# Glass in energy

# Glasses for fuel cells

# and H$_2$ storage

# MAT 498

## Lehigh University

# Fuel cells

# Fuel cells and the hydrogen economy

Fuel cells (FCs) achieve the direct conversion of chemical to electrical energy and will certainly find widespread use as they have very high efficiencies, may use common fuels and can reduce $CO_2$ emissions, at zero noise level, to improve the environment. A primitive fuel cell was demonstrated ~ 160 yrs ago.

Compared to the existing internal combustion engines such as gasoline and diesel, FCs can provide higher generating efficiency between ~ 30 – 60 %. Besides, they practically emit no $CO_2$ nor other exhaust gases, thus drawing much attention as an **environment-friendly**, next-generation power generating system.

Most FCs used $H_2$ as the fuel. Although the introduction of the $H_2$ economy may seem attractive, the cheapest technology for large scale production of hydrogen is the steam reforming of natural gas, which produces significant emissions of greenhouse gases. And the problem of $H_2$ storage is also not solved yet.

For FCs to become widely used one will need optimal choice of fuel and development of alternative materials in the FC stack. Present FC prototypes still use materials selected more than 30 years ago.

# Steam reforming of natural gas

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

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$$CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$$
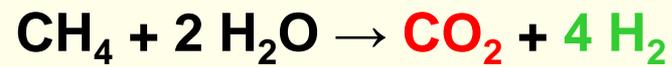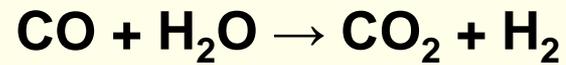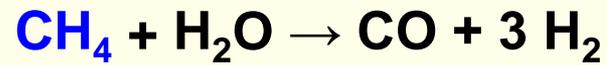
The main constituents of a FC are the electrolyte (ionic conductor) and the two electrodes (cathode and anode). The two main types of FC where this lecture will focus utilize solid electrolytes; they are the intermediate/high temperature Solid Oxide Fuel Cells (SOFCs) and the low temperature Proton Exchange Membrane Fuel Cells (PEMFCs).

At present, only the technologies employing solid electrolytes (SOFC and PEMFC) seem to have real potential.

SOFCs are all ceramic devices which operate in the range of 500 – 1000 $^o$C. One advantage over low T cells is their ability to use CO as a fuel. But their cost is high.

The current PEMFCs use ~ 100 micron thick film Nafion membranes and thus are also known as Polymeric-Electrolyte-Membrane FCs (PEMFCs, as well), but they always require pure H$_2$ fuel supplied to the anode.

The figure sumarizes the different types of FCs under active development. The anode is the fuel electrode and the cathode is the air electrode.

PEMFCs require pure $H_2$ supplied to the anode. But in high T SOFCs e.g. , both $H_2$ and CO can be electrochemically oxidized at the anode.

If there is no breakthrough in the production and storage of $H_2$, the hydrogen economy concept will remain elusive. Then, for FCs to become viable, they will have to operate on alcohol or other hydrocarbon fuels. Otherwise, FC technology will remain a niche market only wherever $H_2$ may be a viable commercial option, like for city bus fleets.
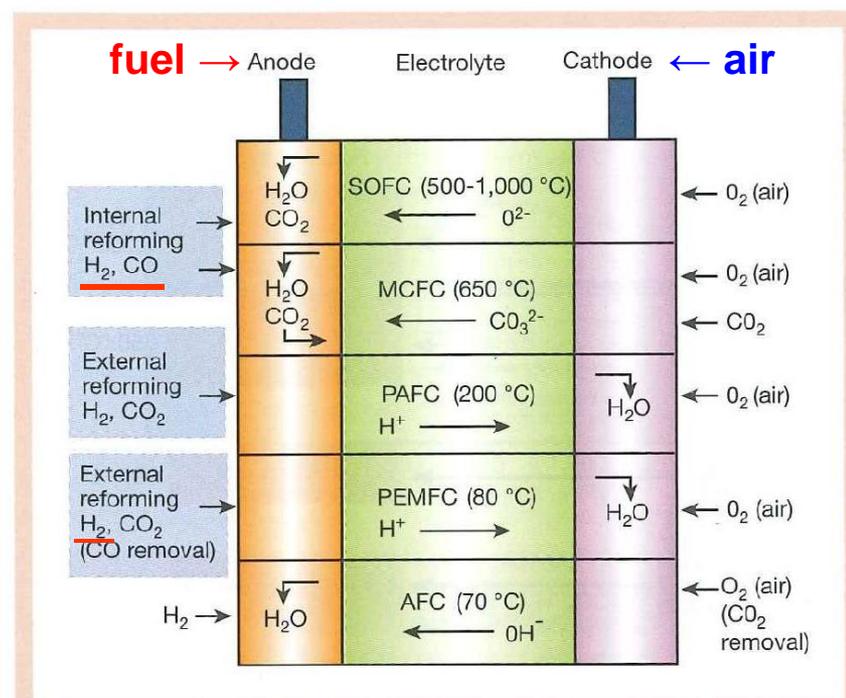


**Figure 1** Summary of fuel-cell types. The oxidation reaction takes place at the anode $(+)$ and involves the liberation of electrons (for example, $O^{2-} + H_2 = H_2O + 2e^-$ or $H_2 = 2H^+ + 2e^-$). These electrons travel round the external circuit producing electrical energy by means of the external load, and arrive at the cathode $(-)$ to participate in the reduction reaction (for example, $1/2O_2 + 2e^- = O^{2-}$ or $1/2O_2 + 2H^+ + 2e^- = H_2O$). It should be noted that as well as producing electrical energy and the reaction products (for example, $H_2O$ and $CO_2$), the fuel-cell reactions also produce heat. The reaction products are formed at the anode for SOFC, MCFC and AFC types, and at the cathode for PAFC and PEMFC types. This difference has implications for the design of the entire fuel-cell system, including pumps and heat exchangers. To maintain the composition of the electrolyte component in the MCFC system, $CO_2$ has to be recirculated from the anode exhaust to the cathode input. Additionally, the composition of the polymeric-membrane electrolyte has to be carefully controlled during operation by an appropriate 'water management' technology.

Adapted from: B.C.H. Steele and A. Heinzel, Nature 414 (2001) 345.

# Charge carriers and fuel cell operation temperature

| FUEL CELL TYPE | ELECTROLYTE | OPERATING TEMPERATURE | CHARGE CARRIER | APPLICATION & FUEL COMMENTS |
|---|---|---|---|---|
| AFC | POTASSIUM HYDROXIDE | ~ 80°C | $OH^-$ | Space<br>Pure $H_2$,<br>CO, $CO_2$ intolerant |
| MCFC | MOLTEN CARBONATES | ~650°C | $CO_3^=$ | Stationary Power<br>Fuel flexibility |
| PAFC | PHOSPHORIC ACID | ~200°C | $H^+$ | Stationary Power, Transportation<br>Relatively pure $H_2$ |
| PEMFC | ION EXCHANGE MEMBRANE | ~50°C | $H^+$ | Transportation<br>Pure $H_2$, CO intolerant |
| SOFC | SOLID METAL OXIDE | 600-1000°C | $O^=$ | Stationary Power, APU<br>Fuel flexibility |

Adapted from: P. Singh and N.Q. Minh, Int. J. Appl. Ceram. Technol. 1 (2004) 5.
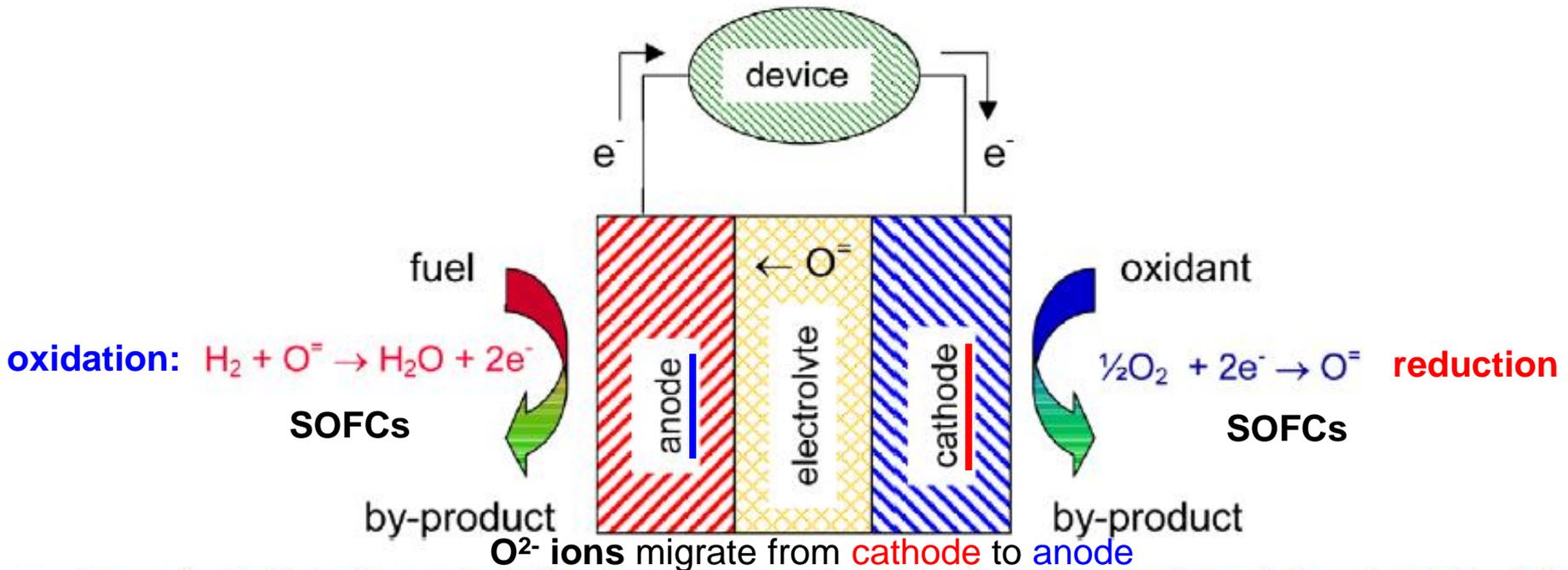
## Classification of Fuel Cells
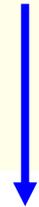
| | (PAFC) Phosphonic Acid Fuel Cell | (MCFC) Molten Carbonate Fuel Cell | (SOFC) Solid Oxide Fuel Cell | (PEFC) Polymer Electrolyte Fuel Cell |
|---|---|---|---|---|
| Electrolytic membrane | Phosphate water solution | Li-Na carbonate | Zirconia ceramic | Polymeric membrane |
| Working temperature range | 200°C | 650~700°C | 900~1000°C | 70~100°C |
| Fuel | Reformed hydrogen (natural gas, etc.) | Natural gas, LP gas | Natural gas, LP gas | Pure hydrogen, refomed hydrogen |
| Generating efficiency | 35~45% | 45~60% | → 45~65% | → 30~40% |
| Characteristics | Works at relatively low temperatures. | Provides high generating efficiency. | Provides high generating efficiency. | Works at low temperatures; downsizing possible. |
| Main applications | Cogeneration; decentralized power source | Substitutes for large-scale thermal power plants; cogeneration | Substitutes for medium-scale thermal power plants; cogeneration | Automotive power source; home cogeneration; Portable power source |

Adapted from:   http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech60.pdf

**Q.**

# Solid Oxide Fuel cells

# SOFCs

$$H_2 + \tfrac{1}{2}\, O_2 \rightarrow H_2O$$



oxidation: $H_2 + O^= \rightarrow H_2O + 2e^-$    $\tfrac{1}{2}O_2 + 2e^- \rightarrow O^=$   reduction

**SOFCs**      **SOFCs**

$O^{2-}$ **ions** migrate from cathode to anode

Schematic of a fuel cell, comprised of an electrolyte, an anode and a cathode. The overall chemical reaction is $H_2 + 1/2\, O_2 \rightarrow H_2O$. Anode and cathode reactions given are appropriate only for oxide ion conducting electrolytes. The reactions would be modified for electrolytes with different mobile ions, but the general principle remains unchanged.

In SOFCs, the cathode and the anode are made from porous ceramic materials and the electrolyte consists of a dense oxygen ion conducting ceramic like Yttria Stabilized Zirconia (YSZ), Lanthanum Strontium Manganite (LSM) or Gadolinium doped Ceria (GDC).

**Classical oxygen ion conductors:**

To introduce mobile oxygen vacancies, tri- or di-valent dopants are added to $ZrO_2$. For a tri-valent dopant, M (e.g. $Y^{3+}$):

$$M_2O_3 \rightarrow 2\ M'_{Zr} + 3\ O_O + V_O^{\cdot\cdot}$$
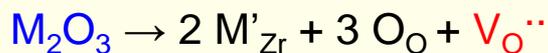
with one oxygen vacancy created for every two M atoms incorporated.
The conductivity increases up until a certain [M], then decreases sharply. The maximum is e.g. 8% Y in YSZ.

Adapted from: Sossina M. Haile, Acta Mater. 51 (2003) 5981.



(a)

(b)
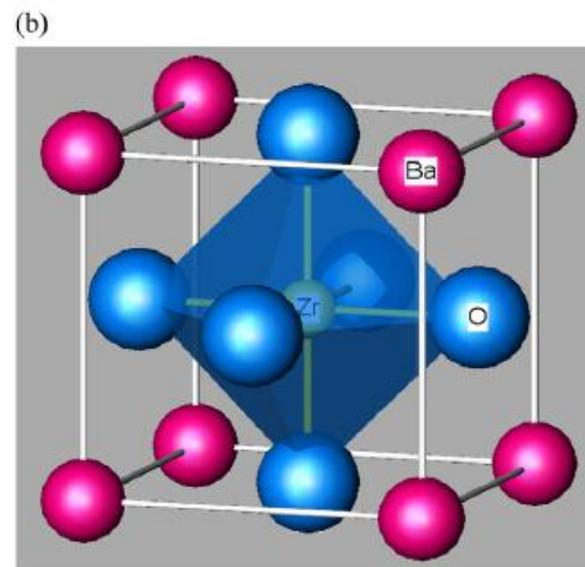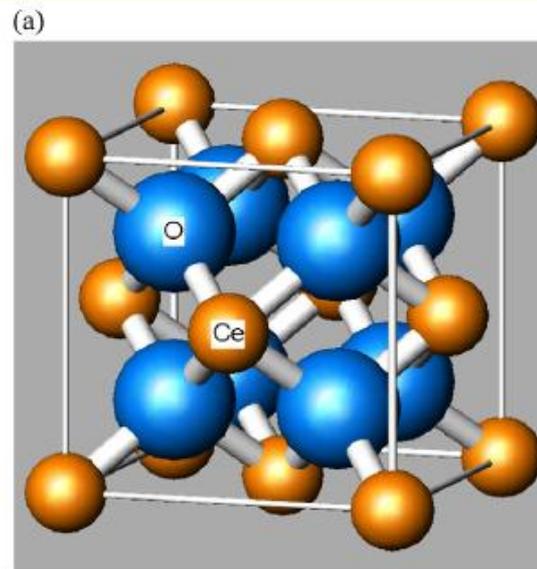
Crystal structure of conducting oxides: (a) fluorite structure, exhibited by stabilized zirconia and by ceria; (b) per-ovskite structure, exhibited by oxygen ion conducting $LaGaO_3$, and by proton conducting $BaZrO_3$.

# Solid oxide fuel cells

Since oxygen ion conductors require high temperature operation for good conductivity, a SOFC operates at **T** ~ 600 - 900 $^o$C: so the key material challenges are related to the thermo-mechanical and thermo-chemical stabilities of the sealant. In SOFCs, lowering the operating temperature will lower costs.

The development of a robust, reliable sealing technology is one of the main technological barriers to the wide-spread commercialization of intermediate temperature SOFCs. Candidates are glasses and glass-ceramics. Namely GCs based on alkaline earth silicate and aluminosilicate materials have been investigated, as these have expansion coefficients ~ 100 - 120 x $10^{-7}$ $K^{-1}$. Another proposal has been to use, instead of rigid seals, non-crystallizing glass compositions that perform as a "viscous gasket" under the operational conditions.

Other critical issues for SOFCs are the electrodes, in particular the anode (fuel electrode). The air electrode (cathode) is a composite of (La,Sr,Mn) oxide (LSM) with YSZ to allow reduction of $O_2$ molecules to oxide ions transporting electrons to the cathode/electrolyte interface. The fuel electrode facilitates the oxidation of the fuel and electron transport from the electrolyte to the fuel/anode interface.

The possible SOFC fuels range from $H_2$ to methane, CO, diesel or coal. But, in fact, fairly pure $H_2$ is used in most cases.

*Large SOFC systems* operate at the *highest temperatures* (HT-SOFCs).

Smaller systems operate at intermediate temperatures (IT-SOFCs), without compromising the internal resistance of the cell and are planar stacks. These could even be used to supply power for A/C units in automotive vehicles.

HT operation places rigorous durability requirements on cell components. While HT operation may be preferred in terms of efficiency, for portable (intermittent) power applications, lower T is favored (IT-SOFCs).

SOFCs may have planar (IT-SOFCs) or tubular (HT-SOFCs) configuration. Seals are necessary in planar stacks.

Planar SOFCs require seals to isolate anode and cathode chambers in a stacked configuration. Literature on the sealants is limited, but these are usually **glasses** or **glass ceramics** (GCs). Still, thermal stress-induced failure at glass seals is a serious problem for planar designs. At present, heating and cooling rates cannot exceed ~ 500 $^o$C/hr, due to stresses associated with the thermal expansion mismatch and with the brittle **glass** and ceramic (GC) **seals.**
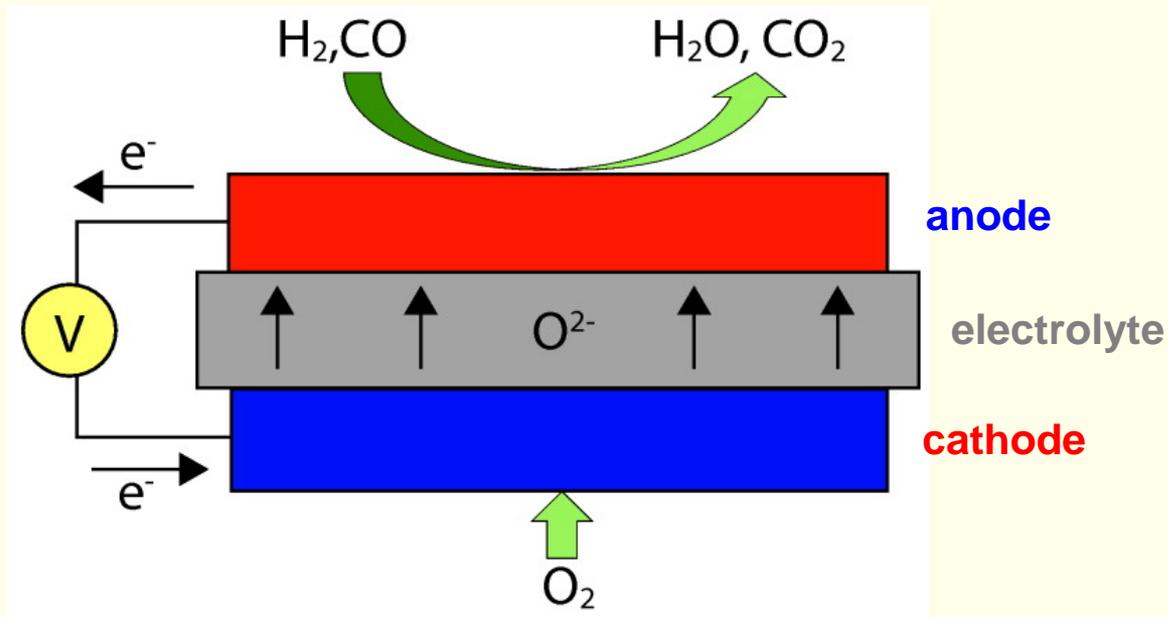


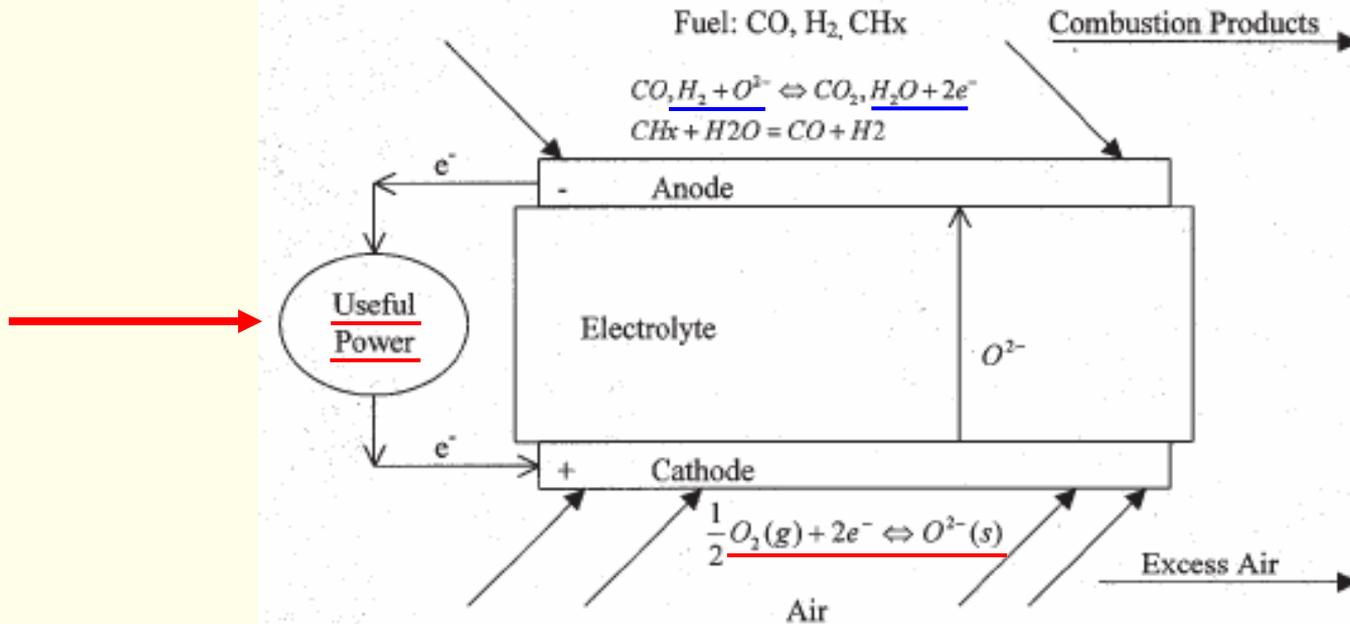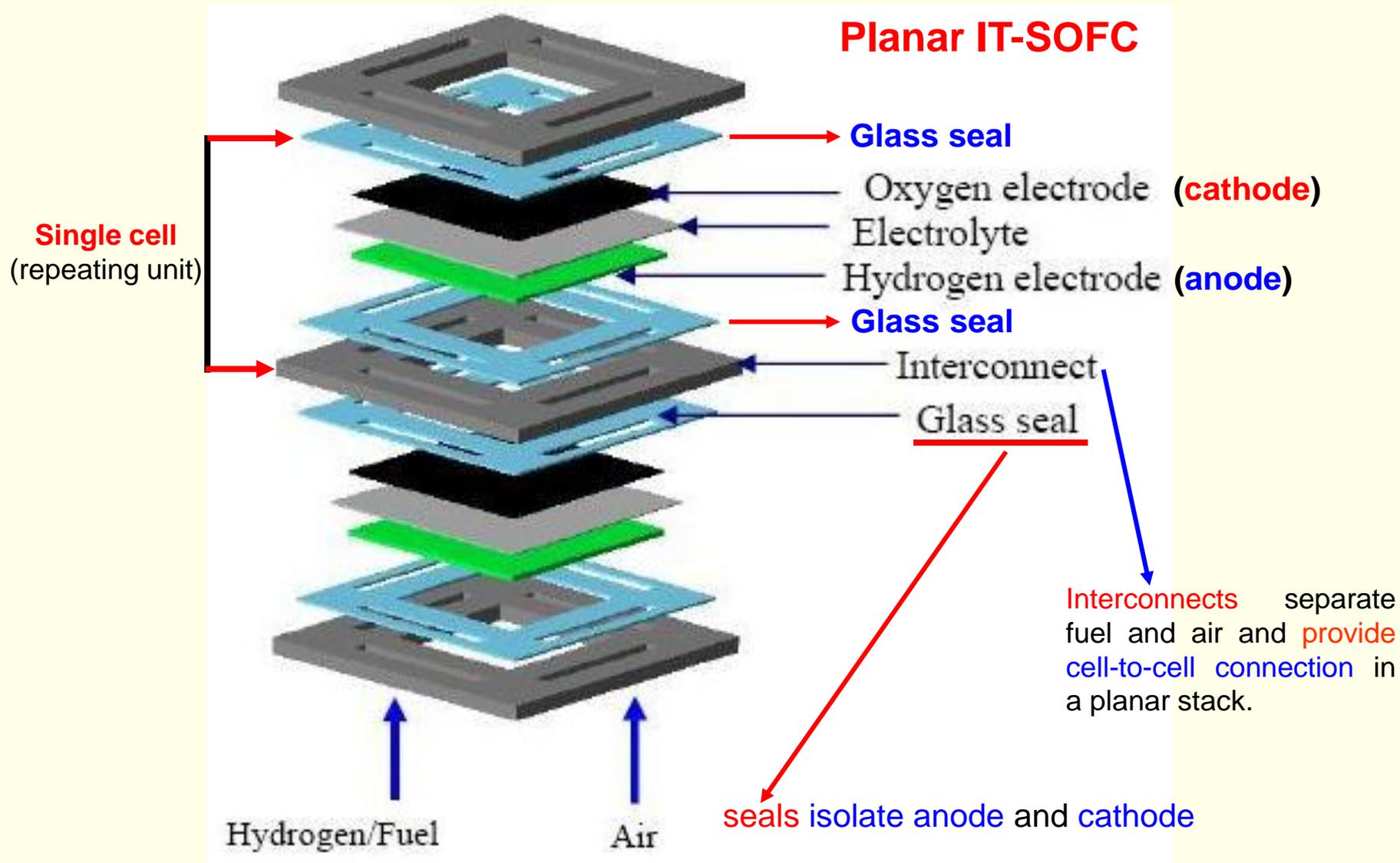**Schemat**ic of SOFC operating on H$_2$ or CO.

Fig. 1. *Schematic of a solid oxide fuel cell. Oxidation of fuel at the anode electrode and reduction of oxygen is shown at the cathode electrodes. Useful power is generated in the external circuit.*

Adapted from: P. Singh and N.Q. Minh, Int. J. Appl. Ceram. Technol. 1 (2004) 5.

Tubular designs in HT-SOFCs (used e.g. by Siemens-Westinghouse, S-W) elliminate the HT sealing problem. S-W use a 1.5 m porous tubular cathode of LSM. Electrochemical vapor deposition (EVD) is used to deposit a dense thick film (30 – 40 μm) of YSZ electrolyte. The anode is porous Ni-YSZ. The S-W tubular design remains the most developed SOFC. Such large systems ~ 70% efficiencies operating at the highest temperatures.

Tubular designs are free of seals, but are very costly, namely due to use of EVD. So nowadays one is trying to reduce the operation temperature to 500 – 600 ºC only (IT-SOFCs).

**The seal problem is the biggest problem for commercialization of IT-SOFCs.**

## Planar IT-SOFC

Glass seal

Oxygen electrode **(cathode)**

Electrolyte

Hydrogen electrode **(anode)**

Glass seal

Interconnect

Glass seal

**Single cell** (repeating unit)

Interconnects separate fuel and air and provide cell-to-cell connection in a planar stack.

seals isolate anode and cathode

Hydrogen/Fuel        Air

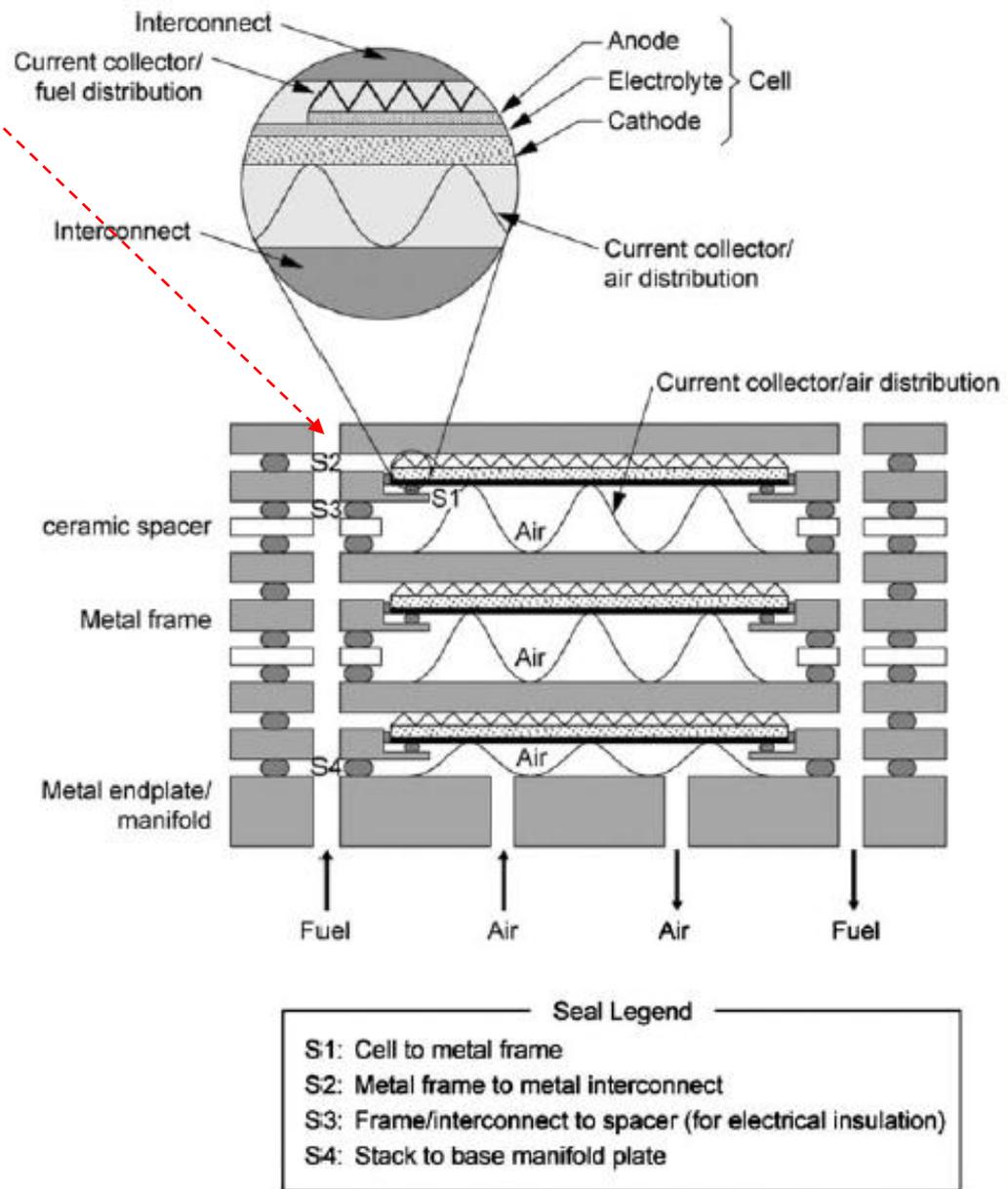Adapted from: http://www.sciencedaily.com/releases/2009/05/090521184437.htm

Schematic of seals **(S1 – S4)** typically found in a planar design SOFC stack with metallic interconnect and metallic internal gas manifold channels (possibly for counter flow pattern of fuel and air gases)

Glass was originally used as seal because it is simple to make and apply. An important property for working with glass is its viscosity.

One normally takes a frit (powdered glass) and mixes it with an organic vehicle to make a paste. The paste is applied and then heated until the organic burns out and ultimately the glass melts, at a temperature at least 1200 $^o$C for soda-lime–silica glass.

After melting and cooling, glass seals are brittle and non-yielding, making them susceptible to cracking because of tensile stresses.



Interconnect
Current collector/ fuel distribution
Anode
Electrolyte } Cell
Cathode
Interconnect
Current collector/ air distribution

Current collector/air distribution
ceramic spacer
Metal frame
Metal endplate/ manifold
S2 S3 S1 Air Air Air S4
Fuel Air Air Fuel

Seal Legend
S1: Cell to metal frame
S2: Metal frame to metal interconnect
S3: Frame/interconnect to spacer (for electrical insulation)
S4: Stack to base manifold plate

Adapted from: Paul A. Lessing, J. Mater. Sci. 42 (2007) 3465.

## Table 1  Viscosity of soda-lime–silica glass [16]

| | Temperature range (°C) | Viscosity range (poise) **1 Pa.s = 10 poise** |
|---|---|---|
| Annealing range | 400–500 | $10^{12.5}$–$10^{13.4}$ |
| Softening point | 700 | $10^{7.6}$ |
| Working range | 700–950 | $10^{4}$–$10^{7.6}$ |
| Melting range | 1200–1400 | $10^{1.5}$–$10^{2.5}$ |

Adapted from: Paul A. Lessing, J. Mater. Sci. 42 (2007) 3465.

Coefficient of thermal expansion for selected glass compositions **(~ 10 – 12 x 10$^{-6}$ °C$^{-1}$)**

| Code | Name | CTE (K$^{-1}$) (0–300 °C) × 10$^{-6}$ | Softening Pt. (°C) |
|------|------|------|------|
| 7740[a] | Pyrex | ~~3.25~~ | 821 |
| 0080[a] | Soda lime | 9.35 | 696 |
| 0139[a] | Potash soda alkali lead | 9.70 | 658 |
| 1990[a] | Potash soda lead | 12.4 | 500 |
| 7567[a] | Lead Zn borate | 12.0 | 358 |
| 7576[a] | Zn boric lead | 10.0 | 372 |
| 7580[a] | Pb Zn borosilicate | 10.0 | 374 |
| 9048[a] | Alkali strontium | 9.90 | 688 |
| SP 712[b] | NA | 9.70 | 628 |
| SP 1360[b] | NA | 12.4 | 632 |

**(Pb)** brackets rows 1990, 7567, 7576, 7580.

[a] Corning Glass
[b] Speciality Glass Inc.

Adapted from: Paul A. Lessing, J. Mater. Sci. 42 (2007) 3465.

| Representative glass–ceramic compositions | | | | | | | |
|---|---|---|---|---|---|---|---|
| Source (Code) | BaO | MgO | SrO | $La_2O_3$ | $B_2O_3$ | $Al_2O_3$ | $SiO_2$ |
| ANL (14) | | | 24.56 | 20.13 | 40.29 | 6.92 | 8.11 |
| PNNL (9) | 36.9 | | | | | 10.5 | 52.6 |
| PNNL (14) | 30.0 | 10.0 CaO | | | 20.0 | 10.0 | 30.0 |
| Julich (10) | | 38.0 | | | 5.0 | 10.0 | 45.0 |
| Julich (BAS) | 45.0 | | | | 5.0 | 5.0 | 45.0 |

ANL = Argonne National Laboratory

PNNL = Pacific Northwest National Laboratory

Alkaline earth aluminosilicate GCs have expansion coefficients ~ 10 – 12 x $10^{-6}$ $K^{-1}$.

Adapted from: Paul A. Lessing, J. Mater. Sci. 42 (2007) 3465.
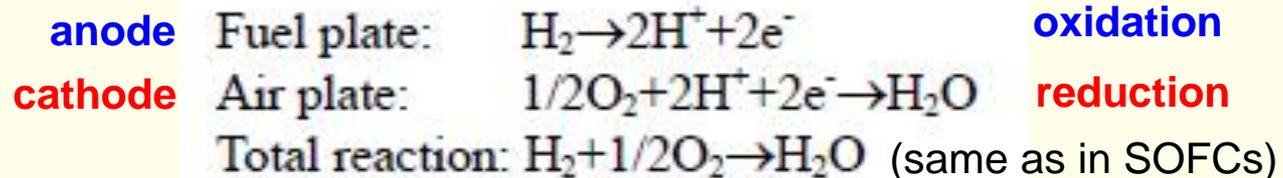
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# PEM Fuel cells

**PEMFCs** are hopefully expected as a new power source for the next-generation vehicles, as these cells can work at relatively low temperatures and also permit to materialize downsized cars with higher power because of their high current density.

There are focused efforts on the research and development of materials that can perfectly seal hydrogen, which is the fuel for these cells, and the establishment of their sealing methods.
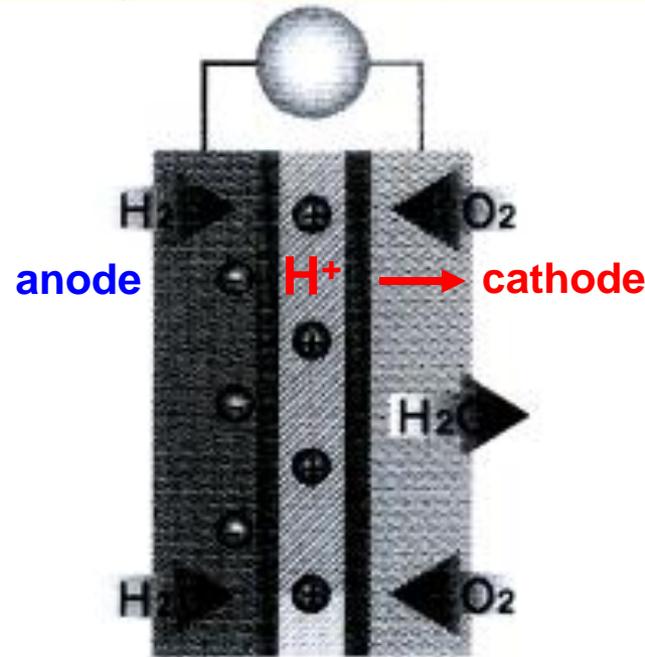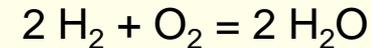
anode    H⁺ ⟶    cathode

The principle of fuel cell

**Protons** migrate from anode to cathode.

| anode | Fuel plate: | $H_2 \rightarrow 2H^+ + 2e^-$ | oxidation |
| cathode | Air plate: | $1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O$ | reduction |
| | Total reaction: | $H_2 + 1/2 O_2 \rightarrow H_2O$ | (same as in SOFCs) |

## PEMFCs

The normal case for PEMFCs is operation with pure $H_2$ and oxygen (or air, with 21% $O_2$) .

These fuel cells produce heat and water:

$$2\ H_2 + O_2 = 2\ H_2O$$

by means of $H_2$ oxidation (at the anode). They require Pt as an electrocatalyst, which adds to the costs.

Polymer Electrolyte MFCs operate at ~ 80 °C. The Nafion membrane is a fluorinated polymer electrolyte (from DuPont). GE initiated the development of these cells in the 1950s. Use of Nafion, also a proton conductor, is more recent. The proton conduction mechanism is based on the migration of hydrated protons ($H_3O^+$).

A significant niche market for PEMFC are the city buses. Other markets may be stationary power and other types of transport, in the future. Also possible are PEMFCs for portable electronic devices.

**Electrolyte**

**Anode**　　**Cathode**

**The fuel cell is a battery-like system.**

**PEMFCs**

$$H_2 \rightarrow 2\,H^+ + 2\,e^-$$

$$2\,H^+ + 2\,e^- + \tfrac{1}{2}\,O_2 \rightarrow H_2O$$

Hydrogen　　Oxygen

Hydrogen　$H^+$　Oxygen

Hydrogen　$H^+$　Oxygen

Catalyst　　　　　　Catalyst

Anode　　　　　　Cathode
**Proton Electrolyte Membrane**

**Fuel Cell Stack**

**Protons** migrate from anode to cathode.

Figure 1. Schematic illustrating multiple fuel cells combined in a stack.

Figure 2. Schematic diagram of the major components and electrochemical reactions in a PEM fuel cell.

Multiple cells connected in series generate more electricity. In PEM cells, each electrode is comprised of a porous, high-surface area material impregnated with an electrocatalyst, typically Pt or a Pt alloy. The electrolyte is a polymeric membrane (such as Nafion) which serves as a proton conductor.

$H_2$ gas is split into protons and electrons at the anode. The protons are conducted through the electrolyte membrane; the electrons flow around the membrane, generating an electrical current. The charged ions ($H^+$ and $e^-$) combine with oxygen at the **cathode**, producing **water** and **heat**.

# Phosphate glasses as electrolytes in PEMFCs

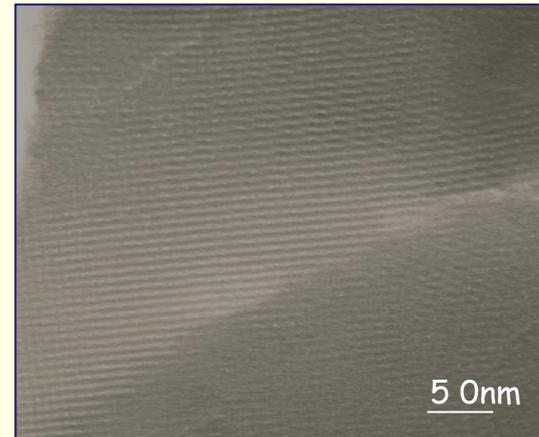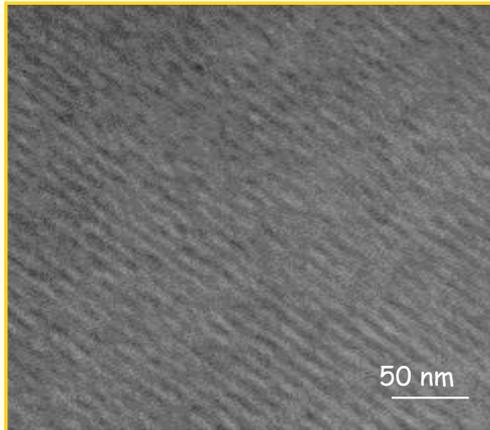**Proton-conducting glasses** have been investigated as possible membrane (electrolyte) materials in **PEMFCs.**

These include proton- conducting phosphate glasses, but with somewhat limited success so far.
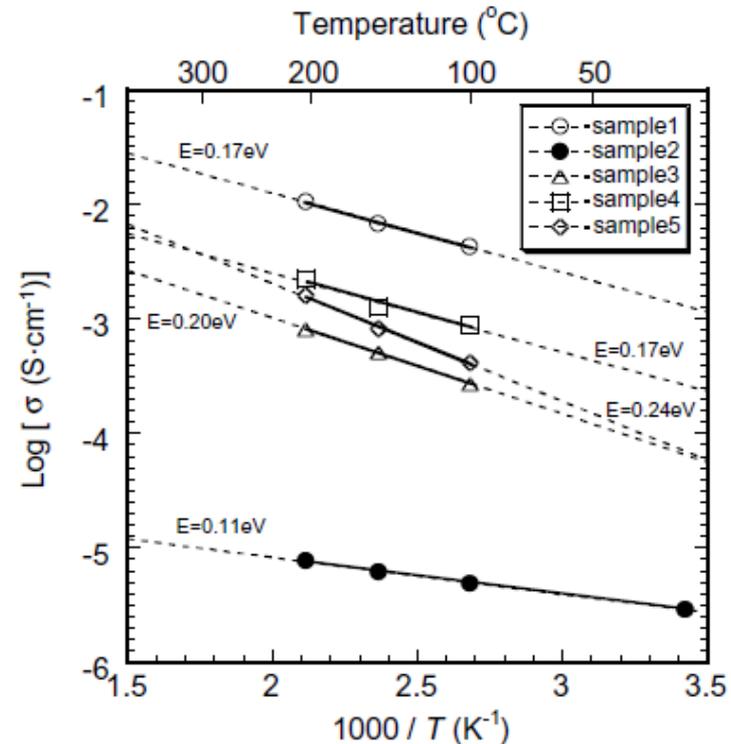


Protonic conductivity versus $1/T$ plots for the glasses obtained by the present processing (in ambient atmosphere, Au-electrode, at 10 kHz). Sample 1: $22BaO–2.5La_2O_3–0.5Al_2O_3–75P_2O_5$ (700 °C). Sample 2: $5SrO–15BaO–10PbO–1Al_2O_3–69P_2O_5$ (600 °C). Sample 3: $6SrO–18BaO–12PbO–64P_2O_5$ (600 °C). Sample 4: $12SrO–12BaO–12PbO–64P_2O_5$ (700 °C). Sample 5: $18SrO–6BaO–12PbO–64P_2O_5$ (800 °C). Sample glasses (in mole ratio) were prepared by heating a mixture of raw materials such as $H_3PO_4$ and metal carbonates at the temperatures given in parenthesis for 30 min, and subsequently by quenching.

Adapted from: Y. Abe et al., J. Non-Cryst. Solids 351 (2005) 2138.

A. Duran and co-workers (ICV, Madrid, Spain) have been developing meso-structured, meso-porous phosphate-based films by self-assembly and **sol-gel**, as possible membranes for PEMFCs:

**$P_2O_5 - SiO_2$**                    **$P_2O_5 - TiO_2$**



The system **$P_2O_5 - SiO_2 - TiO_2$** is also under investigation at present.

In summary, glasses may be used for PEMFCs, as proton conducting membranes (electrolytes); in intermediate temperature SOFCs, glasses and glass-ceramics are used as sealants.

The main trend at present are PEM (polymer) FCs for transportation and HT-SOFCs for large stationary applications.

However, PEMFCs must still reduce costs with Pt catalysts. In HT-SOFCs, the main barrier is the anode; the best so far is Ni-YSZ, but it still has corrosion resistance problems.

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# Hydrogen storage

H₂ adsorption

2 to 8 kJ per mole H₂

Carbon nanotubes    Zeolites    MOF    Clathrates

MgH₂    NaAlH₄

Na
Al
H
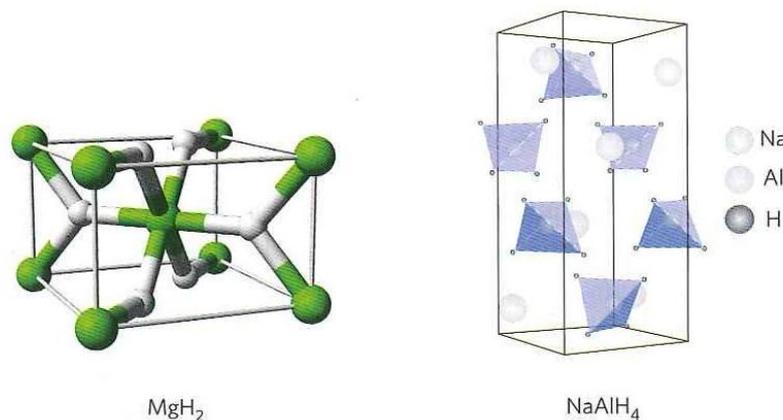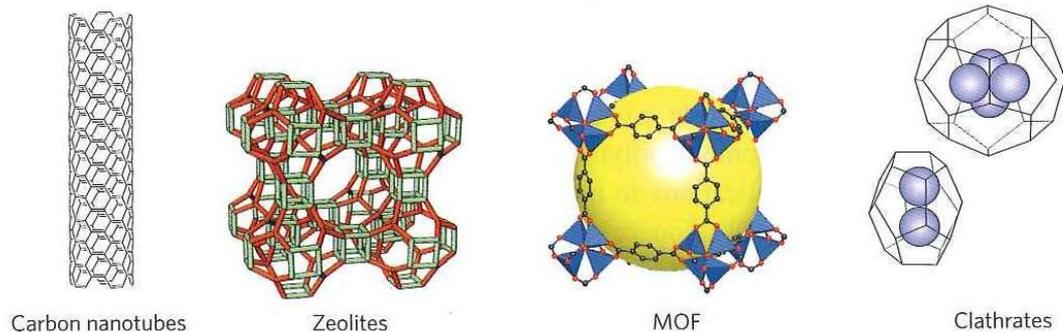
50 to 100 kJ per mole H₂

H₂ absorbtion (= H₂ adsorption + H₂ dissociation)

Hydrogen-storage materials can be split into two classes. Materials that trap molecular $H_2$ by adsorption onto their surfaces and/or into their pores, which include materials such as carbon nanotubes, zeolites, metal–organic frameworks and clathrates (top). Materials such as hydrides ($MgH_2$) or complex hydrides ($NaAlH_4$), which capture atomic hydrogen via a two-step process first by the adsorption of $H_2$ and then by the dissociation and diffusion of H within the bulk of the material (bottom). (Figure courtesy of R. Janot; credits: zeolite, ref. 58 ©2002 NPG; MOF, ref. 59 ©2003 NPG; $MgH_2$, ©Ben Mills.)

**Hydrogen** is the most important component for the operation of fuel cells. But its safe and economical production, storage and transportation present problems.

Reforming of H-containing compounds such as hydrocarbons is not a clean route for the production of $H_2$, so the electrolysis of water may have to be developed in a large scale (but at high cost).

Regarding **storage**, $H_2$ is normally stored at low T as a liquid, or at high pressure as a gas, but an adequate technology is not yet available.

The lack of an infrastructure for $H_2$ distribution seems to be the overriding limitation for its application in vehicles.

Volumes occupied by **4 kg** of $H_2$ compacted in different ways.



**Figure 1** Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

$Mg_2NiH_4$        $LaNi_5H_6$        $H_2$ (liquid)        $H_2$ (200 bar)
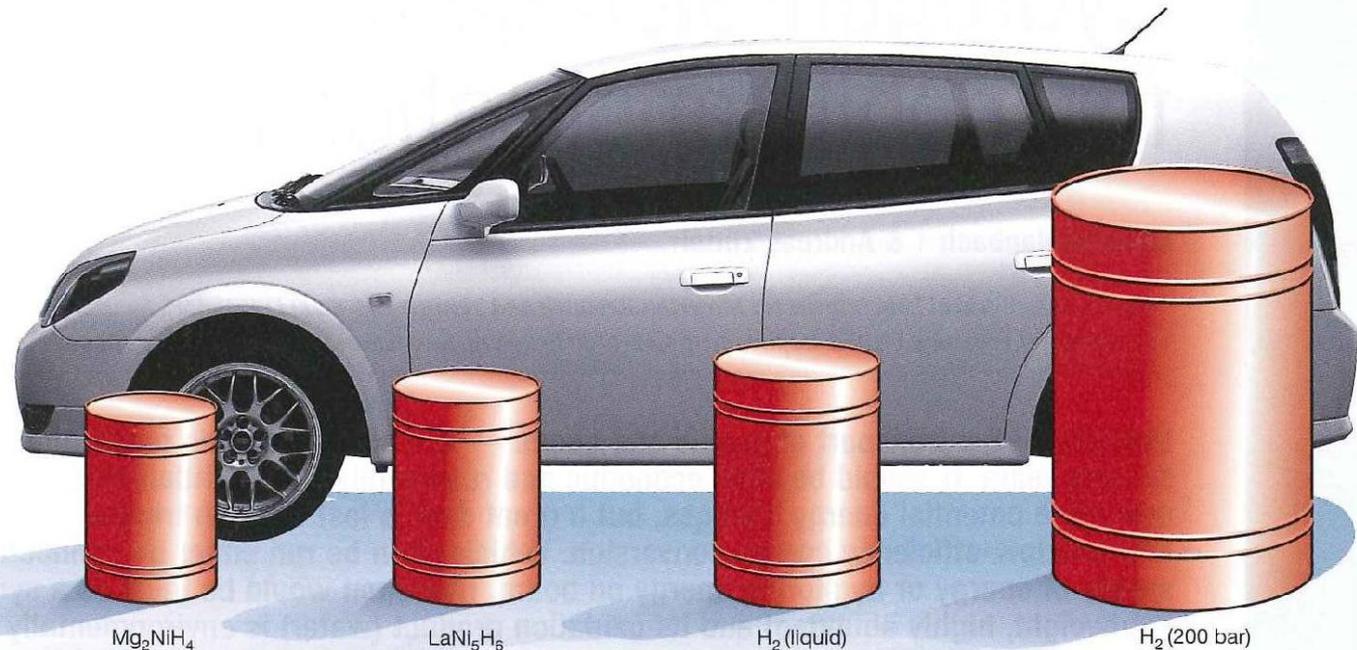
The $H_2$ embrittlement of steel, in particular, calls for new storage techniques.

Adapted from: Louis Schlapbach and Andreas Zuttel, Nature 414 (2001) 353.

## Glass microspheres for hydrogen storage

The use of Hollow Glass Micro Spheres (HGMS) was proposed ~ 15 years ago as a viable alternative for $H_2$ storage and transportation at pressures up to 100 MPa (~ 1000 atm).

Recycled cullet can be used to prepare such spheres and, if one of them breaks, the volume of $H_2$ released is too small to cause any hazard. Sphere size is ~ 50 – 100 μm.

The HGMS can be fabricated by flame spray pyrolysis of glass frit. Glass frit is dropped directly into an oxy-fuel flame, with the glass viscosity becoming low enough for the frit particles to take on a spherical shape (as a result of surface tension), which is retained during quick cooling. The hollow cavity formation inside the spheres is obtained by adding a blowing agent to the glass frit (e.g. $Na_2SO_4$, used as a refining agent in common glass melting), which decomposes and expands.

The $H_2$ loading of the spheres is achieved by placing them in a high pressure hydrogen atmosphere and heating them up to a temperature sufficient for $H_2$ in-diffusion. Outgassing is later forced through re-heating.

**Glass microspheres for hydrogen storage**

Recently, Shelby and co-workers have suggested the occurrence of photo-induced outgassing of $H_2$ from the HGMS, when these are doped with elements such as Fe, Co or Ni and are exposed to near-IR light (~ 2 μm), diffusion is greatly enhanced when compared with heating alone. The rate of $H_2$ release can be controlled by the light intensity and it also increases slightly with an increase in microsphere diameter.
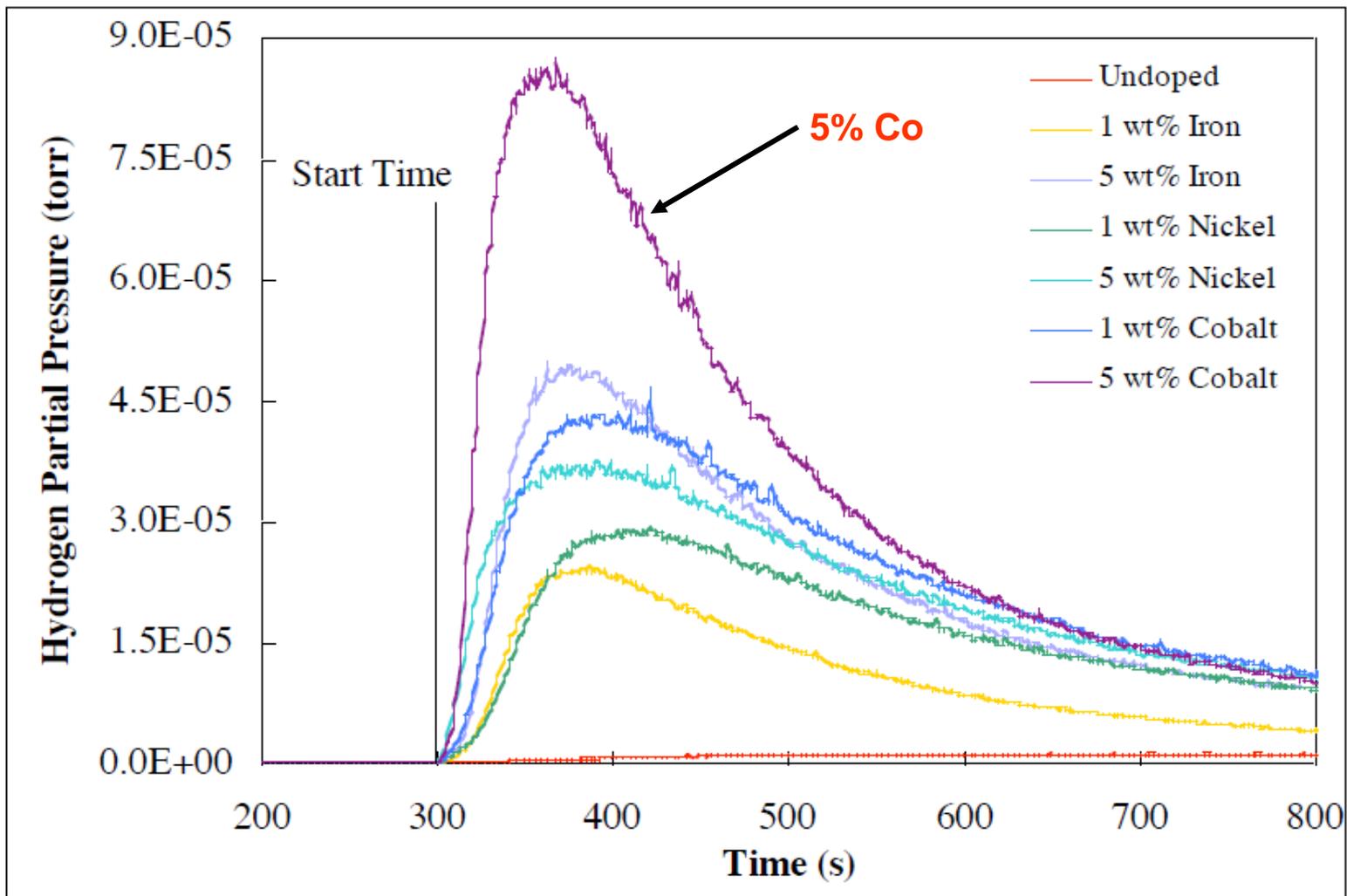
Comparison of hydrogen photo-outgassing from undoped HGMS and 1 and 5 wt% doped HGMS.

**Q.**

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