### Introduction to Fuel Cell Systems

### Overview

- Why Fuel Cells?
- Fuel Cell Fundamentals
- FC Modeling
- FC Applications
- Challenges with FC Utilization
- Various Types of Fuel Cells
- H2 Production

 Clean (CO<sub>2</sub> and emissions), Flexible, Distributed Energy Carrier...

• Electricity!

- Generate with Nuclear, PV, Wind!

Storage Problem in Vehicles
 This is changing...

### • The Pros:

- High Energy Density compared to Batteries
- Continuous energy available as long as hydrogen is supplied
- Portable system able to provide power for a wide range of applications
- Fuel Cells produce the cleanest by-product which is water and heat

- Applications:
- Note: Fuel Cells have a voltage output dependent on the load current demand. Thus a converter is usually used to stabilize the output voltage to a desired value.
- Distributed Generation
- Hybrid Electric Vehicles (HEVs): Fuel Cell in parallel with batteries
- Portable Power Supplies
- Charging Stations
- Single Home Residential Power
- Electricity and Water Generation in Space Shuttle

Conventional Motor

 Fuel → Heat → Mechanical (vehicle)
 Mechanical Power → Electricity (coal plant)
 20% - 30% Fuel → Electricity efficiency

- Fuel Cell: Electrochemical Device
   Fuel (hydrogen) → Electricity (power plant)
   Electricity → Mechanical Power (vehicle)
  - "Steady Flow Battery"

- For vehicles, over 50% reduction in fuel consumption compared to a conventional vehicle with a gasoline internal combustion engine
- 2. Increased reliability of the electric power transmission grid by reducing system loads and bottle necks
- 3. Increased co-generation of energy in combined heat and power applications for buildings
- 4. Zero to near-zero levels of harmful emissions from vehicles and power plants
- 5. High energy density in a compact package for portable power applications

Fossil Fuel Dependant → CO<sub>2</sub>
 – Hydrocarbon Reforming for Hydrogen
 – Electrolysis? (only if you have clean e<sup>-</sup>)

Well to Wheel studies by Stodolsky et al., Mizey et al., and Rousseau et al. (15% → 40%, so CO<sub>2</sub> reduction)

Single Point Emissions

- Without clean e<sup>-</sup>, fuel cells DO NOT solve the CO<sub>2</sub> problem, but they can help alleviate it through higher efficiencies
- Fuel cells DO shift non-CO<sub>2</sub> emissions to single point sources
- Fuel cell easily converts H<sub>2</sub> to e<sup>-</sup> (REVERSE OF WATER ELECTROLYSIS)
- Fuel cells, through H<sub>2</sub> energy carrier, get around the on-board e<sup>-</sup> storage issue.

 Major players: Ballard, zTEK, UTC, Siemens, Plug Power

### Multidisciplinary



### Hydrogen Energy (Economy)

#### Domestic Hydrogen Production Options



#### Road map of Hydrogen R&D

Figure ES-1. Possible Scenarios for Hydrogen Technology Development and Market Transformation

#### Strong Government R&D Role

Strong Industry Commercialization Role



 Technology Development Research to meet technology performance and cost targets and establish technology readiness II. Initial Market Penetration Portable power and stationary/transport systems are validated; infrastructure investment begins with governmental policies III. Expansion of Markets and Infrastructure H, power and transport systems commercially available infrastructure business case realized IV. Fully Developed Markets and Infrastructure H, power and transport systems commercially available in all regions; national infrastructure

The timeframe is long and the investment is large to develop a hydrogen and transportation market that reduces our Nation's dependence on foreign sources of energy while minimizing environmental impacts.

### **Fuel Cells Fundamentals**

- Electrochemical Device
- "Steady Flow Battery"
- Electrochemical "Engine"
- Generate DC power
- # of cells (voltage) and active surface area (current)

#### What is the Difference Between a Fuel Cell and a Rechargeable Battery ?

★ A fuel cell is able to operate for long periods of time without recharging or interruption because reactants are brought in from outside, while a rechargeable battery needs to be charged after discharge.

#### What is a fuel cell ?

A fuel cell is an electrochemical conversion device that converts hydrogen and oxygen into electricity, water, and heat.



http://www.fuelcells.org/whatis.htm

#### Schematic Diagram of H<sub>2</sub>/O<sub>2</sub> PEMFC



Fig. 1. Schematic of a single typical proton exchange membrane fuel cell.



#### \*California Fuel Cell Partnership

#### Schematic Diagram of H<sub>2</sub>/O<sub>2</sub> PEMFC



 ★ Anode: Hydrogen oxidation to protons
 H<sub>2</sub> → 2H<sup>+</sup> + 2e<sup>-</sup>

- ★ The protons migrate through the membrane to the cathode
- ★ Cathode: Oxygen reduction  $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$  $(E_{o25}^oc = +1.23 V \text{ (vs. NHE)})$
- **★** Overall:  $H_2 + \frac{1}{2} O_2 \rightarrow H_2 O$

### Water Management in the PEMFC



$$\begin{array}{c} - \ CF_2 - \ CF - \ CF_2 - \ I \\ 0 \\ I \\ CF_2 \\ I \\ CF - \ CF_3 \\ I \\ 0 \\ I \\ CF_2 \\ I \\ CF_2 \\ I \\ CF_2 \\ I \\ SO_3^- \ H^+ \end{array}$$

 Teflon Backbone (Hydrophobic) Side Chain (Hydrophilic) •Sulfonic Group (weak, dilute acid)

Solid Polymer Electrolyte















\*Ballard Corporation

### BOP

 In addition to the stack, practical fuel cell systems require several other sub-systems and components; the so-called balance of plant (BoP). Together with the stack, the BoP forms the fuel cell system. The precise arrangement of the BoP depends heavily on the fuel cell type, the fuel choice, and the application. In addition, specific operating conditions and requirements of individual cell and stack designs determine the characteristics of the BoP. Still, most fuel cell systems contain:

### BOP

- Fuel preparation. Except when pure fuels (such as pure hydrogen) are used, some fuel preparation is required, usually involving the removal of impurities and thermal conditioning. In addition, many fuel cells that use fuels other than pure hydrogen require some fuel processing, such as reforming, in which the fuel is reacted with some oxidant (usually steam or air) to form a hydrogen-rich anode feed mixture.
- Air supply. In most practical fuel cell systems, this includes air compressors or blowers as well as air filters.
- Thermal management. All fuel cell systems require careful management of the fuel cell stack temperature.
- Water management. Water is needed in some parts of the fuel cell, while overall water is a reaction product. To avoid having to feed water in addition to fuel, and to ensure smooth operation, water management systems are required in most fuel cell systems.
- Electric power conditioning equipment. Since fuel cell stacks provide a variable DC voltage output that is typically not directly usable for the load, electric power conditioning is typically required.
- While perhaps not the focus of most development effort, the BoP represents a significant fraction of the weight, volume, and cost of most fuel cell systems

# Fuel Cell with BOP



Introduction FUEL CELL MODELING

### Fuel Cell Model

Dehydration flooding

- Model→prediction
- Stoichiometric Number: reflects the rate at which a reactant is provided to a fuel cell relative to the rate at which it is consumed. E.g., lamda=2 means that twice as much reactant as needed is being provided to a fuel cell. Choosing an optimal lamda is a delicate task. A large number is wasteful, resulting in parasitic power consumption and/or lost fuel. Too small number will result in reactant depletion effects. Two numbers are needed: for H2, and O2.

### Fuel Cell Model

- Concept "Gibbs Free Energy": the chemical energy released in a reaction can be thought of as consisting 2 parts: an entropy-free part called Gibbs Free Energy and a part that must appear as heat. The Gibbs free energy part can be converted directly into electrical or mechanical work, and thus corresponds to the maximum possible, entropy-free, electrical (or mechanical) output from a chemical reaction. For fuel cell, the ideal maximum efficiency is 83%.
- For fuel cell reaction, the Gibbs free energy is 237.2 kJ per mol of H2, which is the maximum electrical output at STP.

### Fundamentals $H_2 \rightarrow 2H^+ + 2e^-$

# $2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$



 $V_{ideal} = 1.48 \text{ V per cell at STP}$ 

## **Electrochemical Reactions** $H_2 \rightarrow 2H^+ + 2e^-$

 $2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O \quad \text{+ heat}$ 

 $H_2 + \frac{O_2}{2} \rightarrow H_2O$  + HEAT + electrical energy

# Cell potential vs. current density characteristic curve of a typical PEMFC



The reasons for a lower open circuit potential than the thermodynamic value for oxygen reduction on Pt:

Production of some peroxide  $O_2+2H^++2e^- = H_2O_2$  $E^{\circ}_{25}\circ_{C} = + 0.68V$  (Vs. NHE)

×

 $\star$ 

Formation of a range of possible platinum oxides at high potential Pt +H<sub>2</sub>O = Pt-O + 2H<sup>+</sup> + 2e- $E_{25}^{\circ}C$  = + 0.88V (Vs. NHE)
# **Fuel Cell Polarization**



## **Fuel Cell Polarization**



# I-V curve linear equation

### V= 0.85 – 0.25 J

### J: current density, equals I/A

Example: for a 1 kW fuel cell stack, which produces 48 V dc, each cell at 0.6 V, how many cells would be needed and what shaould be the memberance area of each cell?

Use the above approximate formula

# **Fuel Cell Polarization**

- These losses are often referred to as polarization, overpotential or overvoltage, though only the ohmic losses actually behave as a resistance.
- Multiple phenomena contribute to irreversible losses in an actual fuel cell:
- Activation-related losses. These stem from the activation energy of the electrochemical reactions at the electrodes. These losses depend on the reactions at hand, the electro-catalyst material and microstructure, reactant activities (and hence utilization), and weakly on current density.
- Ohmic losses. Ohmic losses are caused by ionic resistance in the electrolyte and electrodes, electronic resistance in the electrodes, current collectors and interconnects, and contact resistances. Ohmic losses are proportional to the current density, depend on materials selection and stack geometry, and on temperature.
- Mass-transport-related losses. These are a result of finite mass transport limitations rates of the reactants and depend strongly on the current density, reactant activity, and electrode structure.

### Power of Fuel Cells



### Fuel Cell Ideal Open Circuit Voltage

- Nomenclature and physical constants:
- q = charge on an electron =  $1.602 \times 10^{-19}$  coulombs
- N = Avogadros number =  $6.022 \times 10^{23}$  molecules/mol
- V = volume of 1 mole of ideal gas at STP=22.4 liter/mol
- n = rate of flow of  $H_2$  into the fuel cell (mol/s)
- I = current (A)
- 1A = 1Coulomb/s
- V<sub>R</sub> = ideal (reversible) voltage across the two electrodes
   (volts)
- P = electrical power delivered (W)

1 Faraday constant = 1 mol of e- = 96,500 C

### Fuel Cell Ideal Open Circuit Voltage

 For each molecule of H2 into an ideal fuel cell, two electrons will pass thru the electrical load. So the current flowing thru the load will be:

$$I(A) = n \left(\frac{mol}{s}\right) \cdot 6.022 \times 10^{23} \left(\frac{moleculesH_2}{mol}\right) \cdot \frac{2electrons}{moleculeH_2} \cdot 1.602 \cdot 10^{-19} \left(\frac{coloumbs}{electron}\right)$$
$$I(A) = 192,945n$$

### Fuel Cell Ideal Open Circuit Voltage

- From the Gibbs free energy of fuel cell reaction, the ideal power in watts delivered to the load will be 237.2 kJ per mol of H2 times the rate of H2 use:  $P(W) = 237.2 \left(\frac{kJ}{mol}\right) \times n \left(\frac{mol}{s}\right) \times 1000 \left(\frac{J}{kJ}\right) \cdot \frac{1W}{J/s}$
- So the reversible voltage produced across the terminals of the ideal fuel cell will be:



 Note that this voltage does not depend on the input rate of H2. But it depends on the temperature and partial pressure of the reactants since realistic operating condition is not STP.

# **Charge Double Layer**

- The charge layer on both electrode-electrolyte interfaces (or close to the interface) is the storage of electrical charges and energy; so it behaves like an electrical capacitor.
- If the current changes, delay affects the activation and concentration potentials. (firstorder)
- Time delay: t = CRa, C is the equivalent capacitance (few farads); Ra is the equivalent variable resistance to the activation and concentration losses.

### **Equivalent Circuit Model**



$$P_{fc} = V_{cell} i_{fc}$$

## **Equivalent Circuit Model**



Diagram of building a dynamic model of PEMFC in SIMULINK

Introduction FUEL CELL APPLICATION

### Hydrogen Fuel Cell Car



\*Green Power, Los Alamos National Lab, LA-UR-99-3231



- FCV
- Entire Drive System
  Contained in "Skateboard"
  Interchangeable, Bolt on Body

- Single Center Electrical Connection
- Drive By Wire (Steering, Accelerator, Braking, etc.)





\* Honda Motor Company







### Sequel, a fuel cell-powered vehicle from General Motors



# Ford Edge hydrogen-electric plug-in hybrid concept



# The Boeing Fuel Cell Demonstrator powered by a hydrogen fuel cell



## Hydrogen Bicycle





#### **Fuel Cell Power Plant Major Processes**





\*Ocean County College, Toms River, NJ

### Major issues in PEFC

- High cost of polymer membrane electrolyte
- Operation temperature limit of present polymer membrane electrolyte
- Reduce the loading of precious metal catalysts, ie. Pt, Ru
- Electro-osmotic drag of water and critical humidification level to maintain the conductivity
   Methanol permeation of the membrane
- Low CO tolerance of present catalysts

- Cold Start
- Hydrogen Storage
  - High Pressure Composite Tanks
  - Cryogenic Storage
  - On-board Hydrocarbon Reforming?

 Carbon Monoxide Poisoning (when H2 is reformed from hydrocarbon fuels such as methanol)

- Durability (up to 5,000 hrs and 40,000 hrs?)
- Clean H<sub>2</sub> Production
- Cost per kW (not just Pt)
- Size
- Weight
- End of Cycle Impact?
- Better than Hybrid Technology?
- Better than EV Technology?

- Low power density compared to batteries
- Susceptible to high and widely variable currents
- Slow responsive action to step loads due to the FC's fuel delivery and regulatory system.

 Current and fuel responsive problems can be remedied with a hybrid FC-Battery/Ultracapacitor system.

FC > DC-DC Converter > Storage Device > Load

An experiment was conducted in order to see the advantages of a hybrid system over a stand-alone FC and converter.

Test included the following materials: -50W PEMFC module by Hampden

- Passive 12V dc-dc boost converter module
- 12V lead acid battery (the type found in electric scooters)
- Programmable variable speed DC motor system as the load

### Example fuel cell system load characteristics without battery (use of passive 12V boost converter)



### Example fuel cell system load characteristics <u>with</u> battery (use of passive 12V boost converter)



- A.D. Little study projects high volume production cost of \$14,700 or \$294/kW (60% Stack, 29% Processor, 11% BOP, Assembly, and Indirect) for fuel cell system
- Platinum cost alone is \$63/kW (21% of total \$)
- ICE engine cost?
- Fuel Cell Vehicle: cell, auxiliary equipment, H<sub>2</sub> storage, power inverters, and electric motors



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#### \* Honda Motor Company


## Various Types of Fuel Cells

- PEMFC (Polymer Electrolyte FC)
- AFC (Alkaline FC)
- PAFC (Phosphoric Acid FC)
- MCFC (Molten Carbonate FC)
- SOFC (Solid Oxide FC)

	PEFC	AFC	PAFC	MCFC	SOFC	
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in LiAlO <sub>2</sub>	Perovskites (Ceramics)	
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite / metal cermet	
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material	
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel	
Operating Temperature	40 – 80 °C	65°C – 220 °C	205 °C	650 °C	600-1000 °C	
Charge Carrier	$\mathrm{H}^{+}$	OH	H <sup>+</sup> CO3 <sup>=</sup>		O <sup>=</sup>	
External Reformer for hydrocarbon fuels	Yes	Yes	Yes No, for some fuels		No, for some fuels and cell designs	
External shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO <sub>2</sub>	to Yes No		No	
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless- based	Ceramic	
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product	
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas	

The most common classification of fuel cells is by the type of electrolyte used in the cells and includes 1) polymer electrolyte fuel cell (PEFC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC), and 5) solid oxide fuel cell (SOFC). Broadly, the choice of electrolyte dictates the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermomechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.).

### Fuel Cell Characteristics Chart

Fuel Cell Type	Electrolyte	Availability	Operating Temp.	Efficiency	Advantages	Disadvantages	Output
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	Currently available	150-200 °C	40%, 85% cogeneration	Can use impure H2 as fuel. Can tolerate up to 1.5% CO at operating temp.	Uses expensive Pt as catalyst, relatively low current generation and large size and weight	Up to 200 kW, units up to 1 MW have been tested
Proton Exchange Membrane (PEM)	Polyperfluoro- sulfonic acid	Under development, prototypes in use	80 °C		High power density, can quickly vary output (good for vehicles), solid electrolyte	Sensitive to fuel impurities	50-250 kW
Molten Carbonate (MCFC)	Carbonate solution	Under development, prototypes in use	650 °C	60%, 85% cogeneration	High operating temperature, therefore, no expensive noble metal catalysts and can operate on cheap fuels.	High operating temperature accelerates corrosion of cell components	10 kW to 2 MW
Solid Oxide (SOFC)	Yttria-stabilized zirconia, or more recently, lanthanide doped ceria	Under development, prototypes in use	1000 °C	60%, 85% cogeneration	High operating temperature, therefore, no expensive noble metal catalysts and can operate on cheap fuels	High operating temperature accelerates corrosion of cell components	Up to 100 kW
Alkaline	KOH(aq) soaked in a matrix	Used by NASA on space missions for decades	150-200 °C	up to 70%	Aqueous electrolyte promotes fast cathode reaction and high performance	High cost	300 -5000 watts
Direct Methanol Fuel Cell (DMFC)	Similar to PEM, however, uses methanol directly	Under development, prototypes in use	50-100 °C	40%	Due to the low operating temperature, good for small portable devices	Problems with fuel passing over the anode with producing electricity	



# **F**uel Cell Technologies



#### PEMFC and SOFC

 Two types of fuel cells have a very bright future. These are the PEMFC and the SOFC. The PEMFC has a bright future for use in automobiles due to the electrolyte and reactants used as well as its low operating temperature and material weight. The SOFC is and will continue to be utilized in distributed generation. The SOGC has a very high operating temperature of 750-1000 degrees Celsius and this waste heat can be used to create steam for turbines. As a result a duel generation can be implemented with this type of fuel cell.



#### SOFC

- High temperature: 750-1000 oC. Waste heat can be used for combined-cycle steam or combined cycle gas turbines.
- Electrolyte: solid ceramic material made of zirconia and yttria.
- Charge carrier that is transported across the electrolyte is oxide O2- ion, which is formed at the cathode when o2 combines with electrons from the anode.

e)

ode'

• Reactions:

$$H_2 + O^{2-} \to H_2O + 2e^-$$
 (Anod  
 $\frac{1}{2}O_2 + 2e^- \to O^{2-}$  (Cathe



#### SOFC Stacks



- SOFC Planar Construction
  - Solid electrolyte, supported by Anode material.
  - Cell interconnects made of stainless steel.

#### **SOFC Cells**



All Courtesy of Versa Power







$$\frac{1}{2}O_{2} + 2OH^{-} \rightarrow 2H_{2}O + 2e^{-} \quad (anode)$$

$$\frac{1}{2}O_{2} + H_{2}O + 2e^{-} \rightarrow 2OH^{-} \quad (cathode)$$

(intolerance of CO2)

http://fuelcellsworks.com/Typesoffuelcells.html http://americanhistory.si.edu/fuelcells/basics.htm http://www.azom.com/details.asp?ArticleID=2962 http://www.corrosion-doctors.org/FuelCell/Types.htm



$$H_{2} + CO_{3}^{2^{-}} \to H_{2}O + CO_{2} + 2 e^{-} \quad (anode)$$
  
$$\frac{1}{2}O_{2} + CO_{2} + 2 e^{-} \to CO_{3}^{2^{-}} \quad (cathode)$$

(tolerance of CO)

#### H2 Production

- Methane Steam Reforming (MSR)
- Partial Oxidation (POX)
- Gasification of Biomass, Coal, or Wastes
- Electrolysis of Water