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

The hydrogen economy

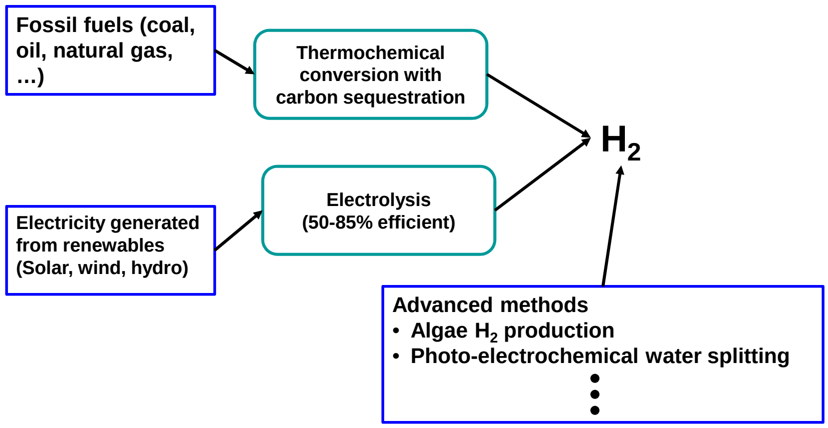
Premise:

$H_2 + O_2 \rightarrow H_2O$
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



Fossil fuels (coal, oil, natural gas, …)

Thermochemical conversion with carbon sequestration

Electricity generated from renewables (Solar, wind, hydro)

Electrolysis (50-85% efficient)

H_2

Advanced methods
- **Algae H_2 production**
- **Photo-electrochemical water splitting**

⋮

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)**

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	$3.3\text{x}10^{4}$	3.48
Diesel	810	42	$3.4\text{x}10^{4}$	3.37
Natural Gas				
@1 bar	0.72	45	$3.2\text{x}10^{1}$(x)	3.25
@100 bar	71		$3.2\text{x}10^{3}$	
LNG (180K, 30bar)	270		$1.22\text{x}10^{4}$	
Methanol	792	20	$1.58\text{x}10^{4}$	3.19
Ethanol	785	26.9	$2.11\text{x}10^{4}$	3.29
Hydrogen				
@1bar	0.082	120	$0.984\text{x}10^{1}$(x)	2.86
@100 bar	8.2		$0.984\text{x}10^{3}$	
Liquid (20K, 5 bar)	71		$8.52\text{x}10^{3}$	

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

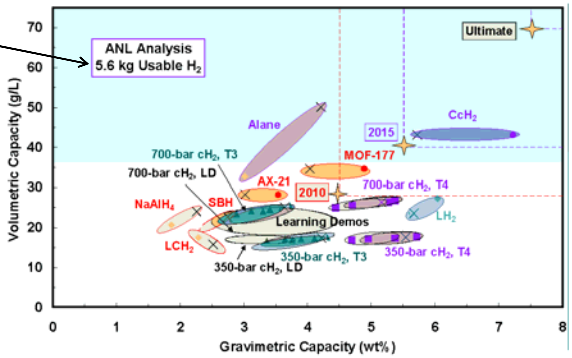
The hydrogen economy
(H2 as transportation fuel)

Obstacles

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

5.6 kg of H2
~700 MJ

Fuel tank capacity
of 50 kg carries
~2200 MJ



CcH2: cryogenic compressed LH2

cH2: compressed H2

MOF: Metal organic framework for LH2

- Infra structure: Supply, safety, …

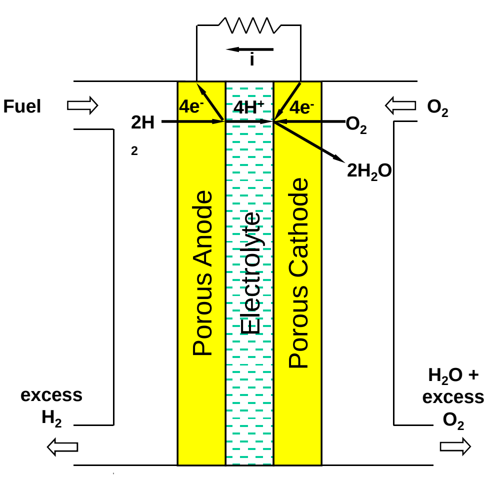
The hydrogen economy has significant hurdles

*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

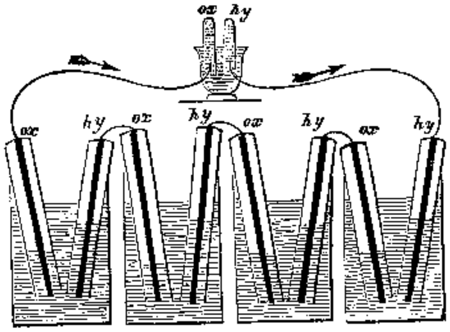


History of Fuel Cell

- **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)

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

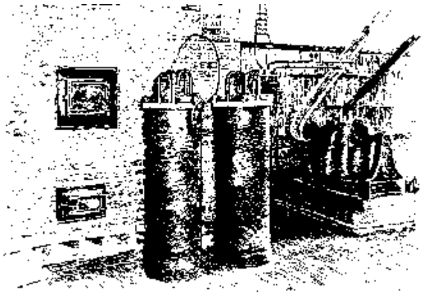
The coal/air cell

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



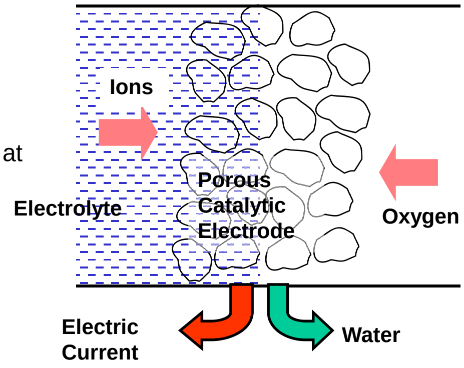
The 1896 W.W.Jacques large carbon cell (30KW)

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)

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

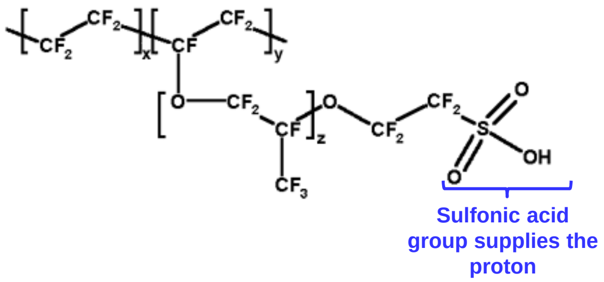
High temperature fuel cells are more tolerant of CO and other deactivating agents

Automotive application

PEM

Nafion (a DuPont product)

Tetrafluoroethylene based copolymer



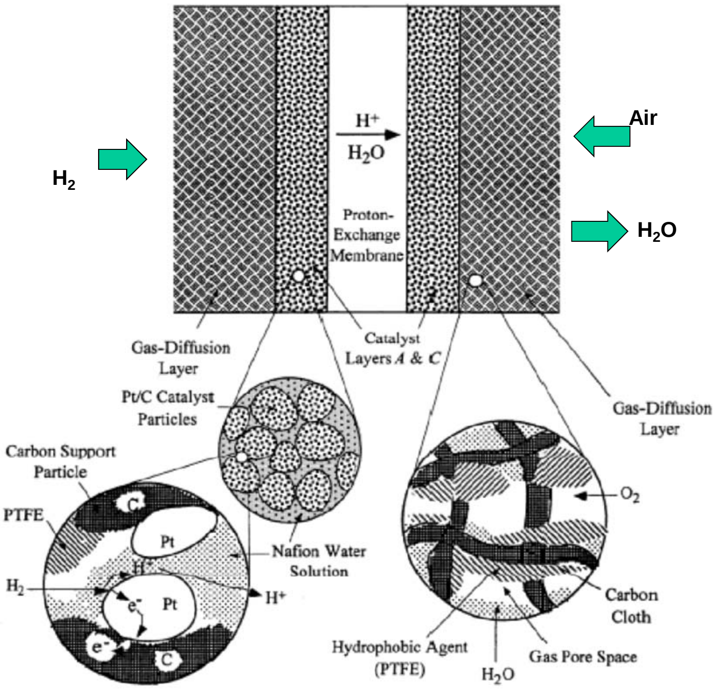
Sulfonic acid group supplies the proton

Function:

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

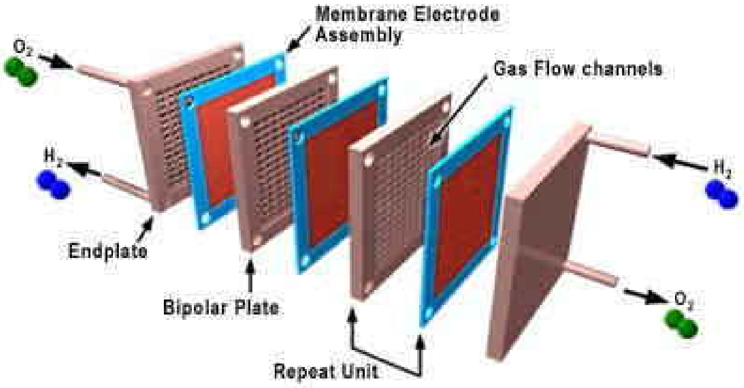
Retail ~$300/m^2$

- 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



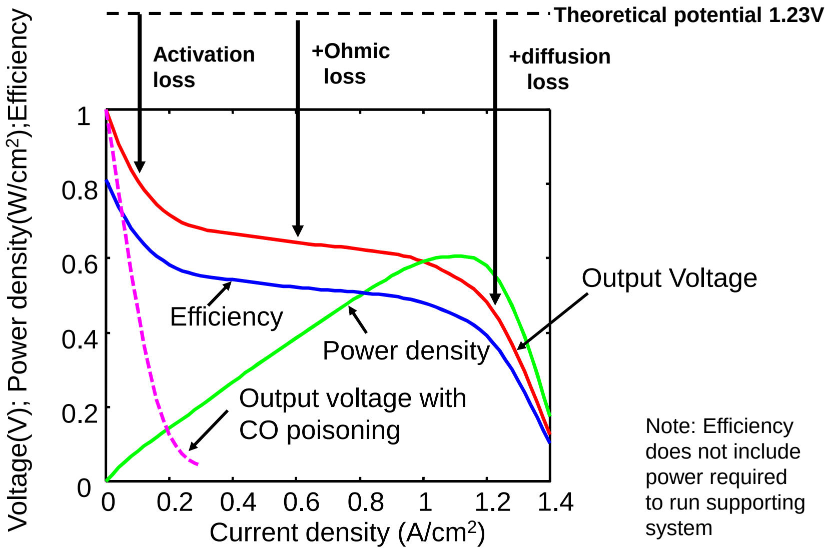
Single cell details

Modern PEM fuel cell stack



(From 3M web site)

Current PEM H_2/O_2 Fuel Cell Performance

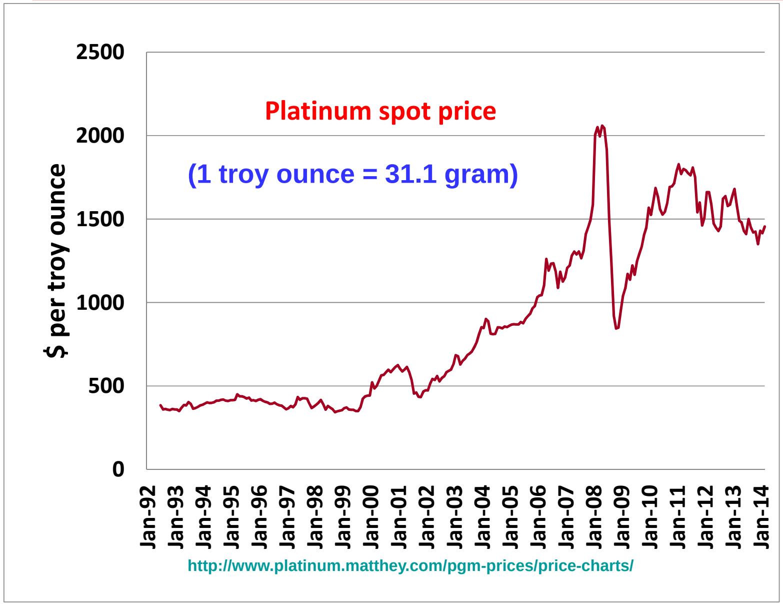


Note: Efficiency does not include power required to run supporting system

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 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)

Price of platinum



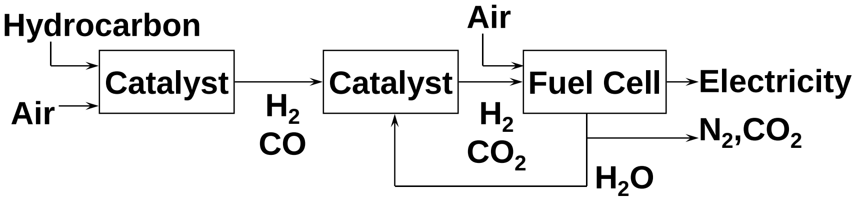
http://www.platinum.matthey.com/pgm-prices/price-charts/

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

The hydrogen problem:
H_2 from reforming petroleum fuel



Hydrocarbon

Air

Catalyst

H_2
CO

Catalyst

H_2
CO_2

Air

Fuel Cell

Electricity

N_2,CO_2

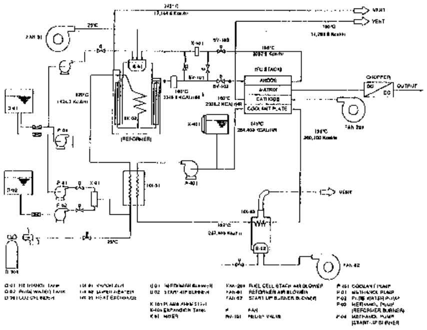
H_2O

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

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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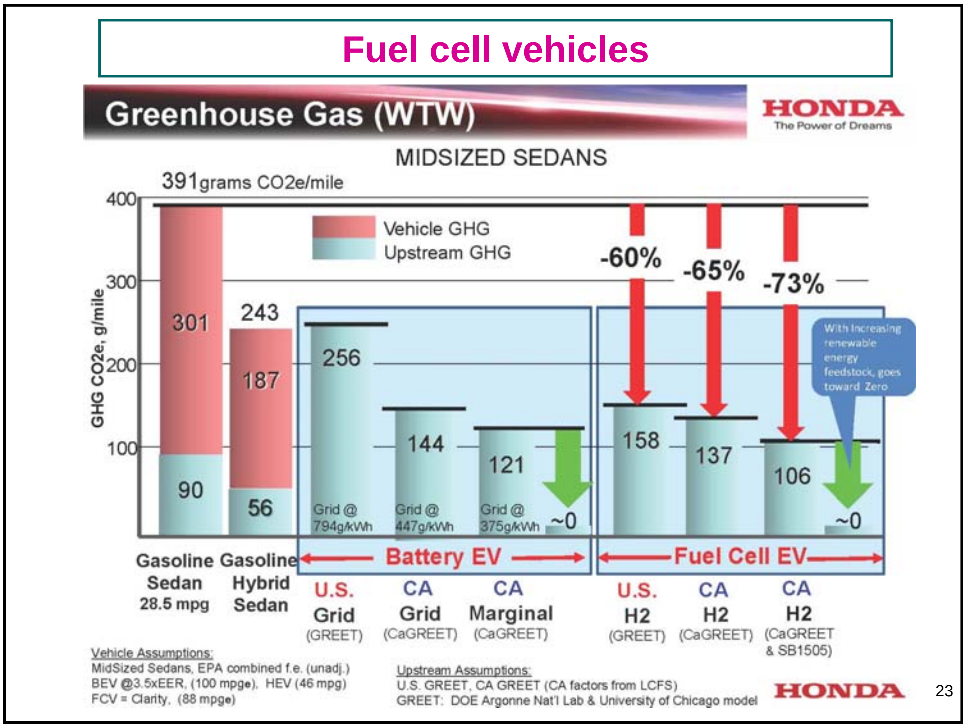
Fuel cell outlook

- 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



Fuel cell vehicles

Greenhouse Gas (WTW)

HONDA
The Power of Dreams

MIDSIZED SEDANS

Vehicle Assumptions:
MidSized Sedans, EPA combined f.e. (unadj.)
BEV @3.5xEER, (100 mpge), HEV (46 mpg)
FCV = Clarity, (88 mpge)

Upstream Assumptions:
U.S. GREET, CA GREET (CA factors from LCFS)
GREET: DOE Argonne Nat'l Lab & University of Chicago model

HONDA

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

Batteries

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

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):

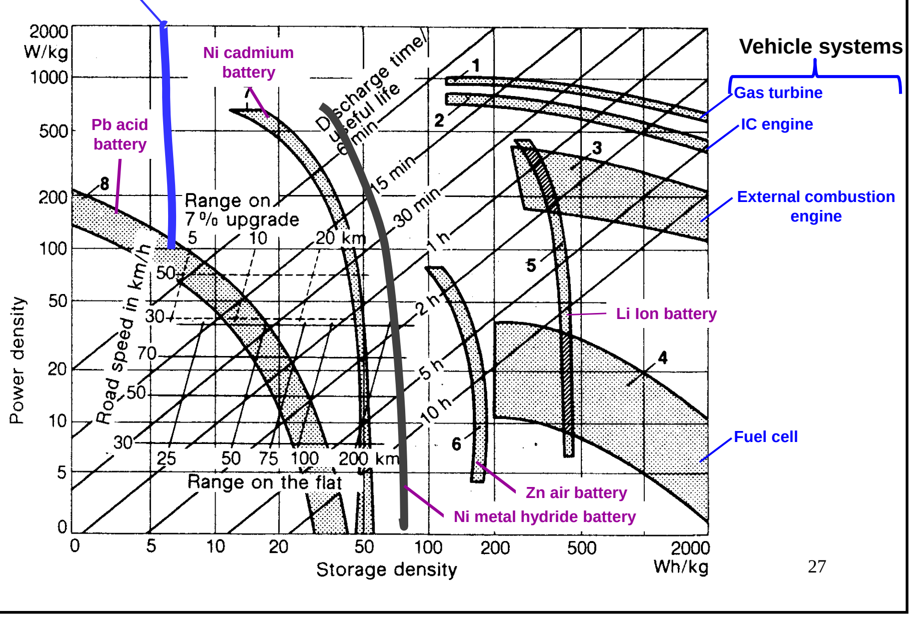
$$LiCoO_2 \rightleftarrows Li_{(1-x)}CoO_2 + xLi^+ + xe^-$$

Cathode (in charging):

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

Ragone Plot: engine/storage system

(From Bosch Automotive Handbook)



Super capacitor Power density up to 10^4 W/kg

Ni cadmium battery

Pb acid battery

Gas turbine

IC engine

External combustion engine

Li Ion battery

Fuel cell

Zn air battery

Ni metal hydride battery

Battery characteristics

Table 2. Relevant energy storage performance overview

	Temperature [°C]	η_E [%]	Energy		Power [W/kg]	Voltage [V]	Self-discharge [%/Month]	Cyclelife @80 %DoD	Cost estimation	
			[Wh/l]	[Wh/kg]					[$/kWh]	[$/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

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

Integrated starter and generator

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

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

Capacitors

Energy storage in the electric field within the capacitor

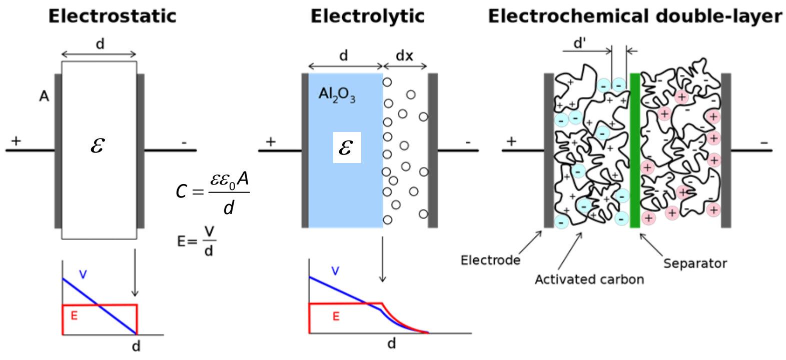


Image from wikipedia

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

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

Hybrid vehicles

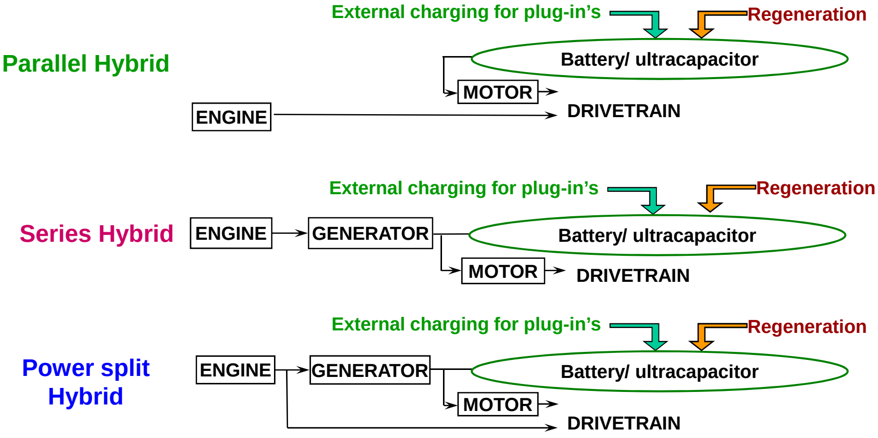
Configuration:

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

Hybrid Vehicles



External charging for plug-in's
Regeneration

Parallel Hybrid

Battery/ ultracapacitor
MOTOR
ENGINE
DRIVETRAIN

External charging for plug-in's
Regeneration

Series Hybrid

ENGINE
GENERATOR
Battery/ ultracapacitor
MOTOR
DRIVETRAIN

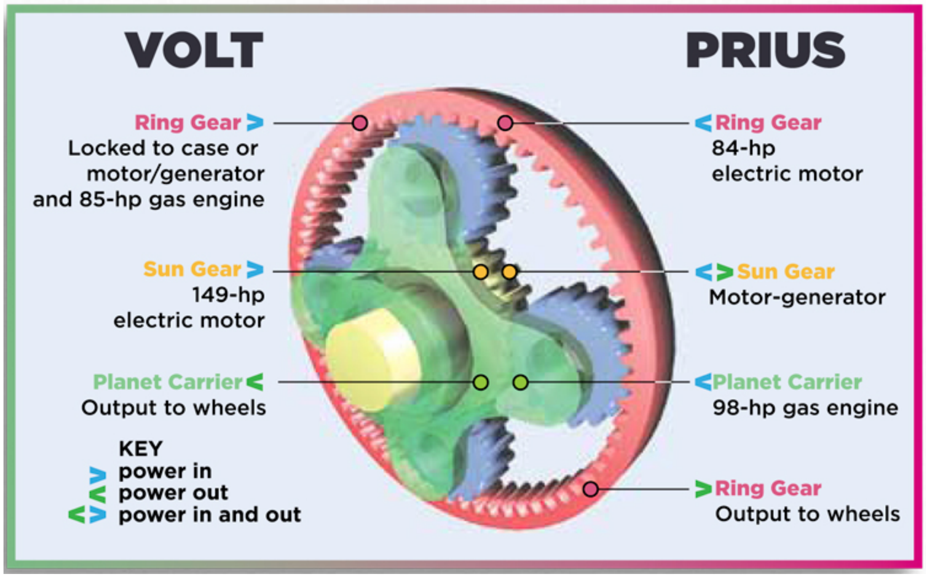
External charging for plug-in's
Regeneration

Power split Hybrid

ENGINE
GENERATOR
Battery/ ultracapacitor
MOTOR
DRIVETRAIN

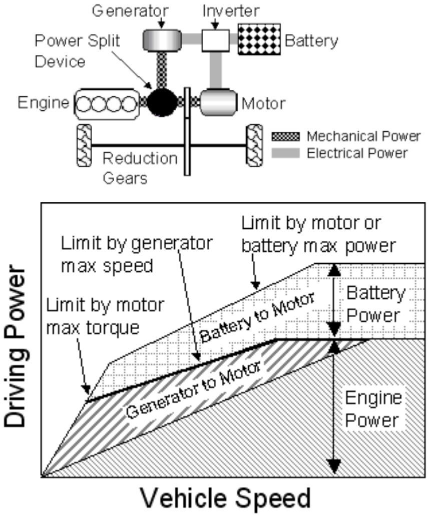
Examples: Parallel hybrid: Honda Insight
Series hybrid: GM E-Flex System
Power split hybrid: Toyota Prius

Power split arrangement

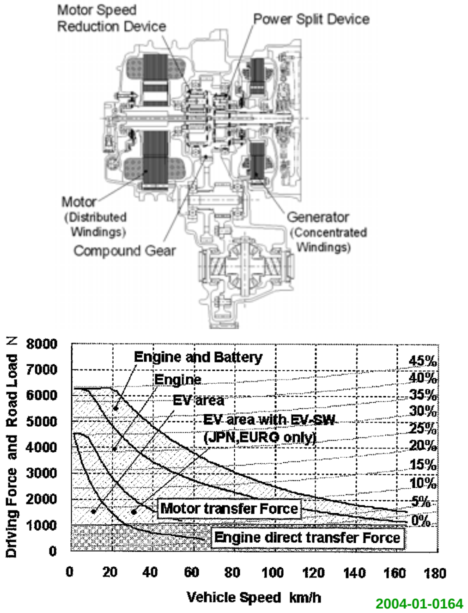


Picture from Motor Trend, Oct. 12, 2010; http://www.motortrend.com/features/editorial/1010_unbolting_the_chevy_volt_to_see_how_it_ticks/

Toyota hybrid power split schedule



From SAE 2009-01-1332



2004-01-0164

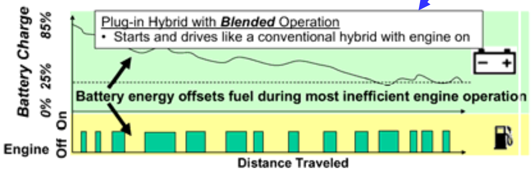
Hybrids and Plug-in hybrids

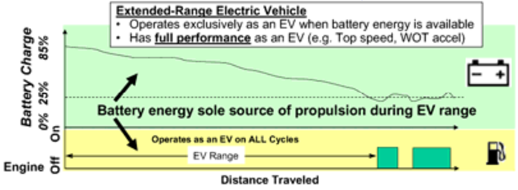
Hybrids (HEV)

- “Stored fuel centered”
  - Full hybrid
  - Mild hybrid /power assist

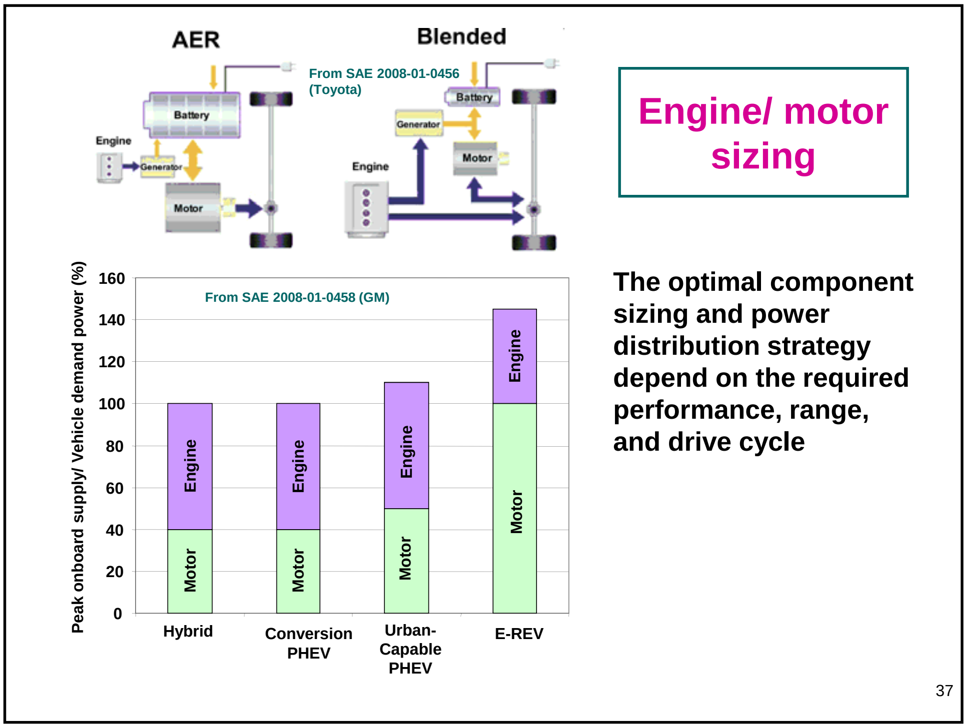
Plug-in hybrids (PHEV)

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





From SAE 2008-01-0458 (GM)

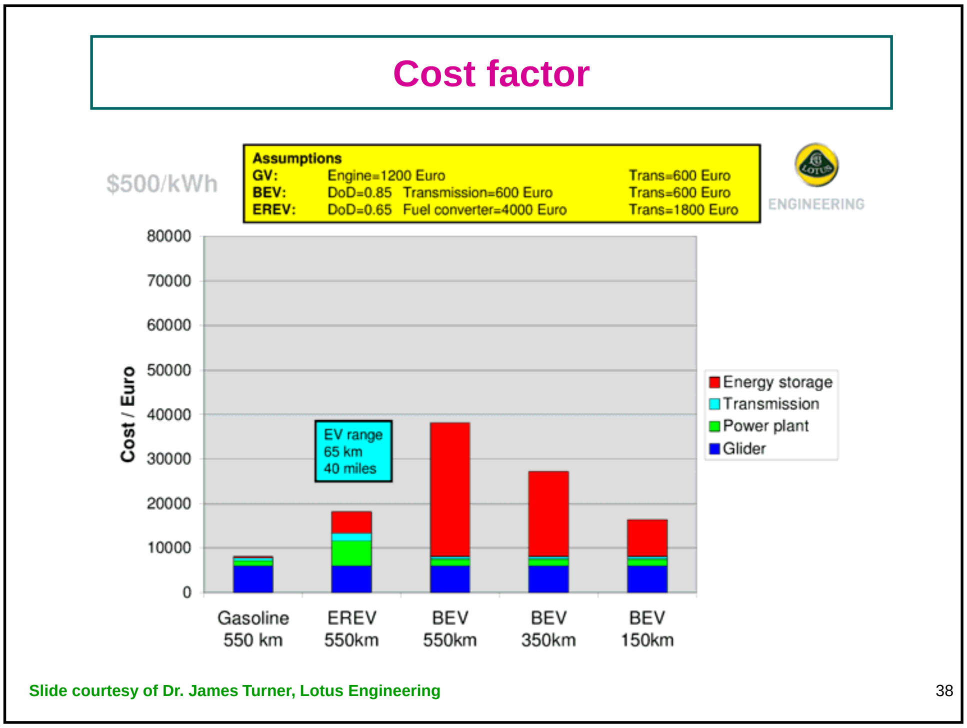


Engine/ motor sizing

From SAE 2008-01-0456 (Toyota)

From SAE 2008-01-0458 (GM)

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



Cost factor

$500/kWh

Assumptions			
GV:	Engine=1200 Euro		Trans=600 Euro
BEV:	DoD=0.85	Transmission=600 Euro	Trans=600 Euro
EREV:	DoD=0.65	Fuel converter=4000 Euro	Trans=1800 Euro

ENGINEERING

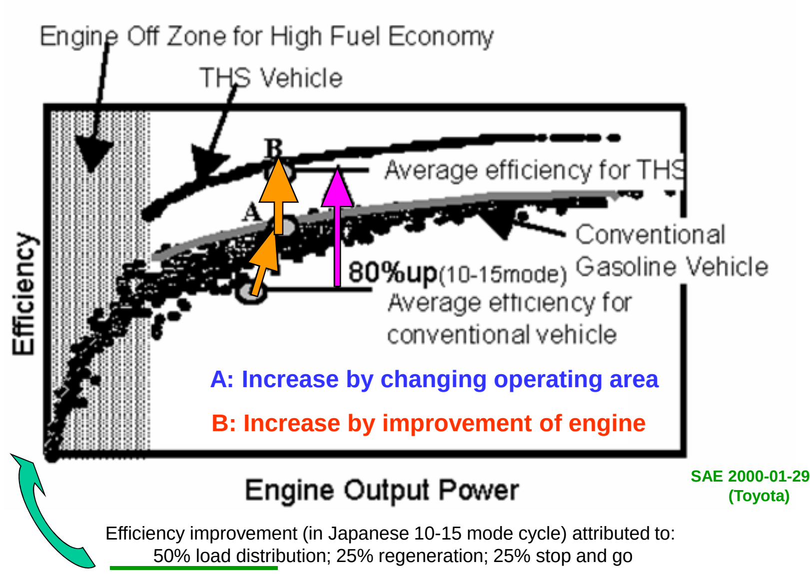
Slide courtesy of Dr. James Turner, Lotus Engineering

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

Efficiency improvement: Toyota Hybrid System (THS)

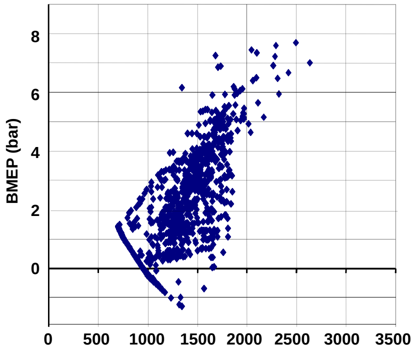


SAE 2000-01-2930
(Toyota)

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

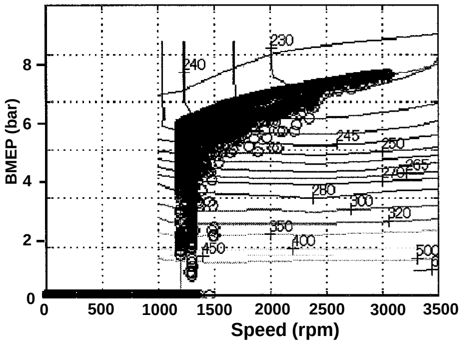
Operating map in LA4 driving cycle

Typical passenger car engine



Toyota THS II

Data from SAE 2004-01-0164



Hybrid cost factor

If Δ\$ 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)

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

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

(excluding interest and battery replacement cost)

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

$$M = \frac{19000 \text{ x } 30}{4 \text{ x } \left(1 - \frac{1}{1 + 2.27}\frac{4}{4.04}\right)} = 204 \text{ K miles}$$

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

Barrier to Hybrid Vehicles

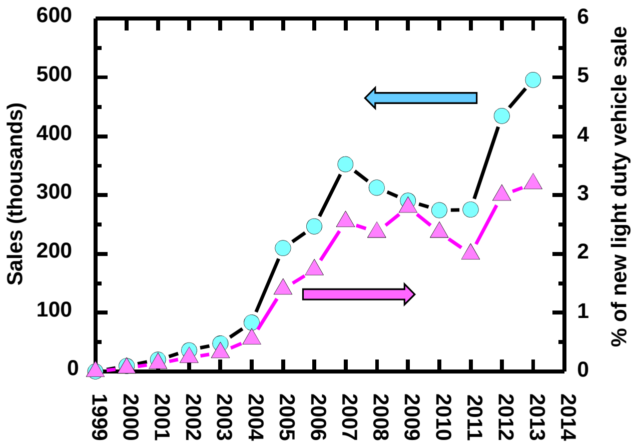
- Cost factor
  - difficult to justify based on pure economics
- Battery replacement **(not included in the previous breakeven analysis)**
  - California ZEV mandate, battery packs must be warranted for 15 years or 150,000 miles : a technical challenge

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

Sales figure for hybrid vehicles



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