January 21, 2004
Fuel Cell Engineering Course
CHEG 320
Taught at UTC Fuel Cells

Fuel Cells

Instructor
James M. Fenton, Professor, Chemical Engineering
University of Connecticut

Teaching Assistants:
1. Ruichun Jiang (rcjiang@engr.uconn.edu)
2. Vijay Ramani (vkramani@engr.uconn.edu)
Fuel Cells in the Public Eye

“Not long ago, the fuel cell was dismissed as an environmentalist's pipe dream. . . . Now it is the subject of a heavily financed research and development race.”

Jeffrey Ball, Wall Street Journal

Fuel cell sales

- 1998 $355 M
- 2003 projected sales $1,295 M
Fuel Cell Market Projections

**World Fuel Cells Market Size**

Market develops ~ 2004/05, exceeding $15 B by 2010
PEM-Fuel Cells for Vehicle Propulsion
Future Alternative to Combustion Engines?

NECAR III (Daimler Benz)

RAV4 - FCEV (Toyota)

Zafira (Opel)
Applications

Stationary (200 kW)

Mobile (50 kW)

International Fuel Cells

Portable ( < 3W)

Toyota

Motorola
Fuel Cell Car & Experiment Kit
Retail Price: $150.00

http://www.thamesandkosmos.com/
Casio: PEM Fuel cell with methanol reformer for laptops
http://www.h2fc.com/tech.html
DaimlerChrysler/Ballard: DMFC go kart
http://www.h2fc.com/tech.html
Toshiba: PDA powered by Direct Methanol Fuel Cell
http://www.h2fc.com/tech.html
## Fuel Cell / Fuel Processing Development Targets

<table>
<thead>
<tr>
<th>Specification</th>
<th>Residential</th>
<th>Commercial</th>
<th>Automotive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale (kWe)</td>
<td>1-7</td>
<td>35-250</td>
<td>40-90</td>
</tr>
<tr>
<td>Fuel</td>
<td>natural gas</td>
<td>natural gas</td>
<td>gasoline</td>
</tr>
<tr>
<td>FPS Cost Target ($/kWe)</td>
<td>300-500</td>
<td>300-500</td>
<td>15-20</td>
</tr>
<tr>
<td></td>
<td>{1500}</td>
<td>{1500}</td>
<td>{60}</td>
</tr>
<tr>
<td>FPS Volume (L/kWe)</td>
<td>~20</td>
<td>~20</td>
<td>~1</td>
</tr>
<tr>
<td>FPS Weight (kg/kWe)</td>
<td>~20</td>
<td>~20</td>
<td>~1</td>
</tr>
<tr>
<td>Life (hours)</td>
<td>40-120K</td>
<td>40-80K</td>
<td>3-6K</td>
</tr>
<tr>
<td>Start-up/Transient (min.)</td>
<td>5-10/-</td>
<td>120/-</td>
<td>1/0.01</td>
</tr>
</tbody>
</table>

Gasoline: natural gas: fuel
Fuel Cell Stack as Automobile Engine

PEM Fuel Cell Module
58 kW-Unit (H\textsubscript{2}/air)

- rated power: 58 kW
- voltage @ rated power: 96 V
- single cell voltage @ r.p.: 0.60 V
- open circuit voltage: 160 V
- rated current: 600 A
- size (without tie rods): 41x41x56 cm\textsuperscript{3}
- volume: 94 l
- weight: 280 kg
- number of cells: 160

integrated H\textsubscript{2}-humidifier

source: Siemens KWU BSPT
Cost Structure of a PEM Fuel Cell Stack (averaged values)

Will Fuel Cells come into Market?

- The costs of an FC stack must be decreased to about $30/kW to compete with conventional ICEs.
- Volume production alone is not enough to reach the cost target. Notable progress in material development is required.
# Comparison of Five Fuel Cell Technologies

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Electrolyte</th>
<th>Operating Temperature (°C)</th>
<th>Electrochemical Reactions</th>
</tr>
</thead>
</table>
| Polymer Electrolyte/Membrane (PEM) | Solid organic polymer poly-perfluorosulfonic acid | 60 - 100                  | Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)  
Cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \)  
Cell: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) |
| Alkaline (AFC)             | Aqueous solution of potassium hydroxide soaked in a matrix | 90 - 100                  | Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)  
Cathode: \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{2(OH)} \)  
Cell: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) |
| Phosphoric Acid (PAFC)     | Liquid phosphoric acid soaked in a matrix         | 175 - 200                 | Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)  
Cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \)  
Cell: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) |
| Molten Carbonate (MCFC)    | Liquid solution of lithium, sodium and/or potassium carbonates, soaked in a matrix | 600 - 1000               | Anode: \( \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \)  
Cathode: \( \frac{1}{2} \text{O}_2 + \text{CO}_3^{2-} + 2\text{e}^- \rightarrow \text{CO}_3^{2-} \)  
Cell: \( \text{H}_2 + \frac{1}{2} \text{O}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 \)  
(CO\(_2\) is consumed at cathode and produced at anode) |
| Solid Oxide (SOFC)         | Solid zirconium oxide to which a small amount of yttria is added | 600 - 1000               | Anode: \( \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \)  
Cathode: \( \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-} \)  
Cell: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) |
## Comparison of Five Fuel Cell Technologies

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Applications</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Polymer Electrolyte/Membrane (PEM) | electric utility portable power transportation | • Solid electrolyte reduces corrosion & management problems  
• Low temperature  
• Quick start-up | • Low temperature requires expensive catalysts  
• High sensitivity to fuel impurities |
| Alkaline (AFC)           | military space                    | • Cathode reaction faster in alkaline electrolyte — so high performance | • Expensive removal of CO₂ from fuel and air streams required |
| Phosphoric Acid (PAFC)   | electric utility transportation    | • Up to 85% efficiency in co-generation of electricity and heat  
• Impure H₂ as fuel | • Pt catalyst  
• Low current and power  
• Large size/weight |
| Molten Carbonate (MCFC)  | electric utility                  | • High temperature advantages* | • High temperature enhances corrosion and breakdown of cell components |
| Solid Oxide (SOFC)       | electric utility                  | • High temperature advantages*  
• Solid electrolyte advantages (see PEM) | • High temperature enhances breakdown of cell components |

*High temperature advantages include higher efficiency, and the flexibility to use more types of fuels and inexpensive catalysts as the reactions involving breaking of carbon-to-carbon bonds in larger hydrocarbon fuels occur much faster as the temperature is increased.
Cross Section of Proton Exchange Membrane Fuel Cell

ANODE: $\text{H}_2 \rightarrow 2\text{H}^+ + 2 \text{ELECTRONS}$
CATHODE: $\text{O}_2 + 4 \text{ELECTRONS} + 4 \text{H}^+ \rightarrow 2 \text{H}_2\text{O}$
Electrodes, Electrolyte, Electrochemical Cell

- “Electrochemistry”
  - Chemistry w/ Combined Chemical & Electrical Effects
- “Electrode”
  - Where Electrochemical Reaction Occurs
- “Electrolyte”
  - Medium in which mobile ions can move – to transfer charge (link two reactions)

- An “electrochemical cell” = 2 electrodes + 1 electrolyte

- Electrode of reaction of interest = Working Electrode (WE)
- Electrode of other (coupled) reaction = Counter Electrode (CE)
- Electrode of Reference = Reference Electrode (RE)

- ANODE = Electrode where OXIDATION reaction happens (GIVES electrons)
- CATHODE = Electrode where REDUCTION rxn. happens (TAKES electrons)

In PEM Fuel Cell:
- Anode = Hydrogen Oxidation Reaction = CE & RE
- Cathode = Oxygen Reduction Reaction = WE
- Membrane = Electrolyte
Fuel Cells

\[ e^- e^- e^- e^- e^- \]

Anode (Oxid.) \[ \rightarrow \]
Electrolyte

Cathode (Reduction)

\[ e^- e^- e^- e^- \]

Positive Ions

Different Electrolytes

\[ \rightarrow \]
Different kinds of Fuel Cells

- Solid Oxide
- Molten Carbonate
- Alkaline
- Phosphoric Acid
- PEM (H_2)
- DMFC = a PEM (MeOH)
**Membrane Electrode Assembly (MEA)**

**Anode**
- \( \text{H}_2 + \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + 2 \text{e}^- \)
- Hydrogen Oxidation

**Cathode**
- \( \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O} \)
- Oxygen Reduction

**Chemical Reactions**
- \( \text{H}_2 + \text{H}_2\text{O} \)
- \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \)

**Details**
- Anode: Proton Conductive Membrane (25-50 µm), Anode Catalytic Layer (10-30 µm), Anode Flow Field
- Cathode: Proton Conductive Membrane (25-50 µm), Cathode Catalytic Layer (10-30 µm), Cathode Flow Field
- Gas Diffusion Layers: Anode (300-500 µm), Cathode (300-500 µm)
Two MEA Technologies

Older (from Phos. A. FC)
Catalyst Layer + GDL
→ GDE (Gas Diffusion Electrode)
GDE + Membrane → MEA

Newer (1992)
Catalyst Layer + Membrane
→ Catalyzed Membrane
Catalyzed Membrane + GDL → MEA

CHEG 320 Spring 2004, UTC Fuel Cells
Dr. J. M. Fenton, Instructor
GDL VS. GDE in PEMFCs

GDE = GDL + Catalyst Layer

Dual-layer GDE
(Adapted from Phosphoric Acid FC)

- Catalyst Layer
  - Pt/C + PTFE
  - 10 – 100 µm
- Macro-porous Substrate
  - 290 – 400 µm

Triple-layer GDE

- Catalyst Layer
  - Pt/C + PTFE + Nafion®
  - 10 – 100 µm
- Micro-porous Layer
  - Carbon + PTFE
  - 10 – 100 µm
- Macro-porous Substrate
  - 290 – 400 µm

GDL
Catalyst on Membrane
Wilson, 1993[2,3]
> Enhanced interface bonding

- Micro-porous Layer
  - Carbon + PTFE
  - 10 – 100 µm
- Macro-porous Substrate
  - 290 – 400 µm

CATHODE is KEY

- **Proton Conductive Membrane**
  - ~30 µm

- **Catalyst Layer**
  - ~30 µm

- **Micro-porous Layer**
  - 10 – 100 µm

- **Macro-porous Carbon Substrate**
  - 290 – 400 µm

Gas Diffusion Electrode

Cathode Electrode
- Reaction Layer
- Oxygen Reduction

Gas Diffusion Layer
- Spatial distribution

Flow Field
Top-View Flow Fields

**Single serpentine**

**Series-sweep** (three channels)

**Triple-serpentine**
MEA Prepared + Cell Hardware → PEMFC

In-house Membrane

Catalyzed Membrane

Sprayed
A: Pt-Ru/C
C: Pt/C

+ 2 GDLs

Membrane Electrode Assembly

GOLD Plated Plates

ANODE
Counter Electrode (CE)
& Reference Electrode (RE)

CATHODE
Working Electrode (WE)

Anode Graphite Flow field

Cathode Graphite Flow field

Heater Pad
Fuel Cell Test Station → Polarization Curves

Apply Current (I) - SET
Measure Voltage (V) – OBTAIN
POWER (P) = I x V

Membrane Electrode Assembly

Anode Mass Flow Controller

Valve

H₂

Anode Humidifier

Anode Exit

Cathode Mass Flow Controller

Valve

O₂ or Air

Cathode Humidifier

Cathode Exit
Ex. Fuel Cell Polarization Curves
(Performance Curves)

- Theory Open Circuit Voltage – Max. Possible Voltage
- Experimental Open Circuit Voltage (no I drawn)
- Real = Experimental Voltage (I drawn)

Irreversibility

Current Density (mA/cm²)
Faraday’s Law

• Tells Amount of Charge Passed ~ Substance Reacted
• Used to Calculate Amount of Reactant Consumed

Mass consumed $\propto$ Current
$\propto$ Time Reacted
$\propto$ MW of Substance
$\propto$ Stoichiometry

$m = s \frac{M I t}{n F}$

Use to Calculate H$_2$, O$_2$ needed for each Current Density
Called “Stoichiometry Needed”
Thermodynamics

Behavior at “equilibrium”

~ Open Circuit Voltage (OCV)

Net reaction rate = zero

Predicts whether a reaction is feasible (spontaneous)
Kinetics

Reaction rate info. provided by kinetic equations

Important when I is drawn from Fuel Cell (non-equilibrium)
Kinetic loss is always there whenever there’s NET reaction

Tell How Fast Reaction Takes Place $\rightarrow$ Fast (Less Voltage Loss)
 Ionic Transport

H⁺ transport in polymer membrane electrolyte

Tells whether ionic transport is effective enough to not significantly add more losses – f (operating conditions)

CAN make “small” through design of membrane

![Graph showing cell voltage vs. current density](image-url)
Mass Transfer

Gas/Liquid Transport Information

Tell whether transport is effective enough for kinetics to take place w/o additional loss or not

Can make “negligible” through design of fuel cell components
In Summary

• Thermodynamics
  – Equilibrium (OCV only)
  – Will be that Voltage if RXN. = REVERSIBLE

• Kinetics
  – Loss whenever rxn. takes place
  – Always there (MOST loss)

• Ionic Transport
  – Loss whenever protons move through membrane
  – Can be “minimized”

• Mass-Transfer
  – Loss whenever reactants move into rxn sites in high demand
  – Can be “minimized”
PEM Fuel Cells
System Definition and Infrastructure for Mobile Applications
Diagram of reformate/air fuel cell “engine” utilizing liquid methanol as fuel.
Schematic of direct methanol fuel cell system.
(Courtesy: Los Alamos National Laboratory)
Low-cost PEM Fuel Cells

Items of cost reduction and targeted data

Membrane:
alternative membrane electrolyte \( \leq 20/m^2 \) (presently: $600/m^2)

System efficiency:
rated power at high cell voltage (0.75 V), low cathode pressure \((\leq 1.5 \text{ bar}_a)\)

Pt-loading:
decrease down to \(< 0.15 \text{ mg/cm}^2\) (at present: up to 4.0 mg/cm²)

Technical targets:
• stack costs \( \leq 30/\text{kW} \)
• high overall efficiency
• high power density

Construction materials:
coated stamped metal
(at present: machined graphite)

Concept of operation:
simplified operational concept
reduction of peripheral devices

Cell design:
simplification of construction,
capable for mass production
**Conceivable applications of PEM Fuel Cells**

**Specific Requirements**

<table>
<thead>
<tr>
<th></th>
<th>Mobile</th>
<th>Decentralized</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Preferred fuel</strong></td>
<td>liquid, i.e. gasoline</td>
<td>natural gas</td>
</tr>
<tr>
<td><strong>Fast start-up</strong></td>
<td>very important</td>
<td>less important</td>
</tr>
<tr>
<td><strong>Start at -30 °C</strong></td>
<td>very important</td>
<td>less important</td>
</tr>
<tr>
<td><strong>Rapid load changes</strong></td>
<td>important</td>
<td>less important</td>
</tr>
<tr>
<td><strong>System size</strong></td>
<td>important</td>
<td>less important</td>
</tr>
<tr>
<td><strong>Required life time</strong></td>
<td>&gt;3,000 h</td>
<td>&gt; 40,000 h</td>
</tr>
</tbody>
</table>

**Portable applications:**

- require simplest possible periphery
- distribution infrastructure for the fuel is essential
Work in Progress at UConn

- Optimization of MEAs
- Material Characterization
- Endurance Testing
- Scale-Up of MEAs
- Performance Characterization
- Short Stack Development

Composite membrane (based on Nafion® and solid proton conductor)
  - Nafion®-Teflon®-phosphotungstic acid (NTPA)
  - Nafion®-Teflon®-zirconium hydrogen phosphate (NTZP)
  - Nafion®-Zirconium hydrogen phosphate (NZP)
  - Nafion®-PVDF (Tri-layer, DMFC)

Catalyst layer:
  - Optimize Proton Conduction
  - Optimize Mass Transfer

Diffusion layer:
  - Enhance Gas Transfer
  - Optimize Hydrophilic/Hydrophobic Regions
**Laboratory Scale HTMEA**

5 cm² HTMEA

**Full-Size Membrane**

300 cm² HTMEA

17 Full-Size HTMEAs in a Stack ~1kW

**Single Cell Assembly**
SEM Images of MEAs

membrane

membrane
UConn Research in PEM Fuel Cells

- Methanol Oxidation Electrocatalysts
- CO Tolerance Electrocatalysts
- Hydrogen Purification Process (recent NSF Funding)
- Low Methanol Crossover Membranes
- High Temperature Membranes
- Membranes Needing No External Humidification
- Selective Oxidation Catalysts
- Reversible PEM Fuel Cells
- Biomass and Landfill Gas Fuel Processing
- Design of PEM FC Powered Toys