

Fuel Cells: Introduction and Current Status

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Why all this excitement about fuel cells?

- Can have zero emissions
- Are highly efficient
- Can be used as long duration portable power sources
- Can use various hydrocarbon fuels (with reformers)
- Are practically noise-free
- Are potential replacements for IC engines (everyone has an opinion on this topic!)



In this talk

- Introduce the basics of fuel cells
- Introduction to various types of fuel cells (PEM in particular)
- Discuss their potential applications
- Current status
- Issues/problems with fuel cells
- Modeling of fuel cells



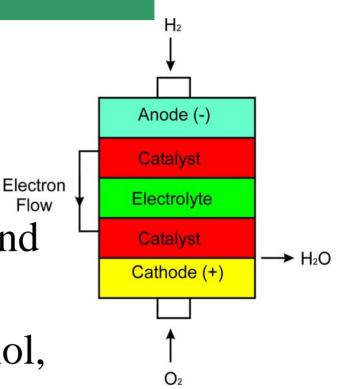
What are fuel cells?

- Use an electrochemical process to convert hydrogen and oxygen into electricity
- No combustion required
- Produces a DC current
- Two electrodes (cathode and anode) are separated by an electrolyte
- Reactants are stored externally and operates continuously



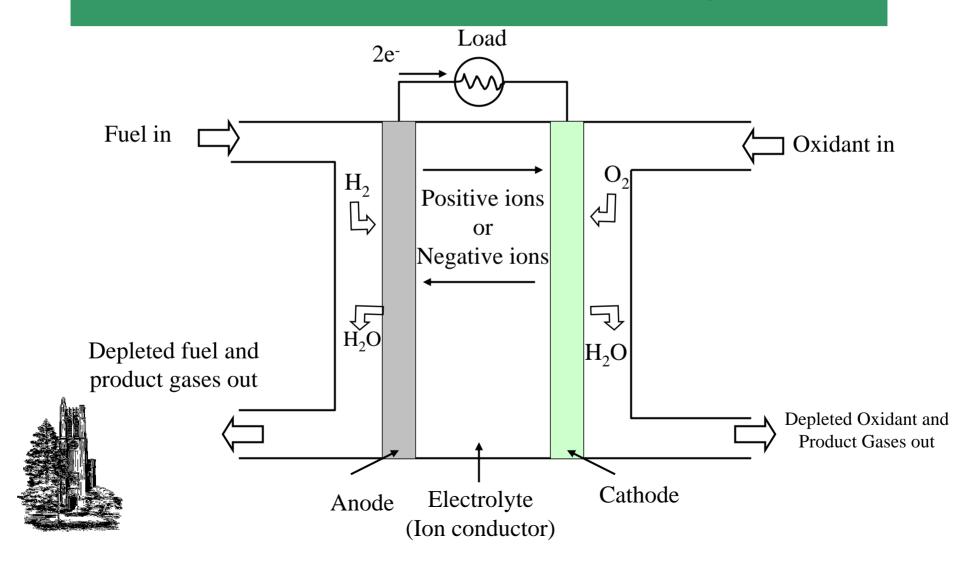
What is a fuel cell?

- Sandwich structure
 - two electrodes
 - one electrolyte
- Generates electricity, water, and heat
- Fuels: H₂, natural gas, methanol, gasoline, etc.





Schematic of a fuel cell system



What are fuel cells? (cont.)

- Numerous types of fuel cells
- Often categorized by the *electrolyte* used
 - Polymer Electrolyte Membrane (PEM)
 - Alkaline fuel cells (AFC)
 - Phosphoric acid (PAFC)
 - Molten carbonate (MCFC)
 - Solid oxide (SOFC)



The Very Basics of Fuel Cells

- Two separate reactions:
 - an oxidation half-reaction at the anode
 - a reduction half-reaction at the cathode

Oxidation half-reaction: $2H_2 \longrightarrow 4H^+ + 2e^-$

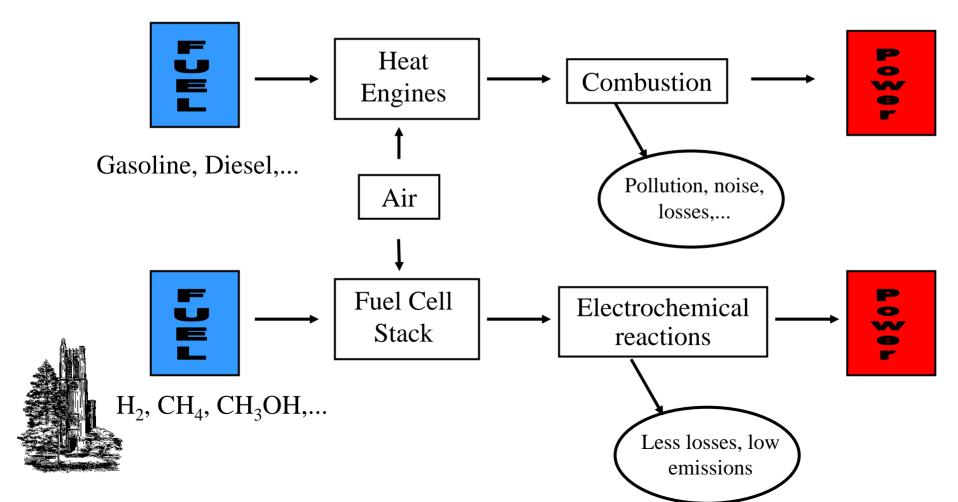
Reduction half-reaction: $O_2+4H^++4e^- \longrightarrow 2H_2O$

Cell reaction: $2H_2+O_2 \longrightarrow 2H_2O$



Catalysts are needed at both anode and cathode to increase the rate of each half-reaction. Pt is the best catalyst, a very expensive material.

Comparison of fuel cells with other energy sources

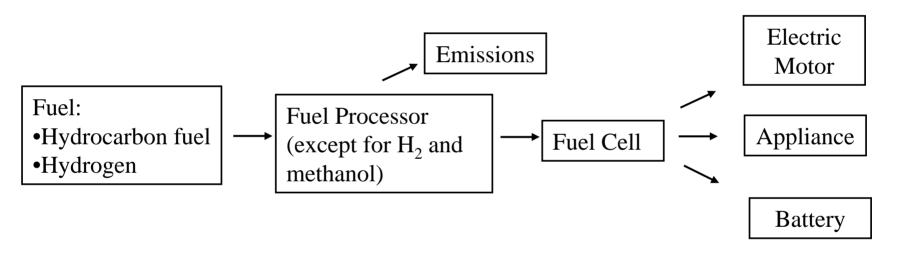


Fuel cells versus heat engines

- A heat engine cannot convert all of its energy supplied into mechanical energy (some of the heat is rejected) even for the ideal Carnot cycle
 - Max Efficiency = $(T_{HIGH} T_{LOW})/T_{HIGH}$
- IC engines use heat from T_{HIGH} source, converts part of the energy into mechanical energy and rejects the rest into a sink at low temperature
- Fuel cells convert chemical energy directly into electrical energy, without conversion of heat to mechanical energy (fuel cells can exceed Carnot efficiency)



Components of a fuel cell system





Engineering

Five Popular Fuel Cells

Fuel Cell	Electrolyte	Operating T	Electrochemical Reactions	
Polymer electrolyte membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60-100	Anode: $H_2 \longrightarrow 2 \text{ H}^+ + 2 \text{ e}^-$ Cathode: $1/2 \text{ O}_2 + 2 \text{ H}^+ + 2 \text{ e}^- \longrightarrow H_2 \text{ O}$ Cell: $H_2 + 1/2 \text{ O}_2 \longrightarrow H_2 \text{ O}$	
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100	Anode: $H_2 + 2(OH)^- \longrightarrow 2 H_2 O + 2 e^-$ Cathode: $1/2 O_2 + H_2 O + 2 e^- \longrightarrow 2(OH)^-$ Cell: $H_2 + 1/2 O_2 \longrightarrow H_2 O$	
Phosphoric Acid (PAFC)	Liquid phosphoric acide soaked in a matrix	175-200	Anode: $H_2 \longrightarrow 2H^+ + 2 e^-$ Cathode: $1/2 O_2 + 2 H^+ + 2 e^- \longrightarrow H_2 O$ Cell: $H_2 + 1/2 O_2 \longrightarrow H_2 O$	
Molten Carbonate (MCFC)	Liquid solution of Li, Na, K carbonates soaked in a matrix	600-1000	Anode: $H_2 + CO_3^2 \longrightarrow H_2 O + CO2 + 2 e^-$ Cathode: $1/2 O_2 + C O_2 + 2 e^- \longrightarrow CO_3^{2-}$ Cell: $H_2 + 1/2 O_2 + C O_2 \longrightarrow H_2 O + C O_2$	
Solid Oxide (SOFC)	Solid zirconium oxide with small amount of ytrria added	600-1000	Anode: $H_2 + O^2 \longrightarrow H_2 O + 2 e^2$ Cathode: $1/2 O_2 + 2 e^2 \longrightarrow O_2 - O_2$ Cell: $H_2 + 1/2 O_2 \longrightarrow H_2 O$	



Popular Fuel Cells (cont.)

	PEM	PAFC (most mature)	MCFC	SOFC
Charge carrier	Hydrogen ion	Hydrogen ion	Carbonate ion	Oxygen ion
Reformer	External	External	Internal or external	Internal or external
Catalyst	Platinum	Platinum	Nickel	Titanate of Calcium (Perovskites)
Efficiency	40-50	40-50	>60	>60
Status	Demo systems between 50- 200kW	Commercial systems 50kW- 11MW	Demo systems up to 2MW	Demo systems up to 100kW



Note: alkaline fuel cells have very high cost, but very high efficiency (>70%)

Various fuel cells

- Phosphoric Acid FC (PAFC):
 - most mature technology,
 - offered commercially in capacities above 100kW
 - some units have operated for n 10,000 hours
 - for power-generating installations that produce both heat and power, landfills, waste water treatment plants, food processors, green facilities.
 - \$4,000/kW, about 3 times the competitive cost
- Molten Carbonate FC (MCFC) and Solid Oxide FC (SOFC)
 - high temperatures (allow to reform fuels internally and ionize hydrogen)
 - MCFC requires a molten electrolyte (slow startup times)

PEM fuel cells

Advantages are linked to low operating temperature (80°C) (see below)



Fuel cell applications

- Electrochemical engines for vehicles (maybe)
- Distributed power plants for buildings/homes (currently used for off-grid sites)
- Battery replacements for portable
 electronics (probable in near future)



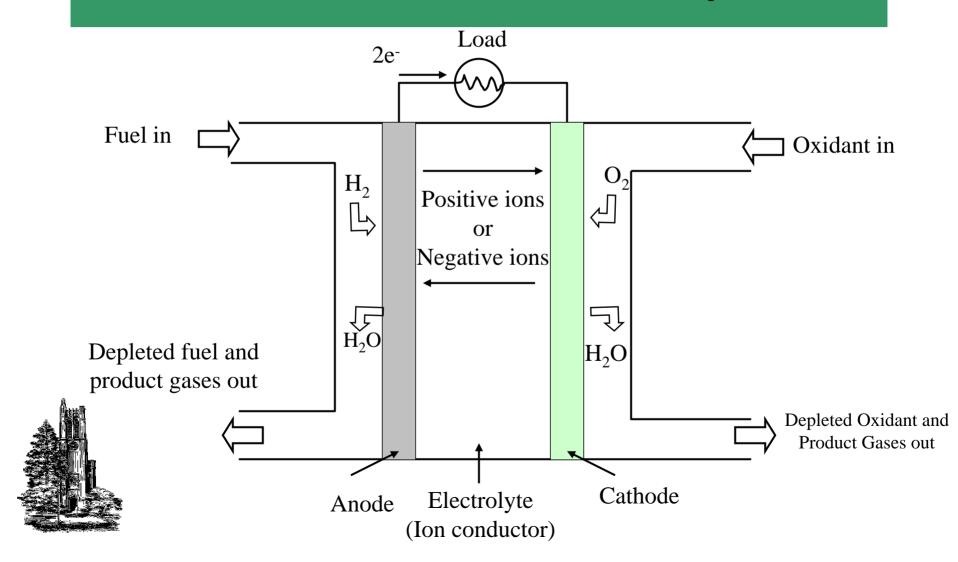


PEM Fuel cells win the popularity contest

- High power and density (low cost/low weight)
- Immobilized membrane simplifies sealing problems, reduces corrosion and provides longer life
- PEMFC have low operating temperatures,
 which implies fast startups and a rapid
 response to changes in demand for power



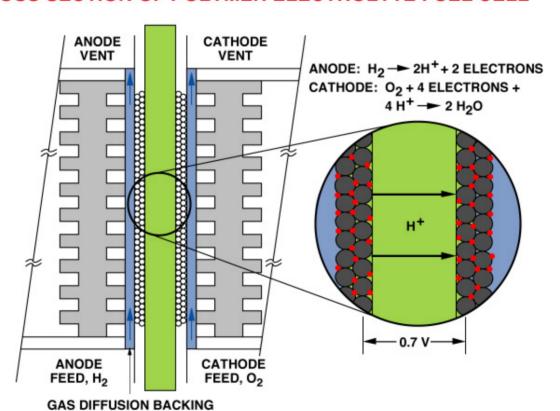
Schematic of a fuel cell system





Focus on the Polymer Electrolyte Membrane (PEM) Fuel Cell

CROSS SECTION OF POLYMER ELECTROLYTE FUEL CELL

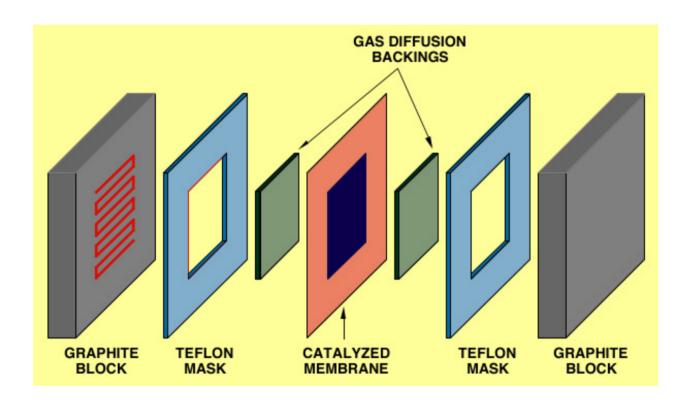






Membrane electrode assembly

SINGLE CELL HARDWARE

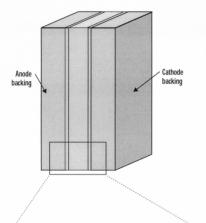




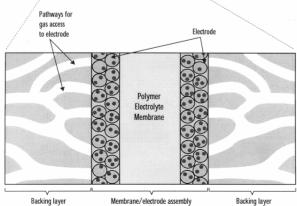


MEA and backing layers

Membrane/electrode assembly with backing layers.



- Backing layers (carbon cloth or paper):
 - •ensure diffusion of reactant to the catalyst
 - assist in water management
 - •allow water to leave
 - •allow water to reach the membrane
 - •if clogged with water, no gas diffusion allowed





Platinum is needed at both electrodes

- Pt is *sufficiently* reactive to bond H and O intermediates to facilitate oxidation or reduction.
- The anode process require Pt sites to bond H atoms when the H₂ molecule reacts, and then release the H atoms as H⁺ and e⁻
- Pt is expensive
- Catalyst layer must have as large a surface area as possible

$$H_2 + 2 \text{ Pt} \longrightarrow 2 \text{ Pt-H}$$

2 Pt-H $\longrightarrow 2\text{Pt} + 2\text{H}^+ + 2\text{e}^-$





Some of the issues with PEM fuel cells

- Reduce the use of Pt
- Water management
- Cold weather
- Manufacturing costs





Water management and PEMFC

- Water comes out as a liquid in PEMFC
- High water content is required in the membrane to ensure ionic conductivity
- Water content is determined by its transport during operation, which is influenced by
 - water drag through the cell
 - back diffusion through cathode
 - diffusion of water in fuel stream through anode

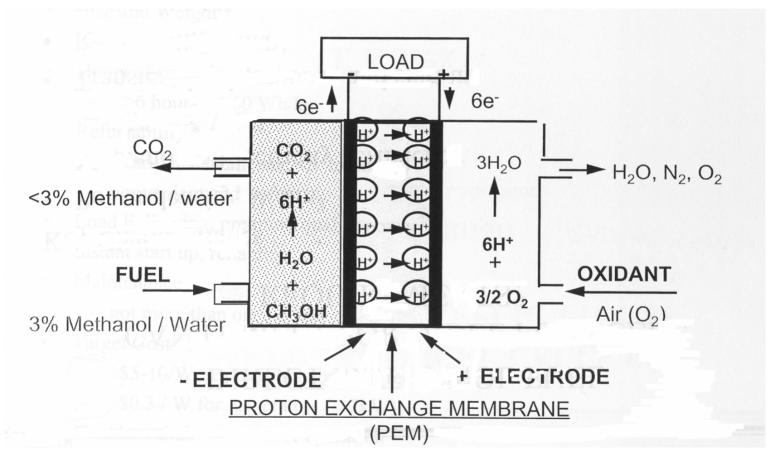


Water management in PEMFC

- Cell output is associated with mass transport issues which are associated to water formation
- Water management is required to avoid imbalance between water production and evaporation (dilution of reactant gases by water, flooding of the electrodes, dehydration of the membrane)



Direct methanol liquid feed fuel cell (DMFC)

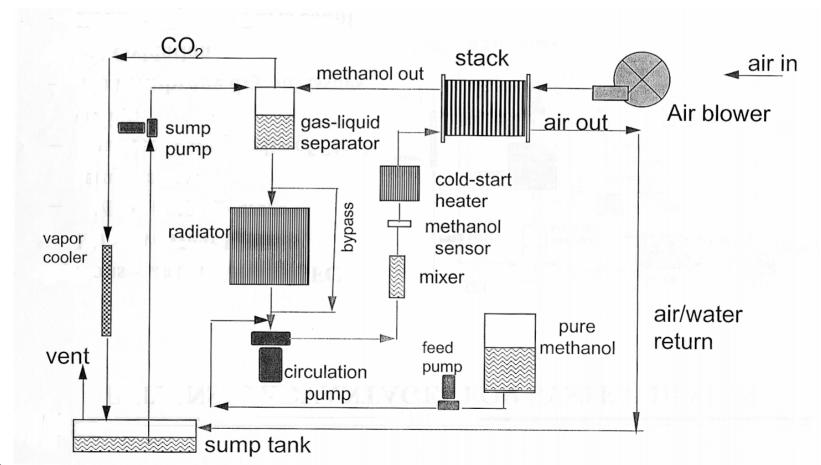




from S.R. Narayanan, NASA-JPL Caltech



A DMFC system





from S.R. Narayanan, NASA-JPL Caltech



Advantages of DMFC

- Aqueous liquid feed
 - effective heat removal
 - more uniform stack temperature
 - reduced complexity of stack design
- Direct oxidation
 - reduces system parts and weight
 - reduces control complexity





Some aspects of DMFC

- Methanol concentration affect performance
 - power density
 - thermal management
- Air flow rates affect performance
 - water balance (evaporation)
 - thermal balance (evaporative cooling)
- Crossover of methanol causes emissions + loss of performance
- Requires accurate concentration monitoring (methanol sensors)
- Requires more catalyst
- Developed as replacements for batteries



Phosphoric Acid Fuel Cell

- The PAFC is the only fuel cell technology that is in commercialization.
- Most of the plants are in the 50 to 200 kW capacity range, but large plants of 1 MW and 5 MW have been built. The largest plant operated to date achieved 11 MW
- Major efforts in the U.S. are concentrated on the improvement of PAFCs for stationary dispersed power plants and on-site cogeneration power plants.





Molten Carbonate Fuel Cell

- Referred to as a second generation fuel cell because it is expected to reach commercialization after PAFCs
- MCFCs differ in many respects from PAFCs because of their higher operating temperature (650 vs 200°C) and the nature of the electrolyte.
- The higher operating temperature of MCFCs provides the opportunity for achieving higher overall system efficiencies (potential for heat rates below 7500 Btu/kWh) and greater flexibility in the use of available fuels.
- Higher operating temperature places severe demands on the corrosion stability and life of cell components, particularly in the aggressive environment of the molten carbonate electrolyte.



Energy Research Corporation's 2MW MCFC power plant demonstration in Santa Clara, California

Solid Oxide Fuel Cell

- No liquid electrolyte (associated with material corrosion and electrolyte management problems).
- The operating temperature of >600°C allows internal reforming,
- Hight Top promotes rapid kinetics with nonprecious materials, and produces high quality byproduct heat for cogeneration or for use in a bottoming cycle, similar to the MCFC.
- The high temperature places stringent requirements on its materials. The development of suitable low cost materials and the low cost fabrication of ceramic structures are presently the key technical challenges



SOFC power plant built by Siemens Westinghouse



Fuel cell applications

- Electrochemical engine for vehicles
- Distributed power plants for buildings/homes (currently used for off-grid sites)
- Battery replacements for portable electronics





Electrochemical engines for vehicles

- Most vehicle manufacturers around the world have a research effort in fuel cells technology
- Research driven by
 - increasingly tighter requirements aimed at reducing emissions





Car industries and fuel cells

• DaimlerChrysler:

 Unveiled a fuel cell concept vehicle based on the Jeep Commander. The engine is a fuel cell/battery hybrid designed to utilize gasoline as fuel. A working methanol hybrid fuel cell system in the Commander planned by the summer of 2000.



Car industries and fuel cells

• Ford:

- Allied with Ballard and Daimler-Benz to develop and market fuel cell engines and electric drive trains.
- Ford unveiled the TH!NK FC5, a family size sedan powered by a Ballard fuel cell electric powertrain using methanol fuel. Based on the 2000 Ford Focus.
- Ford's P2000 Prodigy is a fuel cell powered sedan, running on stored hydrogen.
- introduced a P2000 SUV concept, a sport utility vehicle that will feature a fuel cell engine with a methanol reformer.
- Ford and Mobil are collaborating on a fuel processor to extract hydrogen from hydrocarbon fuels for use in fuel cell vehicles.



Car industries and fuel cells

• General Motors:

- unveiled the Precept concept car, in both hybrid and fuel cell powered forms (four-wheel drive, dual-axle setup).
- introduced the Opel Zafira fuel cell minivan, powered by its seventh generation fuel cell system
- GM intends to have a "production ready" fuel cell vehicle by 2004
- Delphi is working with ARCO and Exxon to develop on-board fuel processing technology to convert gasoline to hydrogen for use in PEM

Car industries and fuel cells

• Ballard Power Systems:

- Is the leading supplier of PEM fuel cells for transportation. Has received orders from auto manufacturers around the world.
- Unveiled its latest fuel cell stack, the Mark 900. It uses low-cost materials and is designed for high volume manufacture.





Car industries and fuel cells

• BMW:

- Joined forces with DELPHI to develop solid oxide fuel cell vehicles.
- Plans to fit 7 Series sedans with fuel cells from International Fuel
 Cells. The vehicle will run on a hydrogen combustion engine; the fuel cell will power the car's on-board electrical system.
- Will develop hydrogen fuelled forklift trucks, 2,000 will be used in the company's own facilities prior to marketing outside.
- De Nora S.p.A., Peugot/Citroen, Renault, Volkswagen/Volvo
 - all involved in fuel cell development efforts



Fuel cells for stationary power

- *Paradigm*: decentralized small units (50kW) could supply power to individual homes/stationary equipment, larger systems will power commercial buildings.
- Markets:
 - Off-grid residential (cottages, villages)
 - Recreational (boats, Rv's, camping)
 - Specialty (pipelines, UPS backup)
 - Deployable systems (generators, telecoms)
 - Residential (home power, cogeneration)
 - Military (electronic equipment support)

Currently used: batteries, generators, grid, solar power



Fuel cells for stationary power

- Fuel cells are of interest to developing countries for environmental reasons (do it right the first time)
- Can improve access to electricity by utilizing clean technologies
- Possible to reduce the number of people who rely on diesel generators



The Asahi brewery in Japan is generating some of its own power with a fuel cell running on hydrogen from the methane gas produced in its brewing process



Fuel cells as portable power sources

- Paradigm: replace the batteries
 - high power density
 - transient load response and start up
 - refuelability
 - fuel cell life
 - cost





Fuel Cell Systems

- Fuel cell power system requires integration of many components
- Efficient system requires more than optimization of stack only
- Implies an efficient and low cost plant
- Desired fuel, emission levels, use of rejected heat, output levels,
 volume/weight,etc



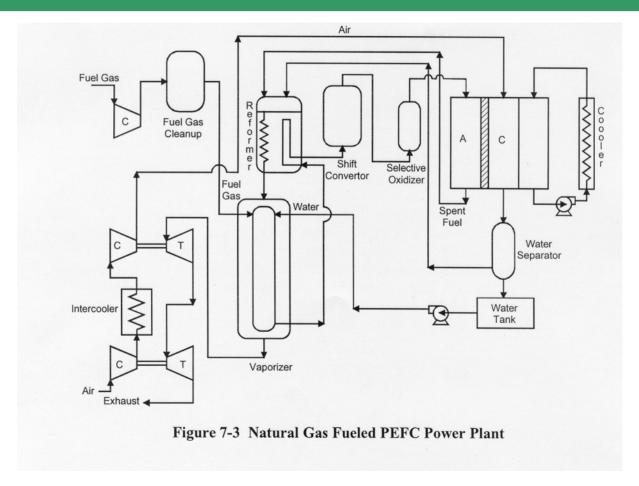
Fuel cell systems: fuel processor

- Required to process other fuels than hydrogen
- Start-up requires burning fuel to reach the transform temperature (emissions)





Fuel cell systems designs





Source: Fuel cell handbook '98



Fuel Cells Systems

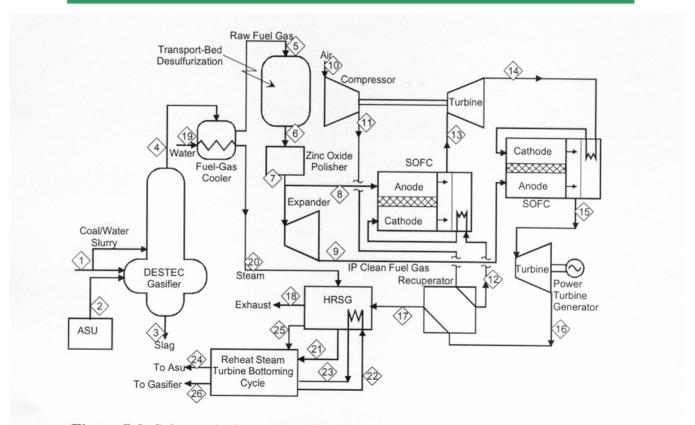




Figure 7-9 Schematic for a 500 MW Class Coal Fueled Pressurized SOFC

Source: Fuel cell handbook '98

System Optimization

- Pressurization
- Temperature
- Fuel Utilization
- Heat recovery
- Humidification/Dehumidification





Current Fuel Cell System Designs

- Natural gas PEM fuel cell
- Natural gas fueled phosphoric acid fuel cell
- Natural gas externally reformed MCFC system
- Natural gas internally reformed MCFC systems
 - Natural gas pressurized SOFC system



New fuel cell systems designs

- Ultra fuel cells
- Natural gas multistage MCFC system
- Coal fueled SOFC system
- Coal fueled multistaged SOFC system
- Coal fueled multistaged MCFC system
- Natural gas fuel pressurized SOFC system

Modeling fuel cells

- 2 possible point of view:
 - thermodynamic models (systems)
 - fairly advanced
 - detailed transport phenomena (component)
 - theory is established but used with 1d or 2d models (1999)



Modeling Transport phenomena in PEM fuel cells

Table 1. Governing equations and source terms.

Governing Equations	Mathematical expressions	Non-zero volumetric source terms and location of application (see Fig. 2)		
Conservation of mass	$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} = S_{m}$	(1)	$S_{m} = S_{H_1} + S_{m\sigma} \text{ at } y = y_3$ $S_{m} = S_{O_2} + S_{o\sigma} \text{ at } y = y_2$	(7)
Momentum transport	$u\frac{\partial(\rho u)}{\partial x} + v\frac{\partial(\rho u)}{\partial y} + w\frac{\partial(\rho u)}{\partial z} = -\frac{\partial P}{\partial x} + \frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial x}\right) + \frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right) + \frac{\partial}{\partial z}\left(\mu\frac{\partial u}{\partial z}\right) + S_{px}$		$S_{pe} = -\frac{\mu u}{\beta_s};$	(8)
	$u\frac{\partial(\rho v)}{\partial x} + v\frac{\partial(\rho v)}{\partial y} + w\frac{\partial(\rho v)}{\partial z} = -\frac{\partial P}{\partial y} + \frac{\partial}{\partial x}\left(\mu\frac{\partial v}{\partial x}\right) + \frac{\partial}{\partial y}\left(\mu\frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial z}\left(\mu\frac{\partial v}{\partial z}\right) + S_{py}$		$S_{py} = -\frac{\mu v}{\beta_y};$	``
	$u\frac{\partial(\rho w)}{\partial x} + v\frac{\partial(\rho w)}{\partial y} + w\frac{\partial(\rho w)}{\partial z} = -\frac{\partial P}{\partial z} + \frac{\partial}{\partial x}\left(\mu\frac{\partial w}{\partial x}\right) + \frac{\partial}{\partial y}\left(\mu\frac{\partial w}{\partial y}\right) + \frac{\partial}{\partial z}\left(\mu\frac{\partial w}{\partial z}\right) + S_{pz}$	(2)	$S_{pz} = -\frac{\mu w}{\beta_z}$ $at z_1 \le z \le z_4$	
Hydrogen transport (anode side)	$u\frac{\partial(\rho m_{H_2})}{\partial x} + v\frac{\partial(\rho m_{H_2})}{\partial y} + w\frac{\partial(\rho m_{H_2})}{\partial z} = \frac{\partial(J_{z,H_2})}{\partial x} + \frac{\partial(J_{y,H_2})}{\partial y} + \frac{\partial(J_{z,H_2})}{\partial z} + S_{H_2}$	(3)	$S_{H_1} = -\frac{I(x, y)}{2F} M_{H_1} A_{cr} \text{ at } y = y_3$	(9)
Water transport (anode side)	$u\frac{\partial(\rho m_{aw})}{\partial x} + v\frac{\partial(\rho m_{aw})}{\partial y} + w\frac{\partial(\rho m_{aw})}{\partial z} = \frac{\partial(J_{x,aw})}{\partial x} + \frac{\partial(J_{y,aw})}{\partial y} + \frac{\partial(J_{z,aw})}{\partial z} + S_{aw}$	(4)	$S_{arr} = -\frac{\alpha(x, y)}{F} I(x, y) M_{H_2O} A_{cr}$ $\alpha t y = y,$	(10)
Oxygen transport (cathode side)	$u\frac{\partial(\rho m_{O_1})}{\partial x} + v\frac{\partial(\rho m_{O_1})}{\partial y} + w\frac{\partial(\rho m_{O_2})}{\partial z} = \frac{\partial(J_{x,O_2})}{\partial x} + \frac{\partial(J_{y,O_2})}{\partial y} + \frac{\partial(J_{z,O_2})}{\partial z} + S_{O_2}$	(5)	$S_{o_1} = -\frac{I(x, y)}{4F} M_{o_1} A_{o_2}$ at $y = y_1$	(11)
Water transport (cathode side)	$u\frac{\partial(\rho m_{cw})}{\partial x} + v\frac{\partial(\rho m_{cw})}{\partial y} + w\frac{\partial(\rho m_{cw})}{\partial z} = \frac{\partial(J_{x,cw})}{\partial x} + \frac{\partial(J_{y,cw})}{\partial y} + \frac{\partial(J_{y,cw})}{\partial y} + S_{cw}$	(6)	$S_{cor} = \frac{1+2\alpha(x,y)}{2F} I(x,y) M_{H_1O} A_{co}$ at $y = y_2$	(12)



Modeling transport phenomena in PEMFC

Table 2. Equations	for modeling	electrochemical	effects.
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Diffusion mass flux of species <i>l</i> in ξ direction	$J_{ij} = -\rho D_{ij} \frac{\partial m_{KI}}{\partial \mathcal{E}}$	(13)
Binary diffusion coefficient (Bird et al., 1966)	$\frac{PD_{i,j}(x,y)}{(P_{c-i} * P_{c-j})^{1/3} \cdot (T_{c-i} T_{c-j})^{5/12} \cdot (\frac{1}{M_i} + \frac{1}{M_j})^{1/2}} = 3.64 \times 10^{-8} \left(\frac{T_{cell}}{\sqrt{T_{c-i} T_{c-j}}}\right)^{2.334}$	(14)
Net water transfer coefficient per proton	$\alpha(x,y) = n_d(x,y) - \frac{F}{I(x,y)} D_w(x,y) \frac{(C_{wc}(x,y) - C_{wc}(x,y))}{t_{m}}$	(15)
Electro-osmotic drag coefficient	$n_{a}(x,y) = 0.0049 + 2.02a_{a} - 4.53a_{a}^{2} + 4.09a_{a}^{3}, a_{a} \le 1$ = 1.59 + 0.159(a_{a} - 1) ; \alpha_{e} > 1	(16)
Water diffusion coefficient	$D_{W} = n_{d} 5.5 \times 10^{-10} \exp(2416(\frac{1}{303} - \frac{1}{T_{d}}))$	(17)
Water concentration for anode and cathode surfaces of the MEA	$C_{wg}(x,y) = \frac{\rho_{w,dry}}{M_{w,dry}} (0.043 + 17.8a_g - 39.8a_g^2 + 36.0a_g^3); a_g \le 1$ $= \frac{\rho_{w,dry}}{M_{w,dry}} (14 + 1.4(a_g - 1)); \text{ for } a_g > 1, \text{ where } K = a \text{ or } c$	(18)
Vater activity	$a_{K} = \frac{X_{w,K}P(x,y)}{P_{w,K}^{set}}$	(19)
ocal current density	$I(x,y) = \frac{\sigma_m(x,y)}{t_m} \{ V_{oc} - V_{cell} - \eta(x,y) \}$	(20)
ocal membrane conductivity	$\sigma_{m}(x,y) = \left(0.00514 \frac{M_{m,dry}}{\rho_{m,dry}} C_{wel}(x,y) - 0.00326\right) \exp\left(1268 \left(\frac{1}{303} - \frac{1}{T_{s}}\right)\right) x 10^{2}$	(21)
ocal over-potential	$\eta(x,y) = \frac{RT_s}{0.5F} \ln\left(\frac{I(x,y) \cdot P(x,y)}{I_o P_{o_1}(x,y)}\right)$	(22)



Some Recent Developments

- Mini/micro fuel cells are on the way
- Silicon PEM fuel cells were recently demonstrated
- High density hydrogen storage based on carbon nanotubes has been reported
- Micro fuel processors were recently developed





Conclusions

- Fuel cells will appear in numerous markets (portable electronic devices and off-grid power sources)
- Most of research need are in the materials area
- Modeling is need at two levels:
 - system models
 - realistic 3d model of transport phenomena in fuel cells (water management)
- Considered as the long-term replacement of IC engines
 (PNGV report)