Lectures and Homework

5/6/2015. Lecture 13:

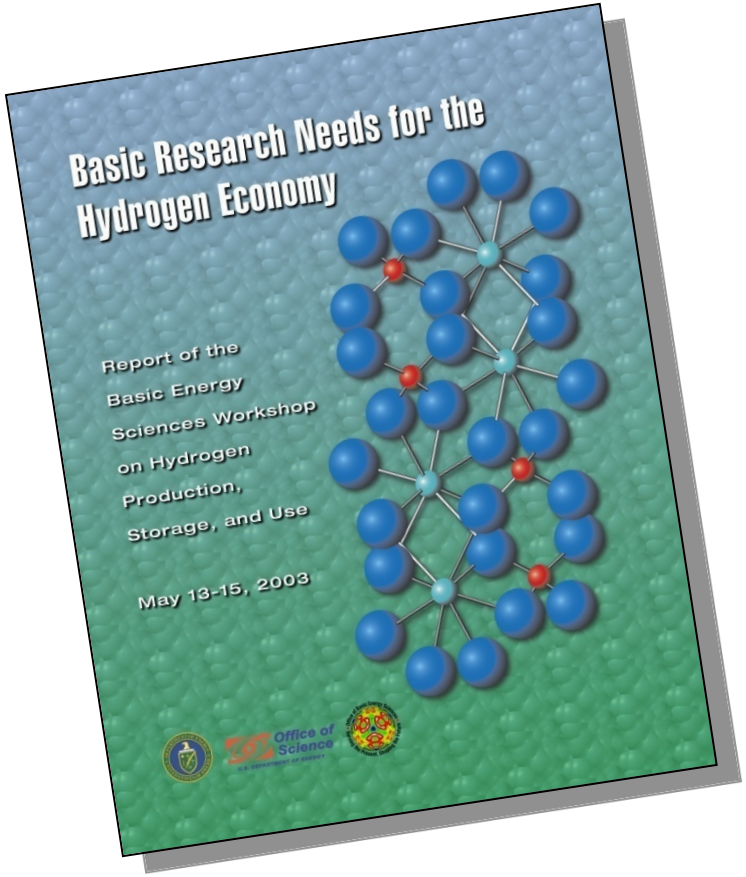
HW: Read Boyle, Renewable Energy, pg. 496-503

Personal energy audit due.5/15.
sign out for kill a watt meters

Midterm Exam: 5/8. closed book, no notes

Homework #3. Assigned 5/8

Basic Research Needs for the Hydrogen Economy



June 24, 2004
DOE Nano Summit
Washington, D.C.

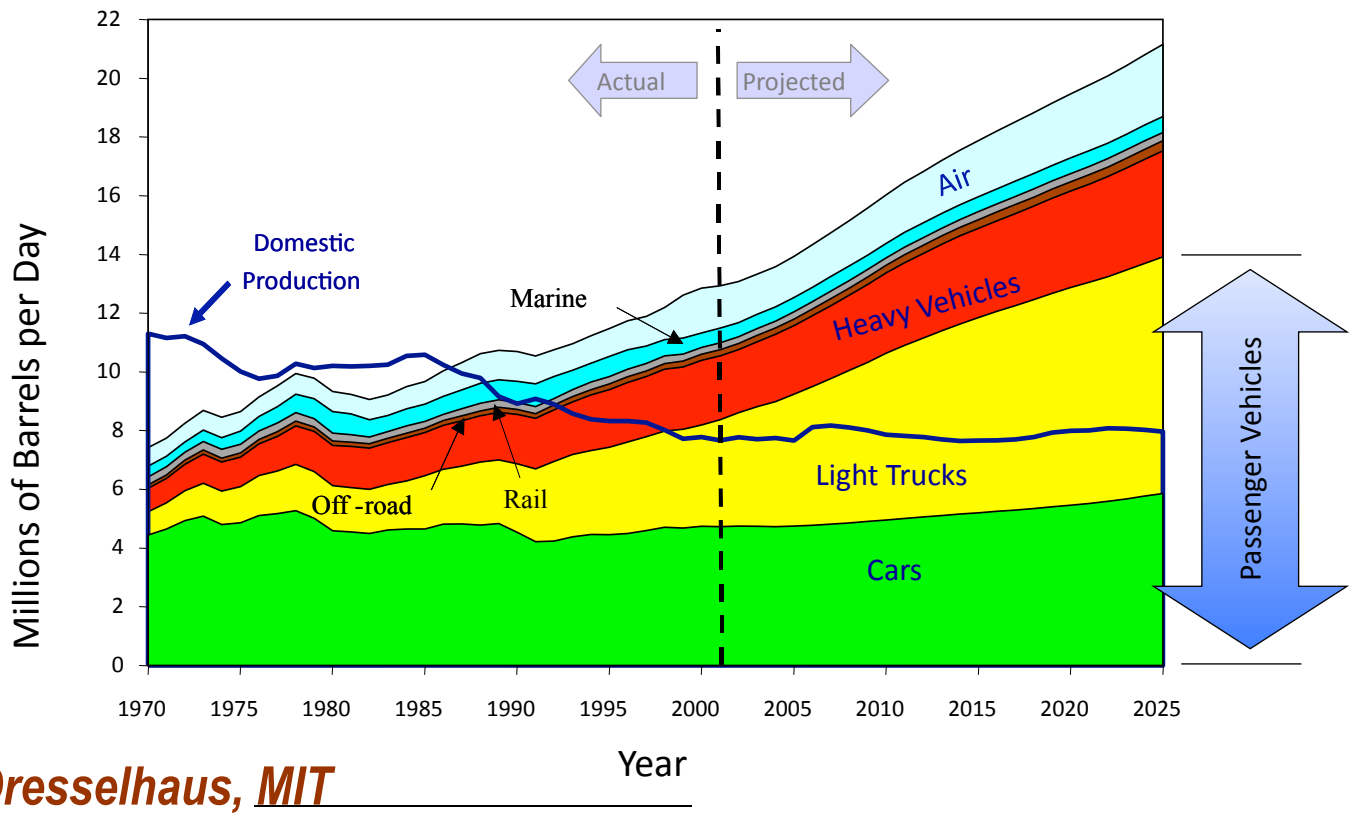
Presented by:
Mildred Dresselhaus
Massachusetts Institute of Technology
millie@mgm.mit.edu
617-253-6864

OFFICE OF SCIENCE
U.S. DEPARTMENT of ENERGY

Drivers for the Hydrogen Economy:

- *Reduce Reliance on Fossil Fuels*
- *Reduce Accumulation of Greenhouse Gases*

Energy Source	% of U.S. Electricity Supply	% of Total U.S. Energy Supply
Oil	3	39
Natural Gas	15	23
Coal	51	22
Nuclear	20	8
Hydroelectric	8	4
Biomass	1	3
Other Renewables	1	1



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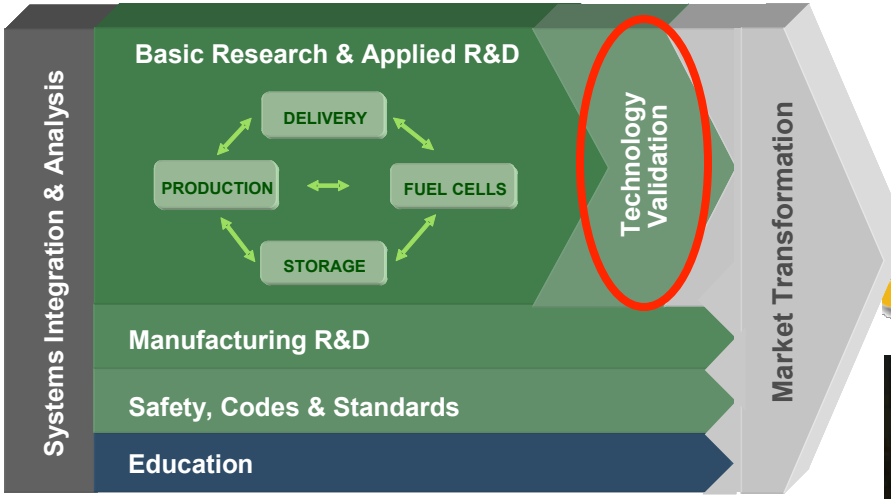
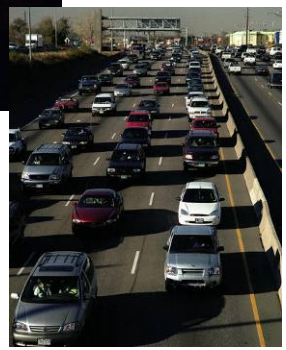
U.S. Department of Energy Hydrogen Program

TODAY

FUTURE

Petroleum-Based Transportation Sector





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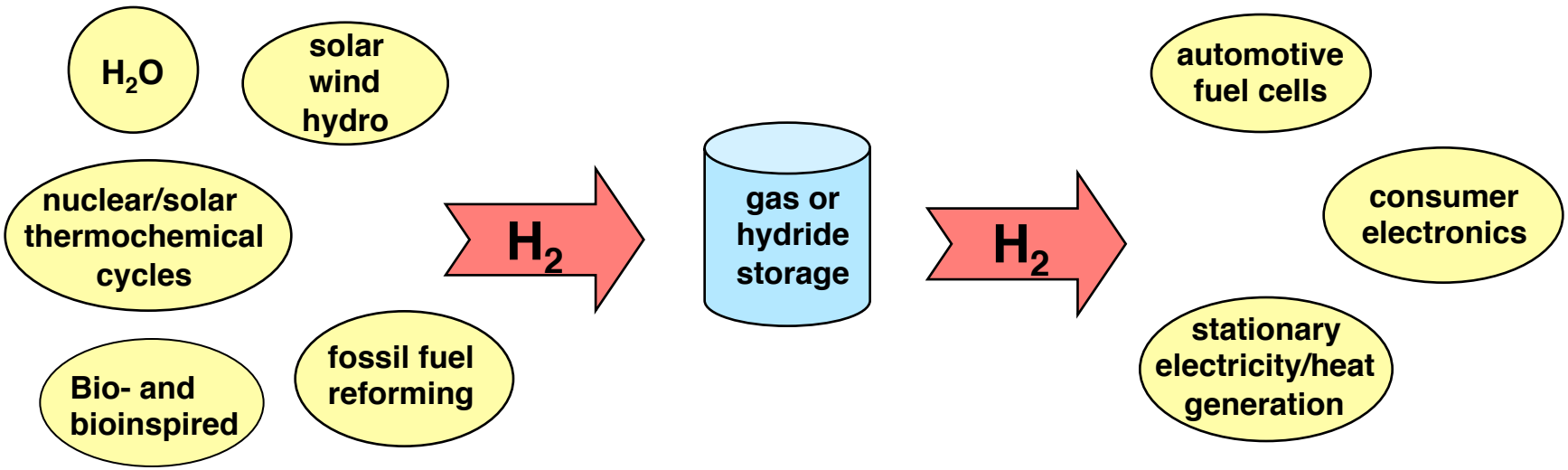
National Renewable Energy Laboratory

The Hydrogen Economy



production	storage	use in fuel cells
9M tons/yr	4.4 MJ/L (Gas, 10,000 psi) 8.4 MJ/L (Liquid H2)	$3000/kW
↓	↓	↓
150 M tons/yr (light cars and trucks in 2040)	9.70 MJ/L (2015 FreedomCAR Target)	$30/kW (Internal Combustion Engine)

M. S. Dresselhaus, MIT

Fundamental Issues

The hydrogen economy is a compelling vision:

- It potentially provides an abundant, clean, secure and flexible energy carrier
- Its elements have been demonstrated in the laboratory or in prototypes

However . . .

- It does not operate as an integrated network
- It is not yet competitive with the fossil fuel economy in cost, performance, or reliability
- The most optimistic estimates put the hydrogen economy decades away

Thus . . .

- An aggressive basic research program is needed, especially in gaining a fundamental understanding of the interaction between hydrogen and materials at the nanoscale

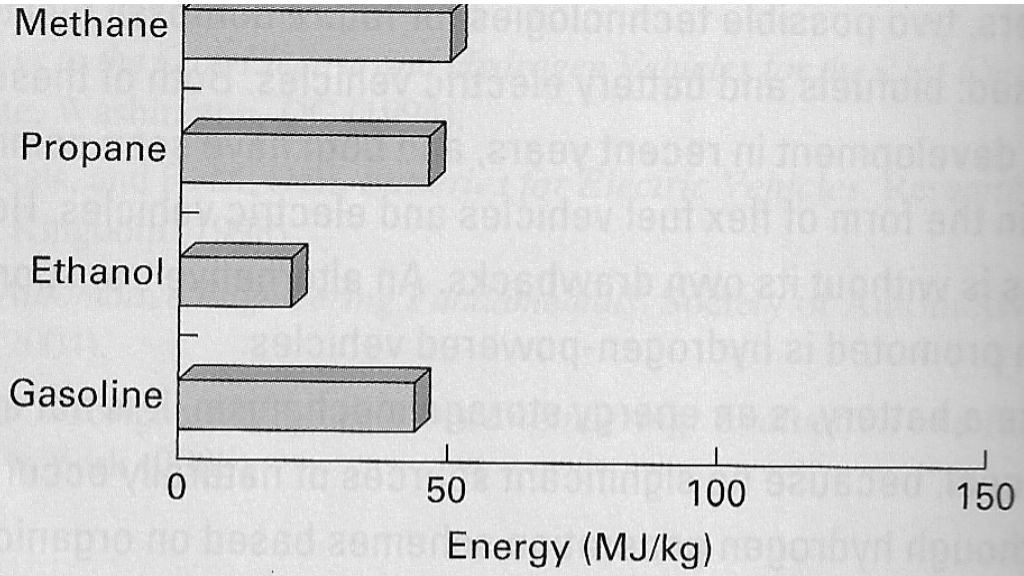


Figure 20.1: Energy content (per kg) of various fuels.

Table 20.1: Specific and volumetric energy densities of gasoline and hydrogen at STP.

Fuel Cell Vehicle Learning Demonstration Project Underway; 3 Years into 5 Year Demo

- Objectives
  - Validate H_2 FC Vehicles and Infrastructure in Parallel
  - Identify Current Status and Evolution of the Technology

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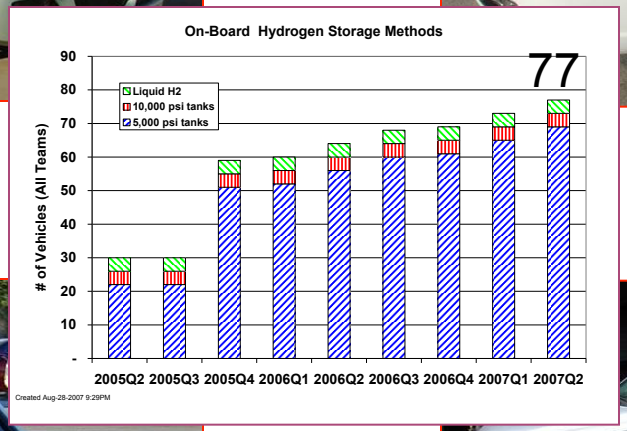
National Renewable Energy Laboratory

Vehicle Status: All of First Generation Vehicles Deployed, 2nd Generation Initial Introduction in Fall 2007



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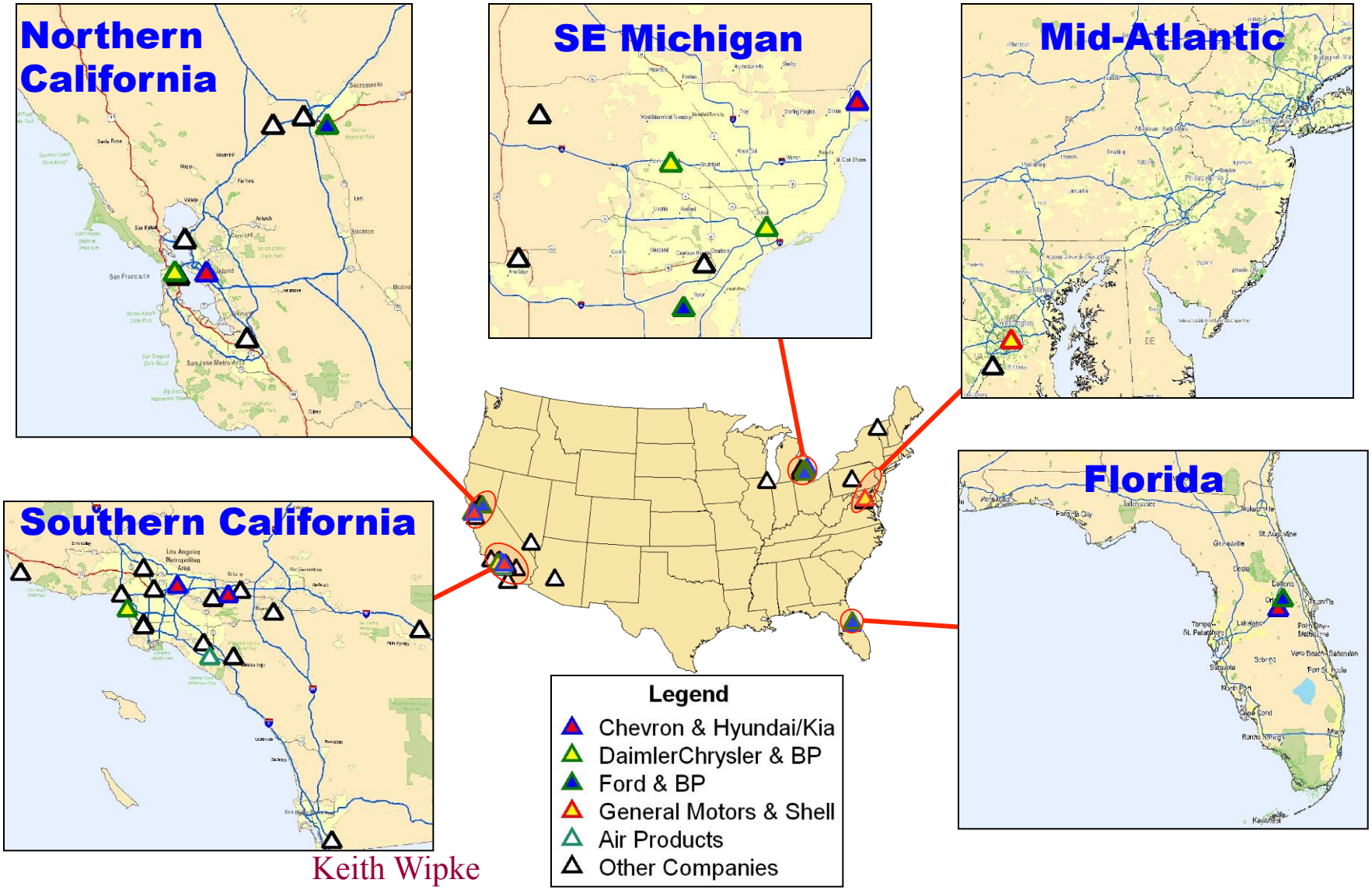
Refueling Stations from All Four Teams Test Vehicle/ Infrastructure Performance in Various Climates



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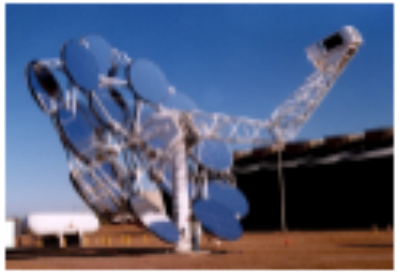
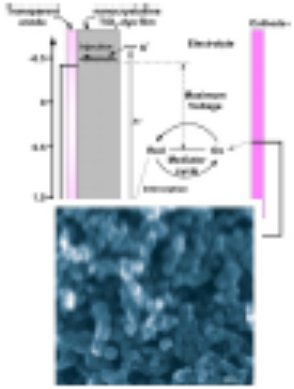
H_2 Production Strategies

Distributed natural gas and electrolysis economics are important for the "transition"

Energy resource diversification is important for the long-term





Source: Steve Chalk, EERE

Hydrogen Production Panel

Panel Chairs: Tom Mallouk (Penn State), Laurie Mets (U of Chicago)

Current status:

- Steam-reforming of oil and natural gas produces 9M tons H_2/yr
- We will need 150M tons/yr for transportation
- Requires CO_2 sequestration.

Alternative sources and technologies:

Coal:

- Cheap, lower H_2 yield/C, more contaminants
- Research and Development needed for process development, gas separations, catalysis, impurity removal.

Solar:

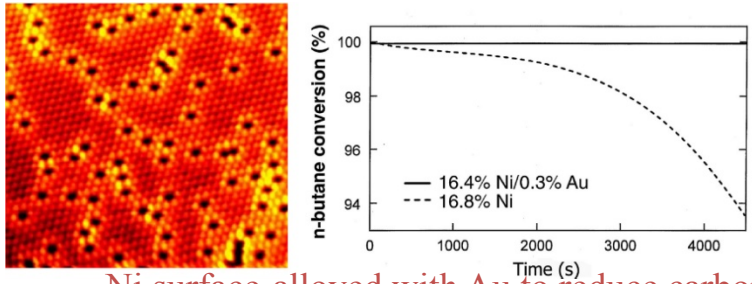
- Widely distributed carbon-neutral; low energy density.
- Photovoltaic/electrolysis current standard – 15% efficient
- Requires 0.3% of land area to serve transportation.

Nuclear: Abundant; carbon-neutral; long development cycle.

Priority Research Areas in Hydrogen Production

Fossil Fuel Reforming Intermediate Term

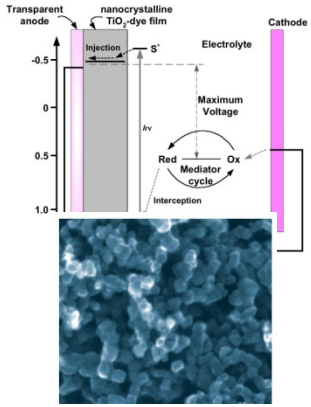
Molecular level understanding of catalytic mechanisms, nanoscale catalyst design, high temperature gas separation



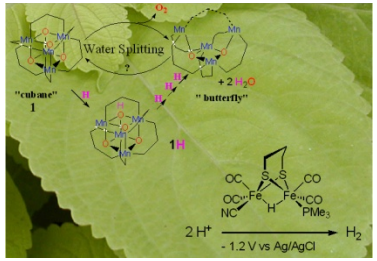
Ni surface-alloyed with Au to reduce carbon poisoning

Solar Photoelectrochemistry/Photocatalysis

Light harvesting, charge transport, chemical assemblies, bandgap engineering, interfacial chemistry, catalysis and photocatalysis, organic semiconductors, theory and modeling, and stability



Dye-Sensitized Solar Cells



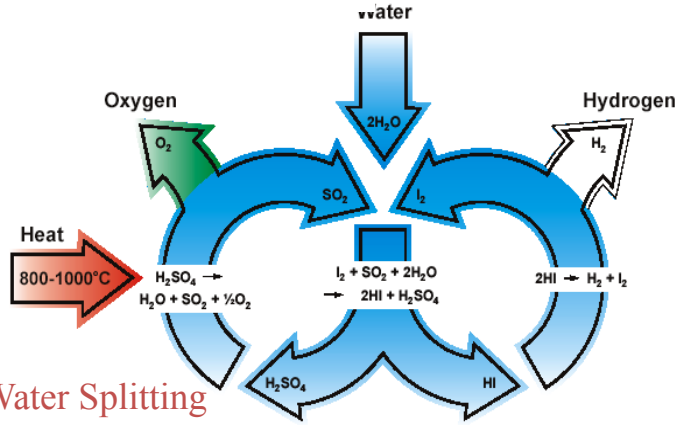
Synthetic Catalysts for H_2 Production

Bio- and Bio-inspired H_2 Production

Microbes & component redox enzymes, nanostructured 2D & 3D hydrogen/oxygen catalysis, sensing, and energy transduction, engineer robust biological and biomimetic H_2 production systems

Nuclear and Solar Thermal Hydrogen

Thermodynamic data and modeling for thermochemical cycle (TC), high temperature materials: membranes, TC heat exchanger materials, gas separation, improved catalysts



Thermochemical Water Splitting

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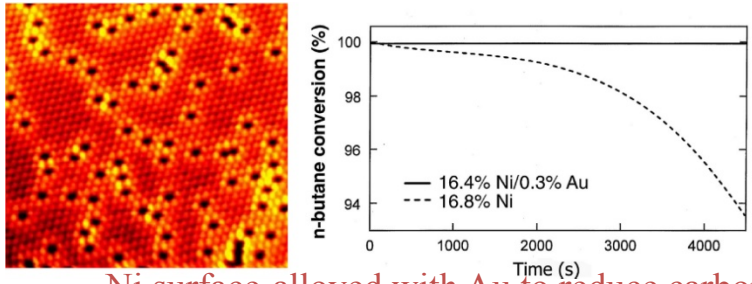

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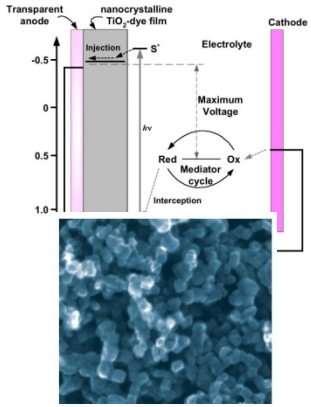

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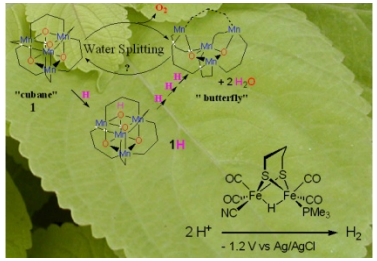

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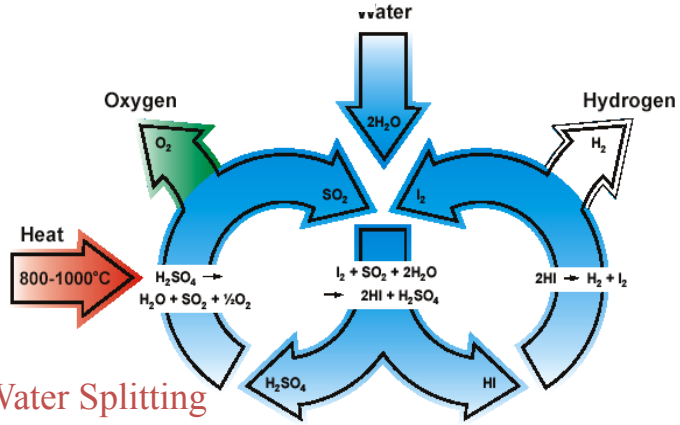


Thermochemical Water Splitting

Hydrogen Storage Panel

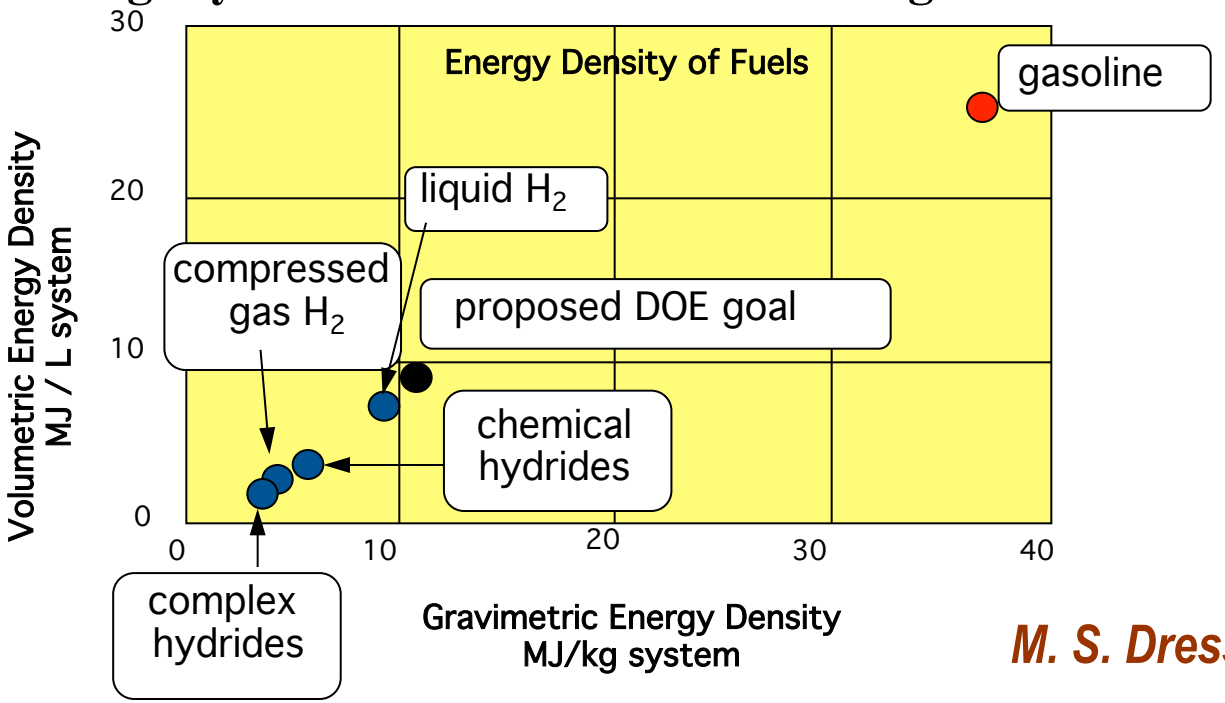
Panel Chairs: Kathy Taylor (GM, Retired) and Puru Jena (Virginia Commonwealth U)

Current Technology for automotive applications

- **Tanks for gaseous or liquid hydrogen storage.**
- **Progress demonstrated in solid state storage materials.**

System Requirements

- **Compact, light-weight, affordable storage.**
- **System requirements set for FreedomCAR: 4.5 wt% hydrogen for 2005, 9 wt% hydrogen for 2015.**
- **No current storage system or material meets all targets.**



M. S. Dresselhaus, MIT

Ideal Solid State Storage Material

- High gravimetric and volumetric density (9 wt %)
- Fast kinetics
- Favorable thermodynamics
- Reversible and recyclable
- Safe, material integrity
- Cost effective
- Minimal lattice expansion
- Absence of embrittlement

FreedomCAR Hydrogen Storage System Targets

	2005	2010	2015
• specific energy (MJ/kg)	5.4	7.2	10.8
weight percent hydrogen	4.5%	6.0%	9.0%
• energy density (MJ/liter)	4.3	5.4	9.72
• system cost ($/kg H_2)	200	133	67
• operating temperature (°C)	-20/50	-30/50	-40/60
• cycle life (cycles)	500	1000	1500
• flow rate (g/sec)	3	4	5
• Max delivery pressure (Atm)	100	100	100
• transient response (sec)	1.75	0.75	0.5
• refueling rate (kg H_2/min)	0.5	1.5	2.0
• loss, permeation, leakage, toxicity, safety			

JoAnn Milliken, DOE/EERE

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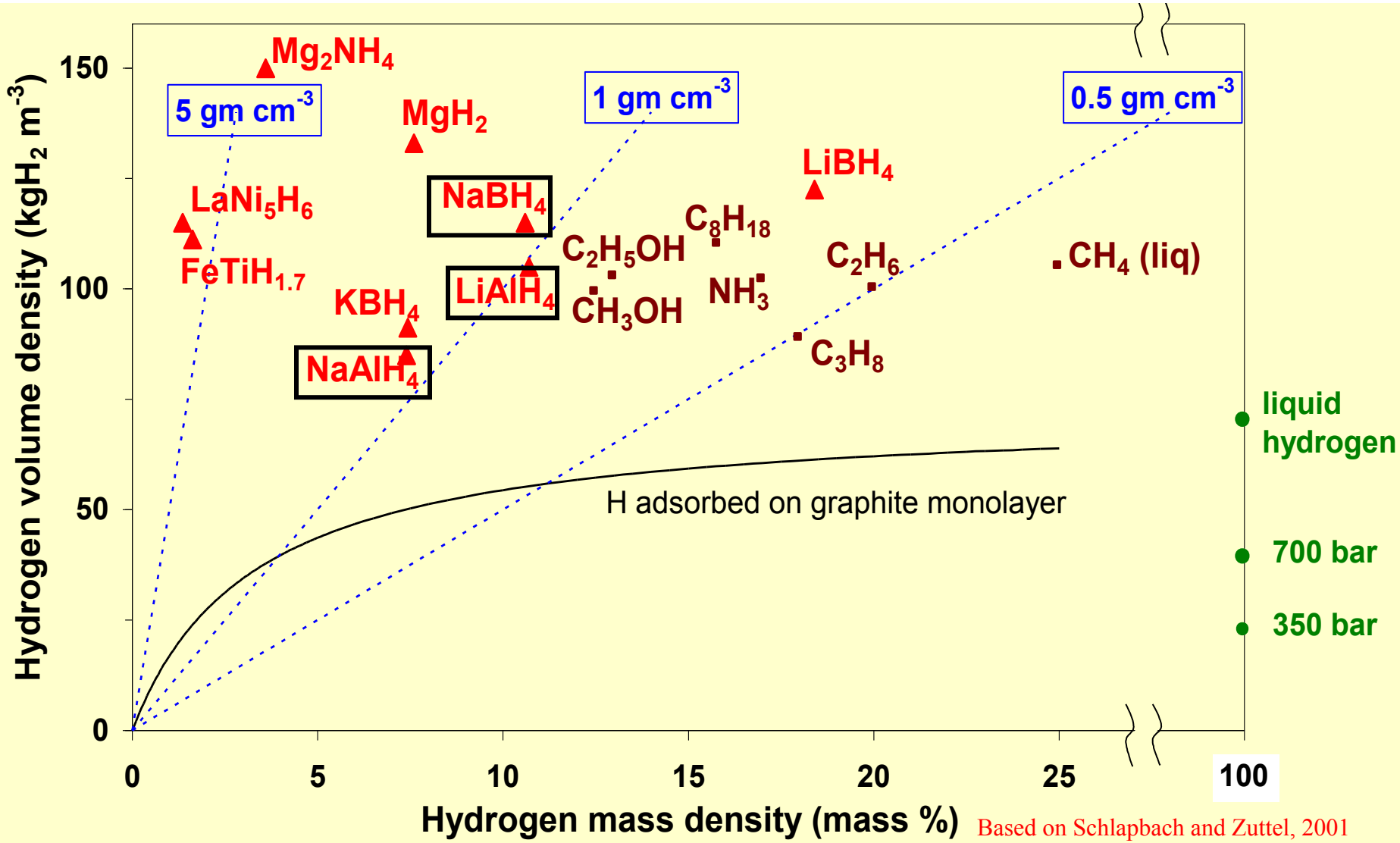
JoAnn Milliken, DOE/EERE

High Gravimetric H Density Candidates



Based on Schlapbach and Zuttel, 2001

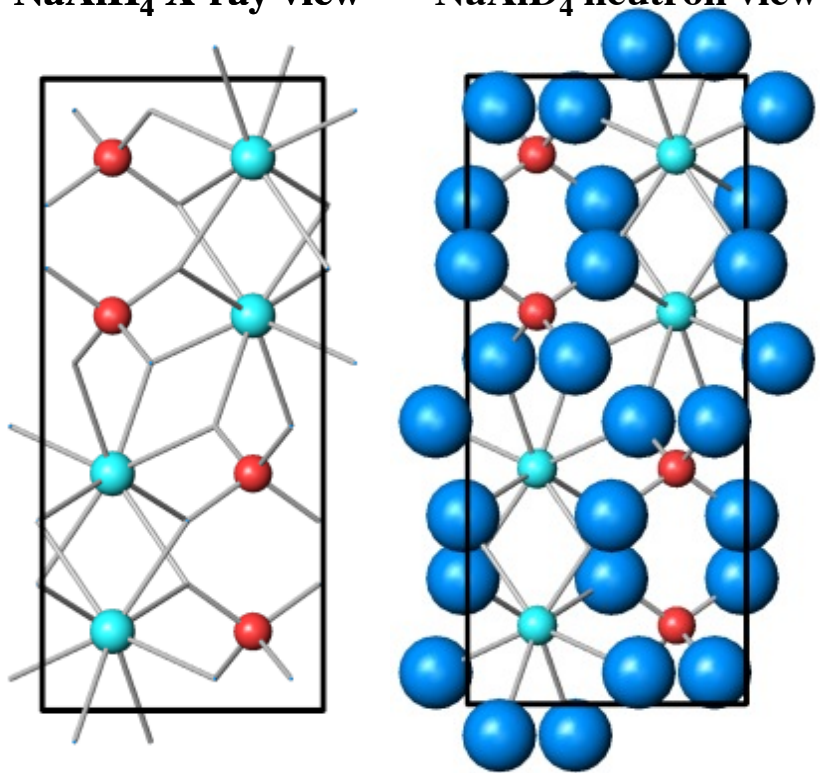
M. S. Dresselhaus, MIT

Priority Research Areas in Hydrogen Storage

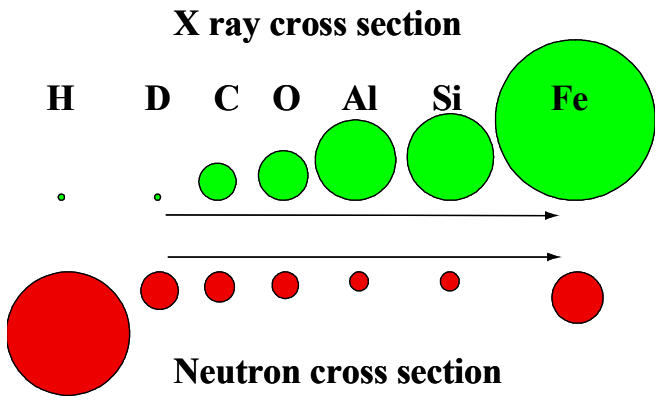
Metal Hydrides and Complex Hydrides

- Metal hydrides such as alanates allow high hydrogen volume density, but temperature of hydrogen release also tends to be high.
- Nanostructured materials may improve absorption volume.
- Incorporated catalysts and nanostructures may improve release.

$NaAlH_4$ X-ray view **$NaAlD_4$ neutron view**



Using Neutrons to "See" Hydrogen



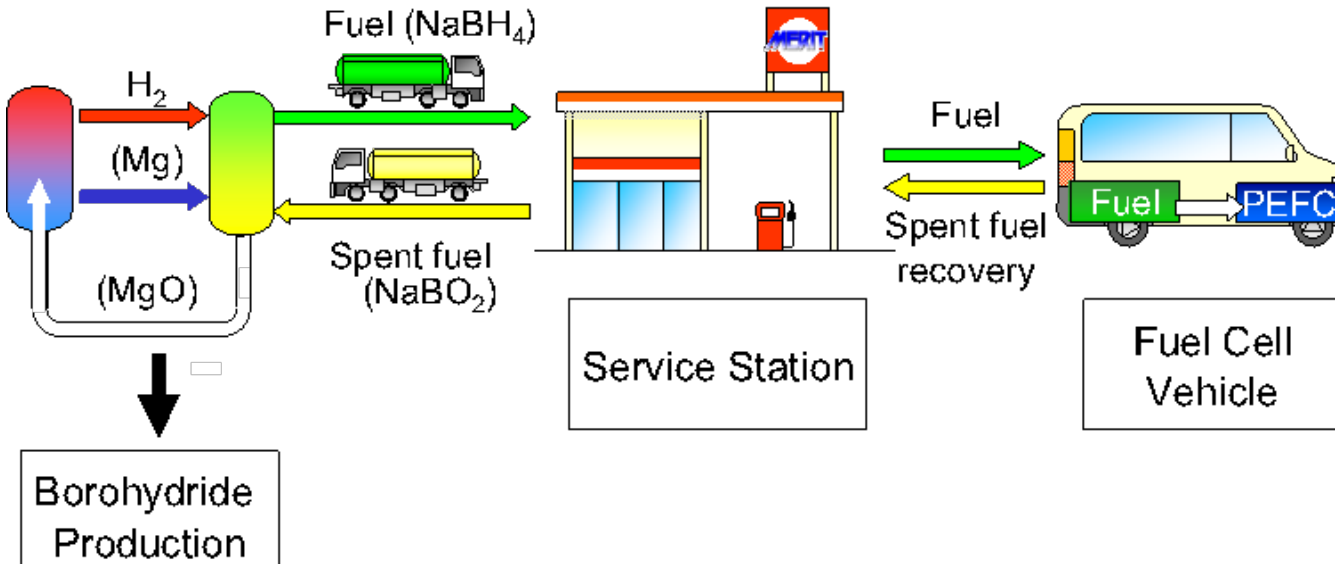
The large neutron cross sections of hydrogen and deuterium make neutrons an ideal probe for in situ studies of hydrogen-based chemical reactions, surface interactions, catalytic reactions and of hydrogen in penetrating through membranes.

M. S. Dresselhaus, MIT

Priority Research Areas in Hydrogen Storage

Using $NaBH_4$ for Automotive Hydrogen Storage

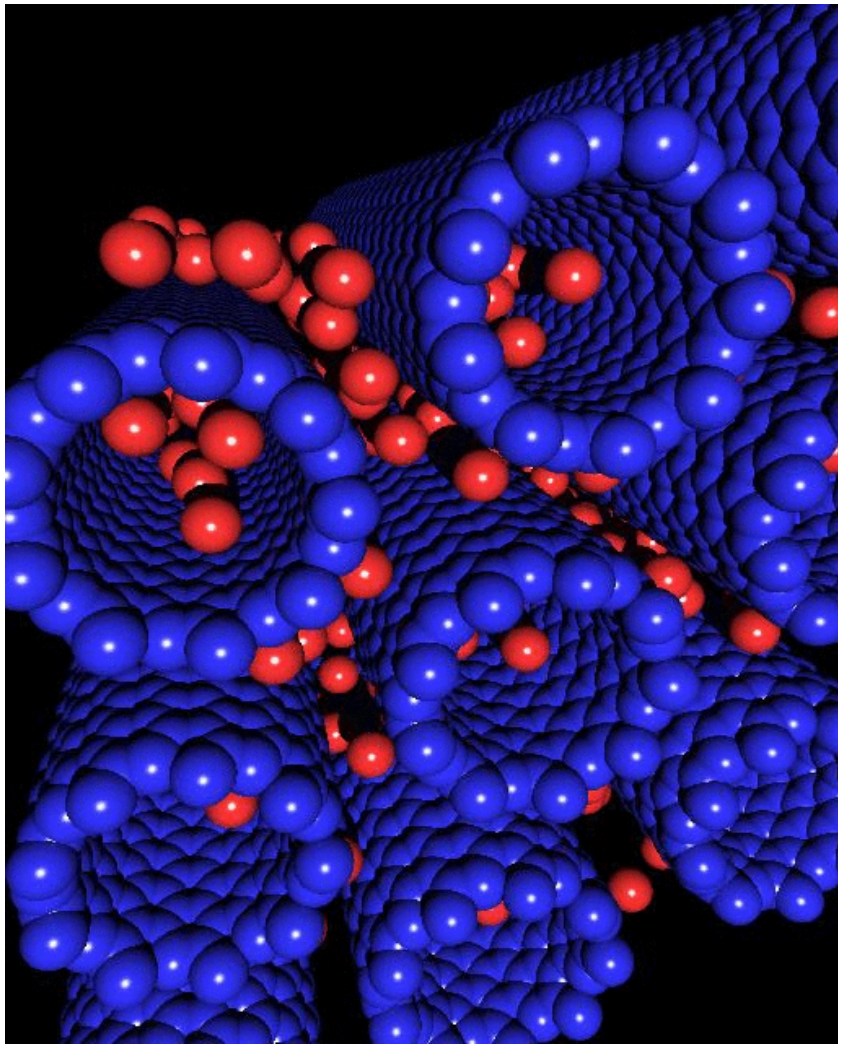
$$NaBH_4 + 2\ H_2O \rightarrow 4\ H_2 + NaBO_2$$



- Hydrogen weight % in $NaBH_4$ is 10.7%
- As a fuel (30% $NaBH_4$, 3 wt% NaOH, 67% H_2O) has a hydrogen content of 6.6 wt%.
- However, $NaBH_4$ as a fuel requires regeneration at a processing plant.
- This is one approach under consideration for a hydrogen fuel cell vehicle.

M. S. Dresselhaus, MIT

Carbon Nanotubes for Hydrogen Storage



- The very small size and very high surface area of carbon nanotubes make them interesting for hydrogen storage.
- Challenge is to increase the H:C stoichiometry and to strengthen the H—C bonding at 300 K.

A computational representation of hydrogen adsorption in an optimized array of (10,10) nanotubes at 298 K and 200 Bar. The red spheres represent hydrogen molecules and the blue spheres represent carbon atoms in the nanotubes, showing 3 kinds of binding sites. (K. Johnson et al)

M. S. Dresselhaus, MIT

Priority Research Areas in Hydrogen Storage

Metal Hydrides and Complex Hydrides

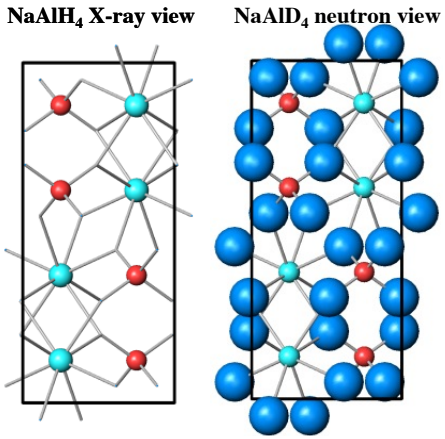
Degradation, thermophysical properties, effects of surfaces, processing, dopants, and catalysts in improving kinetics, nanostructured composites

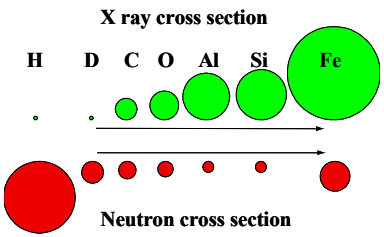
Nanoscale/Novel Materials

Finite size, shape, and curvature effects on electronic states, thermodynamics, and bonding, heterogeneous compositions and structures, catalyzed dissociation and interior storage phase

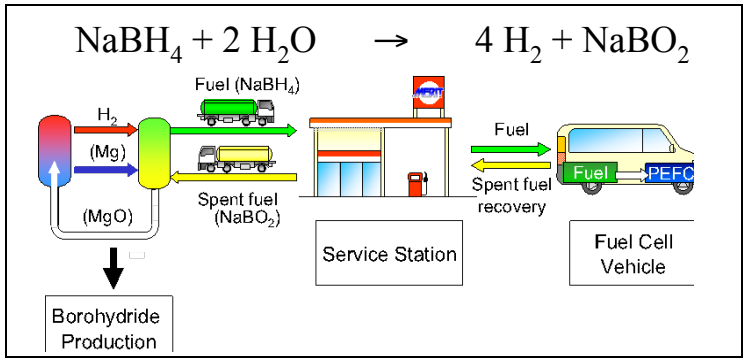
Theory and Modeling

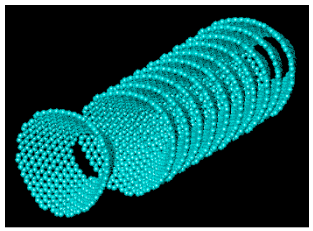
Model systems for benchmarking against calculations at all length scales, integrating disparate time & length scales, first principles methods applicable to condensed phases



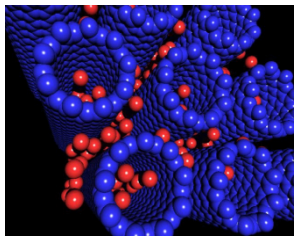


Neutron Imaging of Hydrogen





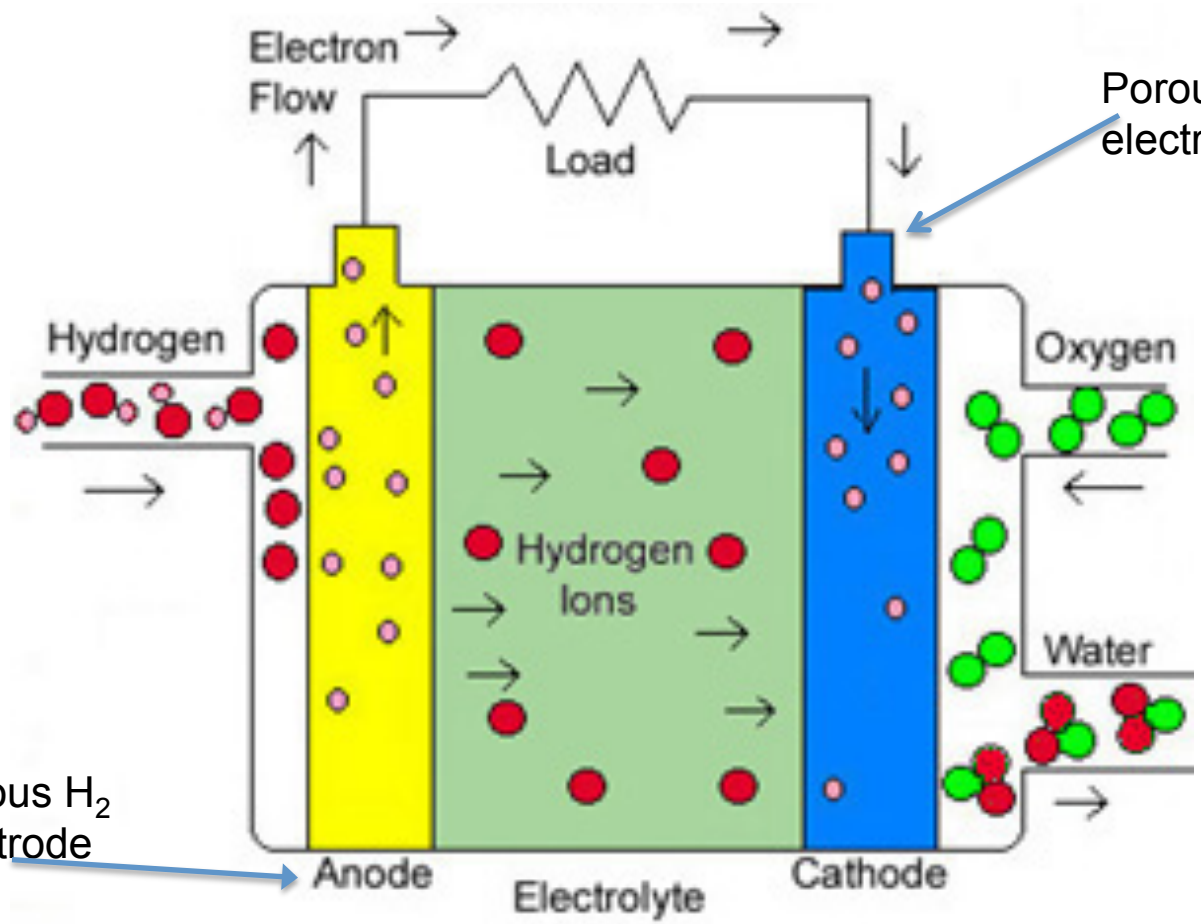
Cup-Stacked Carbon Nanofiber



H Adsorption in Nanotube Array

M. S. Dresselhaus, MIT

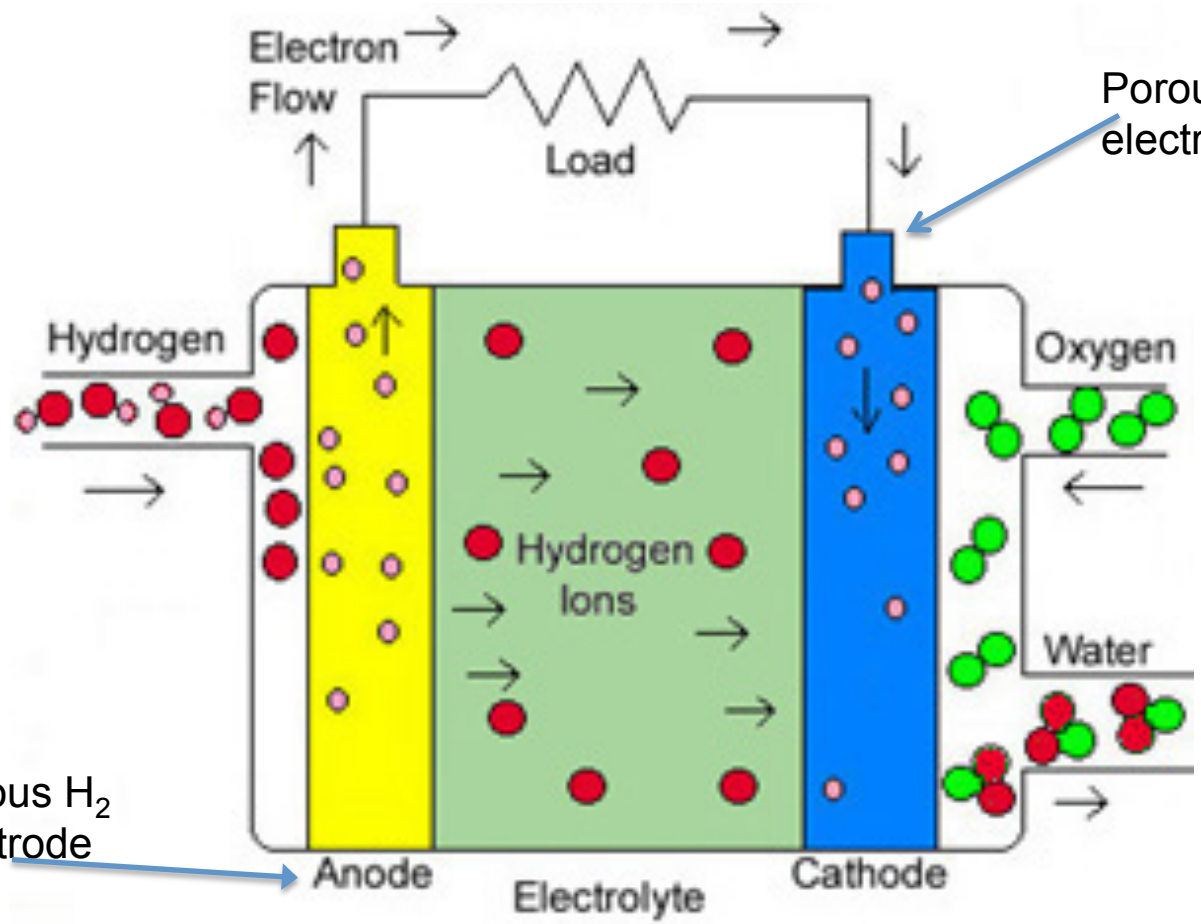
Fuel Cells



Eg. mixture of KOH and H_2O) at lower pressure than ends

$H_2 + 0.5O_2 \rightarrow H_2O$ + electrical energy + heat

Fuel Cells



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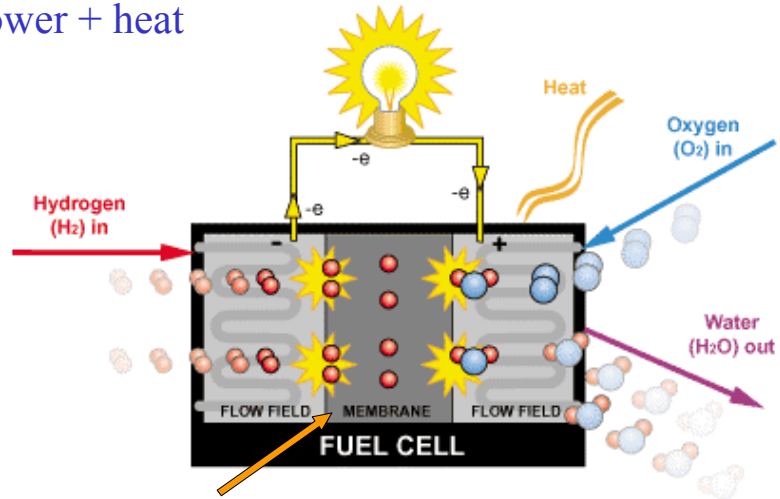
Fuel Cells and Novel Fuel Cell Materials Panel

Panel Chairs: Frank DiSalvo (Cornell), Tom Zawodzinski (Case Western Reserve)

$$2H_2 + O_2 \rightarrow 2H_2O + \text{electrical power} + \text{heat}$$



Membrane conducts protons from anode to cathode
proton exchange membrane (PEM)

Current status:

Limits to performance are materials, which have not changed much in 15 years.

Challenges:

Membranes

Operation in lower humidity, more strength, durability and higher ionic conductivity.

Cathodes

Materials with lower overpotential and resistance to impurities.

Low temperature operation needs cheaper (non- Pt) materials.

Tolerance to impurities: S, hydrocarbons, Cl.

Anodes

Tolerance to impurities: CO, S, Cl.

Cheaper (non or low Pt) catalysts.

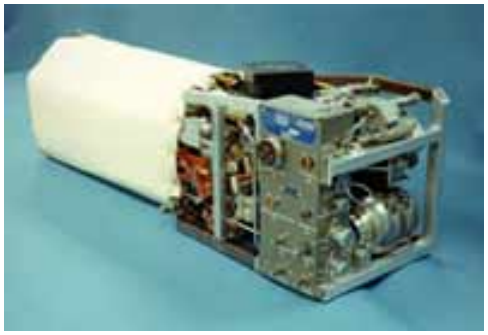
Reformers

Need low temperature and inexpensive reformer catalysts.

M. S. Dresselhaus, MIT

Types of Fuel Cells

Phosphoric Acid FC (PAFC), 250 kW
United Technologies



Alkaline Fuel Cell (AFC), Space Shuttle
12 kW
United Technologies

Low-Temp

High Temp

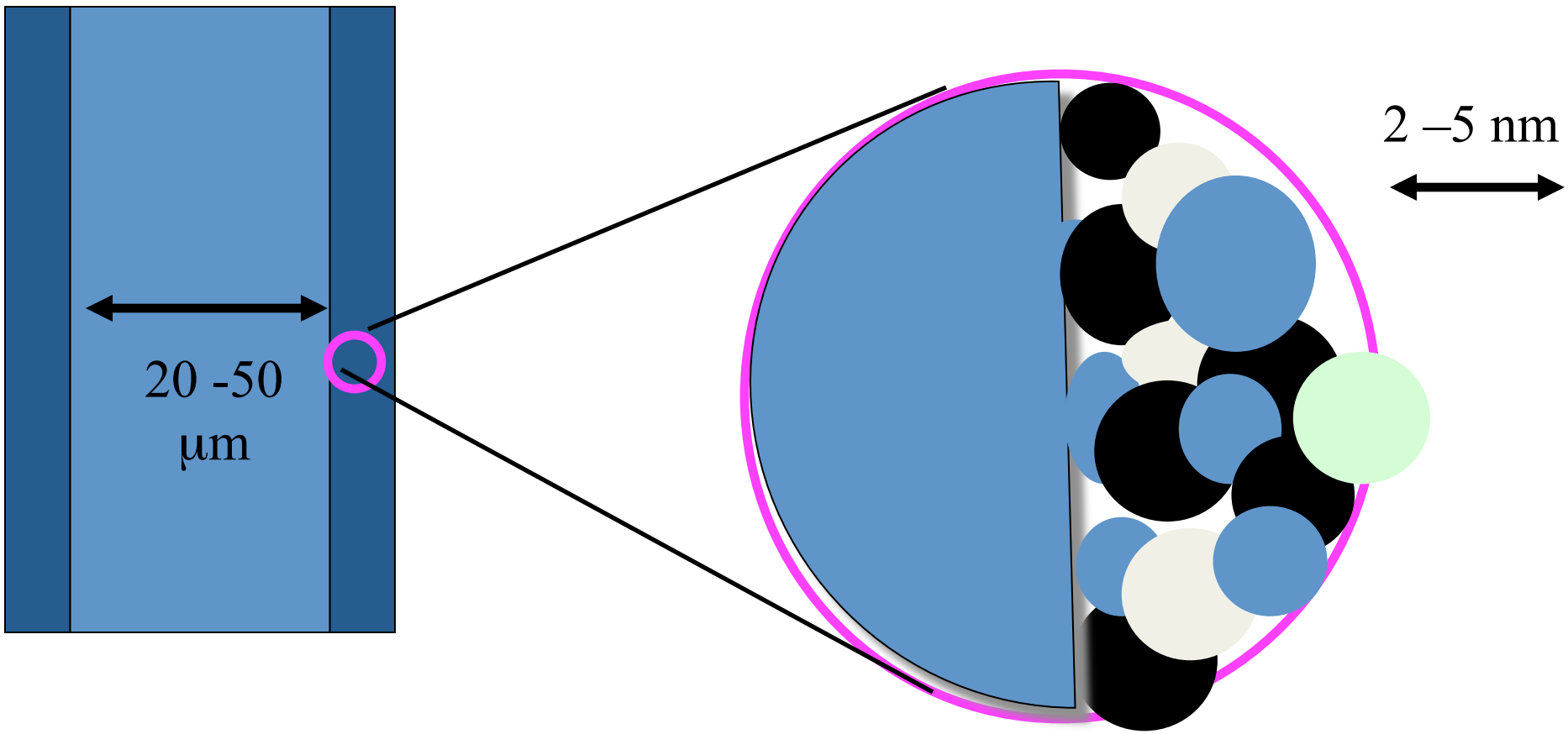
Proton Exchange Membrane (PEM)
50 kW, Ballard

Solid Oxide FC (SOFC) 100 kW
Siemens-
Westinghouse

Molten Carbonate FC (MCFC) 250 kW
FuelCell Energy,

Electrode/Membrane Design

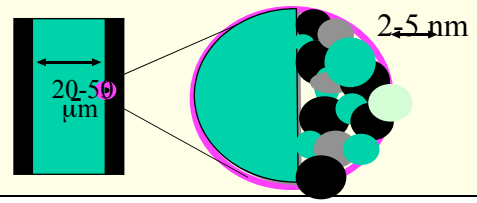
Very challenging. Electrodes need to support three percolation networks: electronic, ionic, fuel/oxidizer/ product access/egress.



Priority Research Areas in Fuel Cells

Electrocatalysts and Membranes

Oxygen reduction cathodes, minimize rare metal usage in cathodes and anodes, synthesis and processing of designed triple percolation electrodes

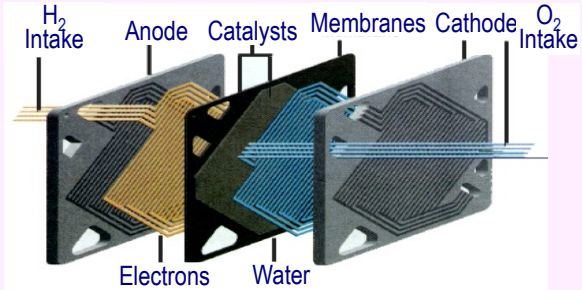


Controlled design of triple percolation nanoscale networks: ions, electrons, and porosity for gases

Low Temperature Fuel Cells

'Higher' temperature proton conducting membranes, degradation mechanisms, functionalizing materials with tailored nano-structures

Internal view of a PEM fuel cell

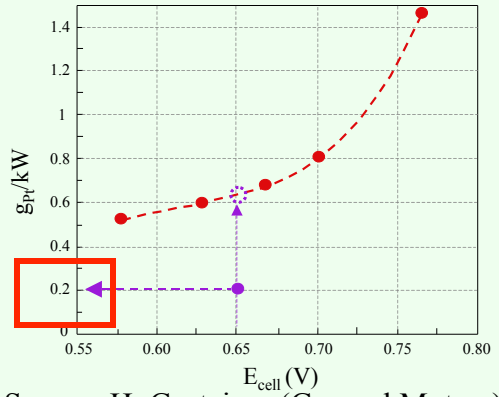


Source: T. Zawodzinski (CWRU)

Solid Oxide Fuel Cells

Theory, modeling and simulation, validated by experiment, for electrochemical materials and processes, new materials-all components, novel synthesis routes for optimized architectures, advanced in-situ analytical tools

Mass of Pt Used in the Fuel Cell — a Critical Cost Issue



Source: H. Gasteiger (General Motors)

YSZ Electrolyte for SOFCs

Porosity can be tailored

Source: R. Gorte (U. Penn)

M. S. Dresselhaus, MIT

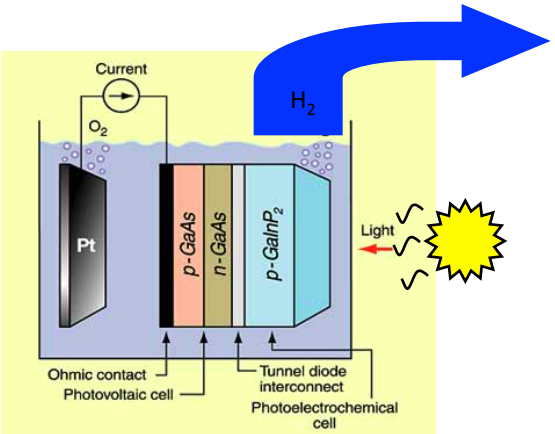
High Priority Research Directions for Hydrogen Economy

- Low-cost and efficient renewable (solar) energy production of hydrogen
- Nanoscale catalyst design
- Biological, biomimetic, and bio-inspired materials and processes
- Complex hydride materials for hydrogen storage
- Nanostructured / novel hydrogen storage materials
- Low-cost, highly active, durable cathodes for low-temperature fuel cells
- Membranes and separations processes for hydrogen production and fuel cells

M. S. Dresselhaus, MIT

Cross-cutting Issue - Materials

the challenge: to understand and control the interaction of hydrogen with materials

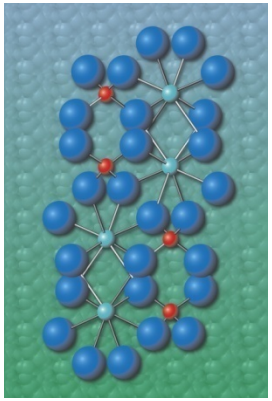


sunlight + $H_2O \rightarrow H_2 + O_2$

transparent semiconductor layers

nanoscale catalysts

nanostructured interfaces

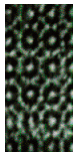


$H_2 \rightarrow NaAlH_4$

new H storage materials

catalytic reactions

nanoscale texture

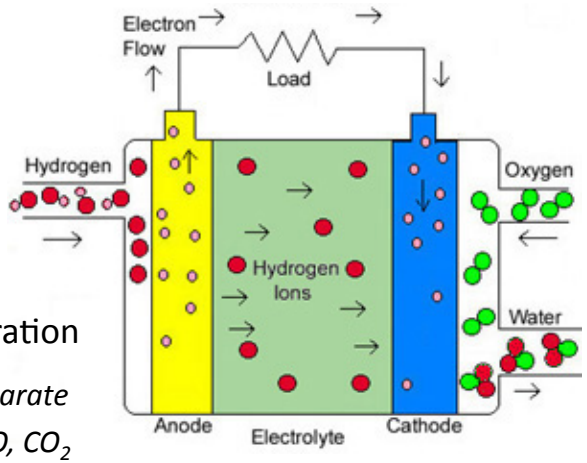


molecular filtration

membranes separate

H_2, O_2, CO, H_2O, CO_2

nanoscale size selection



$H_2 + O_2 \rightarrow H_2O$

fuel cell catalysts

ionic membranes

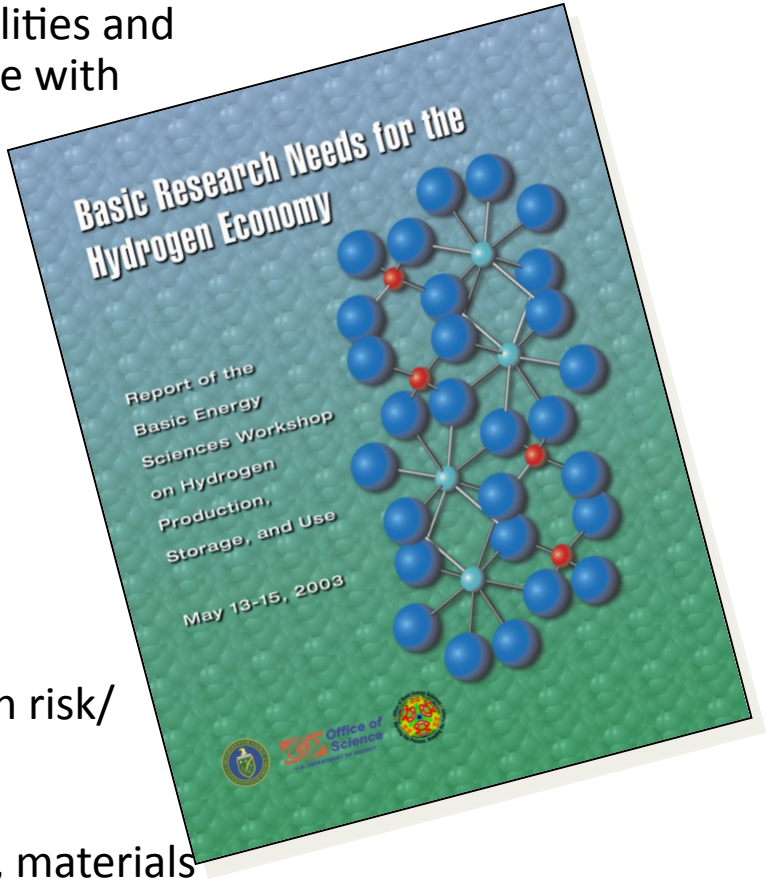
nanoscale architecture

catalysts, nano-materials, membranes needed throughout

M. S. Dresselhaus, MIT

Messages

- Enormous gap between present state-of-the-art capabilities and requirements that will allow hydrogen to be competitive with today's energy technologies
  - production: 9M tons ⇒ 150M tons (vehicles)
  - storage: 4.4 MJ/L (10K psi gas) ⇒ 9.70 MJ/L
  - fuel cells: $3000/kW ⇒ $30/kW (gasoline engine)
- Enormous R&D efforts will be required
  - Simple improvements of today's technologies will not meet requirements
  - Technical barriers can be overcome only with high risk/ high payoff basic research
- Research is highly interdisciplinary, requiring chemistry, materials science, physics, biology, engineering, nanoscience, computational science
- Basic and applied research should couple seamlessly



http://www.sc.doe.gov/bes/hydrogen.pdf

Some Useful References

Basic Research Needs for the Hydrogen Economy (DOE/BES) http://www.sc.doe.gov/bes/hydrogen.pdf

Basic Research Needs to Assure a Secure Energy Future (DOE/BES)
http://www.sc.doe.gov/bes/besac/Basic_Research_Needs_To_Assure_A_Secure_Energy_Future_FEB2003.pdf

Powering the Future - Materials Science for the Energy Platforms of the 21st Century: The Case of Hydrogen (MIT lecture notes)
http://web.mit.edu/mrschapter/www/IAP/iap_2004.html

Hydrogen Programs (DOE/EERE)
http://www.eere.energy.gov/hydrogenandfuelcells/

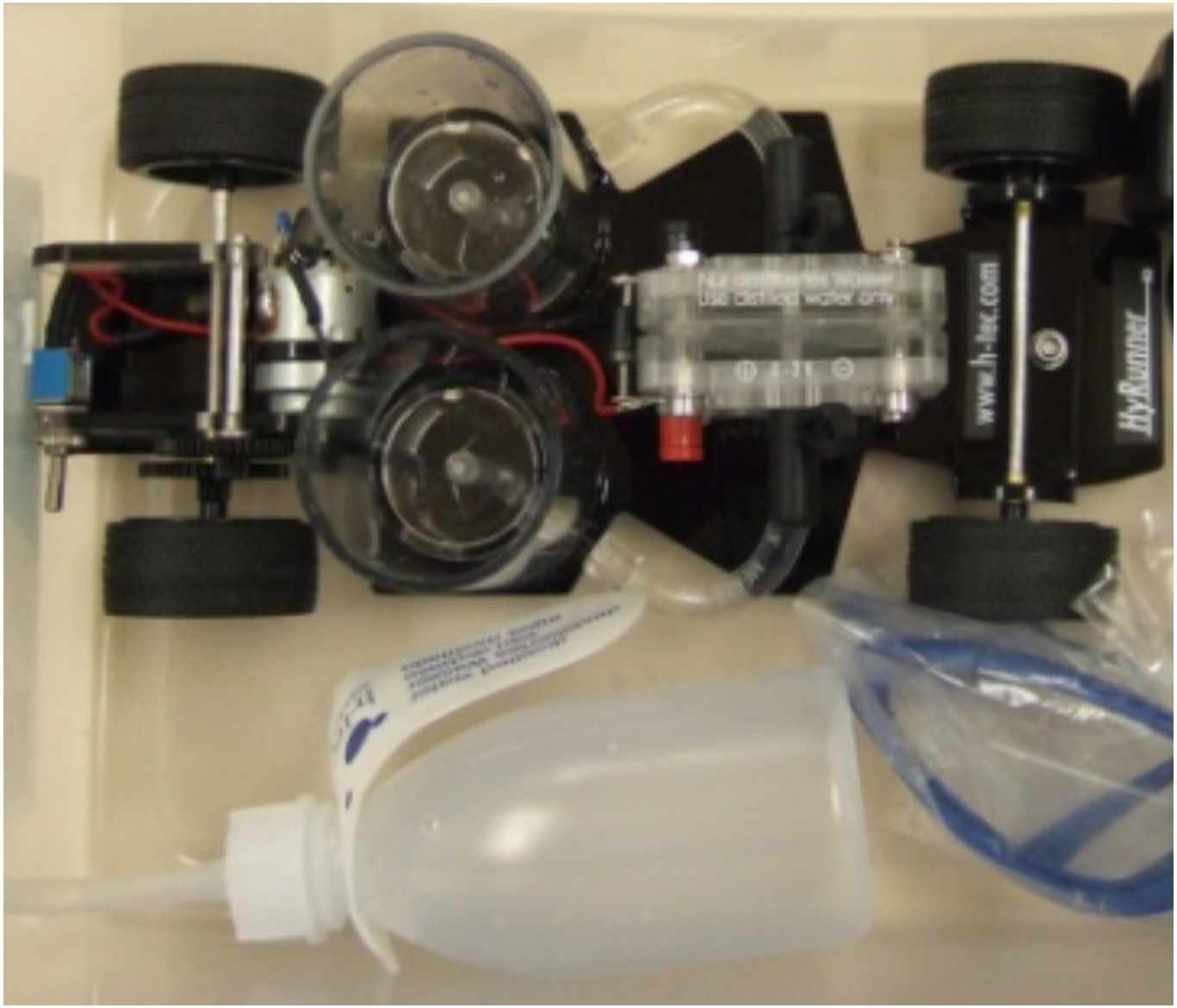
National Hydrogen Energy Roadmap (DOE/EERE) http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/national_h2_roadmap.pdf

FreedomCAR Plan (DOE/EERE)
http://www.eere.energy.gov/vehiclesandfuels/

Fuel Cell Overview (Smithsonian Institution)
http://fuelcells.si.edu/basics.htm

The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs (National Research Council Report, 2004)
http://www.nap.edu/books/0309091632/html/

Hydrogen Fuel Cell Car Lab



Energy Storage Options

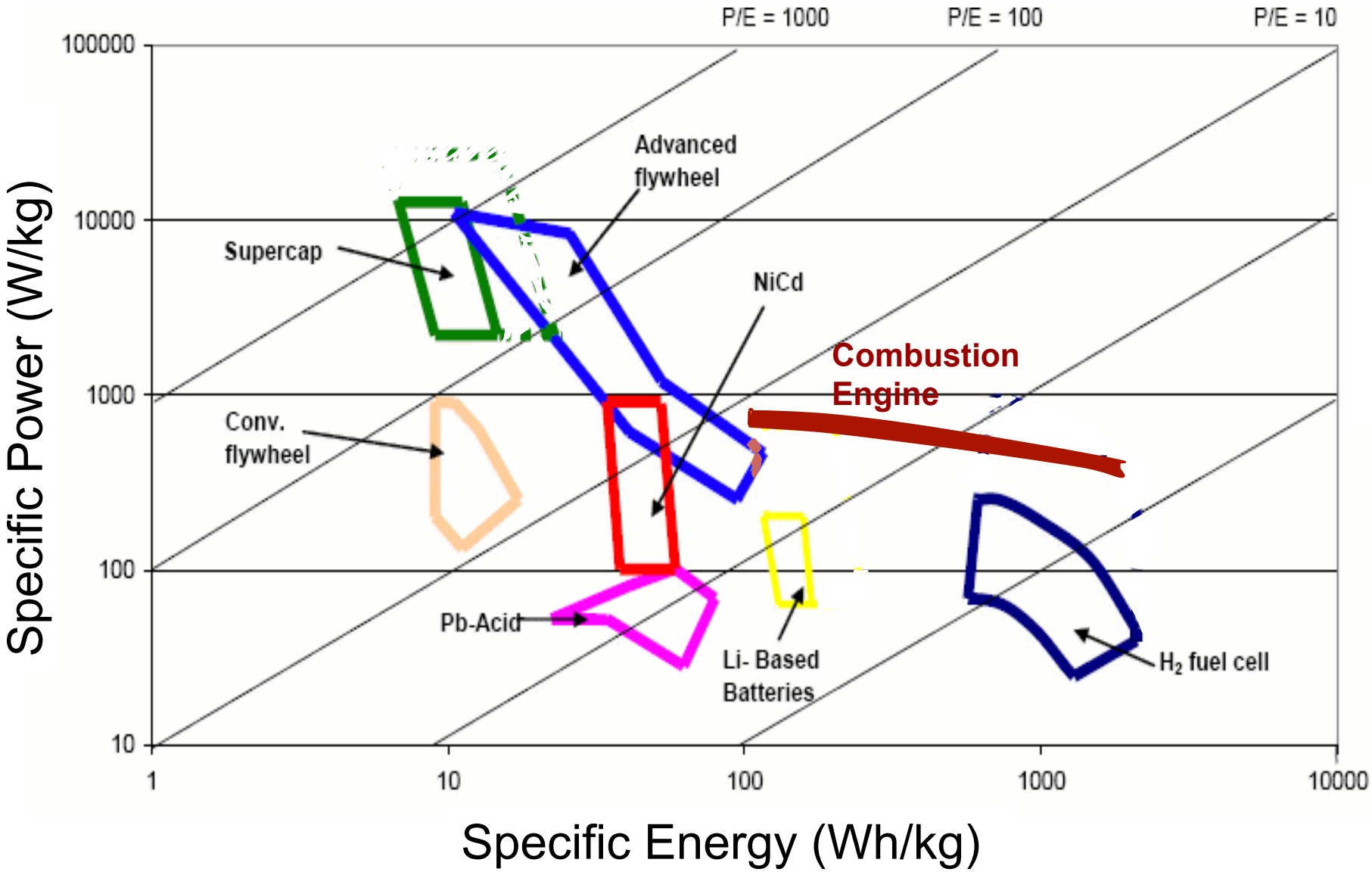


Table 15-1
Selected physical properties of hydrogen, methane, and gasoline[a]

Property	Hydrogen (gas)	Methane (gas)	Gasoline (liquid)
Molecular weight (g/mol)[a]	2.016	16.04	~110
Mass density (kg/m^3)[a,b]	0.09	0.72	720–780
Energy density (MJ/kg)	120[a]	53[c,d]	46[a,c]
Volumetric energy density (MJ/m^3)[a]	11[a]	38[c,d]	35,000[a,c]
Higher heating value (MJ/kg)[a]	142.0	55.5	47.3
Lower heating value (MJ/kg)[a]	120.0	50.0	44.0

[a] *Ogden [2002, Box 2, page 71].*
[b] *at 1 atm and 0° C.*
[c] *Hayden [2001, page 183].*
[d] *Ramage and Scurlock [1996, Box 4.8, page 152].*

Fuel Cell Vehicles: Hype or Hope?

Which technology wins in a head-to-head comparison: fuel cell vehicles or electrics?

Tam Hunt
May 8, 2014

The first mass-market consumer fuel-cell vehicle will soon be available in California: the Hyundai Tucson Fuel Cell SUV. It's taken decades to get to this point, so many enthusiasts are hoping that this will be a tipping point for the technology. It's an exciting development, and by all accounts thus far, it's a great car with a decent range of 250 to 300 miles. However, it's not at all clear that fuel cell vehicles make much sense from a policy perspective. This article delves into the details and compares fuel cell vehicles (FCVs) to electric vehicles (EVs) like the Nissan Leaf and plug-in hybrid electric vehicles (PHEVs) like the Chevy Volt.

EE80J/180J Project Format

Inputs (5%)
Analyses (20%)
Outputs (5%)
Assumptions/Limitations (10%)
Recommended Technologies/Strategies (20%)
Regulation (10%)
Economics and Timeline (10%)
Work Contribution of each member of team (5%)
Sources (10%)
Formatting (5%)

EE80J/180J Project Report Deliverables.1

Inputs (5%): *Specify what data you are using to determine site demands for electricity, natural gas, and transportation fuels? What data are you using to analyze and determine the feasibility of the technologies and strategies you are interested in proposing? Have you found any sources for pricing?*

Analyses (20%): *What analyses are necessary to determine renewable energy requirements? What is your approach to each analysis? What tools have you used in your analyses? Analyses should be primarily focused on technology, and perhaps to a minimal degree to policy mechanisms. Describe your steps briefly either in the body of text or an appendix. Show a summary of your analysis as noted in Outputs, below.*

EE80J/180J Project Report Deliverables.2

Outputs (5%): *What outputs result from your analyses? For example, you were asked to address greenhouse gas emissions in addition to the energy demand/supply balance. What can you get from each technology/strategy in terms of energy and costs/savings?*

Assumptions/Limitations (10%): *Define the scope of your proposal by making your assumptions explicit. All assumptions must be reasonable, transferable, and justifiable through credible sources. It is not acceptable to assume away major energy demands such as transportation. Nor is it acceptable to assume an unlimited budget.*

EE80J/180J Project Report Deliverables.3

Recommended Technologies & Strategies (20%): *The Analyses will answer the question of why but here you should also answer the questions of what (how many, what type, grid tie/ non grid tie), who (i.e.vendors, other applications, sources), when (i.e. in year 20XX), and where. Graphs, tables and charts work well to convey summaries of technologies/strategies/ metrics as well as timelines and fiscal considerations.*
A minimum of one exhibit is required that shows your overall plan for technology/modifications to the site.

Regulation (10%): *What are the overarching regulations governing the technologies and strategies you are recommending on the federal, state and local level? What permits are required? What regulates how the interconnection to the grid will occur? Mention any jurisdictional agencies.*

EE80J/180J Project Report Deliverables.3

Economics & Timeline (10%): *Broadly, how will you finance the technologies and strategies you are proposing? Be thorough in describing what existing incentives exist on the federal, state, and local level? What kind of funding will you seek for the remaining non-incentive funded capital costs? Are there novel funding mechanisms you can propose? What are the general timelines for incentives, permitting, and implementing the phases of your technologies and strategies?*

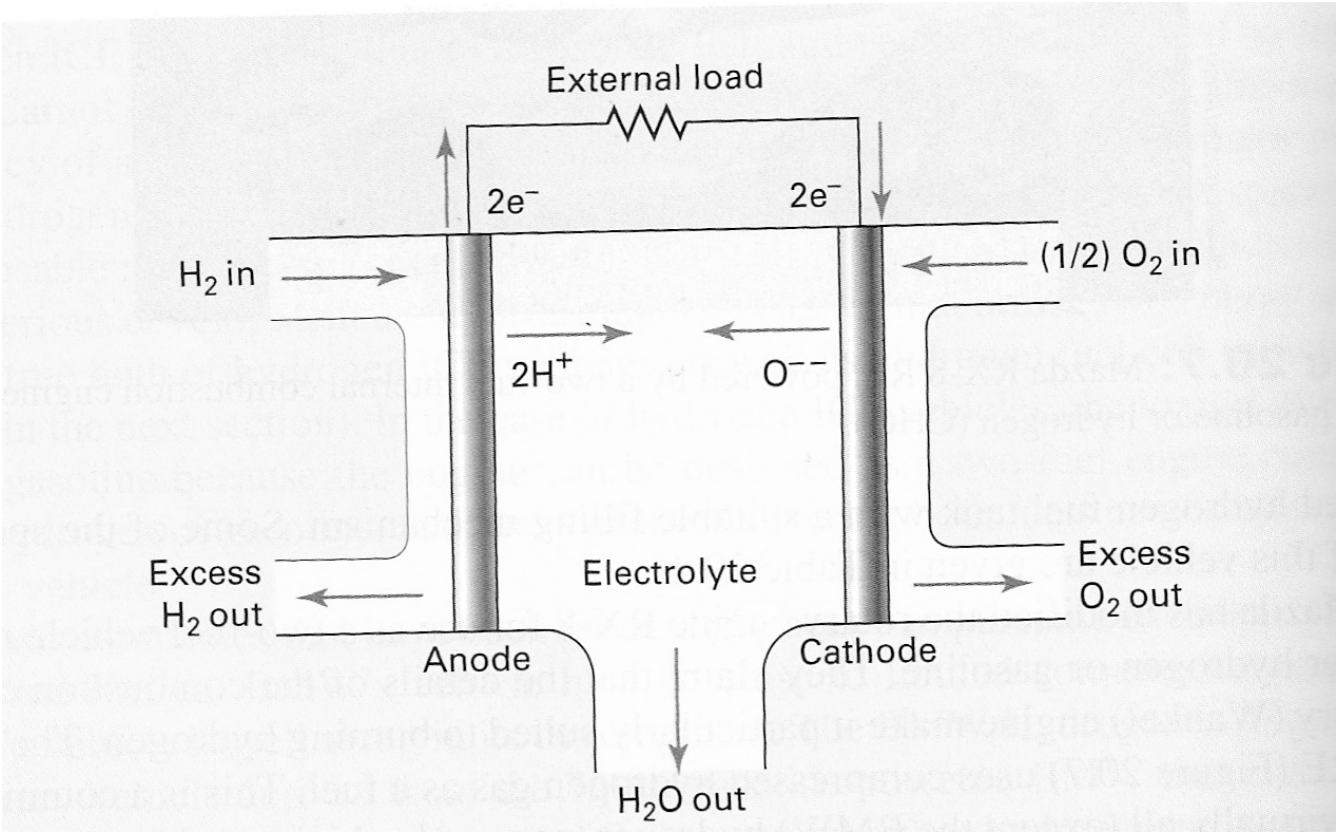
Work Contributions (5%): *Who is doing what and why? Be sure each individual is contributing an equal amount of effort on the proposal.*

EE80J/180J Project Report Deliverables.4

Sources (10%): *A minimum of 10 credible sources should be cited in a 'Literature Cited' section.*
Properly cite within the body of text and in the works cited section.

Formatting (5%): *Please be certain your draft includes a Table of Contents, flows logically, and has been proofread. Moreover, please ensure each person in the group is listed along with the group number on the first page. Also, ensure your sources are properly cited according to MLA or other standard. Lastly, be certain to include attachments of any appendices.*

Fuel Cells



At anode: $H_2 = 2H^+ + 2e-$, at cathode: $2e- + 0.5\ O_2 = H_20^-$

From R. A. Dunlap, Sustainable Energy

Table 20.5: Properties of the common varieties of fuel cells.

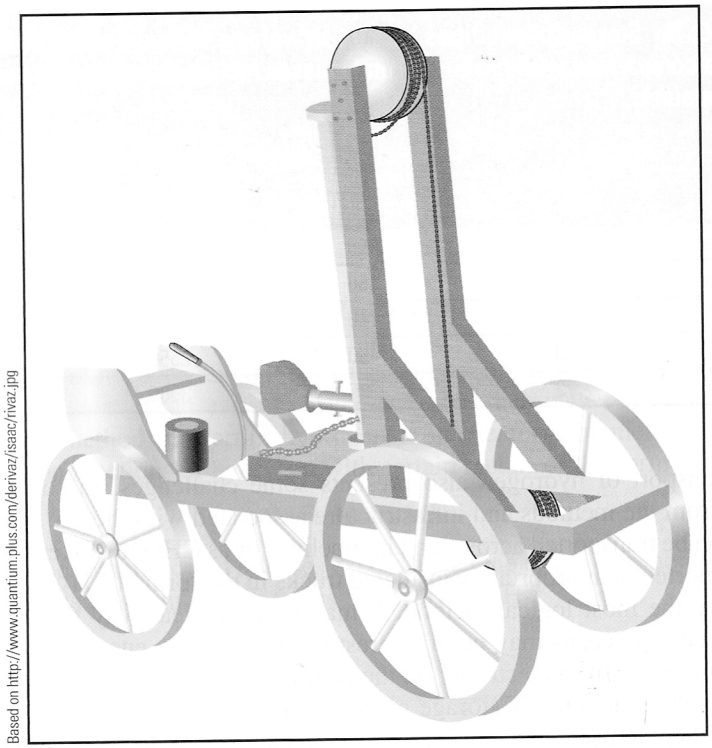
type	electrolyte	operating temperature (°C)	power density (kW/m^2)	typical power output (kW)	lifetime (10^3 h)	efficiency (%)
phosphoric acid	H_3PO_4	~200	0.2	< 200	40	40
alkaline	KOH	−40 to 60	0.25	0.3 to 12	20	70
molten carbonate	K_2CO_3 or Na_2CO_3	~800	0.15	< 2000	40	60
solid oxide	ZrO_2	600–1000	0.3	100	40	60
solid polymer	PEM	60–80	0.5	50–250	40	80

Table 20.3: Storage capabilities for a 0.1-m^3 volume for hydrogen in different forms and a comparison with gasoline. Total masses include the mass of a suitable storage container.

fuel	fuel mass (kg)	total mass, typical (kg)	energy per volume ($MJ/0.1m^3$)	energy per mass (MJ/kg)
CHG (35 MPa)	2.0	100	280	2.8
CHG (70 MPa)	3.5	150	500	3.3
LH_2	7.2	100	1000	10
TiH_2	18	450	2550	5.7
gasoline	72	85	3500	41

~ 3MJ/kg

From R. A. Dunlap



Based on http://www.quantium.plus.com/derivaz/isaac/rivaz.jpg

Figure 20.5: The first automobile was built in 1807 by Francois Isaac de Rivaz of Switzerland. It utilized compressed hydrogen gas as a fuel and used an electric spark produced by means of a battery for ignition.

From R.A.Dunlap

Table 20.4: Specifications of two hydrogen internal combustion engine (ICE) vehicles.

manufacturer	model	fuels	hydrogen range [km (mi)]	gasoline range [km (mi)]
BMW	Hydrogen 7	LH_2/gasoline	200 (124)	480 (298)
Mazda	RX-8 RE	CHG/gasoline	100 (62)	530 (329)

Figure 20.6: BMW Hydrogen 7 powered by a two-fuel internal combustion engine that runs on gasoline or hydrogen (LH_2).