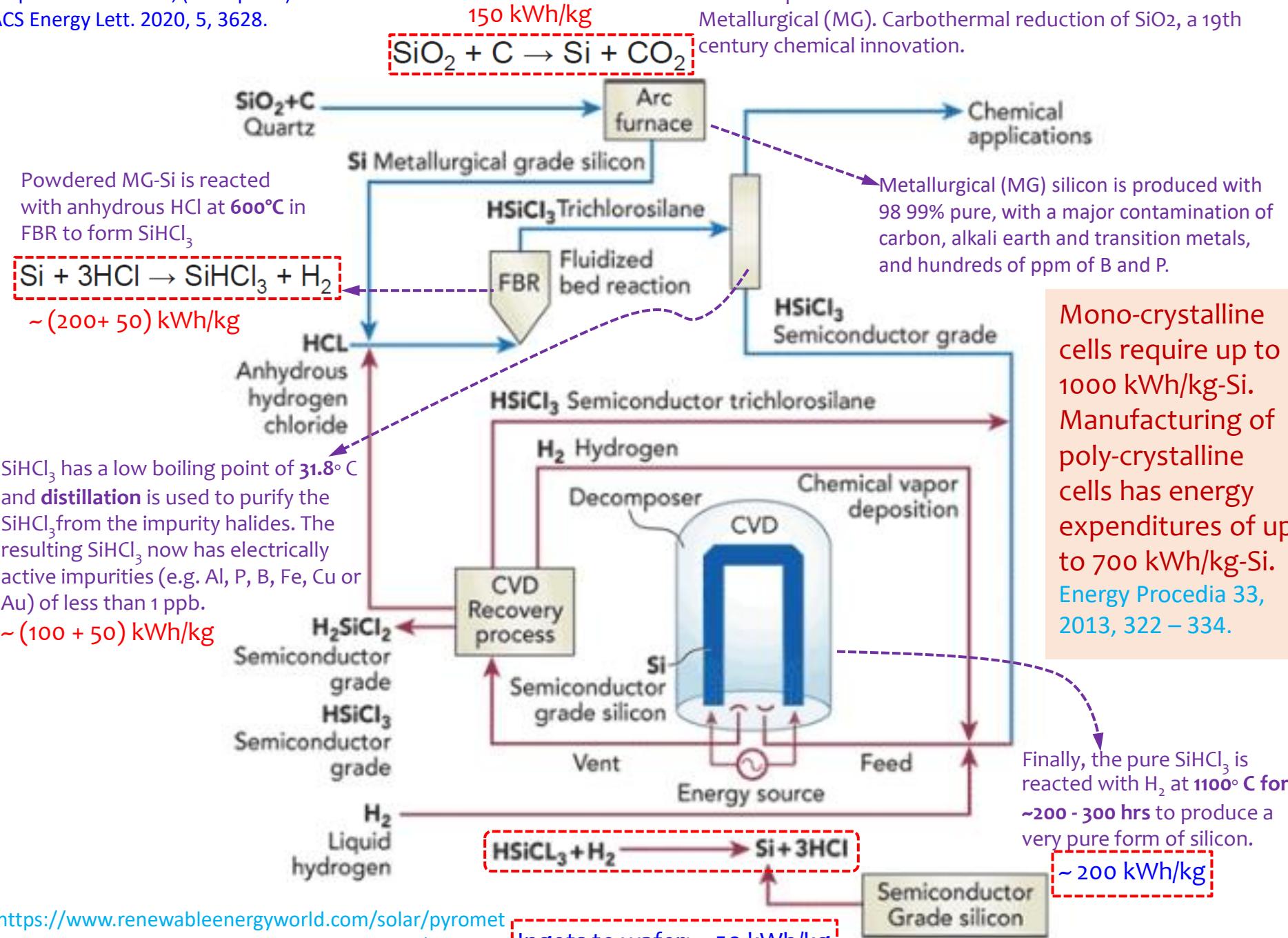


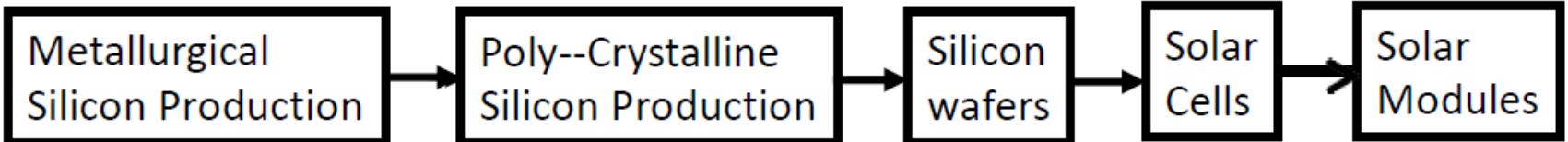
Third Generation Solar Cells

DSSC

Prof. S. Sivaram
Prof. S. Sengupta
Amitava Das

CH5106-17 AD





IS SILICON PV GREEN ENERGY ?

Consider the following facts

- Solar PV manufacturing processes involve converting quartz to metallurgical grade silicon and then to polysilicon ingots which are sliced to form wafers
- Every ton of metallurgical grade silicon production results in 4 tons of silicon tetrachloride; **Material utilization efficiency is a mere 30%**
- 1 ton of crude silicon production results in 10 tons of CO₂; Purification process results in additional 45 tons of CO₂; for manufacturing in China, 70 g CO₂ is generated per kWh of electricity

Total energy expenditure for solar cell manufacturing

The total energy expenditure for solar cell manufacturing is the sum of the aforementioned processes. Mono-crystalline cells require up to 1000 kWh/kg-Si. Manufacturing of poly-crystalline cells has energy expenditures of up to 700 kWh/kg-Si.

Other Issues:

- Silicon production uses SF₆ (to clean the Siemens Reactor: **a potent GHG**), HF (to clean wafers and texture the surfaces), 1,1,1 trichloroethane (**a persistent pollutant**) and large quantities of strong acids.
- Conversion of ingots to wafers requires mechanical sawing, generating up to 10 % waste and a significant amount of fine silicon dust (inhalation hazard)
- Silver that is used for making panels at 5 % of current power demand will consume 50% of current silver produced.
- Little or no recycling of silicon in process waste or end of life panels

1,1,1 trichloroethane (TCA) remains a persistent pollutant at many sites and some of the daughter products that accumulate from intrinsic decay of TCA have been determined to be more toxic than the parent compound. [Water Research, 2011, 45, 2701-2723]

Table 3. Emissions form photovoltaic module and system.

Energy Procedia 33 (2013) 322 – 334

		SO ₂	NO _x	Particles	CO ₂	CH ₄	N ₂ O	Source
Emissions (kg/kW _p)	PV Module 1995/1998	5 - 5.5	4.5 - 5.3	No Info	2.7 - 3.8	No Info	No Info	[5, 6]
	Entire PV System 1998	1.9	1.8	0.11	971,000	1.6	0.0031	[3]

MAKING SILICON IS AN EXPENSIVE PROCESS

- High temperatures, invariably produced using electrical energy
- Long reaction times
- Several unit & Batch processes
- Large number of waste and by products
- Highly corrosive environment

Socio-Economic and Environmental Impacts of
Silicon Based Photovoltaic (PV) Technologies;
Energy Procedia 33 (2013) 322 – 334

Global capacity for solar grade silicon : ~ 0.5 million tons per annum

Minimum viable economic capacity : 10,000 tons per annum

Highly capital intensive : US \$1.5 million per ton of production

By contemporary standards of chemical manufacturing, the process for producing silicon is a highly complex process

Reduce



Reuse



Recycle

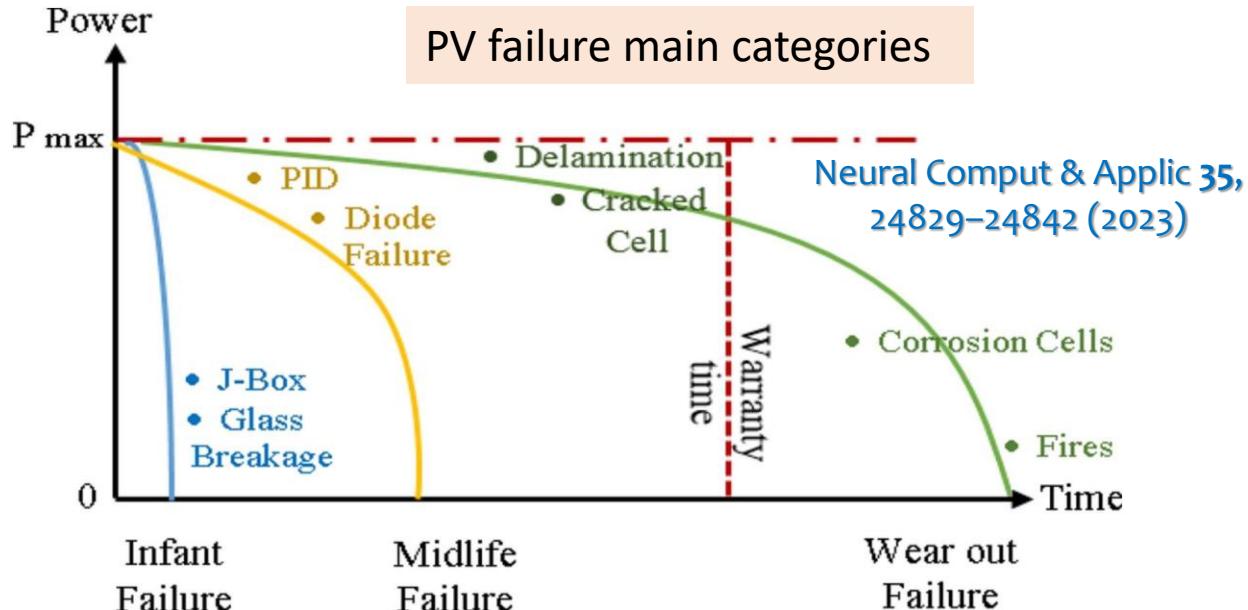


Dispose

Most preferred option

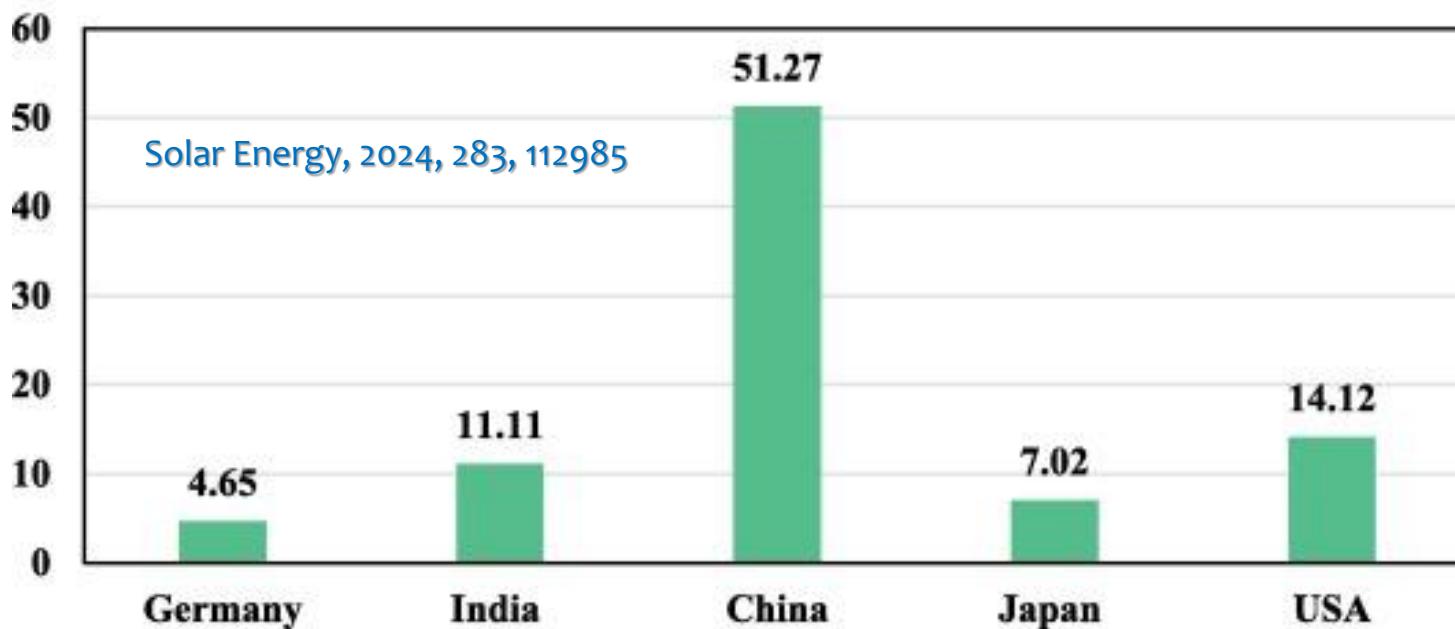


Least preferred option



Solar Energy, 2024, 283, 112985

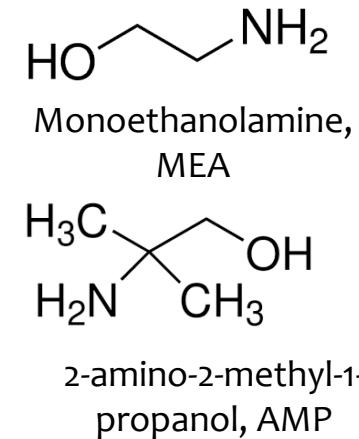
PV waste in 2050 (Mt)



Direct Capture of CO₂ from Air

Basic Concept:

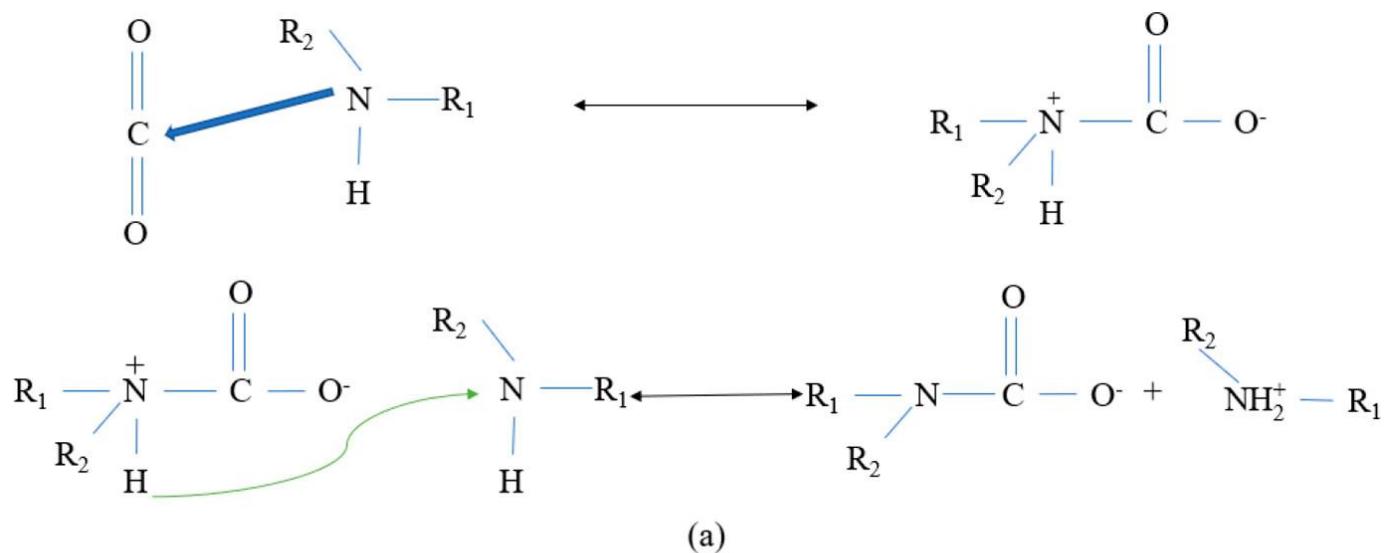
Sterically hindered amines are a special class of amines whose nitrogen atom is surrounded by bulky groups, which partially block access to the nitrogen center. This structural hindrance alters the way CO₂ reacts with the amine. Unlike conventional amines (e.g., monoethanolamine, MEA), **which form a metastable carbamate intermediate**, sterically hindered amines like 2-amino-2-methyl-1-propanol (AMP) tend to form bicarbonate ions instead.



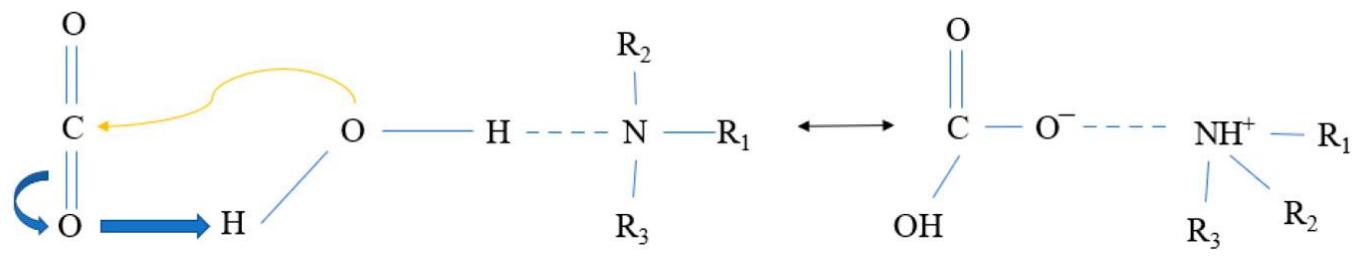
This difference is crucial because:

- The bicarbonate pathway allows higher CO₂ loading capacity (each amine can absorb more CO₂ molecules).
- The weaker bonding between CO₂ and the amine leads to easier regeneration, reducing the energy required for desorption.

As a result, sterically hindered amines offer an efficient and energy-saving alternative for CO₂ capture, making them promising candidates for direct air capture (DAC) and other carbon management applications.

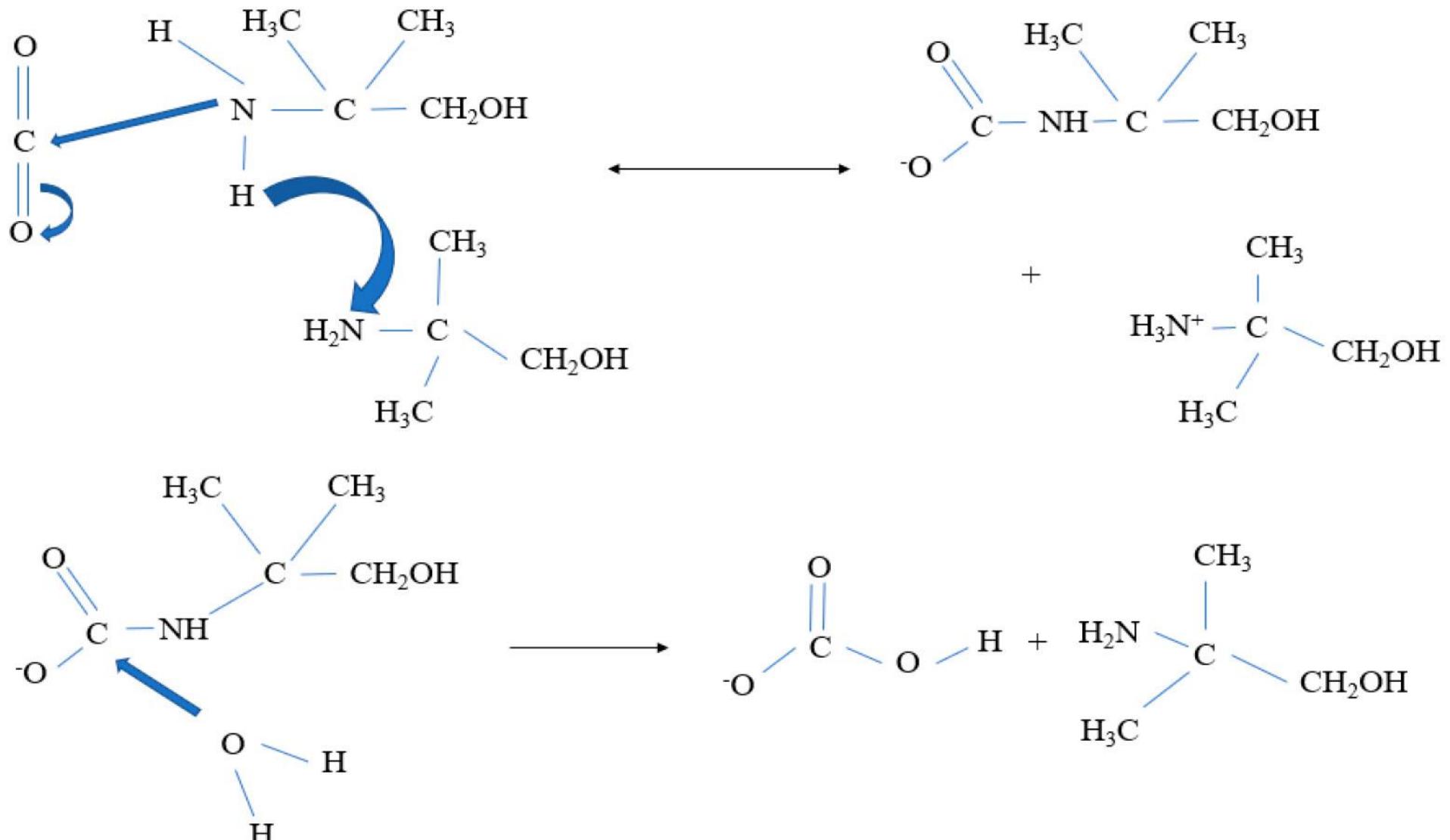


(a)



(b)

- (a) Reaction mechanism of a primary or secondary amine with CO_2 . [J. Phys. Chem. A 2010, 114 (43), 11844–11852]
 (b) Reaction mechanism of a tertiary amine with CO_2 . [Ind. Eng. Chem. Fundam. 1980, 19, 260–266].



Reaction mechanism of SHA (AMP) with CO_2
 [J. Phys. Chem. A 2010, 114 (43), 11844–11852].

Kinetic properties

k_0
absorption capacity
reaction rate
viscosity

Thermodynamic properties

heat of reaction
sensible heat
heat of vaporization
regeneration energy

CO₂ capture based on sterically hindered amine

single amine
blended amine
biphasic amine
non-aqueous amine

Four groups

technical-economic
analysis and life cycle
assessment

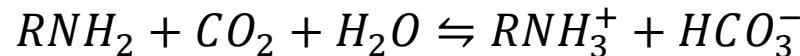
TEA and LCA

When CO₂ interacts with a conventional **primary or secondary amine** (e.g., MEA), the reaction follows a **carbamate formation mechanism**:



Sterically hindered amines (SHA: e.g., 2-amino-2-methyl-1-propanol, AMP) have bulky substituents near the nitrogen, which **impede the formation of carbamates**.

The reaction proceeds primarily through the **bicarbonate pathway**:



CO₂ capture based on sterically hindered amine

Four groups

Kinetic properties

Thermodynamic properties

TEA and LCA

single amine
blended amine
biphasic amine
non-aqueous amine

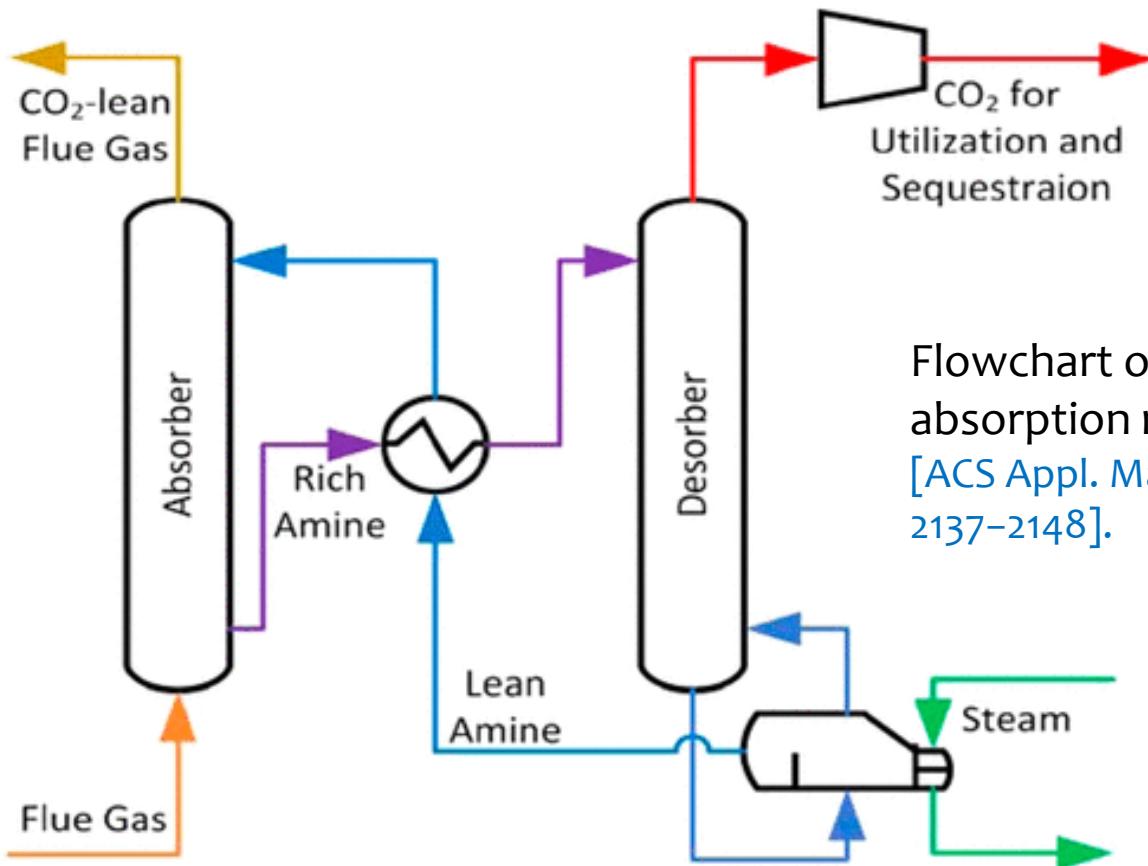
k_0
absorption capacity
reaction rate
viscosity

heat of reaction
sensible heat
heat of vaporization
regeneration energy

technical-economic analysis and life cycle assessment

A **biphasic amine CO₂ capture system** exploits controlled phase separation to concentrate CO₂ in one liquid phase, allowing energy-efficient regeneration and high capture performance — a promising step toward scalable, low-cost carbon capture technologies. (e.g. 2-(Diethylamino)ethanol (DEEA)/3-(Methylamino)propylamine (MAPA))

Reduced regeneration energy (only the CO₂-rich fraction requires heating), Higher cyclic capacity, Lower solvent loss (limited water content reduces evaporation), Enhanced CO₂ loading (phase separation can increase effective capacity).

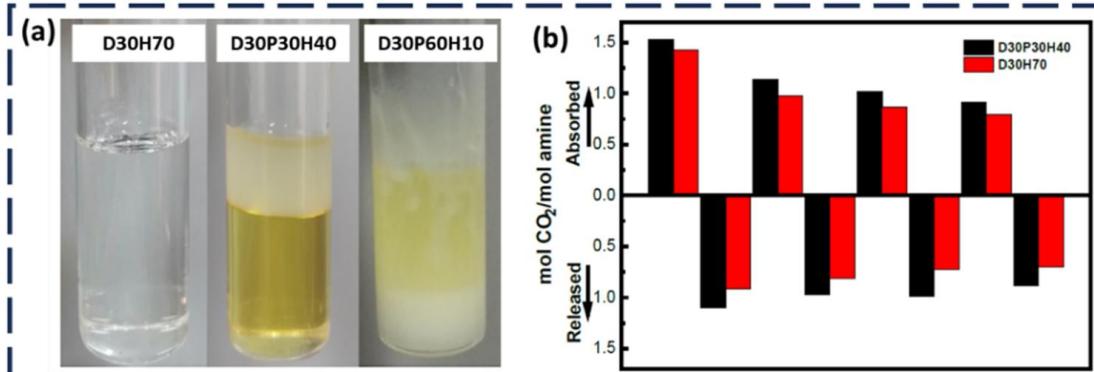


Flowchart of CO₂ capture by a chemical absorption method based on a SHA amine
 [ACS Appl. Mater. Interfaces 2015, 7 (4), 2137–2148].

- ✓ Sterically hindered amines exhibit higher CO₂ absorption capacity because steric hindrance favours bicarbonate formation, although their reaction rate with CO₂ is slower than that of conventional amines.
- ✓ Their heat of desorption is lower owing to the instability of reaction products, leading to reduced regeneration energy requirements.
- ✓ Sterically hindered amines show superior regeneration performance, maintaining stable cyclic capacity over multiple capture–release cycles.

Here are several commercial or near-commercial processes and technologies that employ **sterically hindered amines (SHAs)** for CO₂ capture. Although many are designed for flue gas rather than direct air capture (DAC), they illustrate how SHAs are being applied in real industrial settings.

Company / Process	Solvent (SHA) or concept	Application	Example / scale & status	Key performance note
Mitsubishi Heavy Industries (KM-CDR™ / KS-1™, KS-21)	KS-1™ and newer KS-21 (proprietary sterically hindered amine solvents)	Post-combustion flue gas capture (point sources)	First commercial KS-1 unit delivered 1999 (Malaysia fertilizer plant). Multiple commercial units; large retrofits/demos (e.g., projects capturing ~1.4–1.6 MtCO ₂ /yr reported for major power projects). (Mitsubishi Heavy Industries, Ltd.)	Lower steam/regen energy vs MEA (published/industry estimates ~30–40% lower steam duty; regeneration energy ≈2–3 GJ/tCO ₂ in many reports). (Thunder Said Energy)
ExxonMobil (FLEXSORB™ / FLEXSORB SE)	Proprietary severely sterically hindered amines (gas-treating solvents)	Gas treating (selective H ₂ S removal in presence of CO ₂), industrial gas streams	Proven commercial technology used in >100 units worldwide in refining and gas processing. (exxonmobilchemical.com)	Engineered for selective removal and low solvent circulation; demonstrates industrial robustness of sterically hindered amine chemistries (H ₂ S/CO ₂ separations). (exxonmobilchemical.com)
Decarb Technologies / Decarb (small companies working with SHA-like solvents)	Proprietary water-lean / SHA-class solvent blends (company claims)	Landfill gas, industrial off-gases (commercial/pilot)	Company webpages and pilot claims: >90% capture from landfill gas in pilots; claims 30–45% lower energy vs conventional systems (company data). Status: pilot → early commercial claims. (Decarb Technologies Corp.)	Shows industry interest in water-lean SHA blends to reduce regeneration energy and solvent losses; public metrics are company-reported and need independent verification. (Decarb Technologies Corp.)
Various patented solvent concepts (academic & industry patents)	Hindered amines / promoter-amine blends / phase-separating systems	Flue gas / gas treating / concept for DAC	Multiple patents (e.g., ExxonMobil US9707512B2; EP0705637A1) describe using SHAs, promoters, or phase-separating hindered amines for improved uptake, kinetics or phase change behavior. (Google Patents)	Patents show strategies to improve SHA kinetics (promoters), induce phase separation (biphasic/phase-change) and tailor regeneration energy — many concepts at pilot / IP stage. (Google Patents)



(c)

MEA (monoethanolamine)

MAE (2-(methylamino)ethanol)

EAE (2-(ethylamino)ethanol)

DEA (diethanolamine)

BAE (2-(butylamino)ethanol)

Glycol ethers

EGME (ethylene glycol monomethyl ether)

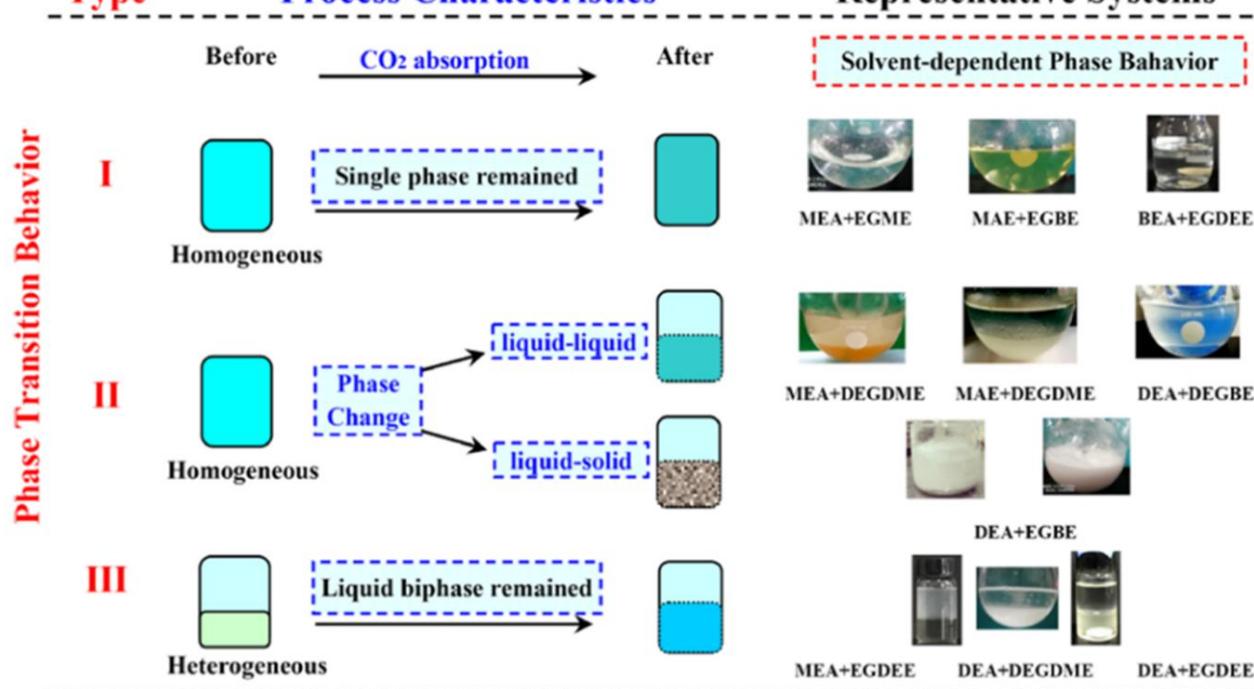
EGEE (ethylene glycol monoethyl ether)

EGBE (ethylene glycol monobutyl ether)

EGDEE (ethylene glycol diethyl ether)

DEGBE (diethylene glycol monobutyl ether)

DEGDME (diethylene glycol dimethyl ether)



(a) Phase separation indications of DETA/1-propanol/H₂O solutions after CO₂ absorption, where the ratio is indicated by the first alphabet of the component followed by the component's percentage. (b) CO₂ absorption/desorption performance for D₃₀P₃₀H₄₀ and D₃₀H₇₀ for 4 cycles. (Conducted at 20 °C and 120 °C for absorption and desorption respectively). Readapted with permission. Copyright 2021 Elsevier B.V. (c) Amines and glycol ethers used it the study, and the different phase transition behavior during CO₂ absorption: Type I: single phase before and after CO₂ absorption; Type II: single phase to biphasic (liquid–liquid or liquid–solid) after CO₂ absorption; Type III: liquid dual phase before and after CO₂ absorption.

1. Why MOFs are effective CO₂ adsorbents

- High surface area & porosity: Many MOFs exceed 5000 m²/g, offering enormous adsorption sites.
- Tailorable pore structure: Pore size and shape can be tuned to match CO₂'s kinetic diameter ($\approx 3.3 \text{ \AA}$).
- Functionalization: Organic linkers can be modified with amine, hydroxyl, or other polar groups to enhance CO₂ affinity via hydrogen bonding or dipole–quadrupole interactions.
- Open metal sites (OMS): Unsaturated metal centers (e.g., in Mg-MOF-74, HKUST-1) strongly coordinate CO₂, through Lewis acid–base interactions.

2. Adsorption mechanisms

- Physisorption: Dominated by van der Waals and electrostatic forces (reversible, low regeneration energy).
- Chemisorption: Occurs in amine-functionalized MOFs via carbamate or bicarbonate formation (higher selectivity but harder regeneration).
- Dual-mode sorption: Some MOFs exhibit both modes depending on temperature and pressure.

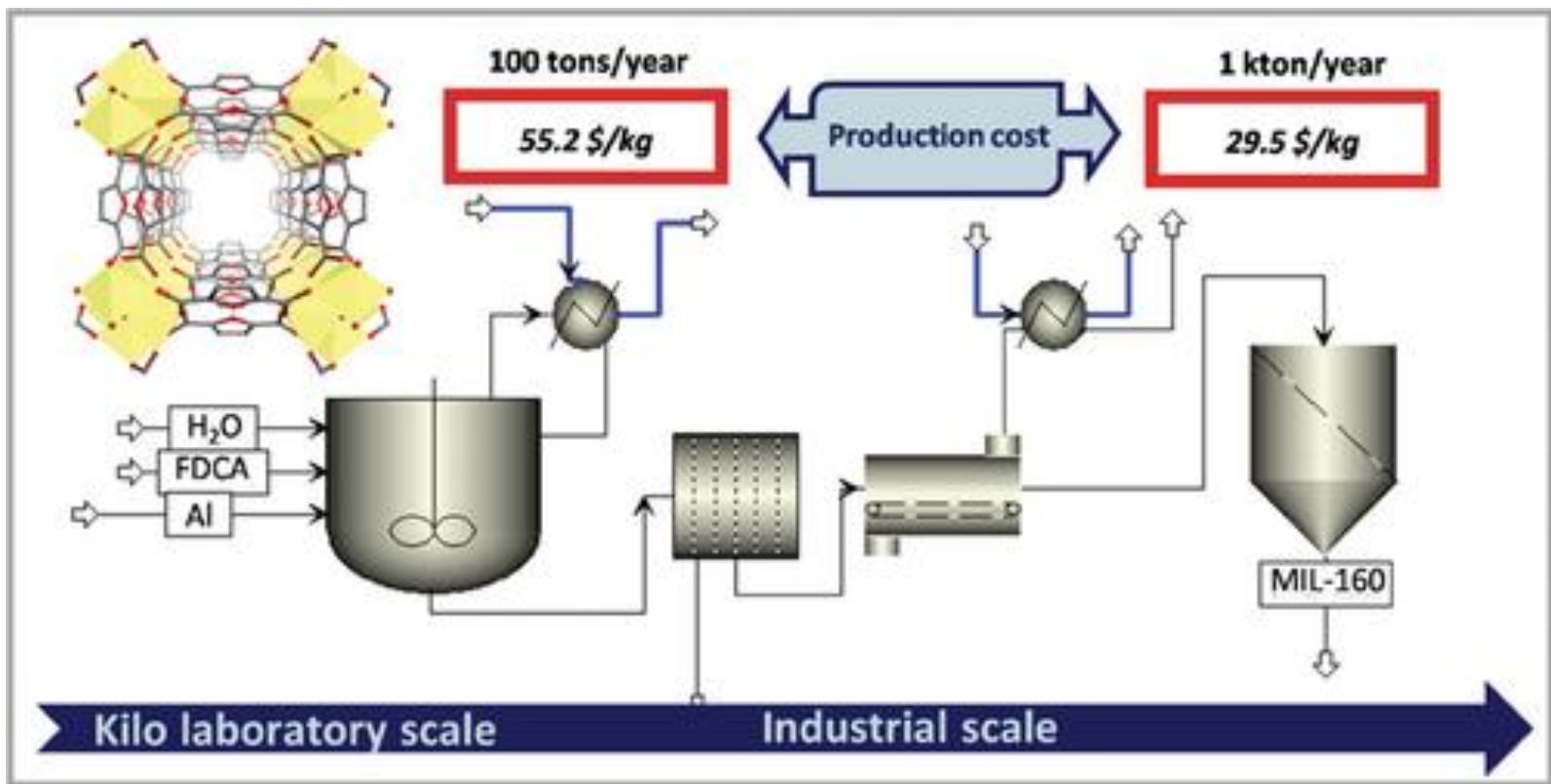
3. Challenges

- Moisture sensitivity: Many MOFs degrade in humid air; stability remains a concern.
- Regeneration cost: Although low for physisorptive MOFs, heat or vacuum regeneration still consumes energy.
- Scalability: Synthesis cost, solvent use, and shaping (pellets, membranes) need optimization for industrial use.
- The inherently low thermal conductivity of many MOFs, combined with the insulating nature of their porous frameworks, limits effective heat transfer during regeneration. This thermal insulation hinders uniform temperature rise throughout the adsorbent bed, thereby slowing the desorption of adsorbed gases and increasing the energy demand for complete regeneration.

4. Emerging directions

- Amine-appended MOFs (e.g., mmen-Mg₂(dobpdc)) for low-pressure CO₂ capture from flue gas.
- Hybrid materials (MOF–graphene, MOF–polymer composites) improving conductivity and moisture tolerance.
- Dynamic MOFs that undergo gate-opening or breathing to enhance selectivity.
- Post-combustion and direct air capture (DAC) applications under realistic humidity and low CO₂ conditions.

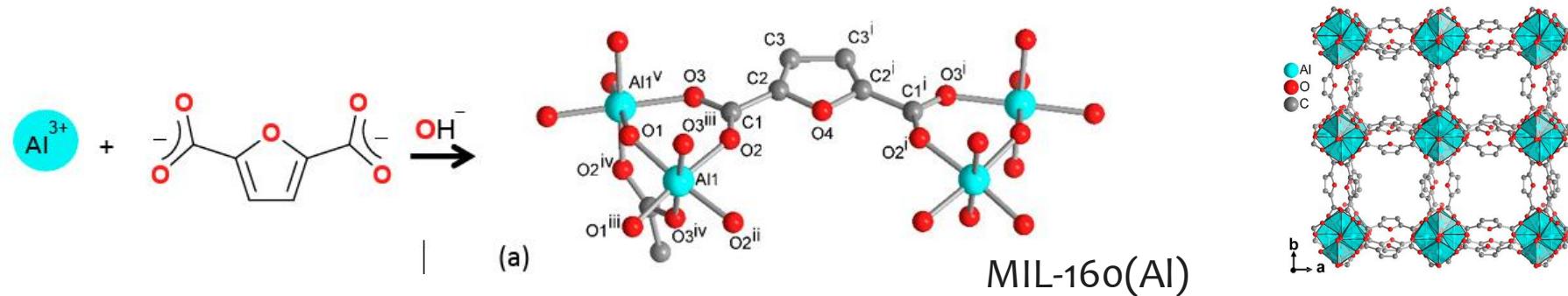
MOF	Key Features	CO ₂ Uptake
Mg-MOF-74 (CPO-27-Mg)	Open Mg ²⁺ sites, strong CO ₂ binding	~8 mmol/g at 298 K, 1 bar
HKUST-1 (Cu-BTC)	Cu paddlewheel nodes, OMS	~6 mmol/g
UiO-66-NH ₂	Zr-based, stable, amine-functionalized	3–4 mmol/g; high selectivity
ZIF-8	Zeolitic topology, robust	Moderate uptake, high stability
SIFSIX-3-Ni	Pillared with SiF ₆ ²⁻ anions, strong electrostatic interaction	Among best CO ₂ /N ₂ selectivity

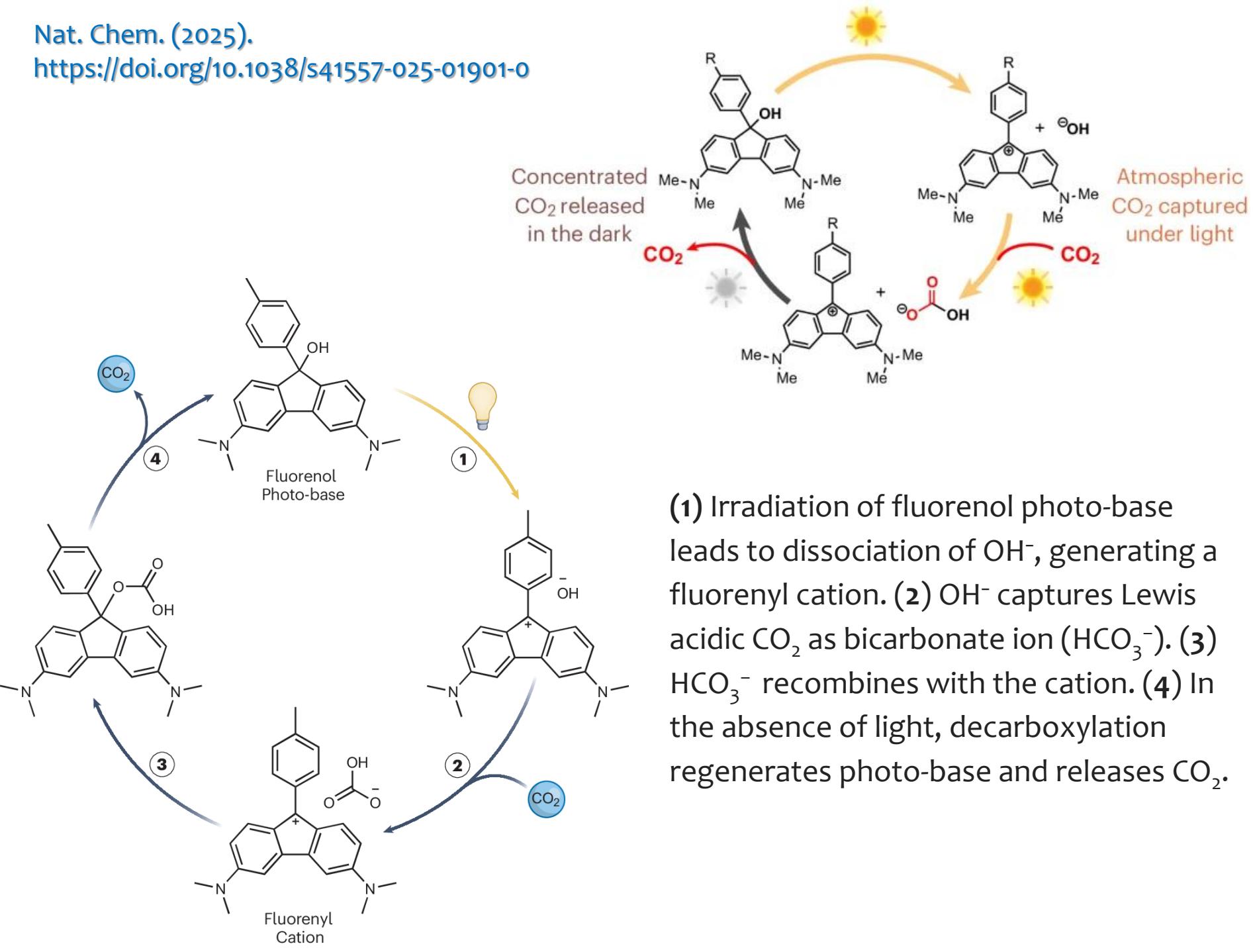


Cost estimation of MIL-160(Al) from laboratory scale to industrial scale.

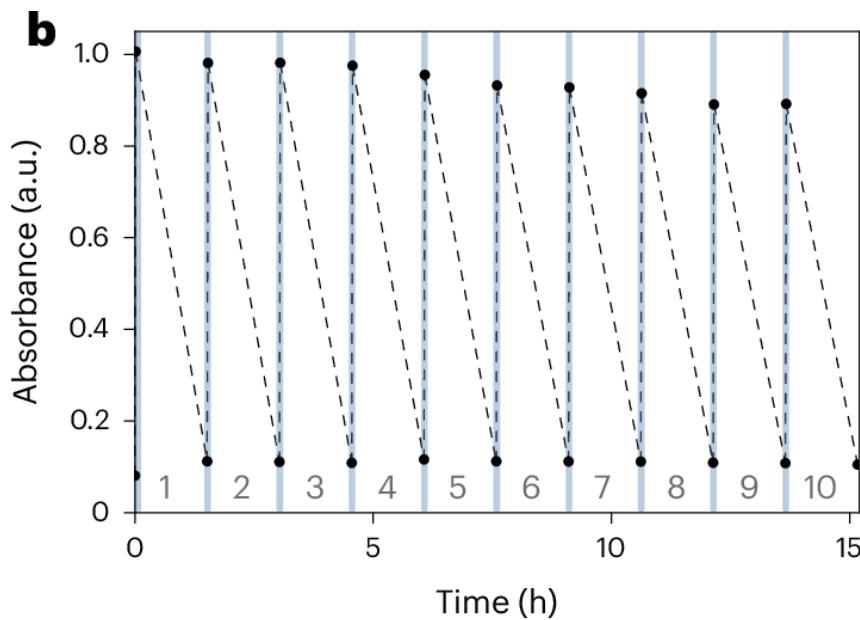
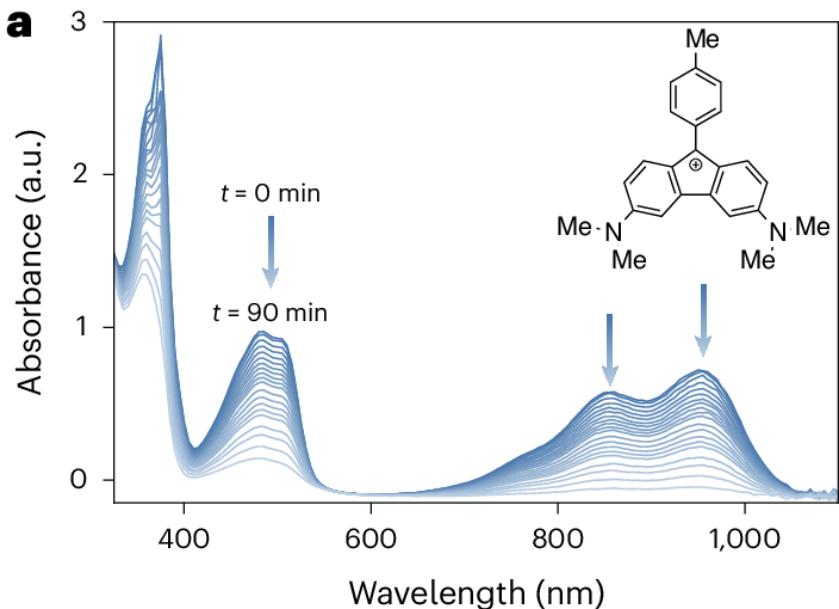
Faraday Discuss., . 2021 Oct 15;231(0):326-341. doi: 10.1039/d1fd00018g.

[Adv. Funct. Mater. 2024, 34, 2309089](#)

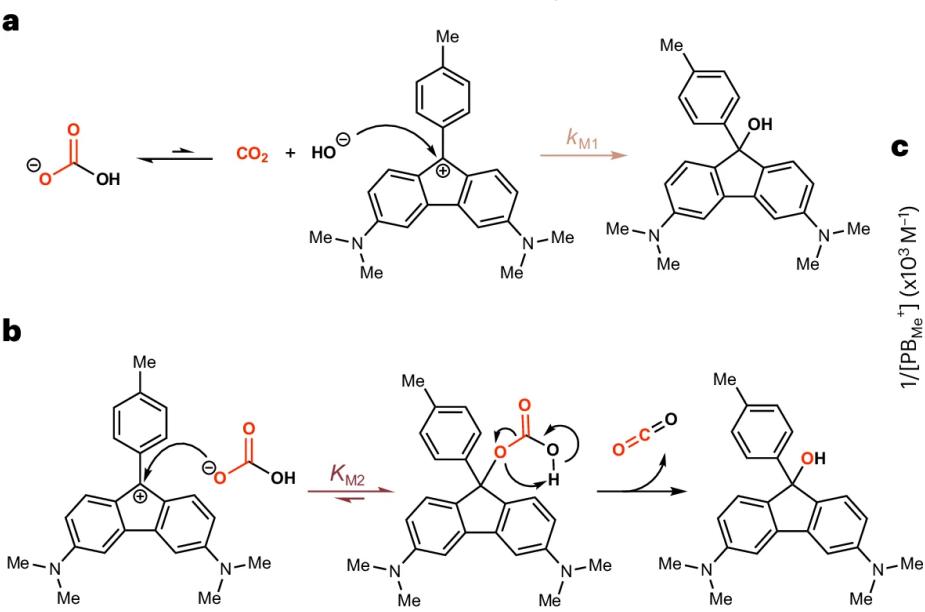




(1) Irradiation of fluorenol photo-base leads to dissociation of OH⁻, generating a fluorenyl cation. **(2)** OH⁻ captures Lewis acidic CO₂ as bicarbonate ion (HCO₃⁻). **(3)** HCO₃⁻ recombines with the cation. **(4)** In the absence of light, decarboxylation regenerates photo-base and releases CO₂.



(a) Decay of photogenerated PB_{Me}^+ cation.



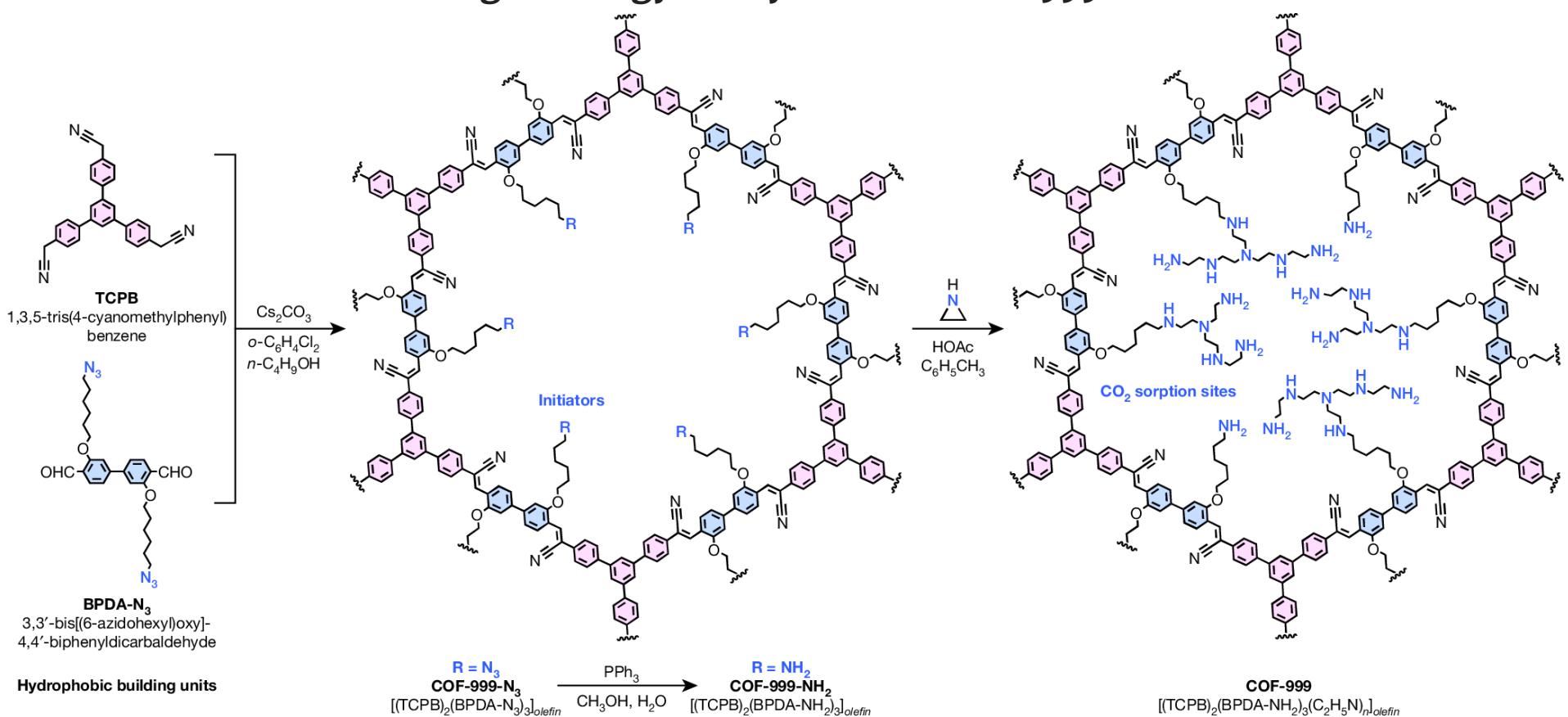
c

$1/[\text{PB}_{\text{Me}}^+] (\times 10^3 \text{ M}^{-1})$

Time (h)

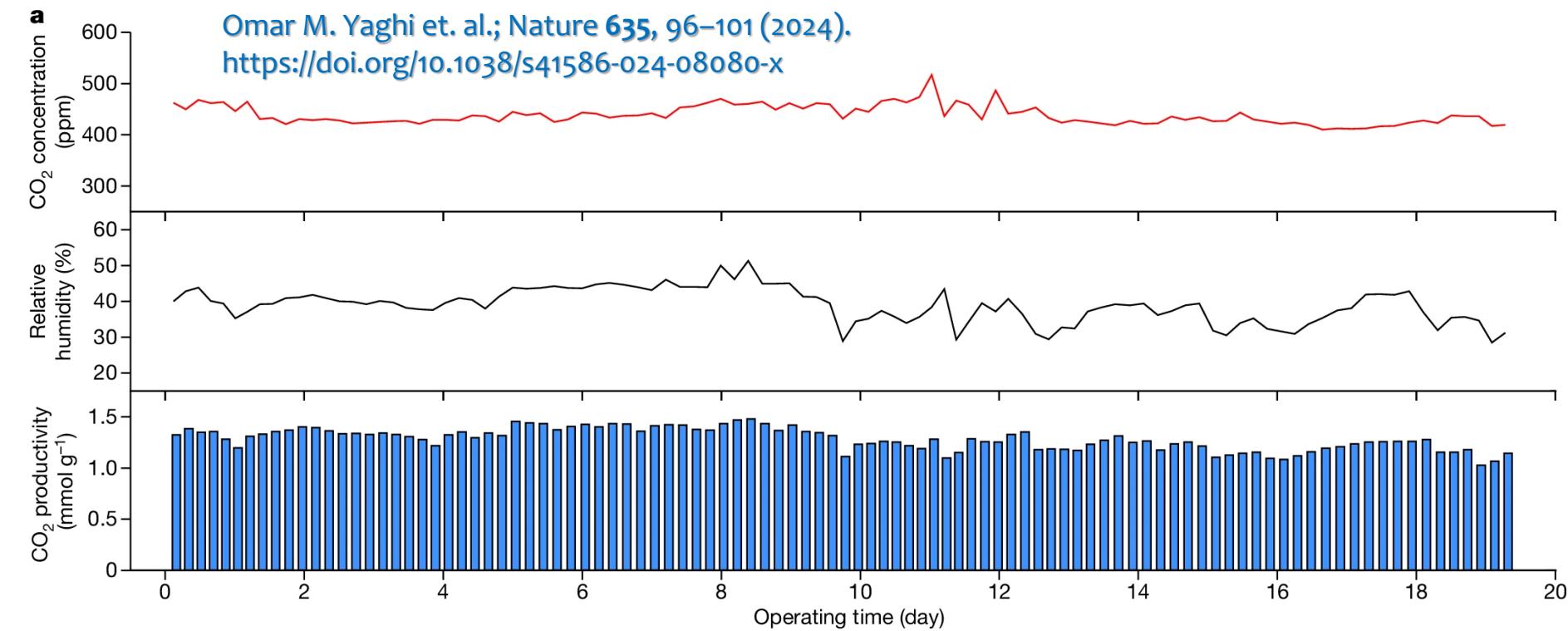
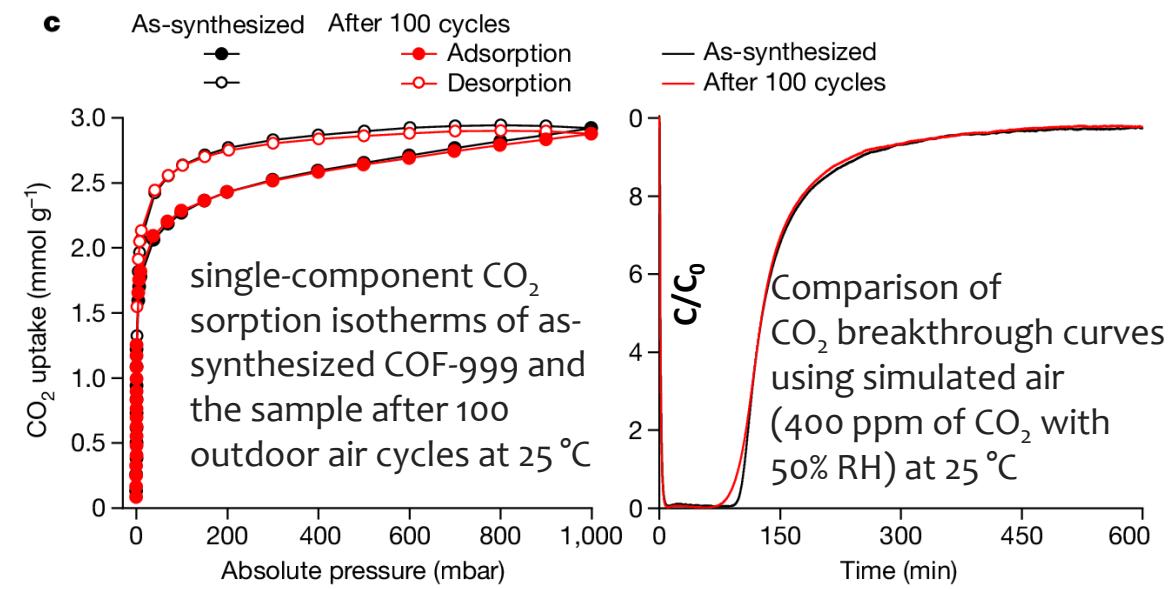
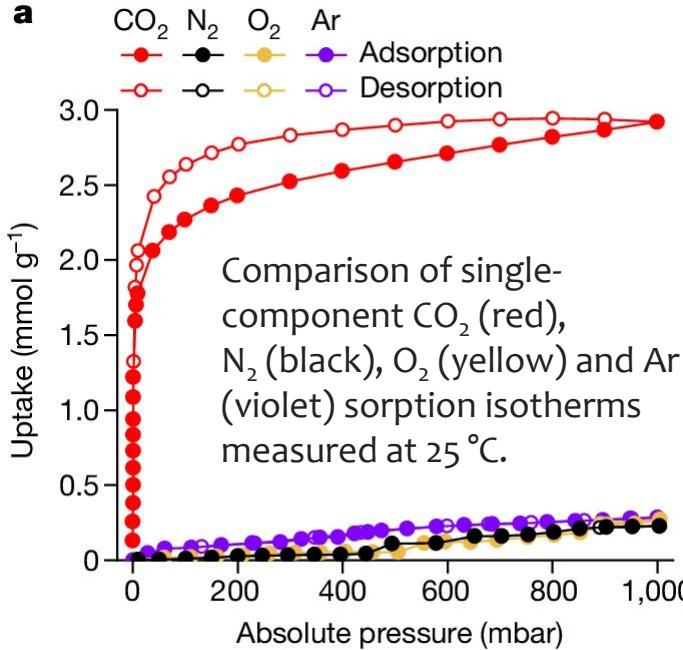
b, Reversible carbocation generation was cycled 10 times over a 15-h period following the rise and decay of the 950-nm absorption peak. Solution is irradiated with 390-nm light (blue region) followed by 90 min in the dark.

Design strategy and synthesis of COF-999



Omar M. Yaghi et. al.; *Nature* **635**, 96–101 (2024).
<https://doi.org/10.1038/s41586-024-08080-x>

COF-999 can capture CO₂ from open air. COF-999 has a capacity of 0.96 mmol g⁻¹ under dry conditions and 2.05 mmol g⁻¹ under 50% relative humidity, both from 400 ppm CO₂. This COF was tested for more than 100 adsorption–desorption cycles in the open air of Berkeley, California, and found to fully retain its performance. COF-999 is an exceptional material for the capture of CO₂ from open air as evidenced by its cycling stability, facile uptake of CO₂ (reaches half capacity in 18.8 min) and low regeneration temperature (60 °C).



Hydrogen Energy

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CH5106

Hydrogen energy involves the use of hydrogen and/or hydrogen-containing compounds to generate energy to be supplied to all practical usages for inclusive growth without compromising the social benefits (human well being), as well as economic competitiveness.

Modern Li-ion batteries have a maximum energy density of ~0.15 to 0.18 kWh per kg.

- Hydrogen: ~33 kWh per kg
- Li-ion: ~0.15 to 0.30 kWh per kg

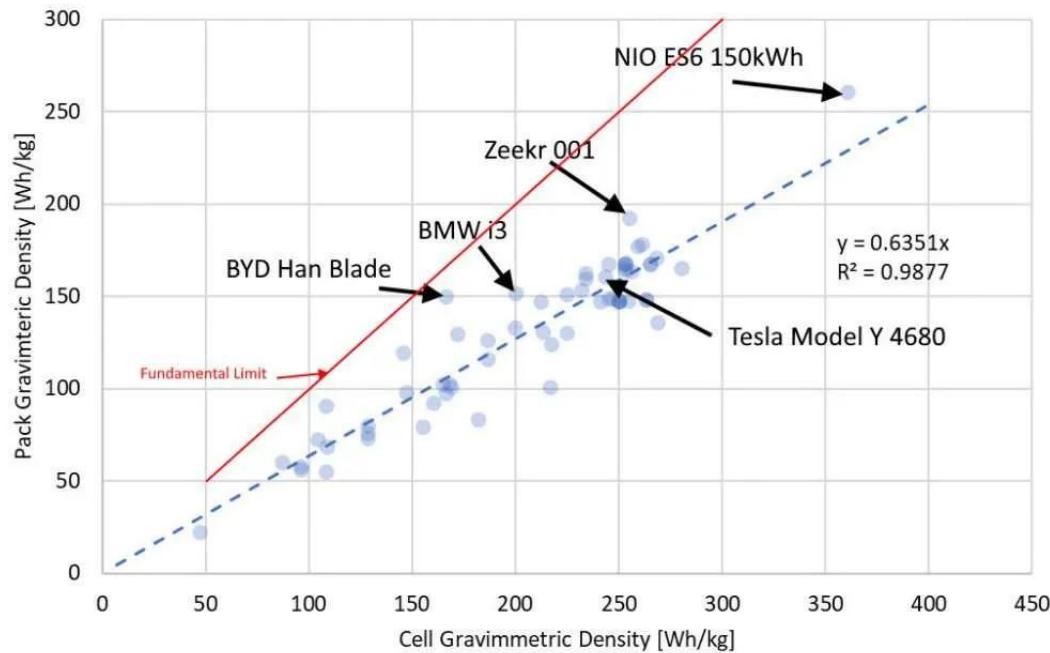
Needed battery mass to match 1 kg of H₂ energy storage:

$$\text{Mass} = \frac{33}{0.15 - 0.30} \approx 110 \text{ to } 220 \text{ kg}$$

- Lead-acid: ~0.037 kWh per kg (roughly)

$$\text{Mass} = \frac{33}{0.037} \approx 892 \text{ kg}$$

<https://www.batterydesign.net/battery-pack-density-fundamental-limit/>



Pack gravimetric energy density: A measure of a battery pack's total energy capacity per unit of weight (Wh/kg).

Cell gravimetric energy density: A measure of the energy per unit of weight for a single cell (Wh/kg).

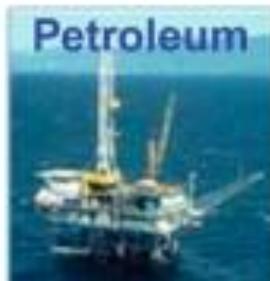
Toward Zero C Emissions



10 atoms of C
for 1 atom of H₂



2 atoms of C
for 1 atom of H₂



1 atom of C
for 2 atoms of H₂

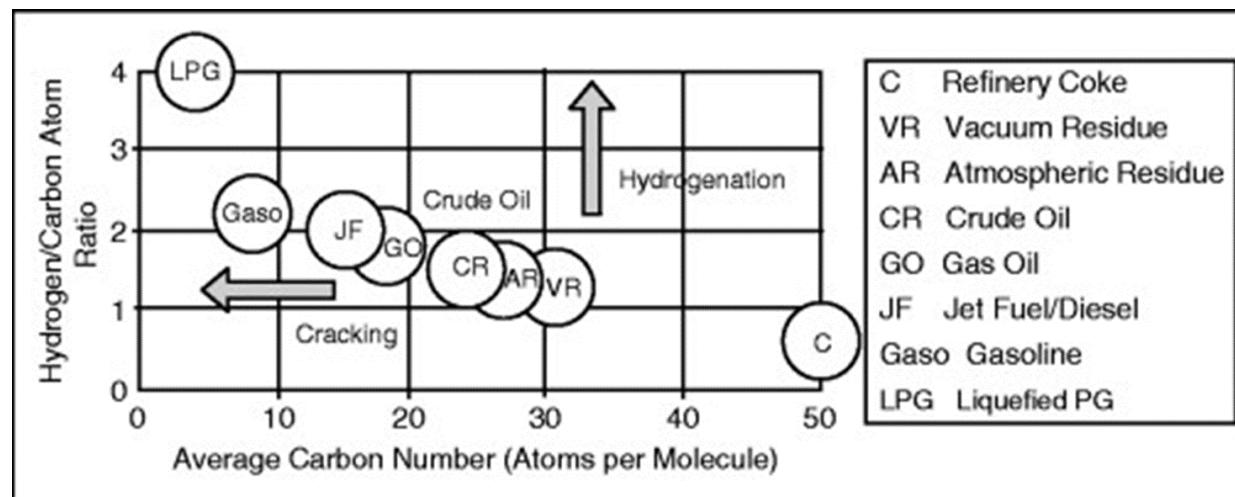


1 atoms of C
for 4 atoms of H₂

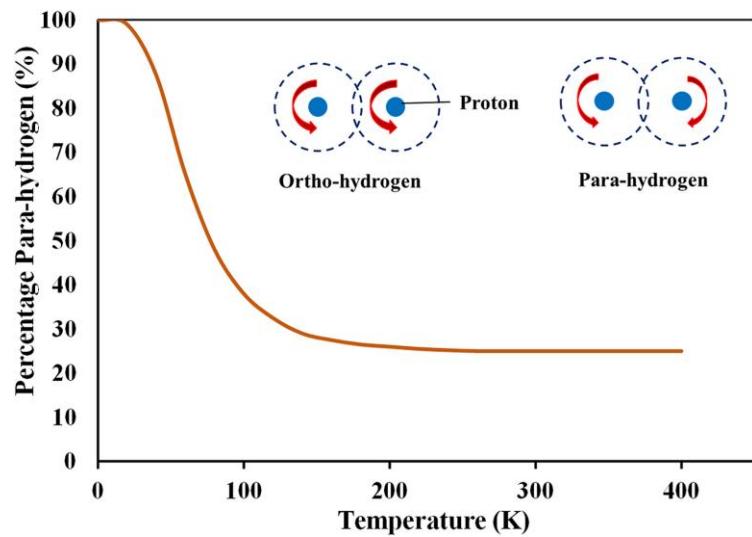


0 atoms of C
for 2 atoms of H₂

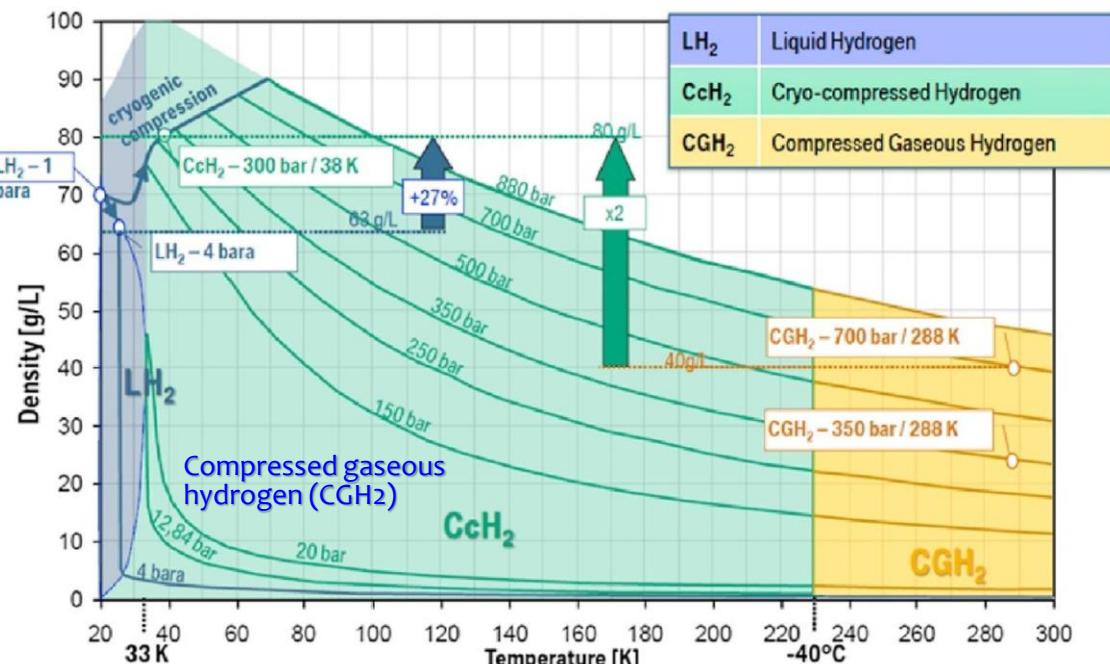
The ratio of the atom numbers of carbon and hydrogen



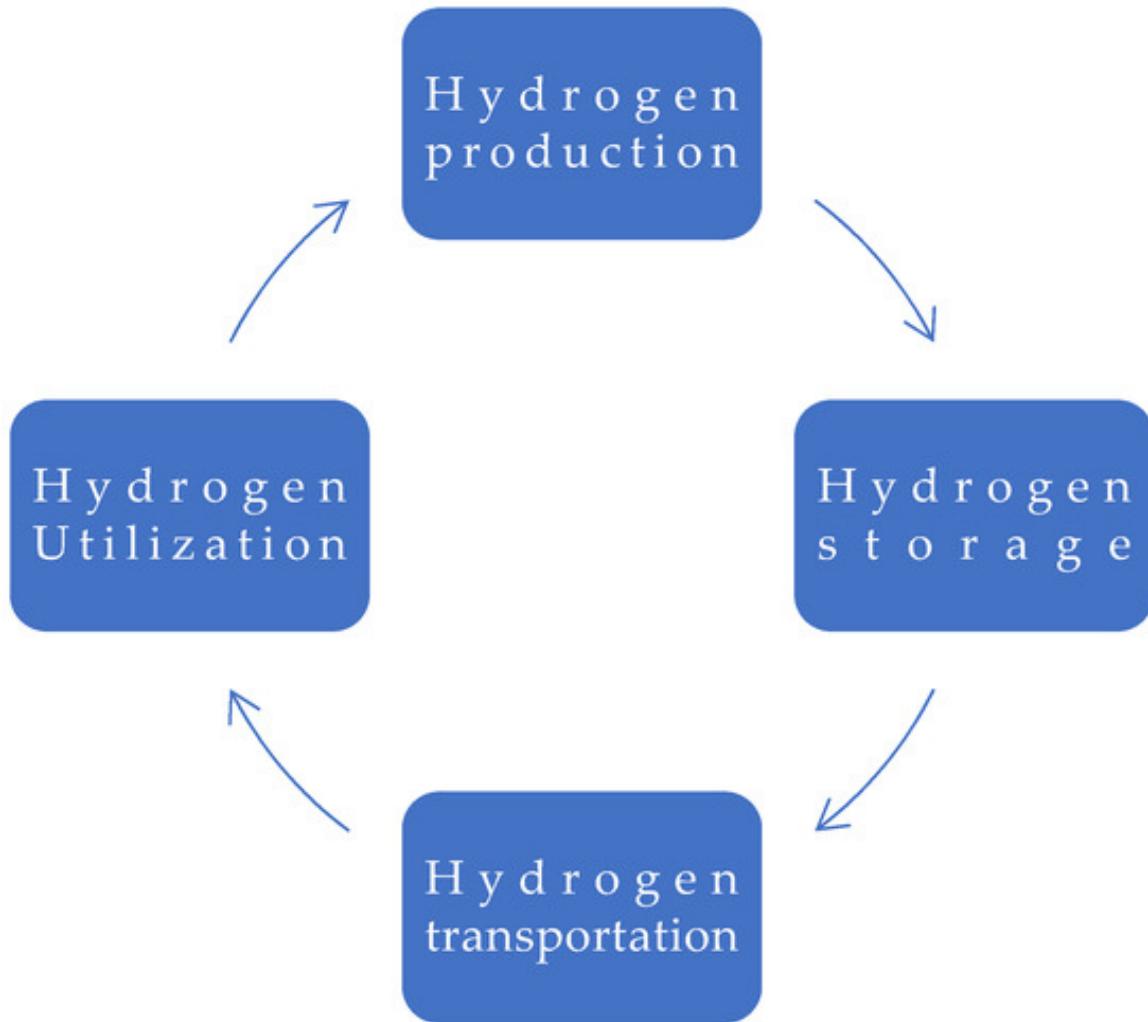
Diatomeric hydrogen (H_2) exists as two spin isomers: ortho-hydrogen (parallel proton spins, $I=1$) and para-hydrogen (antiparallel spins, $I=0$). Proposed by Heisenberg and Hund in 1927, these forms arise from quantum mechanical symmetry of the total wavefunction. At room temperature, the ortho:para ratio is about 3:1, but at low temperatures, para-hydrogen dominates. Their slow interconversion impacts cryogenic hydrogen storage due to the exothermic ortho-to-para transition.



Renewable and Sustainable
Energy Reviews, 2023, 176, 113204



Hydrogen density (y axis) as a function of temperature (x axis) and pressure (iso-lines) for physical based storage



The **ideal storage medium** should allow high volumetric and gravimetric energy densities, quick uptake and release of fuel, operation at room temperatures and atmospheric pressure, safe use, and balanced cost-effectiveness.

How is hydrogen stored?

Physical-based

Compressed Gas



Cold/Cryo Compressed



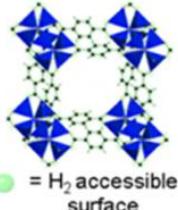
Liquid H₂



Material-based

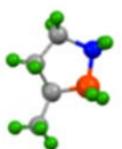
Adsorbent

Ex. MOF-5



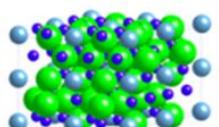
Liquid organic

Ex. BN-methyl cyclopentane



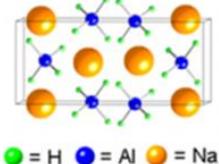
Interstitial hydride

Ex. LaNi₅H₆



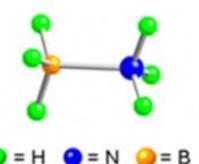
Complex hydride

Ex. NaAlH₄

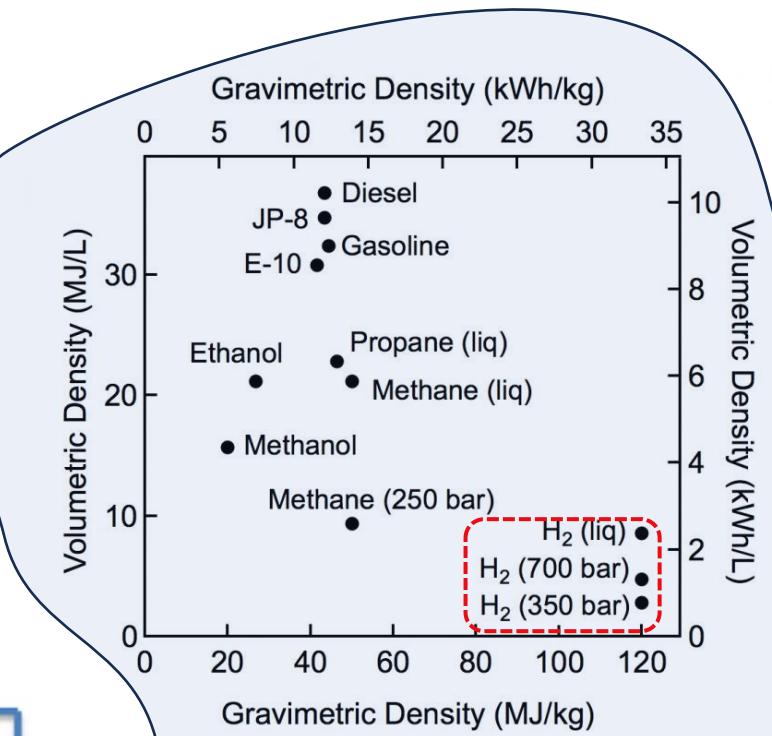


Chemical hydrogen

Ex. NH₃BH₃



Material-based



Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels based on lower heating values.

The Hydrogen and Fuel Cell Technologies Office (HFTO) is pursuing two strategic pathways: near-term and long-term solutions. The near-term approach focuses on compressed gas storage using advanced fiber-reinforced pressure vessels (up to 700 bar) with emphasis on cost reduction. The long-term approach targets (1) cold or cryo-compressed hydrogen storage with higher density and insulated vessels, and (2) materials-based storage technologies such as sorbents, chemical hydrides, and metal hydrides to meet DOE targets.

Targets are set with stakeholder input to ensure competitiveness and guide R&D efforts, shaping HFTO's activity portfolio. Examples include the following.

[efaidnbmnnibpcajpcglclefindmkaj/https://www.energy.gov/sites/default/files/2024-05/hfto-mypp-executive-summary.pdf](https://www.energy.gov/sites/default/files/2024-05/hfto-mypp-executive-summary.pdf)

Clean H₂ production:

- \$2/kg by 2026; \$1/kg by 2031

Electrolyzer systems (low temperature):

- 2026: \$250/kW, 65% efficiency, 80,000-hour durability

Electrolyzer systems (high temperature):

- 2026: \$500/kW, 76% efficiency, 40,000-hour durability

H₂ dispensed for heavy-duty transportation:

- 2028: <\$7/kg

Fuel cell manufacturing for heavy-duty transportation:

- 2030: 20,000 stacks/year (single manufacturing system)

Fuel cell systems for heavy-duty transportation:

- 2030: \$80/kW, 25,000-hour durability

STORAGE PARAMETER	UNITS	2020	2025	ULTIMATE
System Gravimetric Capacity				
Usable, specific-energy from H ₂ (net useful energy/max system mass) ^b	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 (0.055)	2.2 (0.065)
System Volumetric Capacity				
Usable energy density from H ₂ (net useful energy/max system volume) ^b	kWh/L (kg H ₂ /L system)	1.0 (0.030)	1.3 (0.040)	1.7 (0.050)
Storage System Cost				
Storage system cost	\$/kWh net (\$/kg H ₂)	10 (333)	9 (300)	8 (266)
Fuel cost ^c	\$/gge at pump	4	4	4

<https://www.energy.gov/ere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles#:~:text=Useful%20constants>

1 kg H₂ ≈ 1 gal gasoline equivalent (gge) on an energy basis. The volume of 1 kg of H₂ gas at N.T.P. is 11.2 m³.

Hydrogen threshold fuel cost is calculated to be competitive with a gasoline hybrid vehicle. It is defined as the untaxed cost of hydrogen produced, delivered, and dispensed to the vehicle. For material-based storage technologies, the impact of the technology on the hydrogen threshold fuel cost (e.g., off-board cooling, off-board regeneration of chemical hydrogen storage materials, etc.) must be considered.

The MYPP (Multi-Year Program Plan) outlines HFTO's pathways to meet its targets, analyzing key factors in each area and showing how funded efforts address them. For example, this figure highlights major fuel cell cost drivers and potential reductions across manufacturing, power density, components, and durability, with similar charts for electrolyzers and hydrogen storage systems.

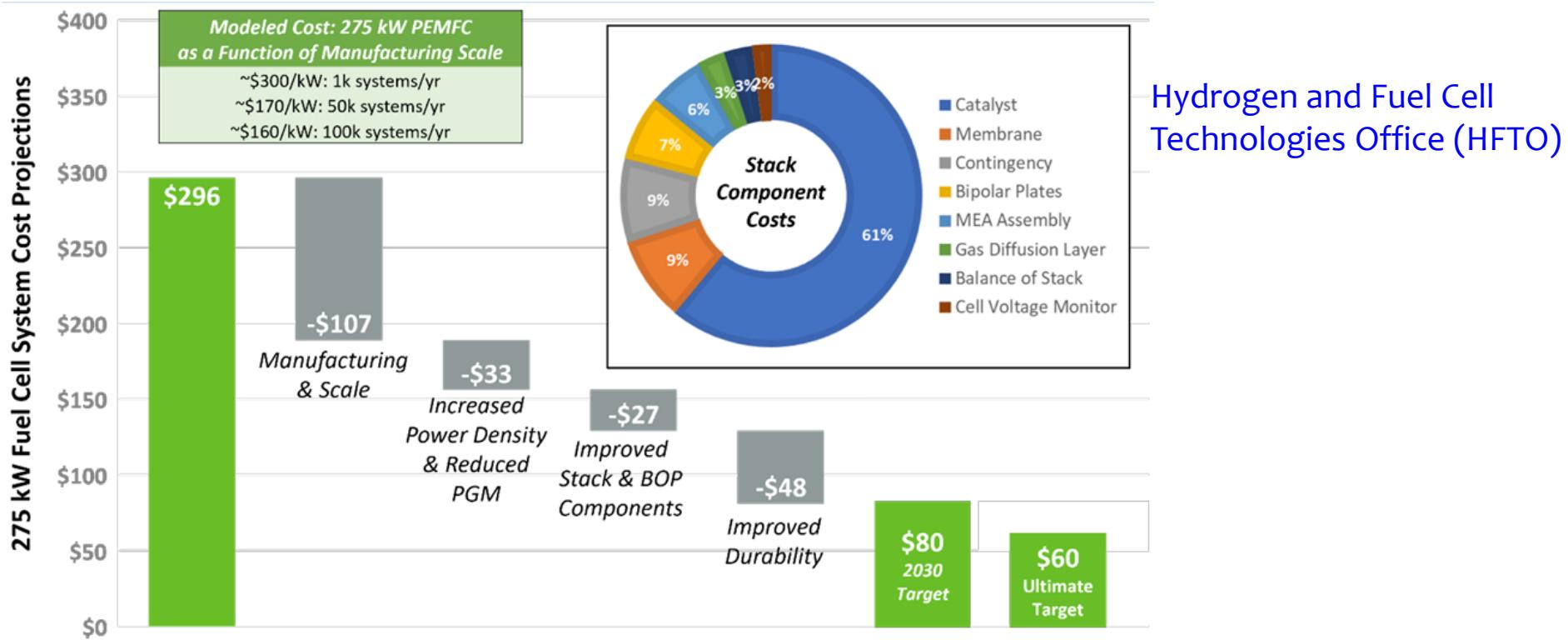
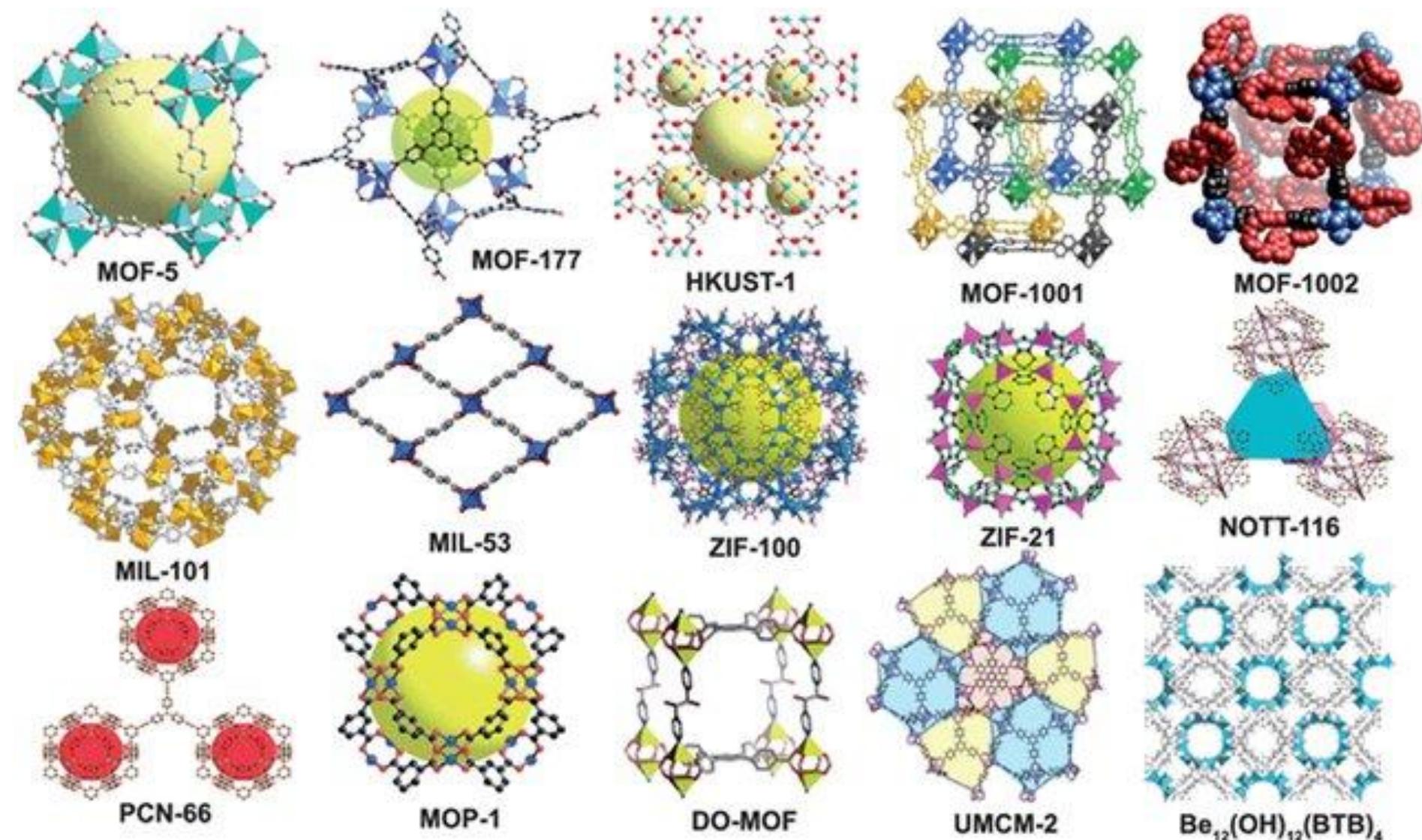
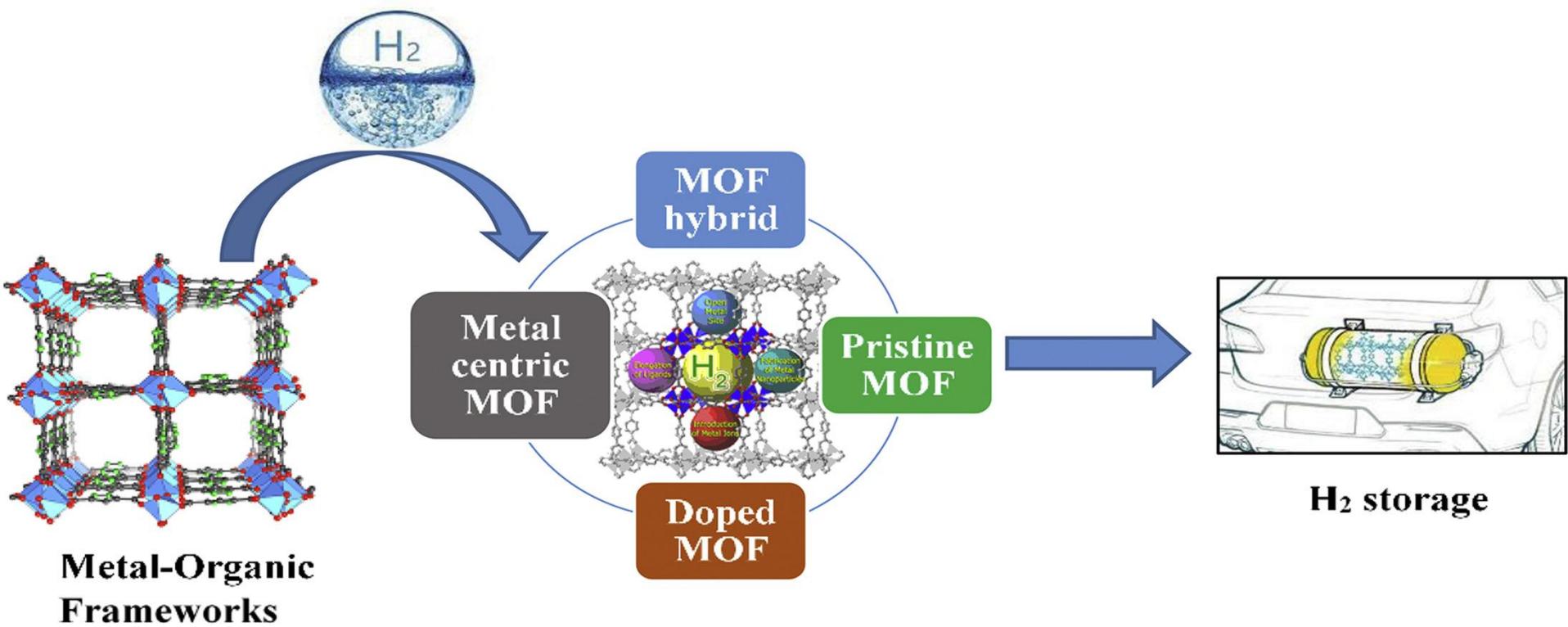


Figure ES.2. Example of “waterfall” chart showing pathways to meeting HFTO cost-reduction targets

[efaidnbmnnibpcajpcglclefindmkaj/https://www.energy.gov/sites/default/files/2024-05/hfto-mypp-executive-summary.pdf](https://www.energy.gov/sites/default/files/2024-05/hfto-mypp-executive-summary.pdf)





Challenges associated with MOF-based H₂ storage:

The hydrogen storage capacity is 7.1 wt.% at 77 K and 40 bar; 10 wt.% at 100 bar; corresponding to 66 g·l⁻¹. The fueling process is quite fast.

Issues: Low thermal conductivity of (0.3 W/(mK)) of MOFs represents an additional challenge for the thermal management in the design of MOF-based storage systems.

The actual 2025 DOE hydrogen storage objectives is a part of the broader U.S. DRIVE initiative, set standards for the complete H₂ storage system. The targets address the need for a balanced approach to storage, considering gravimetric capacity (weight), volumetric capacity (volume), and operational conditions.

<https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles#:~:text=Useful%20constants>

For technological applications, rapid kinetics and full reversibility enable short refuelling times and high cycle life, and so exploration into physisorption in materials is an important area. [Journal of Alloys and Compounds 827 \(2020\) 153548](#)

Liquid hydrogen is the most conceptually simple means of hydrogen storage; however, the complexity and cost associated with the extremely low temperature (20 K) required for hydrogen liquefaction has prompted the consideration of other liquid carriers with moderate storage conditions.

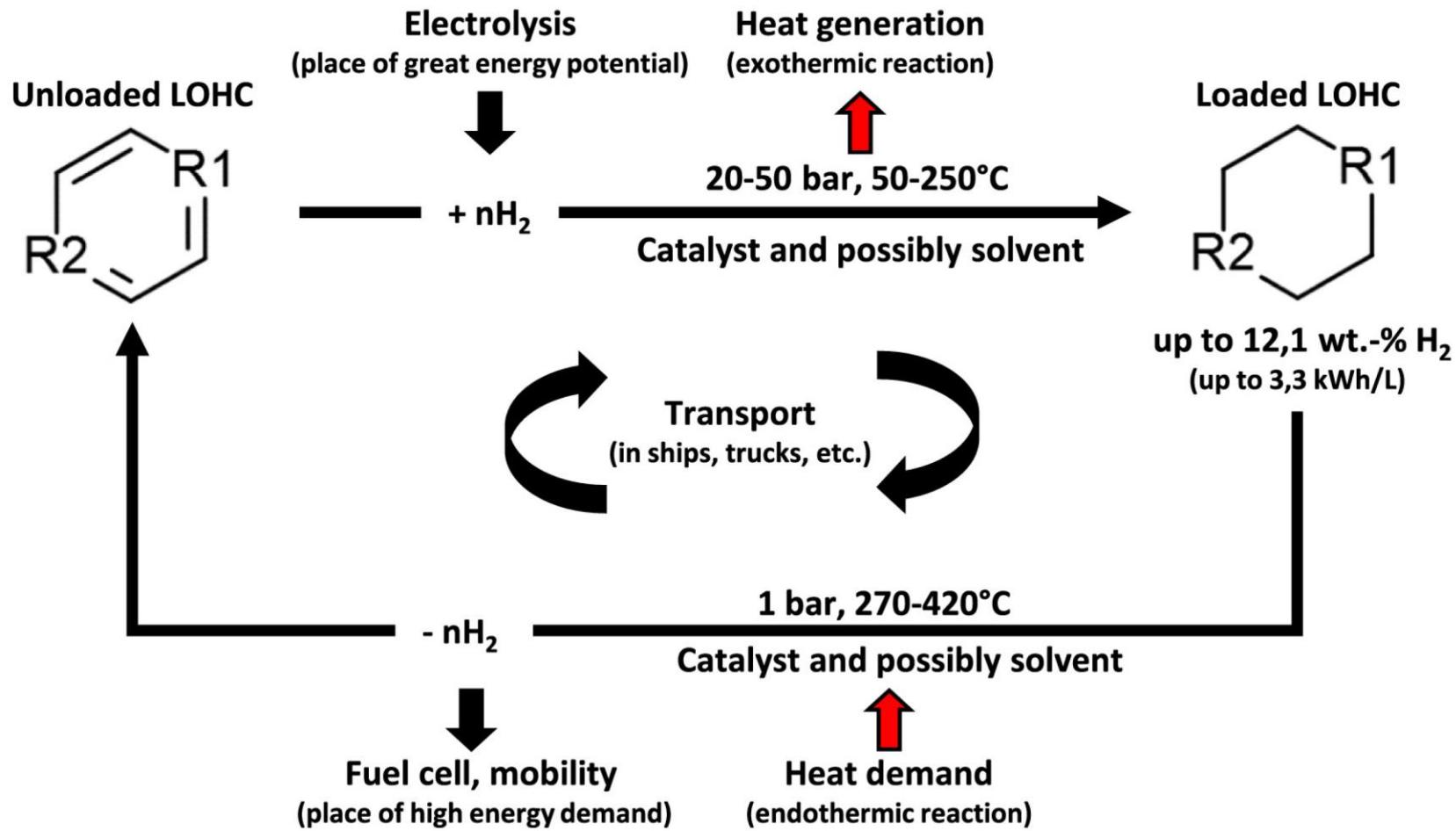
Most attention has been given to two carriers in particular:

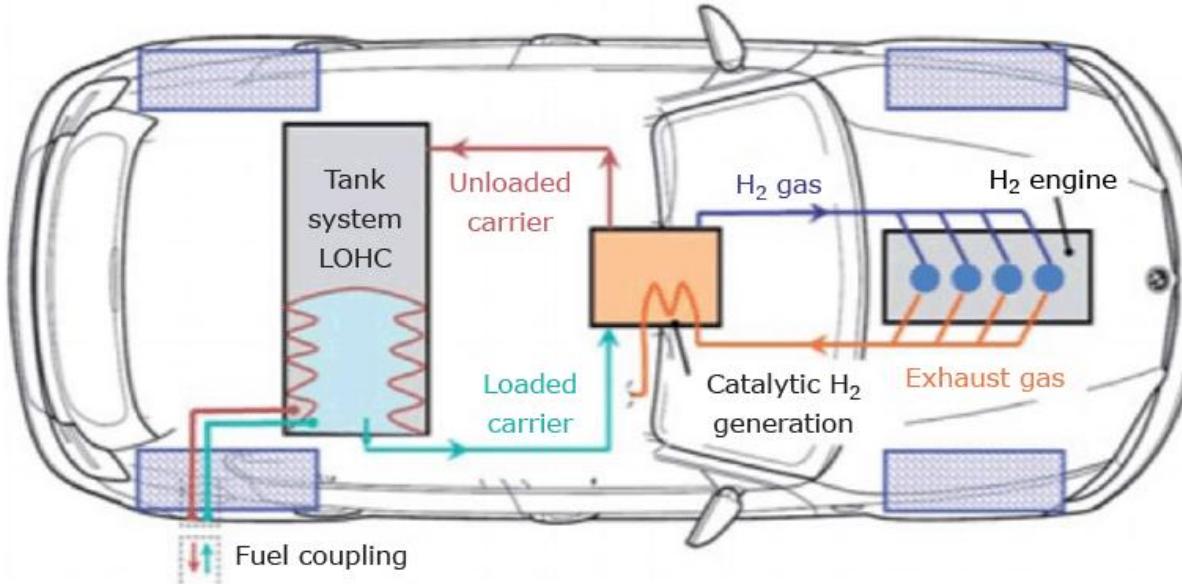
Liquid organic hydrogen carriers (LOHCs) and ammonia. Both have moderate storage requirements and storage costs compared to liquid hydrogen. This has led to the active development of hydrogen supply chains based on conversion to these carriers.

David Milstein & Coworkers, Nature Commun. 2015, 6:6859; DOI: 10.1038/ncomms7859;

Chem. Eur. J. 2020, 26, 15487 – 15490

Päivi T. Aakko-Saksa & Coworkers; Journal of Power Sources, 396 (2018) 803–823



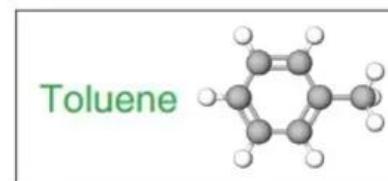
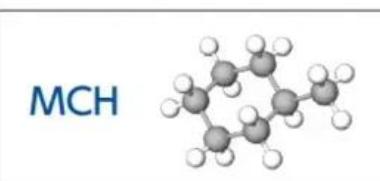
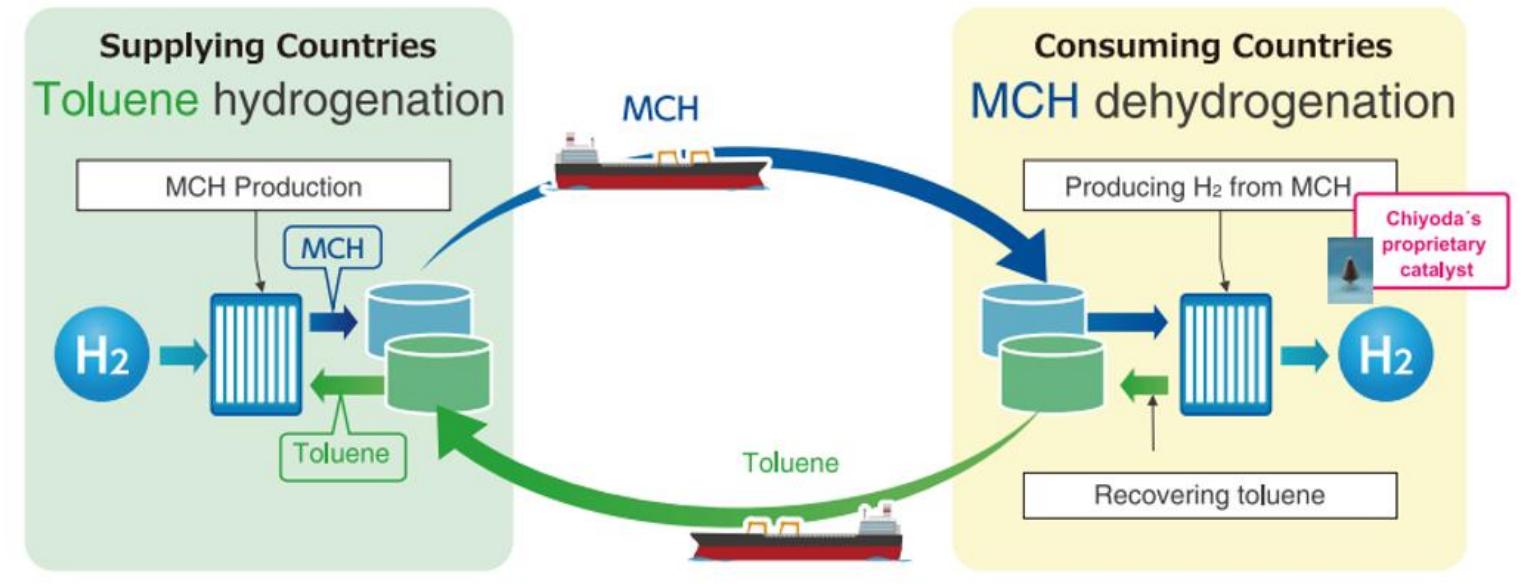


Johnson Matthey Technol. Rev., 2022, 66, (3), 259–270

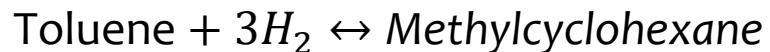
Advantageously, onboard storage of hydrogen in the LOHC would resemble that of gasoline and diesel (liquid state of the LOHC at ambient pressures), which is widely understood, and the safety hazards of storing high-pressure hydrogen are removed. Moreover, a range of 500 km is reportedly achievable using 100 lit of NEC loaded with hydrogen (equivalent to 5 kg of hydrogen) as the LOHC.

Hyundai Motor Company, South Korea, has recently announced plans to develop an onboard LOHC storage technology. This encompasses a partnership with **Hydrogenious LOHC Technologies GmbH**, Germany, which will supply dibenzyl toluene to be used as the LOHC. Initially, the technology will be introduced in South Korea, before being extended to the European market. The development of LOHC-compatible automobiles is expected to raise the profile of the technology as an important tool in the transition to the hydrogen economy [Johnson Matthey Technol. Rev., 2022, 66, (3), 259–270].

Chiyoda Corporation

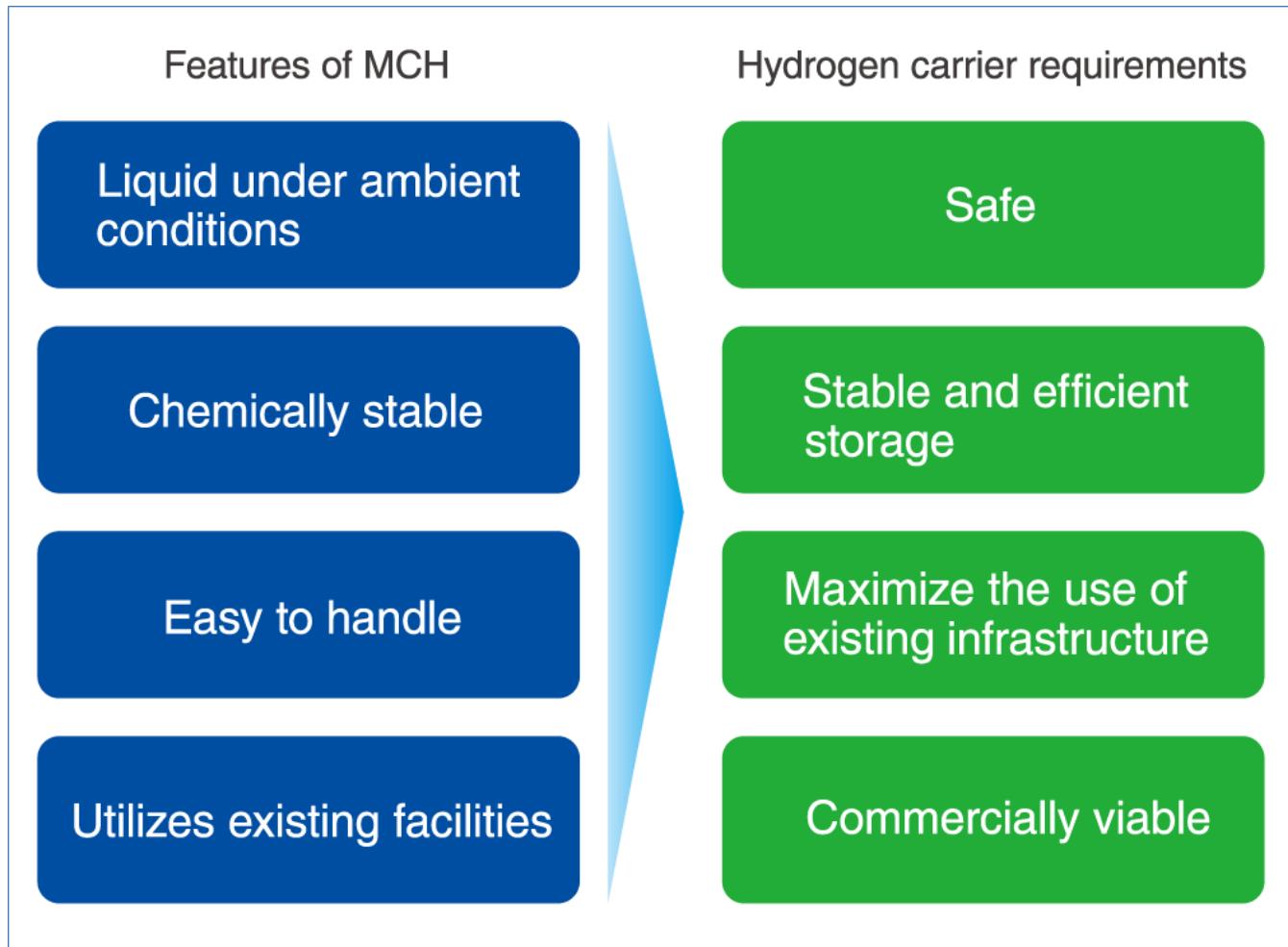


Methylcyclohexane (MCH) is commonly used as a hydrogen carrier in LOHC technology. It stores hydrogen chemically by hydrogenating toluene to form MCH:



https://www.chiyodacorp.com/en/purposesstory/co-creation/spera-hydrogen/?utm_source=chatgpt.com

Chiyoda has developed technology to safely and efficiently store and transport hydrogen using Methylcyclohexane (MCH) as a Liquid Organic Hydrogen Carrier (LOHC) and termed it the ‘SPERA Hydrogen System’ (after “Spera” : Latin for “Hope”).



Where most commercial / pilot activity is focused (2025)

- **Germany / EU:** multiple demos and funded projects (TransHyDE, One Reactor, HyScale, etc.). [Hydrogenious LOHC Technologies+2](#) [Hydrogenious LOHC Technologies+2](#)
- **Japan:** Chiyoda + industrial partnerships pushing SPERA (MCH) for import/export chains and domestic supply. [Chiyoda Corporation](#)
- **Startups & new entrants:** Ayrton Energy (e-LOHC), Honeywell/ENEOS collaborations, and other private investments target commercialization & localized pilots.
- A position-paper states: “Hydrogen carrier technologies—including LOHCs already have a high technology readiness level (TRL 7 or higher as defined by the International Energy Agency/IEA) of the full value chain including hydrogen conversion and reconversion.” [ess.honeywell.com](#)
- The EU’s H2020 call for LOHCs specified: technology starting at TRL 4 and expected to reach **TRL 6** at the end of the project (for demonstration of distribution/storage chain) in the given timeframe. [CORDIS](#)
- According to a recent article: LOHC technology “is being commercialised by Hydrogenious LOHC Technologies ... Having completed the technological proof of concept for LOHC...” [mission-innovation.net](#)

Liquid Organic Hydrogen Carriers are an advanced hydrogen storage technology that utilizes reversible chemical processes to store and release hydrogen. Through hydrogenation, hydrogen molecules are chemically bound to LOHC compounds, significantly enhancing gravimetric and volumetric storage capacities. When needed, hydrogen is released via a dehydrogenation process. Ideal LOHCs are liquid at ambient conditions, safe, cost-effective, and non-toxic, simplifying handling and transportation. Dehydrogenation of LOHCs is normally carried out at temperatures greater than hydrogenation with materials such as perhydro-dibenzyltoluene usually dehydrogenating around a temperature of about 300 °C, while hydrogenation occurs at lower temperatures (Decreasing the dehydrogenation temperature makes it feasible to integrate with low-temperature waste heat and makes energy efficiency better.

[Renew. Sustain. Energy Rev. 2021, 135, 110171](#)

Heat
 $T = 150\text{--}300^\circ\text{C}$
 $\approx -9 \text{ kWh}_{\text{th}}/\text{kg H}_2$

9 H₂

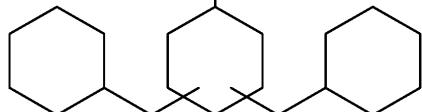
Dibenzyl-toluene as an organic liquid hydrogen carrier (LOHC) molecule.
Materials 2020, 13, 277; doi:10.3390/ma13020277

H₂-Storage
CATALYTIC HYDROGENATION

$P > 20 \text{ bar}$

LOHC⁺ (18H-DBT)

Perhydro-Dibenzyltoluene

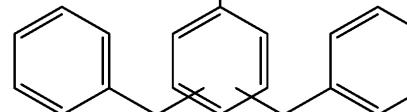


$T_{\text{boil}} = \text{ca. } 370^\circ\text{C}$
(1 atm)

Multi phase
reaction

LOHC⁻ (0H-DBT)

Dibenzyltoluene



$T_{\text{boil}} = \text{ca. } 390^\circ\text{C}$
(1 atm)

$P < 5 \text{ bar}$

H₂-Release
CATALYTIC DEHYDROGENATION

$\approx 16.1 \text{ kg LOHC}^+/\text{kg H}_2$
 $\approx 17.5 \text{ L LOHC}^+/\text{kg H}_2$

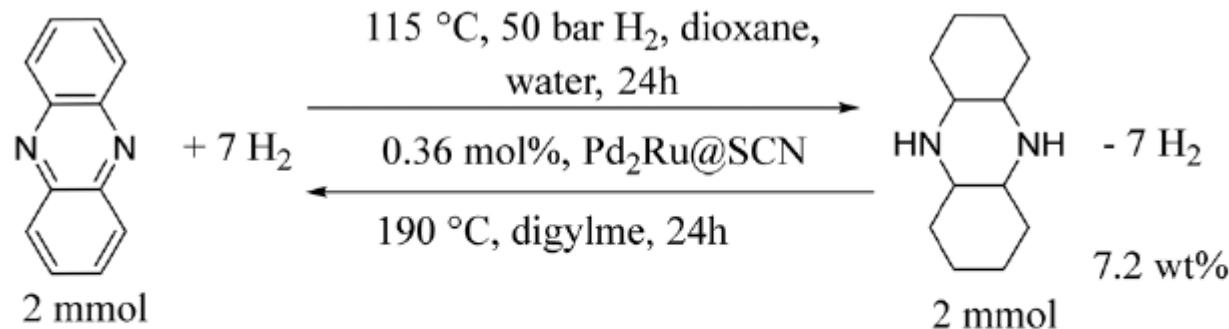
Heat
 $T = 250\text{--}320^\circ\text{C}$
 $\approx +9 \text{ kWh}_{\text{th}}/\text{kg H}_2$

9 H₂

Dibenzyl and benzyl toluenes were introduced commercially by German company Hydrogenious GmbH (<http://www.hydrogenious.net>). In Japan, Chiyoda Corporation (www.chiyodacorp.com) has demonstrated the use of the toluene LOHC system, called SPERA.

N-Heterocycles are considered as one of the most potential candidate media for the reversible storage and release of hydrogen with high hydrogen storage capacity and low energy barrier for catalytic dehydrogenation.

Developing the decentralized supply of pure hydrogen based on the dehydrogenation of N-heterocycles has been rarely studied to date due to problems that include harsh catalytic conditions, complex catalytic system, unstable and expensive catalysts. [Catal. Sci. Technol., 2021, 11, 3990–4007](#)



Scheme 4 The dehydrogenation of H₁₄-PZ and hydrogenation of PZ by Pd₂Ru@SiCN.

The strategy with LOHCs is to hydrogenate an organic compound to store hydrogen and dehydrogenate it when hydrogen is needed.

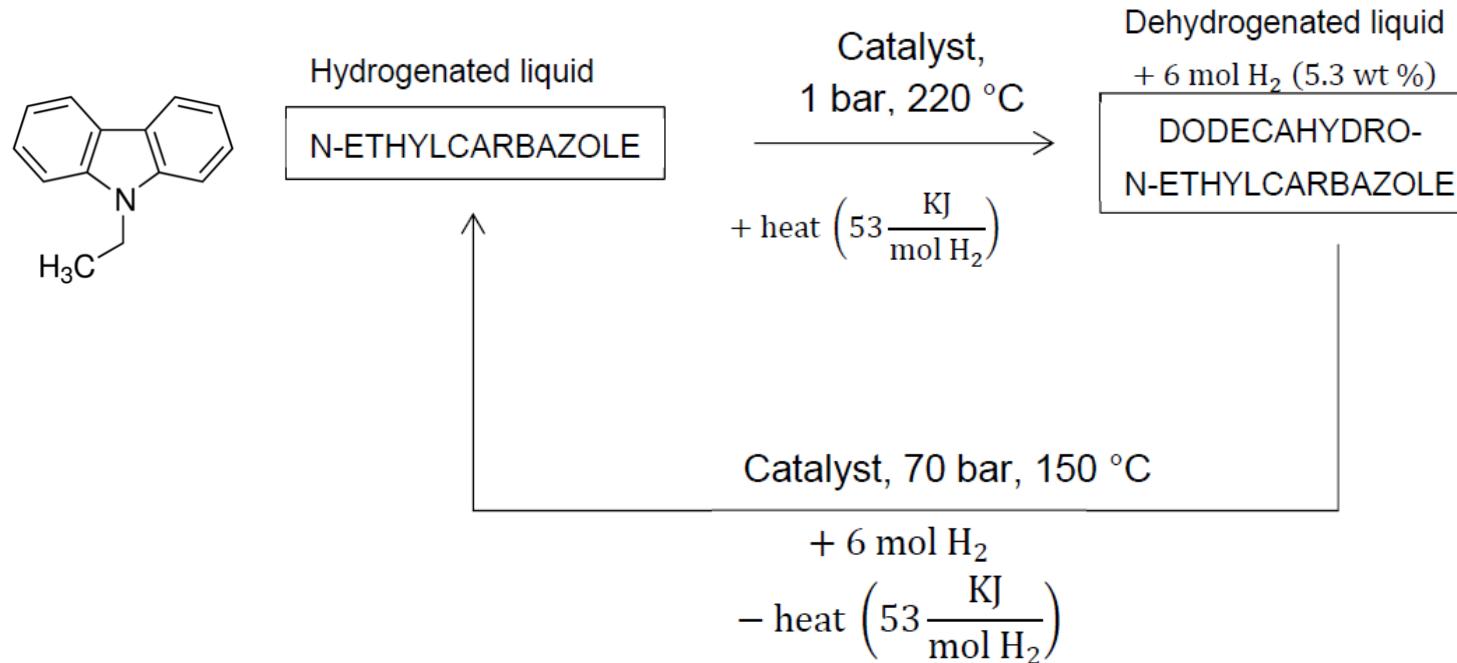
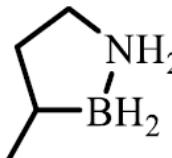
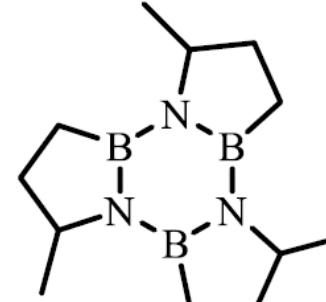


Figure 5. N-ethylcarbazole hydrogen uptake and release. [164].

The price of these precious metals is a major cost driver, and the monetary and environmental costs associated with the extraction of those metals are also significant. Development of stable dehydrogenation catalysts is necessary for decentralized use.

Dehydrogenation of this LOHC involves a significant amount of heat, nearly 60% of the gravimetric energy density of diesel fuel. Therefore, hydrogenation and dehydrogenation of LOHC are more suitable for applications where heat can be conveniently utilized or supplied (e.g. Fuel Cell application) Materials 2019, 12, 1973; doi:10.3390/ma12121973

Storage compound	Hydrogenated form	Dehydrogenated form	H ₂ wt.%	H ₂ g/L
3-Methyl-1,2-BN-cyclopentane ¹⁰⁹			4.7	42

3-Methyl-1,2-BN-cyclopentane has a melting point of -18 °C which indicates a liquid phase for this compound at room temperature. Catalytic dehydrogenation over FeCl₂ or NiCl₂ at 80°C produces 6 equiv. of hydrogen and a cyclohexane shaped trimer over 20 min.

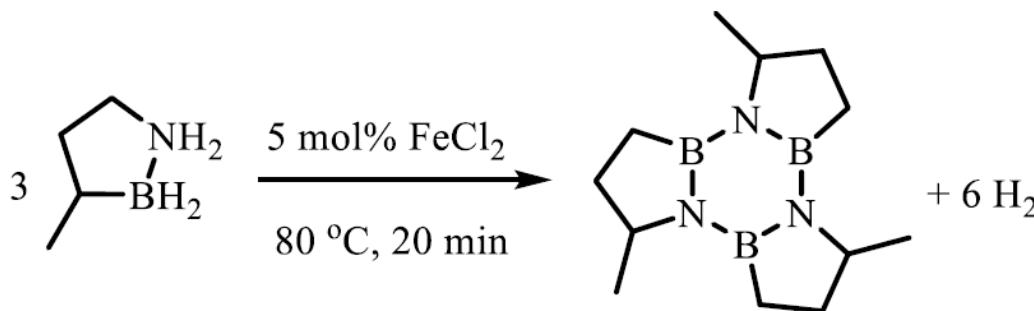
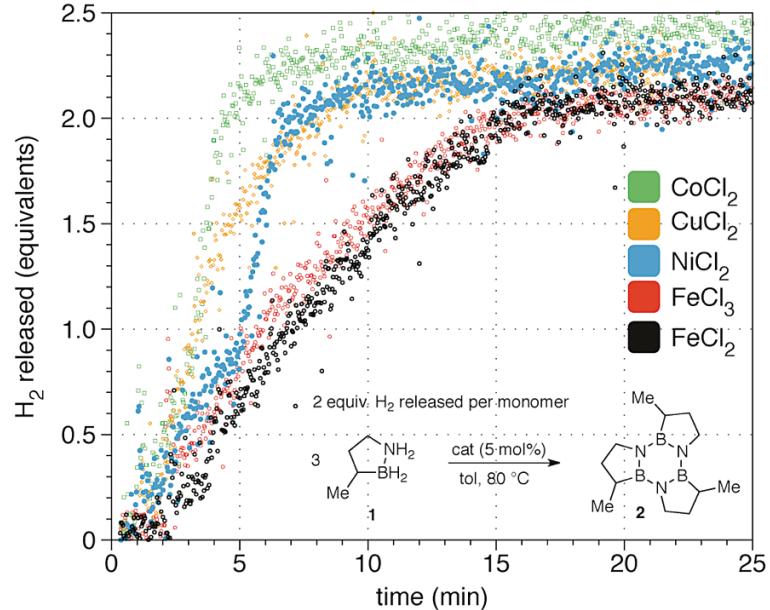


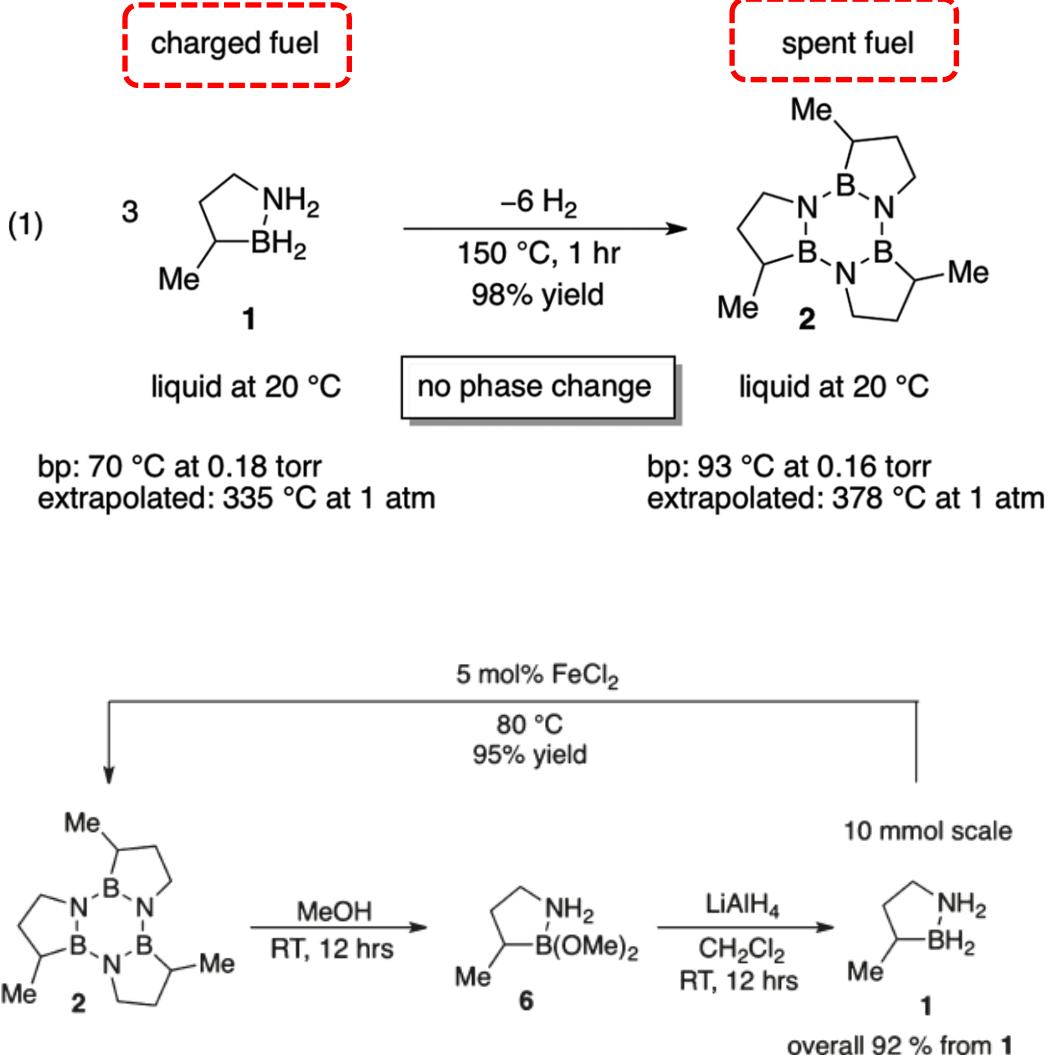
Figure 1.5. Catalytic hydrogen release from 3-methyl-1,2-BN-cyclopentane under mild conditions.¹⁰⁹

Their hydrogen content falls short of the US DOE target, their moderate hydrogen density could be doubled (greater than 9 wt.%) by further catalyzed dehydrogenation of the C-H bonds.

Automated volumetric buret measurements of H₂ release catalyzed by metal chloride complexes



(1)



Conversion of Spent Fuel 2 Back to Charged Fuel 1

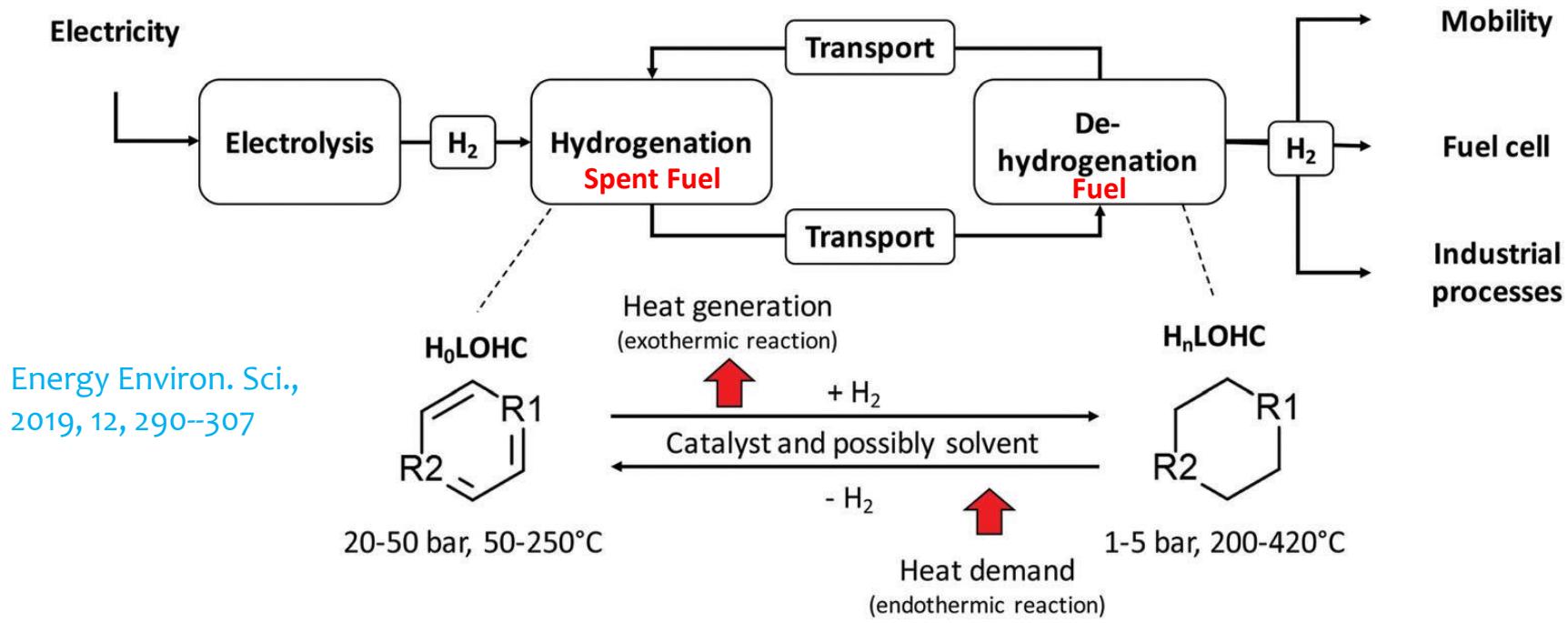
Their hydrogen content falls short of the US DOE target, their moderate hydrogen density could be doubled (greater than 9 wt.%) by further catalyzed dehydrogenation of the C-H bonds.

LOHCs are at **pilot** → **early commercial** stage in 2025. Demonstrations and medium-scale plants exist, major industrial players (Chiyoda, Hydrogenious and several startups) are running pilots or deploying permit-approved systems, and new entrants/partnerships are pushing e-LOHC and scale-up. LOHCs remain promising for long-distance transport and stationary storage, but round-trip energy losses, catalyst & heat management, and system economics still limit widespread on-board vehicle use.

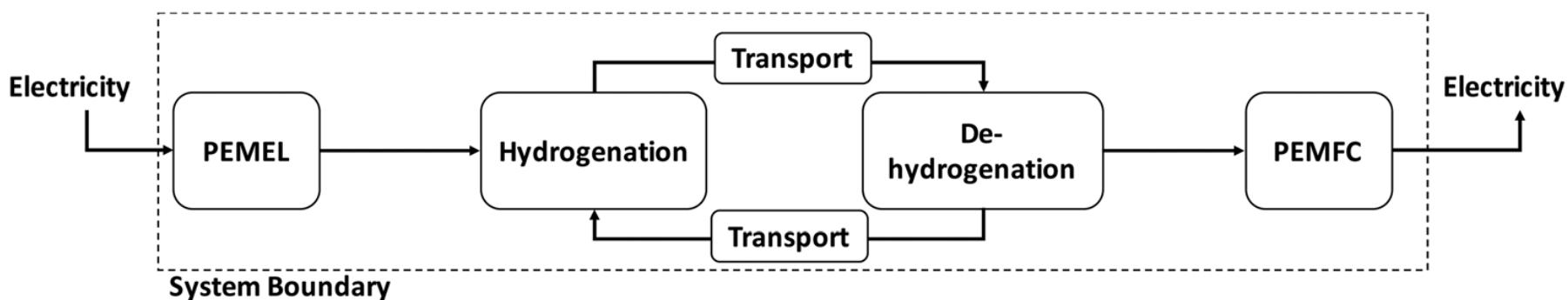
What's technically matured (2025)

Two LOHC families dominate:

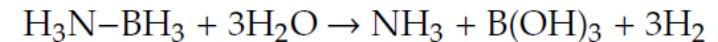
- **MCH / toluene (SPERA)** — championed by Chiyoda (Japan). Well-demonstrated hydrogenation/dehydrogenation chain. [Chiyoda Corporation](#)
- **Hydrogenated dibenzyltoluene / dibenzyltoluene (DBT)** — used by Hydrogenious and partners; good thermal and handling properties for long-term storage/transport.



LOHC storage and transport concept ($H_0\text{LOHC}$: unloaded LOHC; $H_n\text{LOHC}$: loaded LOHC)



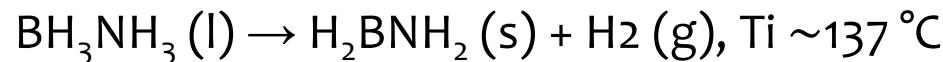
Flow diagram and system boundaries of the process chain (PEMEL: Polymer Electrolyte Membrane Electrolysis, PEMFC: Polymer Electrolyte Fuel Cell).
Process starts with electricity provided by renewable sources of energy and ends again with “green” electricity provided at another place and at another time.



Chemical Hydrogen:

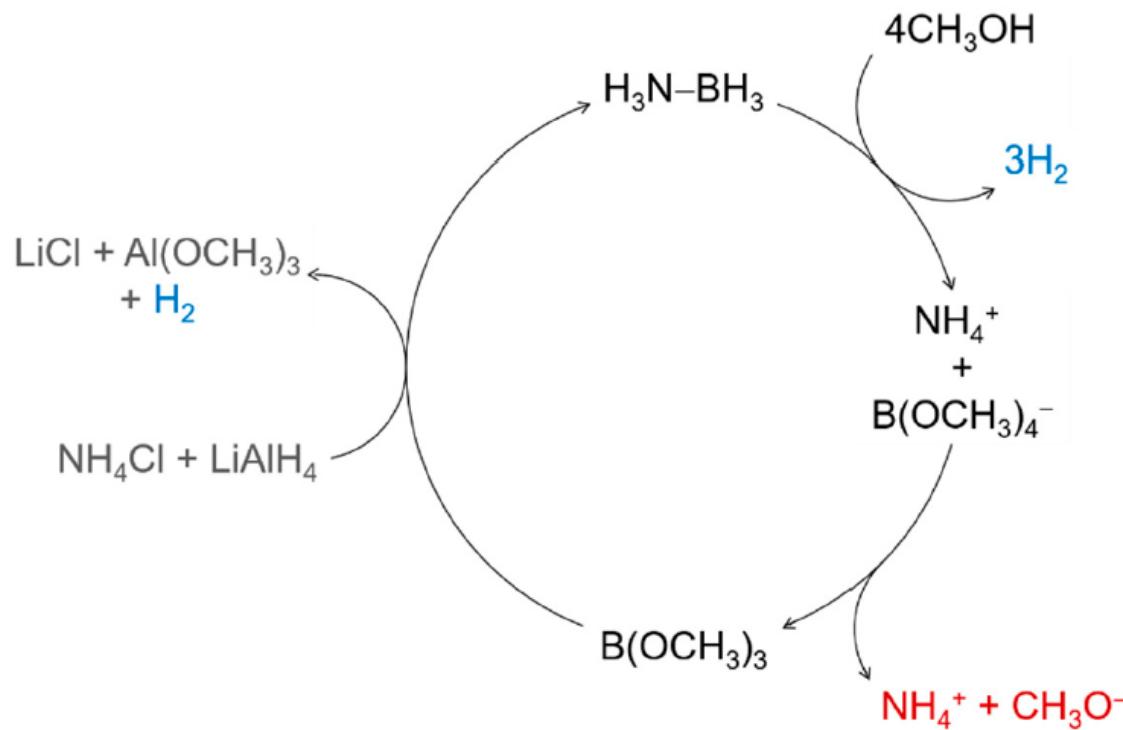
Ammonia borane (NH_3BH_3 , AB) as a source of Hydrogen:

One of the extensively studied hydrogen storage materials is ammonia borane (NH_3BH_3 , AB), which can theoretically contain up to 19.6 wt% hydrogen (practically up to 16 wt%). Melting point of AB is 112–114 °C, but its slow decomposition starts already at 70 °C. In dehydrogenation, 6.5 wt-% hydrogen is released



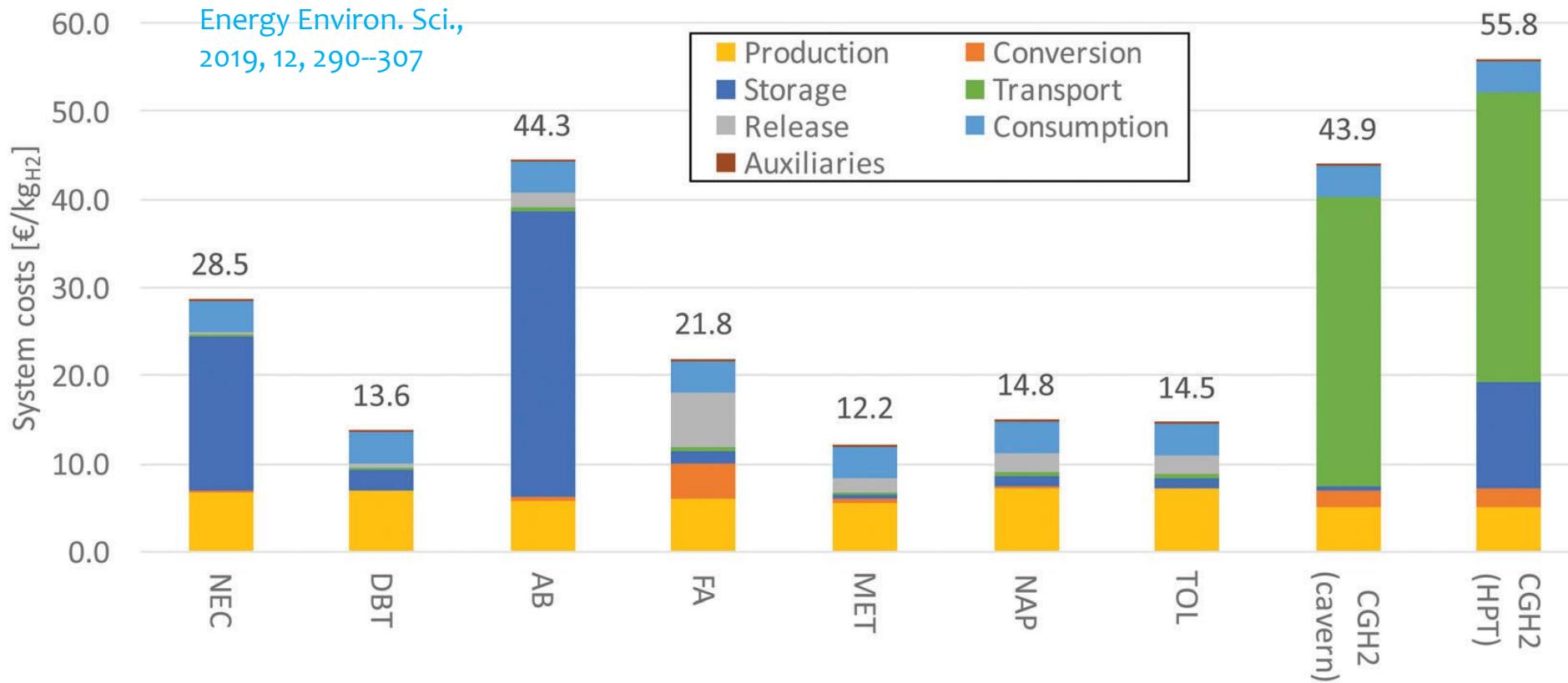
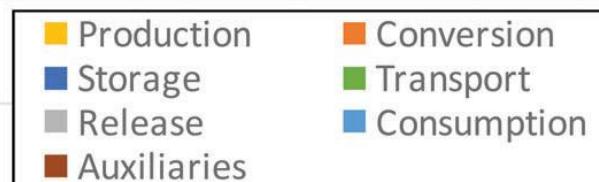
A polymeric polyaminoborane $(\text{BH}_2\text{NH}_2)_n$ is formed, which is followed by borazine $(\text{B}_3\text{N}_3\text{H}_6)$ formation, and finally, a boron nitride (BN) at 450°C.

Regeneration of AB is challenging. The catalytic AB rehydrogenation gives a mixture of $\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3$, $(\text{H}_2\text{NBH}_2)_n$ ($n = 3.5$), $(\text{HBNH})_3$ or $(\text{HBNH})_n$. 10% water solution of AB loses 1.8% of hydrogen in four days and 4.8% in a month when stored at ambient temperature. AB is soluble in water (26 wt%) and methanol (23 wt%), and slightly soluble in ethyl ether, hexane and benzene at room temperature. Purity of hydrogen released from AB is over 99% [Journal of Power Sources, 396 \(2018\) 803–823](#)



A proposed way to close the hydrogen cycle with the couple ammonia borane–methanol, provided that a single by-product forms during the reaction.

[Energies 2020, 13, 3071; doi:10.3390/en13123071](https://doi.org/10.3390/en13123071)



System costs with internal covering of the dehydrogenation heating (NEC: N-ethylcarbazole, DBT: dibenzyltoluene, AB: 1,2-dihydro-1,2-azaborine, FA: formic acid, MET: methanol, NAP: naphthalene, TOL: toluene, CGH₂: compressed hydrogen gas, HPT: high-pressure tank).

Chemical Hydrogen:

The term chemical hydrogen is used to describe the strategy of storing hydrogen by synthesizing molecules that contain hydrogen (e.g. CH₄, NH₃)

- **Ammonia** can be liquefied at room temperature at pressures of 8-10 bar and stored in a similar manner to propane.
- Although it is toxic, its smell can be detected even at safe concentration levels (< 1 ppm).
- Ammonia is actually considered nonflammable when being transported.
- Ammonia is the second most widely produced commodity chemical in the world (second to sulfuric acid), and its worldwide distribution system is well established.
- For ammonia, infrastructure already exists.
- It contains 17% hydrogen by weight, which can be extracted via thermal catalytic decomposition or electro-oxidation. Alternatively, ammonia may be oxidized directly in fuel cells without the need for a separate reactor.
- Ammonia's energy density is comparable to that of compressed natural gas (CNG) and methanol, but lower than gasoline and liquefied propane gas (LPG).
- The life cycle production cost of energy from ammonia is estimated at US\$ 1.2/kWh compared to US\$ 3.8/kWh for methanol and US\$ 25.4/kWh for hydrogen.

NH₃ had a worldwide production of 150 million metric tons in 2023, making it the second-highest-produced chemical commodity after sulfuric acid (H₂SO₄).

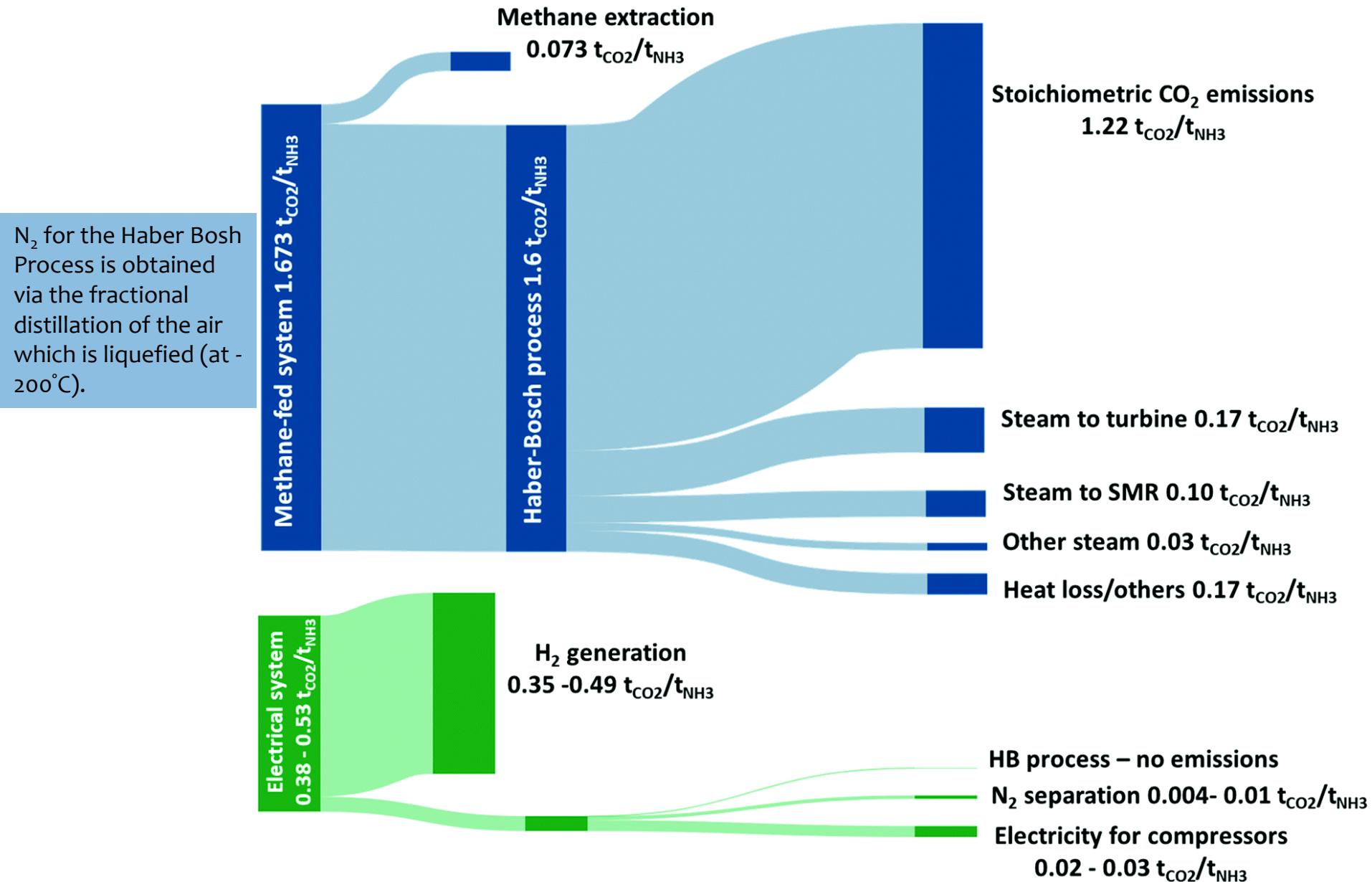
Gray or Brown NH₃: The Haber-Bosch process, responsible for nearly all of the world's 180 million t of annual ammonia production, reacts hydrogen and atmospheric nitrogen. The hydrogen often comes from the steam reformation of methane, a process that emits CO₂.

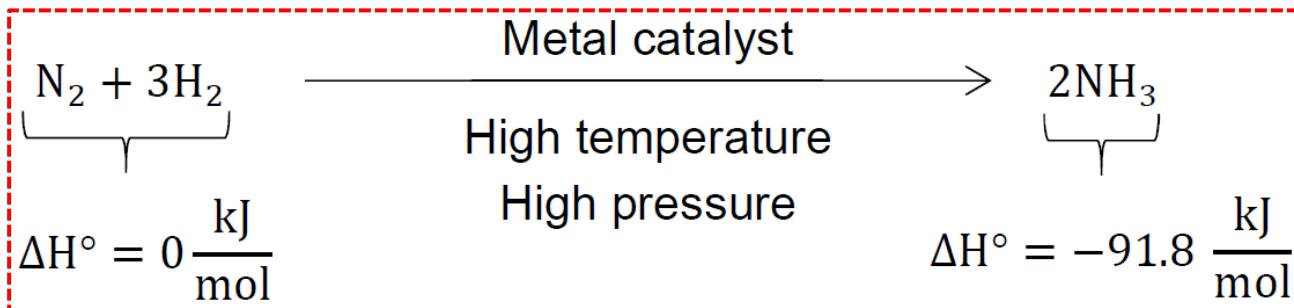
Blue NH₃: Blue ammonia is conventional ammonia with CO₂ has been captured and stored, reducing climate impact compared with gray ammonia. Many fertilizer makers have embarked on such projects in recent years.

Green NH₃: Green ammonia is made with hydrogen that comes from water electrolysis powered by alternative energy. Projects abound, though most are on a modest scale of tens of thousands of tons, an order of magnitude smaller than a typical ammonia plant. A massive project in Saudi Arabia, however, aims to make more than 1 million metric tons of ammonia per year.

Turquoise NH₃: This process uses pyrolysis to convert methane into pure carbon and hydrogen, which is reacted with N₂ to make ammonia. The industry thinks of turquoise ammonia as somewhere between green and blue. A prominent project is Monolith Materials' carbon black plant in Nebraska.

Haber-Bosch process is a capital-intensive and CO₂-producing process.





The energy density of liquid ammonia (17.6 wt %, 11.5 MJ/L) is marginally better than that of liquid hydrogen. A lower vapor pressure of ammonia (9.2 bar at 25 C) significantly simplifies the tank design. **Materials 2019, 12, 1973**

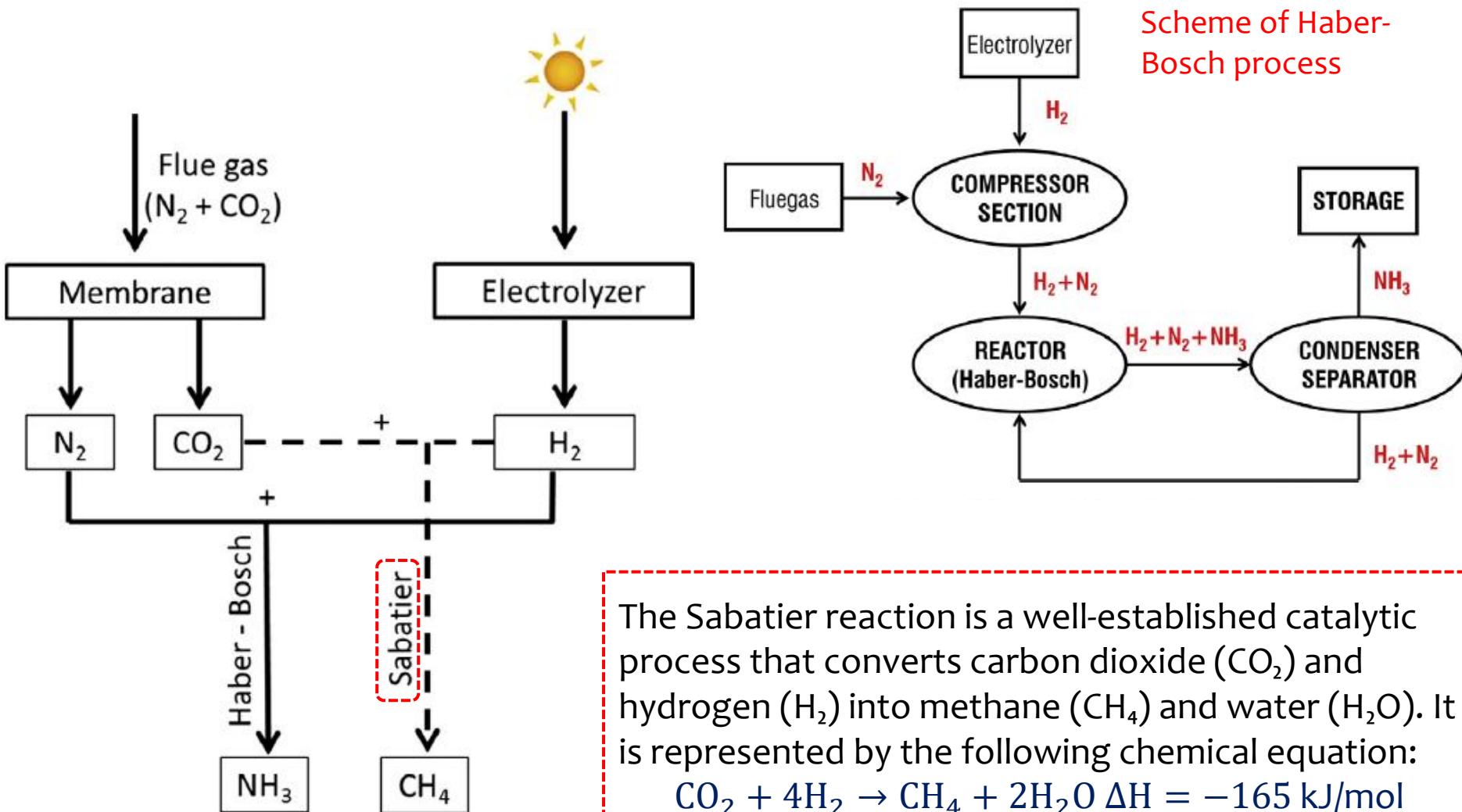
Similar to methane, ammonia utilization is more difficult than pure hydrogen. Solid oxide fuel cells are the most likely route for the use ammonia in fuel cells, but these fuel cells still have durability issues.

Is ammonia the fuel of the future?

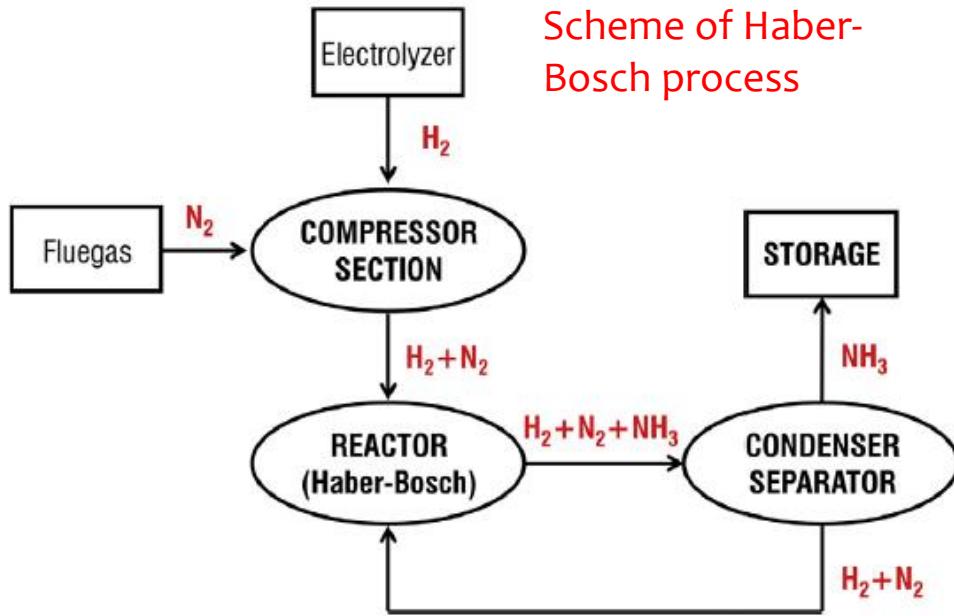
Industry sees the agricultural chemical as a convenient means to transport hydrogen by [Alexander H. Tullo; March 8, 2021 @ C&EN](#) | A version of this story appeared in [Volume 99, Issue 8](#)

“Up to this point, we have made a business by selling the nitrogen value of the molecule. What’s really exciting about this is now there is an opportunity and a market that values the hydrogen portion of the molecule.”

Flue gas treatment by power-to-gas integration for methane and ammonia synthesis
 Energy Conversion and Management 171 (2018) 626–634



Scheme of Haber-Bosch process



Scheme of the combined processes to produce NH_3 and CH_4 from flue gas.

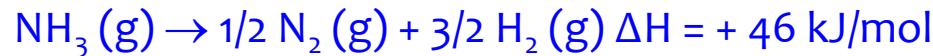
The Sabatier reaction is a well-established catalytic process that converts carbon dioxide (CO_2) and hydrogen (H_2) into methane (CH_4) and water (H_2O). It is represented by the following chemical equation:



- Temperature: $250\text{--}400^\circ\text{C}$
- Pressure: $1\text{--}30 \text{ bar}$

AMMONIA DECOMPOSITION:

Ammonia decomposition (cracking) is simply the reverse of the synthesis reaction.



This reaction is endothermic. The temperature required for efficient cracking depends on the catalyst. There are a wide variety of materials that have been found to be effective, but some (e.g., supported Ni catalysts) require temperatures above 1000°C. Others have high conversion efficiency at temperatures in the range of 650-700°C. These temperatures are well above PEM fuel cell operating temperatures.

The viability of an ammonia-based on board storage system would depend largely on the following factors:

1. Development of high power, small volume, lightweight and efficient integrated ammonia cracking/purification systems capable of supplying hydrogen.
2. Development of lightweight tanks capable of sustaining the weight and vapor overpressure of anhydrous ammonia and with proven long-term integrity in an ammonia environment.
3. Addressing all of the safety issues associated with working with ammonia and ammonia containing systems.