SAND2017-7523PE

Where Does Hydrogen Fit in a Clean Energy Economy?

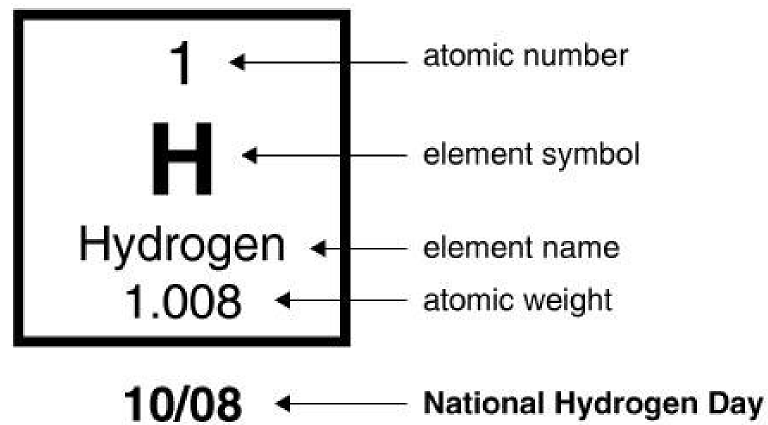
Dr. Mark D. Allendorf

Senior Scientist, Sandia National Laboratories
Livermore, California USA

HyMARC

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

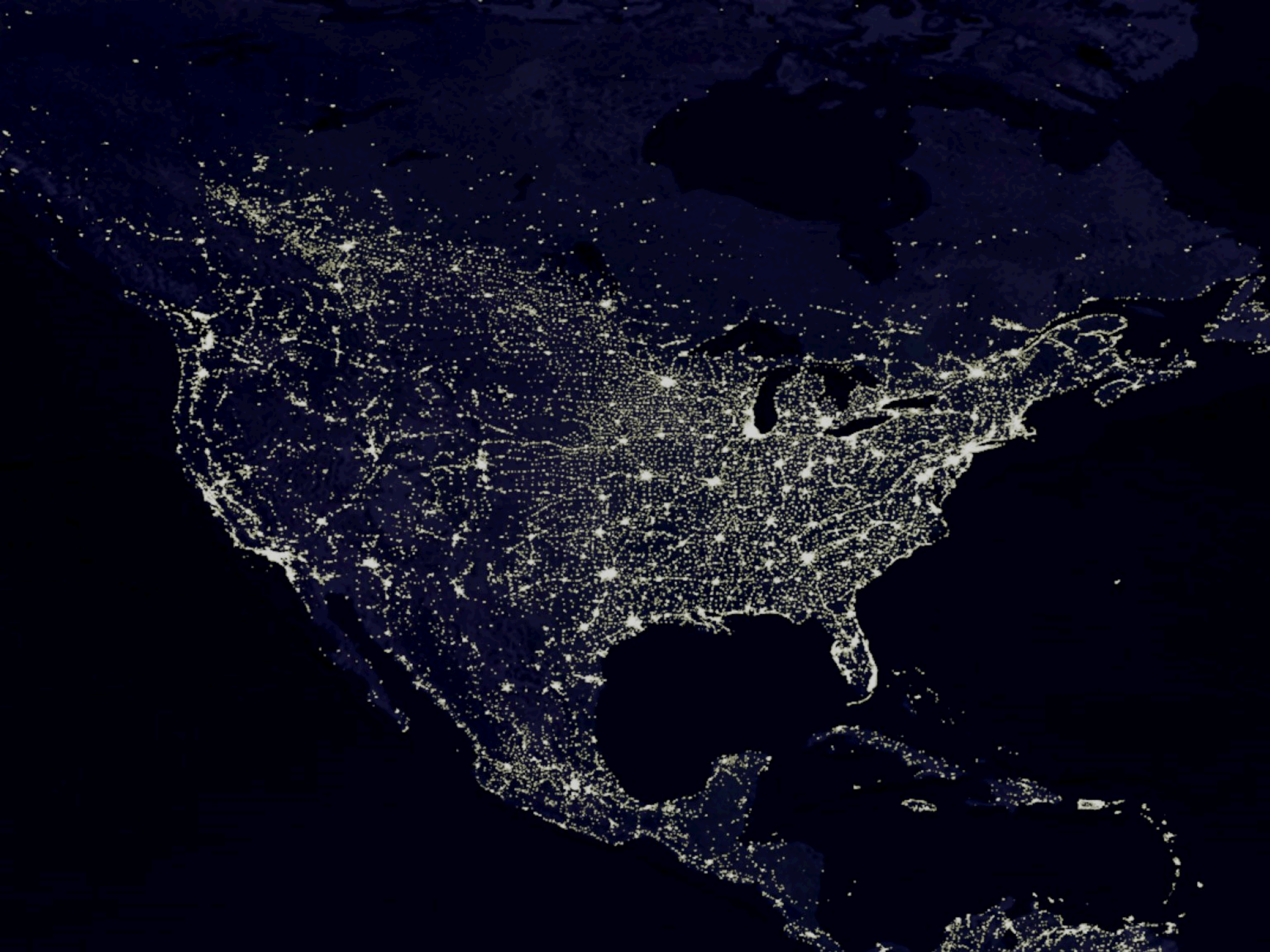
National Hydrogen & Fuel Cell Day | 10·08



#HydrogenNow

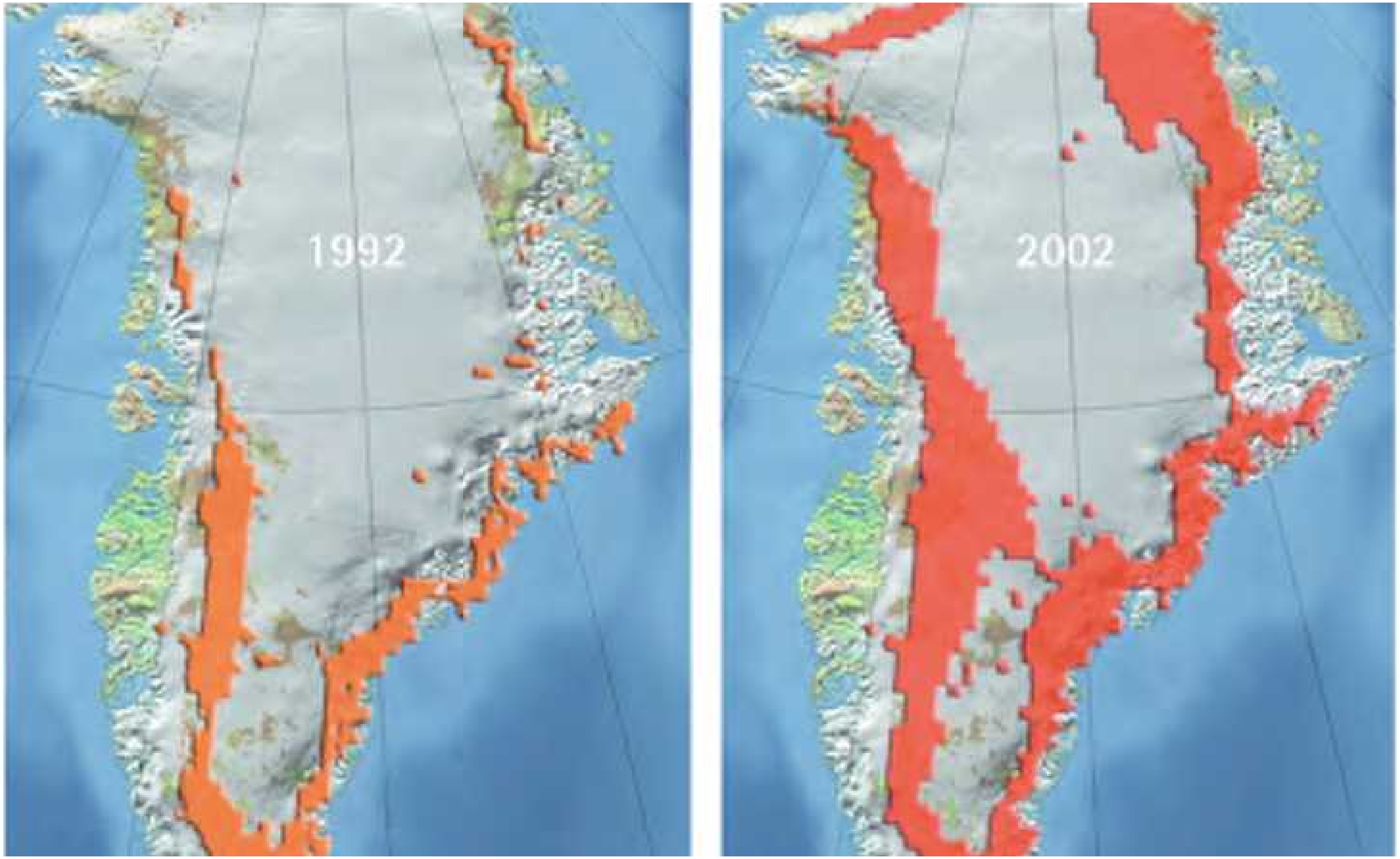
We love our cars…

...and electricity is EVERYWHERE



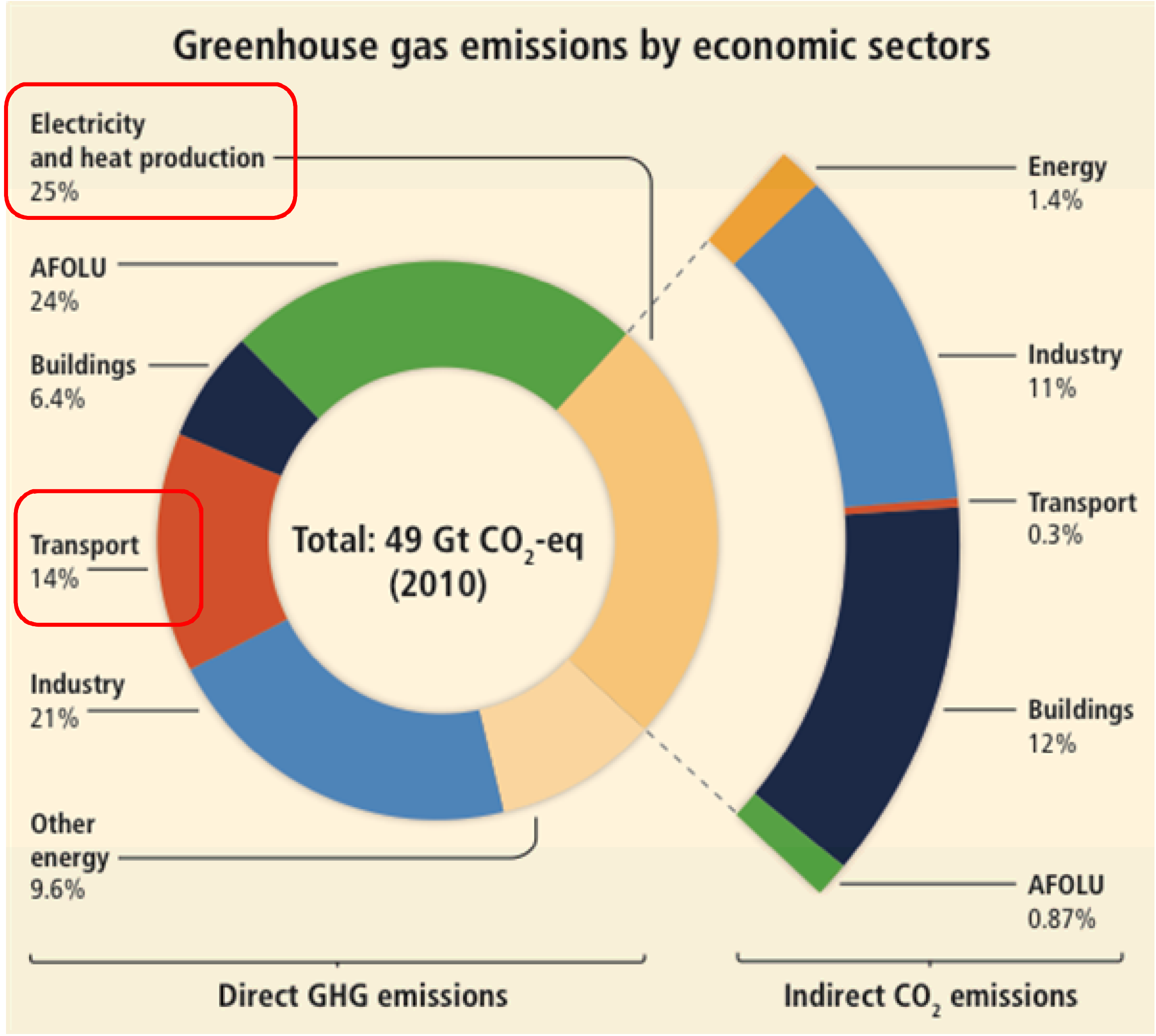
Industrial emissions

Greenland ice sheet melt



Source: Intergovernmental Panel on Climate Change

Power generation + transportation = ~40% of anthropogenic GHG emissions



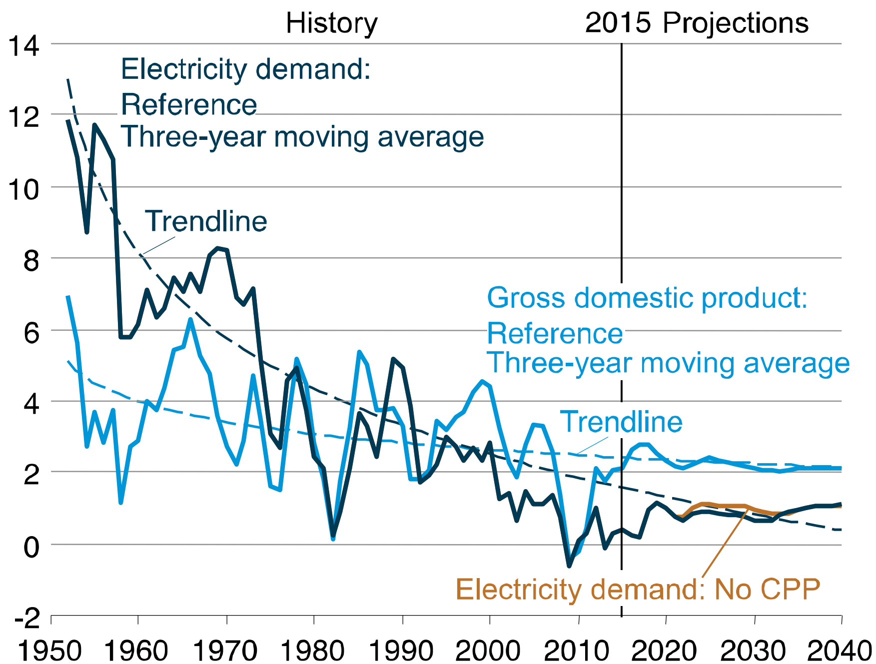
Source: *IPCC 2014 Synthesis Report*

How can we address climate change while simultaneously meeting global energy demands?

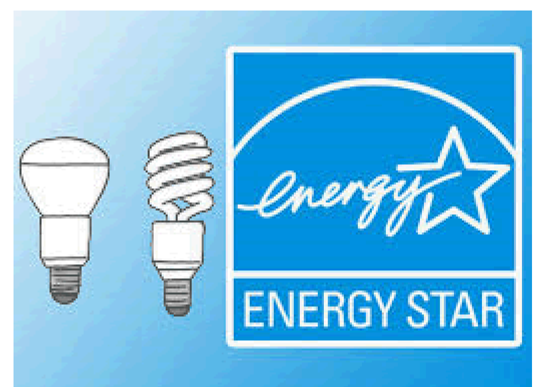
Technology is making a difference: U.S. demand for electricity is actually dropping

Growth in electricity use from 2015 to 2040 slows to 24% with Clean Power Plan (CPP) and to 27% with no CPP

Figure MT-27. U.S. gross domestic product growth and electricity demand growth rates, 1950–2040 (percent, three-year moving average)



Source: U.S. Energy Information Administration | Annual Energy Outlook 2016



Source: International Energy Agency World Energy Outlook 2015

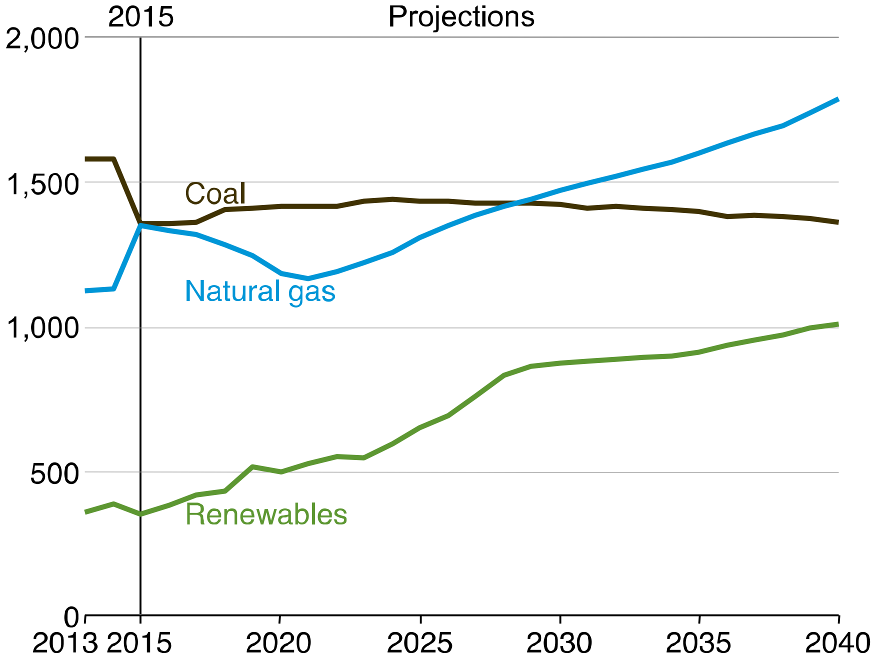
However, global demand is projected to increase >70% by 2040

What about solar and other renewables such as wind?

1 Hour Sunlight = Total World Energy Demand for One Year

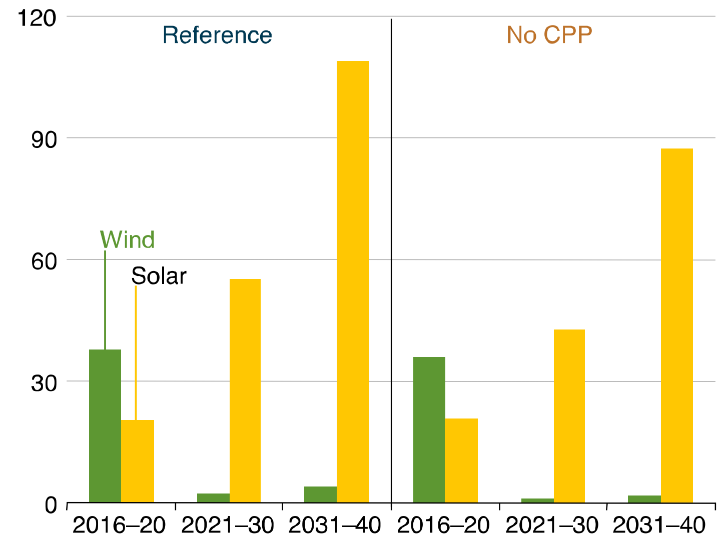
Electricity generation capacity from renewables is projected to grow dramatically, even without the CPP

Figure ES-2. Net electricity generation from coal, natural gas, and renewables in the No CPP case, 2013–40 (billion kilowatthours)



Renewable capacity additions are dominated by solar photovoltaics

Figure MT-36. Wind and solar electricity generation capacity additions in all sectors by energy source in two cases, 2016–20, 2021–30, and 2031–40 (gigawatts)



Source: U.S. Energy Information Administration | Annual Energy Outlook 2016

Limitations of variable inputs: the "duck chart"

Denholm, P.; M. O'Connell; G. Brinkman; J. Jorgenson (2015) Overgeneration from Solar Energy in California: A Field Guide to the Duck Chart. NREL/TP-6A20-65023

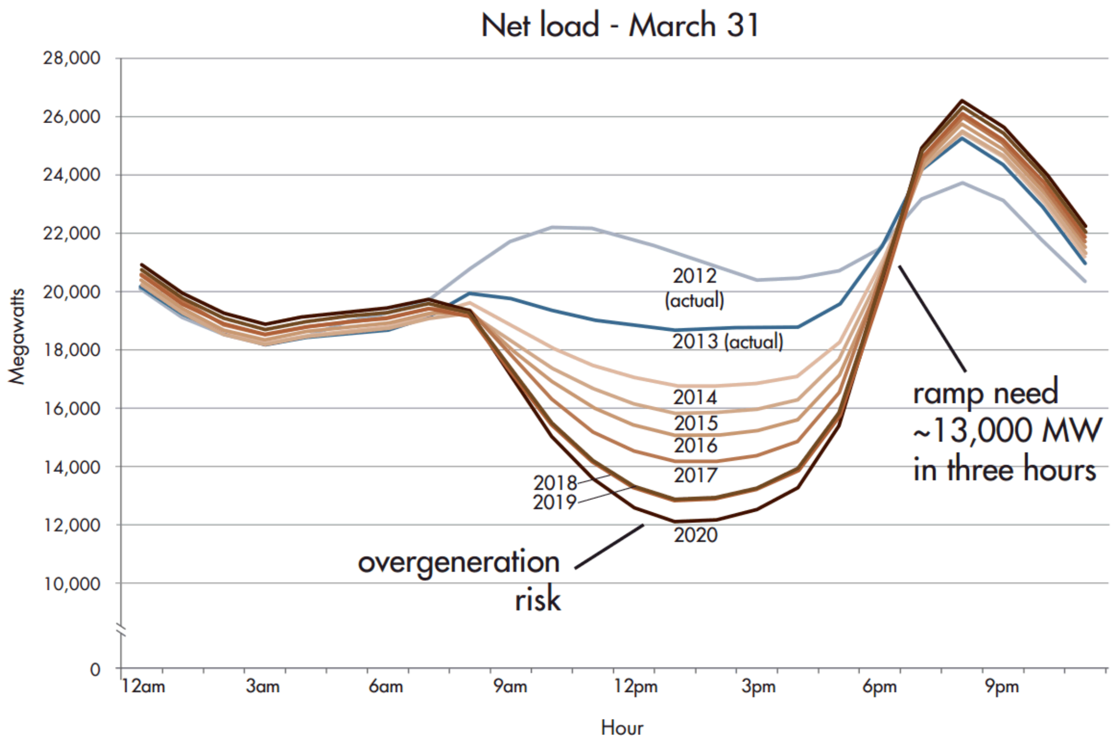
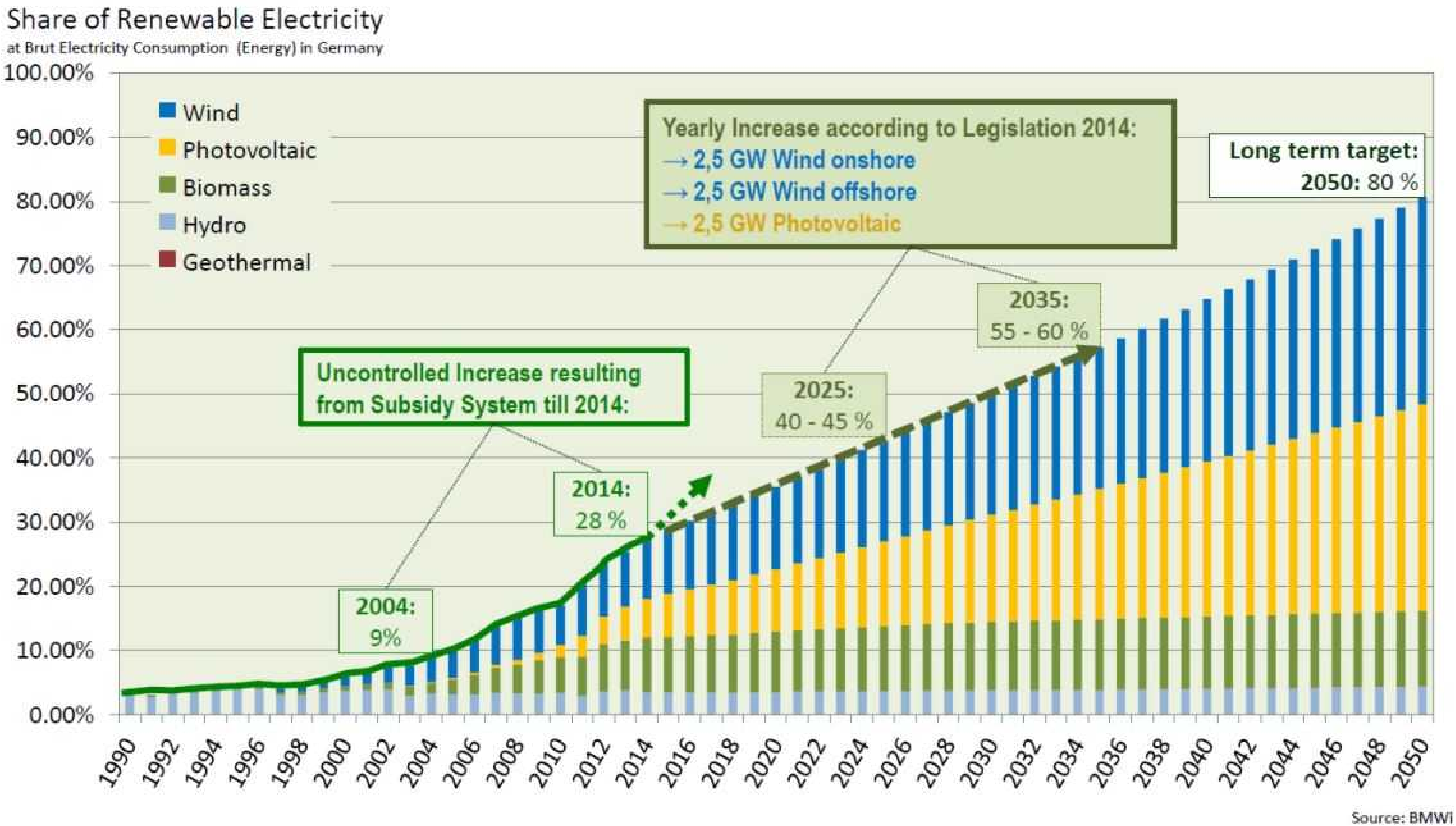


Figure 1. The CAISO duck chart

Source: CAISO 2013

Curtailment will lead to an abundance of low value electrons, and we need solutions that will service our multi-sector demands

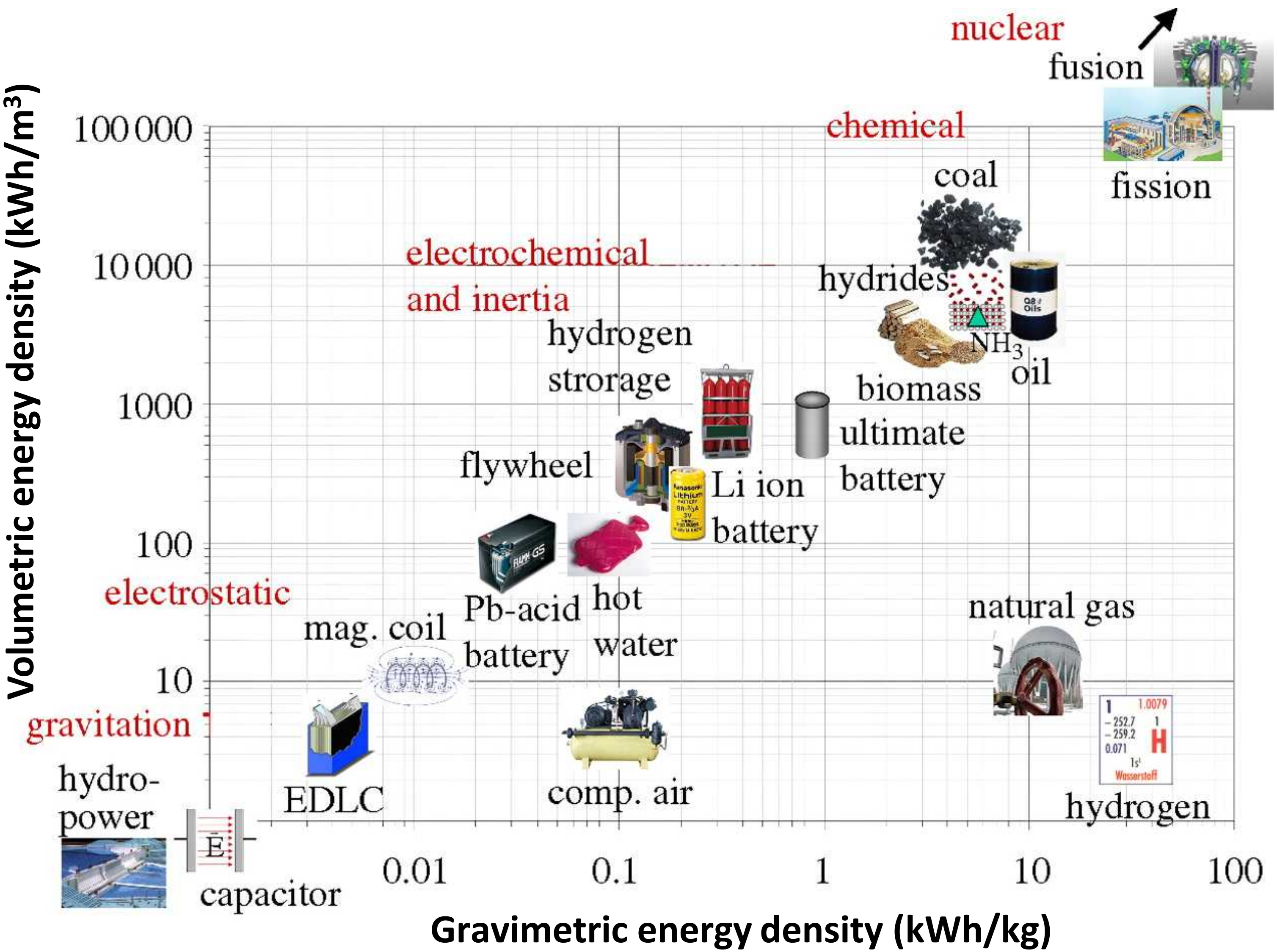
Germany is already limiting the renewable energy penetration rate



So where does hydrogen fit in the grand scheme of renewable energy?

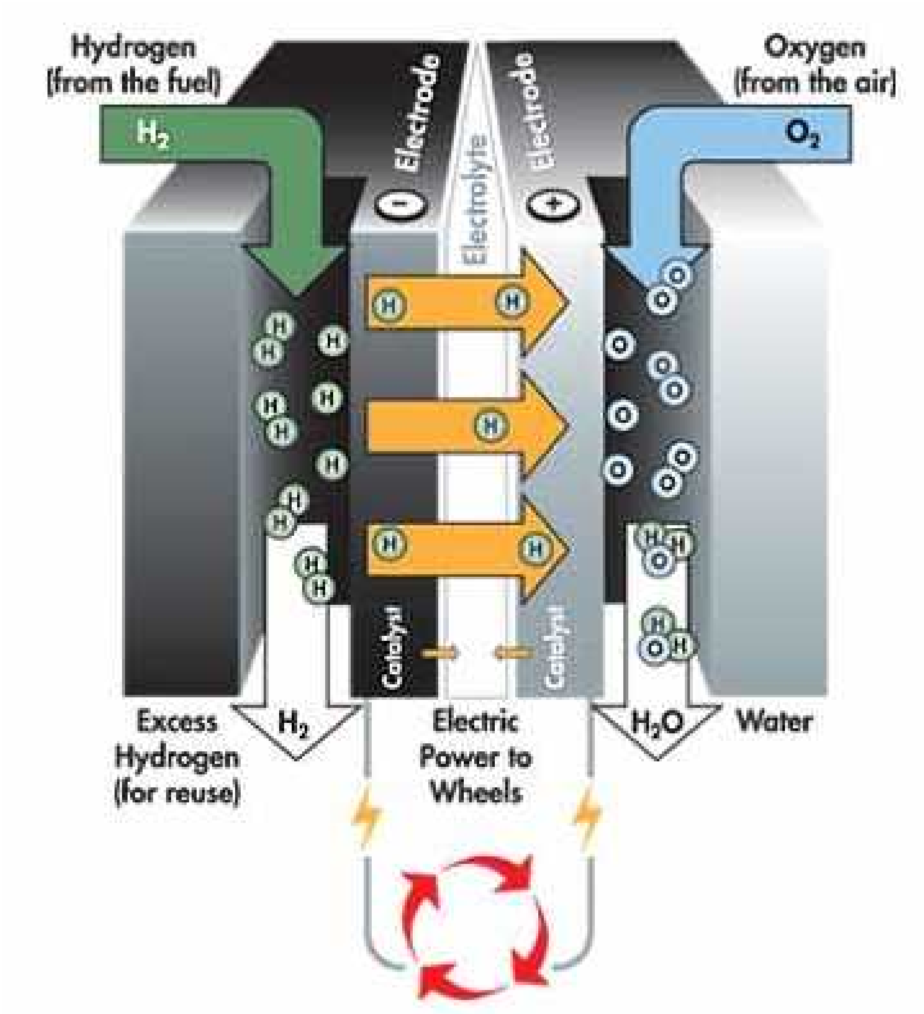
- **On-board vehicular storage**
- **Hydrogen at scale to reduce curtailment problems**
- **Conversion of biofuel production wastes to value-added products**

Hydrogen is an attractive energy carrier based on energy density



Source: A. Züttel *Phil. Trans. A* **368** (2010) 3329

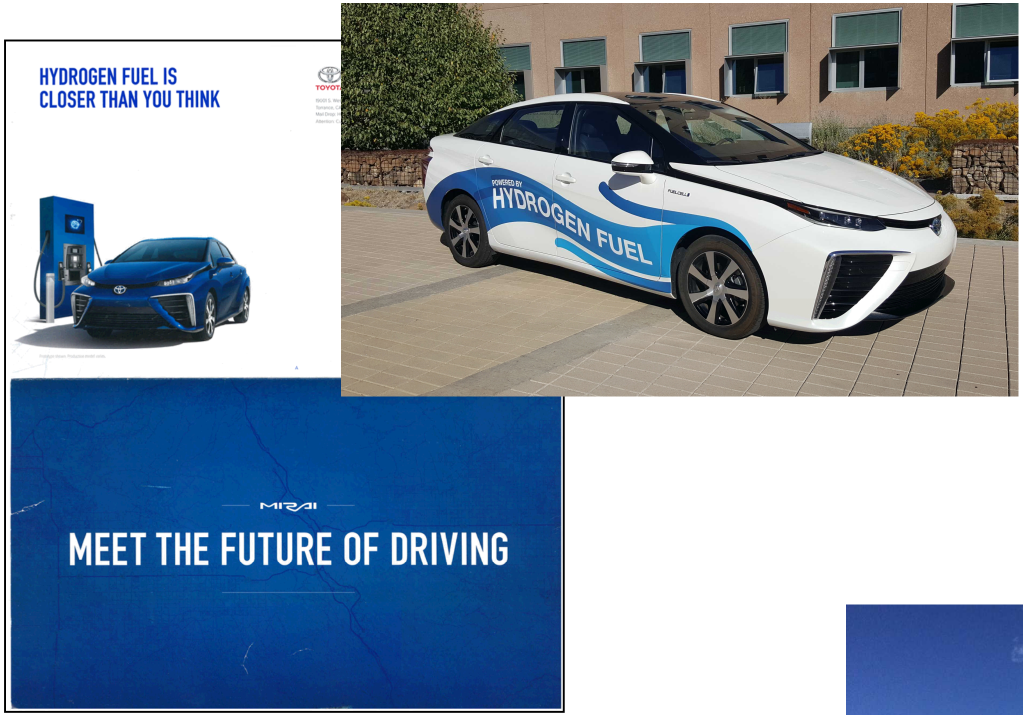
Hydrogen fuel cells



FUEL CELL

Source: U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy

Progress!



- **700 bar pressurized tanks**
- **265 – 312 mile range**
- **Refueling stations being installed in some areas**

SF-BREEZE (San Francisco Bay Renewable Energy Electric vessel with Zero Emissions)

Sandia feasibility study to design, build, and operate a high-speed hydrogen fuel cell passenger ferry and hydrogen refueling station.

Industrial production of hydrogen is not carbon-neutral

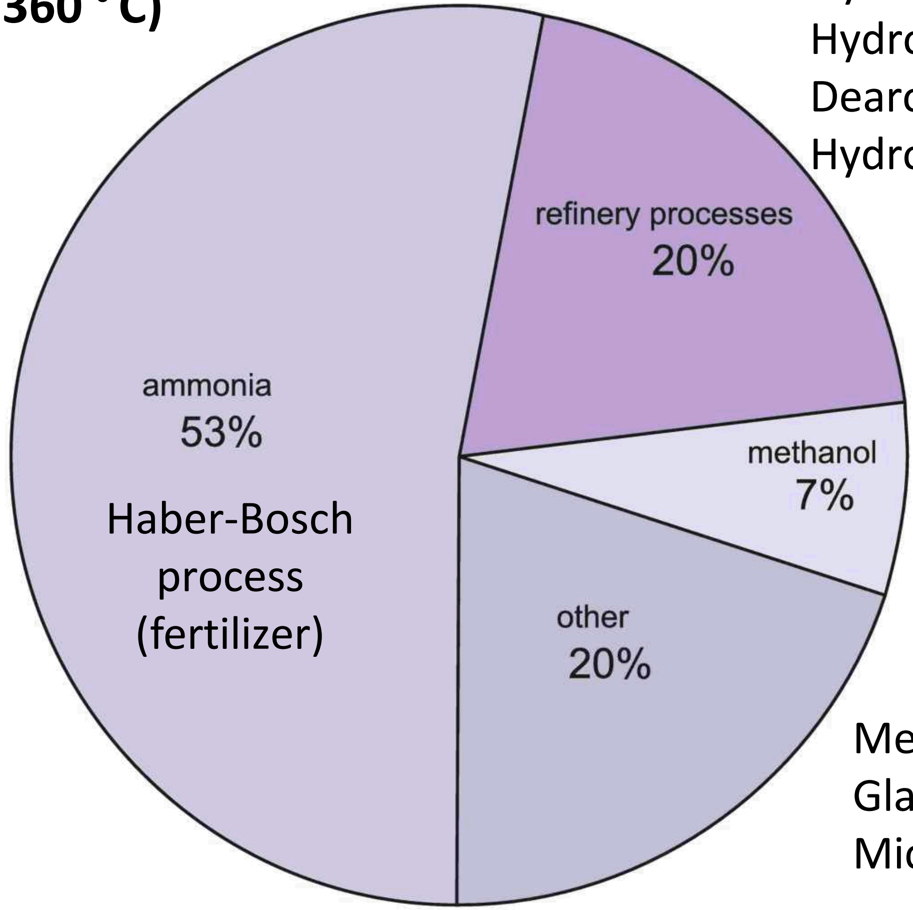
Steam reforming + water-gas shift reactions:

- **$CH_4 + H_2O \rightarrow CO + 3\ H_2$ (700 – 1100 °C)**
- **$CO + H_2O \rightarrow CO_2 + H_2$ (360 ° C)**

Total U.S. production:

- **10 Million tons**
- **≈ current Wind+Solar**

1600 miles of pipeline



Hydrodesulphurisation
Hydroisomerisation
Dearomatisation
Hydrocracking

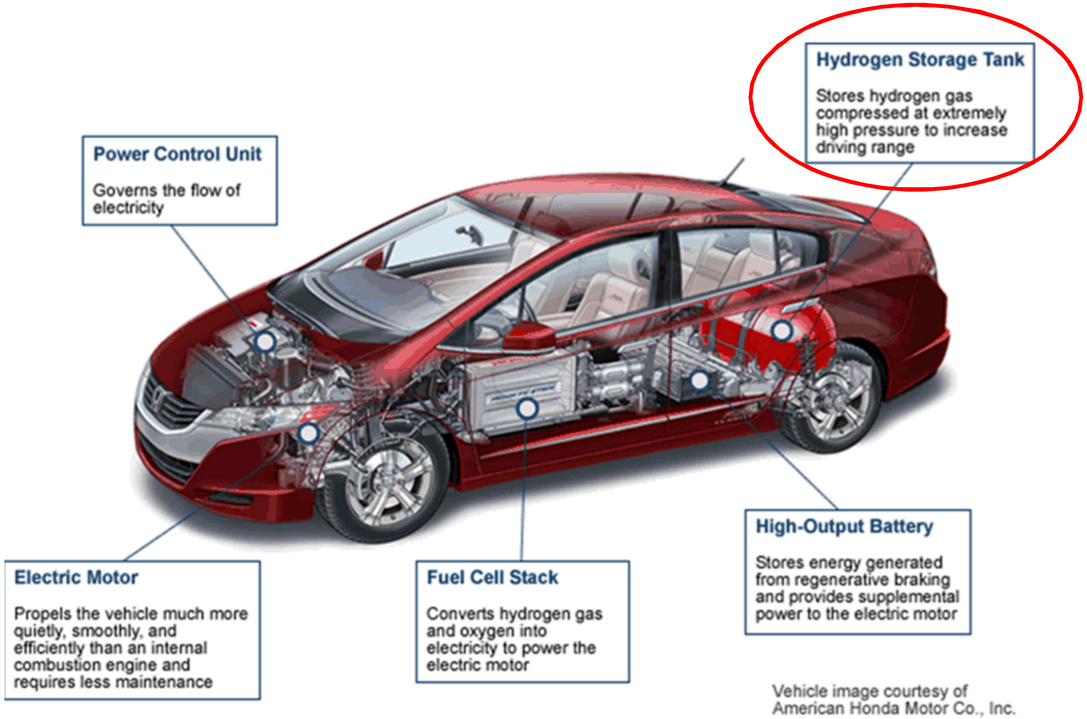
Metals production
Glass
Microelectronics

The hydrogen storage problem

Current hydrogen-fueled vehicles store H_2 as a gas at high pressure

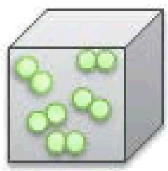
Issues with compressed-gas tanks

- **Cost**
- **Lack of design flexibility**
- **Infrastructure (compressor) costs**
- **DOE storage targets not met**



Long-term strategy: use solid-state materials for storage

Physical Storage



700 bar

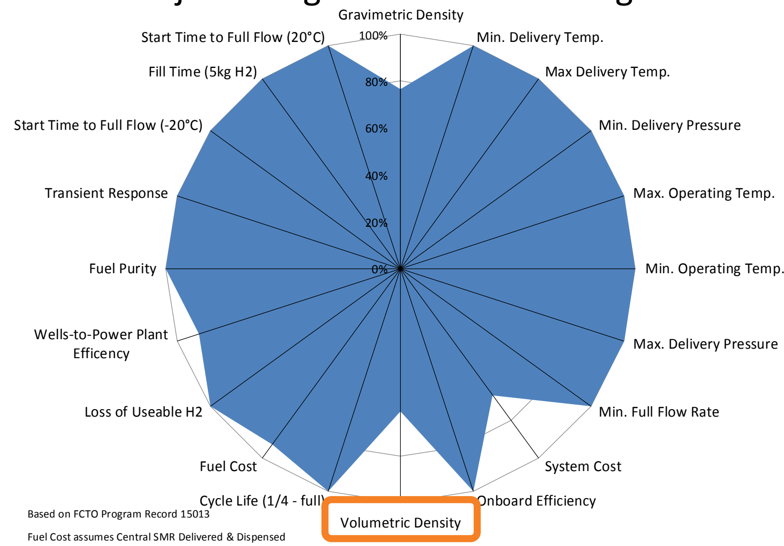
Gen 2 vehicles

40g/L

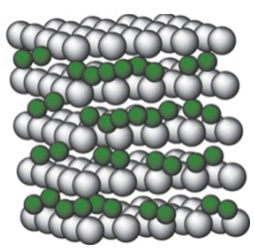
Theoretical limitations prevent 700 bar from meeting all onboard targets

700 Bar H2 Storage System Performance

Projected Against DOE 2020 Targets

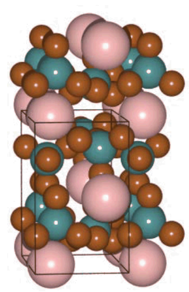


Materials Storage



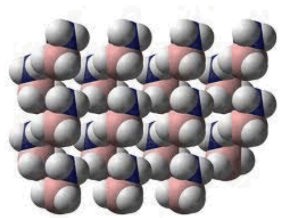
interstitial hydrides

~100-150 g H_2/L



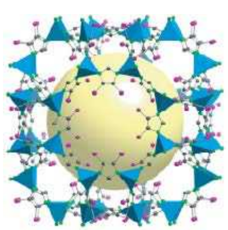
complex hydrides

~70-150 g H_2/L



chemical storage

~70-150 g H_2/L



sorbents

[illegible] $_2$/L

Reference

water

111 g H_2/L

Higher densities = potential to meet system targets

Source U.S. Department of Energy

Basic scientific questions must be addressed to enable solid-state materials to be used for vehicular hydrogen storage

Sorbents: H_2 adsorption enthalpy too low

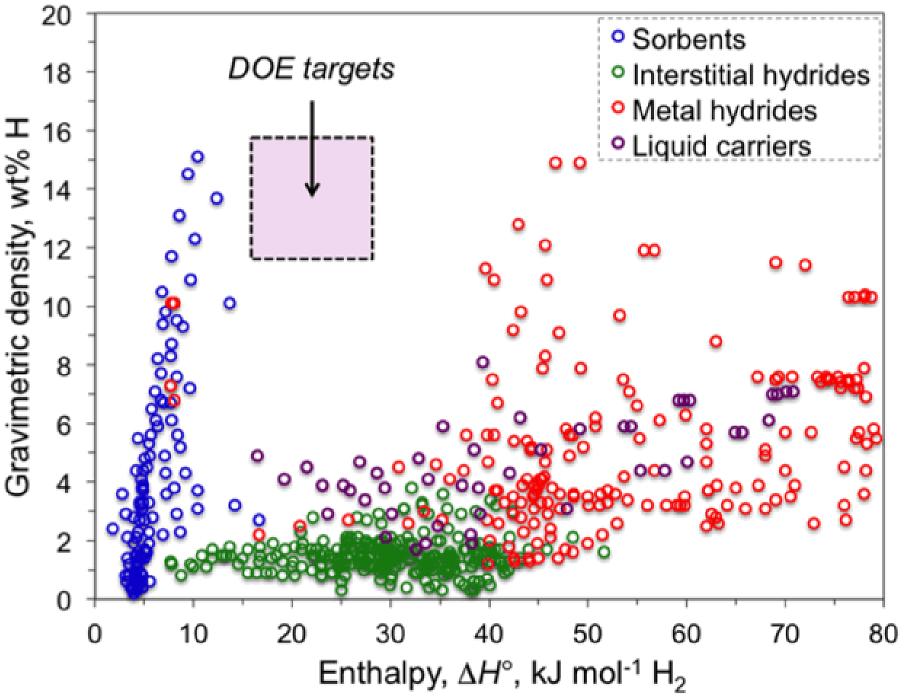
Target desorption enthalpy: 15 – 20 kJ/mol

- Volumetric capacity at target temperature too low
- Usable hydrogen capacity too low

Metal hydrides: H_2 adsorption enthalpy too low, release and uptake too slow

Target desorption enthalpy*: ≤ 27 kJ/mol H_2

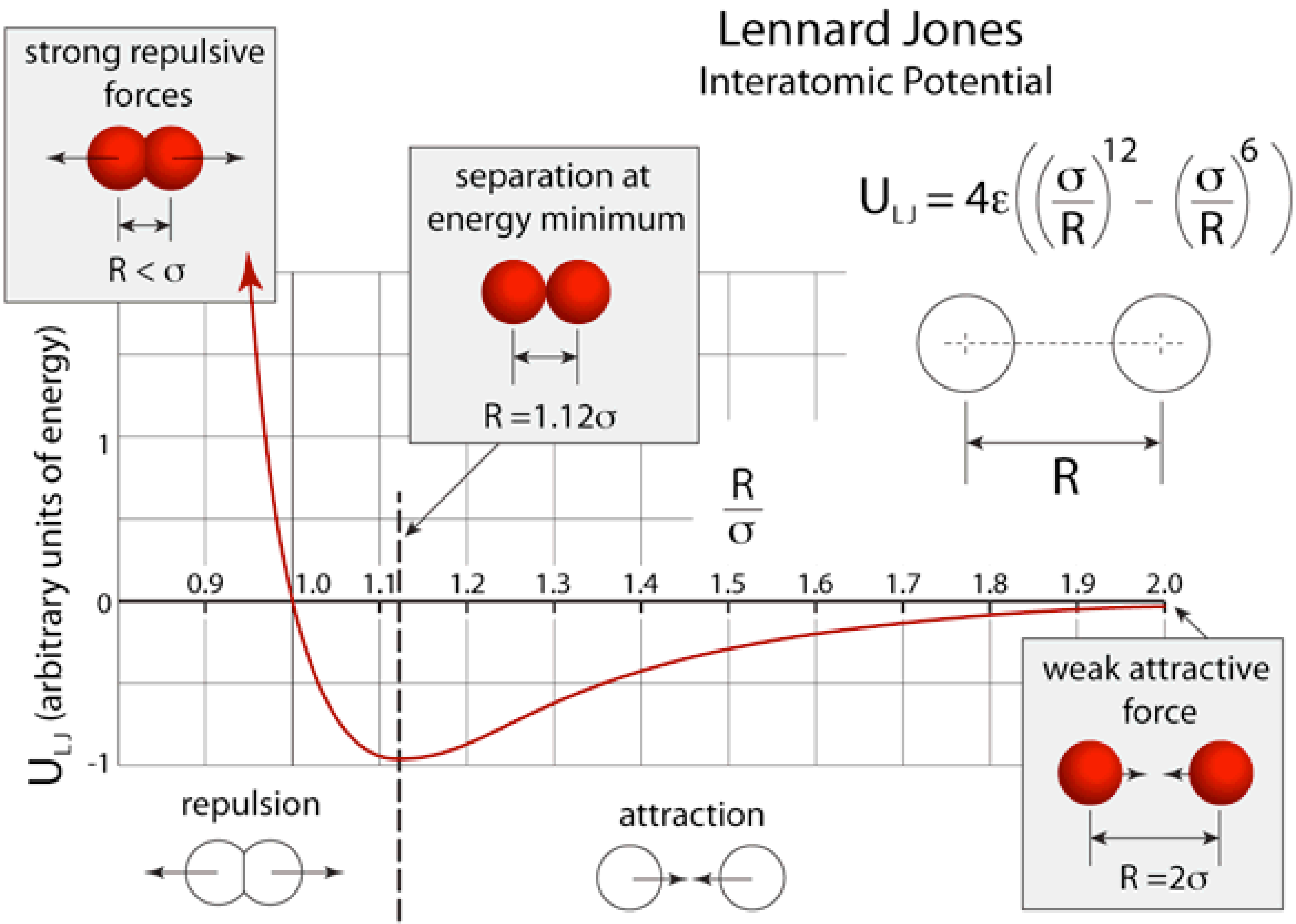
- Poor understanding of:
  - Limited reversibility
  - Slow kinetics
  - Role of interfaces and interfacial reactions
  - Importance and potential of nanostructures



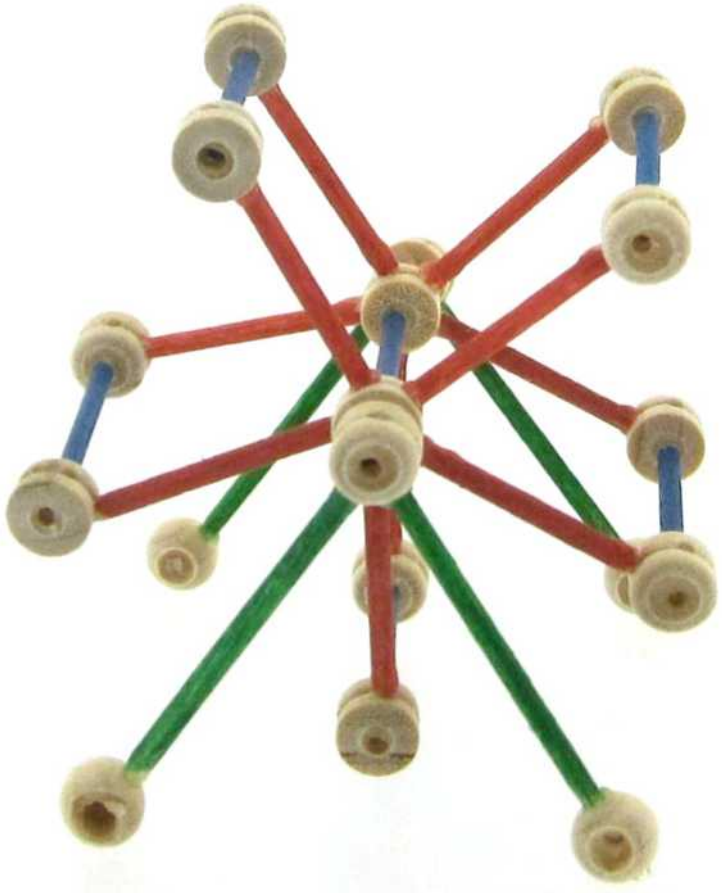
Source: DOE Hydrogen Storage Materials Database

*DOE Engineering Center of Excellence

Van der Waals forces govern the interaction of molecules such as H_2, He, and CH_4, with surfaces



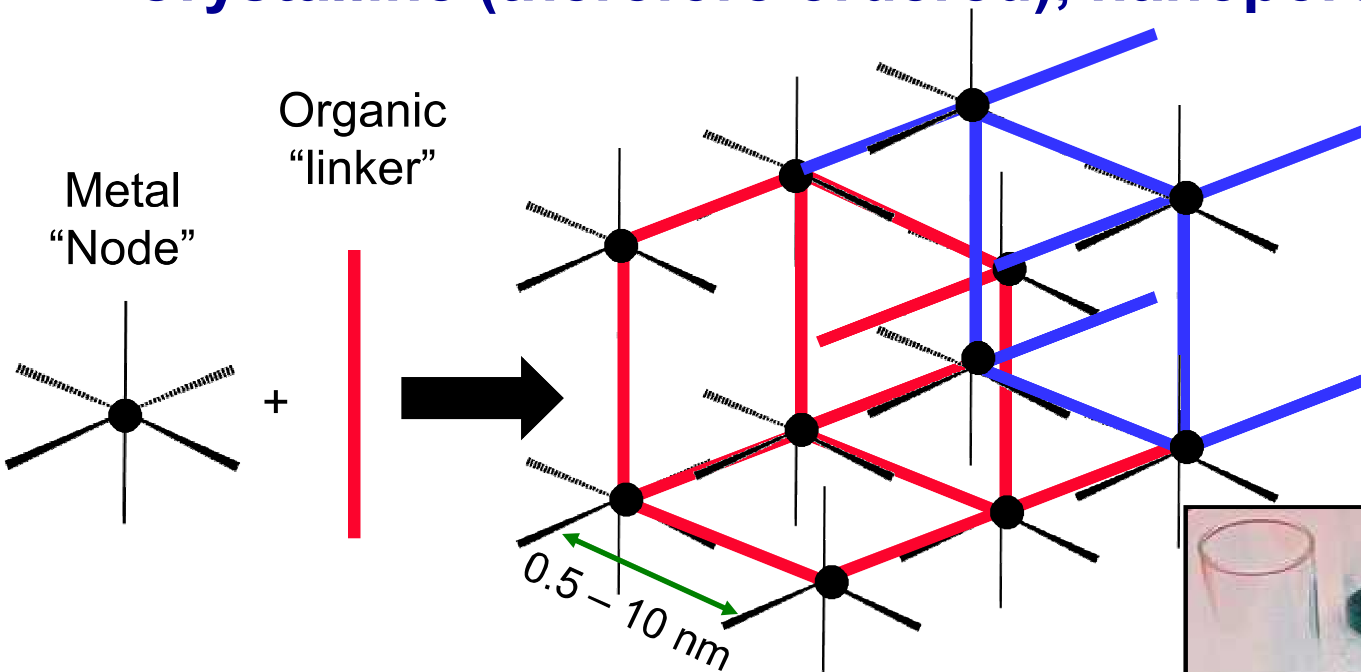
Remember these?

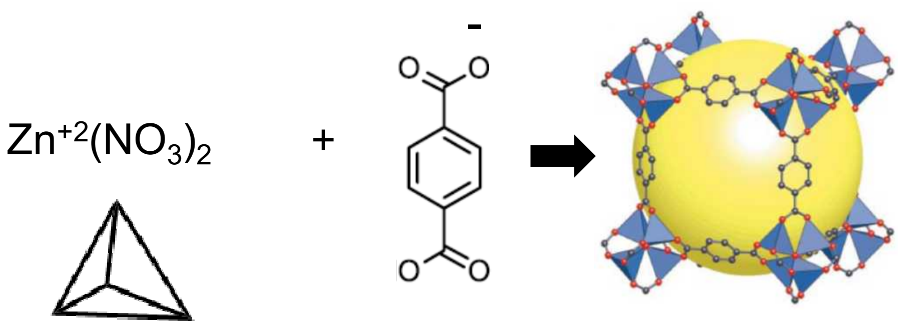


Knowing structure is POWER…because you can relate it to function!

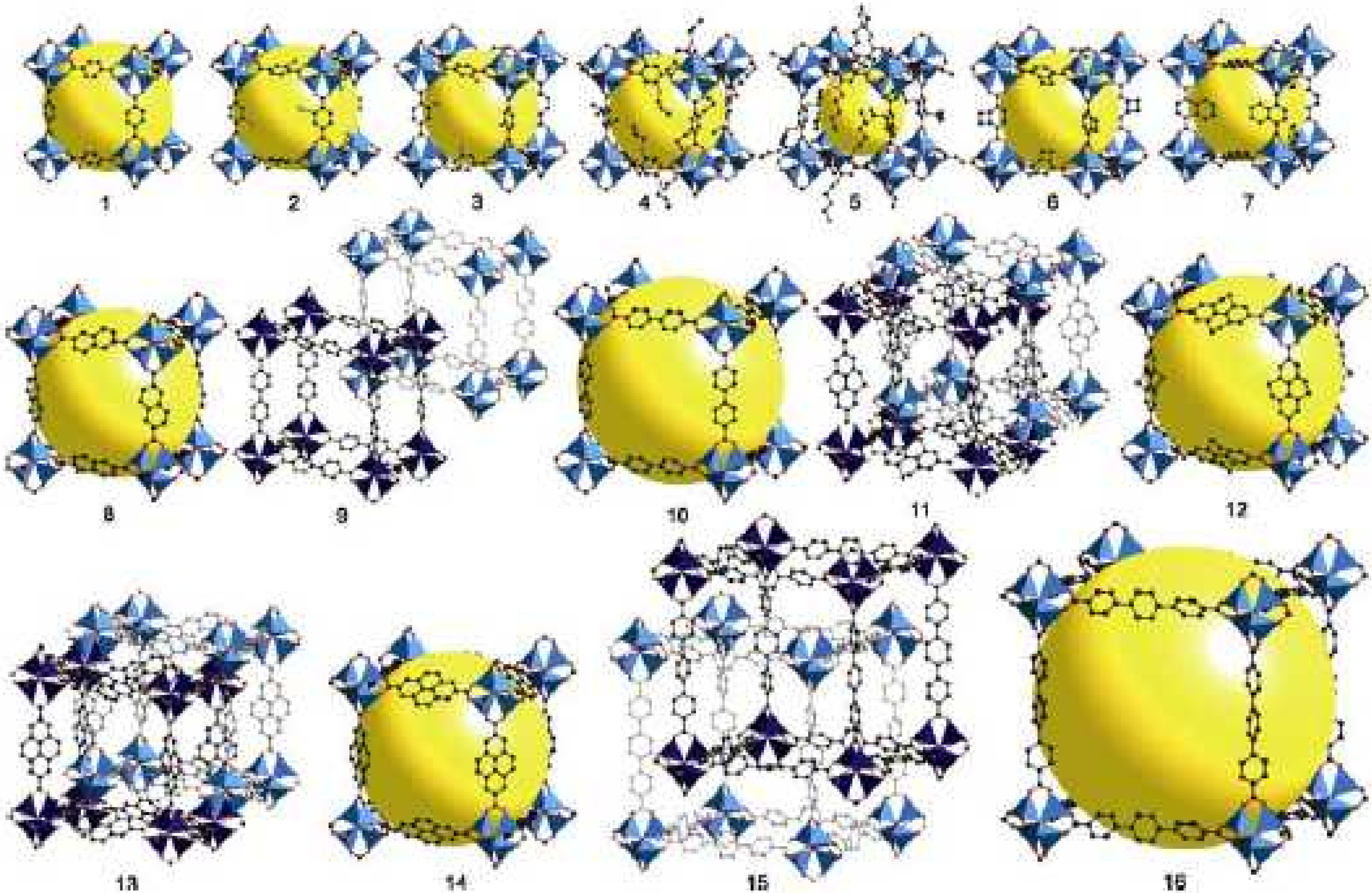
What is a Metal-Organic Framework?

Crystalline (therefore ordered), nanoporous structure





MOFs are a subset of a growing category of self-assembled, nanoporous gas storage materials



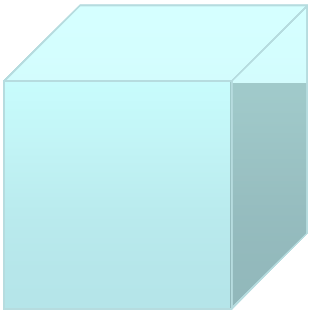
What's the surface area of 1 cm^3 of a MOF (approximately)?

MOF pore diameters are ~ 1 – 3 nm

→ r(pore) ≈ 1 nm = 10^{-9} m

Pore volume = $(4/3)\,\pi r^3 = 4\times10^{-27}\ m^3 = 4\ nm^3$

Surface area = $4\pi r^2 \approx 10^{-17}\ m^2$



How many pores in 1 cm^3 ?

$1\ cm^3 = (10^7\ nm)^3 = 10^{21}\ nm^3$

$10^{21}\ nm^3/(4\ nm^3/pore) = 2.5\times10^{20}$ pores

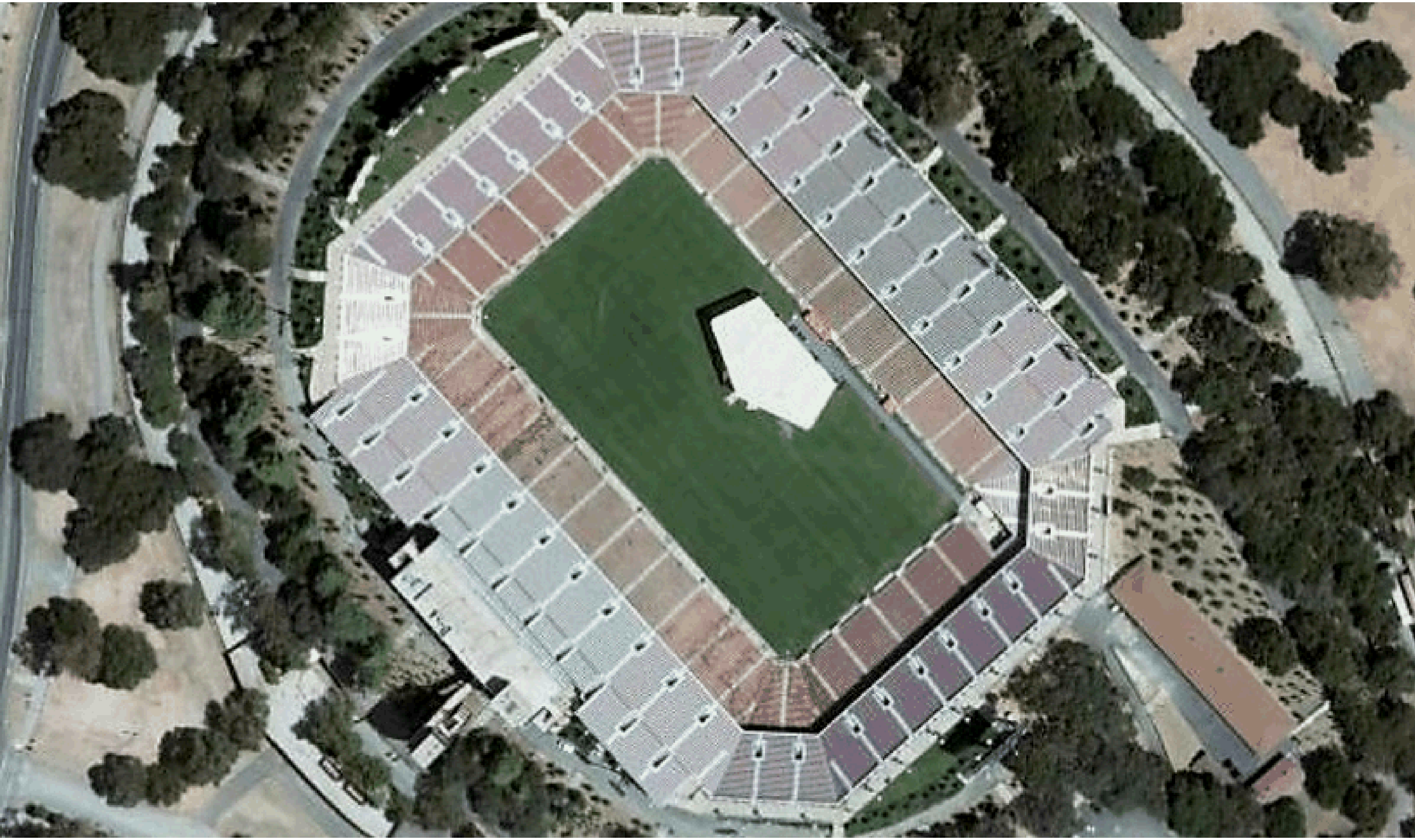
Total surface area = $(2.5\times10^{20}$ pores$)\times(10^{-17}\ m^2/pore)$

= 2,500 m^2/cm^3

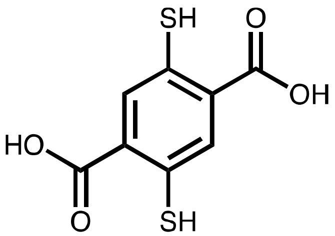
If density = 0.5 g/cm^3, then **5,000 m^2/g!**

(a tennis ball is ~ 0.0002 m^2/g)

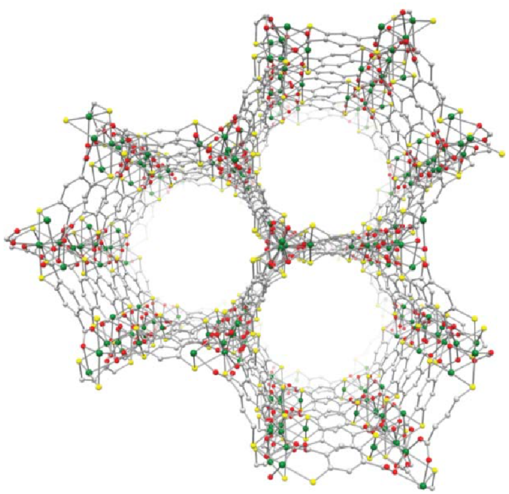
1 football field = 5,351 m^2



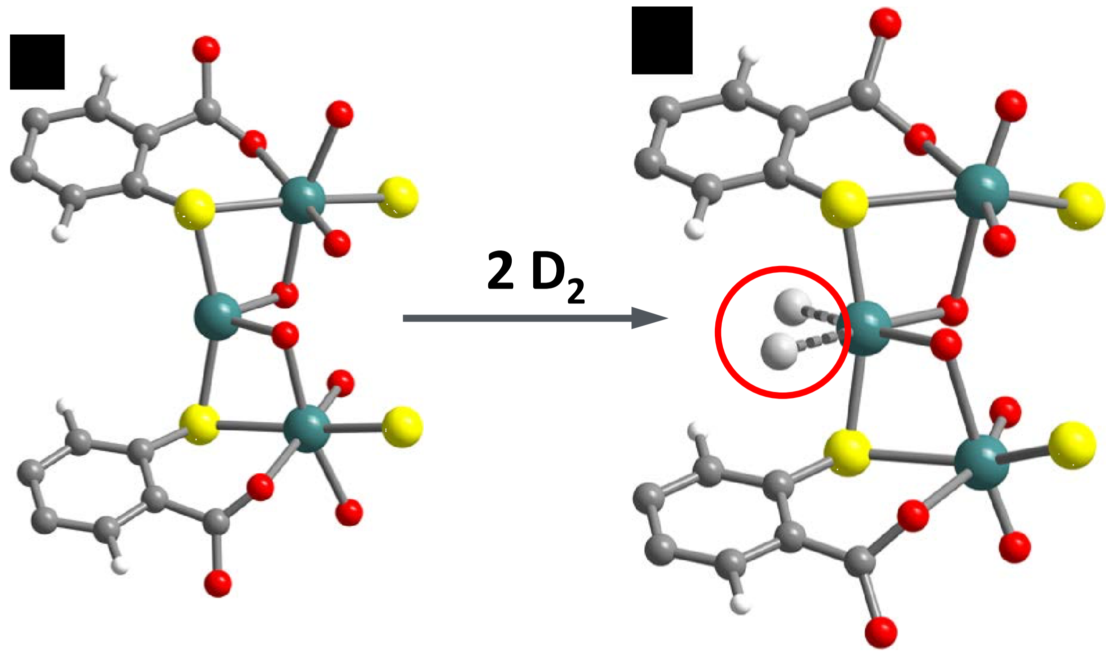
Multiple H_2 binding at a single site in a porous solid



H_4(dsbdc)



Mn_4(dsbdc)



Mn–D_2 distance:

3.07(3) Å

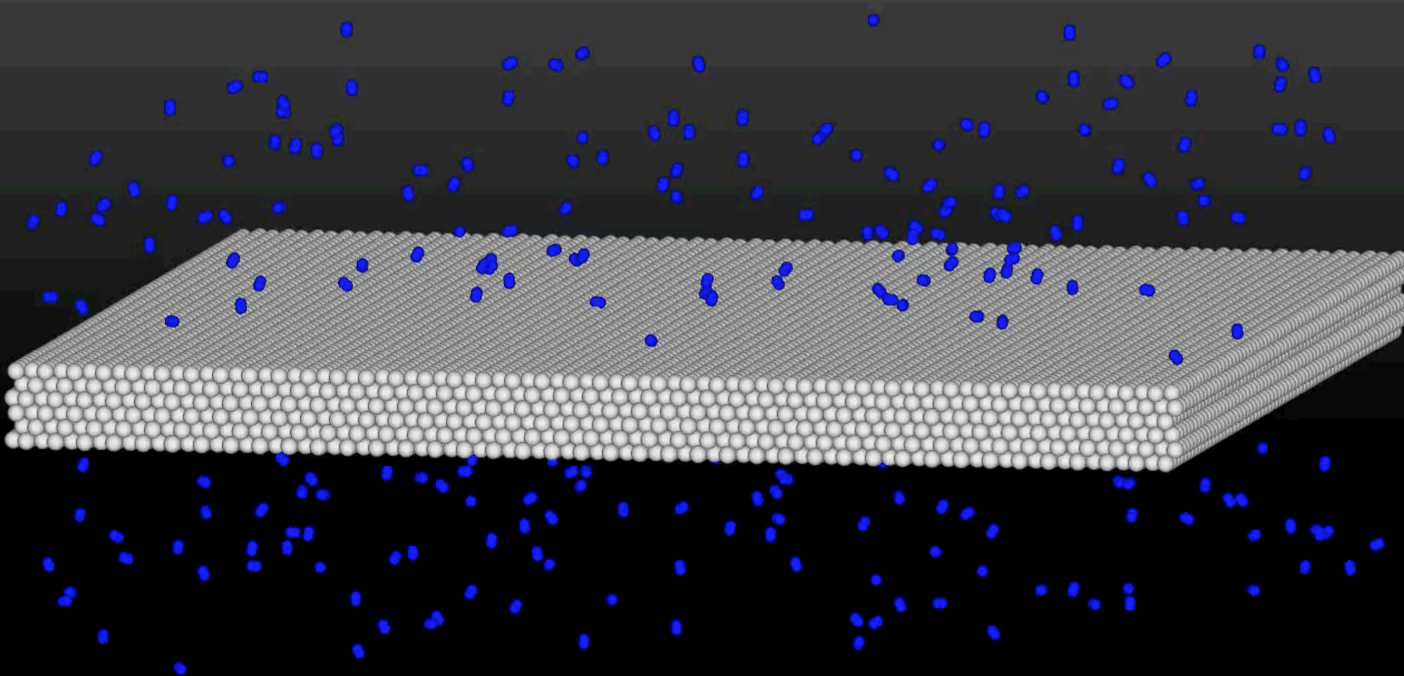
First demonstration of two H_2 molecules binding to a metal center in a MOF

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, *Chem. Commun.* **2016**, *52*, 8251-8254.

Reaction kinetics typically govern H_2 uptake and desorption in metal hydrides

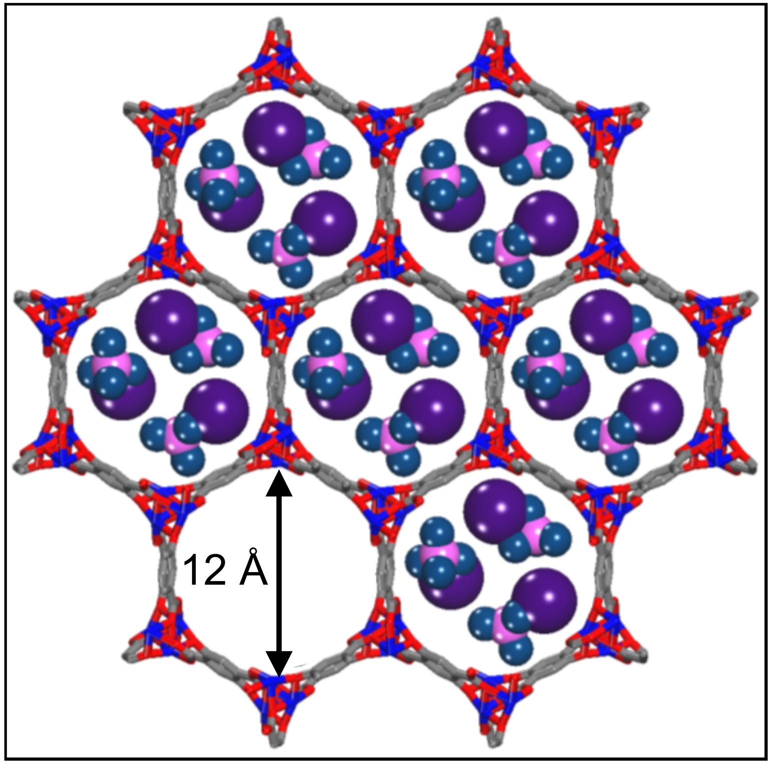
Example: $NaAlH_4 \rightarrow NaH + Al + 1.5\ H_2$

H_2 diffusion into aluminum

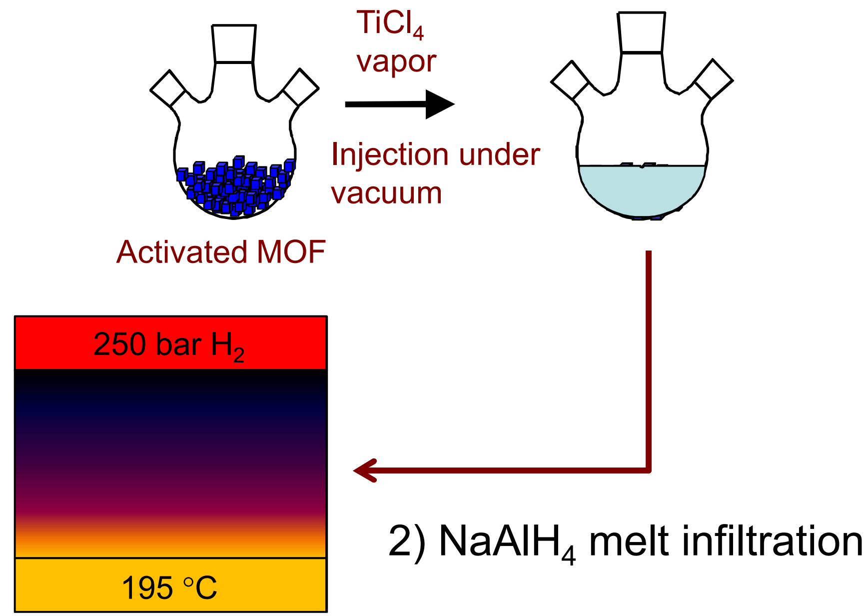


Use a Metal-Organic Framework as a nanoreactor

MOF-74(Mg) withstands $NaAlH_4$ melt-infiltration conditions

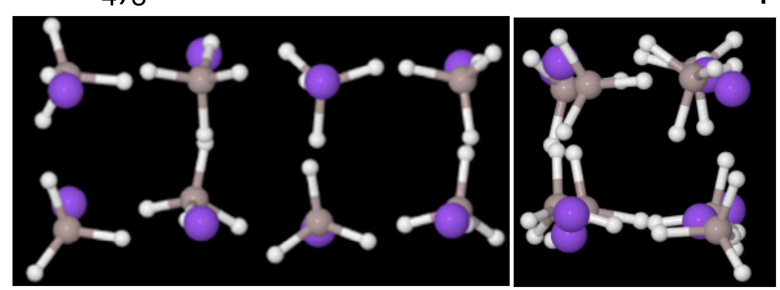


1) Vapor-phase Ti catalyst infiltration



2) $NaAlH_4$ melt infiltration

$(NaAlH_4)_8$ clusters are formed in the MOF pores



- 1530 m^2/g BET surface area, after infiltration → 340 m^2/g
- MOF open metal sites are binding sites for $TiCl_x$ catalyst molecules

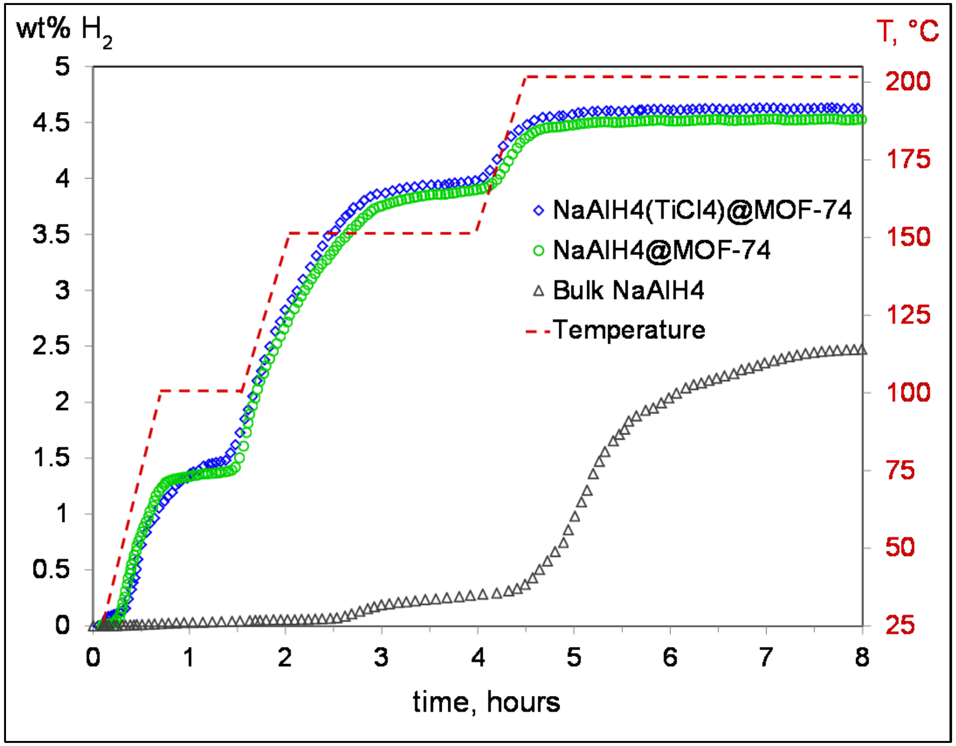
Nanoconfinement dramatically accelerates H_2 desorption

Temperature programmed desorption measurements

- **Highly improved kinetics vs. bulk**
  - Desorption in minutes vs. hours
- **Capacity almost 2X bulk at 200 °C**
- **Minimal effect of Ti on kinetics**

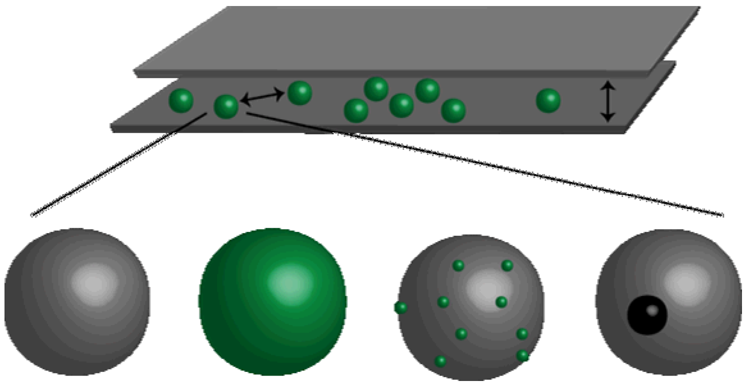
  → Difference almost entirely due to nanoscale and template effects
- **Initial desorption = 4.5 wt%**

  → Nearly complete to NaH + Al



V. Stavila, R.K. Bhakta, T.M. Alam, E.H. Majzoub, M.D. Allendorf, *ACS Nano*, **2012**, *6*, 9807–9817

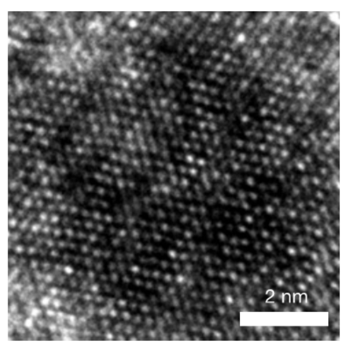
<u>Nanoscale thermodynamics</u>: hierarchically integrated hydrides

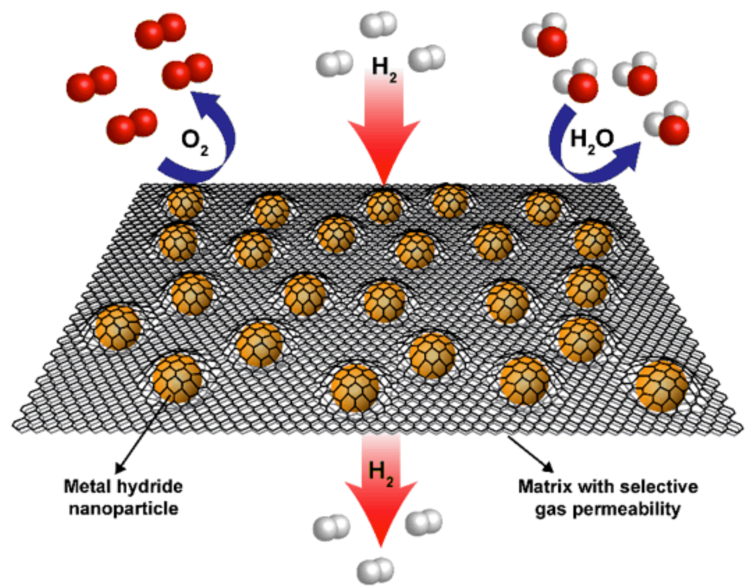


Cho, E., Urban, J. J. et al. *Adv. Mater.* **2015**, in press

- Want to have clear model systems to drive fundamental understanding
- Also push the development of advanced materials: from Mg and Al to complex hydrides such as $LiNH_2$, $Mg(BH_4)_2$

Want to integrate new classes of materials to provide options for modifying thermodynamics, understanding pathways





J. J. Urban et al. *Nature Comm.* 2016

MOLECULAR FOUNDRY
BERKELEY LAB

New Effort: HyMARC
Hydrogen Materials – Advanced Research Consortium

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Individual projects

- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

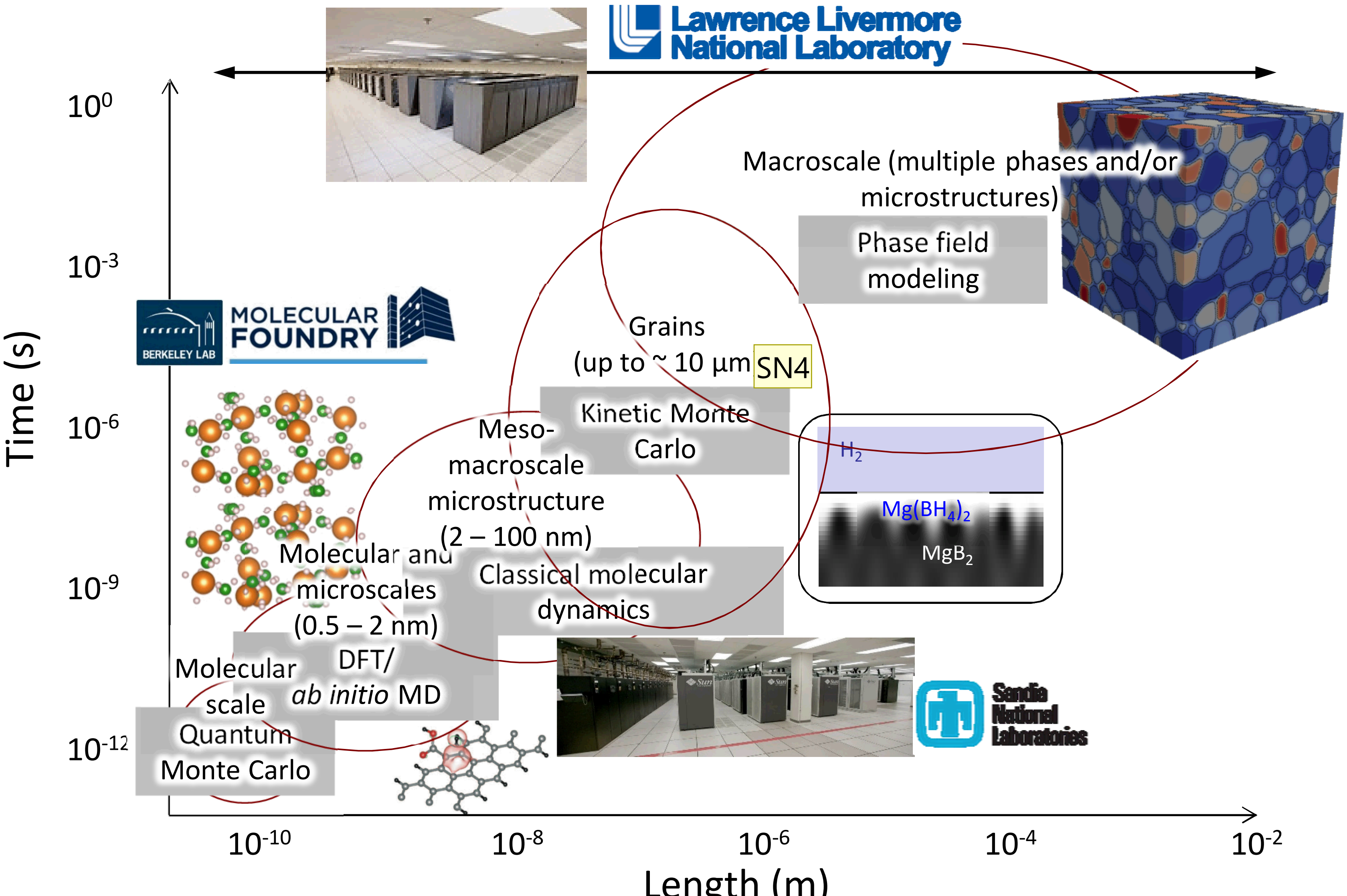
Core National Laboratory Team

- **Material development tools**
  - Foundational R&D
  - Computational modeling development
  - Synthetic/characterization protocol development
- **Guidance to FOA projects**
- **Database development**

Characterization and Validation Team

- **Characterization Resources**
  - Validation of Performance
  - Validation of "Theories"
- **"User-facility" for FOA projects/HyMARC**
- **Characterization Method Development**

HyMARC approach: high-performance National Lab computing allows simulations at all relevant length scales

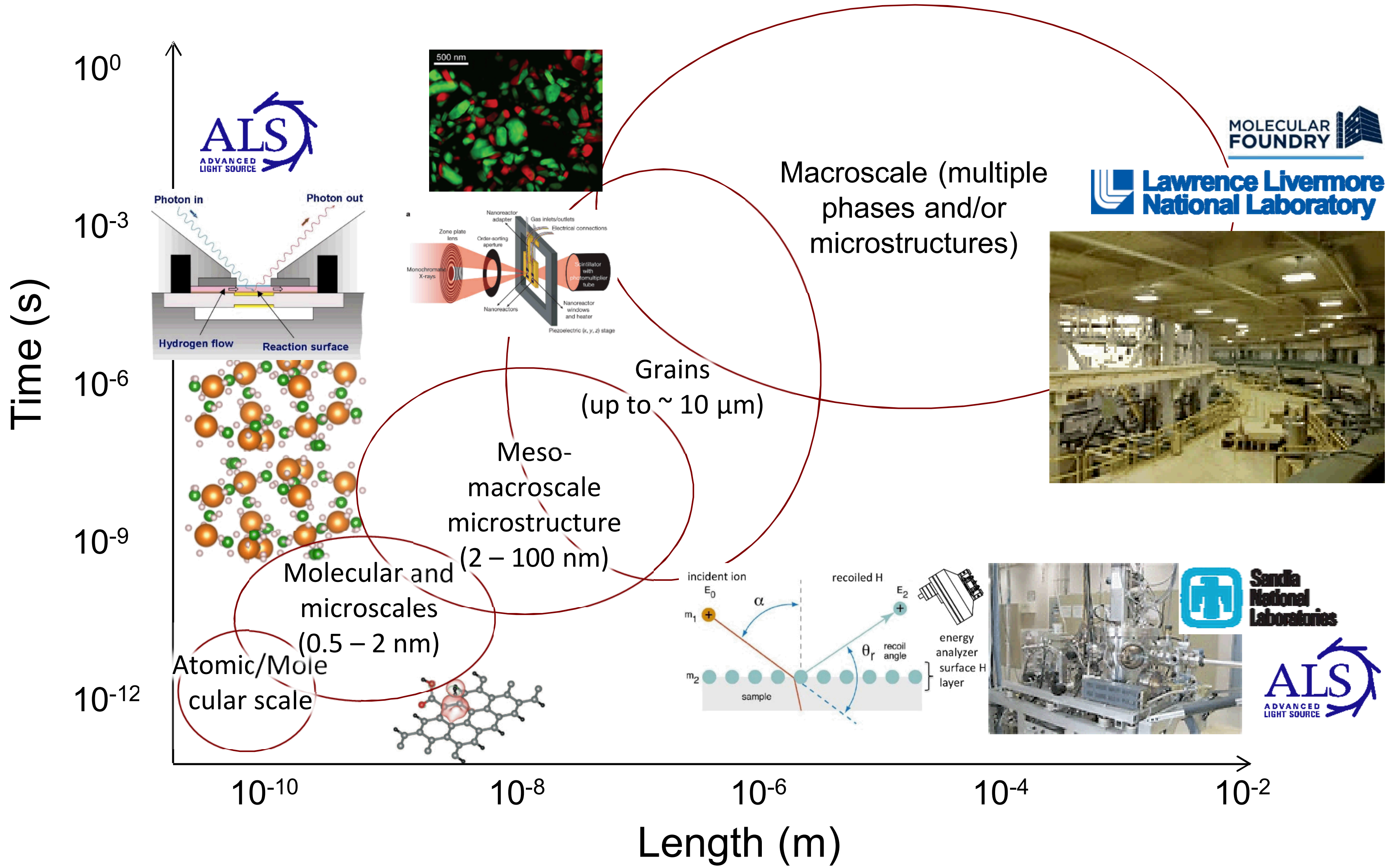


Slide 37

SN4 On my PC, the text boxs within the figure (e.g., Quantum Monte Carlo" are shaded gray. Possibly try saving an an image/picture and pasting into PowerPoint.

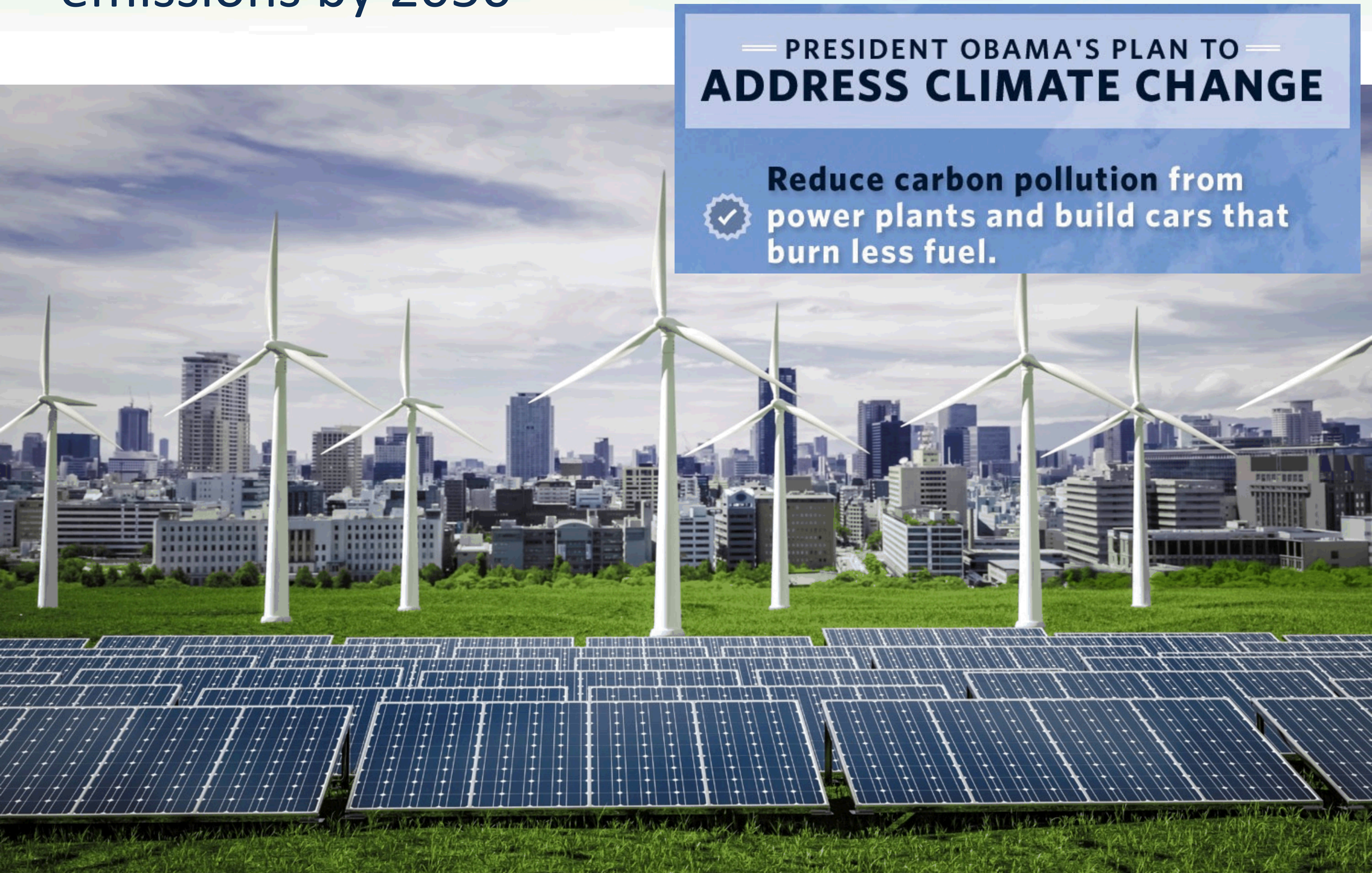
Stetson, Ned, 5/3/2016

HyMAC approach: state-of-the-art characterization tools to probe bulk and surface chemistry, microstructure, phase composition



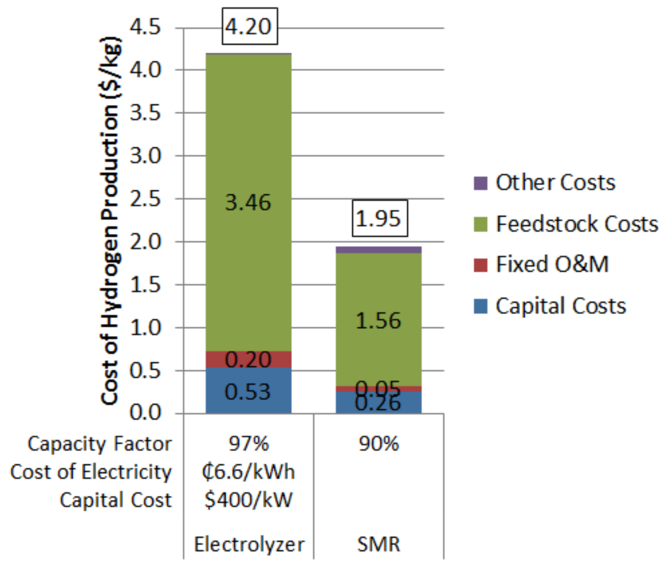
H_2 production at scale

Administration goal of 83% reduction of GHG emissions by 2050

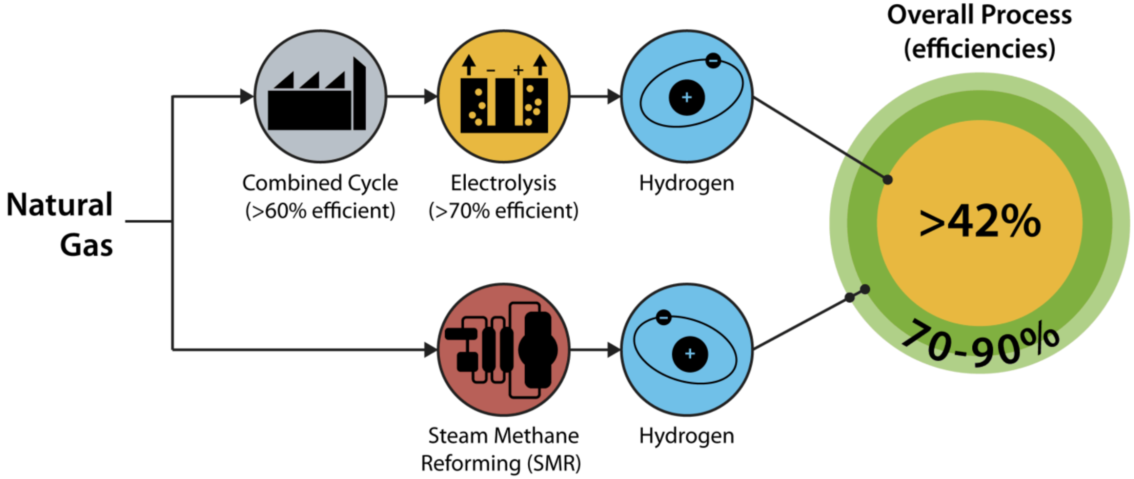


Hydrogen Production (Current)

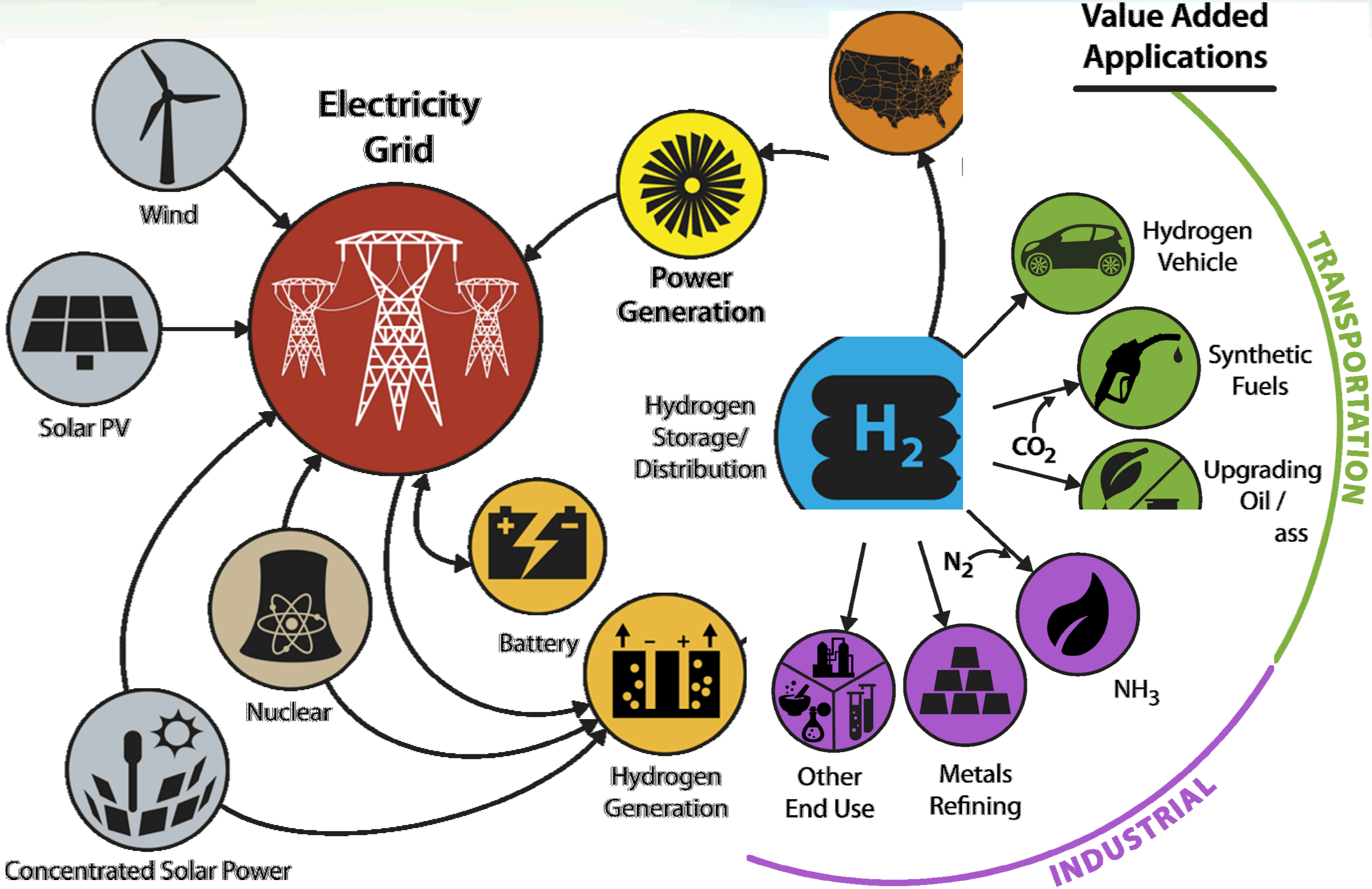
- Today's electrolysis technology (scaled up) is not cost competitive with today's SMR.
- This is expected—it's driven by electricity cost tied to burning fossil fuels and two inefficient processes.



H2A Analysis, Josh Eichman, NREL

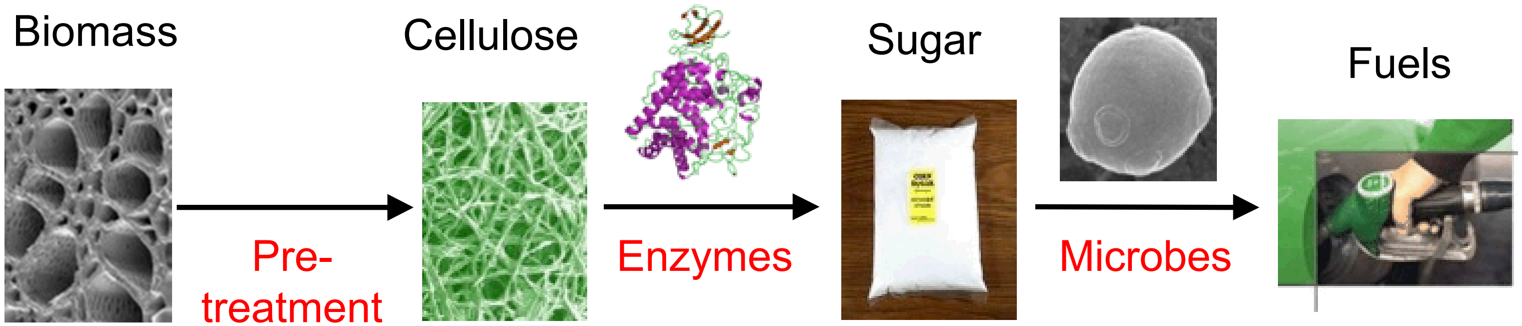


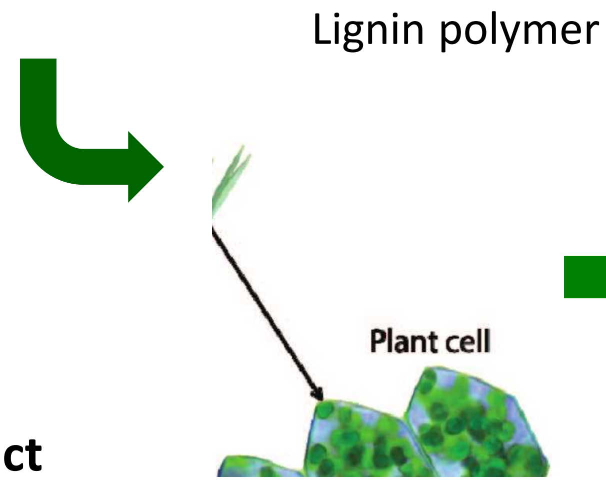
Conceptual low-carbon energy system*



*Illustrative example, not comprehensive; from H2@Scale Big Idea Concept, Pivovar et al

Closing the carbon loop in biofuels production requires new solutions for lignin byproduct





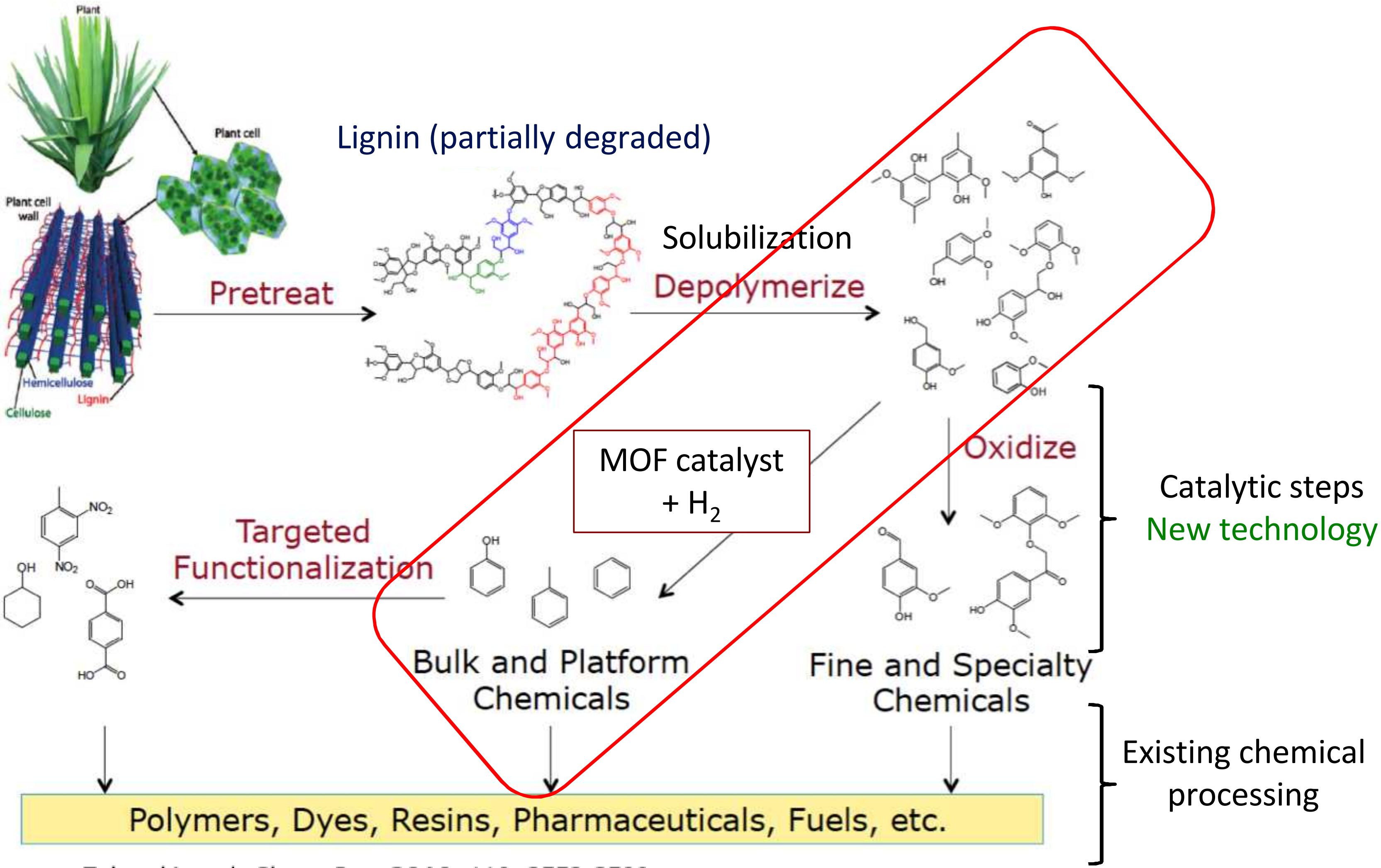
- Carbon fibers
- Engineered plastics
- Thermoplastic elastomers
- Polymeric foams
- Fungible fuels
- Commodity chemicals

Lignin byproduct

- 20 – 30% of biomass by weight
- Regenerated on Earth at a rate of 60 billion tons/year
- 50 Mtons/year waste generated by agriculture and forestry
- Only 2% of waste lignin is used commercially (remainder is burned)
- **Biofuels industry could generate >300 Mton lignin waste a year**

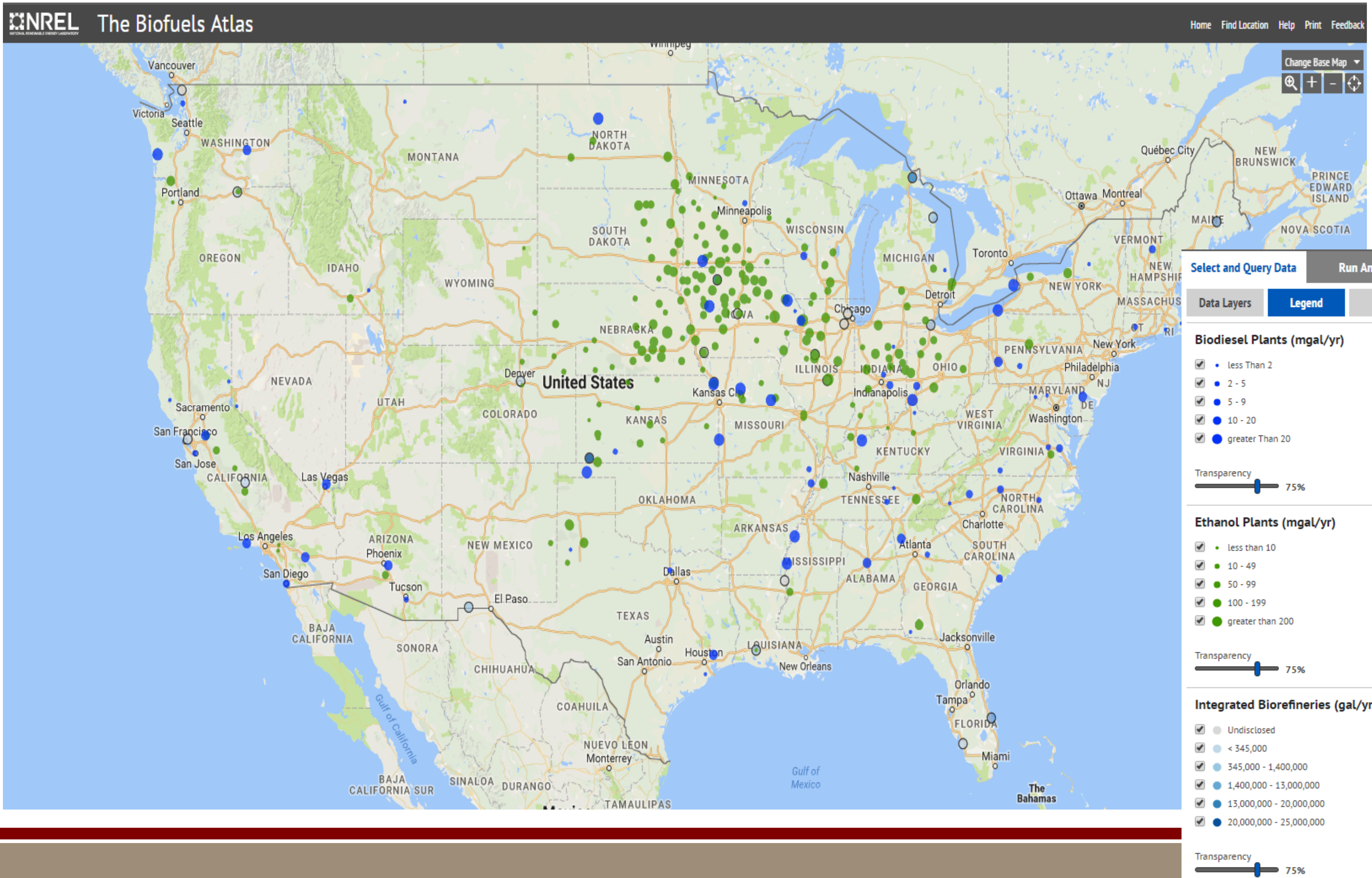
Lignin valorization using hydrogen

Hydrogen is a readily available, low-cost consumable reactant

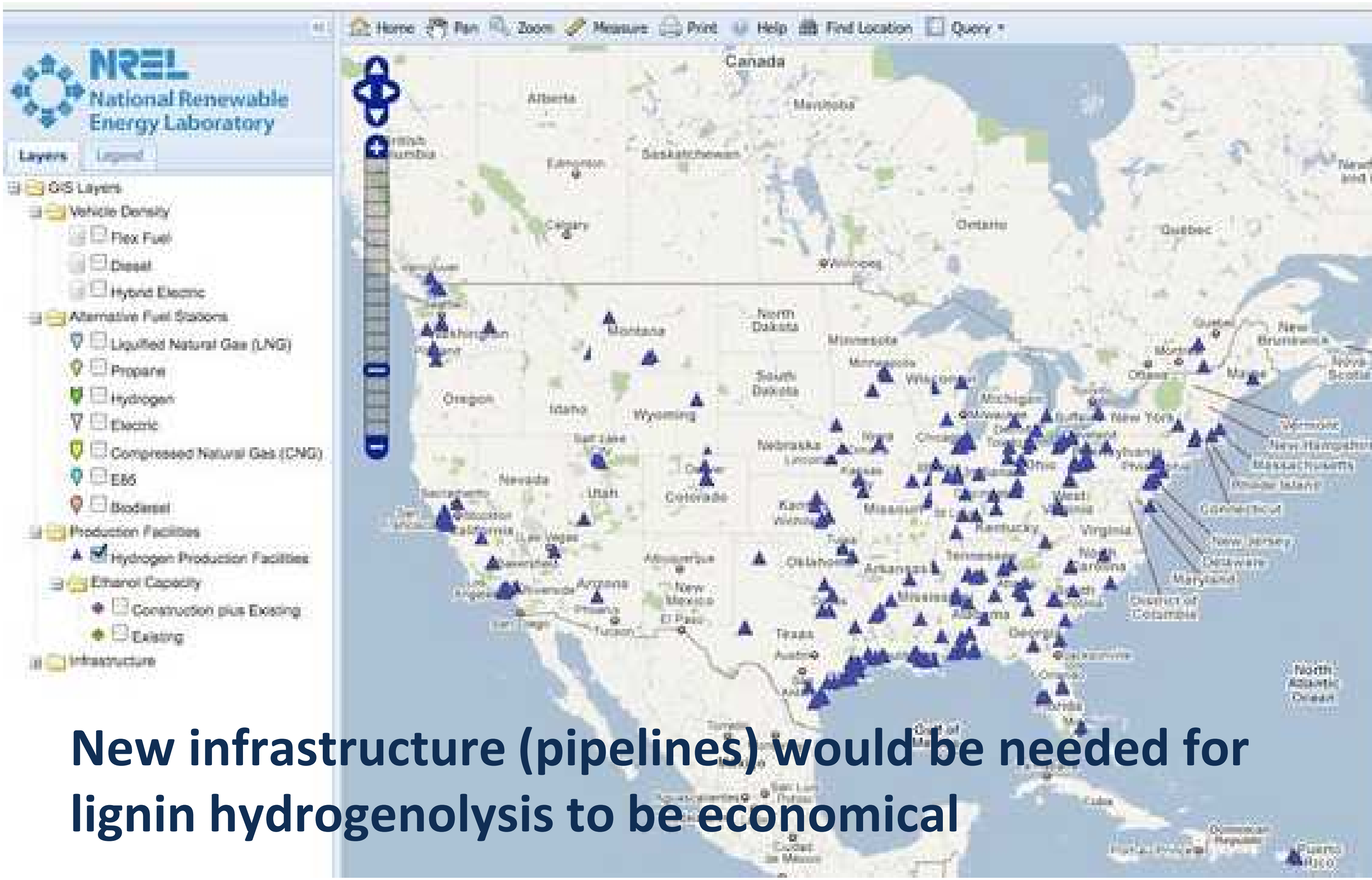


Zakzeski et al. *Chem. Rev.* **2010**, 110, 3552-3599

Biofuel production is concentrated in the upper Midwest



H_2 production tends to be near refineries, primarily on the Gulf Coast and near large cities



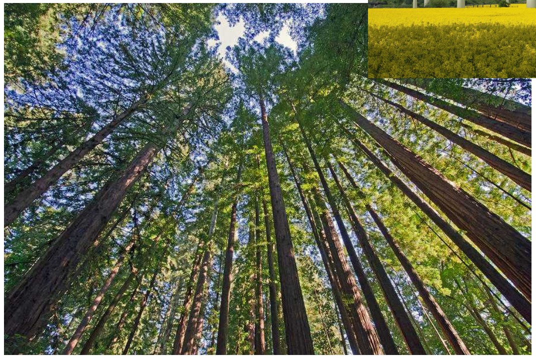
New infrastructure (pipelines) would be needed for lignin hydrogenolysis to be economical

Take-home messages

- Hydrogen-powered fuel cell cars are now commercially available

- A carbon-neutral economy is comprised of many interlinked components

- Hydrogen is much more than a transportation fuel: it can be an important enabler of other renewable energy technologies



We gratefully acknowledge the
EERE Fuel Cell Technologies Office for funding HyMARC

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy