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

The hydrogen economy

Premise:

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \]
\[ \text{LHV} = 120 \text{ MJ/kg (33.3 KW-hr/kg)} \]

- 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)
- Advanced methods
  - Algae H₂ 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

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Density (Kg/m³)</th>
<th>LHV/mass (MJ/Kg)</th>
<th>LHV/mass (MJ/m³)</th>
<th>LHV/Vol of Stoil./Mixture @1 atm, 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>750</td>
<td>44</td>
<td>3.3x10⁴</td>
<td>3.48</td>
</tr>
<tr>
<td>Diesel</td>
<td>810</td>
<td>42</td>
<td>3.4x10⁴</td>
<td>3.37</td>
</tr>
<tr>
<td>Natural Gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>@1 bar</td>
<td>0.72</td>
<td>45</td>
<td>3.2x10¹(x)</td>
<td>3.25</td>
</tr>
<tr>
<td>@100 bar</td>
<td>71</td>
<td>45</td>
<td>3.2x10³</td>
<td></td>
</tr>
<tr>
<td>LNG (180K, 30bar)</td>
<td>270</td>
<td></td>
<td>1.22x10⁴</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>792</td>
<td>20</td>
<td>1.58x10⁴</td>
<td>3.19</td>
</tr>
<tr>
<td>Ethanol</td>
<td>785</td>
<td>26.9</td>
<td>2.11x10⁴</td>
<td>3.29</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>@1 bar</td>
<td>0.082</td>
<td>120</td>
<td>0.984x10¹(x)</td>
<td>2.86</td>
</tr>
<tr>
<td>@100 bar</td>
<td>8.2</td>
<td>120</td>
<td>0.984x10³</td>
<td></td>
</tr>
<tr>
<td>Liquid (20K, 5 bar)</td>
<td>71</td>
<td></td>
<td>8.52x10³</td>
<td></td>
</tr>
</tbody>
</table>

*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 H2
  – 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

• Infrastructure: 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
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
    - Nernst, Haber, Ostwald and others

- Development of Ion Exchange Membrane for application in the Gemini spacecraft in the 1950/1960

- 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

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)


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
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
  - $\text{H}^+$, $\text{O}^{2-}$ (important difference in terms of product disposal)

Types of fuel cell (cont.)

- By electrolyte
  - Solid oxides: ~1000°C
  - Carbonates: ~600°C
  - $\text{H}_3\text{PO}_4$: ~200°C
  - Proton Exchange Membrane (PEM): ~80°C

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

• 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

Retail ~$300/m²

PTFE: polytetrafluoroethylene (trade name teflon)

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Modern PEM fuel cell stack

Typical PEM H₂/O₂ Fuel Cell Performance

Theoretical OCV = 1.229 V

Output Voltage

Efficiency

Power density

Output voltage with CO poisoning

Internal loss

Activation loss

Ohmic loss

Diffusion loss

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/cm², 0.5-0.7 V operating voltage
  – 0.5-0.7 W/cm² 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/cm²
    ➢ 30g for a 60kW stack (Jan., 2014 price ~$1500)
    ➢ (automotive catalyst has ~2-3g)

Price of platinum

Platinum spot price

(1 troy ounce = 31.1 gram)
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 infrastructure
- 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 $\rightarrow$ Catalyst $\rightarrow$ Hydrogen $\rightarrow$ Fuel Cell $\rightarrow$ Electricity
Air $\rightarrow$ Catalyst $\rightarrow$ CO

Note: HC to $H_2$/CO process is exothermic; energy loss $\sim$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 $\sim$70%

Problems:
CO poisoning of anode
Sulfur poisoning
Anode poisoning requires $S<1$ppm
Reformer catalyst poisoning requires $S<50$ppb
Fuel cell powerplant with fuel reforming

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

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

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

Greenhouse Gas (WTW)

MIDSIZED SEDANS

Vehicle GHG
Upstream GHG

-60%
-65%
-73%

Gasoline Sedan
Hybrid Sedan

90
56

256
144
121
158
137
106

Grid @ 90kwh
Grid @ 60kwh
Grid @ 30kwh

U.S. H2
CA H2
CA H2

Battery EV
Fuel Cell EV

Vehicle Assumptions:
Midsized Sedans, EPA combined f.e. (unaided)
BEV (80 km/hr), 100 (mpg)
HSEV (44 mph)
FCV = Clarity (80 mpge)

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

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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!

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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):
\[ \text{PbSO}_4(s) + 2\text{H}_2\text{O}(aq) \rightleftharpoons \text{PbO}_2(s) + \text{HSO}_4(aq) + 3\text{H}^+(aq) + 2e^- \]
Cathode (in charging):
\[ \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \rightleftharpoons \text{Pb}(S) + \text{HSO}_4(aq) \]

**Li ion battery:** e.g. LiCoO2 anode; graphite cathode
Charging (forward) / discharging (reverse)
Anode (in charging):
\[ \text{LiCoO}_2 \rightleftharpoons \text{Li}_{(1-x)}\text{CoO}_2 + x\text{Li}^+ + xe^- \]
Cathode (in charging):
\[ x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6 \]
Super capacitor

Power density up to $10^4$ W/kg

Ragone Plot: engine/storage system

(From Bosch Automotive Handbook)

battery

Pb acid battery

Ni cadmium battery

Range on 7% upgrade

Range on the flat

Li ion battery

Zn air battery

Ni metal hydride battery

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Battery characteristics

Table 2. Relevant energy storage performance overview

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<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Acid</td>
<td>−30 to 60</td>
<td>85</td>
<td>50 to 70</td>
<td>20 to 40</td>
<td>300</td>
<td>2.1</td>
<td>4 to 8</td>
<td>200</td>
</tr>
<tr>
<td>NiMH</td>
<td>−20 to 50</td>
<td>80</td>
<td>40 to 60</td>
<td>1300 to 500</td>
<td>2.9</td>
<td>1.2</td>
<td>20</td>
<td>&gt;2500</td>
</tr>
<tr>
<td>Li-ion</td>
<td>−20 to 55</td>
<td>93</td>
<td>150 to 250</td>
<td>3000 to 800</td>
<td>~3.6</td>
<td>1 to 5</td>
<td>&lt;2500</td>
<td>800</td>
</tr>
<tr>
<td>EDLC</td>
<td>−30 to 65</td>
<td>97</td>
<td>5 to 20</td>
<td>15000</td>
<td>~2.5</td>
<td>30</td>
<td>Not applicable</td>
<td>2000</td>
</tr>
</tbody>
</table>

Electric double layer capacitor (super-capacitor)

Integrated starter and generator

Configuration | P/E (kW/h) | Energy [kWh] | Power [kW] | Voltage [V] |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ISG</td>
<td>&gt; 60</td>
<td>&lt; 0.6</td>
<td>&lt; 6</td>
<td>12</td>
</tr>
<tr>
<td>Mild HEV</td>
<td>30 to 80</td>
<td>&lt; 1</td>
<td>&lt; 13</td>
<td>12 to 42</td>
</tr>
<tr>
<td>Power HEV</td>
<td>20</td>
<td>&lt; 4</td>
<td>20 to 100</td>
<td>&gt; 150</td>
</tr>
<tr>
<td>Plug in HEV</td>
<td>7 to 12</td>
<td>5 to 20</td>
<td>&lt; 80</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>BEV</td>
<td>2 to 3</td>
<td>&gt; 15</td>
<td>20 to 60</td>
<td>NA</td>
</tr>
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</table>


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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

- Electrostatic: \( C = \frac{\varepsilon_0 A}{d} \)
- Electrolytic: \( C = \frac{\varepsilon_0 A}{d} \)
- Electrochemical double-layer

Aluminum oxide layer thickness \(~\mu m\)
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

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

Parallel Hybrid
- External charging for plug-in's
- Battery/ultracapacitor
- Regeneration
- ENGINE → MOTOR → DRIVETRAIN

Series Hybrid
- External charging for plug-in's
- Battery/ultracapacitor
- Regeneration
- ENGINE → GENERATOR → MOTOR → DRIVETRAIN

Power split Hybrid
- External charging for plug-in's
- Battery/ultracapacitor
- Regeneration
- ENGINE → GENERATOR → MOTOR → DRIVETRAIN

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

Toyota hybrid power split schedule

From SAE 2009-01-1332
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)
The optimal component sizing and power distribution strategy depend on the required performance, range, and drive cycle.

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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Operating map in LA4 driving cycle

Typical passenger car engine

Toyota THS II

Data from SAE 2004-01-0164

Hybrid cost factor

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

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

\[
M = \frac{\Delta S \times \text{mph}}{P \times \left( 1 - \frac{1}{1 + \delta P} \right)}
\]

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

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

(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 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

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

*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 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

\[
M = \frac{17480 \times 34}{4 \times (1 - \frac{1}{1 + 1.91})^4 \times 4.04} = 227 \text{ K miles (365x10}^3 \text{km)}
\]

*EPA definition: 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 CO₂ emissions
  - Limited battery life

Sales figure for hybrid & electric vehicles

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