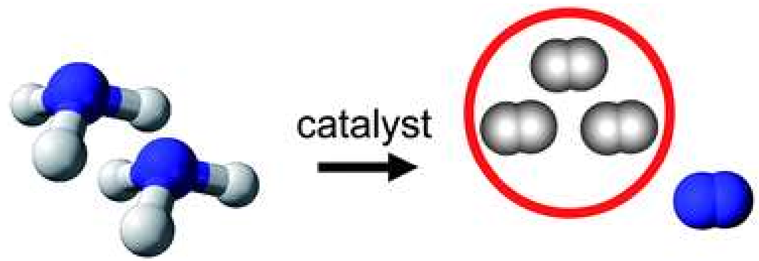

Ammonia's Role in Enabling H2@Scale

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cwolden@mines.edu

AMCHAM, 9/18/24

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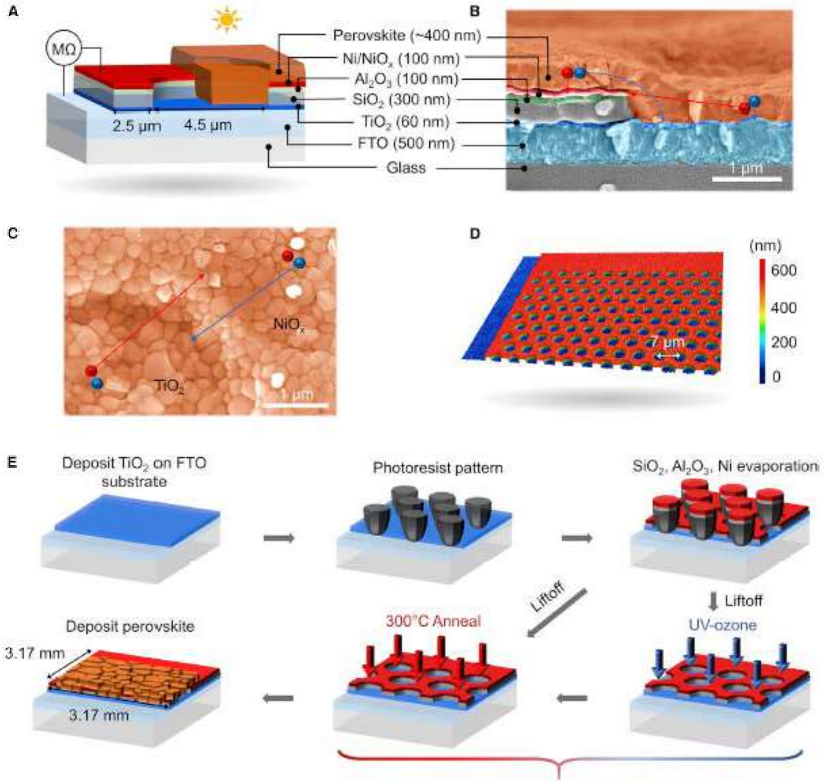
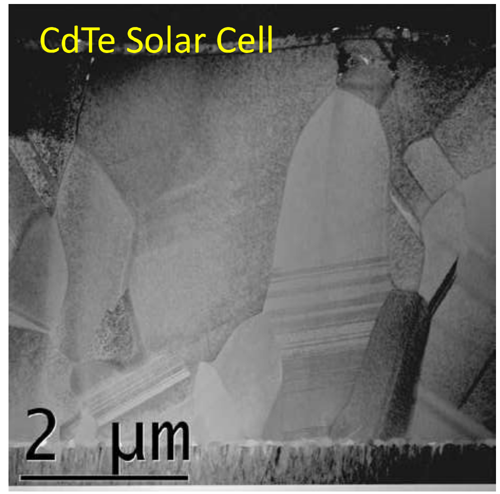
Wolden Group: Thin Film Solar Cells

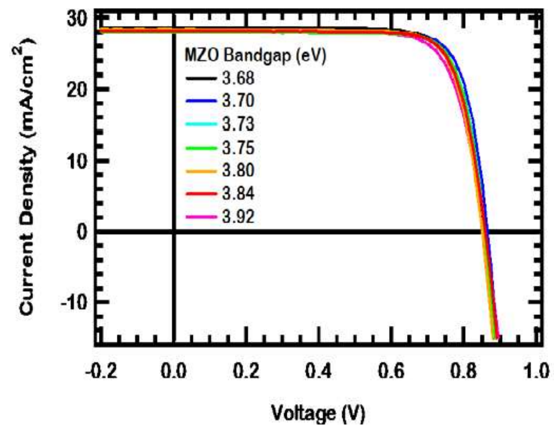
All back contact Perovskites



K. J. Prince, C. P. Muzzillo, M. Mirzokarimov, C. A. Wolden, and L. M. Wheeler, "All-Back-Contact Perovskite Solar Cells Using Cracked Film Lithography," *ACS Applied Energy Materials* (2022).

CdTe-based Solar Cells





G. Yeung, C. Reich, A. Onno, A. Bothwell, A. Danielson, Z. Holman, W. S. Sampath and C. A. Wolden, "Robust passivation of CdSeTe based solar cells using reactively sputtered magnesium zinc oxide," *Solar Energy Materials and Solar Cells* **233,** 111388 (2021).

D. L. McGott, C. P. Muzzillo, C. L. Perkins, J. J. Berry, K. Zhu, J. N. Duenow, E. Colegrove, C. A. Wolden and M. O. Reese, "3D/2D passivation as a secret to success for polycrystalline thin-film solar cells," *Joule* **5,** 1057-1073 (2021).

Wolden Group – Solid State Battery Materials

Solution Synthesis of Anhydrous Metal sulfides (Li_2S, Na_2S)

H_2

Li Metal

Dissolve

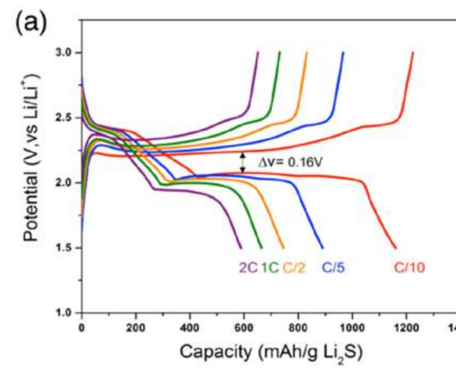
Evaporate

Dry

N_2

H_2S

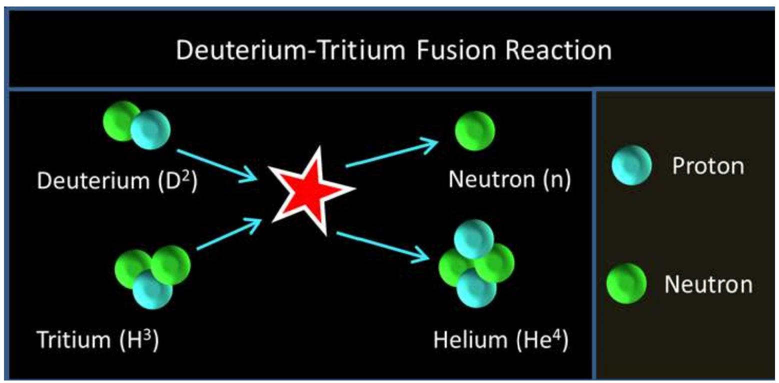
Net: $2Li + H_2S \rightarrow Li_2S + H_2$

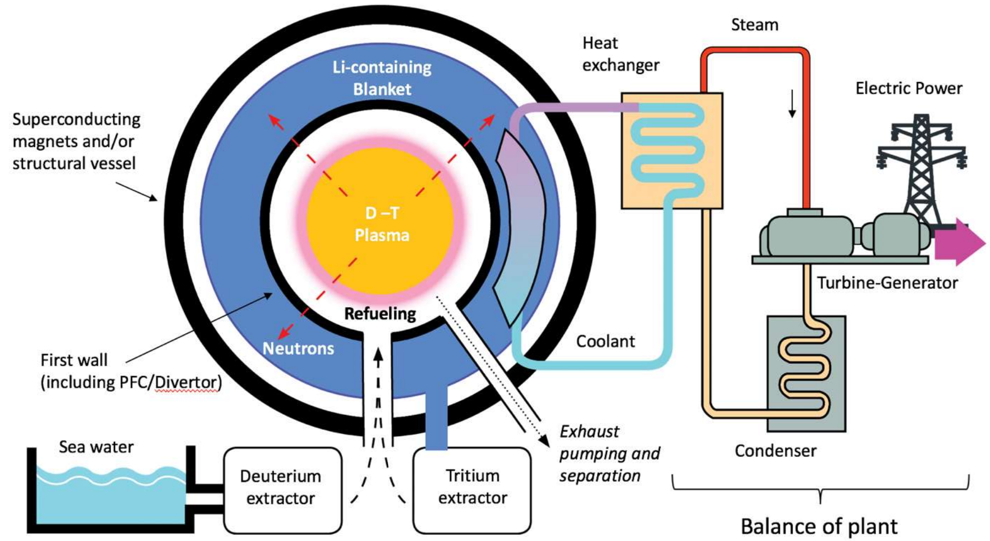


W. H. Smith, J. Birnbaum and C. A. Wolden, "Production and purification of anhydrous sodium sulfide," *Journal of Sulfur Chemistry* **42,** 426-442 (2021).

W. H. Smith, S. A. Vaselabadi, and C. A. Wolden, "Synthesis of high-purity Li_2S nanocrystals via metathesis for solid-state electrolyte applications," *Journal of Materials Chemistry A* **11**, 7652-7661, (2023).

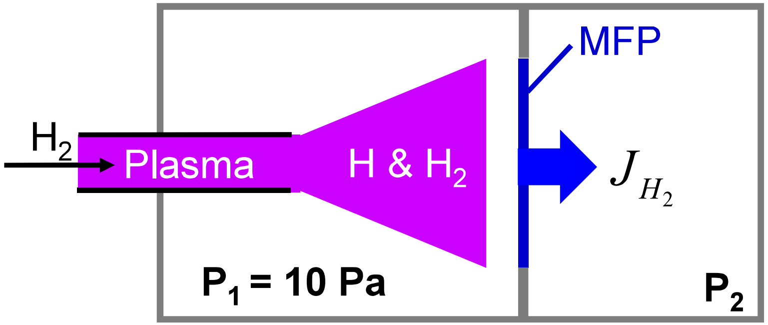
Wolden Group: Fusion Fuel Cycle

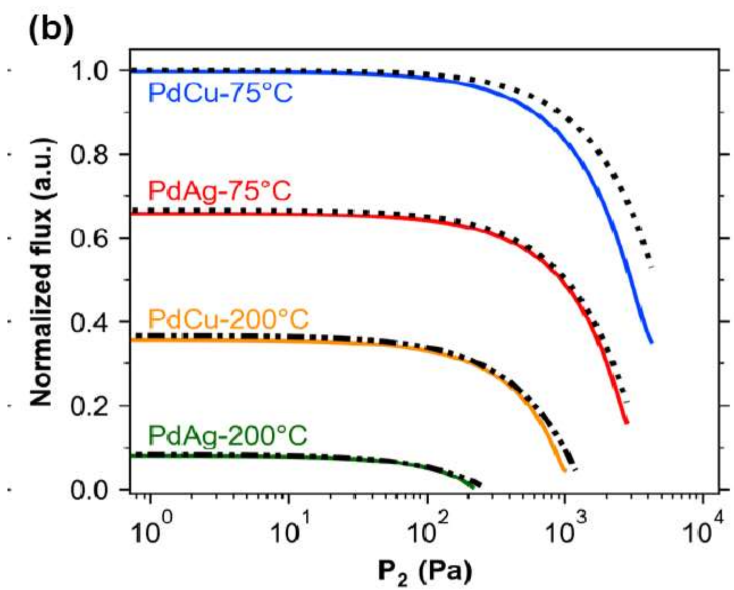




~1% Conversion, Need to purify/recycle DT

Wolden Group: Fusion Fuel Cycle





H2@Scale Vision

Renewable Electricity Growing Fast

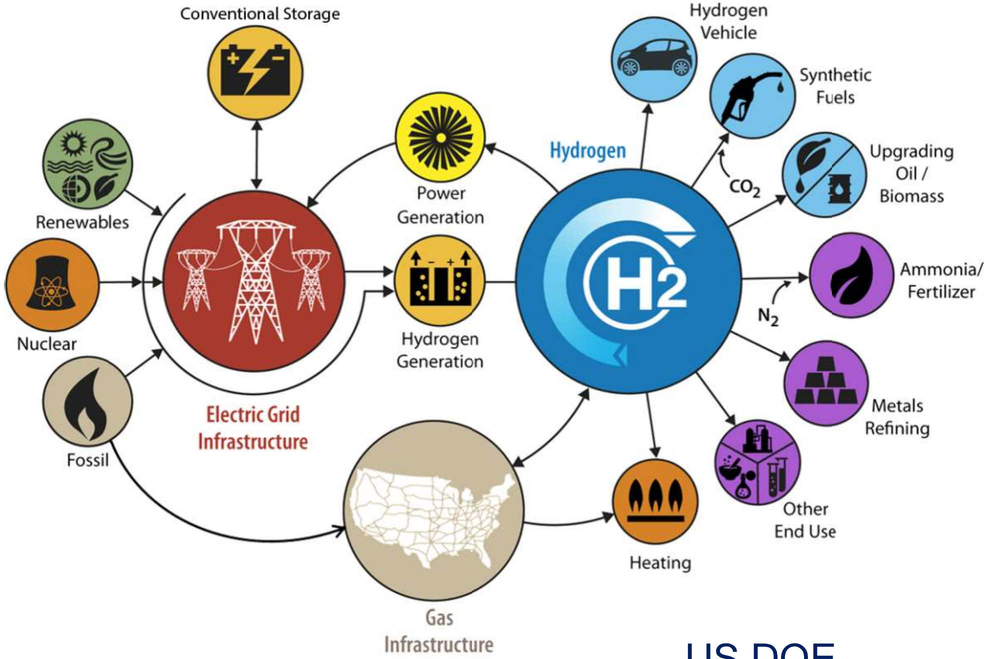
- Wind/solar now competitive with conventional sources
- Challenge: Transportation & Industrial sectors

Hydrogen as the Energy Hub

- Renewable electricity to H_2
- Fuel cell electric vehicles (FCEVs)
- Industrial chemical, fuels, combustion

Challenges

- Distributed vs. centralized production
- Cost of H_2 storage and transportation



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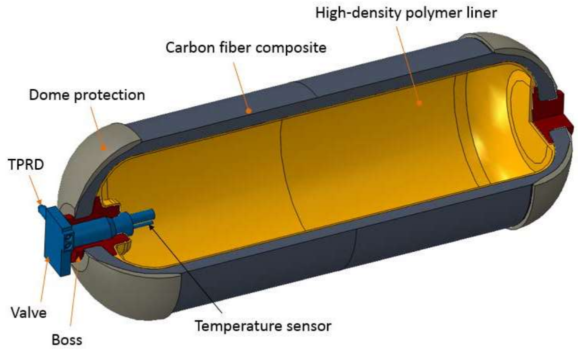
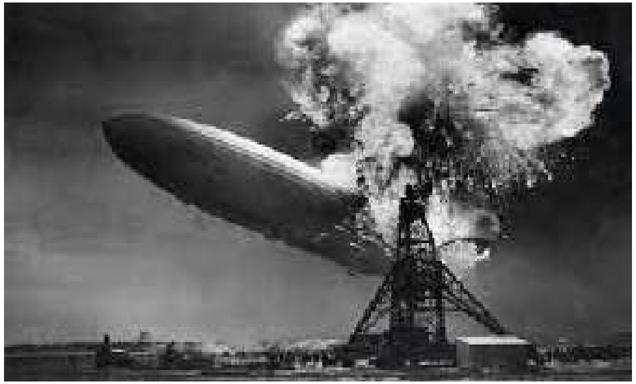
The Challenge with H_2:Storage

Cryogenic liquefaction
T < 20 K

Extreme Compression
P > 700 atm



Safety Concerns
4% Flammability Limit



Produced for
\$2-4/kg H_2

Sold for
>\$20/kg H_2

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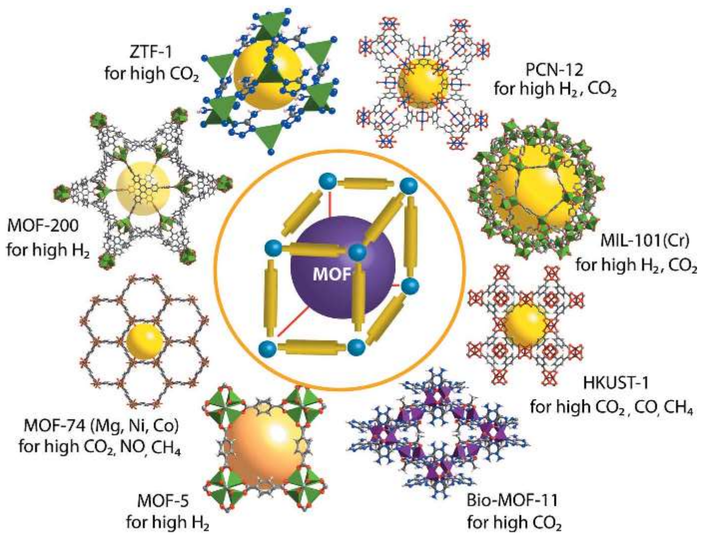
Options for H_2 Storage and Transportation

Solid Carriers

Adsorbents

- MOFs/COFs/ ZIFs

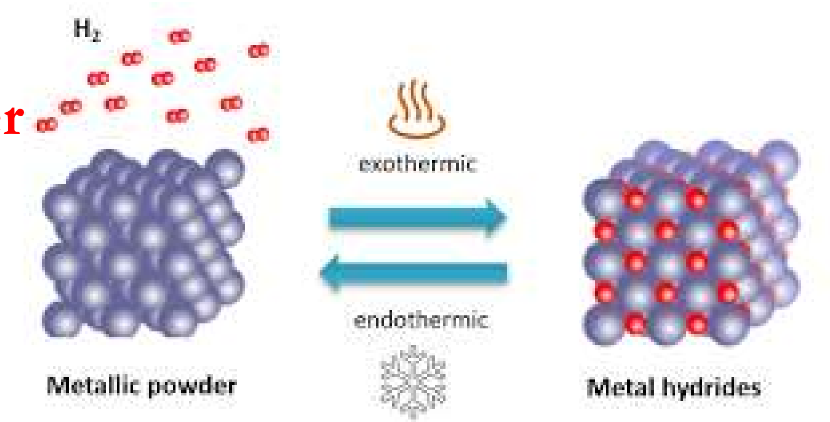


Challenges

- Low capacity
- Two-way carrier
- Reversibility?
- Stability?
- Scalability?

Metal Hydrides

- Li/Mg/B/Al/Alloys

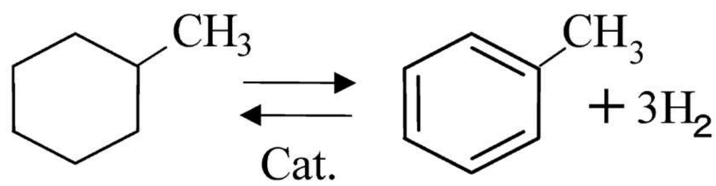


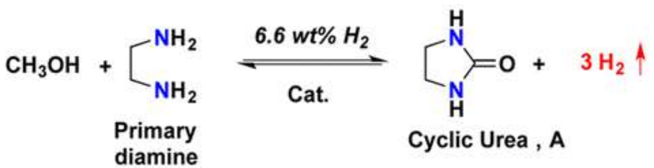
Options for H_2 Storage and Transportation

Liquid Carriers

De/Hydrogenation Couples

- MCH/Toluene
- Amine reduction





- Two-way carrier
- Reversibility?

Reforming

- Ammonia (NH_3)
- Methanol (CH_3OH)
- Formic Acid (HCOOH)
- One-way Carriers

$$2NH_3 \leftrightarrow 3H_2 + N_2 \quad \Delta H^o = 46.4 \text{ kJ/mol } H_2$$

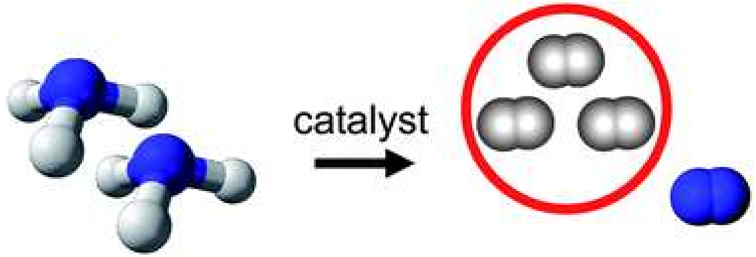
$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2 \quad \Delta H^o = 41.8 \text{ kJ/mol } H_2$$

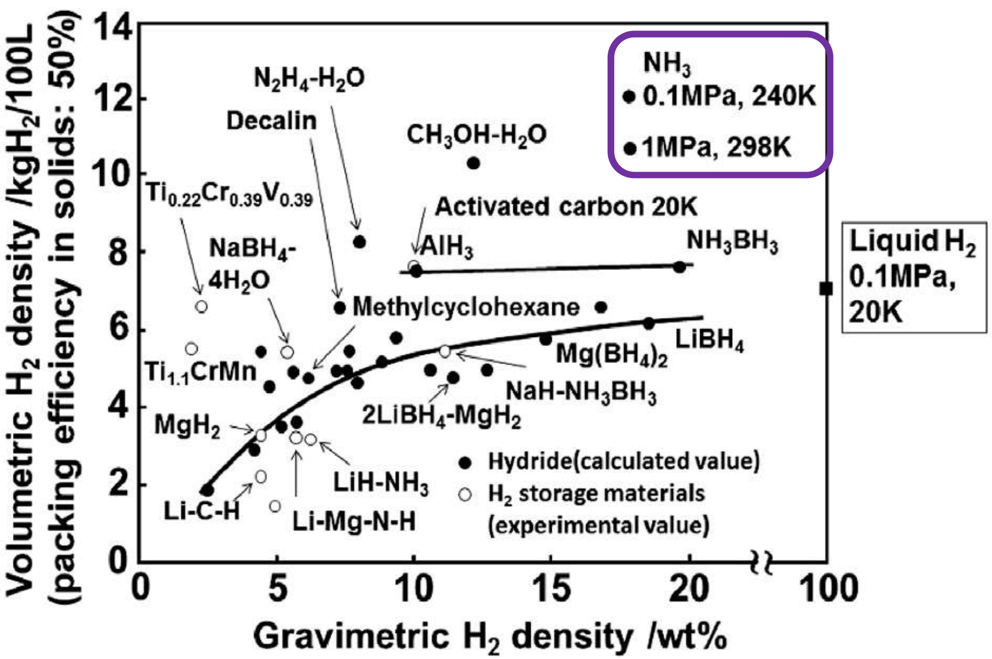
$$HCOOH \leftrightarrow H_2 + CO_2 \quad \Delta H^o = 32 \text{ kJ/mol } H_2$$

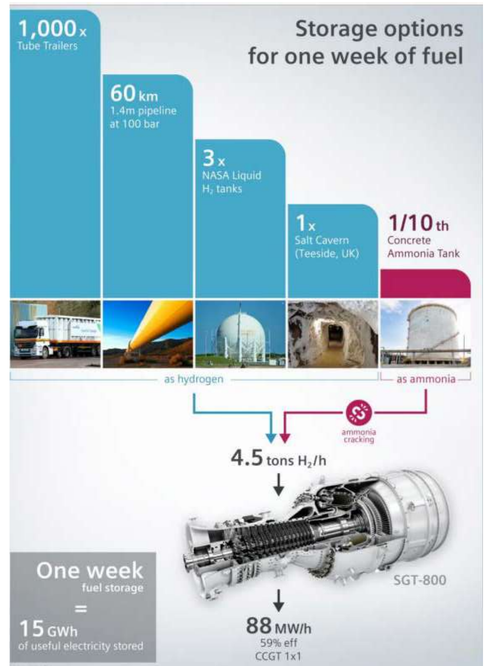
- Endothermic / Purification

J. Kothandaraman, S. Kar, R. Sen, A. Goeppert, G. A. Olah, and G. K. S. Prakash, "Reversible Hydrogen Carrier System Based on Amine Reforming of Methanol," *Journal of the American Chemical Society* **139**, 2549-2552, (2017).

The Case for Ammonia: 1) Capacity







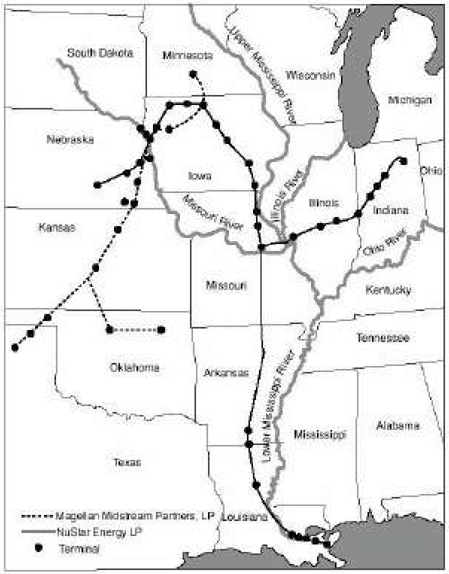
Attributes

- Liquid at modest T/P
- 17.3 wt. %
- 40% more H_2
- 60% more energy
- Relative to liquid H_2

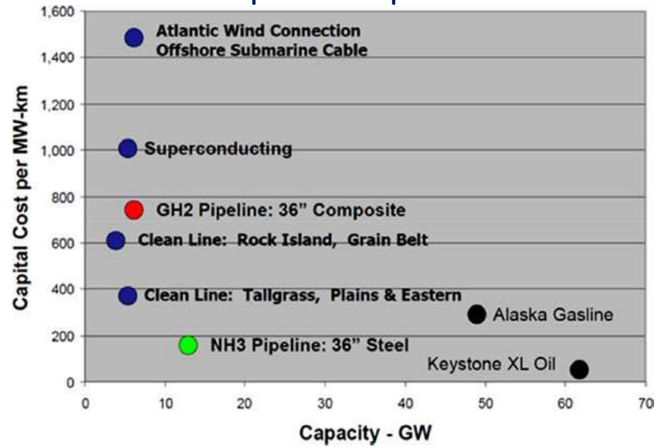
A. Valera-Medina et al., "Ammonia for power," *Progress in Energy and Combustion Science* **69,** 63-102 (2018)

The Case for Ammonia: 2) Infrastructure and Scale

Ammonia pipelines in the US



CapEx Competitive



A. Valera-Medina et al., "Ammonia for power," *Progress in Energy and Combustion Science* **69,** 63-102 (2018)

30,000 MT

- Globally > 200 MMT/yr
- >3000 miles of pipeline
- Regulatory framework in place, proven safety record

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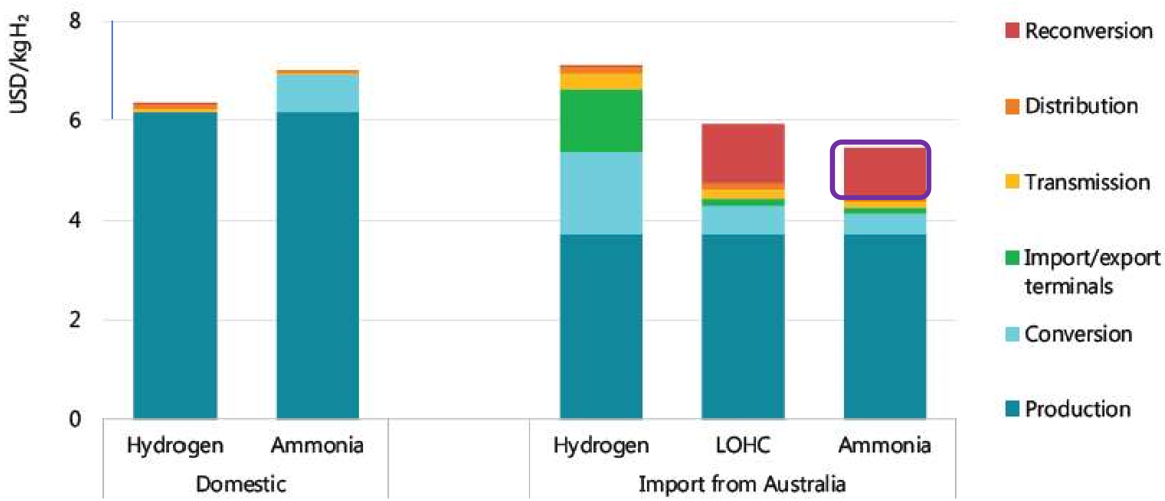
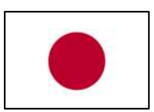
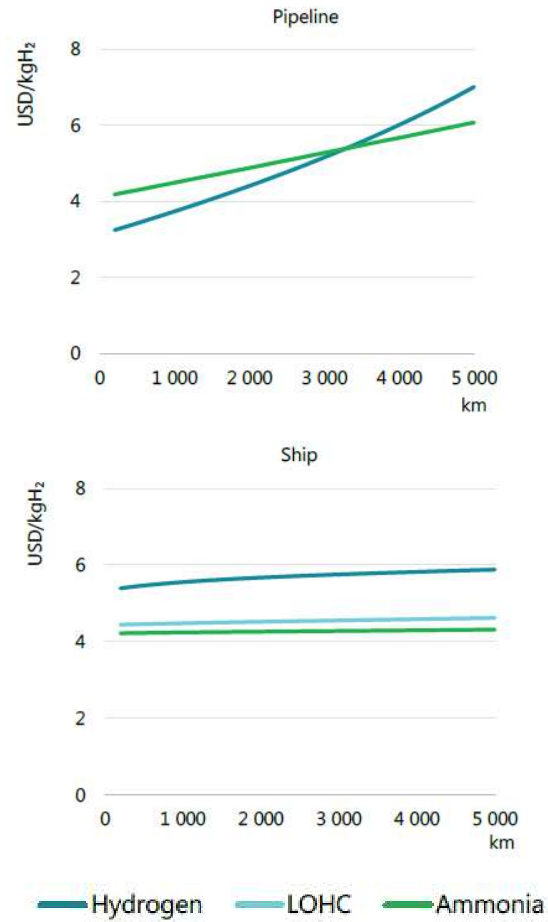
Ammonia@Scale

Australia –Japan Partnership

- Make H_2 in Australia using abundant renewables
- Convert to Ammonia: Ship
- Reconversion to H_2



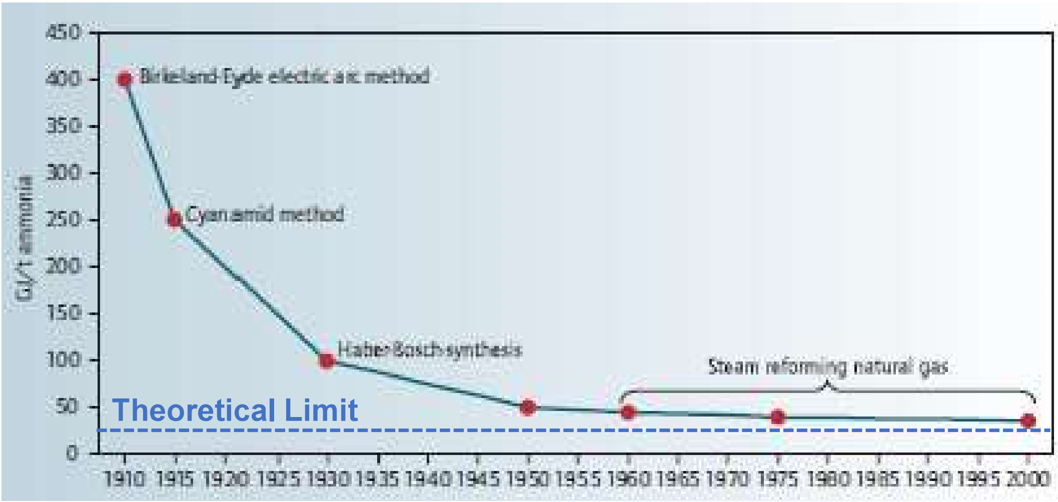




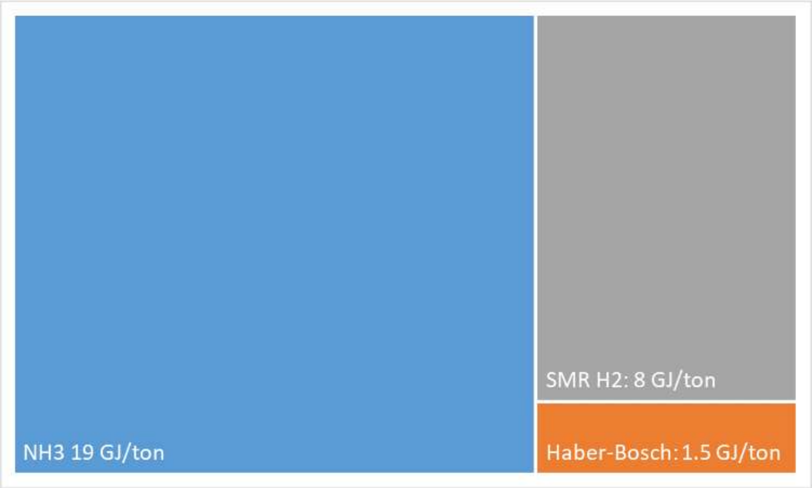
International Energy Agency, "The Future of Hydrogen", *(*2019).

Fallacy: Haber-Bosch is inefficient

Evolution of NH_3 Synthesis



State-of-the-Art: ~28 GJ/ton NH_3



- ~85% of energy losses, CO_2 emissions, costs, associated with hydrogen production

International Energy Agency, "Technology Roadmap: Energy and GHG reductions in the chemical industry via catalytic processes," (2013).

Klerke, A.; Christensen, C. H.; Nørskov, J. K.; Vegge, T., Ammonia for hydrogen storage: challenges and opportunities. *Journal of Materials Chemistry* **18** , 2304 (2018).

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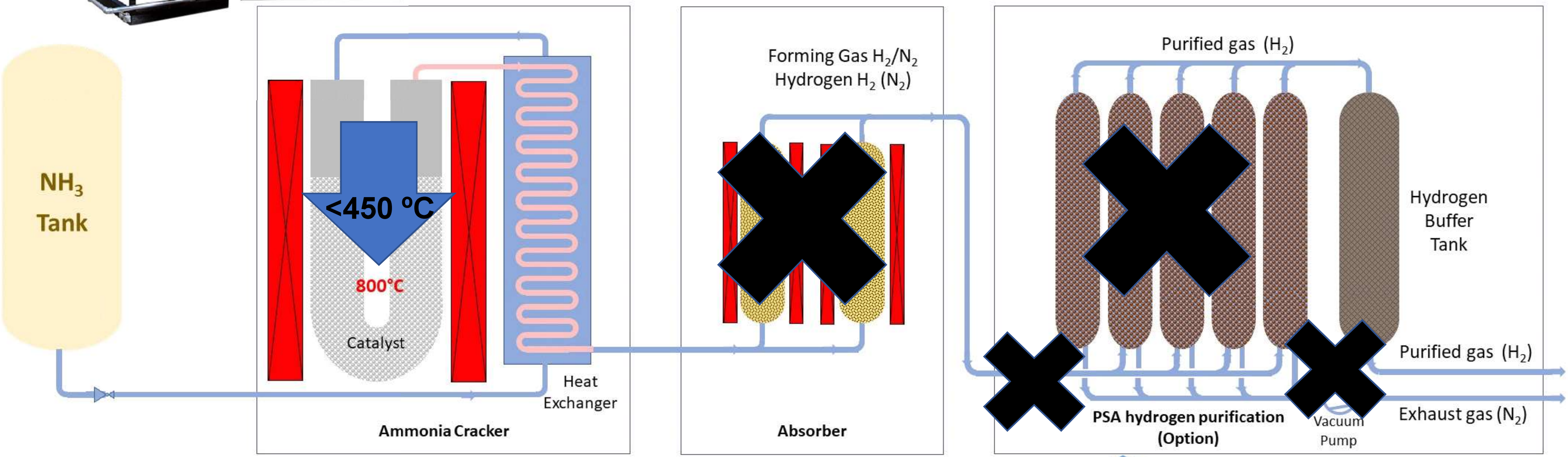
Challenges with Ammonia Decomposition

CapEx & OpEx Intensive

- Very high temperature for complete dissociation
- Compressors, PSA for purification



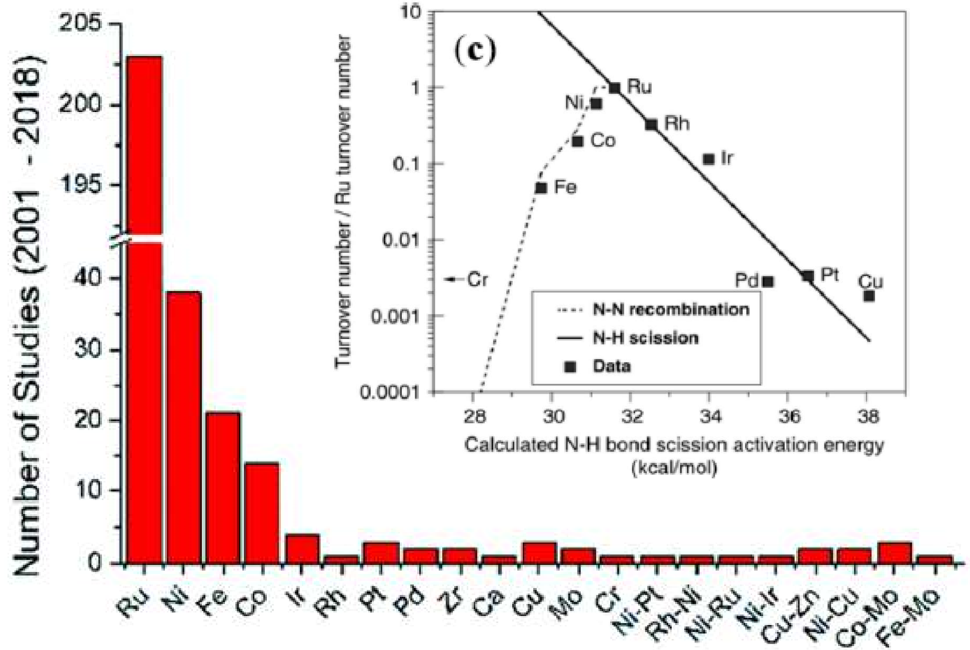
Small Scale: Crystec Technology, Gaztron; Large Scale: Halder-Topsoe, KBR

Strategy 1: Develop New Catalysts

- Goal: Reduce T
- Commercial: Ni-based
- Best: Ru-based ($)
- Novel: Li/Na/Amine/alloys

Strategies

- Control dispersion / faceting
- Novel supports, rare earth oxides
- Alkali promoters (Cs, K, Na, etc.)



T. Su et al., "Review on Ru-Based and Ni-Based Catalysts for Ammonia Decomposition: Research Status, Reaction Mechanism, and Perspectives," *Energy & Fuels* **37**, 8099-8127, (2023).

T. E. Bell and L. Torrente-Murciano, "H_2 Production via Ammonia Decomposition Using Non-Noble Metal Catalysts: A Review," *Topics in Catalysis* 1-20, (2016).

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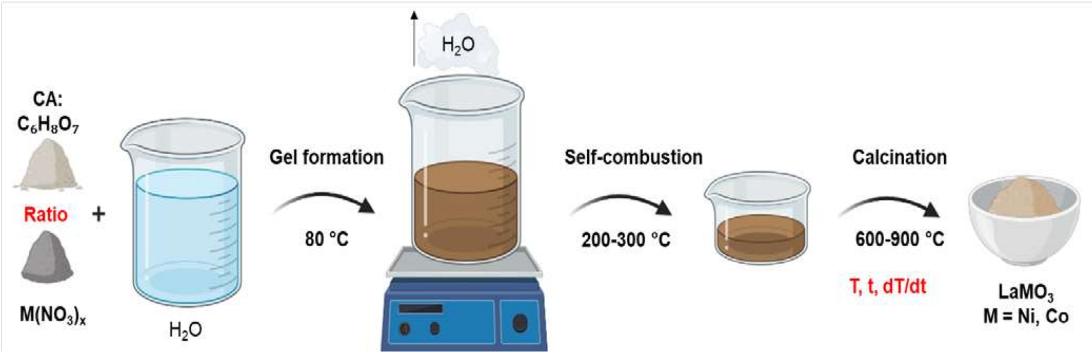
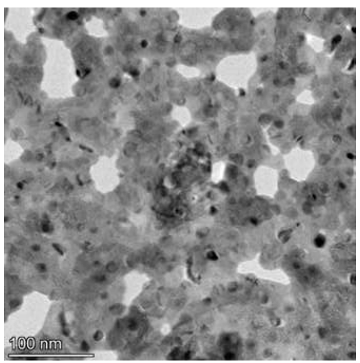
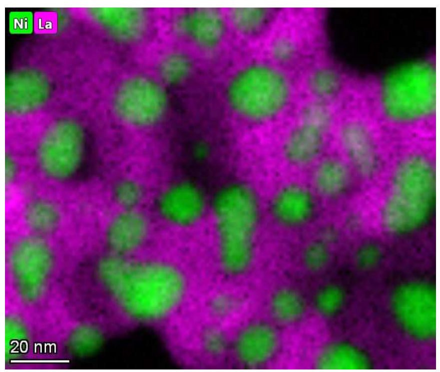
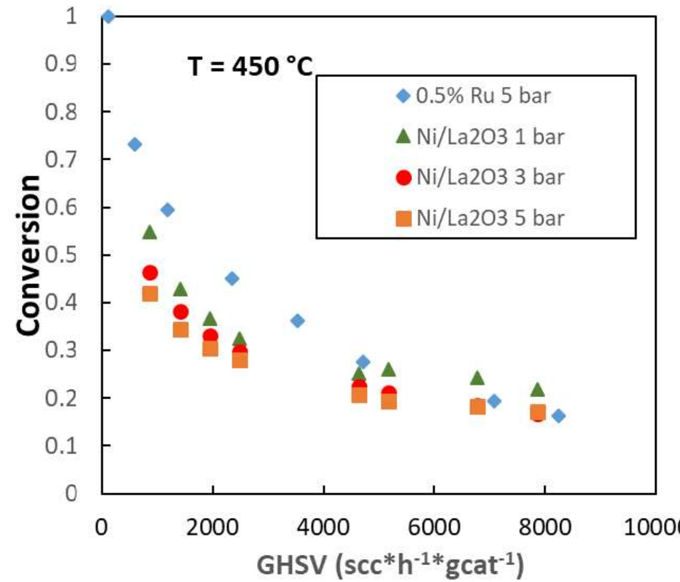
Nanoscale Ni- based Catalysts









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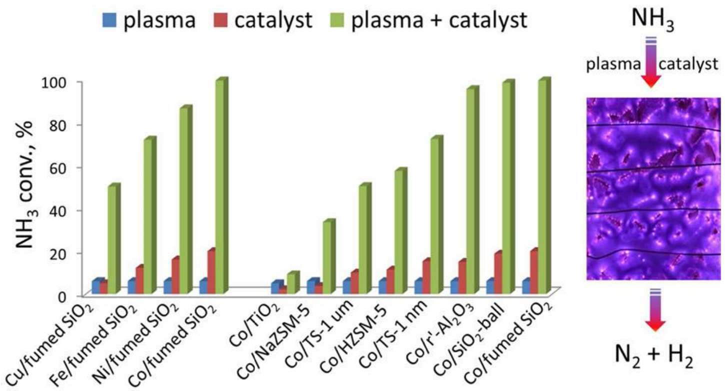
Strategy 2: Novel Processing

Plasmonics

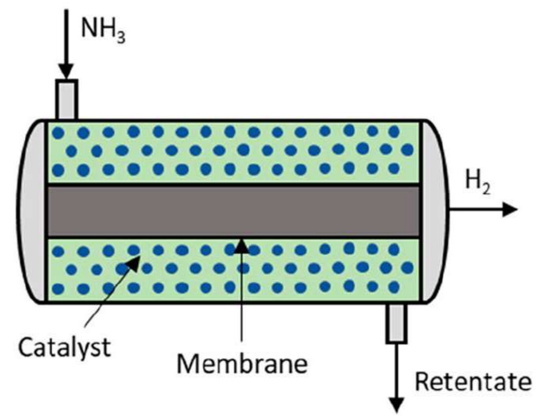
Y. Yuan et al, "Earth-abundant photocatalyst for H_2 generation from NH_3 with light-emitting diode illumination," *Science* **378**, 889, (2022)

Plasma



L. Wang et al, "NH_3 Decomposition for H_2 Generation: Effects of Cheap Metals and Supports on Plasma–Catalyst Synergy," *ACS Catalysis* **5**, 4167, (2015).

Membrane Reactors



V. Cechetto, et al., "Advances and Perspectives of H_2 Production from NH_3 Decomposition in Membrane Reactors," *Energy & Fuels* **37**, 10775, (2023).

Membrane Reactors: Opportunities & Challenges

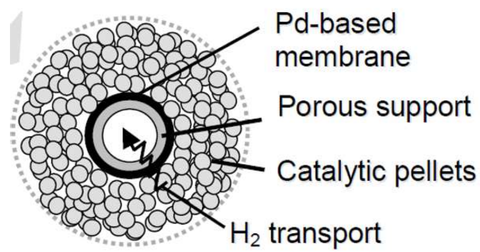
Potential Advantages

- Process intensification
- Accelerate kinetics
- Reduce temperature

$$r = k_f \left[\left(\frac{P_{NH_3}^2}{\cancel{P_{H_2}^3}} \right)^{\beta} - \frac{\cancel{P_{N_2}}}{K_{eq}} \left(\frac{P_{H_2}^3}{P_{NH_3}^2} \right)^{1-\beta} \right]$$

$$r = \frac{kKP_{NH_3}}{1 + KP_{NH_3}} = k' P_{NH_3}^{\alpha}$$

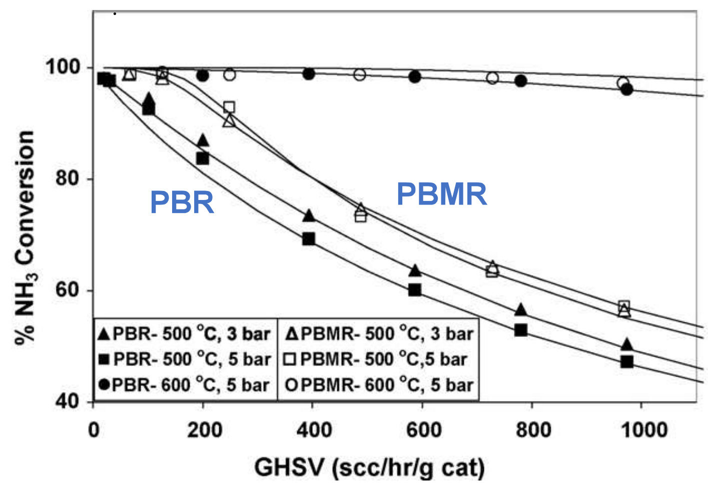
Cross Section



Challenges

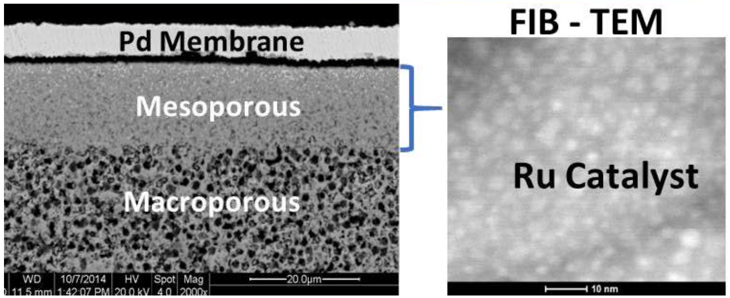
- Transport limitations
- Dispersion /channeling

Israni et al. *Catalysis Today* 139.4 (2009): 299

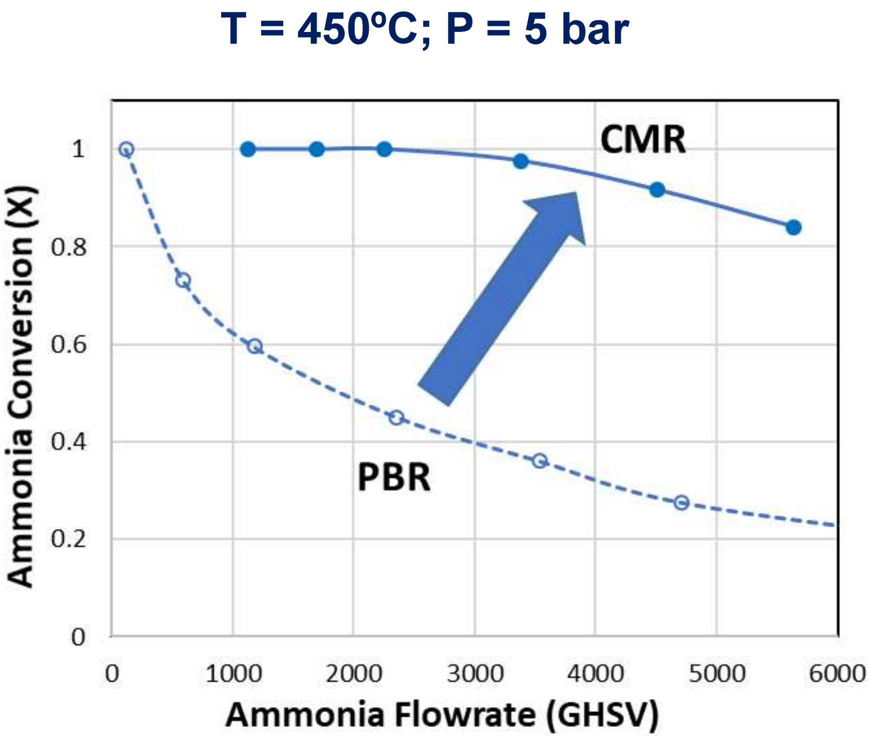


K. Tamaru, "A "new" general mechanism of ammonia synthesis and decomposition on transition metals", *Accounts of Chemical Research* **21,** 88-94 (1988).

Catalytic Membrane Reformer (CMR)

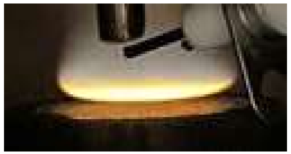


- **Catalyst loaded in support**
- **Higher utilization/throughput**



R. Sitar, J. Shah, Z. Zhang, H. Wikoff, J. D. Way and C. A. Wolden, "Compact ammonia reforming at low temperature using catalytic membrane reactors", *Journal of Membrane Science* **644,** 120147 (2022).

The Case for Ammonia: 3) Utilization



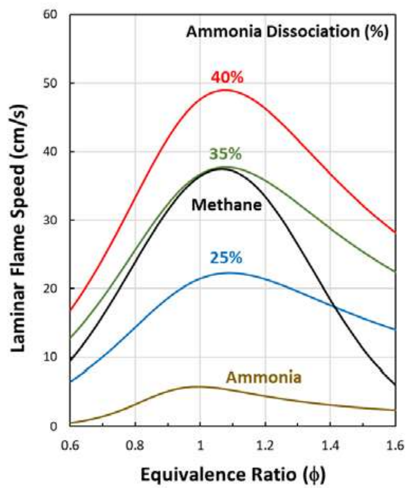
100%: PEMFC

% Dissociation

10% Combustion 50%

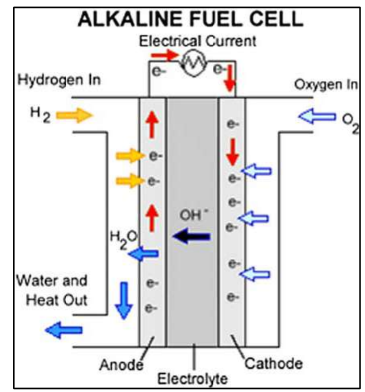
0%: SOFC

90%: AFC



H_2/NH_3 Blends

- NH_3 too Cold
- H_2 too Hot
- Tunable H_2/NH_3
- "Goldilocks"
- No CO_2, but NO_x



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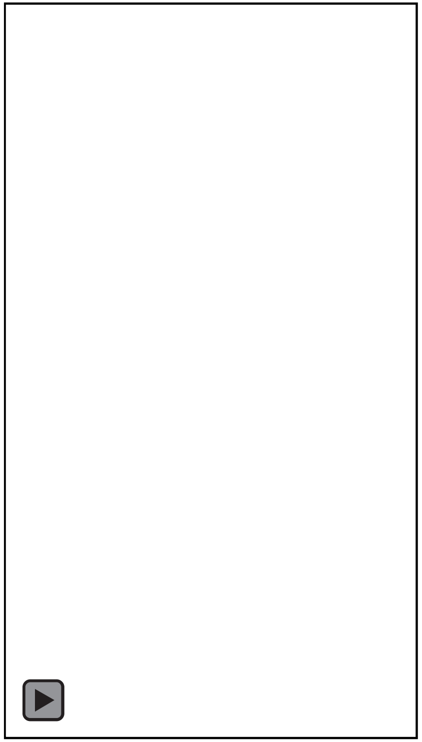
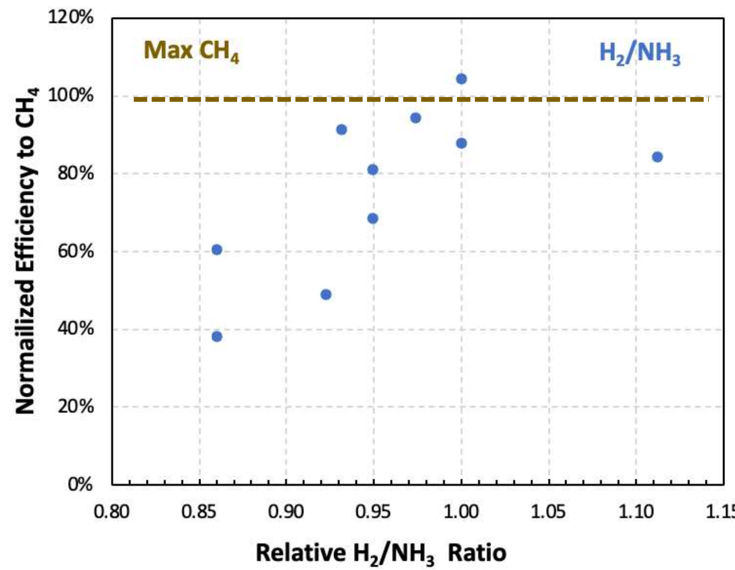
H_2/NH_3 Blends: True Drop-in Fuel

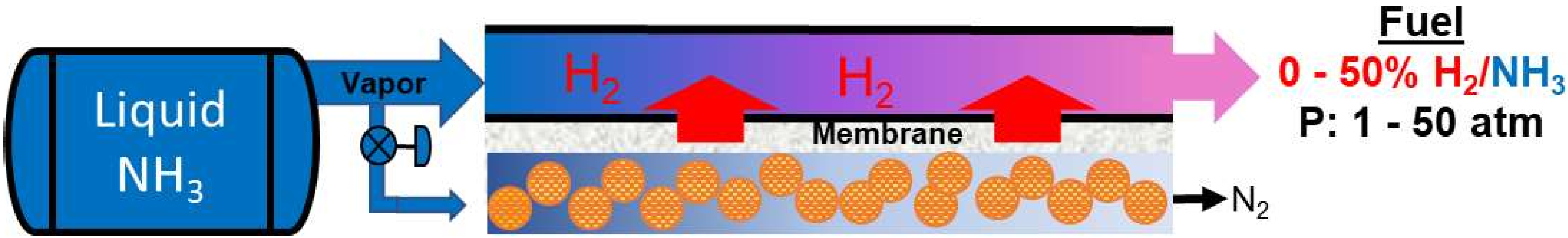


- "Tri-Fuel" Generator
- Gas/LPG/NG
- No Modification
- Vary Load
- $H_2/NH_3 \sim CH_4$
- No ammonia slip
- $NO_x \sim 150$ ppm

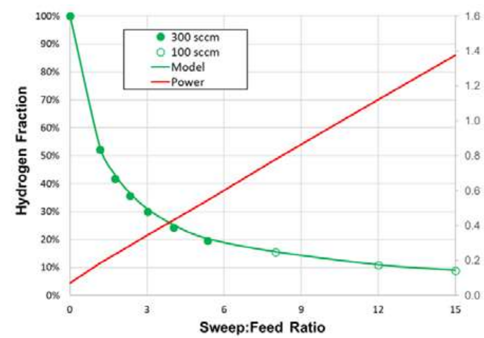
$$\eta = \frac{Electrical\ Power}{\dot{n}_{fuel} \times LHV}$$

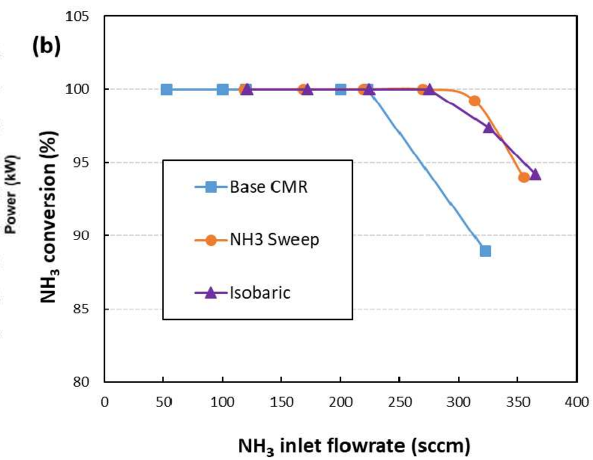


CMR Production of H_2/NH_3 Blends



- Dynamic control of H_2/NH_3
- Even higher efficiency
- High pressure w/o compression
- Reject N_2: More Power, less NO_x





R. Sitar, J. Shah, J. D. Way and C. A. Wolden, "Efficient generation of H_2/NH_3 fuel mixtures for clean combustion", *Energy & Fuels* **36,** 9357-9364 (2022).

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The Case for Ammonia

NH_3

Catalytic Membrane Reformer (CMR)

N_2

$H_2:NH_3$

tunable, drop-in replacement for hydrocarbons

Single, dense liquid fuel source

<\$0.2/kg H_2

1) Capacity
- Dense liquid
- 1 way carrier
- 60% > hydrogen

2) Infrastructure
- Production
- Distribution
- Storage

25X lower storage costs

3) Utilization
- UHP H_2
- Direct as NH_3
- H_2/NH_3 Blends
- Drop-in Fuel

4) CMR Reforming
- High throughput
- Tunable H_2/NH_3
- Isobaric Operation
- Reject N_2

Acknowledgements

Colleagues

- Prof. J. Douglas Way
- Alums: Dr. Zhenyu Zhang (Ammpower), Dr. Thomas F. Fuerst (INL), Prof. Simona Liguori (Clarkson), Dr. Javishk Shah (HyET), Dr. Rok Sitar (Blaze), Hope Wikoff (NREL), Allie d’Aquila (P&G), Liz Golonksi (Army), Izzy Roswell (NREL)
- Current: Nolan Kelley, Ben Ivie, Sean Mathews, Kagan Killough, Ben Baurele, Jon Braford, Dr. Mingyuan Cao

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HyMARC Hydrogen Materials Advanced Research Consortium