2017 Summer Professional Development Course
Advanced Automotive Technology

Topic 1:

Fundamentals of Fuel-Cell Systems for Vehicles

July 10 ~ 11, 2017
Dr. Jimmy C. Chen
Dr. Gene Liao
Wayne State University
fe8369@wayne.edu
geneliao@wayne.edu

WAYNE STATE

NSF

Center for Advanced Automotive Technology
C · A · A · T

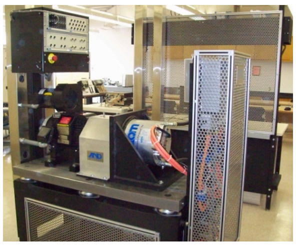
Macomb Community College

Introduction

Jimmy C. Chen
- Assistant Professor of Engineering Technology, Wayne State University.
- Ph.D., Texas A&M University, 2006.
- University projects: NSF, DOL, 2015-present.

Y. Gene Liao
- Professor and Director of Electric-drive Vehicle Engineering & Alternative Energy Technology; Engineering Technology, Wayne State University.
- Doctor of Engineering, University of Michigan-Ann Arbor, 1999.
- Worked as a practicing engineer for over 16 years in automotive sector.
- Consultant to: ASRC Primus/TARDEC, 2007-present.
- University projects: NSF, DOE, DOL, DOC, 2003-present.

Series HEV project with TARDEC



Electric Propulsion Integration Lab – HIL (Hardware-In-the-Loop)

Full HEV project with TARDEC

2

Future Trends for Ground Vehicles

- Hybrid vehicles present medium-term solution
- Long-term solution: **Single** On-board Energy Source/Storage (**Electricity** or ??) for ground vehicles
- How is the electricity supplied by single on-board energy source/storage? From **Battery**, **Fuel Cell**, or ??

Fossil fuel vehicle

HEV/PHEV/EV/FCV …

Micro Stop/Start Mild Full PHEV Range-Ext-EV FC-HEV Electric

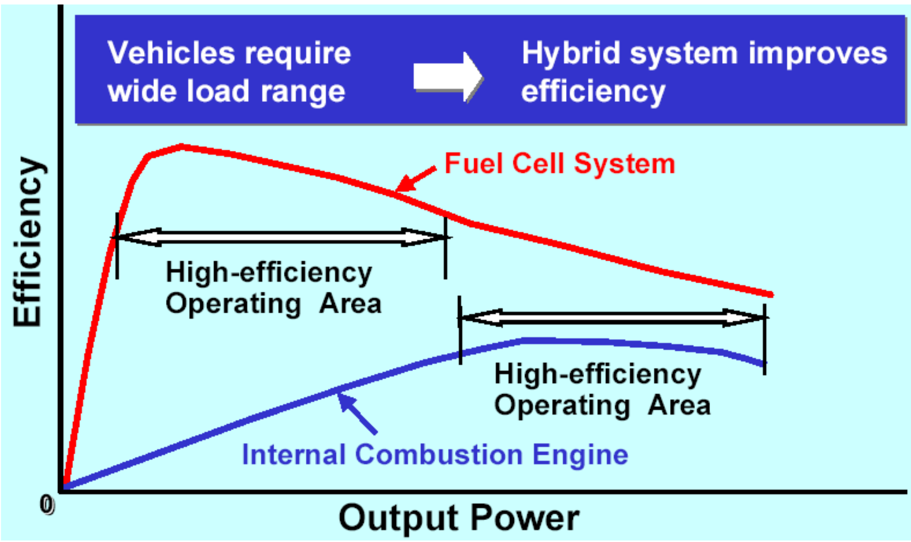
3

Hydrogen Fuel Cell Vehicle (FCV)

- Efficiency
  - More efficient than ICE and gas turbines
  - Can be as efficient for small systems than large ones
- No/low emissions (in principle)
  - True starting from hydrogen
  - Emissions from hydrogen production
- Simplicity, Reliability
  - No moving parts in stack
  - Not true for balance of plant
- Silence
  - True for fuel cell stack
  - Balance of plant
- Dual use technology (stationary power generation and transportation)

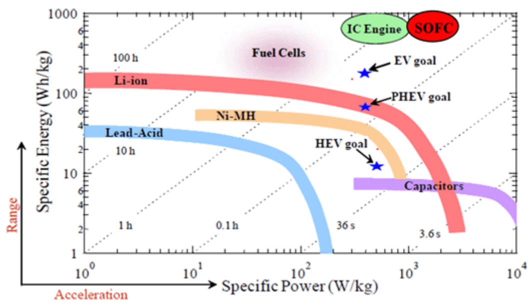
4

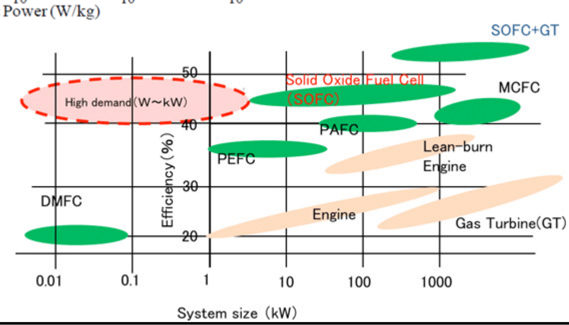
Why Fuel Cells ?



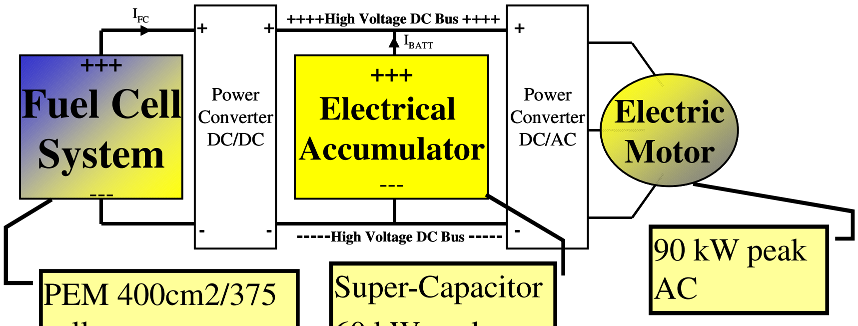
5

Energy and Efficiencies





Experimental Fuel Cell Vehicle



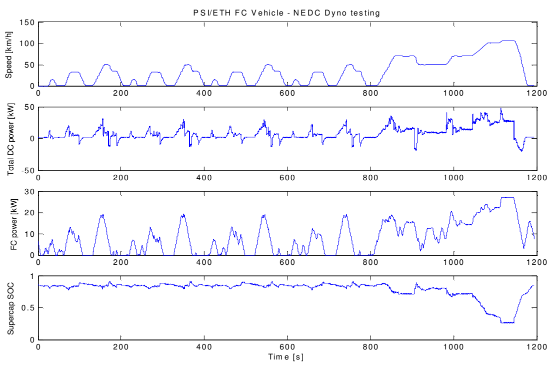
Parameter	VW Bora
Mass [kg]	1960
Frontal area x Drag coefficient [m2]	0.6
Rolling resistance coefficient	0.01

7

Experimental FC Vehicle Results

	NEDC	FUDS	FHDS
H2 consumed [g]	168	185	196
Fuel efficiency ge [l/100km]*	5.64	5.64	4.27
mpgge*	41.6	41.6	55

* SOC corrected gasoline equivalent



NEDC Dyno testing with ECMS

8

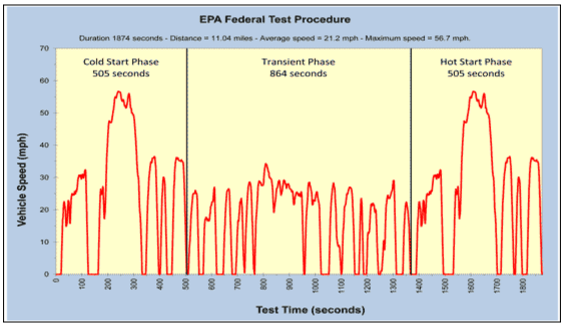
Driving cycles

- A driving cycle is a series of data points representing the speed of a vehicle versus time
- Driving cycles are used to assess the performance of vehicles such as fuel consumption and polluting emissions
- USA:
  - EPA Federal Test: FTP 72/75 (1978) / SFTP US06/SC03 (2008)
- Europe:
  - NEDC: ECE R15 (1970) / EUDC (1990)
- Japan:
  - 10 mode / 10-15 Mode (1983) / JC08 (2008)
- Global harmonized:
  - WLTP (2015)

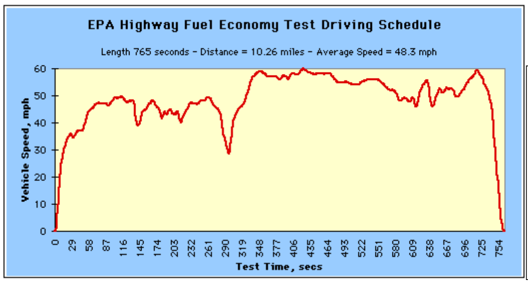
EPA Federal Test Procedure

- The testing was mandated by the Energy Tax Act of 1978, and the current procedure was updated in 2008
- Federal urban driving cycle (FUDS)
  - Also called FTP 72, UDDS or LA-4.
  - It simulates an urban route of 12.07 km (7.5 mi) with frequent stops.
  - The maximum speed is 91.2 km/h and the average speed is 31.5 km/h.
  - The cycle has two phases: a "cold start" phase of 505 seconds over a projected distance of 5.78 km at 41.2 km/h average speed, and a "transient phase" of 864 seconds, for a total duration of 1369 seconds.
  - FTP-75: Additional "hot start" cycle that repeats the "cold start" cycle of the beginning 505 seconds of the UDDS cycle
- Federal highway driving cycle (FHDS)
  - It uses a warmed-up engine and makes no stops, averaging 48 mph (77 km/h) with a top speed of 60 mph (97 km/h) over a 10-mile (16 km)

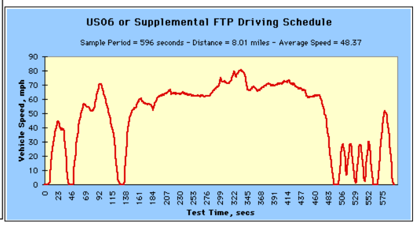
FTP-75



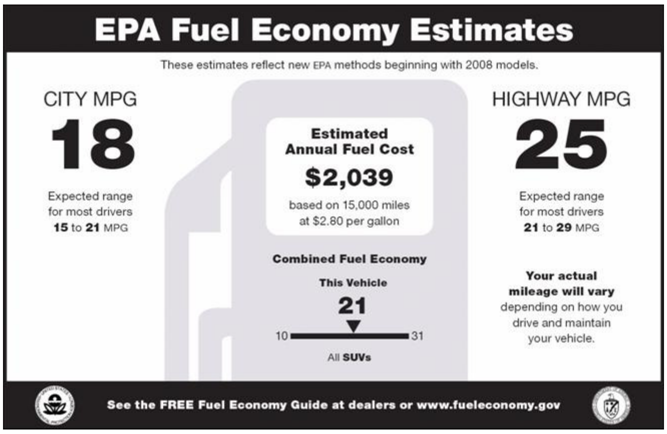
FHDS



The US06 is a high acceleration aggressive driving schedule that is often identified as the "Supplemental FTP" driving schedule.



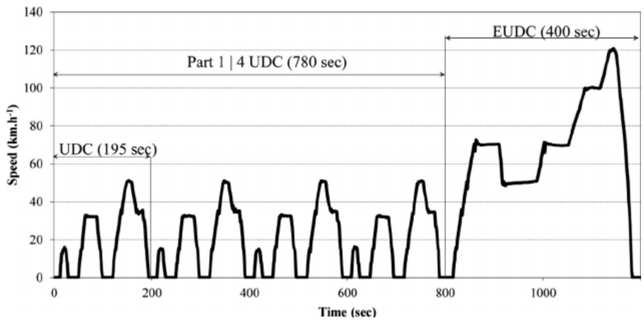
EPA fuel economy sticker



New European Driving Cycle (NEDC)

- Driving cycle last updated in 1997, designed to assess the emission levels of car engines and fuel economy
- Several measurements are performed along the cycle. The figures made available to the general public are:
  - Urban fuel economy (first 780 seconds) ECE-15
  - Extra-Urban fuel economy (780 to 1180 s)
  - Overall fuel economy (complete cycle)
  - CO2 emission (complete cycle)
- The cycle must be performed on a cold vehicle at 20–30 ℃ (typically run at 25 ℃)
- Urban driving Cycle
- Extra-urban driving Cycle
- Combined

NEDC



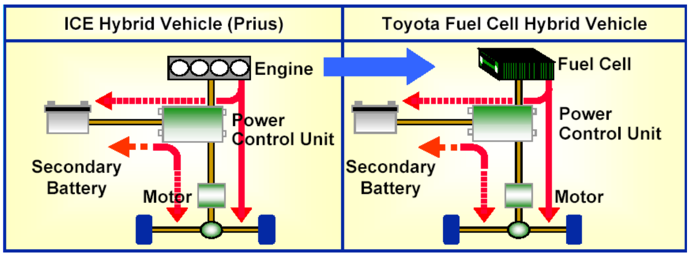
Hybrid Vehicle

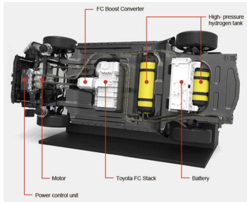
Fuel Cell Vehicle

Engine Tech. ←Good Competitor→ FC Tech.

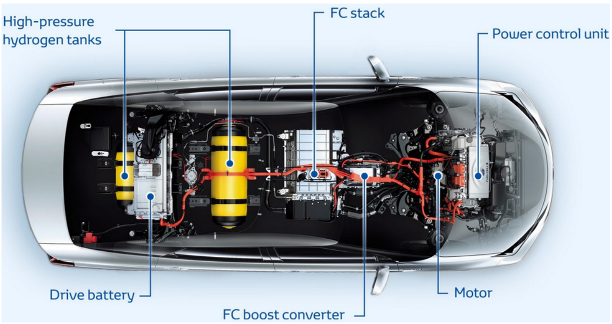
Common Tech.

- >Motor
- >Inverter
- >Battery
- >Vehicle power management
- >Regeneration brake



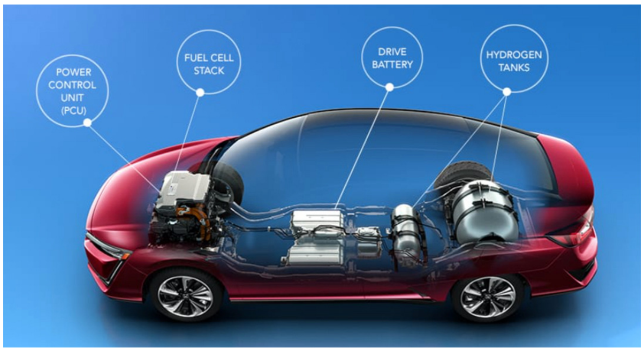


15



2016 Toyota Mirai FCV

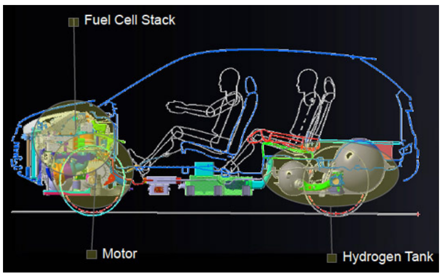
16



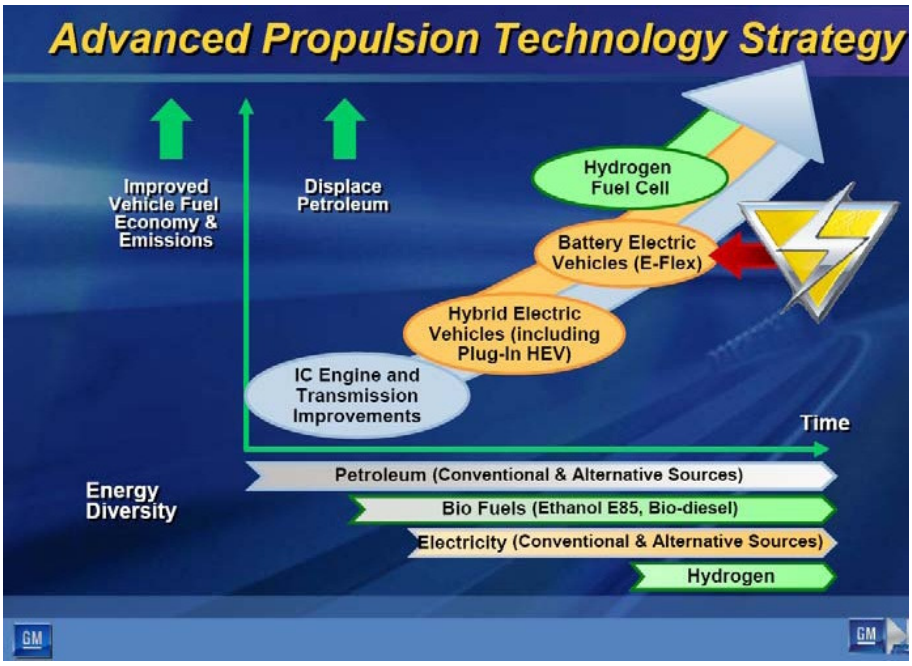
Honda Clarity Fuel Cell

17

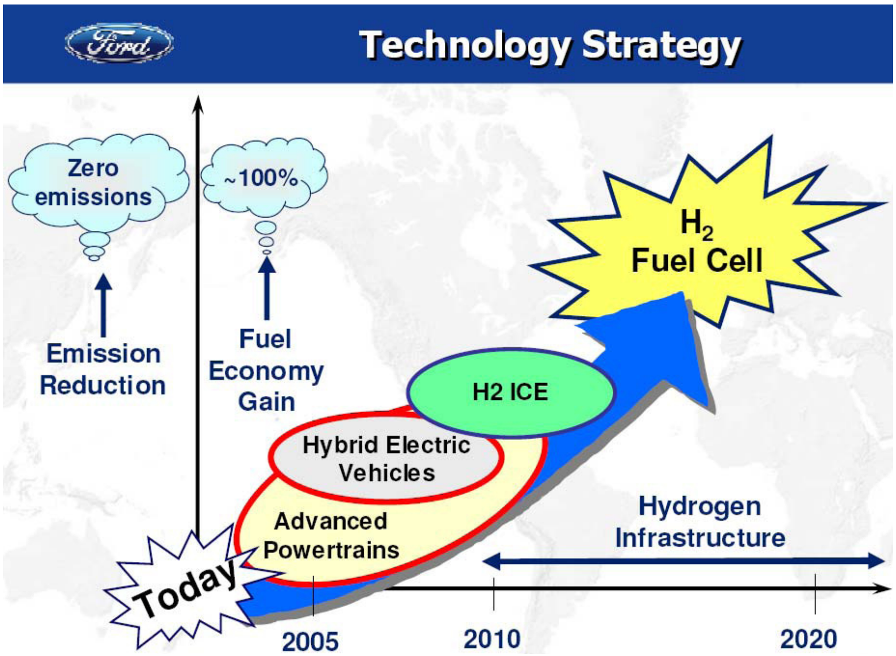
Hyundai ix35 FCEV



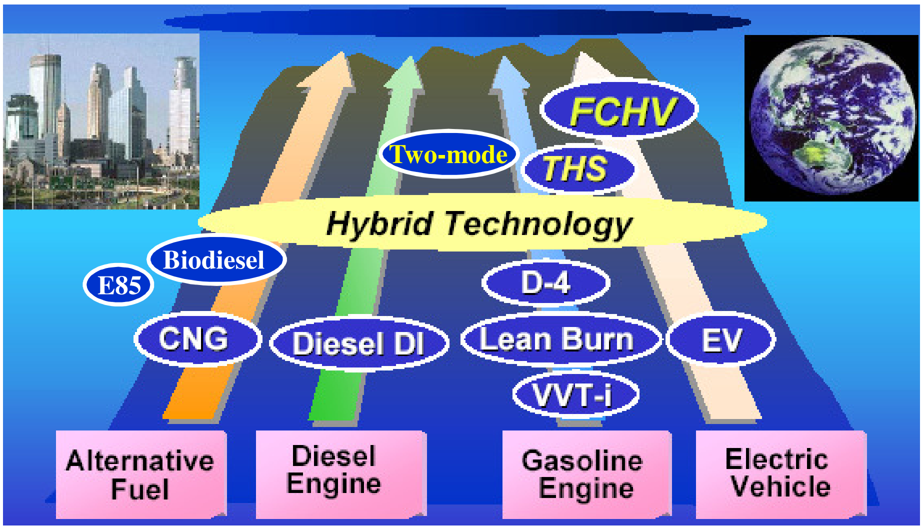
18


Advanced Propulsion Technology Strategy
Improved Vehicle Fuel Economy & Emissions
Displace Petroleum
Hydrogen Fuel Cell
Battery Electric Vehicles (E-Flex)
Hybrid Electric Vehicles (including Plug-In HEV)
IC Engine and Transmission Improvements
Time
Energy Diversity
Petroleum (Conventional & Alternative Sources)
Bio Fuels (Ethanol E85, Bio-diesel)
Electricity (Conventional & Alternative Sources)
Hydrogen
GM
GM

19


Technology Strategy
Zero emissions
~100%
Emission Reduction
Fuel Economy Gain
H_2 Fuel Cell
H2 ICE
Hybrid Electric Vehicles
Advanced Powertrains
Hydrogen Infrastructure
Today
2005
2010
2020

20



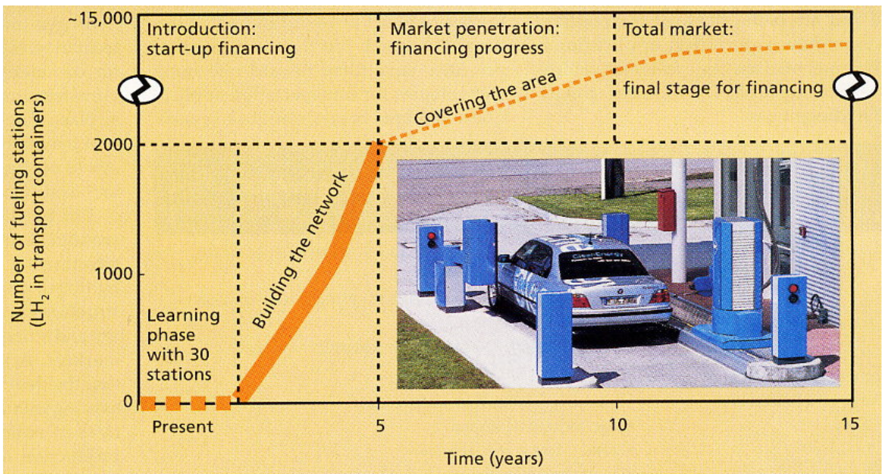
Continuously improved combustion engine, EM, battery, and alternative fuel.

21

Hydrogen Distribution Infrastructure

Hydrogen Infrastructure:

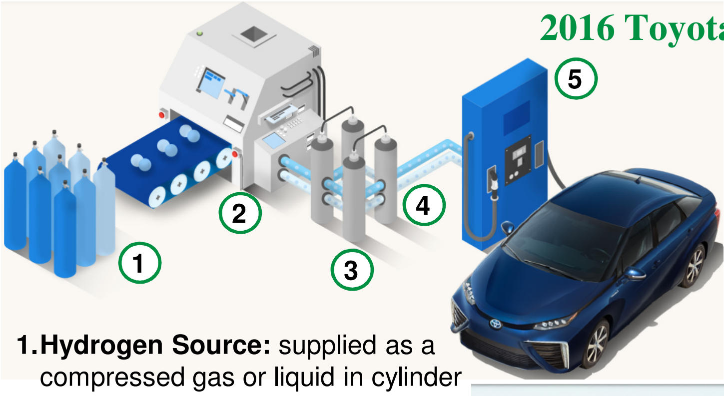
A big unknown, very long and costly



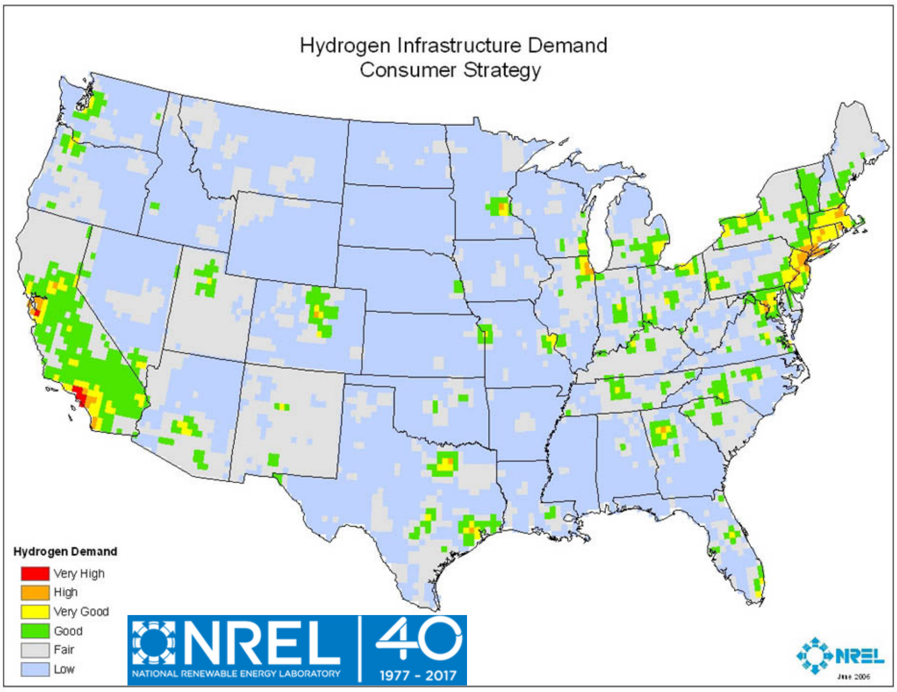
(Source: Automotive Industries, September 2002)

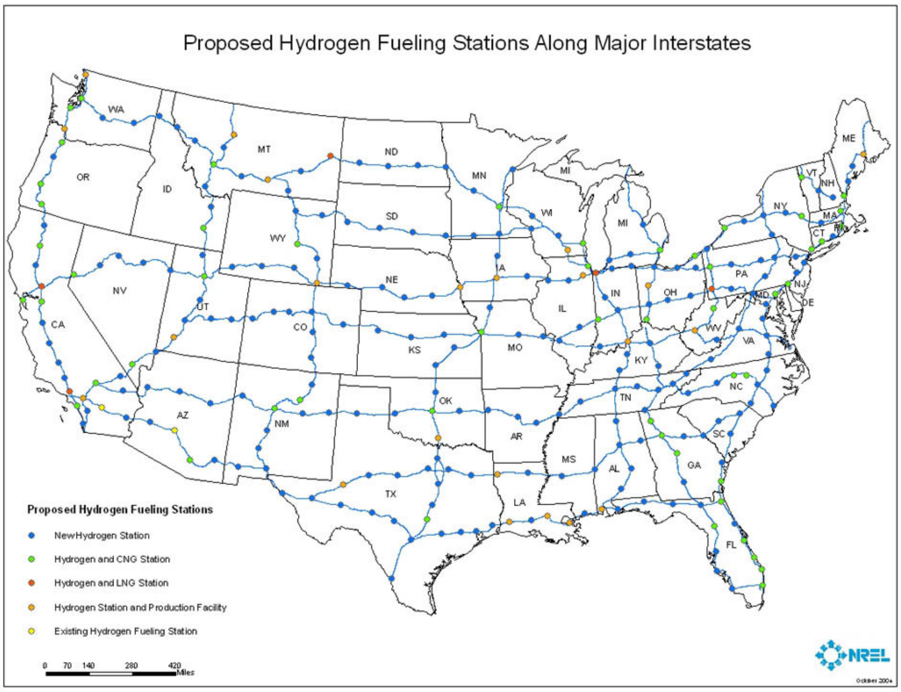
22

2016 Toyota Mirai FCV



1. **Hydrogen Source:** supplied as a compressed gas or liquid in cylinder racks
2. **Compression:** H_2 is compressed
3. **Buffers:** the pressurized H2 is then stored in tubes
4. **Exchanger:** H_2 is cooled in a heat exchanger, enabling for quick fueling
5. **The Dispenser:** the cooled H_2 is transferred to FCV

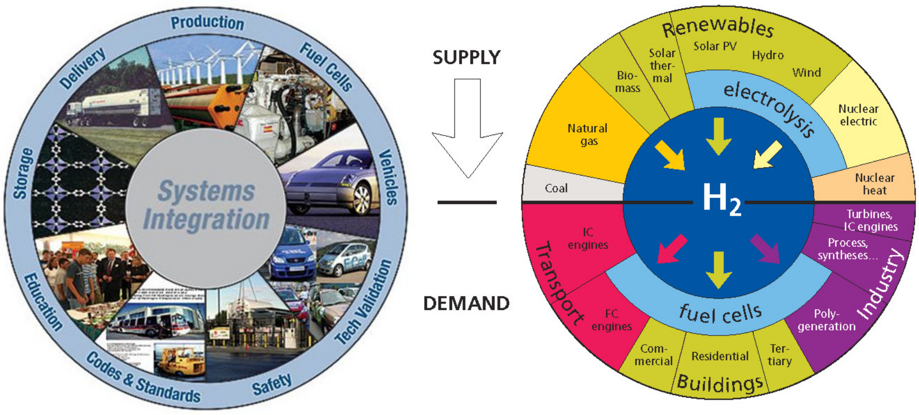




Toyota's Plan in LA Area

Current hydrogen filling stations in blue; planned (2015-2020) stations in orange

The Hydrogen Economy



The Hydrogen Economy

Definition

The Hydrogen Economy is a hypothetical large-scale system in which elemental hydrogen (H_2) is the primary form of energy storage

- Fuel cells would be the primary method of conversion of hydrogen to electrical energy - Efficient and clean; scalable.
- In particular, hydrogen (usually) plays a central role in transportation.

Potential Advantages

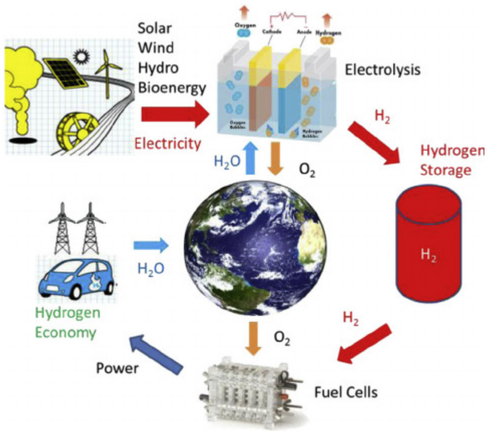
- Clean, renewable
- Potentially more reliable (using distributed generation)

BUT many roadblocks *including potential showstoppers*

- Poses great technological challenges for efficient hydrogen production, storage, and transport.

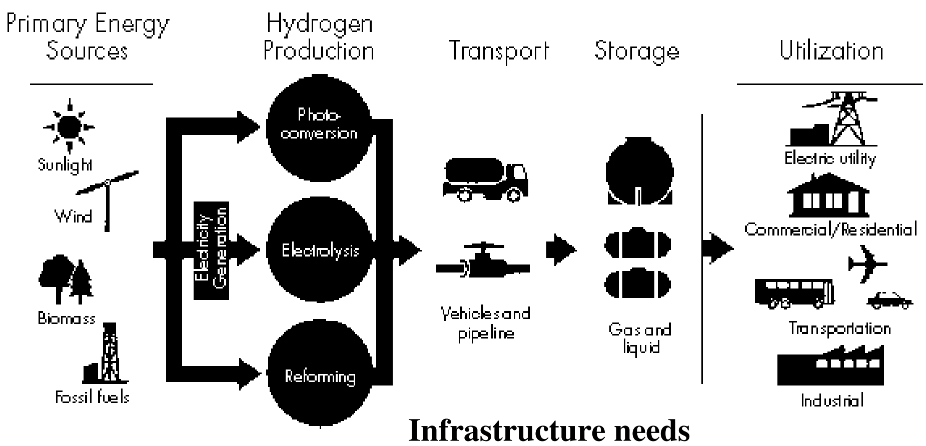
28

Components of the Hydrogen Economy



29

Components of the Hydrogen Economy



Infrastructure needs
- **Production**
- **Storage**
- **Delivery**
- **End use**

30

Hydrogen Production

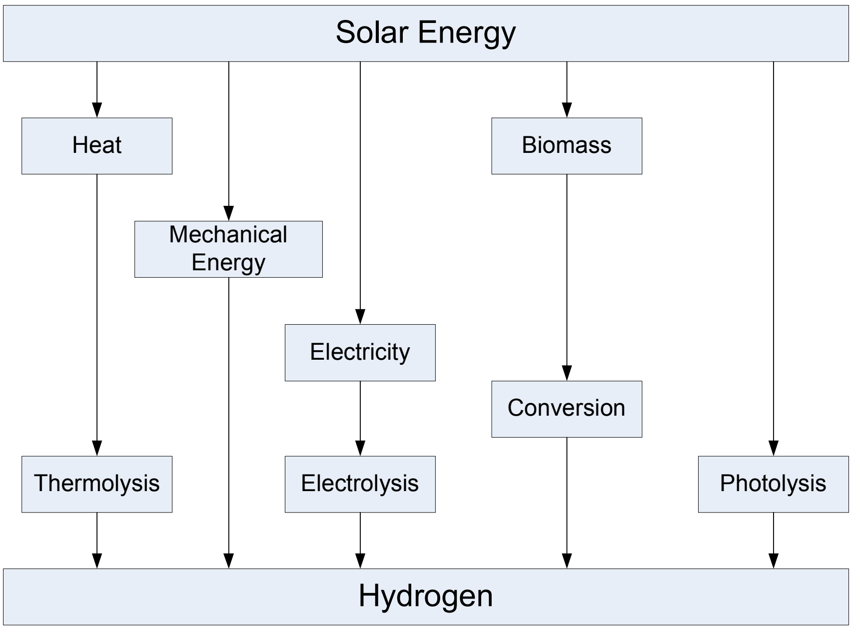
Fossil Fuels
- Steam Reforming of Natural Gas
  - Combination of methane and steam produces hydrogen gas
    - Carbon monoxide is also produced
    - The "water gas shift" reaction can produce further hydrogen from the carbon monoxide. *Carbon dioxide is produced too*.
  - Most economical; main current method
    - Carbon sequestration one method to reduce CO_2 emission
- Partial Oxidation (POX) of Hydrocarbons
  - HC partially oxidized to produce hydrogen and carbon monoxide
- Coal Gasification
  - Gasified at high temps, then processed
  - Can also be used to get hydrogen from biomass

Electrolysis
- Efficiencies 70-85%
- Produces highest purity of hydrogen
- Currently, the electricity consumed is usually worth more than the hydrogen produced

Experimental methods
- Biological hydrogen production
- Direct photolysis
- Thermolysis

31

Renewable Solar Paths to Hydrogen



32

Hydrogen Storage

Large-Scale Stationary Storage
– Underground in depleted oil/gas fields, aquifers, caverns

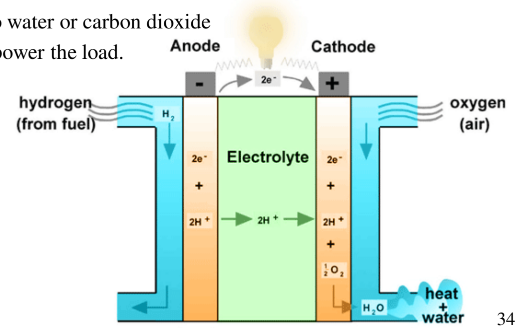
Intermediate- and Small-Scale Stationary/Mobile Storage
– The focus of most current research
– As a liquid
  • Advantage: higher energy density, cheaper transport
  • Disadvantage: economic/energy cost of liquefaction is significant
– As a compressed gas
  • Probably best short-term method, particularly with advanced materials to decrease weight
  • Advantages
    o Rapid charging/discharging
    o Lower costs than liquid storage
  • Disadvantages:
    o Low energy density, Probably still acceptable for ground vehicles
    o Safety (except for public perception)
– As a solid form, metal hydrides
  • Hydrogen is absorbed (into metal mesh) under pressure, released when heated.
  • Less filling pressure needed
  • Low energy density, long recharge time, expensive

Experimental Methods
– Improved hydrides; carbon nanotubes; many other materials (eg conversion to ammonia)

33

Fuel Cell Basics

- Three adjacent segments: the anode, the electrolyte, and the cathode.
- Chemical reactions occur at the interfaces:
  - At the anode a catalyst oxidizes the fuel, hydrogen (or methane), turning the fuel into a positively charged ion and a negatively charged electron
  - The electrolyte is a substance allowing ions to pass but electrons
  - The ions travel through the electrolyte to the cathode and are reunited with the electrons and the two react with a third chemical, usually oxygen, to create water or carbon dioxide
- The net result of the two chemical reactions:
  - Fuel is consumed and turned into water or carbon dioxide
  - An electric current is created to power the load.



34

Fuel Cell Design Features

- The electrolyte substance.
  - The electrolyte substance usually defines the type of fuel cell.
- The fuel that is used.
  - The most common fuel is hydrogen (Methane will produce CO_2).
- The anode catalyst breaks down the fuel into electrons and ions.
  - The anode catalyst is usually made up of very fine platinum powder.
- The cathode catalyst turns the ions into the waste chemicals like water or carbon dioxide.
  - The cathode catalyst is often made up of nickel but it can also be a nanomaterial-based catalyst.
- A typical fuel cell produces a voltage from 0.6 V to 0.7 V at full rated load.
- To deliver the desired amount of energy, the fuel cells can be combined in series and in parallel to form a fuel cell stack

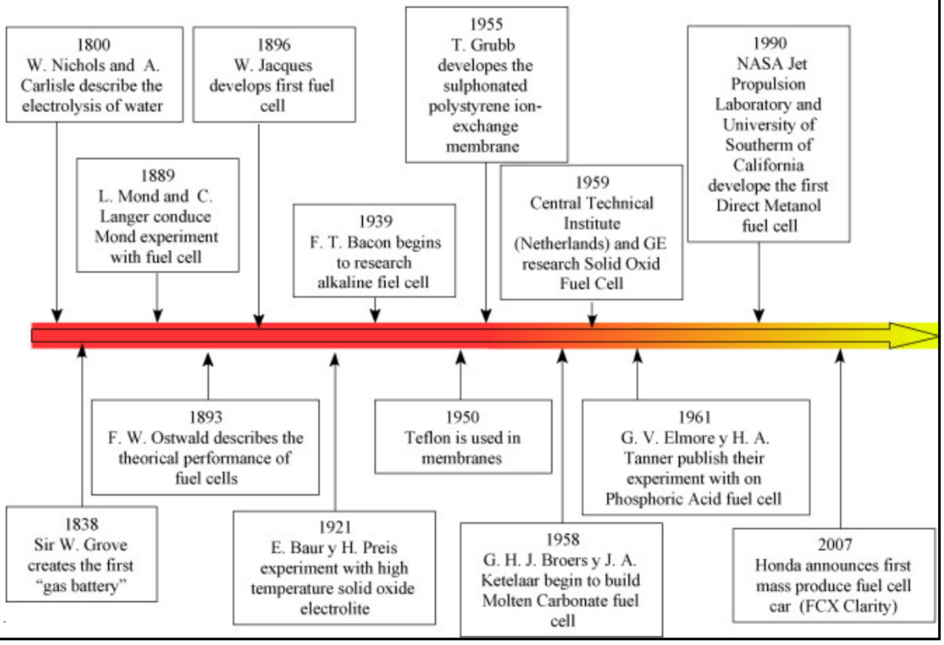
35

Major Types of Hydrogen Fuel Cells

- Proton Exchange Membrane (PEM) or Polymer Electrolyte Fuel Cell (PEFC)
  - ⇒ The technology of choice for FC vehicles, or certainly the most common
- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)
  - ⇒ An alternate technology considered for FC vehicles

36

Historical review of fuel cells



Types of Hydrogen Fuel Cells

Proton Exchange Membrane (PEM) or Polymer Electrolyte Fuel Cell (PEFC)

- Only liquid is water
- Electrodes are made a proton exchange membrane (polymer, such as fluorinated sulfuric acid polymer or equiv.)
- Water management in membrane is critical
- Low operating temperature (<120°C, typically 80-85 °C)
- Use hydrogen rich gas as fuel, with no or very low CO (poisoning)
- High catalyst loading (Pt usually) required at both electrodes

⇒ The technology of choice for FC vehicles

38

PEMFC / PEFC

- PEMFCs are built out of membrane electrode assemblies (MEA) including electrodes, electrolyte, catalyst, and gas diffusion layers
- Hydrogen is delivered to the anode side of MEA and is catalytically split into protons (H^+)and electrons (oxidation half-cell reaction):

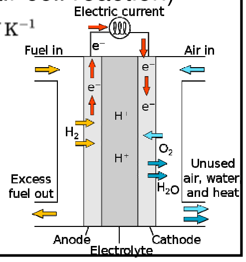
$$\mathrm{H_2 \rightarrow 2H^+ + 2e^-} \qquad E^\circ = 0\,\mathrm{V} \quad \frac{\mathrm{d}E^\circ}{\mathrm{d}T} = 0\,\mathrm{mV\,K^{-1}}$$

- The protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, creating the current output
- Oxygen is delivered to the cathode side of MEA and reacts with the protons and the electrons to form water (reduction half-cell reaction)

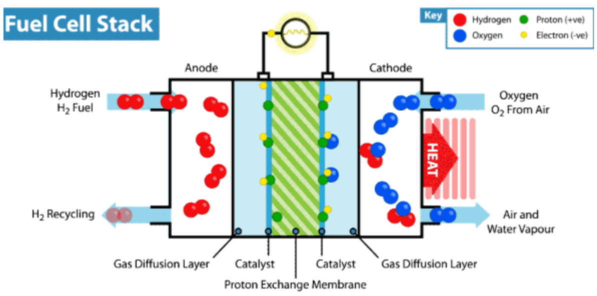
$$\frac{1}{2}\mathrm{O_2 + 2H^+ + 2e^- \rightarrow H_2O} \qquad E^\circ = 1.2291\,\mathrm{V} \quad \frac{\mathrm{d}E^\circ}{\mathrm{d}T} = -0.8456\,\mathrm{mV\,K^{-1}}$$

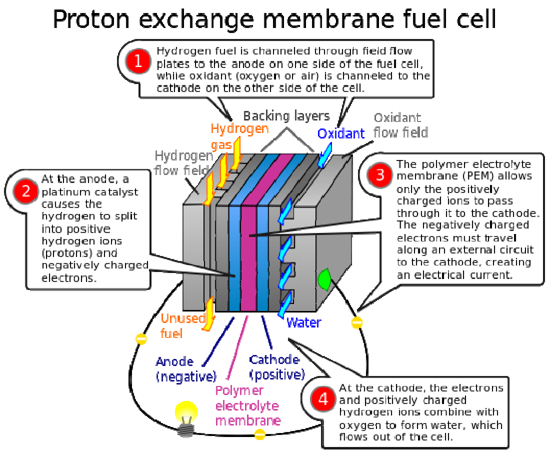
- Overall reaction:

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2 \rightarrow H_2O} \qquad E^\circ = 1.2291\,\mathrm{V} \quad \frac{\mathrm{d}E^\circ}{\mathrm{d}T} = -0.8456\,\mathrm{mV\,K^{-1}}$$



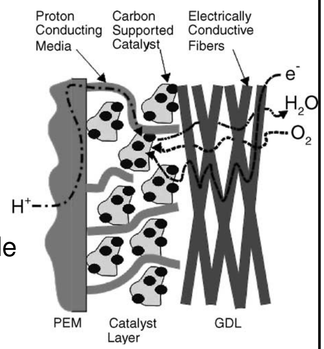
PEM Fuel Cell

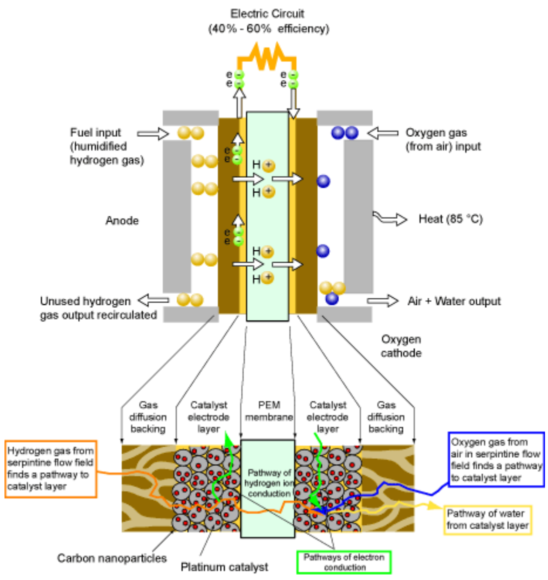




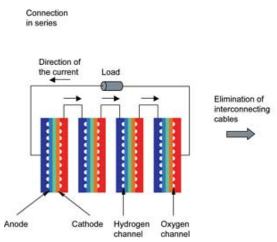
PEM-MEA

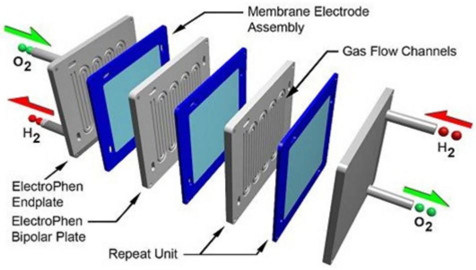
- MEA is an assembled stack of proton exchange membranes (PEM), catalyst and flat plate electrode
- PEM is sandwiched between the anode and cathode which have the catalyst embedded in them. The electrodes are electrically insulated from each other by the PEM
- PEM is a fluoropolymer (PFSA) proton permeable but electrical insulator barrier.
- The most commonly used Nafion PEMs are Nafion XL, 112, 115, 117, and 1110.
- The electrodes materials commonly are carbon cloth or carbon fiber papers heat pressed onto the PEM.
- Platinum is one of the most commonly used catalysts, however other platinum group metals are also used.

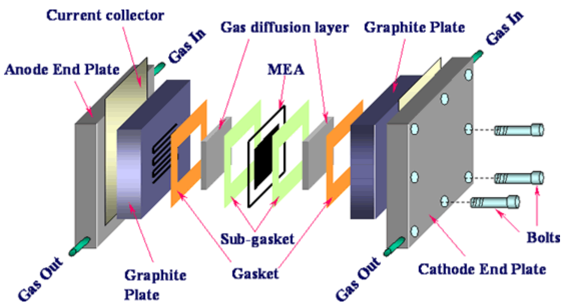




PEM Structure







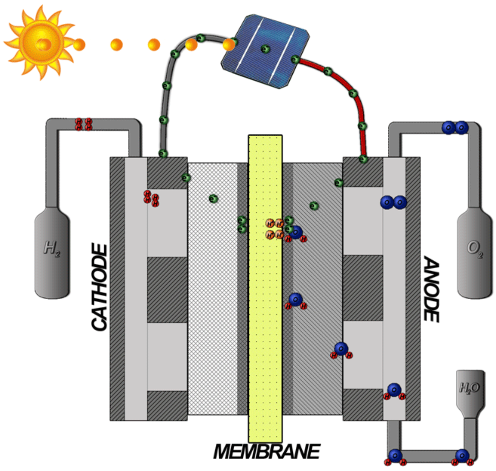
Assemble a PEM FC

http://www.homepages.ucl.ac.uk/~ucecoya/pemfc.html

PEM FC Design Issues

- Cost
  - In 2013, the Department of Energy estimated that 80-kW automotive fuel cell system costs of US$67(55) per kilowatt could be achieved, assuming volume production of 100,000 (500,00) automotive units per year.
- Water and air management
  - The membrane must be hydrated, requiring water to be evaporated at precisely the same rate that it is produced
- Temperature management
  - The same temperature must be maintained throughout the cell in order to prevent destruction of the cell through thermal loading
- Durability and lifetime
  - Automotive fuel cells require a 5,000-hour lifespan (the equivalent of 240,000 km (150,000 mi) under extreme temperatures. Current service life is 2,500 hours
- Limited carbon monoxide tolerance of some (non-PEDOT) cathodes

PEM Reverse Reaction w/ Solar Cells



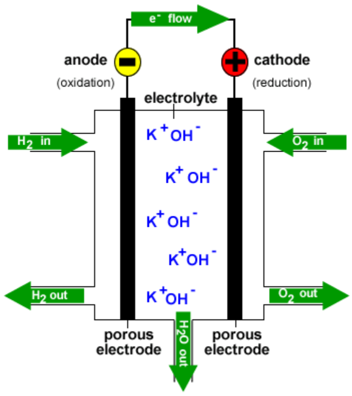
Alkaline Fuel Cell (AFC)

- Electrolyte is concentrated KOH (35 to 85%)
- Electrolyte in matrix (asbestos usually)
- Many catalysts used (Ag, Ni, etc.)
- Temperature range (120°C to 250°C)
- Very sensitive to CO poisoning as well as CO_2
- Aqueous alkaline solutions do not reject CO_2 so the fuel cell can become "poisoned" by the conversion of KOH to potassium carbonate (K_2CO_3) blocking the electrode pores
- They are among the most efficient fuel cells, having the potential to reach 70%
- Technology is being phased-out, except for space applications

48

Alkaline Fuel Cell (AFC)

- Fuel cell chemistry:
  - Anode: hydrogen is oxidized
    $$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$
  - Cathod:
    $$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$
  - The net reaction consumes one oxygen molecule and two hydrogen molecules in the production of two water molecules.
- CO_2 poisoning chemistry:
  $$CO_2 + 2KOH \longrightarrow K_2CO_3 + H_2O$$



Alkaline Fuel Cell (AFC)

- Design
  - Static (immobilized) electrolyte:
    - Was used in the Apollo space craft and the Space Shuttle.
    - Typically use an asbestos separator saturated in potassium hydroxide.
    - Water production is controlled by evaporation from the anode
    - Typically use platinum catalysts to achieve maximum efficiencies.
  - Flowing electrolyte
    - Use a more open matrix that allows the electrolyte to flow either between the electrodes (parallel to the electrodes) or through the electrodes transversely
    - Parallel flow: water produced is retained in the electrolyte, and old electrolyte may be exchanged
    - Transverse flow (EloFlux): has the advantage of low-cost construction and replaceable electrolyte but so far has only been demonstrated using oxygen.
  - Other: metal hydride fuel cell and the direct borohydride fuel cell.
- Applications
  - Spacecrafts
  - The world's first Fuel Cell Ship HYDRA, an AFC system with 5 kW net output

Alkaline anion exchange membrane fuel cells (AAEMFC)

- Also known as hydroxide exchange membrane fuel cells (HEMFCs), anion-exchange membrane fuel cells (AEMFCs), or alkaline membrane fuel cells (AMFCs)
- AAEMFCs are functionally similar to AFCs, but employ a solid polymer electrolyte while AFCs use aqueous (KOH) as electrolyte
- AAEMFCs solve the problems of electrolyte leakage and carbonate precipitation (by K_2CO_3), though still taking advantage of benefits of operating a fuel cell in an alkaline environment.
- AAEMFC can use hydrogen or methanol as fuel
- Under alkaline conditions, oxygen reduction reaction kinetics at the cathode of AAEMFC are much more facile than in PEMFCs, allowing use of non-noble metal catalysts such as silver or iron phthalocyanines for the cathode and nickel for the anode
- The biggest challenge in developing AAEMFCs is the anion exchange membrane (AEM) for the movement of free OH^- ions.

Phosphoric Acid Fuel Cell (PAFC)

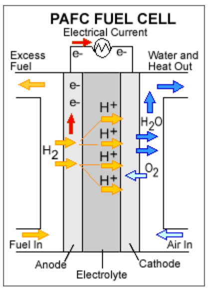
- Electrolyte is pure phosphoric acid (H_3PO_4) a non-conductive electrolyte to pass positive hydrogen ions from the anode to the cathode
- Electrolyte in matrix of silicon carbide
- Pt used as catalyst for both electrodes to increase reaction rates
- Temperature range is higher (100°C to 220°C), causing heat and energy loss. Using this heat in cogeneration can enhance the efficiency of phosphoric acid fuel cells from 40–50% to about 80%

Phosphoric Acid Fuel Cell (PAFC)

- Electrode reactions
  - Anode reaction: $2H_2(g) \rightarrow 4H^+ + 4e^-$
  - Cathode reaction: $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$
  - Overall cell reaction: $2\ H_2 + O_2 \rightarrow 2H_2O$
- PAFCs are CO_2-tolerant and even can tolerate a CO concentration of about 1.5%
- At lower temperatures phosphoric acid is a poor ionic conductor, and CO poisoning of the platinum electro-catalyst in the anode becomes severe
- Disadvantages:
  - low power density
  - corrossive electrolyte

Phosphoric Acid Fuel Cell (PAFC)

- Applications
  - Most commercially developed FC
  - Combined both heat and electric output
  - Fuel flexibility – allow impure hydrogen
  - Reliable and commercially available with high price
  - Used for stationary power generators with output in the 100 kW to 400 kW range
  - Used in large vehicles (bus)
  - Submarines
  - Doosan Fuel Cell America Inc. (PureCell System), Fuji Electric



PureCell System 400 CEP

Molten Carbonate Fuel Cell (MCFC)

- Electrolytes are alkali (K, Na) carbonate salts
- Temperature Range (600°C to 700°C) for molten salts
- Electrolyte in ceramic matrix of $LiAlO_2$
- The salt liquefies at high temperatures, allowing for the movement of charge within the cell
- Usually Ni anode and Ni oxide cathode are used, while Ni also plays catalyst so no additional catalyst required
- Molten carbonate fuel cells can reach efficiencies approaching 60%
- When the waste heat is captured and used, overall fuel efficiencies can be as high as 85%
- Molten carbonate fuel cells are not prone to poisoning by carbon monoxide or carbon dioxide. Carbon oxides is even used as fuel

55

Molten Carbonate Fuel Cell (MCFC)

- The operating pressure is between 1-8 atm while the temperatures are between 600-700 °C
- MCFCs don't require an external reformer to convert more energy-dense fuels to hydrogen. Due to the high temperatures at which MCFCs operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming
- Reactions:
  - Internal Reforming

$$CH_4 + H_2O = 3H_2 + CO$$

  - Anode

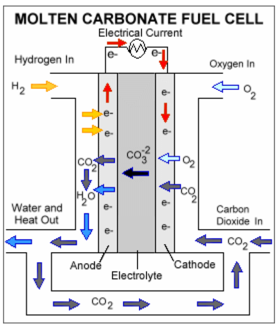
$$H_2 + CO_3^{-2} = H_2O + CO_2 + 2e^-$$

  - Cathode

$$\frac{1}{2}O_2 + CO_2 + 2e^- = CO_3^{-2}$$

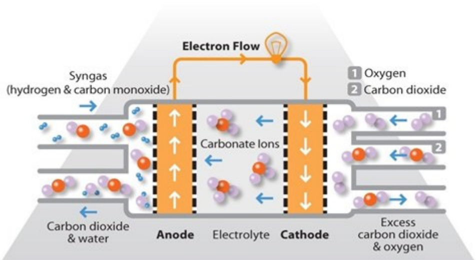
  - Cell

$$H_2 + \frac{1}{2}O_2 + CO_2 = H_2O + CO_2$$

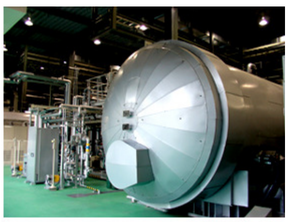


Molten Carbonate Fuel Cell (MCFC) Materials

- The anode material typically consists of a porous (3-6 μm, 45-70% material porosity) Ni based alloy.
- Ni is alloyed with either Chromium or Aluminum in the 2-10% range
- The cathode material is composed of a porous lithiated nickel oxide (lithium is intercalated within the NiO crystal structure).
- The pore size within the cathode is in the range of 7-15 μm with 60-70% of the material being porous.
- NiO can dissolute when contacting CO_2 and it leads to precipitation of Ni metal in the electrolyte and since it is electrically conductive, the fuel cell can get short circuited
- Magnesium oxide serves to reduce the solubility of Ni2+ in the cathode and decreases precipitation in the electrolyte
- Common MCFC electrolytes contain 62% Li_2CO_3 and 38% K_2CO_3
- A greater fraction of Li carbonate is used due to its higher ionic conductivity but is limited to 62% due to its lower gas solubility, ionic diffusivity of oxygen, and having the lowest corrosion rate



MCFC


Molten Carbonate Fuel Cell (MCFC)

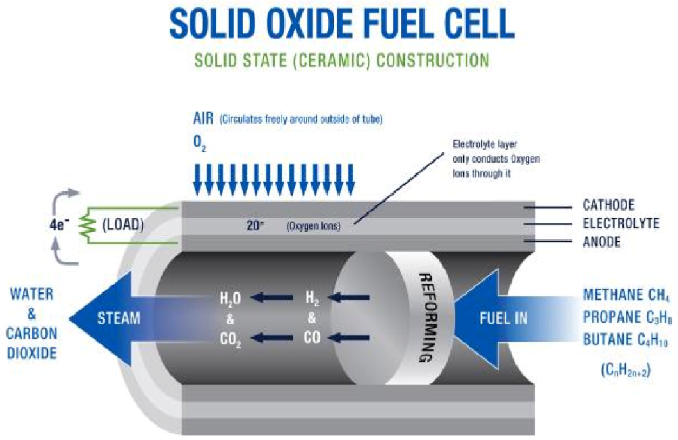
Component	Ca. 1965	Ca. 1975	Current Status
Anode	• Pt, Pd, or Ni	• Ni-10 Cr	• Ni-Cr/Ni-Al/Ni-Al-Cr • 3-6 μm pore size • 45 to 70 percent initial porosity • 0.20 to .5 mm thickness • 0.1 to1 m^2/g
Cathode	• Ag_2O or lithiated NiO	• lithiated NiO	• lithiated NiO-MgO • 7 to15 μm pore size • 70 to 80 percent initial porosity • 60 to 65 percent after lithiation and oxidation • 0.5 to 1 mm thickness • 0.5 m^2/g
Electrolyte Support	• MgO	• mixture of α-, β-, and γ-$LiAlO_2$ • 10 to 20 m^2/g • 1.8 mm thickness	• γ-$LiAlO_2$, α-$LiAlO_2$ • 0.1 to12 m^2/g • 0.5 to1 mm thickness
Electrolyte[a] (wt percent)	• 52 Li-48 Na • 43.5 Li-31.5 Na-25 K • "paste"	• 62 Li-38 K • hot press "tile" • 1.8 mm thickness	• 62 Li-38 K • 60 Li-40 Na 51 Li-48 Na • tape cast • 0.5 to1 mm thickness

Solid Oxide Fuel Cell (SOFC)

- Electrolyte is solid, non-porous, ceramic, metal oxide; usually yttria-stabilized zirconia (YSZ): Y_2O_3 (yttria)-stabilized ZrO_2(zirconia)
- Temperature range (650°C to 1000°C)
- SOFCs are made entirely of solid materials, they are not limited to the flat plane configuration but often designed as rolled tubes.
- Oxygen ions travel from the cathode to the anode instead of positively charged hydrogen ions travelling from the anode to the cathode like other types of fuel cells
- SOFC systems can run on fuels other than pure hydrogen gas but must contain hydrogen atoms with internal reform.
- Anode can be Co-ZrO_2 and cathode can be Sr-doped $LaMnO_3$
- The theoretical overall efficiency can be as high as 80%–85% if waste heat from SOFC systems can be captured and reused.

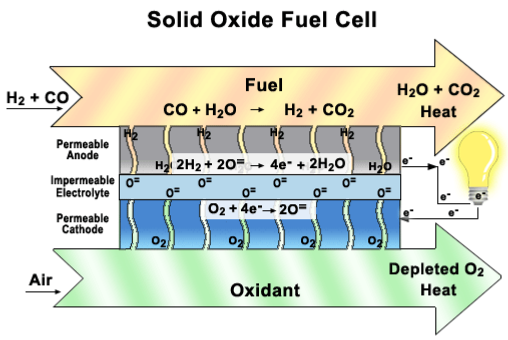
⇒ An alternate technology considered for FC vehicles

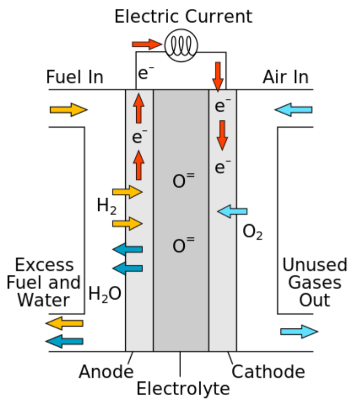
59



Solid Oxide Fuel Cell (SOFC)

- The chemical reactions:
  - Anode: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$
  - Cathode: $O_2 + 4e^- \rightarrow 2O^{2-}$
  - Cell: $2H_2 + O_2 \rightarrow 2H_2O$





Solid Oxide Fuel Cell (SOFC) Electrodes

- The ceramic anode layer must be very porous to allow the fuel to flow through
- The common anode material is a cermet made up of Ni or Co mixed with the ceramic material used for the electrolyte, typically YSZ
- YSZ part helps stop the grain growth of Ni or Co because large grains would reduce the contact area and lower the cell's efficiency
- The anode is commonly the thickest and strongest layer in each individual cell, for its smallest polarization losses, and being often the layer that provides the mechanical support
- The cathode, or air electrode, is a thin porous layer on the electrolyte where oxygen reduction takes place
- Cathode materials are minimum electronically conductive. Currently, lanthanum strontium manganite (LSM, $La_{1-x}Sr_xMnO_3$) is the cathode material of choice for commercial use because of its compatibility with doped zirconia electrolytes

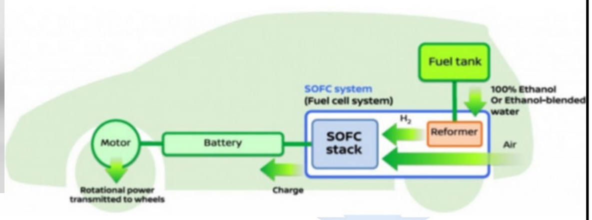
Solid Oxide Fuel Cell (SOFC) Electrolyte

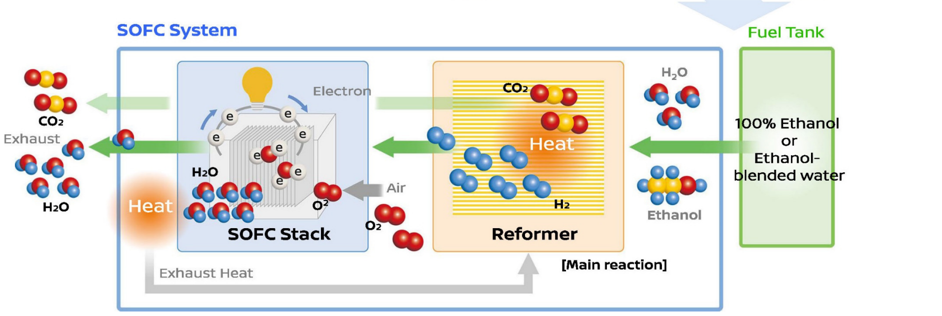
- The electrolyte is a dense layer of ceramic metal oxide that conducts oxygen ions
- Low electronic conductivity to prevent losses from leakage currents and short circuits
- Popular electrolyte materials
  - yttria (Y_2O_3)-stabilized zirconia (ZrO_2) (YSZ) (often the 8% form 8YSZ)
  - scandia stabilized zirconia (ScSZ) (usually 9 mol%Sc2O3 – 9ScSZ)
  - gadolinium doped ceria (GDC) (Gd:CeO_2), lower operating temperature
  - Cubic Bismuth Oxide (Bi_2O_3)

Solid Oxide Fuel Cell (SOFC)

- SOFCs are capable of internally reforming light hydrocarbons such as methane (natural gas), propane and butane
- High operating temperatures result in the potential for carbon dust to build up on the anode, slowing down the internal reforming process
- SOFC systems have slow start-up time, making SOFCs less useful for mobile applications
- High operating temperature provides an advantage by removing the need for a precious metal catalyst like platinum, thus reducing cost.
- Reusing waste heat from SOFC systems increase the theoretical overall efficiency to as high as 80%–85%
- Nissan announced development of the world’s first SOFC-powered vehicle system that runs on bio-ethanol electric power

Nissan SOFC-powered vehicle





Types of Hydrogen Fuel Cells

Summary of Basic Chemical Reactions of Various Types of Fuel Cells

Fuel Cell	Anode Reaction	Cathode Reaction
Proton Exchange Membrane	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Alkaline	$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
Phosphoric Acid	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten Carbonate	$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^= \rightarrow 2CO_2 + 2e^-$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^=$
Solid Oxide	$H_2 + O^= \rightarrow H_2O + 2e^-$ $CO + O^= \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^= \rightarrow 2H_2O + CO_2 + 8e^-$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$

CO - carbon monoxide
CO_2 - carbon dioxide
$CO_3^=$ - carbonate ion
e^- - electron
H^+ - hydrogen ion
H_2 - hydrogen
H_2O - water
O_2 - oxygen
OH^- - hydroxyl ion

66

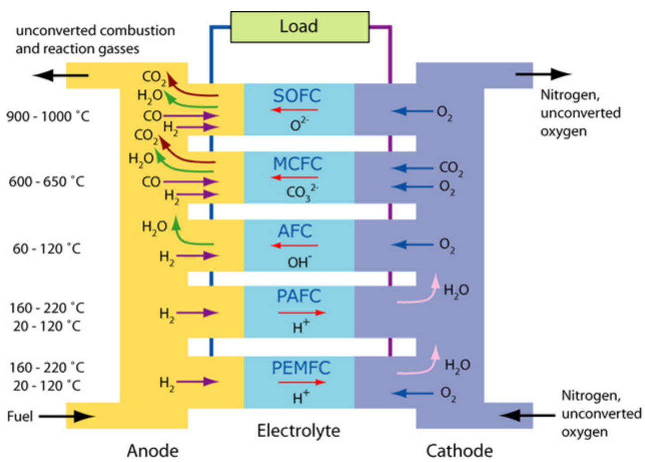
Types of Hydrogen Fuel Cells

Summary of Characteristics of Various Types of Fuel Cells

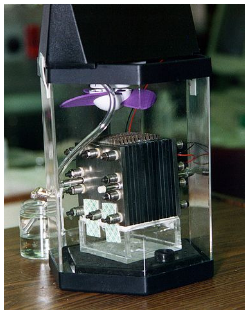
	PEFC	PAFC	MCFC	SOFC
Electrolyte	Ion Exchange Membrane	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic
Operating Temperature	80°C	205°C	650°C	800-1000°C now, 600-1000°C in 10 to 15 years
Charge Carrier	H^+	H^+	$CO3^=$	$O^=$
External Reformer for CH_4 (below)	Yes	Yes	No	No
Prime Cell Components	Carbon-based	Graphite-based	Stainless Steel	Ceramic
Catalyst	Platinum	Platinum	Nickel	Perovskites
Product Water Management	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas

67

Types of Hydrogen Fuel Cells

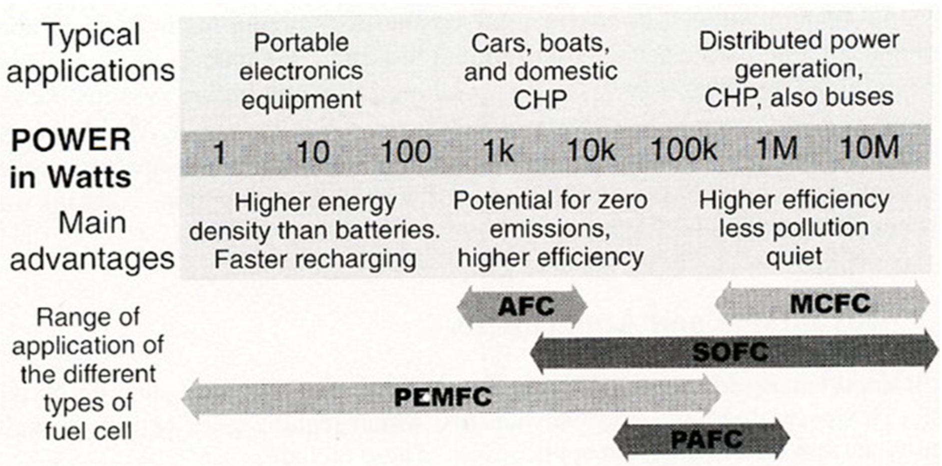


Other Types of Fuel Cells



- **Direct-methanol fuel cells (DMFCs)**:
  - A subcategory of proton-exchange fuel cells in which methanol is used as the fuel.
  - Their main advantage is the ease of transport of methanol, an energy-dense yet reasonably stable liquid at all environmental conditions
- **Solid acid fuel cell (SAFC)**:
  - The use of a solid acid material as the electrolyte.
  - They operate at mid-range temperatures, from 200 to 300 ℃.
  - Solid acids are chemical intermediates between salts and acids, such as CsHSO4, or chemistry is based on oxyanion groups (SO_4^{2-}, PO_4^{3-}, SeO_4^{2-}, AsO_4^{3-}).
- Etc.…

Types of Fuel Cells and Applications

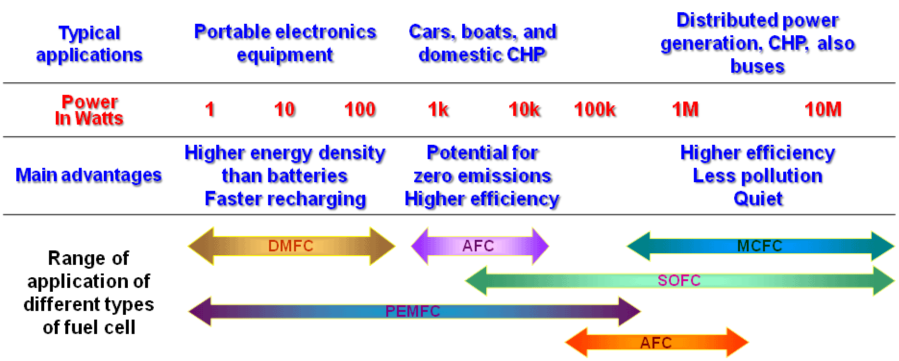


Fuel Cell Types by Use (after Larminie and Dicks, 2000)

70

Data for different types of fuel cells

Fuel cell type	Operating temperature [C°]	Electric Efficiency [%]	Applications and notes
Alkaline (AFC)	60 - 100	50	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	60 - 120	40	Vehicles and mobile applications, and for lower power CHP systems.
Direct Methanol (DMFC)	20-90	20	Suitable for portable electronic systems of low power, running for long times.
Phosphoric acid (PAFC)	180 - 200	40	Large numbers of 200-kW CHP systems in use.
Molten carbonate (MCFC)	600 - 700	50 - 55	Suitable for medium- to large-scale CHP systems, up to MW capacity.
Solid oxide (SOFC)	800 - 1000	50 - 55	Suitable for all sizes of CHP systems, 2kW to multi-MW.



Fuels for Fuel Cell Systems

- Hydrogen
- Alcohols (methanol, ethanol, etc)
- Natural gas/gaseous hydrocarbons (methane, ethane, propane, butane, coal gas, syn-gas, etc.)
- Liquid hydrocarbons (gasoline, Diesel, kerosene, naphta, etc)
- Others (ammonia, hydrazine, etc.)

Gas species	PEM Fuel Cell	AFC	PAFC	MCFC	SOFC
H_2	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (>10ppm)	Poison	Poison (>0.5%)	Fuel [a]	Fuel [a]
CH_4	Diluent	Diluent	Diluent	Diluent [b]	Diluent [b]
CO_2 and H_2O	Diluent	Poison [c]	Diluent	Diluent	Diluent
S (as H_2S and COS)	Few studies, to date	Unknown	Poison (>50 ppm)	Poison (>0.5 ppm)	Poison (>1.0 ppm)

a – In reality CO reacts with H_2O producing H_2 and CO_2 via the shift reaction (7.3) and CH_4 with H_2O reforms to H_2 and CO faster than reacting as a fuel at the electrode.

b – A fuel in the internal reforming MCFC and SOFC.

c – The fact that CO_2 is a poison for the alkaline fuel cell more or less rules out its use with reformed fuels

Fuel Sources

- Petroleum
- Natural gas
- Coal
- Bio-mass
- Electricity (fossil fuel, nuclear, hydro, solar…)

(after Larminie and Dicks, 2000)

72

Hydrogen Storage

- Targets were set by the FreedomCAR Partnership in January 2002 between the United States Council for Automotive Research (USCAR) and U.S. DOE (Targets assume a 5-kg H_2 storage system). The ultimate goal for volumetric storage is still above the theoretical density of liquid hydrogen.
- In 2010, only two storage technologies were identified as having the potential to meet DOE targets: MOF-177 exceeds 2010 target for volumetric capacity, while cryo-compressed H2 exceeds more restrictive 2015 targets for both gravimetric and volumetric capacity

Storage Parameter	2005	2010	2015
Gravimetric Capacity (Specific energy)	1.5 kWh/kg 0.045 kg H_2/kg	2.0 kWh/kg 0.060 kg H_2/kg	3.0 kWh/kg 0.090 kg H_2/kg
System Weight:	*111 Kg*	*83 Kg*	*55.6 Kg*
Volumetric Capacity (Energy density)	1.2 kWh/L 0.036 kg H_2/L	1.5 kWh/L 0.045 kg H_2/L	2.7 kWh/L 0.081 kg H_2/L
System Volume:	*139 L*	*111 L*	*62 L*
Storage system cost	$6 /kWh	$4 /kWh	$2 /kWh
System Cost:	*$1000*	*$666*	*$333*
Refueling rate	.5 Kg H_2/min	1.5 Kg H_2/min	2.0 Kg H_2/min
Refueling Time:	*10 min*	*3.3 min*	*2.5 min*

Hydrogen Storage

Chemical storage

- Metal hydrides (MgH_2, $NaAlH_4$, $LiAlH_4$, LiH, $LaNi_5H_6$, $TiFeH_2$)
- Non-metal hydrides
- Carbohydrates (polymeric $C_6H_{10}O_5$)
- Synthesized hydrocarbons
- Liquid organic hydrogen carriers (LOHC)
- Ammonia
- Amine borane complexes
- Imidazolium ionic liquids
- Phosphonium borate
- Carbonite substances
- Metal-organic frameworks
- Encapsulation

Physical storage

- Cryo-compressed
- Carbon nanotubes
- Clathrate hydrates (crystalline water-based solids)
- Glass capillary arrays
- Glass microspheres

Hydrogen Storage for Fuel Cell

Methods

- Compressed in gas cylinders
- Cryogenic liquid
- Reversible metal hydrides
- Alkali metal hydrides

Requirements

- Safe to handle
- Require little energy to supply hydrogen
- Easy to supply hydrogen
- Gravimetric storage efficiency
- Volumetric storage efficiency

Name	Formula	Percent hydrogen	Specific gravity	Vol. (L) to store 1 kg H_2	Notes
Simple hydrides					
Liquid H_2	H_2	100	0.07	14	Cold, -252°C
Lithium hydride	LiH	12.68	0.82	6.5	Caustic
Beryllium hydride	BeH_2	18.28	0.67	8.2	Very toxic
Diborane	B_2H_6	21.86	0.417	11	Toxic
Liquid methane	CH_4	25.13	0.415	9.6	Cold –175°C
Ammonia	NH_4	17.76	0.817	6.7	Toxic, 100 ppm
Water	H_2O	11.19	1.0	8.9	
Sodium hydride	NaH	4.3	0.92	25.9	Caustic, but cheap
Calcium hydride	CaH_2	5.0	1.9	11	
Aluminium hydride	AlH_3	10.8	1.3	7.1	
Silane	SiH_4	12.55	0.68	12	Toxic 0.1 ppm
Potassium hydride	KH	2.51	1.47	27.1	Caustic
Titanium hydride	TiH_2	4.40	3.9	5.8	
Complex hydrides					
Lithium borohydride	$LiBH_4$	18.51	0.666	8.1	Mild toxicity
Aluminium borohydride	$Al(BH_4)_3$	16.91	0.545	11	Mild toxicity
Lithium aluminium hydride	$LiAlH_4$	10.62	0.917	10	
Hydrazine	N_2H_4	12.58	1.011	7.8	Toxic 10 ppm
Hydrogen absorbers					
Palladium hydride	Pd_2H	0.471	10.78	20	
Titanium iron hydride	$TiFeH_2$	1.87	5.47	9.8	

(after Larminie and Dicks, 2000)

75

Hydrogen Storage for Fuel Cell

Compressed Hydrogen

- Stored in metal cylinders at high pressures (340 bars [5000 psi] currently)
- Pressures increasing to 10,000 psi shortly
- Typically aluminum liner with epoxy composite shell
- Low storage efficiency (both volumetric and gravimetric)
- Limited to relatively small quantity to storage density:
  : A stretch to package in automobiles and meet range requirements!
- Unlimited storage time and no restrictions on purity
- Not very "user-friendly" at refueling station due to high pressure
- Safety is a concern due to high pressure (rather than hydrogen explosion risk, except in confined spaces)

	2 L steel, 200 bar	147 L composite, 300 bar
Mass of empty cylinder	3.0 kg	100 kg
Mass of hydrogen stored	0.036 kg	3.1 kg
Storage efficiency (% mass H_2)	1.2 %	3.1 %
Specific energy	0.47 $kWh.kg^{-1}$	1.2 $kWh.kg^{-1}$
Volume of tank (approx.)	2.2 L (0.0022 m^3)	220 L (0.22 m^3)
Mass of H_2 per litre	0.016 $kg.L^{-1}$	0.014 $kg.L^{-1}$

(after Larminie and Dicks, 2000)

76

Hydrogen Storage for Fuel Cell

Liquid Hydrogen – LH_2

- Cryogenically stored at about 22ºK
- Low pressure, typically 2-3 bars
- Vacuum double wall tanks
- "Slow" release of hydrogen gas
- Relatively "user-friendly" to refill
- Good volumetric and gravimetric storage efficiency
- Require ultra low temperature (-253ºC)
- Liquefaction is energy expensive (60% efficiency typically)
- Has received more attention in Europe

Mass of empty container	51.5 kg
Mass of hydrogen stored	8.5 kg
Storage efficiency (% mass H_2)	14.2 %
Specific energy	5.57 $kWh.kg^{-1}$
Volume of tank (approx.)	0.2 m^3
Mass of H_2 per litre	0.0425 $kg.L^{-1}$

(after Larminie and Dicks, 2000)

77

Hydrogen Storage for Fuel Cell

Alkali Metal Hydride

- Calcium or sodium hydride typically
- React with water to produce hydrogen
- Not easily reversible
- Liquid hydroxide by-product (caustic)
- Requires large excess water as hydroxides are hydrophylic
- Atmospheric pressure and temperature storage
- Storage efficiency comparable to other methods
- Safe except caustic liquid
- "Refilling" means disposal of by-product and replenishment
  - *Not desirable for automotive applications*

$$NaH + H_2O \rightarrow NaOH + H_2$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

Mass of container and all materials	45 kg
Mass of hydrogen stored	1.0 kg
Storage efficiency (% mass H2)	2.2 %
Specific energy	0.87 $kWh.kg^{-1}$
Volume of tank (approx.)	50 L
Mass of H_2 per litre	0.020 $kg.L^{-1}$

(after Larminie and Dicks, 2000)

78

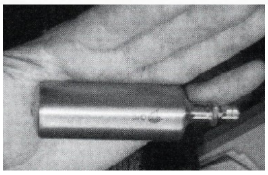
Hydrogen Storage for Fuel Cell

Reversible Metal Hydride - MH_2

- Metal (alloys) of titanium, iron, manganese, nickel, chromium, etc.
- Reversible reaction
- Well suited for low pressure (2 bar), room temperature storage
- Storage is mildly exothermic (rate limiting for refilling)
- Release is mildly endothermic, self limiting with pressure
- Capable of several hundreds of charge/discharge cycles (thermally managed)
- Storage affected by impurities
- Volumetric storage efficiency as good as LH2
- Gravimetric storage efficiency like compressed H2
- Very safe
- Slow refilling

Mass of empty container	0.26 kg
Mass of hydrogen stored	0.0017 kg
Storage efficiency (% mass H_2)	0.65 %
Specific energy	0.26 $kWh.kg^{-1}$
Volume of tank (approx.)	0.06 L
Mass of H_2 per litre	0.028 $kg.L^{-1}$

$$M + H_2 \leftrightarrow MH_2$$



(after Larminie and Dicks, 2000)

79

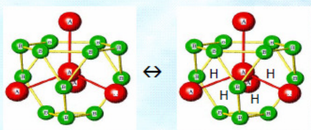
Solid Hydrogen Storage System

Reversible

Safe

Compact

$$M + H_2 \leftrightarrows MH + \Delta H$$



Design Requirements:
- Suitable MH Alloy
- Efficient Heat Exchanger
- Proper Powder Packaging

H_2 Desorption Process

- Gaseous hydrogen withdrawn from the tank to operate the engine or fuel cell
- process absorbs heat
- MH powder cools to a point at which hydrogen desorption will stop
- External heat is required to sustain the desorption process

H_2 Absorption Process

- Hydrogen is chemically bonded to a host metal alloy that is contained in powder form within the storage tank.
- When gaseous hydrogen is introduced to the tank, it is chemically absorbed by the host metal, which is transformed into a metal hydride (MH)
- Heat is released

80

Applications

Features

- DOT approved
- CGA certified components
- >3300 units worldwide

Standard products

Model	diameter (in.)	length (in.)	weight (lbs.)	capacity (liters)
7G250	2.0	6	2	75
10G250	2.5	5	2	100
25G250	2.5	12	5	280
85G250	3.5	17	14.5	900

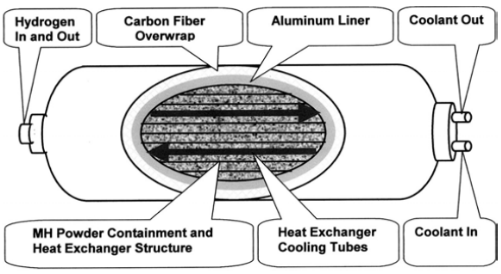
Applications

Portable power

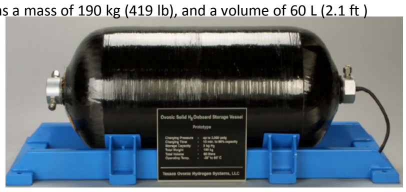
Vehicular

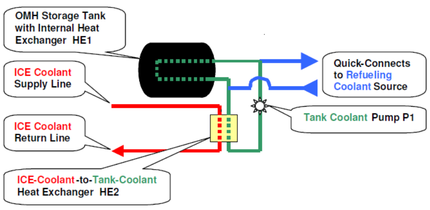
Stationary power

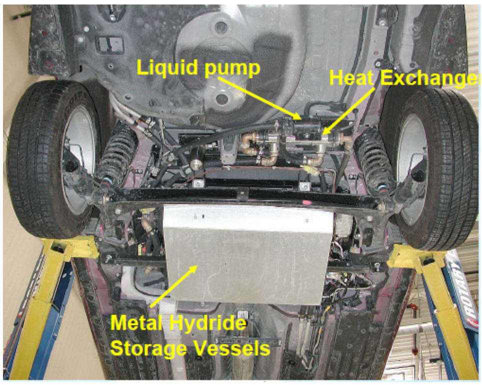
81



Ovonics metal solid hydride storage tank. The nameplate indicates the system shown can store 3 kg (6.6 lb) 3 of hydrogen, has a mass of 190 kg (419 lb), and a volume of 60 L (2.1 ft)



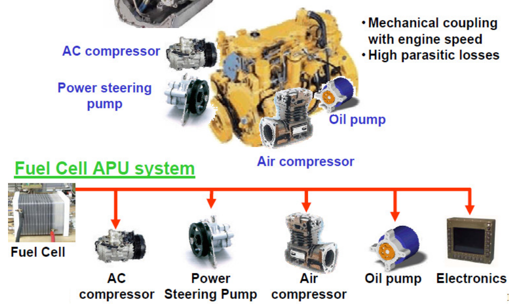




82

Fuel Cell Application: Electricity for Vehicle Auxiliary Power Unit (APU)

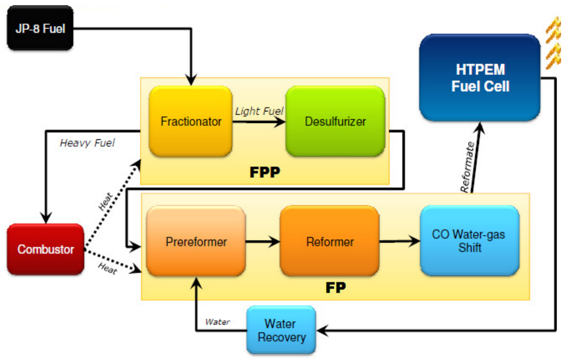
- Engine Idling (alternator power)
  - –Significant noise and heat generation
  - –Low Fuel Efficiency
- Battery
  - –Limited silent watch duration
    - 3 h @ 1kW, 1 h @ 2.4 kW with only one cranking
    - Needs 6.5 hours to recharge
    - Deep cycling reduces battery life
- Auxiliary Power Unit (APU)
  - –IC engine or gas turbine + generator
  - –*Fuel Cell*



83

Fuel Cell Application: Silent Watch Support

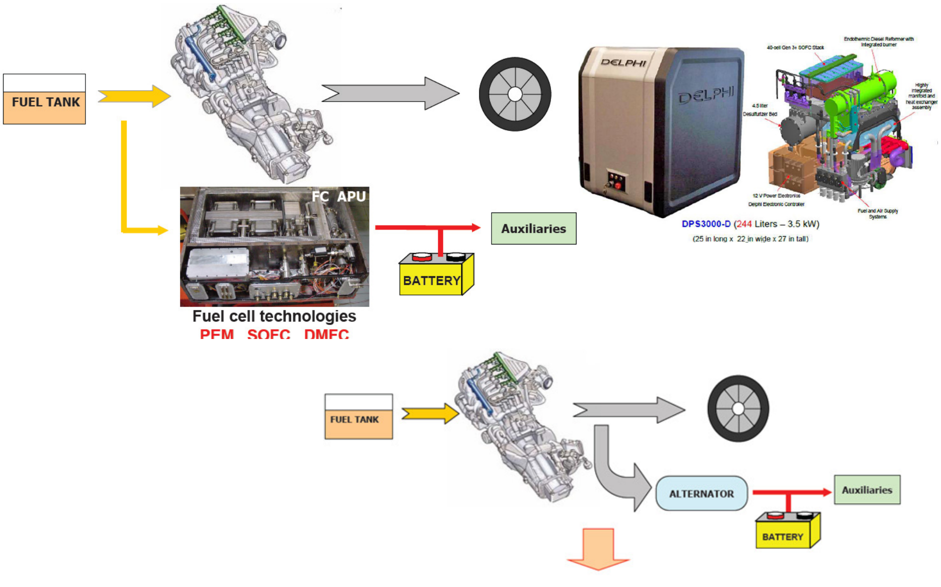
- Engine Idling (alternator power)
  - –Significant noise and heat generation
  - –Low Fuel Efficiency
- Battery
  - –Limited silent watch duration
    - 3 h @ 1kW, 1 h @ 2.4 kW with only one cranking
    - Needs 6.5 hours to recharge
    - Deep cycling reduces battery life
- Auxiliary Power Unit (APU)
  - –IC engine or gas turbine + generator
  - –*Fuel Cell*



Abrams, Bradley and Stryker APU Performance Requirements			
Continuous Power	8 kW (Threshold) / 10 kW (Objective)		
Mission Duration	> 12 hours		
Fuel Consumption	1.75 gal / hour (Threshold) / 1.5 gal / hour (Objective)		
NPS Volume	 ABRAMS 225 Liters	BRADLEY 200 Liters	STRYKER 180 Liters
NPS Weight	453 lbs. – Requires its own cooling system		254 lbs. - Can integrate into engine's cooling system
Procurement Cost	< $40K		

84

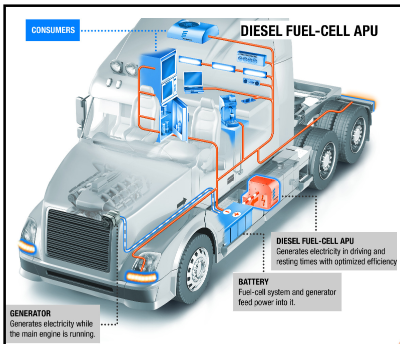
Fuel cell APU: On-board Reforming for H_2



Weak point: low efficiency running (<15%) idling (<5%)

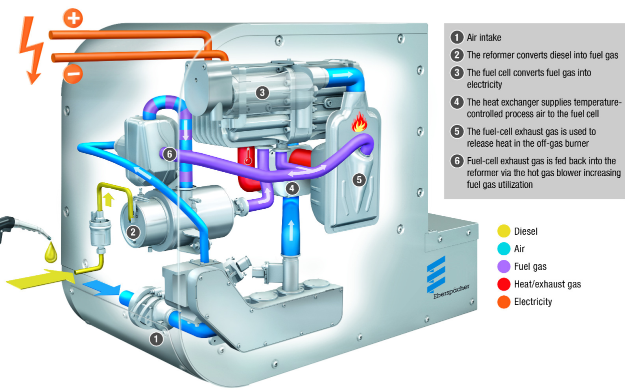
Strong point: simple, cheap and reliable

85



Eberspaecher presents a fuel-cell APU (auxiliary power unit) that converts diesel very efficiently to electricity and thereby supplies all on-board consumer components.

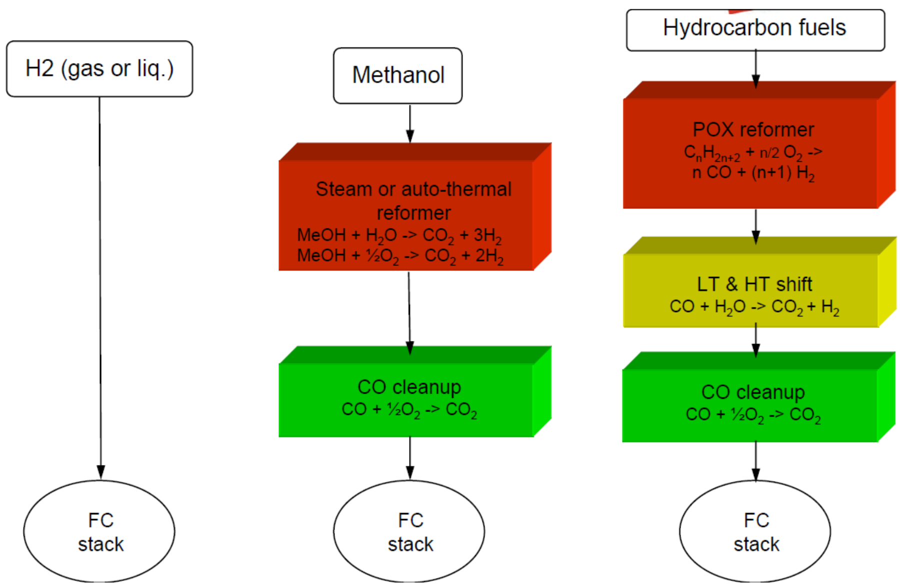
BASIC PRINCIPLE OF DIESEL FUEL-CELL APU



On-board Reforming for H_2

- Steam reforming of gaseous hydrocarbons is a potential way to provide fuel for fuel cells on-board to avoid H_2 distribution problems.
- Issues and challenges of reforming:
  - Fossil fuel reforming reduces the CO_2 emissions and nearly eliminates CO emissions as compared to the conventional combustions due to increased efficiency but does not eliminate carbon dioxide release completely
  - Carbon capture and storage become possible by reforming with additional costs
  - The reforming reacts at high temperatures, making it slow to start up and requiring costly high temperature materials.
  - Sulfur compounds in the fuel will poison certain catalysts, making it difficult to run this type of system from ordinary gasoline.
  - Low temperature polymer fuel cell membranes can be poisoned by CO produced by the reactor, making complex CO-removal system necessary.
  - The thermodynamic efficiency of the process is between 70% and 85% (LHV basis) depending on the purity of the hydrogen product.
  - Fuel Cell APU turns out a more realistic option for reforming applications

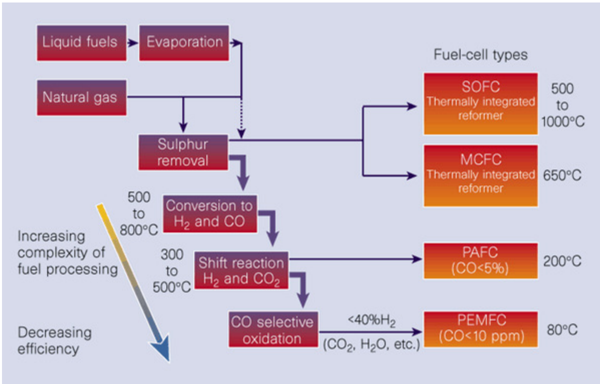
Choice of Fuel: On-board Reforming for H_2



P. Ekdunge, PEM fuel cells for automotive applications: auxiliary power, 2007

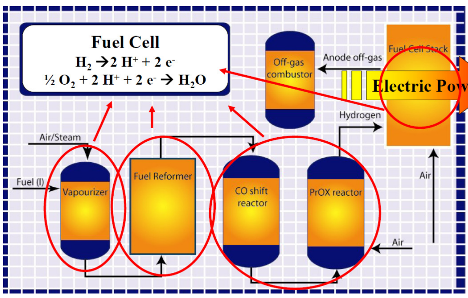
88

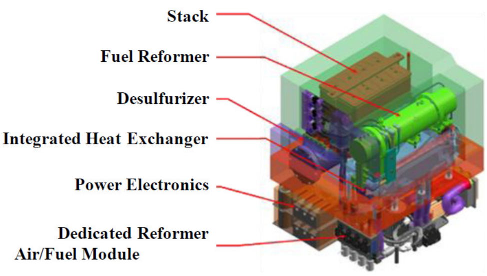
Fuel processing reactions (reforming of methane to hydrogen fuel) and their influence on the complexity and efficiency of different types of fuel cell.



Nature 400, 619-621(12 August 1999)

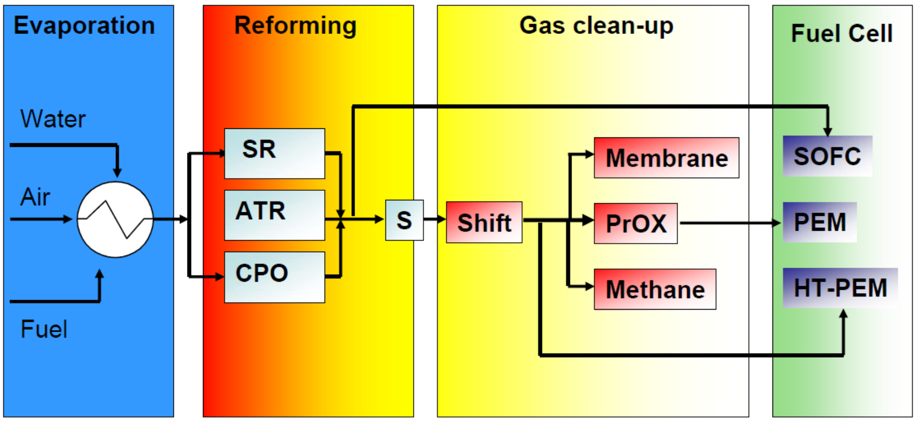
Reforming Process





P. Ekdunge, PEM fuel cells for automotive applications: auxiliary power, 2007

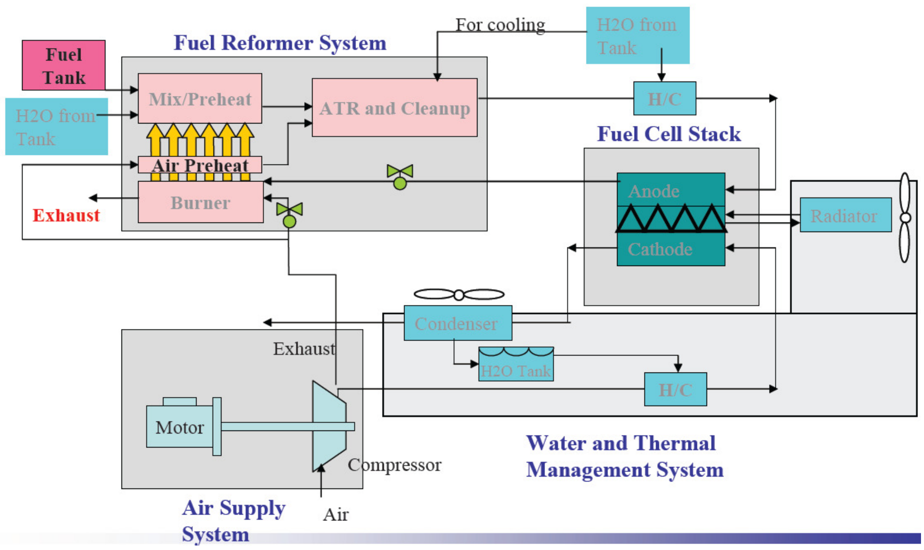
Reforming Systems



P. Ekdunge, PEM fuel cells for automotive applications: auxiliary power, 2007

91

Reforming Process



P. Ekdunge, PEM fuel cells for automotive applications: auxiliary power, 2007

92