Solid Oxide Fuel Cells (SOFCs)

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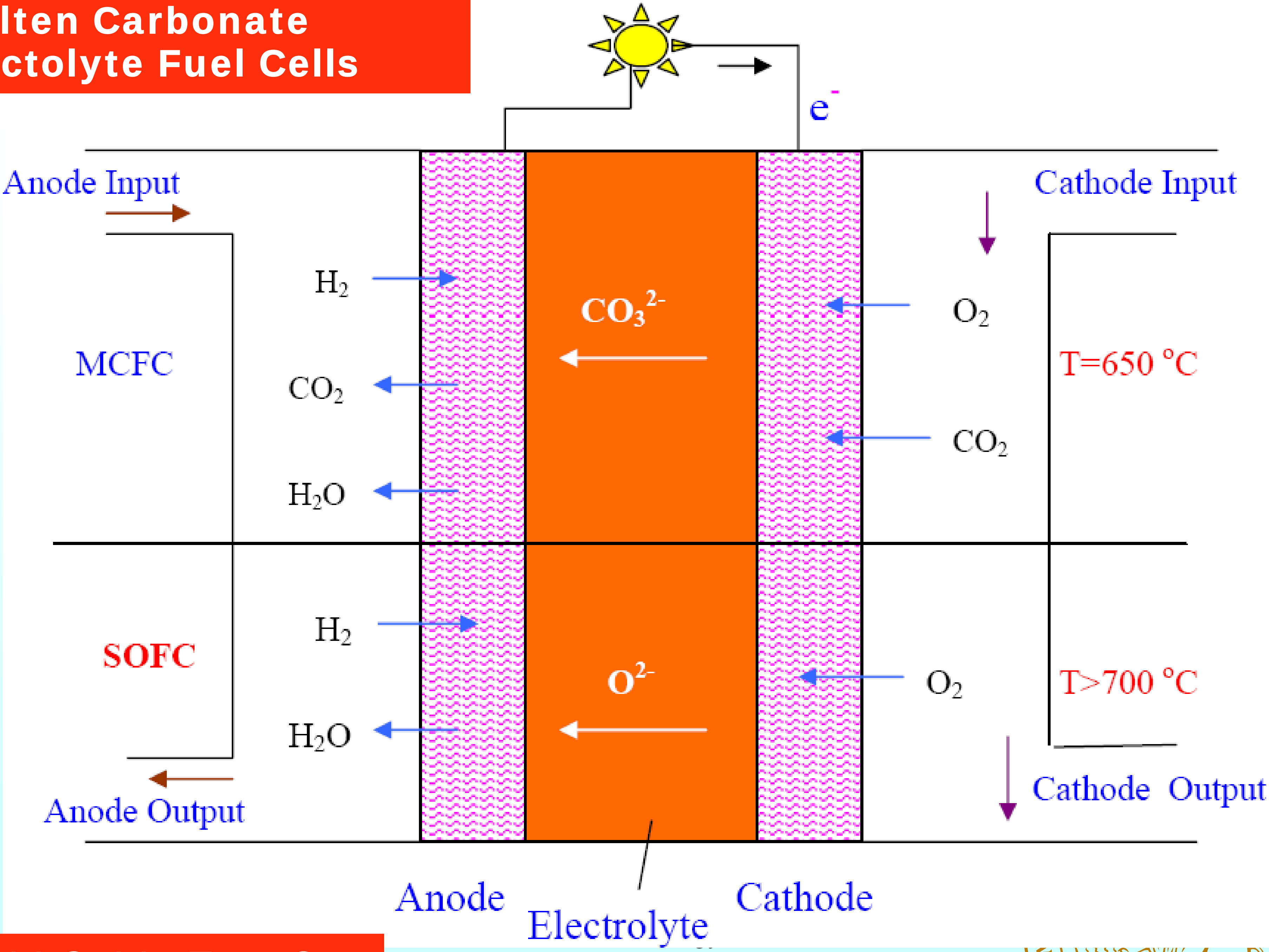
Molten Carbonate Electolyte Fuel Cells



Solid Oxide Fuel Cell

Why SOFCs

- Employ Solid State Electrolyte;
- Corrosion **Reduced**;
- Water Management **Eliminated**;
- Very **Thin** Layers/Cell Components Possible;
- Fuel **Flexibility** High;
- Precious Metal Electrocatalysts not needed
- **Internal Reforming** and **Combined** Heat/ Power Cycles Possible, etc….

Introduction

- **The electrochemical reactions proceed more quickly at high temperatures, and noble metal catalysts are often not needed;**
  - **The temperature (cell / exhaust gas) is high enough to facilitate the extraction of hydrogen;**
- **High temperature fuel cells enable combined ” heat and power (CHP) system”;**
  - **High temperature exhaust gas can be used to run a gas turbine-bottoming cycle.**

Solid Oxide Fuel Cells (SOFCs), Intermediate Temperature (IT-)SOFCs to be discussed.

Cell Components

- **Electrolytes and interconnects must be chemically, morphologically, and dimensionally stable for both oxidizing and reducing conditions:**
  - The components must be chemically stable in order to limit chemical interactions with other cell components;
  - No components may exhibit any significant change in volume between room temperature and the fabrication temperature;

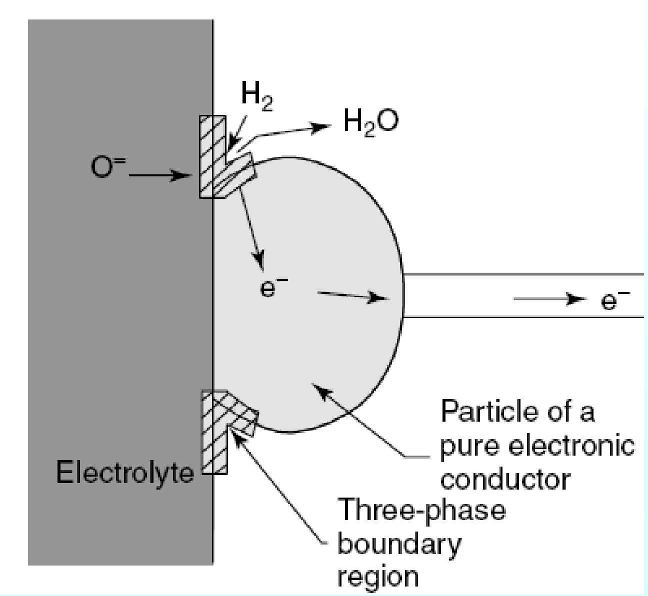
Conductivities or Resistivities

- The resistivities of typical cell components at 1,000^{o}C are 10 ohm-cm (ionic) for the electrolyte (8-10 mol% Y_2O_3 doped ZrO_2), 1 ohm-cm (electronic) for the cell interconnect (doped LaCrO3), 0.01 ohm-cm (electronic) for the cathode (doped LaMnO3), and 3 x 10^{-6} ohm-cm (electronic) for the anode (Ni/ZrO2 cermet).

- It is apparent that the solid oxide electrolyte is worst conductive of the cell components, followed by the cell interconnect.

SOFC Electrodes and Interconnects

Anode: a porous cermet made of metallic nickel (Ni) and a YSZ skeleton; The zirconia serves to inhibit sintering of the metal particles and provides a comparable thermal expansion coefficient.

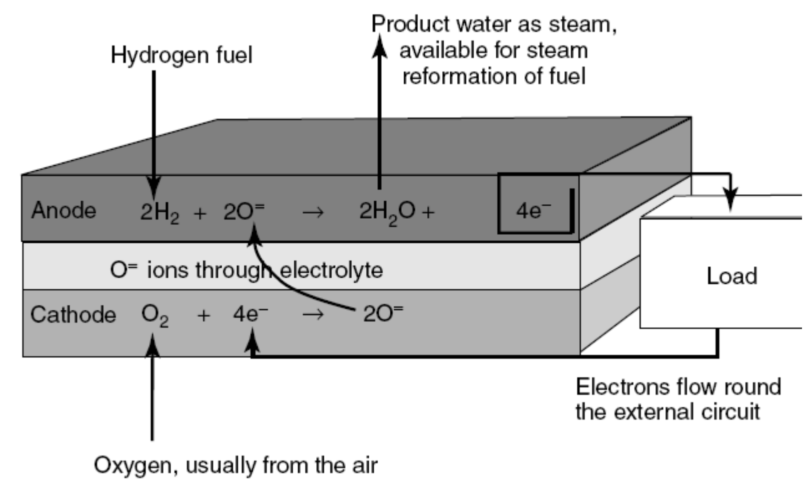


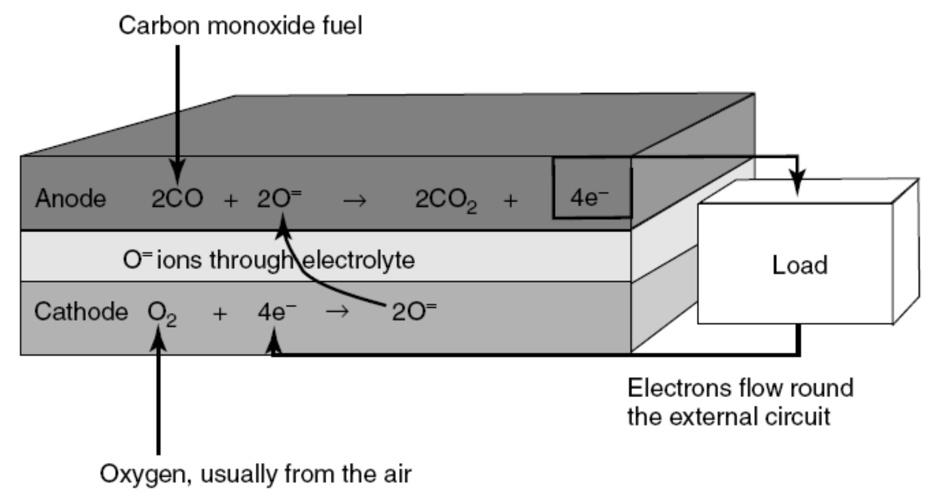
•Cathode: strontium-doped lanthanum manganite (La0.84Sr0.16)MnO3,a *p*-type semiconductor.

•Interconnect: metals (stainless steels) or alloys to be compatible in terms of chemical stability and mechanical compliance (similar thermal expansion coefficients).

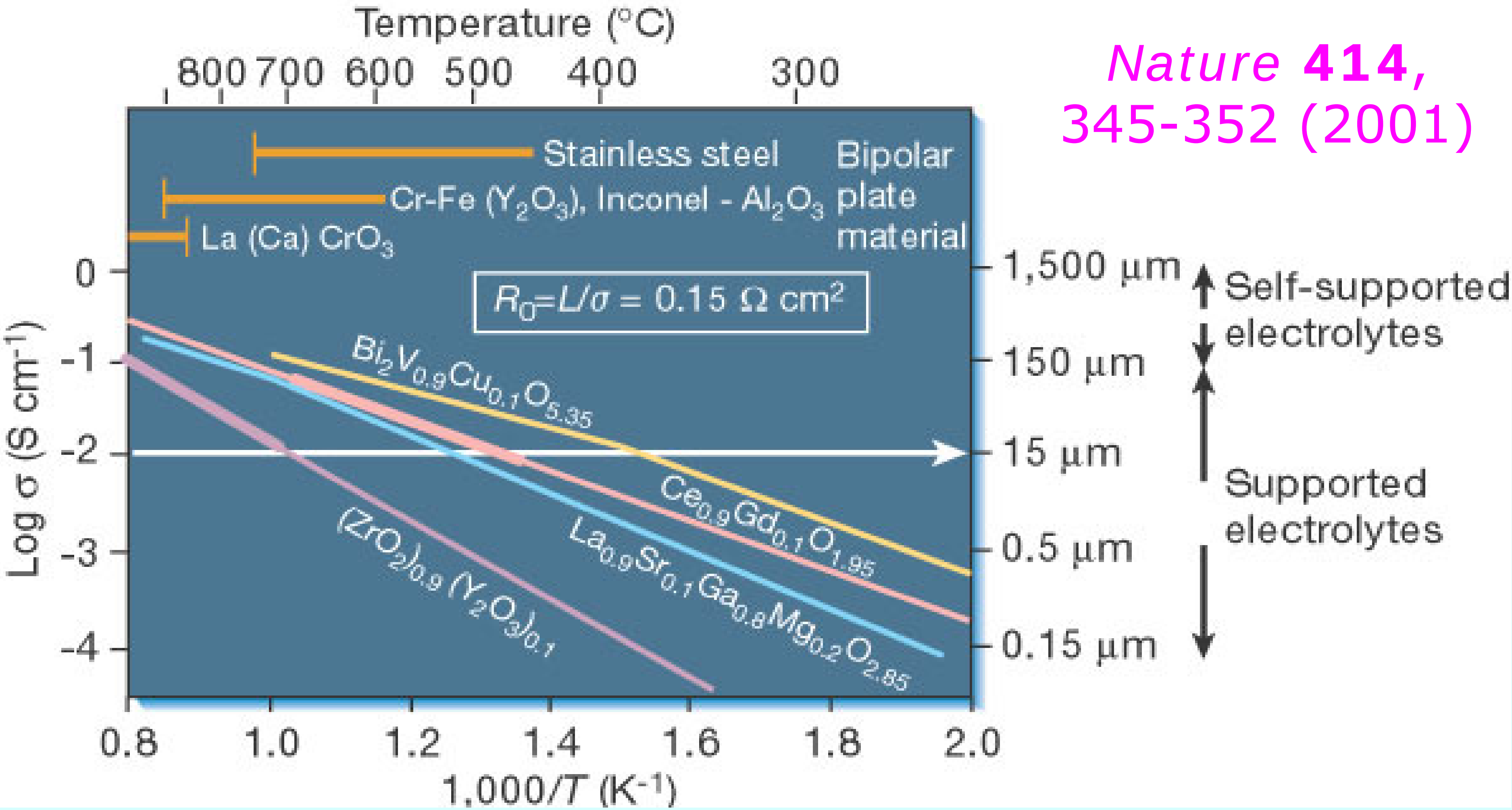
SOFC Electrolyte

- An oxide ion-conducting ceramic material as the electrolyte with only two phases (gas and solid) processes;
- Both hydrogen and carbon monoxide can act as fuels;





- Originally zirconia (ZrO_2) as an oxygen ion conductor, then zirconia stabilised with the addition of a small percentage (8-10 mole%) of yttria (Y_2O_3), so called YSZ.



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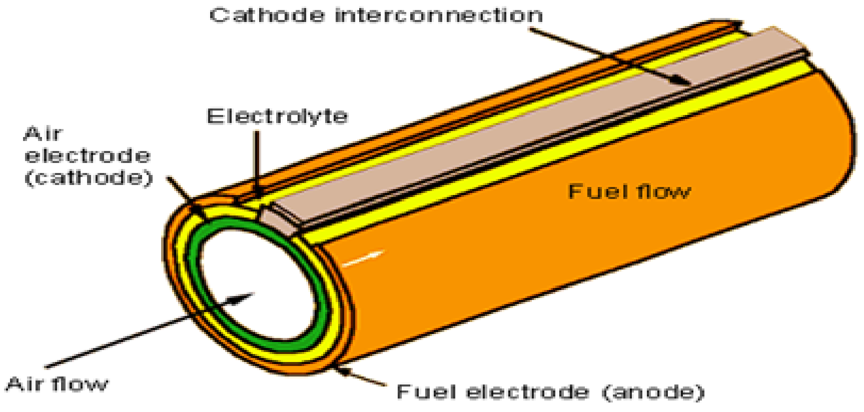
Films of oxide electrolytes can be reliably produced using cheap, conventional ceramic fabrication routes at thicknesses down to 15μm. The specific conductivity of the electrolyte must exceed 10^{-2} *S/cm*. This is achieved at 500 °C for the electrolyte $Ce_{0.9}Gd_{0.1}O_{1.95}$, and at 700 °C for the electrolyte $(ZrO2)_{0.9}(Y2O3)_{0.1}$.

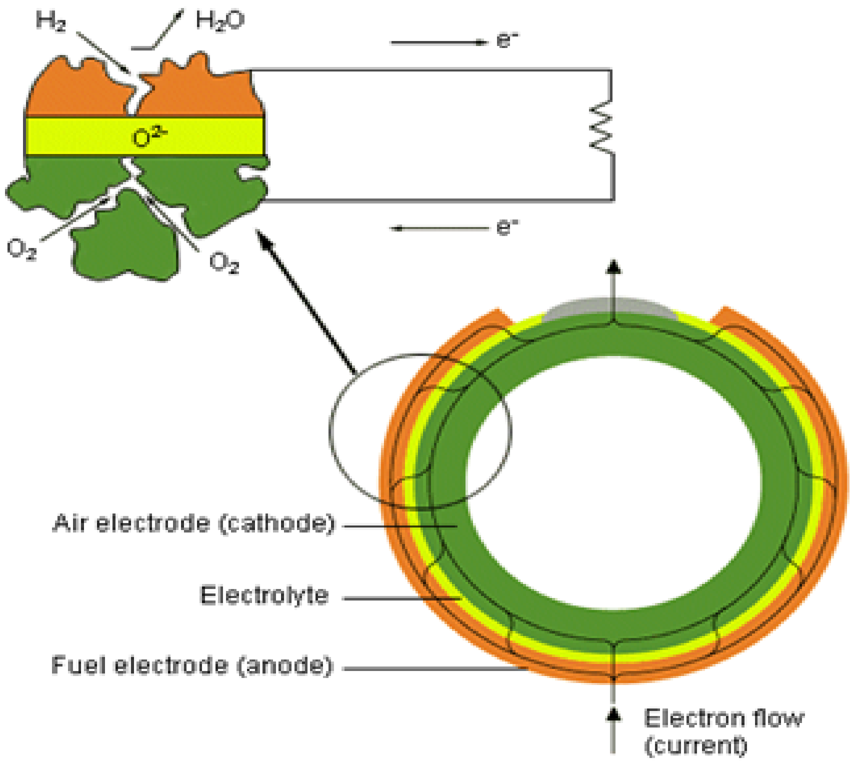
- Two different design configurations are being developed for solid oxide fuel cells, motivated by 1) considerations of how to seal the anode and cathode compartments, 2) ease of manufacturing, and 3) minimizing losses due to electric resistance.

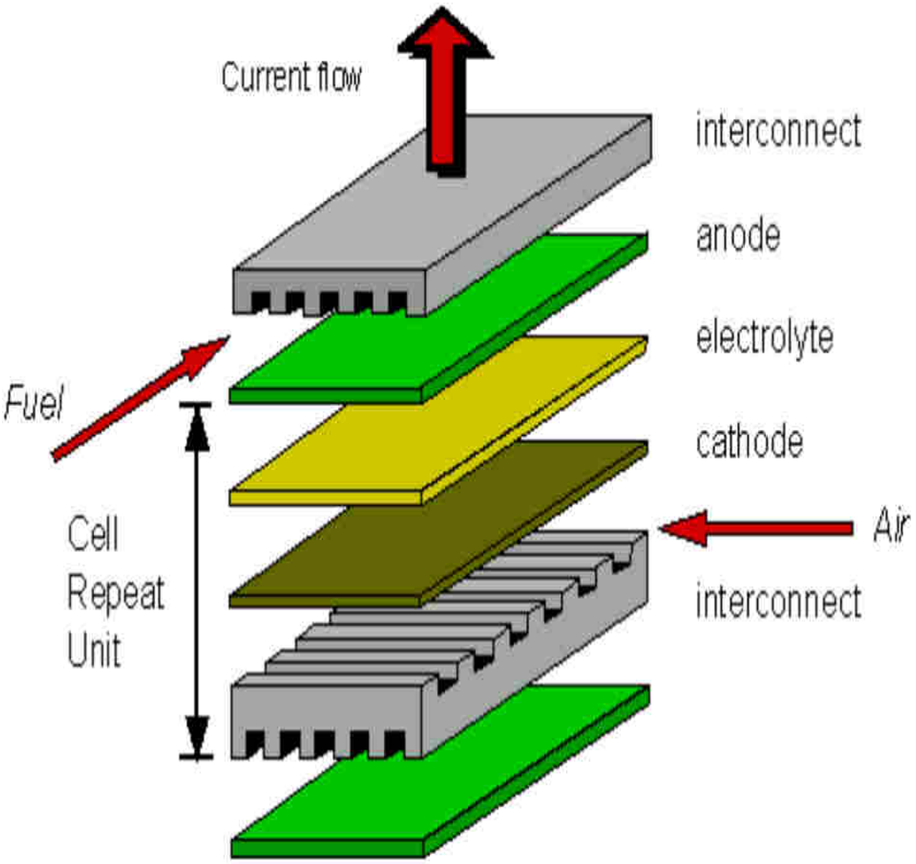
- The two principal types are tubular and planar. The tubular SOFC has undergone development since the late 1950s. Operating between 900-1,000°C, the long tubes have relatively high electrical resistance but are simple to seal. Some tubular designs eliminate the need for seals and allow for thermal expansion. Several tubular units are presently operating in the field, with tens of thousands of hours of demonstrated operation.

- The planar one is composed of flat, thin ceramic plates. It operates at 800°C or even below. Ultra-thin electrode /electrolyte sheets have low electrical resistance in order to achieve high efficiency. Operation at temperature lower than the tubular SOFC enables less exotic materials of construction, thus cost saving.

Various Structures of SOFCs (Tubular and Planar)







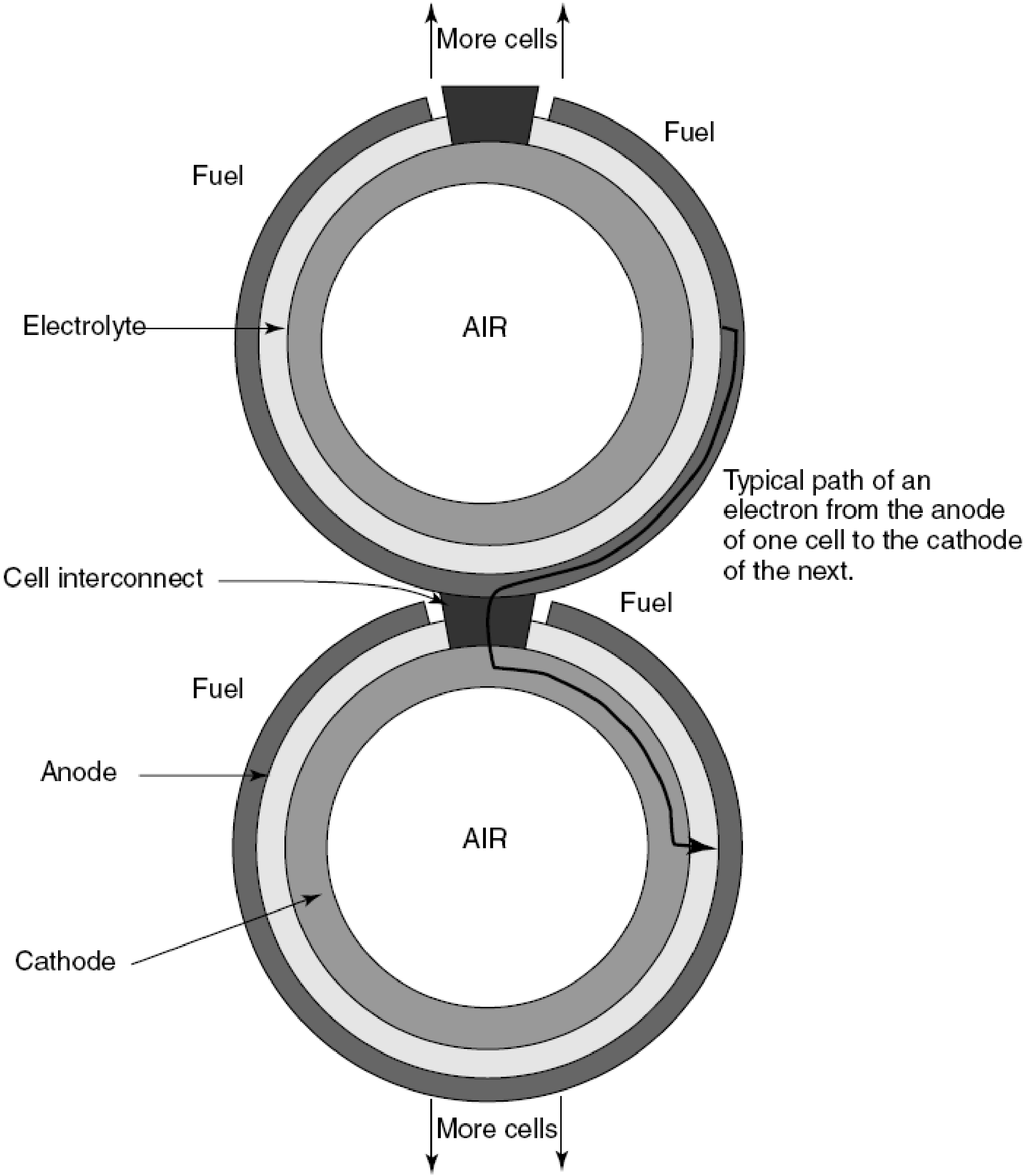
Tubular (left) and planar SOFC technology

Tubular SOFC Designs

- **Tubular SOFCs:** the cathode tube is fabricated first with a porosity of 30 - 40% to permit rapid transport of the reactant and product gases to the cathode/ electrolyte interface where the electrochemical reactions occur. The electrolyte is applied to the cathode tubes by electrochemical vapor deposition (EVD). In this technique, the appropriate metal chloride vapor is introduced on one side of the tube surface, and O_2/H_2O is introduced on the other side.

Cross Section of Tubular Cells

Siemens Westinghouse design, the electrolyte and the anode are built onto the air cathode.



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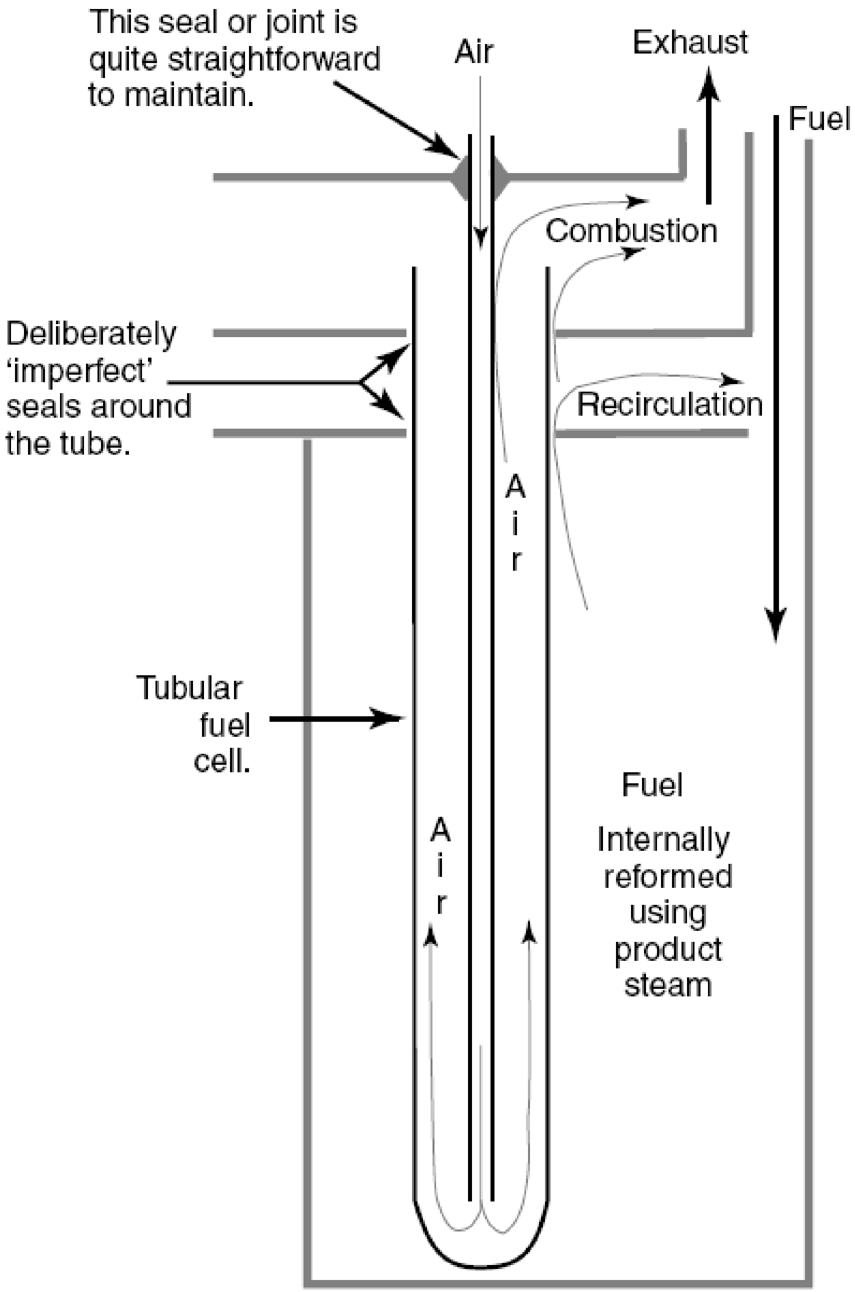
- Fuel flows along the outside of the tube, air is fed through a thin alumina air supply tube located centrally. Heat generated within the cell brings the air up to the operating temperature. The air then flows through the fuel cell back-up to the open end.
- Air and unused fuel from the anode exhaust mix are instantly combusted and so the cell exit is above 1000°C. This combustion provides additional heat to preheat the air supply tube.
- Thus the tubular SOFC does not require high-temperature seals.



Siemens cylindrical-tube SOFC technology

Seal-less, high internal ohmic losses

A typical SOFC stack

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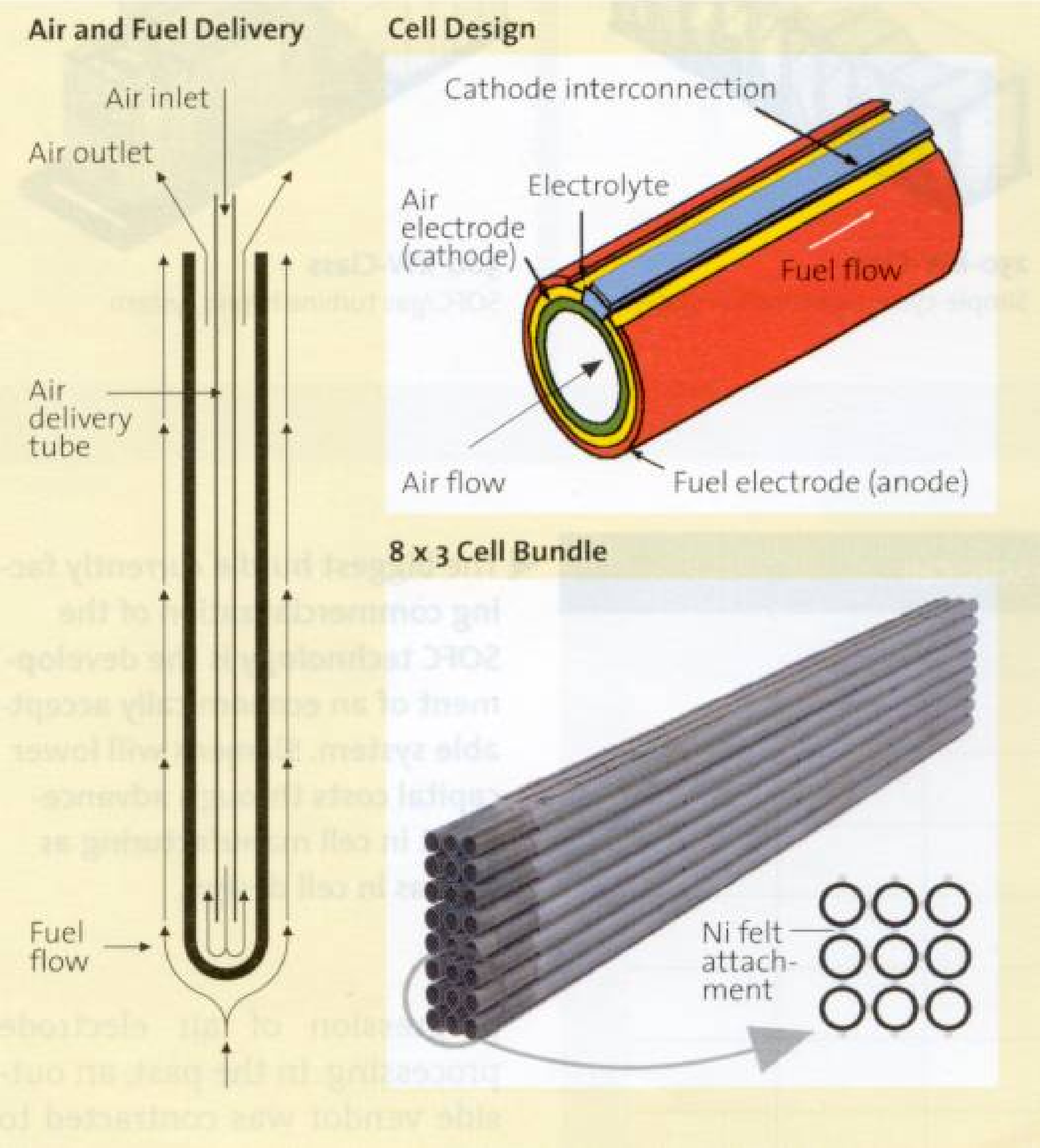
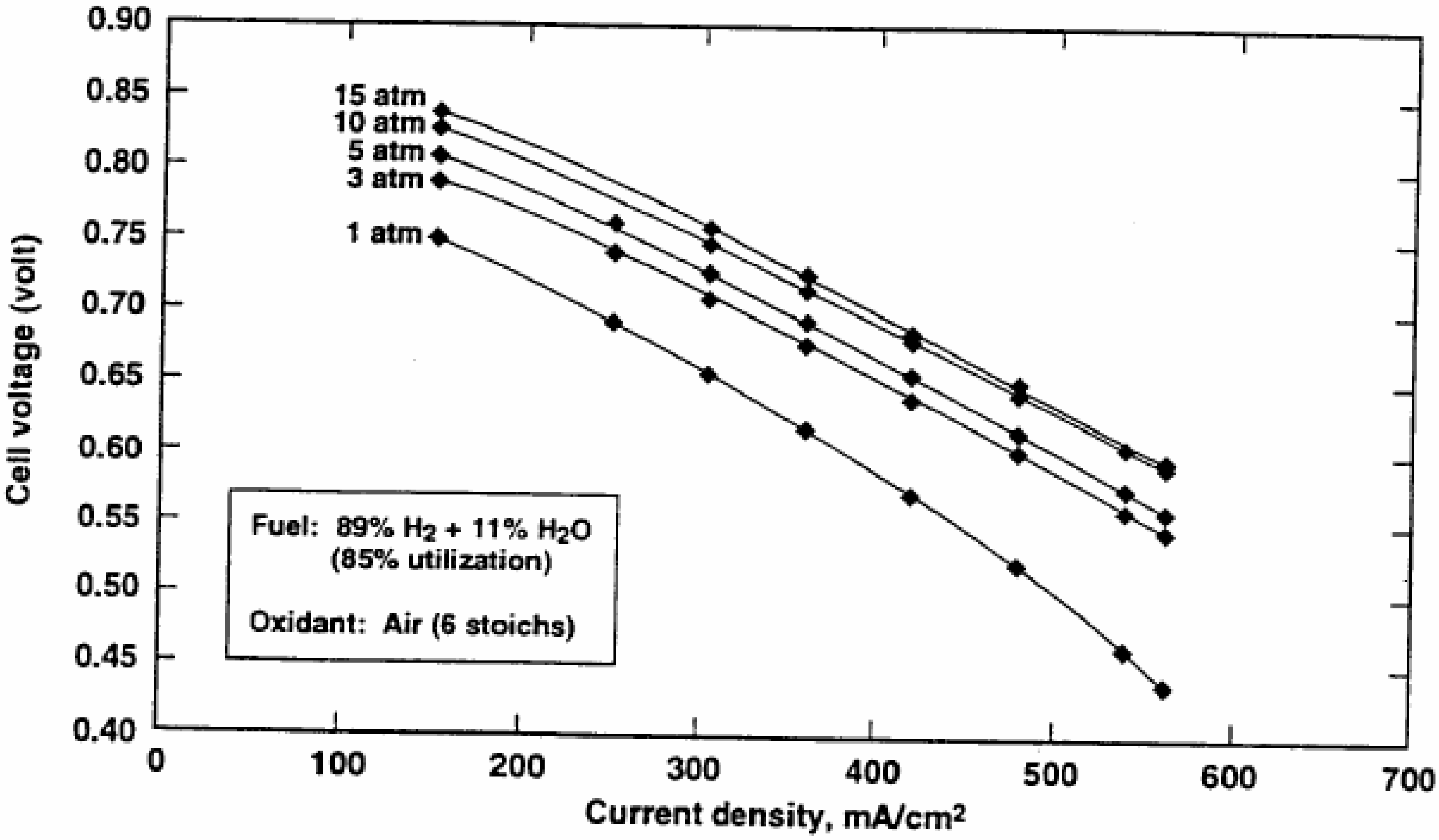
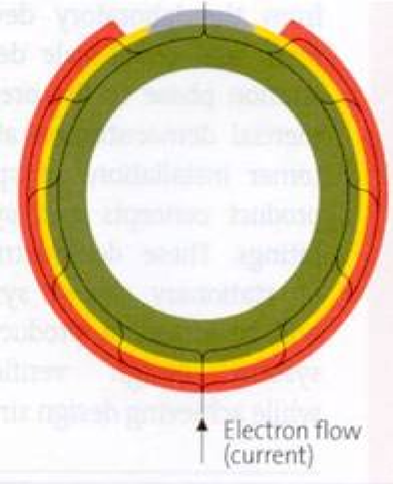
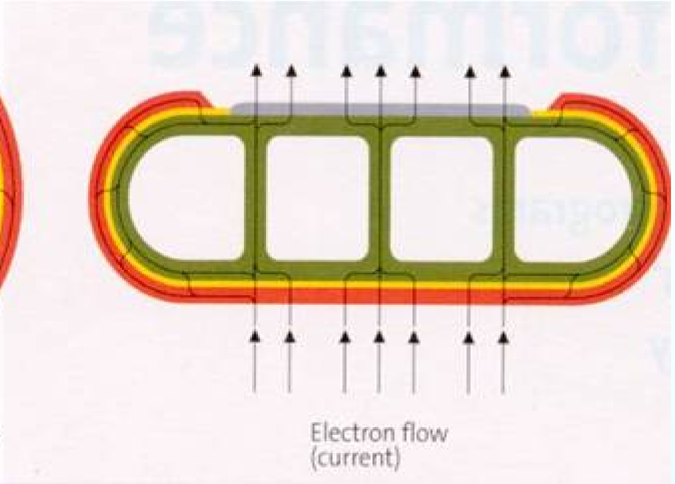


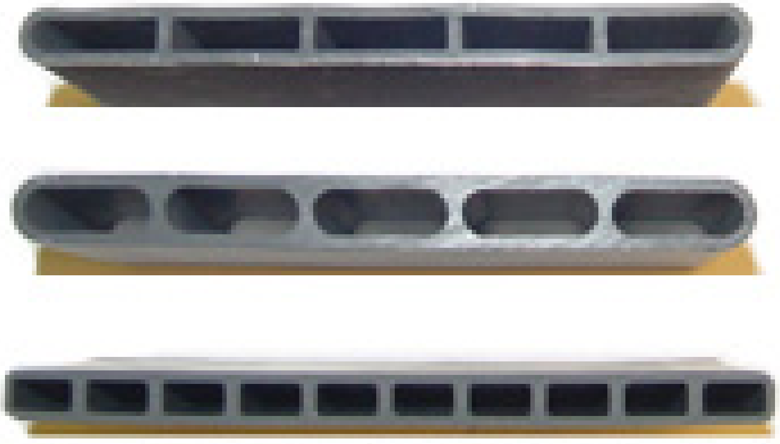
Siemens Westinghouse Tubular Cell Performance at 1,000°C (2.2 cm diameter,150 cm active length)



The high power density SOFC (Siemens)

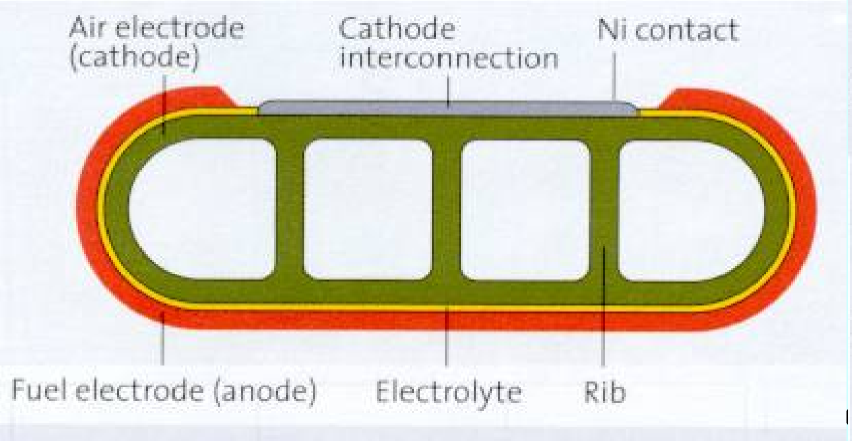


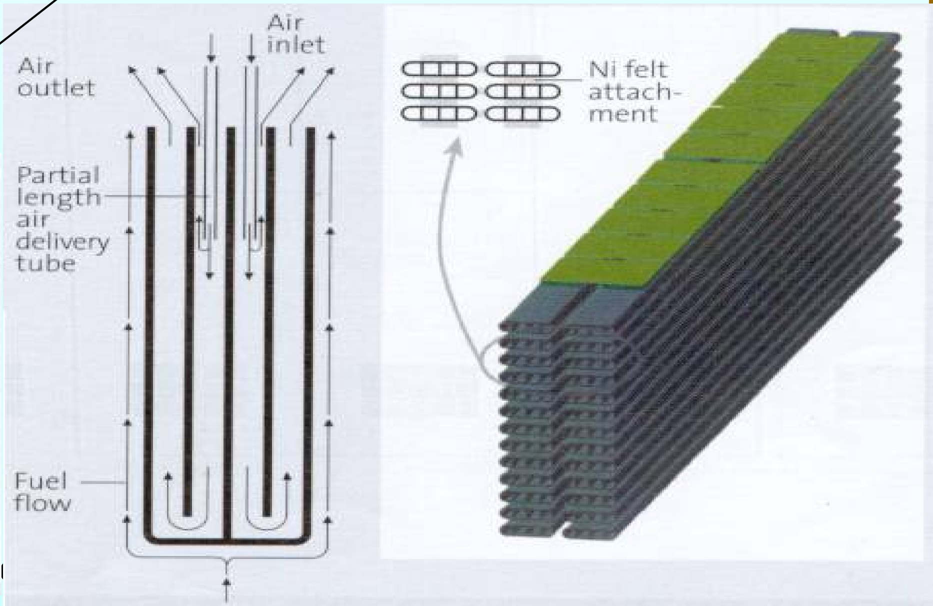




Conventional

new design



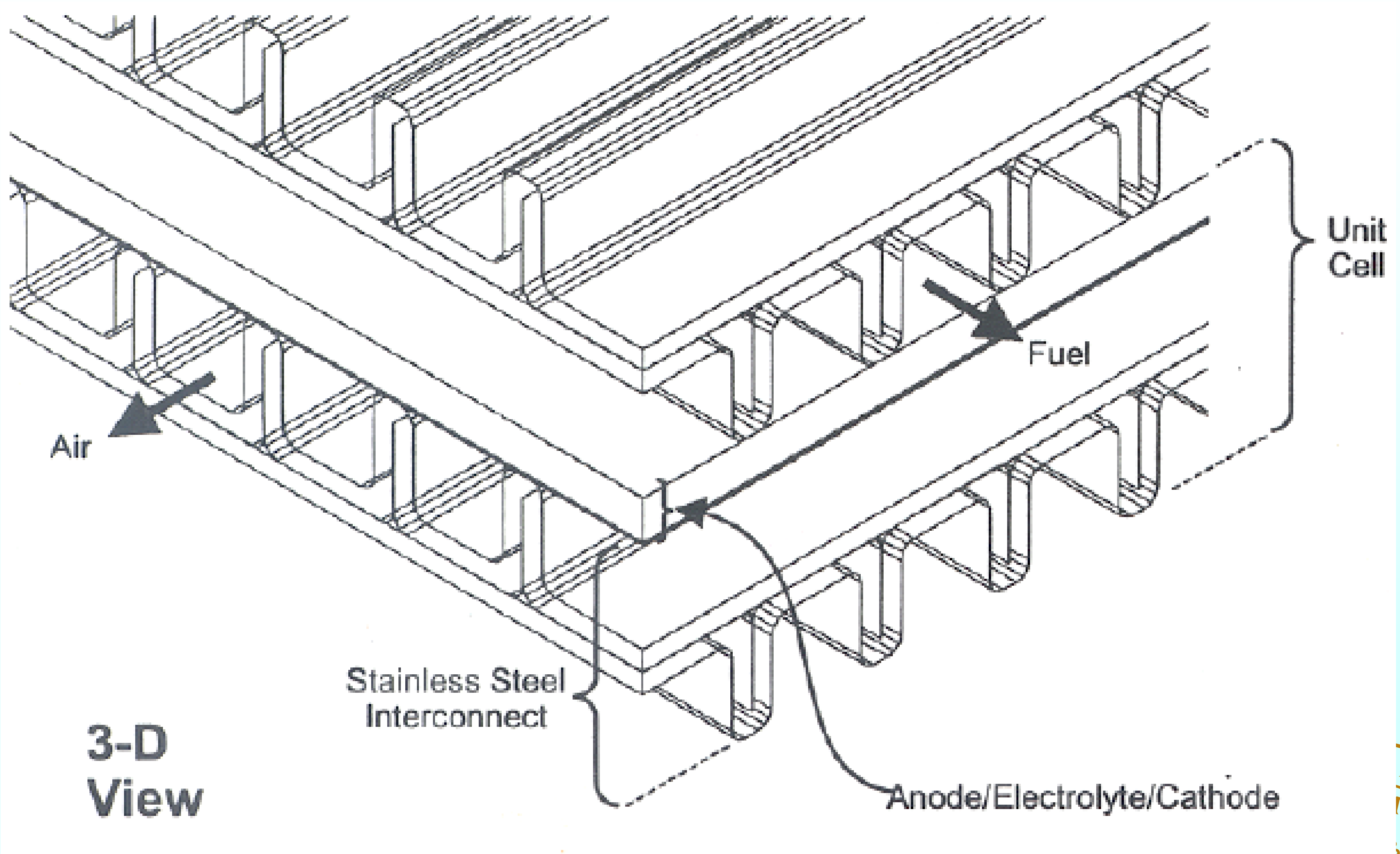


Planar SOFC Designs

- In the planar configuration, the anode, electrolyte, and cathode form thin, flat layers that are sintered together, and then separated by bipolar plates similar to the design of other types of fuel cells. The plates can be either rectangular, square, circular, or segmented in series and can be manifolded externally or internally. Many planar designs use metallic bipolar plates and operate at a lower temperature than the all-ceramic tubular design.

- **The planar SOFCs can be categorized on the basis of the supporting component of the cathode / electrolyte / anode structure. Two approaches are at hand, i.e., electrode- or electrolyte-supported cells.**

Planar SOFC with a Cross-Flow Stack Configuration



Planar SOFCs

- **Problems?**

  A recent development has been to use a bipolar interconnect made of ferritic stainless steel; this cannot be used in the manufacture higher-temperature fuel cells, because most steels oxidize quite readily at temperatures above 800°C. To limit corrosion on the air side, the operating temperature of the planar SOFC must be maintained below 800°C. However, the conductivity of the electrolyte decreases with falling temperature.

- **Reduced Temperature SOFCs:**

Dropping the Operating Temperature to Below 800°C — called *Intermediate Temperature SOFCs.*

ITSOFC design options

- There are two options for mitigating decreased performance. The well-established YSZ electrolyte can be used at temperatures as low as 700°C when the thickness is about 15 micrometers.

- To go to even lower temperatures, more conductive electrolytes such as lanthanum gallate, scandium doped zirconia, or gadolinium doped ceria (GDC) can be used. Also, at significantly-reduced operating temperature, the lanthanum manganite cathode material becomes kinetic rate limiting to the point that it must be modified or replaced.

Anode-Supported ITSOFCs

- A newer stack configuration is the anode-supported concept. This design has a thick anode, which acts as the supporting structure. The electrolyte and cathode are very thin in comparison.

- These stacks operate within a temperature range of 700 – 800^{o}C. Each individual cell is “sandwiched” or held between metal interconnecting plates that act as air and fuel flow channels as well as the electrical connection between each cell in a stack.

- The advantage of this concept is the fact that metals are more durable than ceramics. By using the metallic bipolar plate as the main load-bearing component of the stack, the fracture resistance and thermal stress tolerance might be improved.

Intermediate Temperaute (IT) SOFCs

- **Critical Issues : Reduced Temperature Causes Lower Electrolyte Ionic Conductivity and Electrode Catalytic Activity;** $ASR_{electrolyte} < 0.15\ \Omega cm^2$.

- **Option 1: For Conventional *YSZ* Materials, Thinner Electrolyte and Electrode-Supported Structure Employed.**

Temperature (^oC)	Conductivity (Scm^{-1})	Thickness (μm)	Structures
950	0.1	150	Self-Supported
700	0.01	15	Electrode-Supported

ITSOFCs

- **Option 2:** **New Ceramic Materials Employed for Electrolyte and/or Electrodes. For example:**

Materials	Temperature (^oC)	Conductivity (Scm^{-1})	Thickness (μm)	Structures
YSZ	700	0.01	15	Thin Electrolyte
Samarium Doped Ceria and Li_2SO_4	400-700	0.01-0.4	500	Thick Electrolyte

Performance of ITSOFC at Reduced Temperatures