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 CO₂ 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 CO₂ nor other exhaust gases, thus drawing much attention as an environment-friendly, next-generation power generating system.

Most FCs used H₂ as the fuel. Although the introduction of the H₂ 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 H₂ 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

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2 \]
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 °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 H₂ fuel supplied to the anode.
The figure summarizes the different types of FCs under active development. The anode is the fuel electrode and the cathode is the air electrode.

PEMFCs require pure H₂ supplied to the anode. But in high T SOFCs e.g., both H₂ and CO can be electrochemically oxidized at the anode.

If there is no breakthrough in the production and storage of H₂, 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 H₂ may be a viable commercial option, like for city bus fleets.

<table>
<thead>
<tr>
<th>FUEL CELL TYPE</th>
<th>ELECTROLYTE</th>
<th>OPERATING TEMPERATURE</th>
<th>CHARGE CARRIER</th>
<th>APPLICATION &amp; FUEL COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>POTASSIUM HYDROXIDE</td>
<td>~ 80°C</td>
<td>OH⁻</td>
<td>Space, Pure H₂, CO, CO₂ intolerant</td>
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<tr>
<td>MCFC</td>
<td>MOLTEN CARBONATES</td>
<td>~ 650°C</td>
<td>CO₃⁻</td>
<td>Stationary Power, Fuel flexibility</td>
</tr>
<tr>
<td>PAFC</td>
<td>PHOSPHORIC ACID</td>
<td>~ 200°C</td>
<td>H⁺</td>
<td>Stationary Power, Transportation, Relatively pure H₂</td>
</tr>
<tr>
<td>PEMFC</td>
<td>ION EXCHANGE MEMBRANE</td>
<td>~ 50°C</td>
<td>H⁺</td>
<td>Transportation, Pure H₂, CO intolerant</td>
</tr>
<tr>
<td>SOFC</td>
<td>SOLID METAL OXIDE</td>
<td>600-1000°C</td>
<td>O⁻</td>
<td>Stationary Power, APU, Fuel flexibility</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Classification of Fuel Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolytic membrane</td>
</tr>
<tr>
<td>Working temperature range</td>
</tr>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>Generating efficiency</td>
</tr>
<tr>
<td>Characteristics</td>
</tr>
<tr>
<td>Main applications</td>
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Adapted from: http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech60.pdf
Solid Oxide Fuel cells
SOFCs

H₂ + ½ O₂ → H₂O

 oxidation:  H₂ + O²⁻ → H₂O + 2e⁻

Schematic of a fuel cell, comprised of an electrolyte, an anode and a cathode. The overall chemical reaction is H₂ + ½ O₂ → H₂O. 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.

Solid oxide fuel cells

Since oxygen ion conductors require high temperature operation for good conductivity, a SOFC operates at $T \sim 600 - 900 \, ^\circ\text{C}$: 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 $\sim 100 - 120 \times 10^{-7} \, \text{K}^{-1}$. 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 °C/hr, due to stresses associated with the thermal expansion mismatch and with the brittle glass and ceramic (GC) seals.

![Schematic of SOFC operating on H₂ or CO.](http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=105700873)
Tubular designs in HT-SOFCs (used e.g. by Siemens-Westinghouse, S-W) eliminate 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 °C only (IT-SOFCs).
The seal problem is the biggest problem for commercialization of IT-SOFCs.

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

seals isolate anode and cathode

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

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

<table>
<thead>
<tr>
<th></th>
<th>Temperature range (°C)</th>
<th>Viscosity range (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing range</td>
<td>400–500</td>
<td>$10^{12.5}$ – $10^{13.4}$</td>
</tr>
<tr>
<td>Softening point</td>
<td>700</td>
<td>$10^{7.6}$</td>
</tr>
<tr>
<td>Working range</td>
<td>700–950</td>
<td>$10^{4}$ – $10^{7.6}$</td>
</tr>
<tr>
<td>Melting range</td>
<td>1200–1400</td>
<td>$10^{1.5}$ – $10^{2.5}$</td>
</tr>
</tbody>
</table>

1 Pa.s = 10 poise


<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>CTE (K⁻¹) (0–300 °C) × 10⁻⁶</th>
<th>Softening Pt. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7740ᵃ</td>
<td>Pyrex</td>
<td>3.25</td>
<td>821</td>
</tr>
<tr>
<td>0080ᵃ</td>
<td>Soda lime</td>
<td>9.35</td>
<td>696</td>
</tr>
<tr>
<td>0139ᵃ</td>
<td>Potash soda alkali lead</td>
<td>9.70</td>
<td>658</td>
</tr>
<tr>
<td>1990ᵃ</td>
<td>Potash soda lead</td>
<td>12.4</td>
<td>500</td>
</tr>
<tr>
<td>7567ᵃ</td>
<td>Lead Zn borate</td>
<td>12.0</td>
<td>358</td>
</tr>
<tr>
<td>7576ᵃ</td>
<td>Zn boric lead</td>
<td>10.0</td>
<td>372</td>
</tr>
<tr>
<td>7580ᵃ</td>
<td>Pb Zn borosilicate</td>
<td>10.0</td>
<td>374</td>
</tr>
<tr>
<td>9048ᵃ</td>
<td>Alkali strontium</td>
<td>9.90</td>
<td>688</td>
</tr>
<tr>
<td>SP 712ᵇ</td>
<td>NA</td>
<td>9.70</td>
<td>628</td>
</tr>
<tr>
<td>SP 1360ᵇ</td>
<td>NA</td>
<td>12.4</td>
<td>632</td>
</tr>
</tbody>
</table>

ᵃ Corning Glass
ᵇ Speciality Glass Inc.

(~ 10 – 12 x 10⁻⁶ °C⁻¹)
Alkaline earth aluminosilicate GCs have expansion coefficients $\sim 10 - 12 \times 10^{-6} \text{ K}^{-1}$.
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.

**Protons** migrate from anode to cathode.

**PEMFCs**

- **Anode**: Fuel plate: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)
- **Cathode**: Air plate: \( 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \)
- **Total reaction**: \( \text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \)

(same as in SOFCs)

Adapted from: http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech60.pdf
The normal case for PEMFCs is operation with pure H\textsubscript{2} and oxygen (or air, with 21\% O\textsubscript{2})
. These fuel cells produce heat and water:

\begin{equation}
2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}
\end{equation}

by means of H\textsubscript{2} oxidation (at the anode). They require Pt as an electrocatalyst, which adds to the costs.

Polymer Electrolyte MFCs operate at \~ 80 \degree 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\textsubscript{3}O\textsuperscript{+}).

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.
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.

Adapted from: http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=105700873
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.

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:

\[
P_2O_5 - \text{SiO}_2\quad \text{and}\quad P_2O_5 - \text{TiO}_2
\]

The system \( P_2O_5 - \text{SiO}_2 - \text{TiO}_2 \) 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.
Hydrogen storage
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 H₂, so the electrolysis of water may have to be developed in a large scale (but at high cost).

Regarding storage, H₂ 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 H₂ distribution seems to be the overriding limitation for its application in vehicles.

Volumes occupied by 4 kg of H₂ compacted in different ways.

The H₂ embrittlement of steel, in particular, calls for new storage techniques.

Glass microspheres for hydrogen storage

The use of Hollow Glass Micro Spheres (HGMS) was proposed ~ 15 years ago as a viable alternative for H\textsubscript{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\textsubscript{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\textsubscript{2}SO\textsubscript{4}, used as a refining agent in common glass melting), which decomposes and expands.

The H\textsubscript{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\textsubscript{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 $\text{H}_2$ 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 $\text{H}_2$ 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.

References: