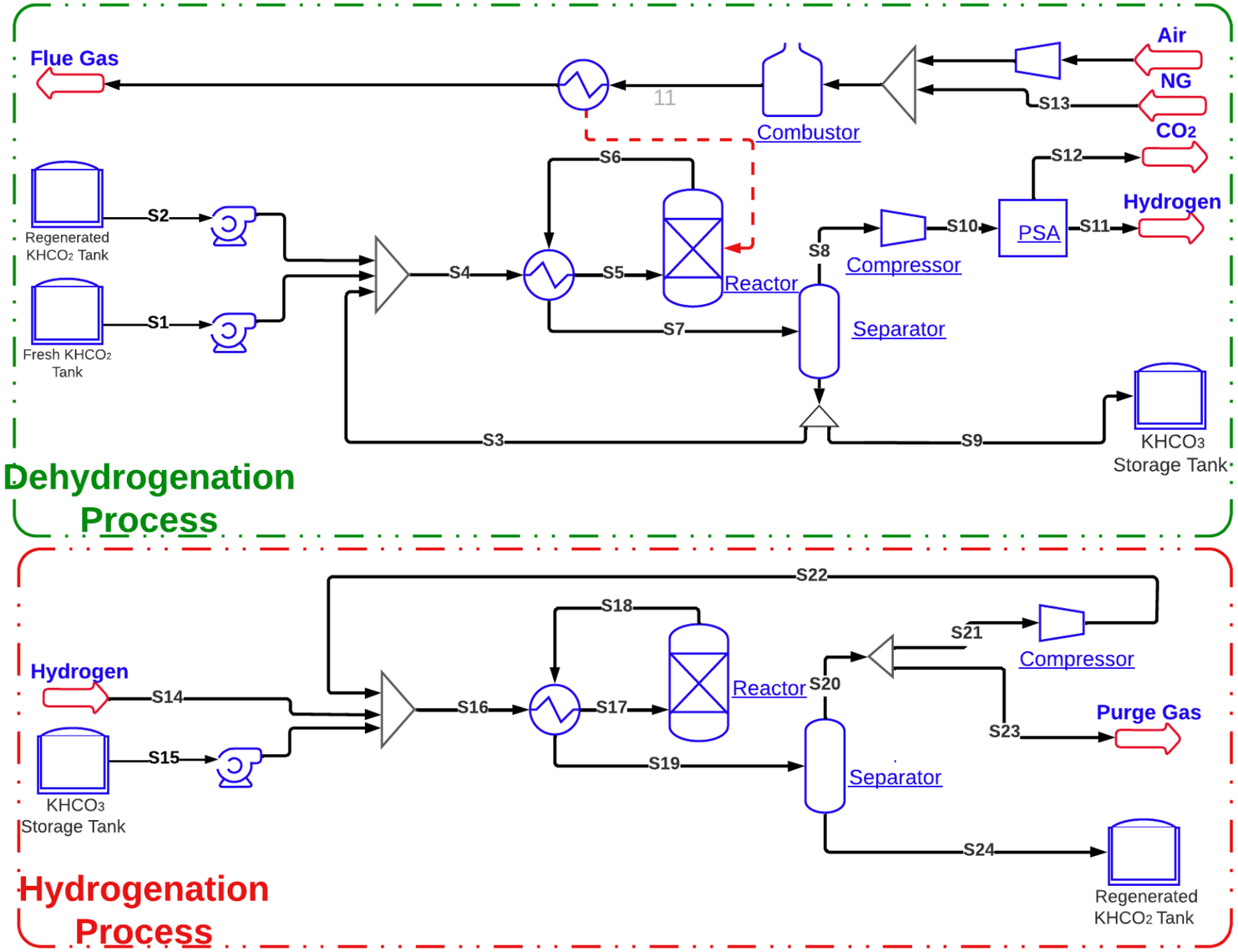




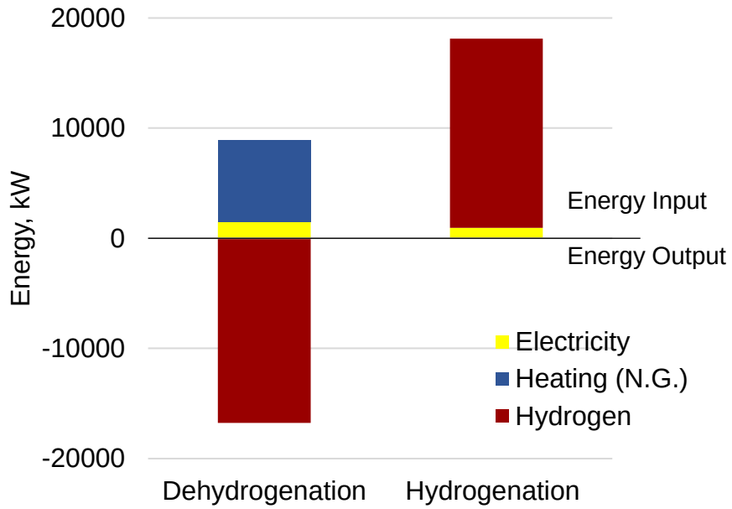
- The system allows for continuous dehydrogenation of aqueous formate salts
  - System is highly modular, which allows for easy exchange of:
    - ✓ Catalyst
    - ✓ Feed
    - ✓ Temperature
    - ✓ Size of the column

Provides first crucial step to scaling up of carrier systems, assisting seedling projects in catalyst testing

Accomplishments: Analysis of potassium formate as a carrier



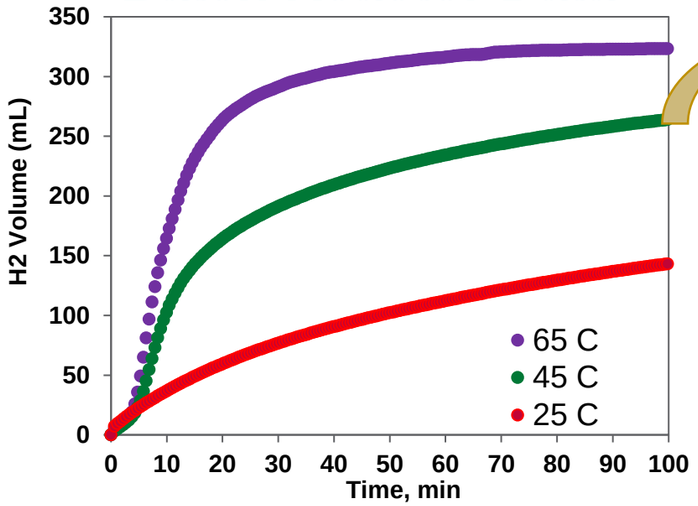
- The system capacity is *500 kg/hr hydrogen* for providing *10MW electricity*.
- The overall *energy efficiency* is *62%* based on reaction equilibrium data.
- The *heating duty* for dehydrogenation part counts for *28%* of the energy input, if we can utilize the waste heat from the fuel cell and *energy efficiency* can potentially increase up to *90%*.
- *Fresh formate* can be potentially *reduced* in the cycles if the CO_2 can be *stored* in the *dehydrogenation and utilized* in the *hydrogenation*.



Utilizing the waste heat from fuel cell can boost the energy efficiency to 90%.

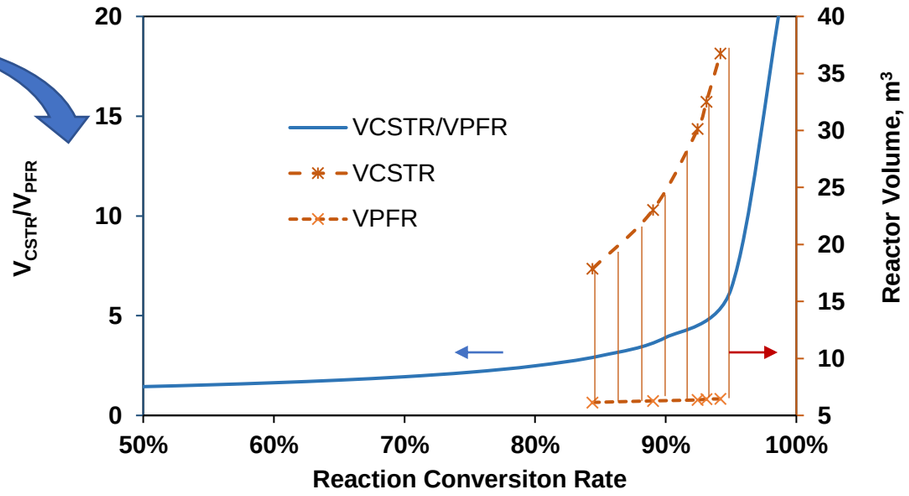
Accomplishments: Analysis of potassium formate as a carrier

Batch Reactor Data

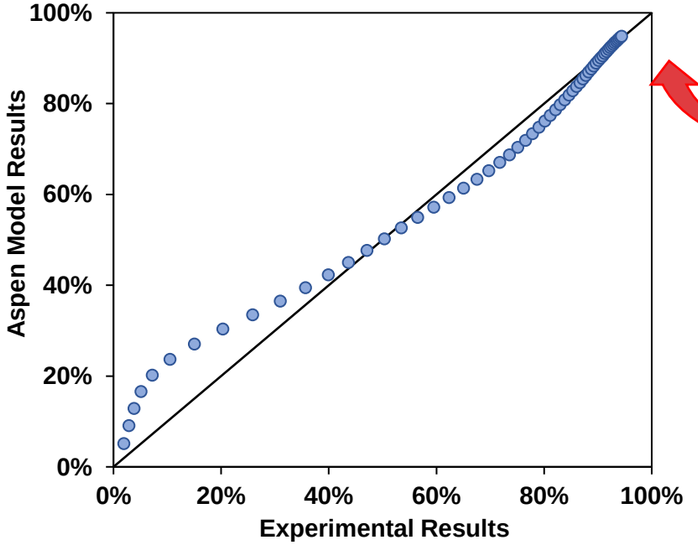


Kinetics Model Development

- first order model is built based on the batch reactor experimental data
- $r = Ae^{\frac{-Ea}{RT}} C_{f0}$
- $\mathrm{Ea} = 54\ \mathrm{kJ/mol}$
- A = 12,400 L/s
- Assuming 3wt% Pd/C



Aspen Model Results

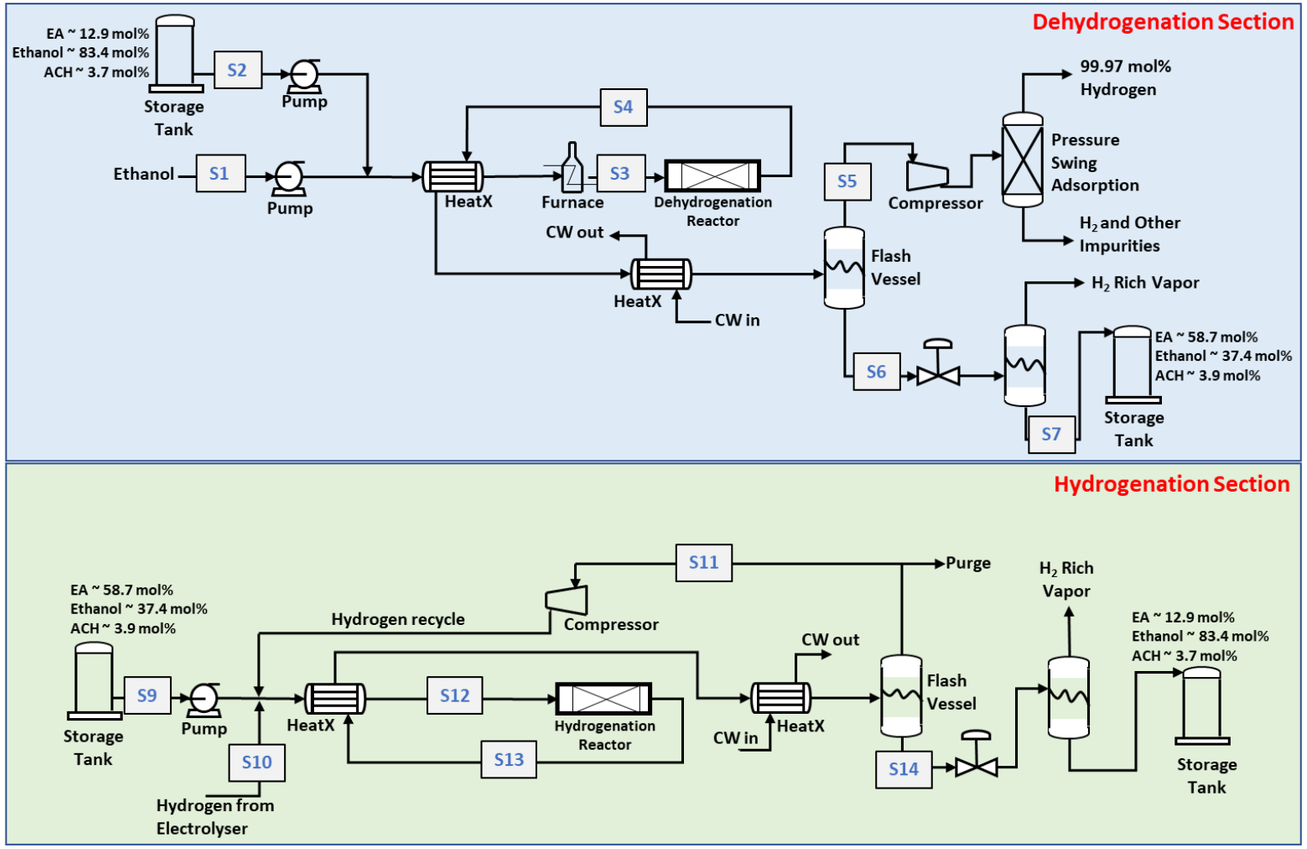


Progress

- Dehydrogenation reaction behaves as a first order reaction based on the batch experimental data with Pd/C catalyst.
- The *500 kg/hr hydrogen* production capacity requires dehydrogenation reactor size ranging from *6 – 37 m³* depending on the reactor types, overall conversion rate, et al.

Kinetics study indicates dehydrogenation reactor sizes ranging from 24-148 L/mol H_2.

Accomplishments: Analysis of ethanol as a carrier

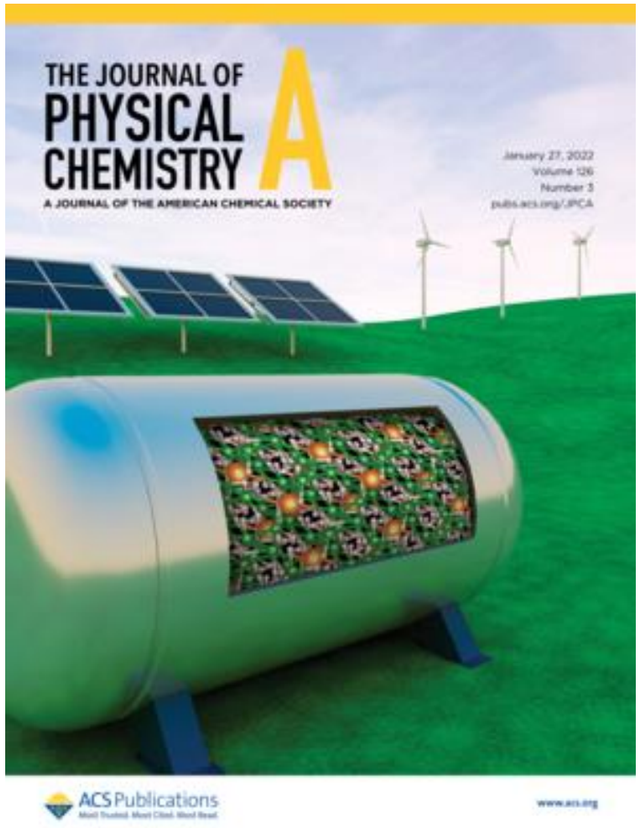


Energy Input	kWh
Electricity (Elec)	433
Pumps and Compressors	378
Cooling Water Circulation	55
Make-up ethanol	6460
Natural Gas (NG)	3,442
Dehydrogenation Feed Heat	2,126
Dehydrogenation Reactor	1,316
Hydrogen (H_2, LHV)	20,903
Energy Output	kWh
Hydrogen (99.97 mol%, LHV)	16,691
Purge Streams (PS, LHV)	15,427
Dehydrogenation Section	11,070
Hydrogenation Section	4,357
Energy Efficiency	88 %

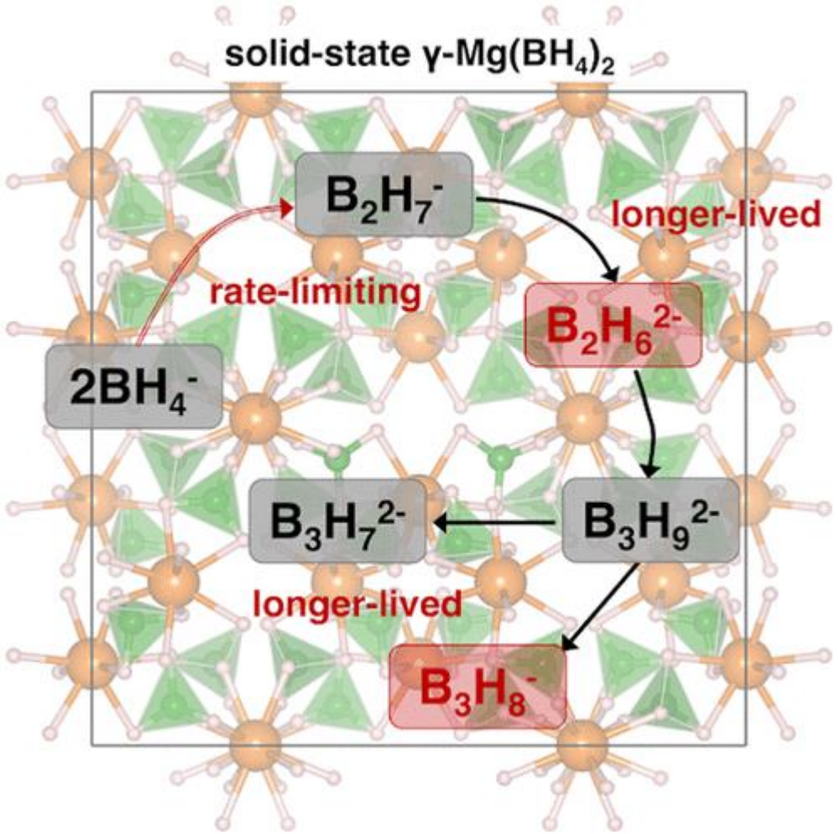
- Previous work showed that ethanol could supply a small neighborhood microgrid, but liquid phase dehydrogenation consumed more energy than the energy content of the H_2 released (doi.org/10.1021/acssuschemeng.1c01513)
- An Aspen model for both dehydrogenation and hydrogenation shows greatly improved energy efficiency

Gas-phase cycling of ethanol ⇌ ethyl acetate improves energy efficiency to 88%.

Accomplishments: Understanding $B_3H_8^-$ formation & stability



Analysis of Intermediates and Products from the Dehydrogenation of $Mg(BH_4)_2$. Iffat H. Nayyar, Bojana Ginovska, Mark Bowden, Gary Edvenson, Ba Tran, and Tom Autrey. The Journal of Physical Chemistry A 2022 126 (3), 444-452
DOI: 10.1021/acs.jpca.1c09690

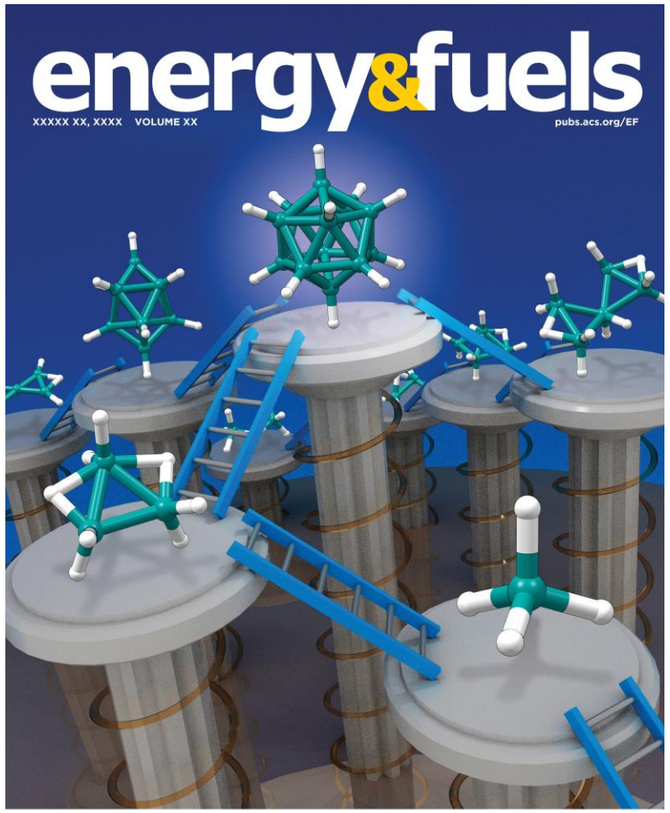


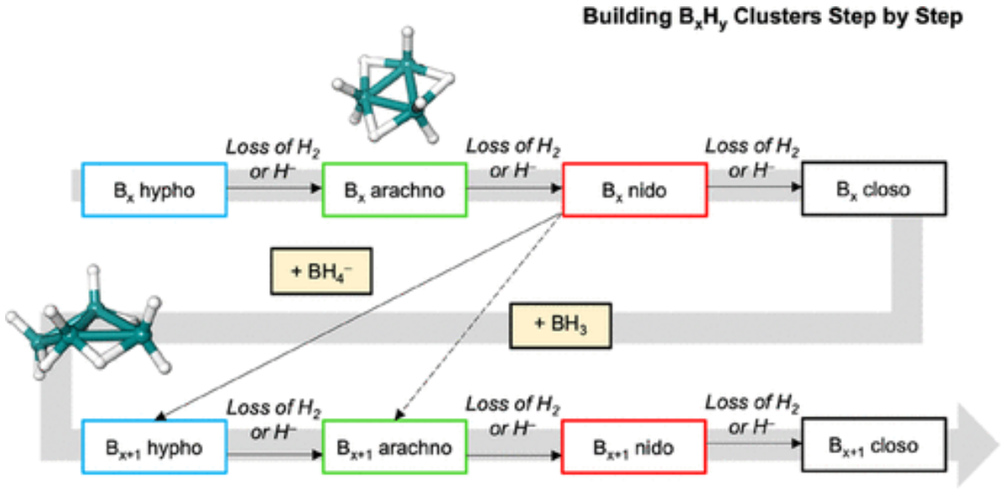
First-Principles Elucidation of Initial Dehydrogenation Pathways in $Mg(BH_4)_2$. Liwen F. Wan, Tom Autrey, and Brandon C. Wood. J. Phys. Chem. Lett. 2022, 13, 8, 1908–1913

- Literature theory predicts that $Mg(B_3H_8)_2$ is unstable
  - Nayyar *et al*… Disordered Mg-H-B_3H_8 is more stable than crystalline compounds, making it a feasible intermediate in the decomposition of $Mg(BH_4)_2$.
  - Wan *et al*… $B_3H_8^-$ is a key metastable intermediate embedded in the $Mg–BH_4–Mg$ matrix with a high activation energy for further reaction

$B_3H_8^-$ has at least two forms: an unstable $Mg(B_3H_8)_2$ compound and metastable $B_3H_8^-$ formed *in situ*.

Accomplishments: Understanding $Mg(BH_4)_2$ decomposition





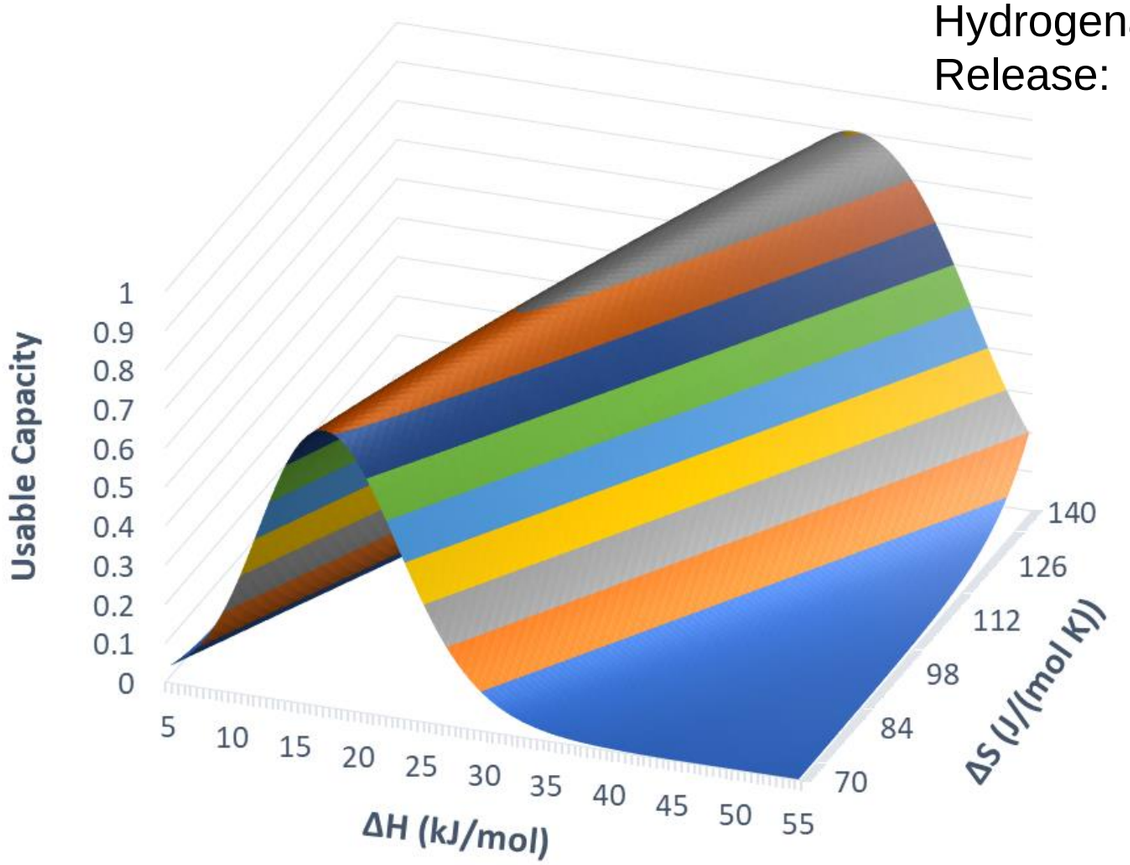
Exploring Detailed Reaction Pathways for Hydrogen Storage with Borohydrides Using DFT Calculations. Samantha I. Johnson, Jonathan M. DeMaria, Bojana Ginovska, Gary M. Edvenson, Hans Hagemann, and S. Tom Autrey. *Energy & Fuels* **2022** (in press)

- Developed a universal pathway explaining key intermediates observed during H_2 release from $Mg(BH_4)_2$
  - Anions up to $B_6H_x^-$ are formed from sequential condensation pathway
  - Larger clusters are formed from dimerization which becomes more energetically favorable

DFT calculations unravel complex mechanism for hydrogen release from $Mg(BH_4)_2$.

Accomplishments: Calculation of ideal thermodynamics

Hydrogenation: 25 °C, 30 bar H_2
Release: 125 °C, 5 bar



- The ideal Gibbs free energy can be calculated for proposed temperatures and pressures for uptake and release
  - Combinations of ΔH and ΔS can be used to obtain the ideal ΔG
- We have extended this analysis to calculate thermodynamic values when the uptake and release temperatures are <u>different</u>

The usable capacity (fraction of theoretical) is the difference between the equilibrium compositions at release and hydrogenation conditions

Targets optimum thermodynamic properties for practical uptake and release.

Collaborations

- National Renewable Energy Laboratory
  - Thermal decomposition and thermogravimetric measurements
- Lawrence Livermore National Laboratory
  - Theoretical calculations of solid-state materials and interfaces
- Lawrence Berkeley National Laboratory, Argonne National Laboratory
  - Technoeconomic analysis, life cycle assessment
- Sandia National Laboratory
  - Chemistry of novel Mg-B compounds
- University of Hawaii
  - Borohydride chemistry
- Washington State University
  - Heterogeneous catalysts for formate hydrogenation/dehydrogenation
- University of Southern California
  - Homogeneous formic acid catalysts
- University of Rostock, Germany
  - Process energy analysis
- University of Geneva, Switzerland
  - Borohydride chemistry

Remaining challenges and barriers

- Improving heterogeneous catalyst stability for formate dehydrogenation
- Increasing delivered H_2 purity
  - Removal of CO_2 from formate dehydrogenation
  - Capture of volatiles in organic carrier systems
- Establish boundary conditions for comparing life cycle assessment across a wide range of carriers
- Developing cost-effective carrier processes with more than a single outcome or purpose
- Bridging gap between laboratory and large-scale applications

Proposed future work

- In Phase 3 of HyMARC consortium:
  - Obtain data to support prototype demonstrations of H_2 carriers
  - Develop continuous flow-through hydrogenation reactor
    - Demonstrate multiple cycles of reversible hydrogen release and uptake in a continuous process
  - Improve catalyst stability for formate dehydrogenation
  - Investigation of ancillary benefits of different hydrogen carriers
  - TEA and LCA for formate system, supplying a 10 MW use case
  - Investigate solutions for stranded energy applications
    - Understand bottlenecks and challenges

Proposed future work is subject to change based on funding levels

Summary

- Demonstrated multiple cycles of hydrogen release and uptake in aqueous formate/bicarbonate (batch reactor)
- Constructed continuous flow reactor for long-term studies of carrier systems
  - Demonstrated continuous release of hydrogen from aqueous formate for 5 days
- Resolved experiment/theory discrepancy over $B_3H_8^-$ stability during $Mg(BH_4)_2$ dehydrogenation
  - Identified initial steps of H_2 release from $Mg(BH_4)_2$ using advanced theoretical approach
- Used process engineering to improve energy efficiency of ethanol/ethyl acetate cycle to 88%
  - Use of gas phase reactor avoids wasteful refluxing
- Completed investigations of $Mg(BH_4)_2$ dehydrogenation
  - Six peer-reviewed papers published in 2021-22

Presentations

Presentations

- Mark Bowden and Tom Autrey. "HyMARC Consortium: System Properties and Materials for Hydrogen Storage." Presented by M. Bowden at U.S. – Turkey Hydrogen Energy & Fuel Cell Technologies Forum, June 16, 2021
- Mark Bowden, Ba Tran, Kriston Brooks and Tom Autrey. "A Rational Strategy for Linking the Properties of Hydrogen Carriers with the Needs of Energy Storage Use Cases." Presented by M. Bowden at MRS 2020 Fall virtual meeting, Online Conference, United States, December 6 2021
- Tom Autrey “Energy storage at scale – hydrogen carriers are the superheroes”. Presented by Tom Autrey at PacificChem Symposium Hydrogen-Rich Systems: Materials Chemistry for Energy Storage and Delivery, Online Conference, Dec 20 2021
- Mark Bowden, Ba Tran, Noemi Leick, Tamara Allen, Craig Jensen and Tom Autrey. “The Effect of Glyme Additives on $Mg(BH_4)_2$ Dehydrogenation” Presented by M. Bowden at PacificChem Symposium Hydrogen-Rich Systems: Materials Chemistry for Energy Storage and Delivery, Online Conference, Dec 20 2021
- Ba Tran. “Long duration energy storage at scale – hydrogen carriers for all seasons”. Presented by Ba Tran at the ACS National Meeting Spring 2022, San Diego, March 23, 2022
- Kriston Brooks, Tom Autrey, Ba Tran and Mark Bowden. “Development of Application-Based Technical Targets for Hydrogen Carriers”. Presented by K. Brooks at the ACS National Meeting Spring 2022, San Diego, March 23, 2022

Publications

1. Samantha I. Johnson, Jon DeMaria1, Bojana Ginovska, Gary M. Edvenson, Hans Hagemann, Tom Autrey. *Exploring detailed reaction pathways for hydrogen storage with borohydrides using DFT calculations*. (in press) Energy and Fuels. **2022** doi: /10.1021/acs.energyfuels.2c00331
2. Liwen Wan, Tom Autrey, Brandon Wood. *First-principles elucidation of initial dehydrogenation pathways in Mg(BH4)2*. The Journal of Physical Chemistry Letters. **2022** https://doi.org/10.1021/acs.jpclett.2c00112
3. Iffat H. Nayyar, Bojana Ginovska, Mark Bowden, Andrew Lipton, Angelina Gigante, Hans Hagemann, Craig Jensen and Tom Autrey. *An experimental and computational study of the thermodynamically unstable Mg(B3H8)2 intermediate formed during release of H2 from Mg(BH4)2*. J. Phys Chem A. **2022** doi.org/10.1021/acs.jpca.1c09690
4. Mark D. Allendorf, Jonathon Snider, Vitalie Stavila, Matthew Witman, Tom Autrey, Ba Tran, Mark Bowden, Kriston Brooks. *The Chemical Goldilocks Challenges for Transport and Storage of Hydrogen.* Invited perspective. in review. Nature Chemistry, **2022**. NCHEM-20102341A.
5. Peng Peng, Aikaterini Anastasopoulou, Kriston Brooks, Hiroyasu Furukawa, Mark Bowden, Jeffrey Long, Thomas Autrey, Hanna Breunig. *Techno-Economic Analysis of Hydrogen Storage using Metal-Organic Frameworks for Data Center Backup Power*. in press Nature Energy, **2022.** NENERGY-21061107A.
6. Ba L. Tran, Samantha I. Johnson, Kriston Brooks, Tom Autrey. *Ethanol as a Liquid Organic Hydrogen Carrier for Seasonal Microgrid Application: Catalysis, Theory, and Engineering Feasibility*. ACS Sustainable Chem. Eng **2021**. doi.org/10.1021/acssuschemeng.1c01513.
7. Ba L. Tran, Tamara N. Allen, Mark E. Bowden, Tom Autrey, Craig M. Jensen. *Effects of Glymes on the Distribution of $Mg(B_{10}H_{10})$ and $Mg(B_{12}H_{12})$ from the Thermolysis of $Mg(BH_4)_2$. Invited. Inorganics **2021**, 9, (6):41. DOI: 10.3390/inorganics9060041*.
8. Angelina Gigante, Noemi Leick, Andrew S. Lipton, Ba Tran, Nicholas Strange, Madison Martinez, Romain Moury, Thomas Gennett, Hans Hagemann, Tom Autrey. *Thermal conversion of unsolvated $Mg(B_3H_8)_2$ to BH_4^- in the presence of MgH_2*. ACS Applied Energy Materials. *DOI: 10.1021/acsaem.1c00159* **2021**
9. Robert T. Bell, Nicholas A. Strange, Noemi Leick, Vitalie Stavila, Mark Bowden, Tom Autrey, Thomas Gennett. *$Mg(BH_4)_2$ Based Hybrid Metal-Organic Borohydride System Exhibiting Enhanced Chemical Stability in Melt*. ACS Applied Energy Materials. doi.org/10.1021/acsaem.0c02861 **2021**

- Mevawala, Chirag; Brooks, Kriston; Bowden, Mark; Tran, Ba; Gutiérrez, Oliver; Autrey, S. Tom; Müller, Karsten, Hanna Breunig. *The ethanol - ethyl acetate system as a biogenic hydrogen carrier*. Submitted to ACS Sustainable Chemistry & Engineering
- Noemi Leick, Ba L. Tran, Mark E. Bowden, Thomas Gennett, Tom Autrey. *Thermodynamic studies on the mixtures of $Mg(BH_4)_2$ and glymes.* Accepted for publication in Dalton Transactions (2022)
- Erika Michela Dematteis, Mads B. Amdisen, Tom Autrey, Jussara Barale, Mark E. Bowden, Craig E. Buckley, Young Whan Cho, Stefano Deledda, Martin Dornheim, Petra de Jongh, Jakob B. Grinderslev, Valerio Gulino, Bjørn C. Hauback, Michael Heere, Tae Wook Heo, Terry D. Humphries, Torben R. Jensen, Shin Young Kang, Young-Su Lee, Hai-Wen Li, Sichi Li, Kasper T. Møller, Peter Ngene, Shin-ichi Orimo, Mark Paskevicius, Marek Polanski, Shigeyuki Takagi, Liwen Wan, Brandon Wood, Michael Hirscher, Marcello Baricco. *New trends in properties and applications of complex hydrides systems*. invited accepted. Progress in Energy (IOP)

Acknowledgements

This work was supported by the Hydrogen Materials—Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office. Thanks to Ned Stetson, Jesse Adams, and Zeric Hulvey for technical and programmatic guidance

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Kat Grubel

Oliver Gutierrez

Sam Johnson

Jothi Kothandaraman

Shuyun Li

Chirag Mevawala

Ba Tran

Peter Valdez