

ESP5403 Nanomaterials for Energy Systems

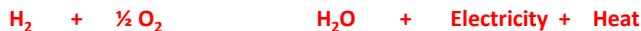
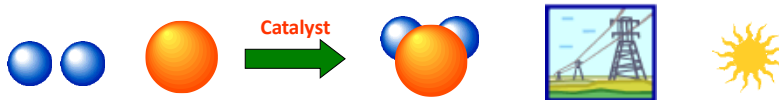
FUEL CELL TECHNOLOGY

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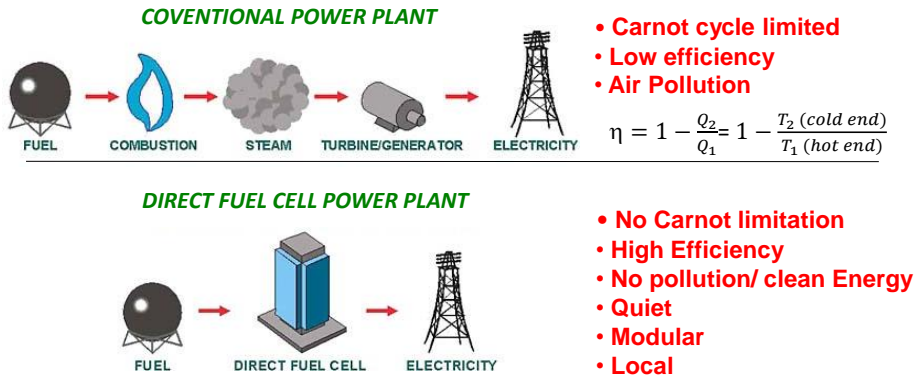
What is a fuel cell?



A fuel cell may be one of a variety of electrochemical power sources, but is more precisely a device designed to convert the energy of a chemical reaction directly to electrical energy

- Fuel cell is an Energy Conversion Device (like battery), which converts continuously the free energy change of a chemical reaction between a fuel and oxygen directly into electricity and heat with appropriate electrodes and electrolyte.
- Although the operation of a fuel cell is, in principle, similar to a battery, it does not require the time consuming process of recharging
- Fuel cells can provide electricity continuously, unlike the batteries, as long as the fuel and oxidant are supplied

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Advantages of Fuel Cells

- There is no combustion, redox reactions generate energy, with only water-vapor emissions
- There are no moving parts, therefore, fuel cells are quiet and reliable
- Electricity is created electrochemically, rather than by combustion (burning in air), so thermodynamic laws that limit a conventional power plant are not applicable, therefore, fuel cells are more efficient in extracting energy
- The fuel, hydrogen, and the product, water are considered renewable and green, therefore, fuel cells will be essential to a sustainable energy program.

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Glossary of Terms Used in Describing Fuel Cell Technology

Electrochemical reaction: A reaction involving the transfer of electrons from one chemical substance to another.

Contact Electrode: An electrical terminal that conducts an electric current into or out of a fuel cell (where the electrochemical reaction occurs).

Anode: Electrode where oxidation reaction happens (electrons are released).

Cathode: Electrode where reduction reaction occurs (electrons are acquired).

In a fuel cell, hydrogen is oxidized at the anode and oxygen reduction occurs at the cathode.

Electrolyte: A chemical compound that conducts ions from one electrode to the other (with high ionic conduction and negligible electronic conduction)

Ion: An atom that carries a positive or negative charge due to the loss or gain of an electron. Anion is a negative ion, cation is a positive ion.

An electrochemical cell consists of 2 electrodes + 1 electrolyte

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Terminology (cont.)

Catalyst: A substance that participates in a reaction, increasing its rate, but is not consumed in the reaction.

Polymer: A natural or synthetic compound made of giant molecules which are composed of repeated links of simple molecules (monomers).

Inverter: A device used to convert direct current electricity produced by a fuel cell to alternating current.

Reformer: A device that extracts pure hydrogen from hydrocarbons.

Stack: Individual fuel cells connected in series within a generating assembly.

Cogeneration: The use of waste heat to generate electricity. Harnessing otherwise wasted heat boosts the efficiency of power-generating systems.

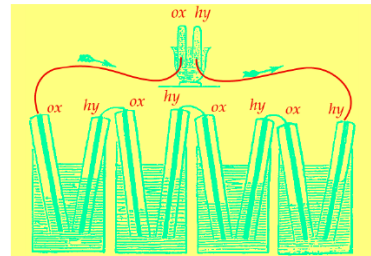
Direct Fuel Cell: A type of fuel cell in which a hydrocarbon fuel is fed directly to the fuel cell stack, without requiring an external "reformer" to generate hydrogen.

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A Very Brief History

Fuel cell principle first discovered by Sir William Grove in 1839.

Grove used four large cells, each containing hydrogen and oxygen, to produce electric power which was then used to split the water in the smaller upper cell.



Commercial potential was first demonstrated by NASA in the 1960's with the usage of fuel cells on the Gemini and Apollo space flights. However, these fuel cells were very expensive.

Fuel cell research and development has been actively taking place since the 1970's, resulting in many commercial applications ranging from low cost portable systems for cell phones and laptops to large power systems for buildings.

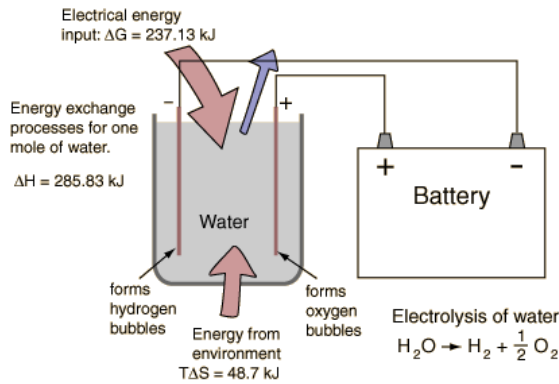


1 kW dismantable fuel cell stack

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Electrolysis

“What does this have to do with fuel cells?”



By providing energy from a battery, water (H_2O) can be dissociated into the diatomic molecules of hydrogen (H_2) and oxygen (O_2).

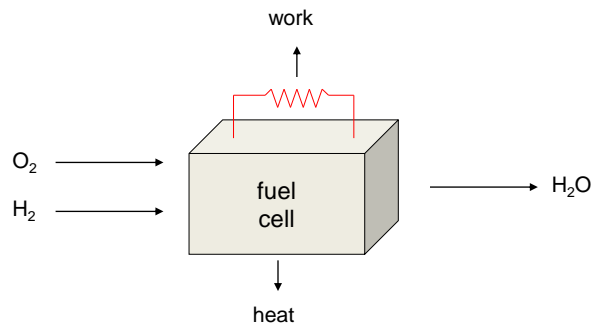
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Fuel Cell Basics

“Put electrolysis in reverse.”

The familiar process of electrolysis requires work to proceed, if the process is put in reverse, it should be able to do work for us spontaneously.

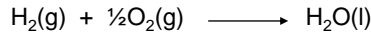
The most basic “black box” representation of a fuel cell in action is shown below:



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Fuel Cell Basics

Thermodynamics



Other gases in the fuel and air inputs (such as N_2 and CO_2) may be present, but as they are not involved in the electrochemical reaction, they do not need to be considered in the energy calculations.

Thermodynamic properties at 1Atm and 298K

	H_2	O_2	$\text{H}_2\text{O} (\text{l})$
Enthalpy (H)	0	0	-285.83 kJ/mol
Entropy (S)	130.68 J/mol·K	205.14 J/mol·K	69.91 J/mol·K

Enthalpy is defined as the energy of a system plus the work needed to make room for it in an environment with constant pressure.

Entropy can be considered as the measure of disorganization of a system, or as a measure of the amount of energy that is unavailable to do work.

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Fuel Cell Basics

Thermodynamics

Enthalpy of the chemical reaction using Hess' Law:

$$\begin{aligned}\Delta H &= \Delta H_{\text{reaction}} = \sum H_{\text{products}} - \sum H_{\text{reactants}} \\ &= (1\text{mol})(-285.83 \text{ kJ/mol}) - (0) \\ &= -285.83 \text{ kJ}\end{aligned}$$

Entropy of chemical reaction:

$$\begin{aligned}\Delta S &= \Delta S_{\text{reaction}} = \sum S_{\text{products}} - \sum S_{\text{reactants}} \\ &= [(1\text{mol})(69.91 \text{ J/mol}\cdot\text{K})] - [(1\text{mol})(130.68 \text{ J/mol}\cdot\text{K}) + (\frac{1}{2}\text{mol})(205.14 \text{ J/mol}\cdot\text{K})] \\ &= -163.34 \text{ J/K}\end{aligned}$$

Heat gained by the system:

$$\begin{aligned}\Delta Q &= T\Delta S \\ &= (298\text{K})(-163.34 \text{ J/K}) \\ &= -48.7 \text{ kJ}\end{aligned}$$

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Fuel Cell Basics

Thermodynamics

The Gibbs free energy is then calculated by:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (-285.83 \text{ kJ}) - (-48.7 \text{ kJ}) \\ &= -237 \text{ kJ}\end{aligned}$$

The external work done on the reaction, assuming reversibility and constant temp.

$$W = \Delta G$$

The work done on the reaction by the environment is:

$$W = \Delta G = -237 \text{ kJ}$$

The heat transferred to the reaction by the environment is:

$$\Delta Q = T\Delta S = -48.7 \text{ kJ}$$

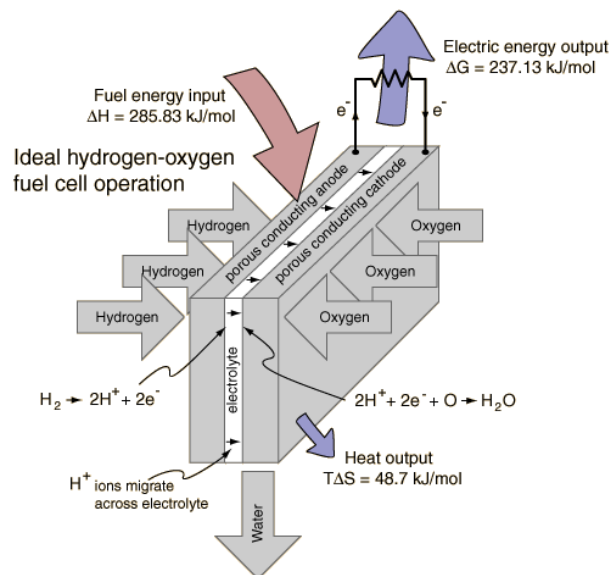
More simply stated:

The chemical reaction can do 237 kJ of work and produces 48.7 kJ of heat to the environment.

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Fuel Cell Basics

Putting it together

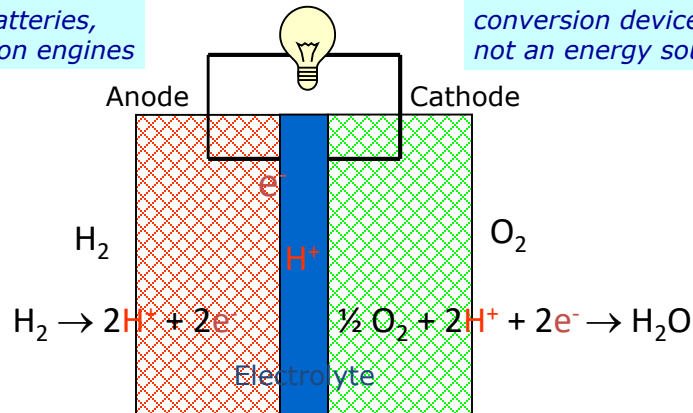


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Fuel Cell: Principle of Operation

*best of batteries,
combustion engines*

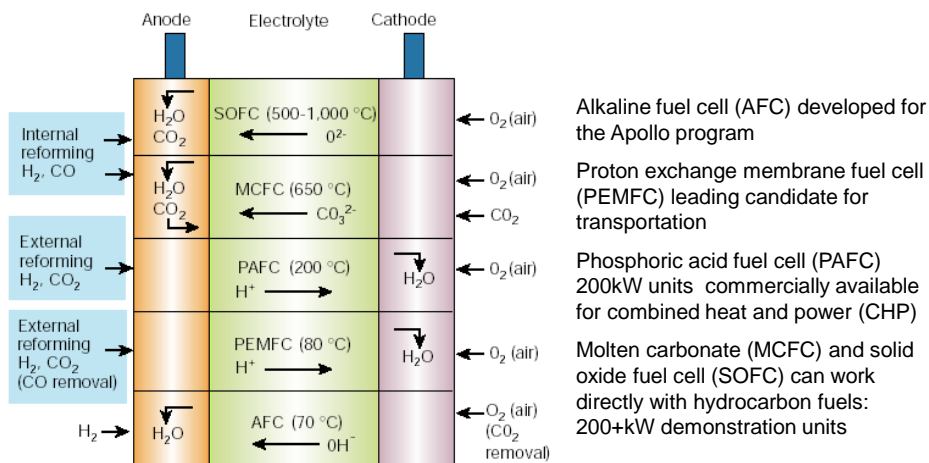
*conversion device,
not an energy source*



- A fuel cell is a multi-component device with two electrodes (anode and cathode), separated by an ionic conductive membrane
- At the anode the oxidation reaction (loss of electrons) occurs
- At the cathode the reduction reaction (gain of electrons) occurs.

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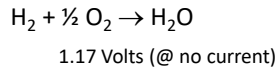
Fuel Cell Types



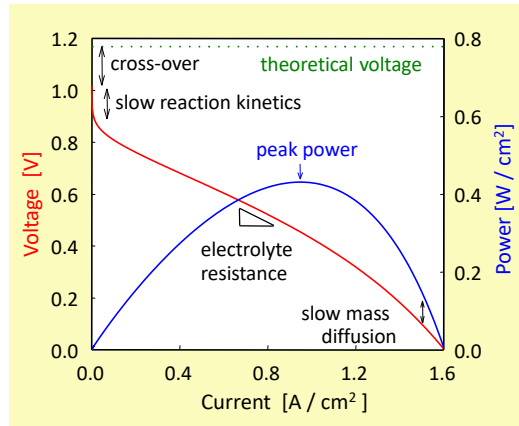
B. C. H. Steele & A. Heinzl, Nature, 414 (2001) 345

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Fuel Cell Performance



- voltage losses
 - fuel cross-over
 - reaction kinetics
 - electrolyte resistance
 - slow mass diffusion
- power = $I \cdot V$
- peak power at mid I



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Fuel Cell Voltage

In a fuel cell, **two** electrons pass round the external circuit for each water molecule produced and each molecule of hydrogen used. So, for one *mole* of hydrogen used, $2N$ electrons pass round the external circuit – where N is Avogadro's number. If $-q$ is the charge on one electron, then the charge that flows is

$$-2Nq = -2F \text{ coulombs}$$

F being the Faraday constant, or the charge on one mole of electrons.

If E is the voltage of the fuel cell, then the electrical work done moving this charge round the circuit is

$$\text{Electrical work done} = \text{charge} \times \text{voltage} = -2FE \text{ joules}$$

If the system is reversible (or has no losses), then this electrical work done will be equal to the Gibbs free energy released ΔG_f . So

$$\Delta G_f = -2F \cdot E$$

Thus

$$E = \frac{-\Delta G_f}{2F}$$

This fundamental equation gives the electromotive force (EMF) or reversible open circuit voltage of the hydrogen fuel cell.

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Fuel Cell Voltage

For example, a hydrogen fuel cell operating at 200°C has $\Delta G = -220 \text{ kJ}$, so

$$E = \frac{220,000}{2 \times 96,485} = 1.14 \text{ V}$$

ΔG , maximum EMF (or reversible open circuit voltage), and efficiency limit (HHV basis) for hydrogen fuel cells

Form of water product	Temp °C	ΔG kJ mol ⁻¹	Max EMF V	Efficiency limit %
Liquid	25	-237.2	1.23	83
Liquid	80	-228.2	1.18	80
Gas	100	-225.2	1.17	79
Gas	200	-220.4	1.14	77
Gas	400	-210.3	1.09	74
Gas	600	-199.6	1.04	70
Gas	800	-188.6	0.98	66
Gas	1000	-177.4	0.92	62

$E = 1.481 \text{ V}$ at 0°C (using Higher Heating Value of H₂)

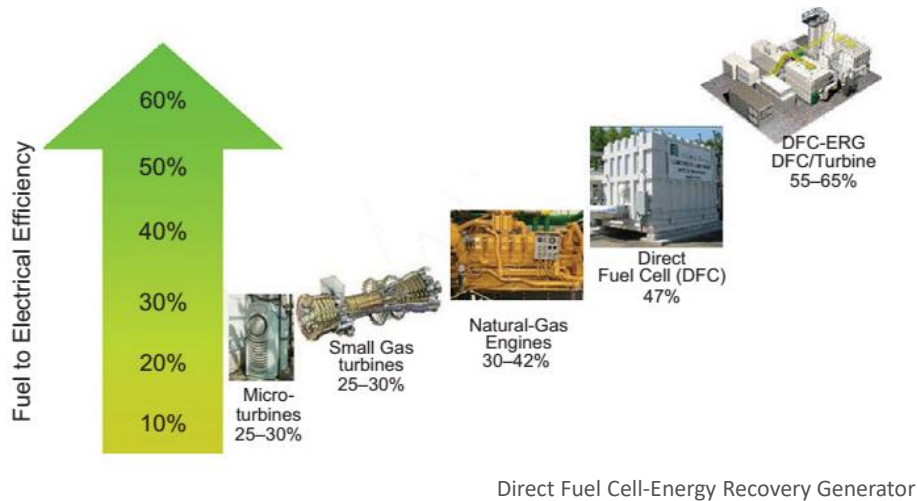
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Hydrogen Fuel Cell Efficiency

- 40% efficiency converting methanol to hydrogen in reformer
- 80% of hydrogen energy content converted to electrical energy
- 80% efficiency for inverter/motor
 - Converts electrical to mechanical energy

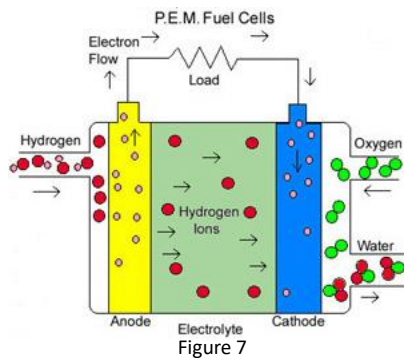
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Fuel Cell Efficiency: A Comparison



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Proton Exchange Membrane Fuel Cell (PEMFC)



Thin permeable polymer sheet electrolyte

40 – 50% efficiency

50 – 250 kW

80°C operating temperature

Electrolyte will not leak or crack

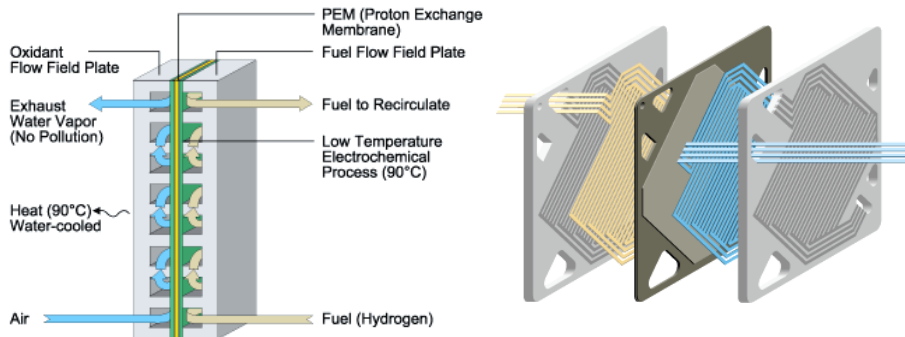
Temperature good for home or vehicle use

Platinum catalyst on both sides of membrane → \$\$

<https://www.youtube.com/watch?v=6UwSazq8GTU>

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PEMFC

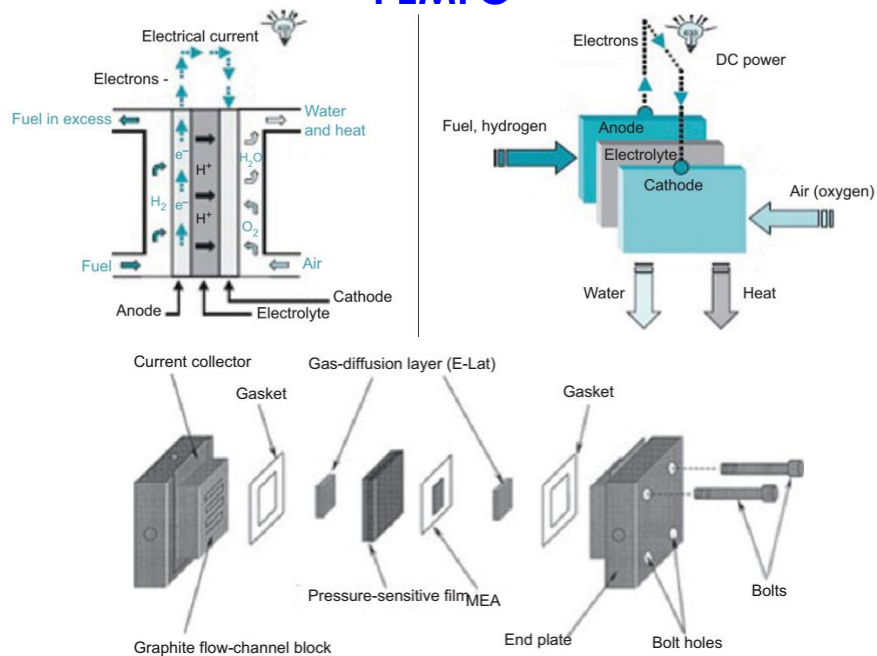


- Electrodes (anode and the cathode) separated by a polymer membrane electrolyte.
- Each of the electrodes is coated on one side with a thin platinum catalyst layer.
- The electrodes, catalyst and membrane form the membrane electrode assembly (MEA).
- Hydrogen and air are supplied on either side through channels formed in the flow field plates

Ballard® fuel cell

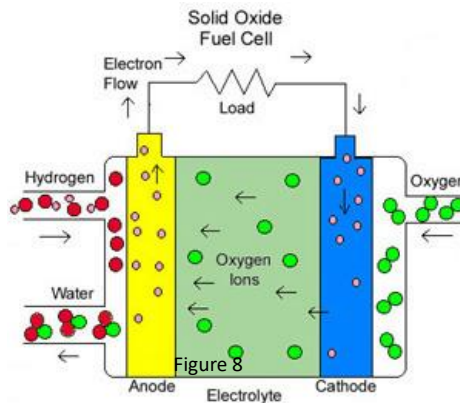
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PEMFC



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Solid Oxide Fuel Cell (SOFC)

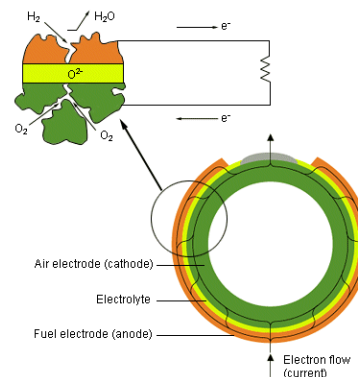
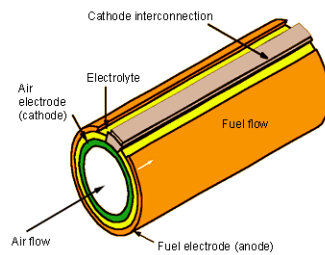


- Hard ceramic oxide electrolyte
- ~60% efficient
- ~1000°C operating temperature
- Cells output up to 100 kW

- high temp / catalyst can extract the hydrogen from the fuel at the electrode
- high temp allows for power generation using the heat, but limits use
- SOFC units are very large
- solid electrolyte won't leak, but can crack

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SOFC

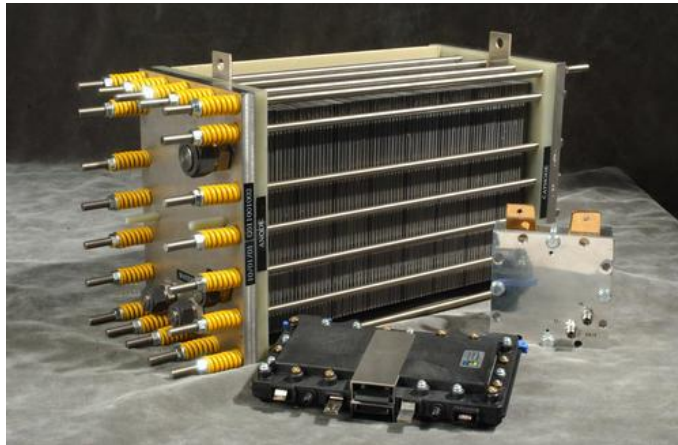


Cathode	(La,Sr)MnO ₃	1.5 m extruded tubular (2.2 mm) porous cathode
Interconnection	(La,Sr)CrO ₃	plasma spraying (85 μm)
Electrolyte	8%Y ₂ O ₃ -ZrO ₂	thick-film (30–40 μm)
Anode	Ni/ 8%Y ₂ O ₃ -ZrO ₂	porous layer (100 μm) by a slurry-spray process

Siemens Westinghouse fuel cell

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Fuel Cell Stack



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<http://www.nrel.gov/hydrogen/photos.html>

Fuel Cell Choices

Temperature sets operational parameters & fuel choice

- | | |
|--|---|
| <ul style="list-style-type: none"> • Ambient Temperature <ul style="list-style-type: none"> ✓ Rapid start-up ✗ H_2 or CH_3OH as fuels ✗ Catalysts easily poisoned • Applications <ul style="list-style-type: none"> – Portable power – Many on/off cycles – Small size | <ul style="list-style-type: none"> • High Temperature <ul style="list-style-type: none"> ✓ Fuel flexible ✓ Very high efficiencies ✗ Long start-up • Applications <ul style="list-style-type: none"> – Stationary power – Auxiliary power in portable systems |
|--|---|

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Technical Challenges

Many Challenges in Materials and Materials Processing

- CO tolerant electrocatalysts
- Better membranes for PEMFC
- Intermediate temperature high performance electrodes
- Low cost fabrication processes for SOFC
- New materials!

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Fuel Cell Innovations

- New Electrolytes
 - Intermediate temperature operation
 - Lower the temperature below solid oxide fuel cells
 - Raise the temperature above polymer fuel cells
- New Catalysts
 - Enhance reaction kinetics (improve efficiency)
 - Reduce susceptibility to poisons (reduce complexity)
- Novel integrated designs
 - Dramatically improve thermal management
 - Utilize micromachining technologies: micro fuel cells

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