Hydrogen, fuel cells, batteries, super capacitors, and hybrids

The hydrogen economy

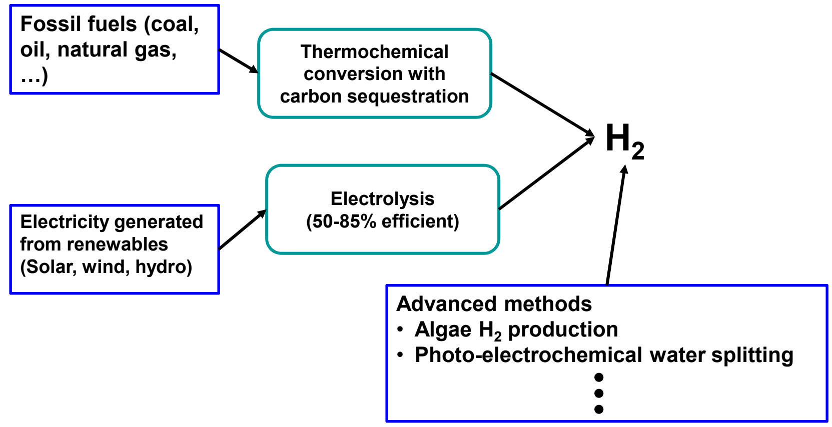
Premise:

$H_2 + O_2 \rightarrow H_2O$
LHV = 120 MJ/kg (33.3 KW-hr/kg)

- Energy production via combustion or fuel cell
- No green house gas; clean

The hydrogen economy

Source of hydrogen



Current production (without CO2 sequestration):

- 48% from natural gas, 30% from oil, 18% from coal, 4% from electrolysis

Usage:

- Half for producing ammonia to be used for fertilizers; remaining for petroleum refining (hydro-cracking)

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Transportation Fuels

Fuels	Density	LHV/mass*	LHV/Vol.**	LHV/Vol. of Stoi.Mixture @1 atm,300K
	(Kg/m^3)	(MJ/Kg)	(MJ/m^3)	(MJ/m^3)
Gasoline	750	44	3.3×10^4	3.48
Diesel	810	42	3.4×10^4	3.37
Natural Gas				
@1 bar	0.72	45	3.2×10^1(x)	3.25
@100 bar	71		3.2×10^3	
LNG (180K, 30bar)	270		1.22×10^4	
Methanol	792	20	1.58×10^4	3.19
Ethanol	785	26.9	2.11×10^4	3.29
Hydrogen				
@1bar	0.082	120	0.984×10^1(x)	2.86
@100 bar	8.2		0.984×10^3	
Liquid (20K, 5 bar)	71		8.52×10^3	

*Determines fuel mass to carry on vehicle
**Determines size of fuel tank
***Determines size of engine

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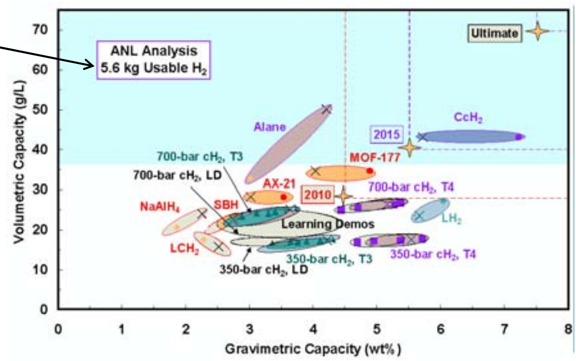
The hydrogen economy
(H2 as transportation fuel)

Obstacles

- Storage: Low energy density; need compressed or liquid H_2
  - Compressing from 300°K, 1 bar to 350 bar, ideal compressor work = 16% of LHV; practical energy required upwards of 35% of LHV
  - Liquefaction (20°K, 1 bar LH2) work required is upwards of 60% of LHV*

5.6 kg of H2
~700 MJ

Petroleum fuel tank capacity of 50 kg carries ~2200 MJ



CcH2: cryogenic compressed LH2

cH2: compressed H2

MOF: Metal organic framework for LH2

Alane is aluminum hydride

- Infra structure: Supply, safety, …

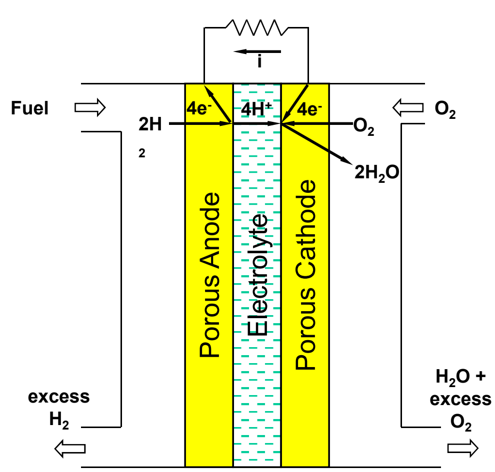
The hydrogen economy has significant hurdles 5

*Value adopt from NREL/TP-570-25106

What is a fuel cell?

Direct conversion of fuel/oxidant to electricity
- Example: $2H_2 + O_2 \rightarrow 2H_2O$
- Potentially much higher efficiency than IC engines

H_2 - O_2 system



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History of Fuel Cell

- **Sir William Grove** demonstrated the first fuel cell in 1839 (H2 – O2 system)
- Substantial activities in the late 1800's and early 1900's
  - Theoretically basis established
    - Nerst, Haber, Ostwald and others
- Development of Ion Exchange Membrane for application in the Gemini spacecraft in the 1950/1960
  - W.T. Grubb (US Patent 2,913,511, 1959)
- Development of fuel cell for automotive use (1960s to present)

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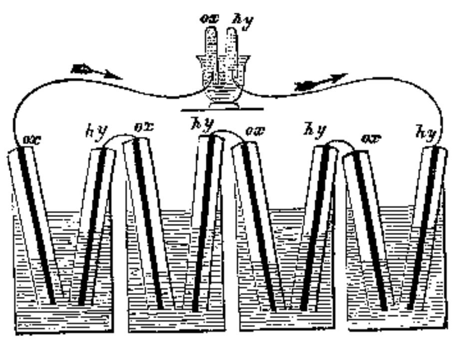
The Grove Cell (1839)

- Important insights to fuel cell operation
  - H2-O2 system (the most efficient and the only practical system so far)
  - Platinum electrodes (role of catalyst)
  - recognize the importance of the coexistence of reactants, electrodes and electrolyte



W.R.Grove, 'On Gaseous Voltaic Battery," Pil. Mag., **21**,3,1842
As appeared in Liebhafsky and Cairns, *Fuel Cells and Fuel Batteries*, Wiley, 1968

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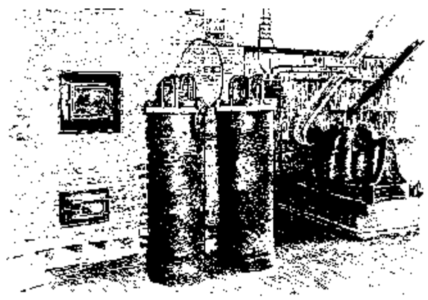
The coal/air cell

Wilhelm Ostwald (1894)

"The way in which the greatest of all industrial problems – that of providing cheap energy – is to be solved, must be found by electrochemistry"

Status at 1933

- Low efficiency and contamination of electrodes doomed direct coal conversion



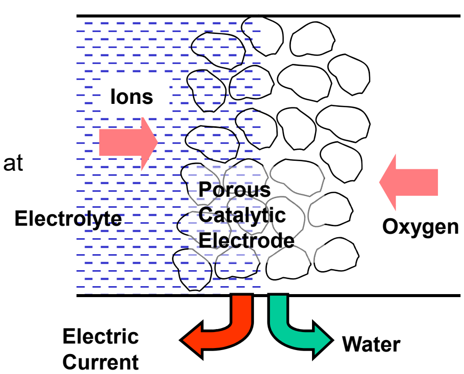
The 1896 W.W.Jacques large carbon cell (30KW)

Picture and quote from Liebhafsky and Cairns, *Fuel Cells and Fuel Batteries*, Wiley, 1968

Critical processes

- Reactions (anode and cathode)
  - Pre-electrochemical chemical reaction
  - Electrochemical reaction
  - Post-electrochemical chemical reaction
- Transport
  - Transport of ions in electrolyte
  - Fuel/oxidant/ion/electron transport at electrodes
- Role of the electrolyte
  - To provide medium for electrochemical reaction
  - to provide ionic conduction and to resist electron conduction
  - separation of reactants

Cathode of H_2/O_2 cell



Types of fuel cell

- Classification by fuel
  - Direct conversion
    - ➢Hydrogen/air (pre-dominant)
    - ➢Methanol/air (under development)
  - Indirect conversion
    - ➢reform hydrocarbon fuels to hydrogen first
- Classification by charge carrier in electrolyte
    - ➢H^+, O^{2-} (important difference in terms of product disposal)

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Types of fuel cell (cont.)

- By electrolyte
  - Solid oxides: ~1000^{o}C
  - Carbonates: ~600^{o}C
  - H_3PO_4: ~200^{o}C
  - Proton Exchange Membrane (PEM): ~80^{o}C

High temperature fuel cells are more tolerant of CO and other deactivating agents

Automotive application

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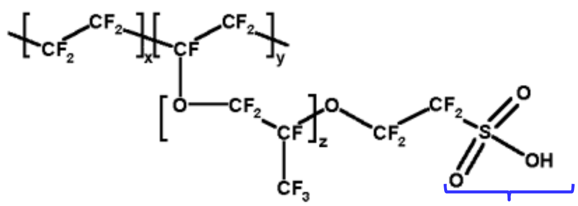
PEM

Nafion (a DuPont product)

Tetrafluoroethylene based copolymer



Sulfonic acid group supplies the proton

Function:

- As electrolyte (provide charge and material carrier)
- As separator for the fuel and oxidant

Retail ~$300/m^2$

- PEM must be hydrated properly
  - If dry, resistance increase; eventually crack and reactants leak through
  - Excess water formation: flood electrodes; prevent reactants from reaching electrode

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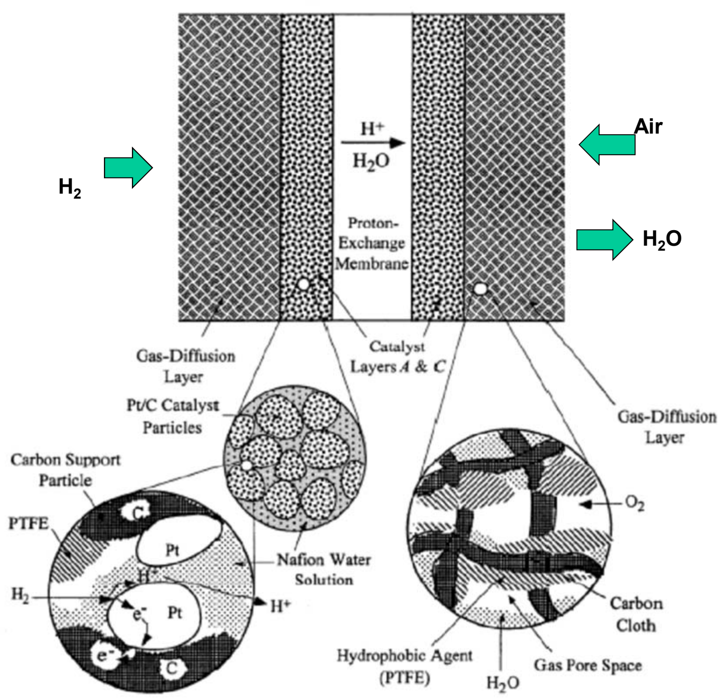

Single cell details

PTFE: polytetrafluoro-ethylene (trade name teflon)

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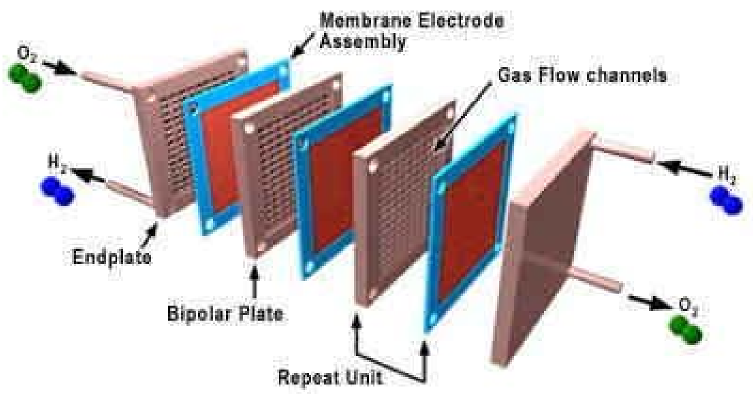
Modern PEM fuel cell stack



(From 3M web site)

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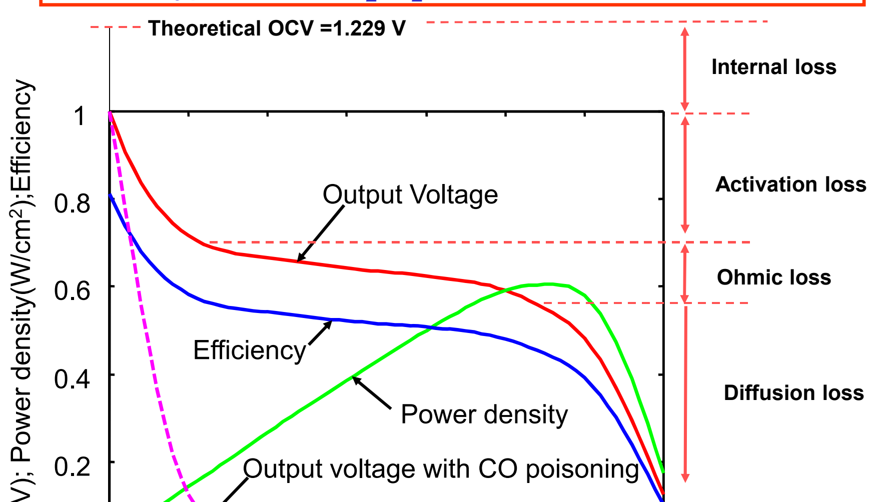
Typical PEM H_2/O_2 Fuel Cell Performance



Note: Efficiency does not include power required to run supporting system

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Fuel cell as automotive powerplant

- Typical fuel cell characteristics
  - 1A/cm^2, 0.5-0.7 V operating voltage
  - 0.5-0.7 W/cm^2 power density
  - stack power density 0.7 kW/L
  - System efficiency ~50%
  - $500/kW
    - ➢DOE goal $35/KW at 500,000 per year production
    - ➢compared to passenger car engine at $15-20/kW
  - Platinum loading ~0.3 mg/cm^2
    - ➢30g for a 60kW stack (Jan., 2014 price ~$1500)
    - ➢(automotive catalyst has ~2-3g)

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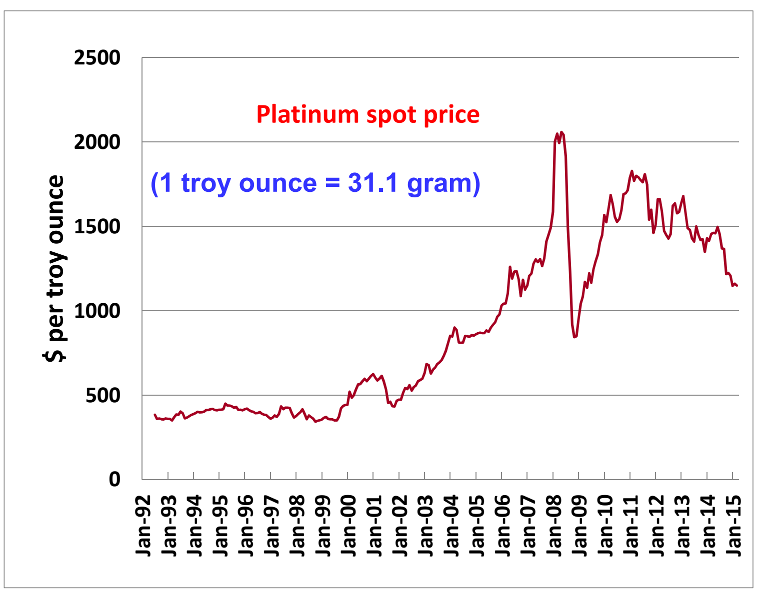
Price of platinum



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The Hydrogen problem:

Fundamentally H_2 is the only feasible fuel in the foreseeable future

- Strictly, hydrogen is not a “fuel”, but an energy storage medium
  - Difficulty in hydrogen storage
  - Difficulty in hydrogen supply infra structure
- Hydrogen from fossil fuel is not an efficient energy option
- Environmental resistance for nuclear and hydroelectric options

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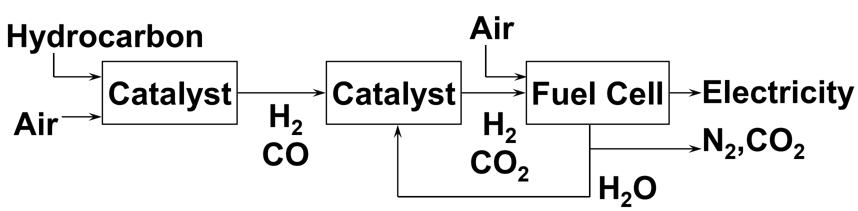
The hydrogen problem:
H_2 from reforming petroleum fuel



Note: **HC to H_2/CO process is exothermic;**
energy loss ~20% and needs to cool stream
(Methanol reforming process is energy neutral, but energy loss is similar when it is made from fossil fuel)

Current best reformer efficiency is ~70%

Problems:
CO poisoning of anode
Sulfur poisoning
Anode poisoning requires S<1ppm
Reformer catalyst poisoning requires S<50ppb

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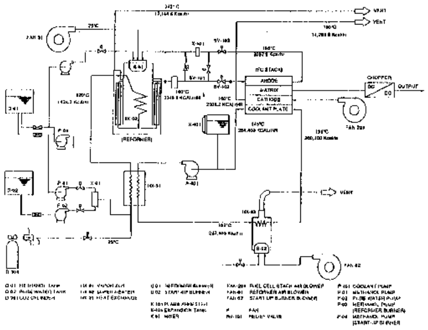
Fuel cell powerplant with fuel reforming



Practical Problems
Start up/shut down
Load Control
Ambient temperature
Durability

GM (May, 2002) Chevrolet S-10 fuel cell demonstration vehicle powered by onboard reformer

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Fuel cell outlook

- Too many barriers
  - Cost: unlikely to come down because of price of precious metal
  - System complexity
    - Management of hydration, temperature, cold start, cold climate, …
  - Hydrogen supply
    - Source
    - Infra structure
- Battery is a more practical option

Unless there is exceptional break through, fuel cell is not going to be a transportation powerplant component

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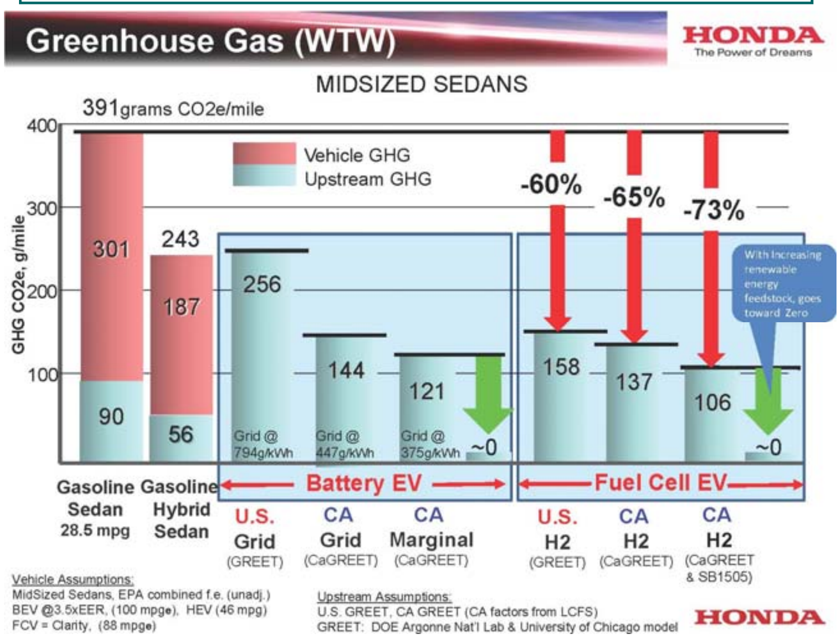
Fuel cell vehicles



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FCX Clarity Deployments in California

First Fuel Cell Vehicle Dealership Network

- Three Official Clarity/FCX dealerships: Santa Monica, Torrance, and Costa Mesa
- Clarity dealership responsibilities:
  - Sales, Service, Parts, Customer Relations

First Customers

- First deliveries in July, 2008 (25 to-date)
- 3 year lease ($600/month)
- Primary car utility
- Extremely positive feedback
- More stations needed!

Property of American Honda Motor Co., Inc. HONDA

Honda June 2011 presentation

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Batteries

- Electrochemical energy source
- Rechargeable batteries
  - Electrical energy storage
- Attributes
  - Energy density (by mass and volume)
  - Power density
  - Cost

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Battery electrochemistry

Lead acid battery: lead electrodes; dilute sulfuric acid as electrolyte

Charging (forward) / discharging (reverse)

Anode (in charging):

$$PbSO_4(s) + 2H_2O(aq) \rightleftarrows PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$$

Cathode (in charging):

$$PbSO_4(s) + H^+(aq) + 2e^- \rightleftarrows Pb(S) + HSO_4^-(aq)$$

Li ion battery: e.g. LiCoO2 anode; graphite cathode

Charging (forward) / discharging (reverse)

Anode (in charging):

$$LiCoO_2 \rightleftarrows Li_{(1-x)}CoO_2 + xLi^+ + xe^-$$

Cathode (in charging):

$$xLi^+ + xe^- + 6C \rightleftarrows Li_xC_6$$

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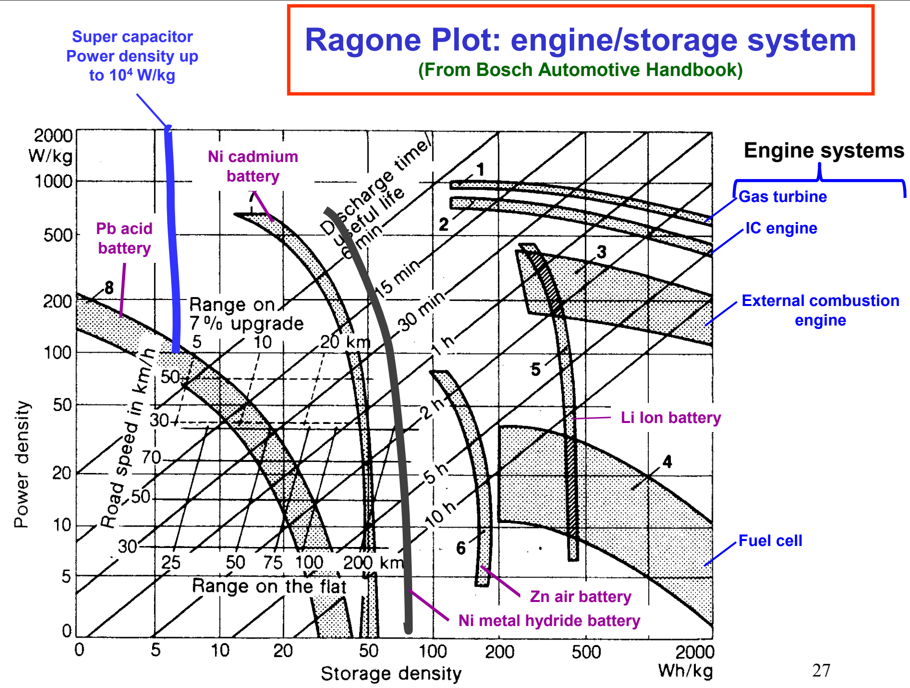
Ragone Plot: engine/storage system

(From Bosch Automotive Handbook)



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Battery characteristics

Table 2. Relevant energy storage performance overview

	Temperature [°C]	η_E [%]	Energy [Wh/l]	Energy [Wh/kg]	Power [W/kg]	Voltage [V]	Self-discharge [%/Month]	Cyclelife @80 %DoD	Cost estimation [$/kWh]	Cost estimation [$/kW]
Lead Acid	−30 – 60	85	50 – 70	20 – 40	300	2,1	4 – 8	200	150	10
NiMH	−20 – 50	80	200	40 – 60	1300 – 500	1,2	20	>2500	500	20
Li-ion	−20 – 55	93	150 – 250	100 – 200	3000 – 800	~3,6	1 – 5	<2500	800	50 – 75
EDLC	−30 – 65	97	5	5 – 20	15000	~2,5	30	Not applicable	2000	50

EDLC: Electric double layer capacitor (super-capacitor)

Configuration	P/E (hr⁻¹)	Energy [kWh]	Power [kW]	Voltage [V]
ISG	>60	<0,6	<6	12
Mild HEV	30 – 80	<1	<13	12 – 42
Power HEV	20	<4	20 – 100	>150
Plug In HEV	7 – 12	5 – 20	<80	>200
BEV	2 – 3	>15	20 – 60	NA

ISG: Integrated starter and generator

Source: Conte, Elektrotechnik & Informationstechnik (2006) 123/10: 424–431

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Battery for the Chevy Volt

40 miles range

- 288 cell Li-ion battery; 16 kW-hr capacity
  - System weight 190 kg
  - Package as 3 cells in parallel as one unit; 96 units in series
  - 360 VDC; peak current 40A over 30 sec
- Thermal management
  - Cool and heated by 50/50 de-ionized water and glycol
  - 1.8 kW heater for heating in cold climate

Source: Parish et al, SAE Paper 2011-01-1360

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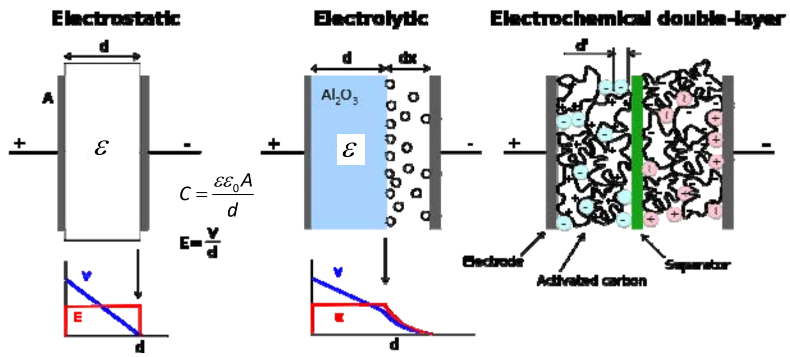
Capacitors

Energy storage in the electric field within the capacitor



Aluminum oxide layer thickness ~μm
Double layer thickness ~0.3-0.8 nm

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EDLC (super-capacitor)

Transportation application: **Complementary to battery**

- Advantages
  - Charging/discharging by charge transfer; no chemistry involved fast rates
    - ➢ High power density (10x to 100x that of conventional battery)
    - ➢ Fast charging time
  - Almost unlimited life cycle (millions of cycles)
  - Low internal resistance; high cycle efficiency (95%)
- Disadvantages
  - Low energy density (10% of conventional battery)
  - High self discharge rate
  - Very high short circuit current; safety issue
  - High cost ($5K-10K/kW-hr)
    - ➢ cost in the activated carbon electrode manufacturing

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Hybrid vehicles

Configuration:

IC Engine + Generator + Battery + Electric Motor

Concept

- Eliminates external charging
- As "load leveler"
  - Improved overall efficiency
- Regeneration ability
- Plug-in hybrids: use external electricity supply

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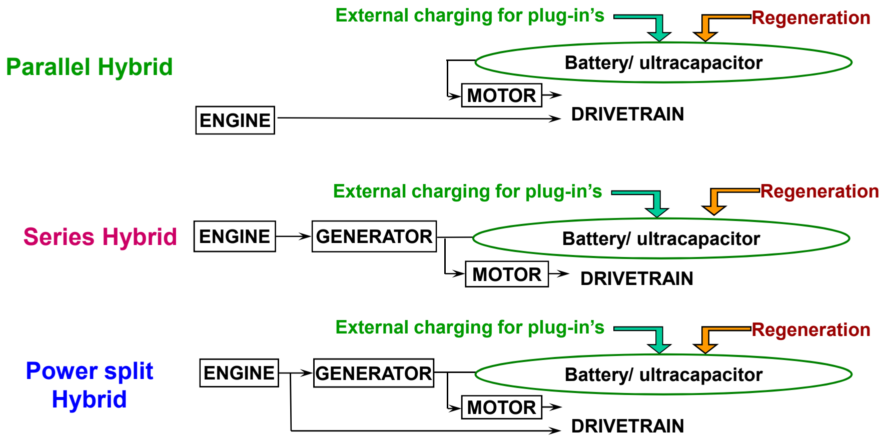
Hybrid Vehicles



Examples: Parallel hybrid: Honda Insight
Series hybrid: GM E-Flex System
Power split hybrid: Toyota Prius

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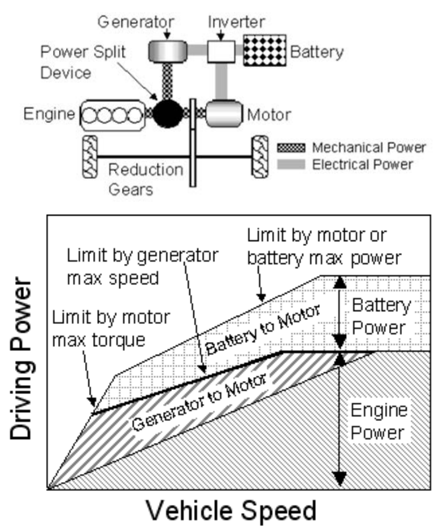
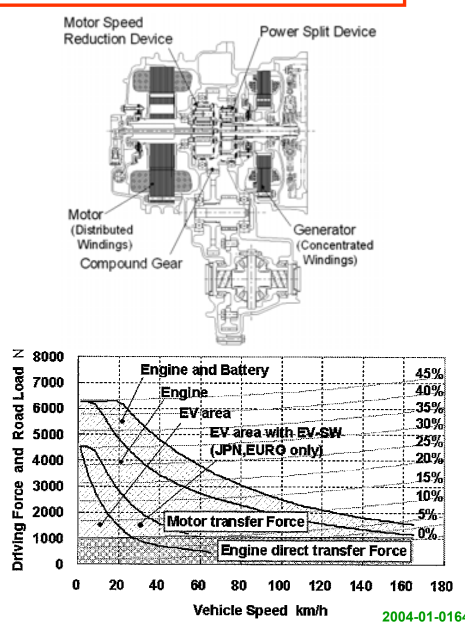
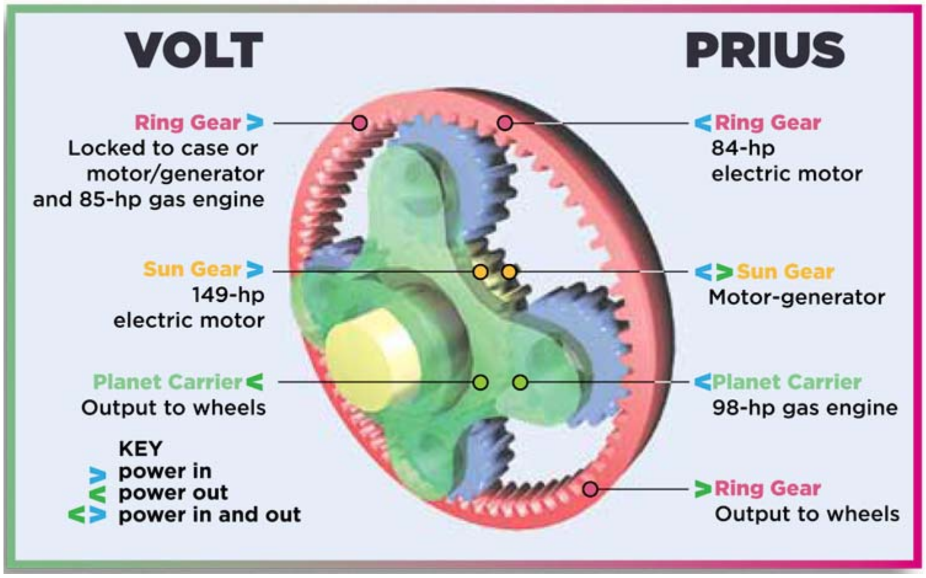
Toyota hybrid power split schedule





From SAE 2009-01-1332

Power split arrangement



Picture from Motor Trend, Oct. 12, 2010.

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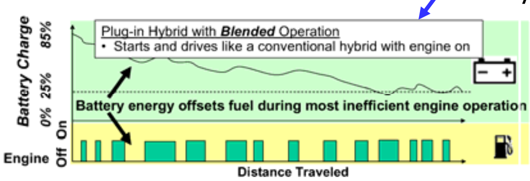
Hybrids and Plug-in hybrids

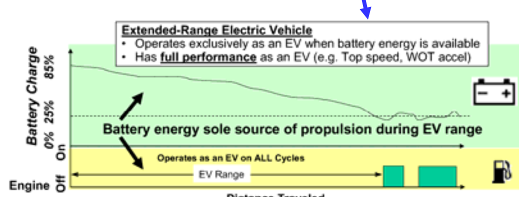
Hybrids (HEV)

- "Stored fuel centered"
  - Full hybrid
  - Mild hybrid /power assist

Plug-in hybrids (PHEV)

- "Stored electricity centered"
  - Blended PHEV
  - Urban capable PHEV
  - AER/ E-REV





From SAE 2008-01-0458 (GM)

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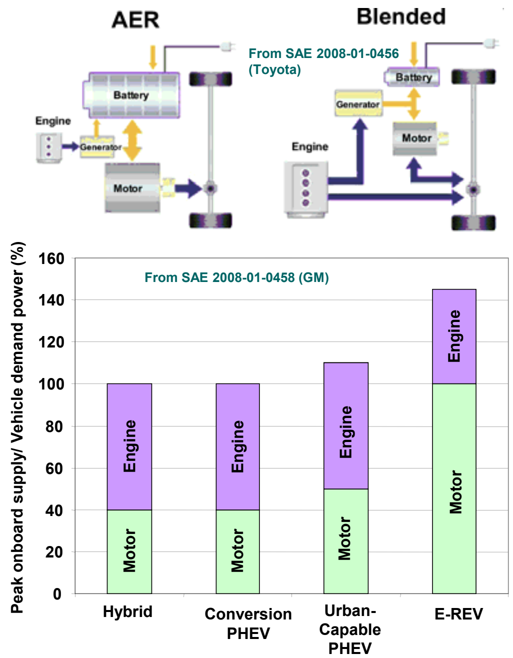

Engine/ motor sizing

The optimal component sizing and power distribution strategy depend on the required performance, range, and drive cycle

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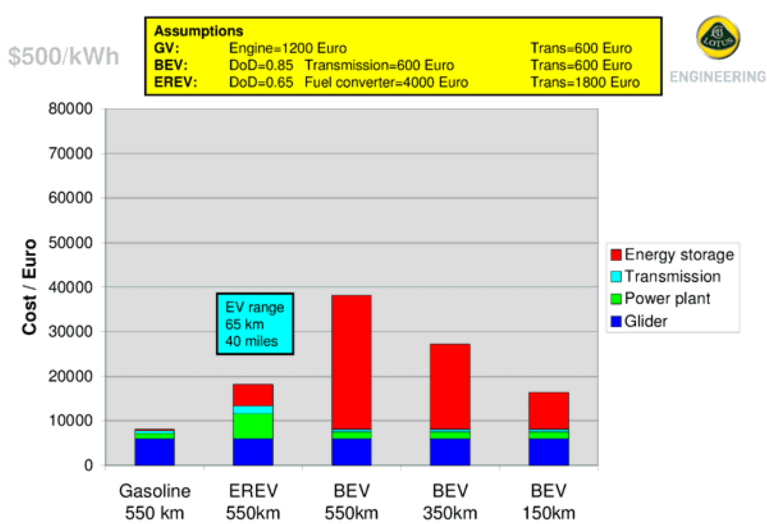
Cost factor



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HEV TECHNOLOGY

Toyota Prius

- Engine: 1.5 L, Variable Valve Timing, Atkinson/Miller Cycle (13.5 expansion ratio), Continuously Variable Transmission
  – 57 KW at 5000 rpm
- Motor - 50 KW
- Max system output – 82 KW
- Battery - Nickel-Metal Hydride, 288V; 21 KW
- Fuel efficiency:
  – 66 mpg (Japanese cycle)
  – 43 mpg (EPA city driving cycle)
  – 41 mpg (EPA highway driving cycle)
- Efficiency improvement (in Japanese cycle) attributed to:
  – 50% load distribution; 25% regeneration; 25% stop and go
- Cost: ~$20K

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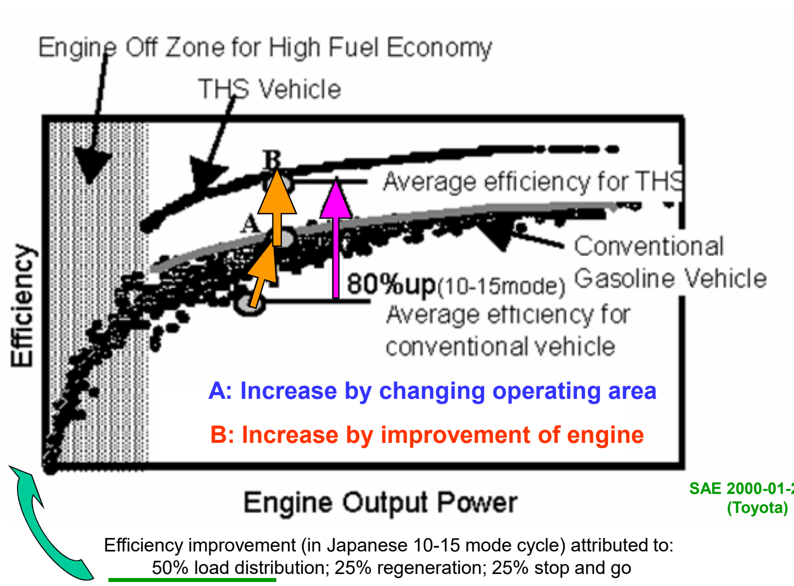
Efficiency improvement: Toyota Hybrid System (THS)



SAE 2000-01-2930 (Toyota)

Efficiency improvement (in Japanese 10-15 mode cycle) attributed to:
50% load distribution; 25% regeneration; 25% stop and go

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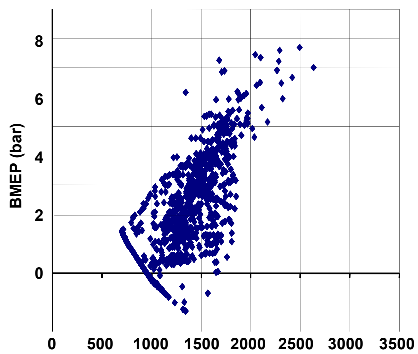
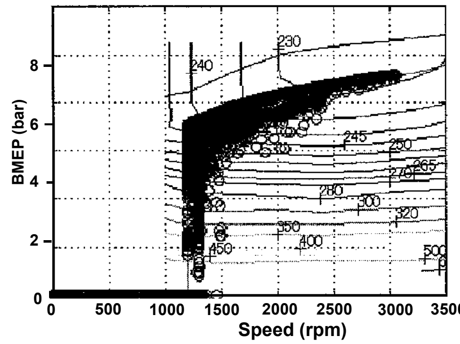
Operating map in LA4 driving cycle

Typical passenger car engine



Toyota THS II Data from SAE 2004-01-0164



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Hybrid cost factor

If $\Delta\$$ is price premium for hybrid vehicle
P is price of gasoline (per gallon)
δ is fractional improvement in mpg

Then mileage (M) to be driven to break even is

$$M = \frac{\Delta\$ \text{ x mpg}}{P \text{ x } \left(1 - \frac{1}{1+\delta}\frac{E}{P}\right)}$$

For hybrid E=P
For E-REV, E is cost of electricity for energy equivalent of 1 gallon of gasoline

(assume that interest rate is zero and does not account for battery replacement cost)

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Hybrid cost factor

Example:
Ford Fusion and Ford Fusion-Hybrid

Price premium (Δ$, MY13 listed) = \$5300 (\$27200-\$21900)
mpg (city and highway combined) = 27 mpg (47 for hybrid)
hybrid improvement in mpg(%) = 74%

At gasoline price of \$4.00 per gallon, mileage (M) driven to break even is

$$M = \frac{5300 \text{ x } 27}{4 \text{ x } \left(1 - \frac{1}{1+0.74}\right)} = 84 \text{ K miles } (135\text{x}10^3 \text{km})$$

(excluding interest and battery replacement cost)

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EREV cost factor

Example:
Chevrolet Cruise versus Volt (EREV)

Price premium (Δ$, MY13 listed) = \$19000 (\$39145-\$20145)
mpg (city and highway combined) = 30 mpg vs 98 mpg_e for PHEV
hybrid improvement in mpg(%) = 227%

At gasoline price of \$4.00 per gallon, and electricity of \$0.12/KWhr (\$4.04/gallon equivalent*), mileage (M) driven to break even is

$$M = \frac{19000 \text{ x } 30}{4 \text{ x } \left(1 - \frac{1}{1+2.27}\frac{4.04}{4}\right)} = 206 \text{ K miles } (332\text{x}10^3 \text{km})$$

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*EPA definition: Energy of 1 gallon of gasoline=33.7 KWhr

BEV cost factor

Example:

Nissan Sentra versus Leaf (BEV)

Price premium (Δ$, MY13 listed) = $17480 ($35200-$17720)
mpg (city and highway combined) = 34 mpg vs 99 mpg_e for BEV
hybrid improvement in mpg(%) = 191%

At gasoline price of $4.00 per gallon, and electricity of $0.12/KWhr ($4.04/gallon equivalent*), mileage (M) driven to break even is

$$M = \frac{17480x34}{4x(1 - \frac{1}{1+1.91} x \frac{4.04}{4}} = 227 \text{ Kmiles } (365x10^3 km)$$

*EPA definition: 1gallon of gasoline=33.7 KWhr

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Barrier to Hybrid Vehicles

- Cost factor
  – difficult to justify based on pure economics
- Battery replacement (not included in the previous breakeven analysis)
  – California ZEV mandate, battery packs must be warranted for 15 years or 150,000 miles : a technical challenge

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Hybrid Vehicle Outlook

- Hybrid configuration will capture a significant fraction of the passenger market
  - Fuel economy requirement
  - **Additional cost is in the affordable range**

- Plug-in hybrids
  - Much more expansive (hybrid + larger battery)
  - Weight penalty (battery + motor + engine)
  - No substantial advantage for overall CO_2 emissions
  - Limited battery life

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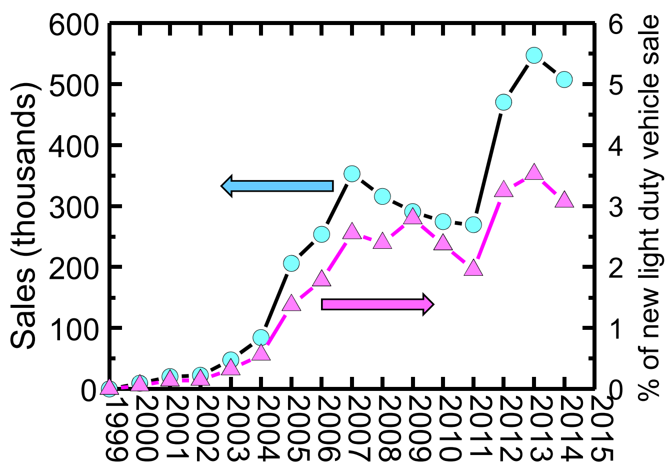
Sales figure for hybrid & electric vehicles



Expect substantial increase in market penetration by 2025 because of fuel economy target requirement

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