



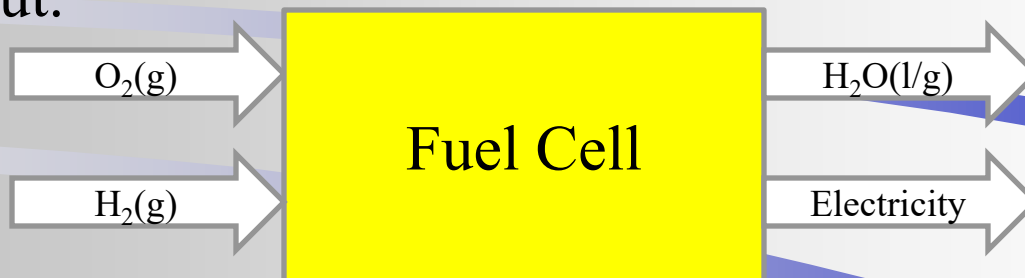
# Electrochemistry

CHEM 5390

# Fuel Cells

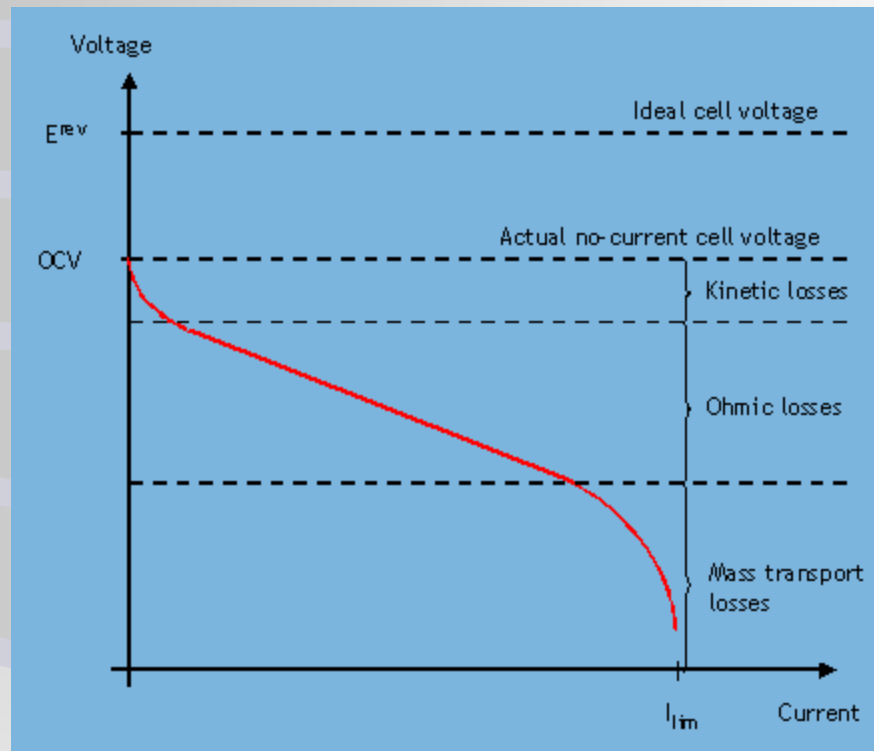
An electro-chemical energy conversion device

A “factory” that takes fuel as input and produces electricity as output.



Converts chemical energy → electricity without intermediate heat step.

# Fuel Cells



# Fuel Cells

There are five major types of fuel cells categorized according to their electrolyte.

- ▣ Phosphoric acid fuel cell (PAFC)
- ▣ Polymer electrolyte membrane fuel cell (PEMFC)
- ▣ Alkaline fuel cell (AFC)
- ▣ Molten carbonate fuel cell (MCFC)
- ▣ Solid oxide fuel cell (SOFC)

# Fuel Cells

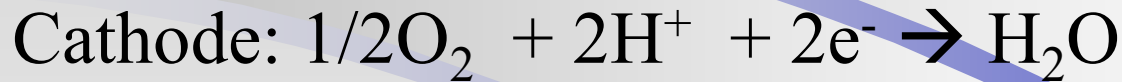
	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Polymer membrane	Liquid $\text{H}_3\text{PO}_4$	Liquid KOH	Molten carbonate	Ceramic
Charge carrier	$\text{H}^+$	$\text{H}^+$	$\text{OH}^-$	$\text{CO}_3^{2-}$	$\text{O}^{2-}$
Operating Temperature	80°C	200°C	60-220°C	650°C	600-1000°C
Catalyst	Pt	Pt	Pt	Ni	Perovskites
Cell components	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic based
Fuel compatibility	$\text{H}_2$ , methanol	$\text{H}_2$	$\text{H}_2$	$\text{H}_2$ , $\text{CH}_4$	$\text{H}_2$ , $\text{CH}_4$ , CO

# Fuel Cells

## Polymer (Proton) Electrolyte Membrane (PEM) Fuel Cells

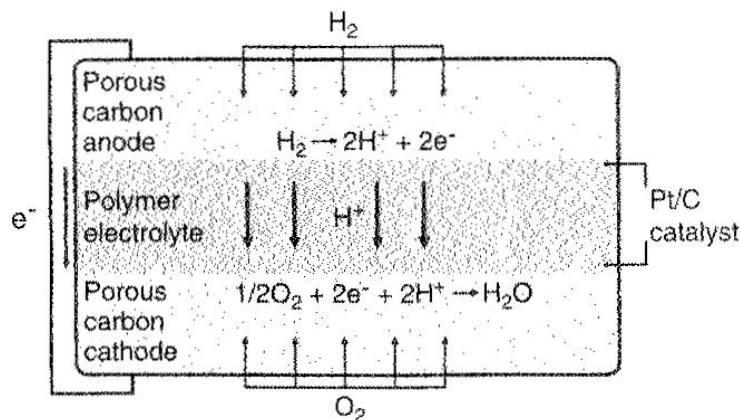
Polymer electrolyte membrane (PEM) fuel cells are also called proton exchange membrane fuel cells.

The PEMFC is constructed from a proton-conducting polymer electrolyte membrane, usually a perfluorinated sulfonic acid polymer.



# Fuel Cells

## PEM Fuel Cells



**Figure 8.3.** Schematic of  $H_2$ — $O_2$  PEMFC. Porous carbon electrodes (often made from carbon paper or carbon cloth) are used for both the anode and the cathode. The electrodes are coated with a Pt catalyst mixture. Water is produced at the cathode.

PEM fuel cells use a solid polymer in the form of a thin, permeable sheet as an electrolyte and porous carbon electrodes containing a platinum catalyst.

They need only hydrogen, oxygen from the air, and water to operate.

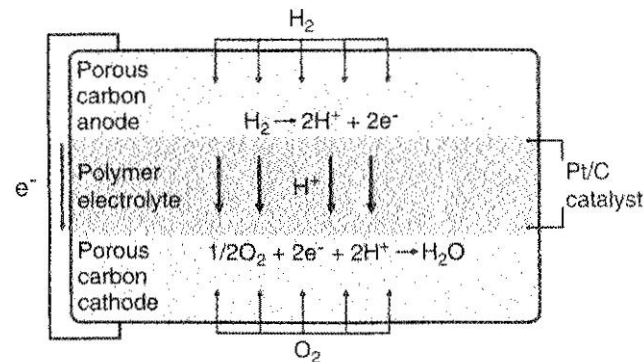
# Fuel Cells

## PEM Fuel Cells

The polymer membrane

- thin (20-200  $\mu\text{m}$ )
- flexible
- transparent

It is coated on either side with a thin layer of Pt-based catalyst and porous carbon electrode support material.



**Figure 8.3.** Schematic of  $\text{H}_2$ — $\text{O}_2$  PEMFC. Porous carbon electrodes (often made from carbon paper or carbon cloth) are used for both the anode and the cathode. The electrodes are coated with a Pt catalyst mixture. Water is produced at the cathode.

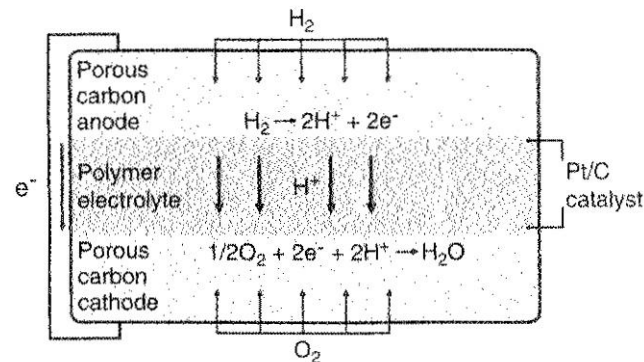
# Fuel Cells

## PEM Fuel Cells

This sandwich structure is referred to as a membrane electrode assembly (MEA).

The entire MEA is less than 1 mm thick. Since the membrane must be hydrated, the operating temperature is limited to 90°C or lower.

Low operating temperatures necessitate the need for Pt-based catalyst.



**Figure 8.3.** Schematic of H<sub>2</sub>—O<sub>2</sub> PEMFC. Porous carbon electrodes (often made from carbon paper or carbon cloth) are used for both the anode and the cathode. The electrodes are coated with a Pt catalyst mixture. Water is produced at the cathode.

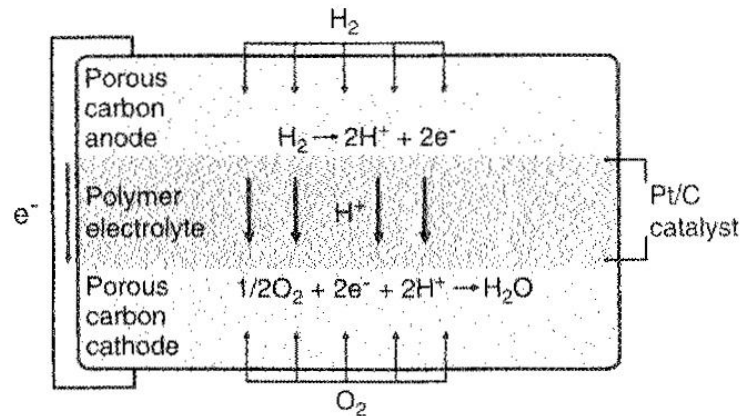
# Fuel Cells

## PEM Fuel Cells

### Fuel

- H<sub>2</sub> (preferred)
- liquid methanol
- formic acid

The direct methanol fuel cell (DMFC) is a PEMFC that directly oxidizes CH<sub>3</sub>OH to provide electricity. Since 2005 there has been an upturn in research on DMFCs.



**Figure 8.3.** Schematic of H<sub>2</sub>—O<sub>2</sub> PEMFC. Porous carbon electrodes (often made from carbon paper or carbon cloth) are used for both the anode and the cathode. The electrodes are coated with a Pt catalyst mixture. Water is produced at the cathode.

# Fuel Cells

## Polymer (Proton) Electrolyte Membrane (PEM) Fuel Cells

PEM fuel cells are used primarily for transportation applications and some stationary applications.

Example - a Honda FCX powered by PEMFCs

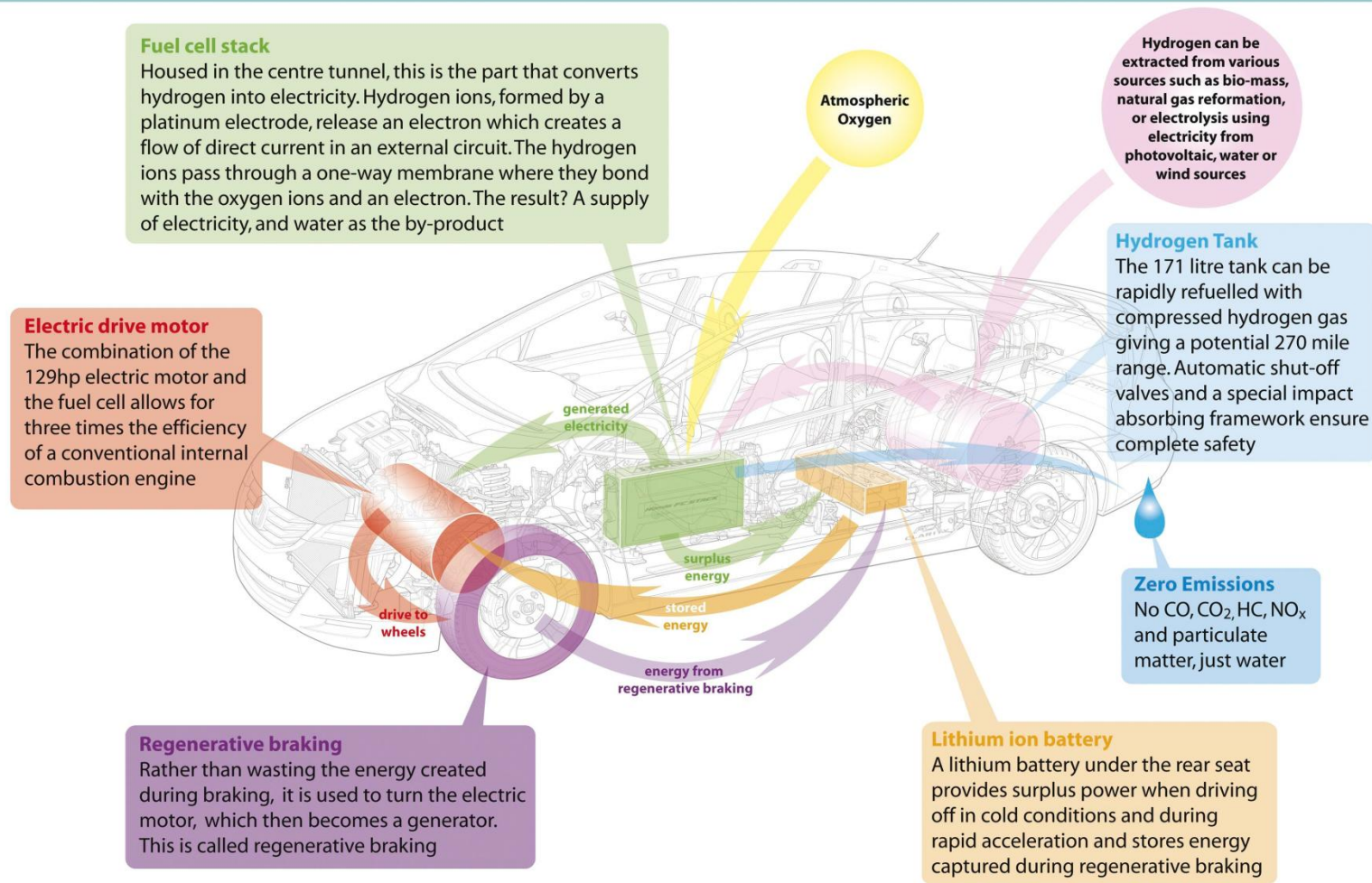


# Fuel Cells

FCX  
CLARITY

## How it works

HONDA  
The Power of Dreams



# Fuel Cells

## Polymer Electrolyte Membrane (PEM) Fuel Cells

### Advantages:

Deliver high-power density and offer the advantages of low weight and volume, compared with other fuel cells. (highest of fuel cell classes)

Low-temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability.

Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

The solid, flexible electrolyte will not leak or crack, and these cells operate at a low enough temperature to make them suitable for homes and cars. (portable applications)

# Fuel Cells

## Polymer Electrolyte Membrane (PEM) Fuel Cells

### Disadvantages:

Fuels must be purified, and a platinum catalyst is used on both sides of the membrane, raising costs.

The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers are currently exploring platinum/ruthenium catalysts that are more resistant to CO. Also S is a problem.

Polymer membrane and ancillary components are expensive.

Active water management is often required.

# Fuel Cells

## **Polymer Electrolyte Membrane (PEM) Fuel Cells**

### Disadvantages:

A significant barrier to using these fuel cells in vehicles is hydrogen storage.

Most fuel cell vehicles (FCVs) powered by pure hydrogen must store the hydrogen on-board as a compressed gas in pressurized tanks.

Due to the low-energy density of hydrogen, it is difficult to store enough hydrogen on-board to allow vehicles to travel the same distance as gasoline-powered vehicles before refueling, typically 300–400 miles.

# Fuel Cells

## Polymer Electrolyte Membrane (PEM) Fuel Cells

Disadvantages:

- Can use higher-density liquid fuels
- methanol
- ethanol
- natural gas
- liquefied petroleum gas
- gasoline

But must have an on-board fuel processor to reform the methanol to hydrogen.

This requirement increases costs and maintenance.

The reformer also releases carbon dioxide (a greenhouse gas), though less than that emitted from current gasoline-powered engines.

# Fuel Cells

## PEMFC Electrolyte Materials

Electrolyte materials must

- Conduct ions, but not electrons, must possess high ionic conductivity
- Must be gas impermeable to prevent anode and cathode gasses from mixing
- Must be ultra thin to minimize resistance
- Must have good mechanical properties

Most electrolytes are based on thin polymeric membranes that conduct  $H^+$  ions and many rely on water-based vehicle mechanisms.

# Fuel Cells

## PEMFC Electrolyte Materials

Nafion

Most popular electrolyte for PEM and DMFCs

Nafion has a teflon backbone structure with sulfonic acid functional groups.

The backbone provides mechanical strength while the functional groups provide charge sites for proton transport.

Must hydrate Nafion to maintain conductivity.

Nafion is expensive ( $> \$400/\text{m}^2$ )

# Fuel Cells

## PEMFC Electrolyte Materials

### Sulfonated Hydrocarbon Polymers

There are several advantages to using hydrocarbon polymers over perfluorinated polymers:

- more diverse and less expensive
- hydrocarbon polymers containing polar groups have high water uptake over a wide temperature range
- more easily recycled by conventional methods

#### Disadvantages

- less stable
- lower ionic conductivity

# Fuel Cells

## PEMFC Electrolyte Materials

Most common Sulfonated Hydrocarbon Polymers is polyaryletherketone = PEEK

PEEK polymers are chemically and thermally stable. Depending on the ratios of ether to ketone are known as PEEK, PEEKK, PEK, and PEKKEK – but for shorthand – PEEK.

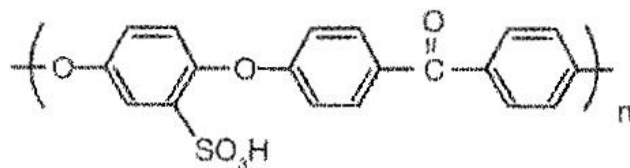


Figure 9.1. General chemical structure of sulfonated PEEK.

These polymers are also typically sulfonated to provide proton conductivity – but are cheaper to produce.

Must go above 150 °C to compete with Nafion ionic conductivities.

# Fuel Cells

## PEMFC Electrolyte Materials

### Phosphoric Acid Doped Polybenzimidazole (PBI)

Has a proton conduction mechanism that does not require water and so can operate above 100°C.

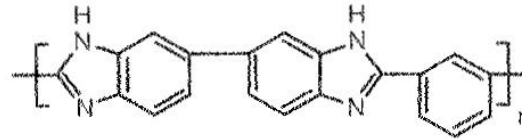


Figure 9.2. Chemical structure of Poly-2,2'-m-(phenylene)-5,5'-bibenzimidazole, commonly called polybenzimidazole, or PBI.

PBI is similar to PEEK but instead of sulfonating the structure, ionic conductivity is created by doping with a strong acid (typically  $\text{H}_3\text{PO}_4$ ).

PBI is thermally stable, has high mechanical strength, can be used at 200°C, and is less expensive than Nafion.

PBI has durability issues (acid-leaching), oxidative degeneration problems, slow kinetics of  $\text{O}_2$  reduction, and difficult to blend with Pt catalyst.

# Fuel Cells

## PEMFC Electrode/Catalyst Materials

Electrodes must provide high electrical conductivity and high porosity as well as high catalytic activity.

Since PEMFCs use Pt catalyst - try to use as little as possible.

Electrodes typically fabricated as dual-layers

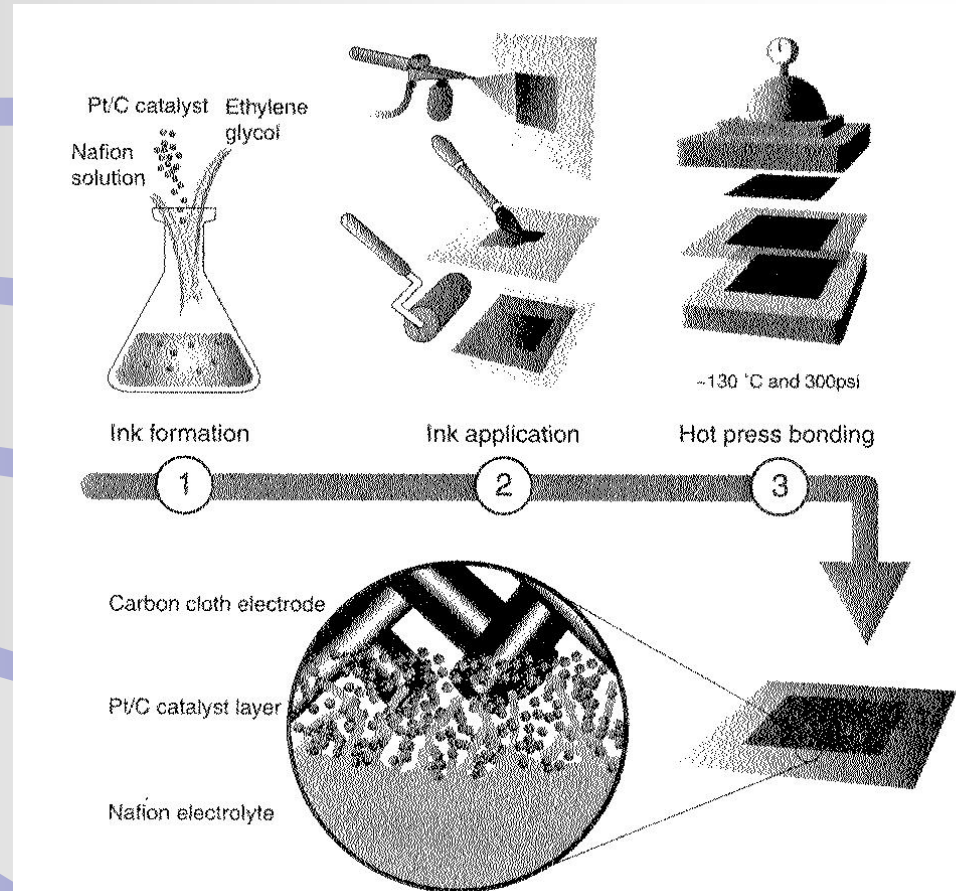
- A thin (10-30  $\mu\text{m}$ ) catalyst Pt/C layer and electrolyte on
- A thicker (100-500  $\mu\text{m}$ ) inexpensive, porous, and electrically conductive electrode layer

Dual layer maximizes catalytic activity, gas access, product removal, and electrical conductivity while minimizing cost.

# Fuel Cells

## PEMFC Electrode/ Catalyst Materials

1. A catalyst “ink” is formulated containing Pt/C material mixed with 5% Nafion, water, and glycerol.
2. The ink is deposited onto both sides of an electrolyte membrane by spray-deposition, painting, or screen printing.

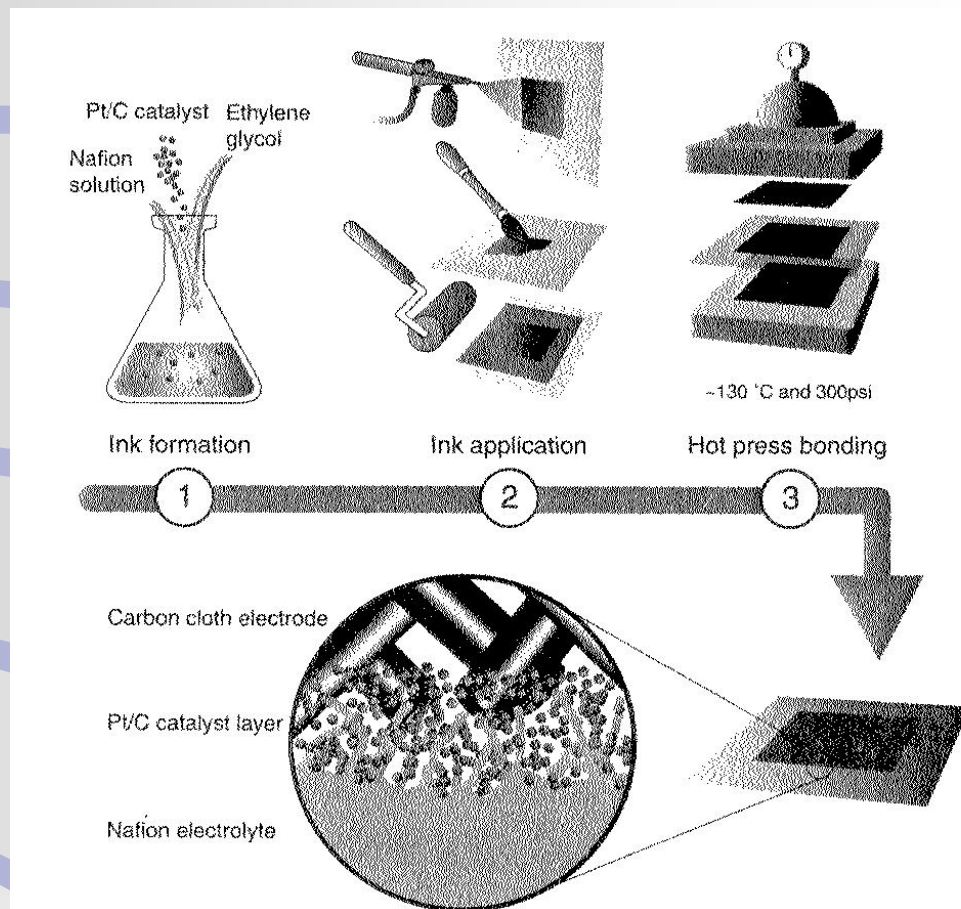


**Figure 9.3.** The typical PEMFC MEA fabrication process (1) Pt/C catalysts are mixed with water, 5% Nafion solution, and ethylene glycol to form a catalyst ink. (2) The catalyst ink is applied to the electrolyte membrane using one of several techniques. (3) Carbon-cloth or carbon paper electrodes are hot-press bonded onto either side of the catalyst-coated membrane. Detail drawing shows the desired final MEA microstructure.

# Fuel Cells

## PEMFC Electrode/ Catalyst Materials

3. Electrode attachment: porous carbon-cloth or carbon paper electrodes are bonded to both sides of the membrane via a hot-press embossing ( $\sim 120\text{-}140\text{ }^{\circ}\text{C}$ ). These porous electrodes protect the catalyst and hold it in place.



**Figure 9.3.** The typical PEMFC MEA fabrication process (1) Pt/C catalysts are mixed with water, 5% Nafion solution, and ethylene glycol to form a catalyst ink. (2) The catalyst ink is applied to the electrolyte membrane using one of several techniques. (3) Carbon-cloth or carbon paper electrodes are hot-press bonded onto either side of the catalyst-coated membrane. Detail drawing shows the desired final MEA microstructure.

# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### Dual-Layer (Gas-diffusion layer/catalyst layer) approach

Catalyst layers are expensive so mix with high surface area carbon powders (Vulcan XC-72) and immobilize catalyst on carbon support.

#### Catalyst Layer requirements

- High catalytic activity
- High surface area/high density of TPBs
- Percolating electrical and ionic conductivity
- High stability/corrosion resistance
- Excellent poison/impurity tolerance
- Minimal degradation
- Low cost

# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### Dual-Layer (Gas-diffusion layer/catalyst layer) approach

Gas diffusion layer (GDL) plays a significant role in the removal of water.

#### Gas Diffusion Layer requirements

- High electrical conductivity
- High gas permeability
- High stability/corrosion
- Facilitate water removal
- Good mechanical properties
- Low cost

# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### GDL Electrode Materials

Most PEMFCs use carbon-fiber based GDL materials.

Most common are carbon fiber cloths (woven) and carbon fiber paper (nonwoven).

Carbon fibers are used because they have good electrical conductivity, high porosity (>70%), excellent stability, corrosion resistance, and good mechanical properties.

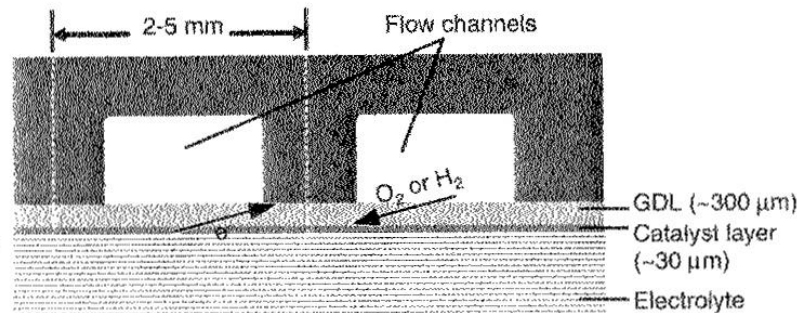
# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### GDL Electrode Materials

Carbon-fiber materials exhibit anisotropy in electrical conductivity.

In-plane electrical conductivity is higher than through plane by 10-50 times.

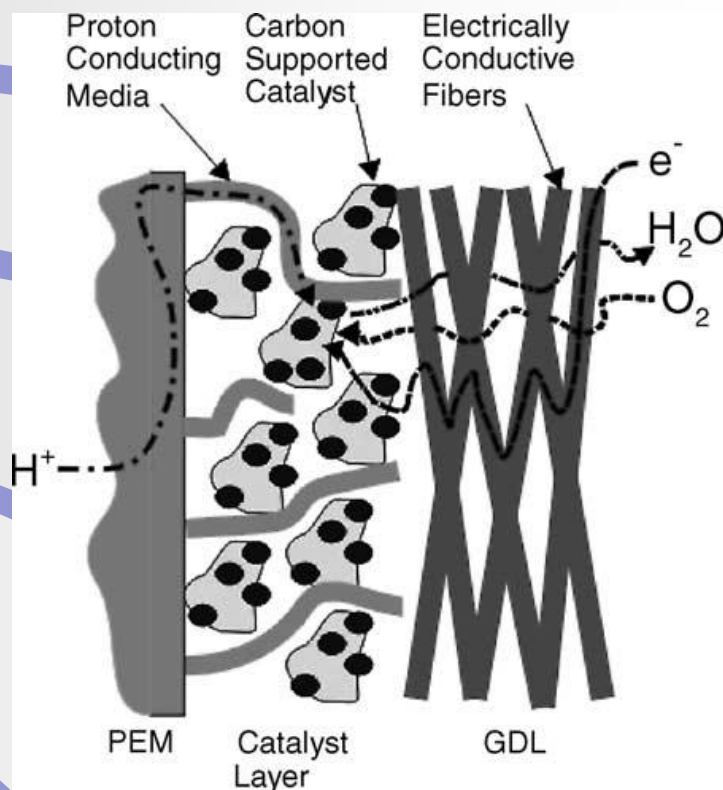
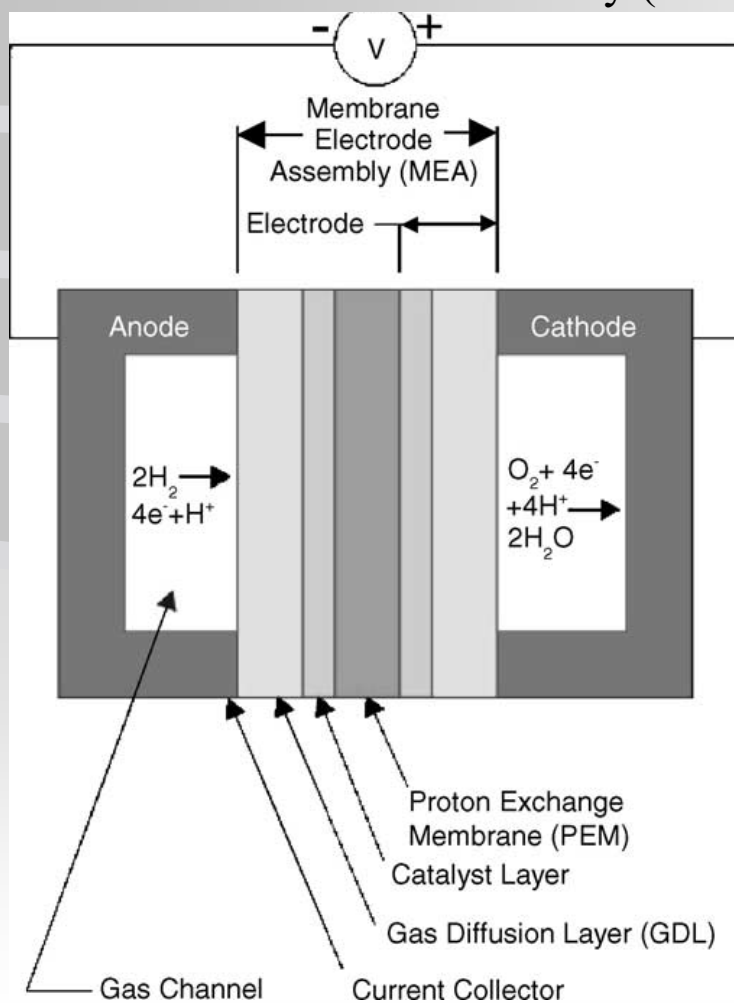


**Figure 9.4.** Gas and electron transport within the fuel cell GDL. In the GDL, lateral (in-plane) transport is more important than vertical (out-of-plane) transport. For example, electrons generated under the middle of a fuel cell flow channel must be transported laterally 1-2 mm, but must only transport  $\sim 300 \mu\text{m}$  vertically to reach the current collecting rib structures. Similarly, gas from the flow channel must transport  $\sim 1-2 \text{ mm}$  laterally, but only  $\sim 300 \mu\text{m}$  vertically to reach reaction zones under the channel ribs.

# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### Membrane electrode Assembly (MEA)



# Fuel Cells

## PEMFC Electrode/Catalyst Materials

### GDL Electrode Materials

#### Carbon Cloth

Produced using a textile process that weaves carbon fiber filaments into a thin, flexible, fabric material.

#### Carbon Paper

Produced by bonding a random “haystack” arrangement of carbon fibers into a thin, stiff, lightweight sheet. Binding material is added to carbonized resin fill some of the pores between fibers.

#### Hydrophobic Treatment

If water accumulates on the GDL layers, it will block supply and deteriorate performance. To prevent water accumulation GDL materials are treated with PTFE (Teflon).

# Fuel Cells

## PEMFC Anode Catalyst

Platinum (for H<sub>2</sub> fuel cells)

Pt facilitates the hydrogen oxidation reaction (HOR) due to the optimal bonding affinity between Pt and H<sub>2</sub>.

Metals like W, Mo, Nb, and Ta form too strong a bond with H<sub>2</sub> giving a stable hydride phase.

Metals like Pb, Sn, Zn, Ag, Cu, and Au form too weak a bond.

Typical Pt loadings in Pt/C is around 0.05 mg Pt/cm<sup>2</sup>.

# Fuel Cells

## PEMFC Anode Catalyst

### Platinum Alloys (for Direct Alcohol Fuel Cells)

These fuel cells tend to form CO which poisons pure Pt by irreversibly absorbing on the Pt.

Pt is alloyed with Ru, Sn, W, or Re to improve CO tolerance.

Ru creates new absorption sites to bind  $\text{OH}_{\text{abs}}$  species which reacts with bound CO to produce  $\text{CO}_2$  and  $\text{H}^+$ .

While Pt/Ru works well for methanol oxidation it is ineffective for ethanol oxidation – use Pt/Sn.

# Fuel Cells

## PEMFC Cathode Catalyst

Pt facilitates the oxygen reduction reaction (ORR), however it is less active for the ORR meaning much higher loading.

Need to develop new Pt-alloy catalyst or Pt-free catalyst.

A number of Pt-alloys have been investigated: Pt-Ni, Pt-Cr, Pt-Co, Pt-Mn, Pt-Fe, and Pt-Ti

so far  $\text{Pt}_3\text{Co}$  and  $\text{Pt}_3\text{Cr}$  have shown the most promise enhancing ORR up to 2-4 times over pure Pt.

There are problems with alloys:

- Harder to deploy as high surface area (small particle size) dispersions on carbon supports
- Co and Cr can poison PEMFC if leached from catalyst
- Are more susceptible to accelerated degradation, corrosion, and deactivation

# Fuel Cells

## PEMFC Cathode Catalyst

Pt-free catalyst are attractive because of the cost.

However it is difficult to find a stable replacement that can withstand the harsh (acidic) environment.

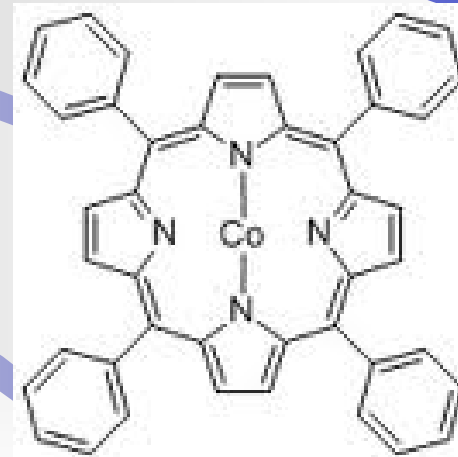
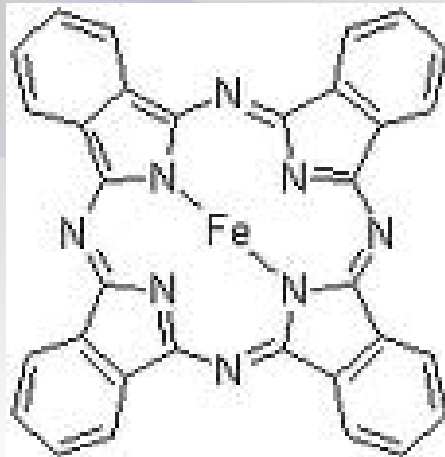
However none of the Pt-free catalyst have achieved the activity of Pt and tend to degrade.

# Fuel Cells

## PEMFC Cathode Catalyst

Candidates include:

- Metal macrocycles – typically Co or Fe stabilized by nitrogen atoms bound into an aromatic or graphite like carbon structure.
- Heteropoly acid catalyst (HPA) – large inorganic oxides such as V and Fe substituted HPAs
- Doped carbon – carbon doped with Fe, N, B or other elements

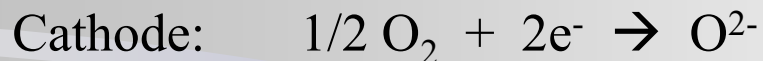


# Fuel Cells

## Solid Oxide Fuel Cells

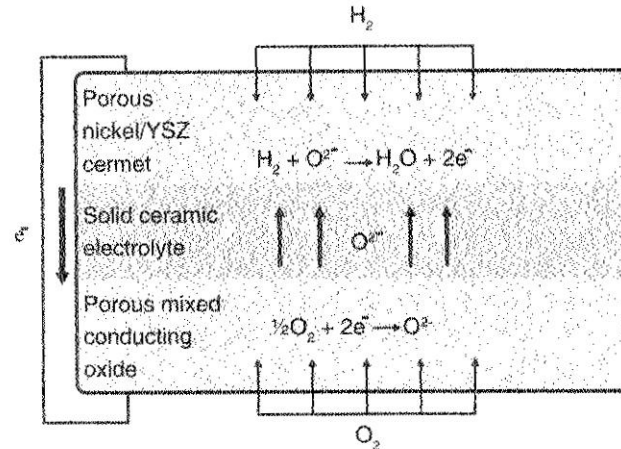
SOFC uses a solid ceramic electrolyte – the most popular is yttria-stabilized zirconia (YSZ), which is an oxygen ion (oxygen vacancy) conductor.

Since  $O^{2-}$  is the mobile conductor:



# Fuel Cells

## Solid Oxide Fuel Cells



**Figure 8.9.** Schematic of H<sub>2</sub>-O<sub>2</sub> SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperatures. Water is produced at the anode.

In SOFC, water is produced at the anode, rather than the cathode, as in PEMFC.

The anode and cathode materials are different.

The fuel electrode must be able to withstand the highly reducing high-temperature environment of the anode, while the air electrode must be able to withstand the highly oxidizing high temperature environment of the cathode.

# Fuel Cells

## Solid Oxide Fuel Cells

Most common anode material is a Ni-YSZ cermet.

The nickel provides conductivity and catalytic activity.

The YSZ adds ion conductivity, thermal expansion compatibility, and mechanical stability and maintains the high porosity and surface area of the anode structure.

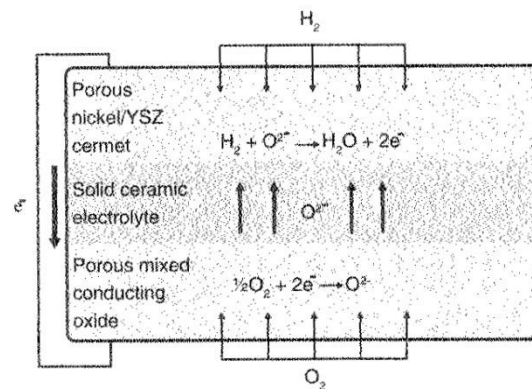


Figure 8.9. Schematic of  $H_2$ - $O_2$  SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperatures. Water is produced at the anode.

# Fuel Cells

## Solid Oxide Fuel Cells

Most common cathode materials is a mixed ion-conducting and electronically conducting (MIEC) ceramic material.

Typical cathode materials include:

- strontium-doped lanthanum manganite (LSM)  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$
- lanthanum-strontium ferrite (LSF)  $\text{La}_{0.80}\text{Sr}_{0.20}\text{FeO}_3$
- lanthanum-strontium cobaltite (LSC)
- lanthanum strontium cobalt iron oxide  $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_3$

These materials show good oxidation resistance and high catalytic activity.

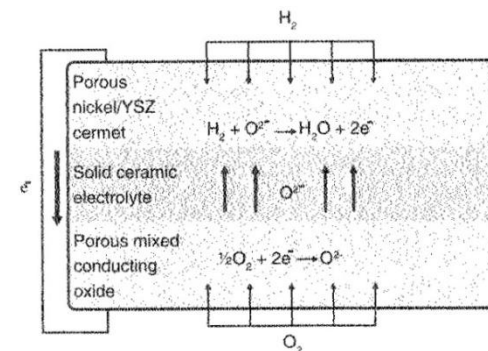


Figure 8.9. Schematic of  $\text{H}_2\text{-O}_2$  SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperatures. Water is produced at the anode.

# Fuel Cells

## Solid Oxide Fuel Cells

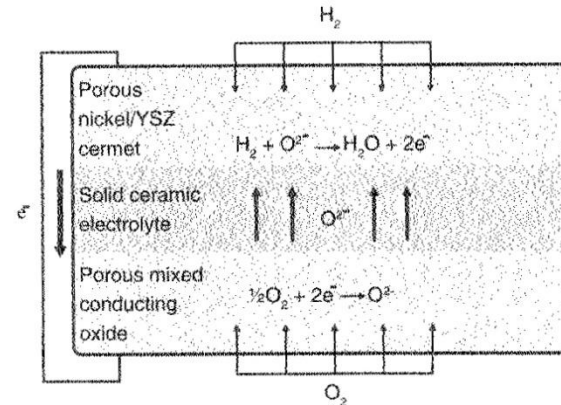


Figure 8.9. Schematic of H<sub>2</sub>-O<sub>2</sub> SOFC. The ceramic electrolyte is solid state. A nickel-YSZ cermet anode and a mixed conducting ceramic cathode provide the required thermal, mechanical, and catalytic properties at high SOFC operating temperatures. Water is produced at the anode.

The operating temperatures are between 600-1000°C for SOFCs.

Scientists are currently exploring the potential for developing lower-temperature SOFCs operating 400-700°C that have fewer durability problems and cost less.

Efficiency is about 60 percent however in applications designed to capture and utilize the system's waste heat (co-generation), overall fuel use efficiencies could top 80%–85%.

Cells output is up to 100 kW.

# Fuel Cells

## **Solid Oxide** fuel cells (SOFC)

### Advantages:

High-temperature operation removes the need for precious-metal catalyst, thereby reducing cost.

At such high temperatures a reformer is not required to extract hydrogen from the fuel, and waste heat can be recycled to make additional electricity.

SOFCs are also the most sulfur-resistant fuel cell type; they can tolerate several orders of magnitude more of sulfur than other cell types. In addition, they are not poisoned by carbon monoxide (CO), which can even be used as fuel. This property allows SOFCs to use gases made from coal. (fuel flexibility)

High-quality waste heat for cogeneration applications.

Relatively high power density.

# Fuel Cells

## **Solid Oxide** fuel cells (SOFC)

### Disadvantages:

High-temperature operation has disadvantages.

It results in a slow startup and requires significant thermal shielding to retain heat and protect personnel, which may be acceptable for utility applications but not for transportation and small portable applications.

The high operating temperatures also place stringent durability requirements on materials. The development of low-cost materials with high durability at cell operating temperatures is the key technical challenge facing this technology.

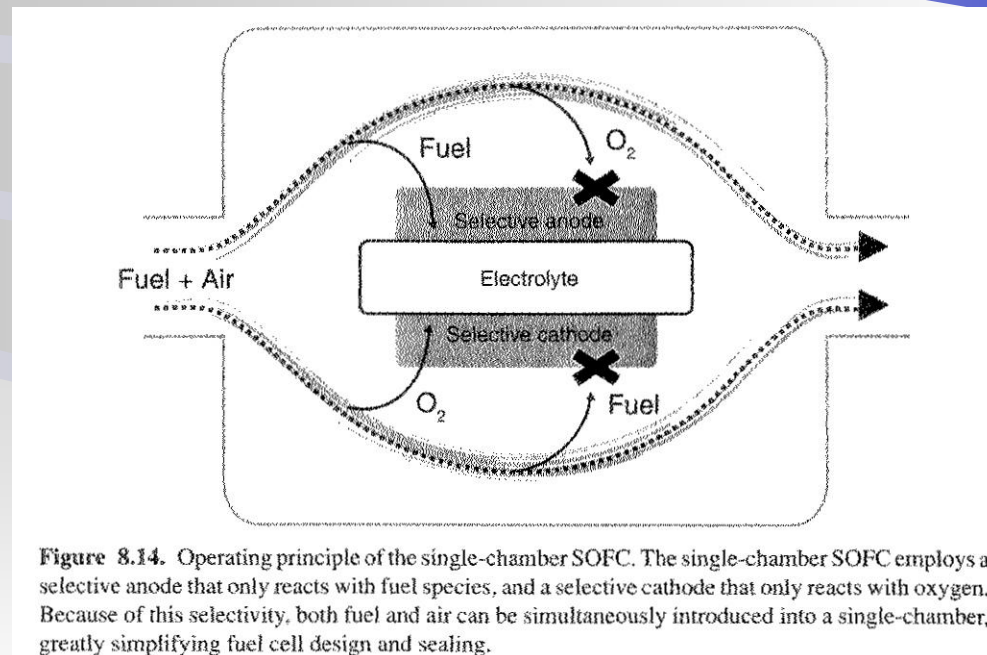
While solid electrolytes cannot leak, they can crack.

Relatively expensive components/fabrication.

# Fuel Cells

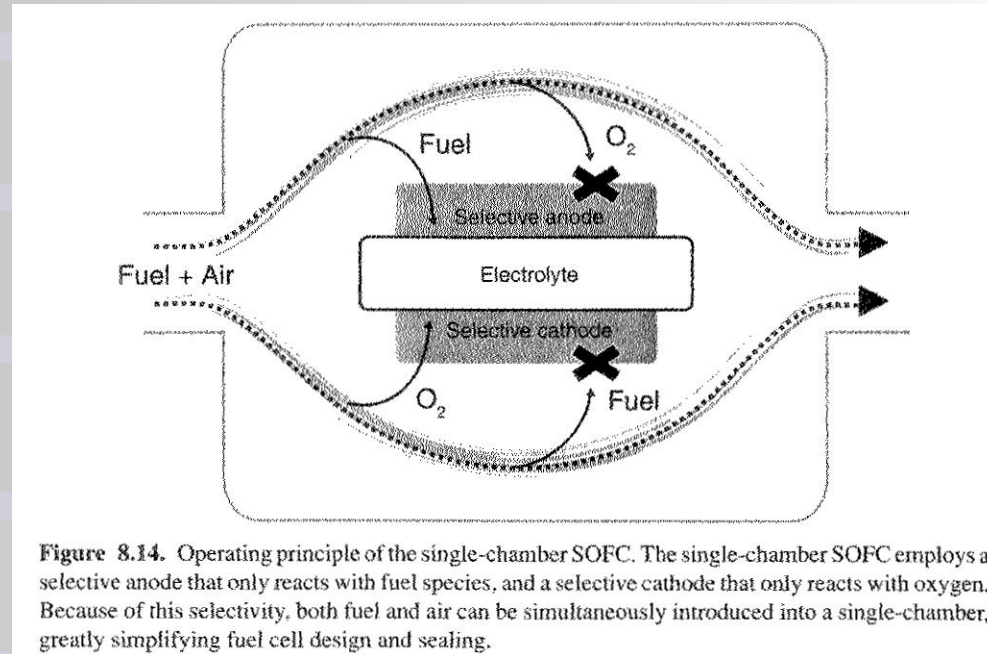
## Single Chamber SOFC

The single chamber SOFC is a type of solid oxide fuel cell that is designed to operate in a single chamber where both the fuel and air are supplied in combination.



# Fuel Cells

## Single Chamber SOFC



For the single channel to work, highly selective anode and cathodes must be used.

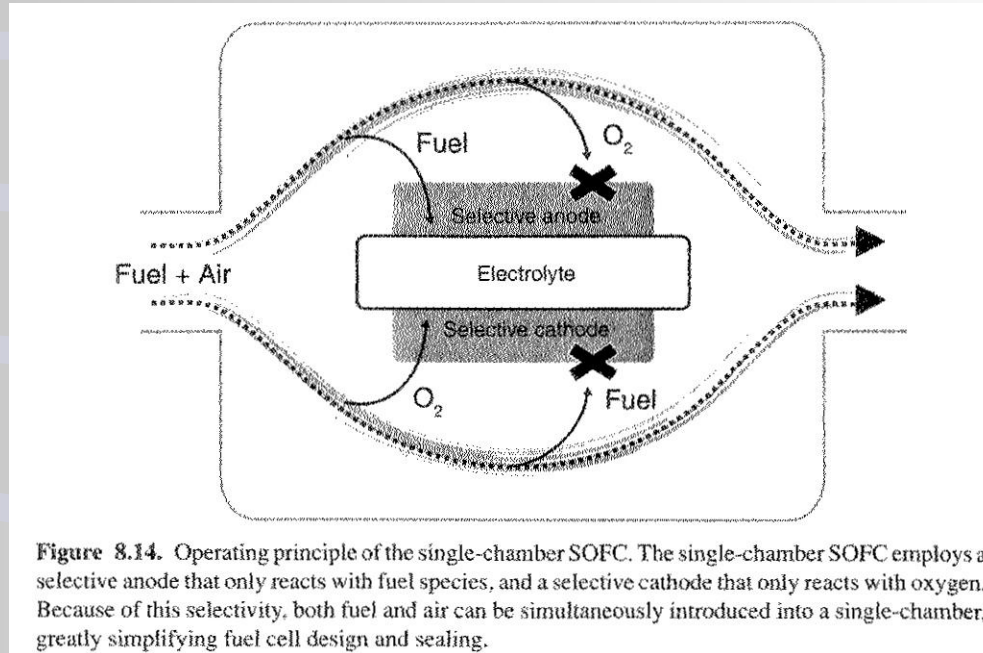
The anode materials must be chosen that only oxidizes fuel (and ignore oxygen) while the cathode materials must be chosen that only reduces oxygen and ignores fuel.

Pt cannot be used, since Pt catalyzes both the oxidation of fuel and reduction of oxygen.

Also Ni-YSZ and LSM are not selective enough.

# Fuel Cells

## Single Chamber SOFC



Some selective electrodes that have been developed are:

Ni-GDC (GDC = gadolinium-doped ceria) cermets for the anode and  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$  (SSC) for the cathode.

# Fuel Cells

## Single Chamber SOFC

### Advantages:

- Design is simple
- Requires no high temperature seals
- Electrolyte does not have to be gas-tight
- Size reduction

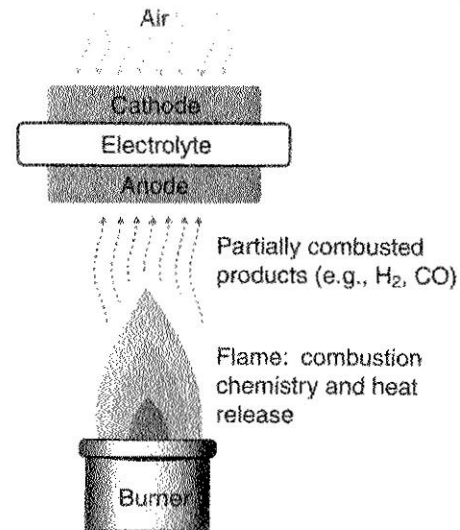
### Disadvantages:

- Risk of fuel/air mixture explosion is high
  - Must use very dilute mixtures (4%)
  - Decreases performance
- Electrodes are not 100% selective leading to parasitic reactions
  - Decreases efficiency

# Fuel Cells

## Direct Flame SOFC

Use an open flame  
with a SOFC



**Figure 8.15.** Schematic illustration of the direct flame fuel cell. A direct flame fuel cell is designed to operate in a “zero-chamber” mode, where the anode side is exposed to a flame combustion source, which provides both heat and partially combusted fuel species, while the cathode faces the ambient air.

A fuel rich flame is placed a few mm away from the anode.  
The cathode is exposed to ambient air.

# Fuel Cells

## SOFC Electrolyte Materials

Ion conductivity in ceramic oxide electrolytes is below that of most polymeric proton conductors. To obtain high ion conductivity must operate at temperatures above 700-800 °C.

Fluorite crystal structure electrolyte materials include YSZ and GDC.

YSZ (yttria-stabilized zirconia) is most common since it has excellent chemical stability and inertness. Also has one of the highest fracture toughness values of all metal oxides. YSZ has good ionic conductivity and little or no electronic conductivity.

GDC (gadolinia-doped ceria) has higher ionic conductivity than YSZ but has significant electronic conductivity under reducing conditions.

Other electrolyte materials include doped-perovskites.

# Fuel Cells

## SOFC Electrolyte Materials

Ion conductivity in ceramic oxide electrolytes is below that of most polymeric proton conductors. To obtain high ion conductivity must operate at temperatures above 700-800 °C.

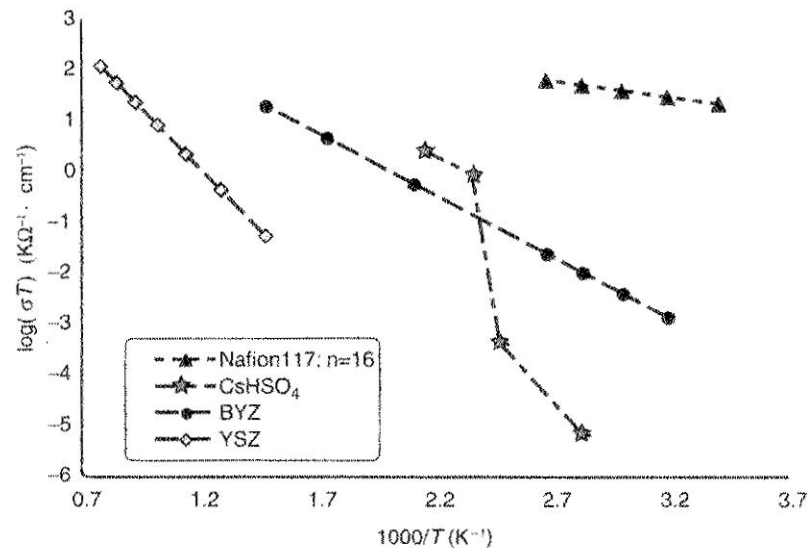


Figure 9.5. Conductivity of a proton conducting polymer (Nafion), a solid acid (CsH<sub>2</sub>O<sub>4</sub>), an oxide ion conductor (YSZ), and a proton-conducting oxide (BZY) as a function of  $1/T$ .

# Fuel Cells

## SOFC Electrolyte Materials

### Yttria-Stabilized Zirconia (YSZ)

Created by doping  $\text{ZrO}_2$  with 8%  $\text{Y}_2\text{O}_3$ . The fluorite crystal structure of the zirconia host is retained. Two zirconium cations ( $\text{Zr}^{4+}$ ) are replaced by two yttrium cations ( $\text{Y}^{3+}$ ) producing one empty oxygen site ( $\text{O}^{2-}$ ) to maintain charge balance. This leads to significant conductivity. Conductivity peaks at 6-8%  $\text{Y}_2\text{O}_3$ .

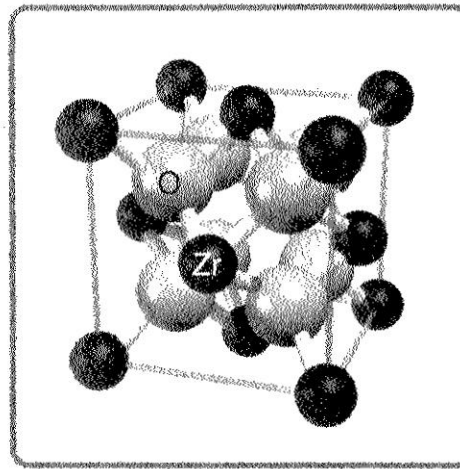


Figure 9.6. The fluorite crystal structure exhibited by stabilized zirconia and by doped ceria.

# Fuel Cells

## SOFC Electrolyte Materials

### Doped Ceria

Obtained by doping ceria ( $\text{CeO}_2$ ) with a second lanthanide metal to give  $\text{Ce}_{1-\delta}(\text{Ln})_{\delta}\text{O}_{2-1/2\delta}$

These doped structure also have the fluorite structure.

Doped ceria has higher conductivity than YSZ and the most common dopants are Sm (SDC) or Gd (GDC) (10-20%)

However under reducing conditions,  $\text{Ce}^{4+}$  is partially reduced to  $\text{Ce}^{3+}$ , which induces n-type electronic conductivity – also the lattice parameter will increase leading to mechanical failure.

# Fuel Cells

## SOFC Electrolyte Materials

Ceria

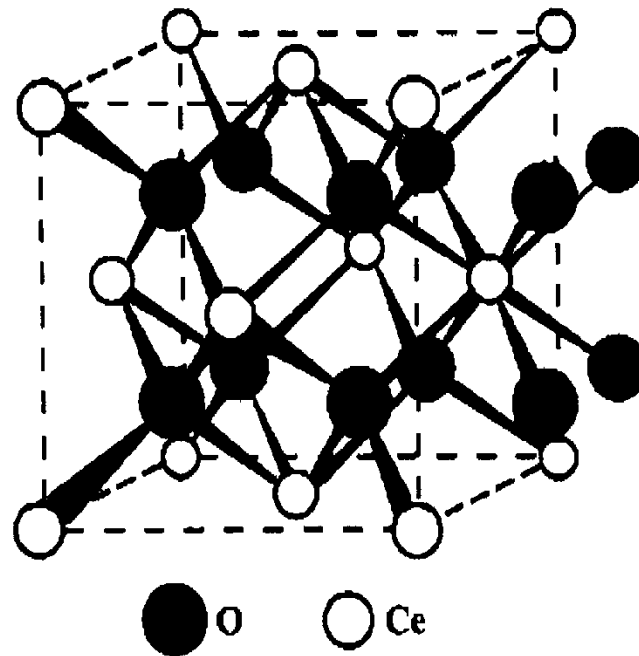


FIG. 1. The fcc cell of CeO<sub>2</sub> with the fluorite structure.

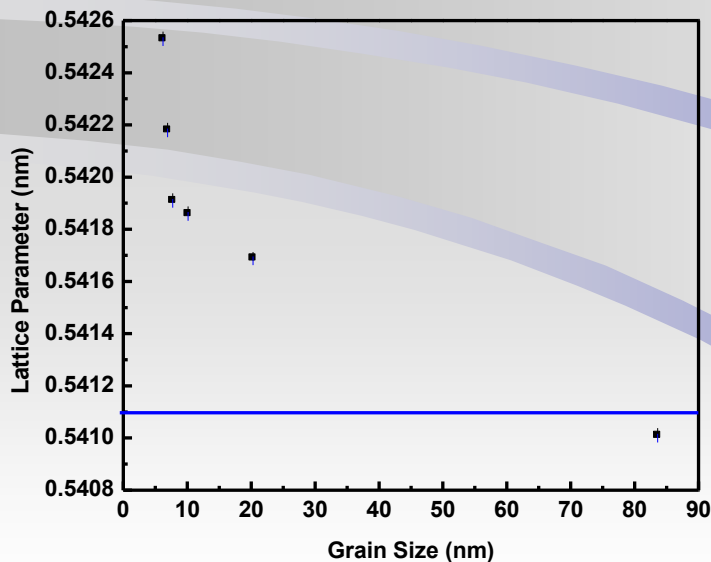
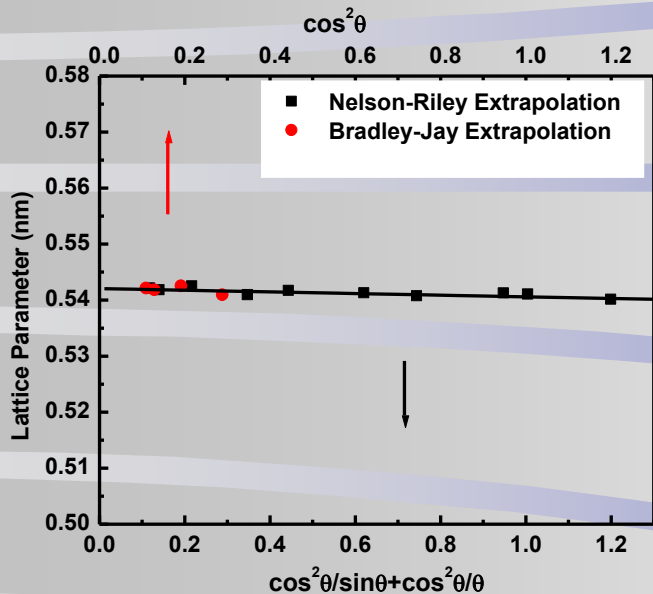
# Fuel Cells

## Lattice Relaxation of Nanocrystalline Cerium Oxide

Precise calculated lattice parameter of “green” powdery (6.22 nm) cerium oxide is 0.54268, 0.54264 and 0.54253 nm using Cohen’s, B-J, and N-R method, respectively.

B-J and N-R extrapolations are shown on the left

Lattice parameter increases with decreasing particle size of cerium oxide. Blue line represents the theoretical lattice parameter for stoichiometric FCC  $\text{CeO}_2$ .



# Fuel Cells

Estimation of Ce<sup>3+</sup> percentage and oxygen vacancies in electrosynthesized nanosized CeO<sub>y</sub>

Grain Size (nm)	Lattice Parameter (nm)	Ce <sup>3+</sup> / (Ce <sup>4+</sup> + Ce <sup>3+</sup> ) (%)		Oxygen Vacancies (%)		y in CeO <sub>y</sub>	
		<i>M's</i>	<i>T's</i>	<i>M's</i>	<i>T's</i>	<i>M's</i>	<i>T's</i>
6.21752	0.54253	5.787	7.418	2.8935	3.7091	1.9710	1.9629
6.91599	0.54218	4.457	5.710	2.2285	2.8551	1.9777	1.9714
7.72579	0.54191	3.429	4.392	1.7145	2.1962	1.9829	1.9780
10.10909	0.54186	3.238	4.148	1.6190	2.0742	1.9838	1.9793
20.30101	0.54169	2.591	3.319	1.2955	1.6593	1.9870	1.9834

Note: *M's* refers the results calculated using the method established by McBride and colleagues. *T's* refers the results calculated using the method suggested by Tsunekawa and colleagues. Grain sizes and lattice parameters are measured by XRD.

# Fuel Cells

## Transport in flow structures: Convective Transport

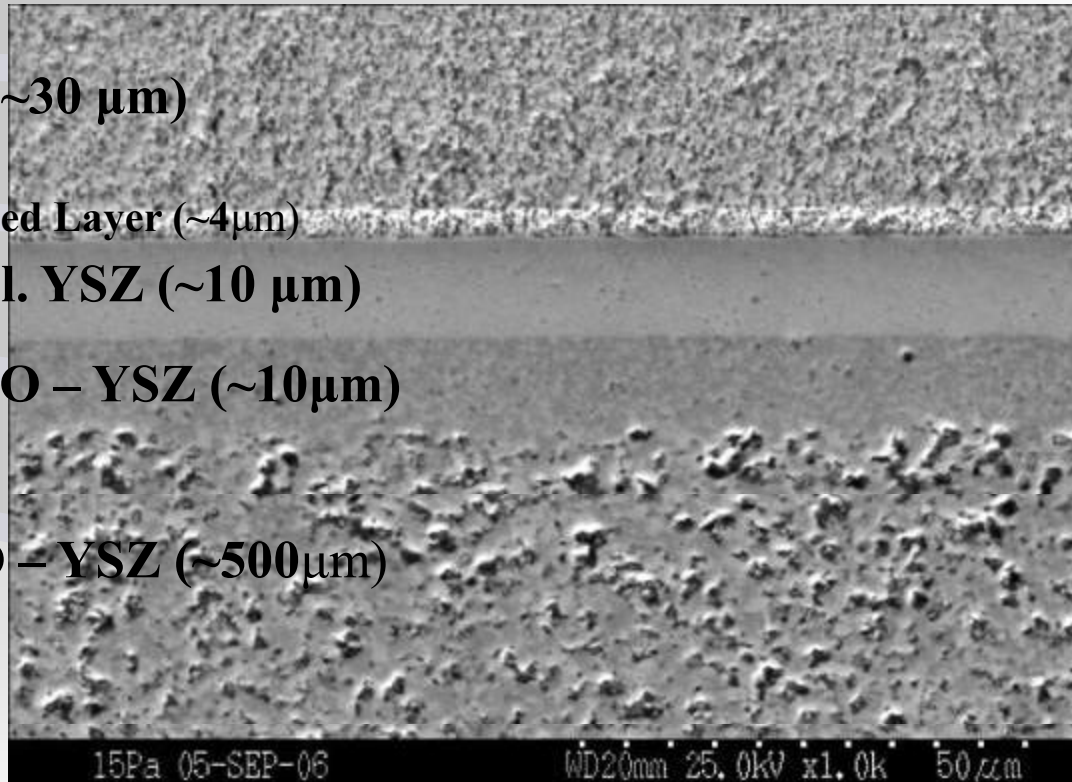
**Cathode: LSCF ( $\sim 30 \mu\text{m}$ )**

**Interlayer: Ceria Based Layer ( $\sim 4 \mu\text{m}$ )**

**Electrolyte: 8 mol. YSZ ( $\sim 10 \mu\text{m}$ )**

**Active Anode: NiO – YSZ ( $\sim 10 \mu\text{m}$ )**

**Bulk Anode: NiO – YSZ ( $\sim 500 \mu\text{m}$ )**



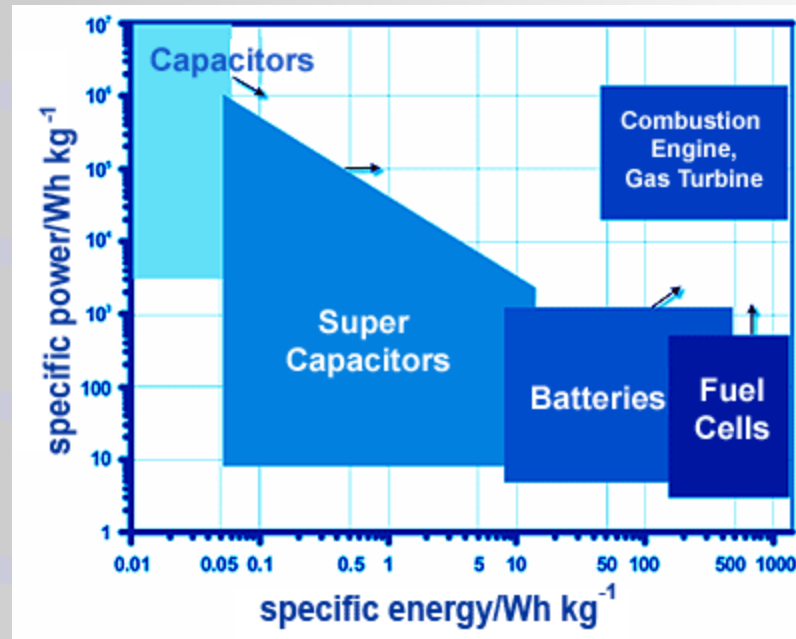
# Fuel Cells

Department of Energy and NSF Funding:

Programs want research in several focus areas:

- Cathodes
- Anodes
- Electrolytes
- Coal Contaminants
- Fuel Processing
- Modeling and Simulation
- Manufacturing, Power Plants

# Fuel Cells



Simplified Ragone plot showing how fuel cells compare favorably in specific energy per unit mass to other energy storage systems.

(Winter et.al., Chem. Rev., ACS,2004, Vol. 104, No. 10)

# Fuel Cells

## Summary

- The five major fuel cells are PAFC, PEMFC, AFC, MCFC, and SOFC – they differ based on their electrolyte.
- PEMFC and SOFC appear poised to best meet potential applications. PEMFCs are especially suited for portable and small stationary applications while SOFCs appear suited for distribution-power and utility-scale power applications.
- PEMFC advantages include high power density, low operating temperature, and good start-stop cycle. Disadvantages include the requirement for expensive Pt catalyst, high-cost membrane and cell components, poor poison tolerance, and water management issues.

# Fuel Cells

## Summary

- SOFC advantages include fuel flexibility, nonprecious metal catalyst, and the production of high-quality waste heat. Disadvantages include system complexity, corrosive molten electrolyte, and relatively expensive cell materials.
- While all fuel cells run best on H<sub>2</sub> gas, the high temperature fuel cells can also run on simple hydrocarbon fuels or CO via direct electrooxidation or internal reforming.

# Class Assignment

- Research paper – due Dec 2<sup>nd</sup>
- Final – Dec 9<sup>th</sup> 8 – 10 am