Lecture on the subject of Fuel Cells given at the IMIA Conference in Stockholm on 16th September 2003 by Manfred Schäfer, Securitas Versicherung, Germany.

Fuel Cells

A fuel Cell is a electrochemical energy conversion device. A fuel cell produces electricity, water, and heat directly from hydrogen or hydrogen rich gases and oxygen in the air.

In a fuel cell, the fuel and the oxidant gases themselves comprise the anode and cathode respectively. Thus, the physical structure of a fuel cell is one where the gases are

directed through flow channels to either side of the electrolyte.

The electrolyte is the distinguishing feature between different types of fuel cells. Different electrolytes conduct different specific ions.

In principle, all fuel cells consist of two electrodes — an anode and a cathode — and an electrolyte.

The anode, or negative (=fuel) electrode, is made of a substance that is readily oxidized (releases electrons).

The cathode, or positive (=oxidant) electrode, is made of a substance that is readily reduced (=accepts electrons).

To achieve that electrons can flow from the anode to the cathode through anexternal load, the anode and cathode are separated by an electrolyte.

The anode material dissolves into the electrolyte forming positively charged cations and leaves behind a corresponding buildup of free electrons within the anode. This buildup of electrons manifests itself as a negative charge.

In short, electrons flow from the anode to the cathode by way of theexternal load and then join the positively charged ions that migrate through the electrolyte.

The Electrolyte

The electrolyte is the core component of the fuel cell. The fuel cells are named after it.

A electrolyte is a substance which conducts electric current as a result of a dissociation into positive and negative ions, which migrate toward and frequently are discharged at the negative and positive electrodes.

Ions with a positive charge have lost one or more electrons and are known as positive ions or "protons" or "cations".

Ions with a negative charge have gained one or more electrons and are known as negative ions or "anions".

Electrolytes can be liquid or solid; some operate at high temperature, and some at low temperature.

The most familiar electrolytes are acids, bases and salts, which ionize in solution in such solvents as water etc. Many salts, such as sodium chloride, behave as electrolytes when melted in the absence of any solvent.

In a fuel cell the electrolyte has also the requirement to keep the hydrogen fuel separate from the oxidant. If this fails it comes to an accidental reaction between fuel and oxidant.

The Catalyst

Fuel cells tend to require a noble metal catalyst, typically platinum, to encourage the electrode reactions.

A catalyst is a special material that facilitates, accelerates etc. a chemical reaction retaining its own properties and without being consumed. In a fuel cell it facilitates the reaction of oxygen and hydrogen. In low temperature it is usually made of platinum powder very thinly coated onto carbon paper, cloth or a polymer. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen.

The Electrodes

A electrode is a conductor through which electricity enters or leaves an electrolyte. Fuel cells have a negative electrode (the anode) and a positive electrode (the cathode).

Types of Fuel Cells

Proton Exchange Membrane Fuel Cells (PEM)

Proton exchange membrane (PEM) (or "solid polymer") fuel cells use an electrolyte that conducts hydrogen ions (H+) from the anode to the cathode. The electrolyte is composed of

a solid polymer film that consists of a form of acidified Teflon.

PEM fuel cells are currently the most promising type of fuel cell for automotive use and have been used in the majority of prototypes built to date.

PEM fuel cells typically operate at 70 to 90 ºC (160 to 195 ºF) and a pressure of 15 to 30 psig (1 to 2 bar). Each cell can produce up to about 1.1 VDC.

Advantages and Disadvantages

The advantages of PEM fuel cells are that they:

- are tolerant of carbon dioxide. As a result, PEM fuel cells can use unscrubbed air as oxidant, and reformate as fuel.
- operate at low temperatures. This simplifies materials issues, provides for quick startup and increases safety.
- use a solid, dry electrolyte. This eliminates liquid handling, electrolyte migration and electrolyte replenishment problems.

- use a non-corrosive electrolyte. Pure water operation minimizes corrosion problems and improves safety.
- have high voltage, current and power density
- operate at low pressure which increases safety
- have good tolerance to differential reactant gas pressures
- are compact and rugged
- have relatively simple mechanical design
- use stable materials of construction

The disadvantages are that they:

- can tolerate only about 50 ppm carbon monoxide
- can tolerate only a few ppm of total sulphur compounds
- need reactant gas humidification Humidification is energy intensive and increases the complexity of the system. The use of water to humidify the gases limits the operating temperature of the fuel cell to less than water's boiling point and therefore decreases the potential for co-generation applications.
- use an expensive platinum catalyst
- use an expensive membrane that is difficult to work with
- DMFC cannot be used until it reaches 100 mW/cm2. Up to year 2003 the output density is said to be 50 mW/cm2.

Direct Methanol PEM Fuel Cells (DMFC)

PEM fuel cells can also run using methanol fuel directly, rather than hydrogen. Although the energy released during this reaction is less than when using pure hydrogen, it results

in a much simpler fuel storage system and circumvents the need to produce hydrogen.

In a direct methanol PEM fuel cell, the cells are supplied with a liquid mixture of methanol and water at the anode, and air at the cathode. At 130 ºC (266 ºF) , a noble catalyst

immediately decomposes the methanol.

PEM Fuel Cell Stack Construction

Individual fuel cells have an maximum output voltage on the order of 1 VDC. Substantial voltages and power outputs are obtained by connecting many cells electrically in series to

form a fuel cell stack.

Each fuel cell consists of a membrane electrode assembly (MEA), which consists of the anode, cathode, electrolyte and catalyst, sandwiched between two flow field

plates made of graphite. The plates channel the fuel and air to opposite sides of the MEA.

Coolant is used to regulate the fuel cell reaction temperature.

To facilitate this, cooling plates are placed between each fuel cell. These cooling plates channel the coolant past the fuel cells to absorb or supply heat as required. Seals

between the graphite plates ensure that the oxidant, fuel and coolant streams never mix within the fuel cells.

Critical areas of concern are seals, flow field pattern tolerances and cell alignment. As

with any commercial product, the resulting design must be reliable, manufacturable, economically viable and have a significant operating life.

The Membrane Electrolyte (PEM)

The solid polymer electrolyte is the ultimate distinguishing characteristic of a PEM fuel cell.

The electrolyte is a thin membrane of a plastic-like film that ranges in thickness from 50 to 175 microns. These membranes are composed of perfluorosulfonic acids, which are Teflon-like fluorocarbon polymers

Thus, PEM fuel cells ultimately use an acidic electrolyte just like phosphoric acid fuel cells.

All acidic solid polymer electrolytes require the presence of water molecules for hydrogen ion conductivity since hydrogen ions move together with water molecules during the ion exchange reaction. The ratio of water to hydrogen ions for effective conductivity is typically about 3:1.

For this reason, the gases in contact with the membrane must be saturated with water for effective fuel cell operation.

A number of commercial membranes are available such as Nafion, produced by

Dupont, and others by the Dow Chemical Company

All electrolytes must perform the fundamental functions of being a proton conductor, an electron insulator and a gas separator. In addition, manufacturers strive to produce membranes that have reasonable mechanical strength, dimensional stability (resistance to swelling), high ionic conductivity, low equivalent weight (the weight of polymer relative to the number of acid sites), and that are easily manufacturable.

Optimizing of membranes construction is on-going. Fundamental research into the catalyst layer/membrane interface is needed to further understand the processes involved in current generation.

Membrane Electrode Assembly (MEA)

If the polymer electrolyte membrane is coated on each side with porous carbon electrodes and with integrated platinum partides it is called a MEA.

The Electrodes

The electrodes provide the interface between the reactant gases and electrolyte.

A catalyst is added to the surface of each electrode where it contacts the electrolyte in order to increase the rate at which the chemical reaction occurs. A Platinum-catalyst promotes a chemical reaction by providing ready reaction. Platinum is very expensive, so

the amount used (known as the catalyst loading) is a significant factor in the cost of a fuel cell. Fuel cell designers strive to minimize the amount of platinum used while maintaining

good cell performance.

Flow Field Plates

The flow field plates channel fuel and oxidant to opposite sides of the MEA.

Each flow field plate contains a single gas channel of serpentine design that maximizes gas contact with the MEA. The specific shape of the gas channels is critical for uniform

power generation, stable cell performance and correct product water management.

The plates are typically made of graphite into which the flow channels are either machined or pressed. Graphite is the preferred material due to its excellent conductivity, low contamination and relatively low cost. Coolant plates, placed between each fuel cell, are of similar design and construction to the gas flow field plates. Coolant flow channels are designed for effective heat management.

Alkaline Fuel Cells (AFC)

Alkaline fuel cells use an electrolyte that conducts hydroxyl (OH^-) ions from the cathode to the anode. This is opposite to many other types of fuel cells that conduct hydrogen ions from the anode to the cathode.

The electrolyte is typically composed of a molten alkaline mixture such as potassium hydroxide (KOH).

The electrolyte can be mobile or immobile.

Mobile alkaline electrolyte fuel cells use a fluid electrolyte that continuously circulates between the electrodes. The product water and waste heat dilute and heat the liquid electrolyte but are removed from the cell as the electrolyte circulates.

Immobile alkaline electrolyte fuel cells use an electrolyte that consists of a thick paste retained by capillary forces within a porous support matrix such as asbestos. The paste itself provides gas seals at the cell edges. Product water evaporates into the source hydrogen gas stream at the anode from which it is subsequently condensed. The waste heat is removed by way of a circulating coolant.

Alkaline fuel cells operate at about 65 to 220 ºC (150 to 430 ºF) (and a pressure of about 1 bar (15 psi)). Each cell can produce up to between 1.1 and 1.2 VDC.

Advantages and Disadvantages

The advantages of alkaline fuel cells are that they:

- operate at low temperature
- have fast start up times (50% rated power at ambient temperature)
- have high efficiency
- need little or no expensive platinum catalyst
- have minimal corrosion
- have relative ease of operation
- have low weight and volume

The disadvantages are that they:

- are extremely intolerant to CO_2 (about 350 ppm maximum) and somewhat intolerant of CO. This is a serious disadvantage and limits both the type of oxidant and fuel that can be used in an alkaline fuel cell.

The oxidant must be either pure oxygen or air that has been scrubbed free of carbon dioxide. The fuel must be pure hydrogen due to the presence of carbon oxides in reformate.

- have a liquid electrolyte, introducing liquid handling problems
- require complex water management: Thus, the fuel cell produces water that either evaporates into the source hydrogen stream (in an immobile system) or is flushed out of the cells along with the electrolyte (in a mobile system). This water must be continually removed to facilitate further reaction.

Phosphoric Acid Fuel Cells (PAFC)

Phosphoric acid fuel cells use an electrolyte that conducts hydrogen ions (H+) from the anode to the cathode. As its name implies, the electrolyte is composed of liquid phosphoric

acid within a silicon carbide matrix material. (Some acid fuel cells use a sulphuric acid electrolyte.)

Phosphoric acid fuel cells operate at about 150 to 205 ºC (300 to 400 ºF) and a pressure of about 1 bar (15 psi).

Each cell can produce up to about 1.1 VDC.

A new form of acid fuel cell currently under development uses a solid acid electrolyte.

These cells are made of compounds and operate at temperatures up to 250 ºC (480 ºF) with open circuit voltages of 1.11 V.

They offer the advantage of operation without humidity, moderate carbon monoxide tolerance, and support autoreforming of methanol. They suffer from disadvantages of sulphur degradation, high ductility at temperatures above 125 ºC, (257 ºF) and water solubility. Practical manufacturing techniques have not yet been developed.

<u>Advantages and Disadvantages</u>

The advantages of phosphoric acid fuel cells are that they:

- are tolerant of carbon dioxide (up to 30%). As a result, phosphoric acid fuel cells can use unscrubbed air as oxidant, and reformate as fuel.

- operate at low temperature, but at higher temperatures than other low-temperature fuel cells. Thus, they produce higher grade waste heat that can potentially be used in co-generation applications.
- have stable electrolyte characteristics with low volatility even at operating temperatures as high as 200ºC (392 ºF) .

The disadvantages are that they:

- can tolerate only about 2% carbon monoxide
- can tolerate only about 50 ppm of total sulphur compounds
- use a corrosive liquid electrolyte at moderate temperatures, resulting in material corrosion problems
- have a liquid electrolyte, introducing liquid handling problems. The electrolyte slowly evaporates over time.
- allow product water to enter and dilute the electrolyte
- are large and heavy
- cannot auto-reform hydrocarbon fuels
- have to be warmed up before they are operated or be continuously maintained at their operating temperature.
- the fuel cell produces water that accumulates at the cathode. This product water must be continually removed to facilitate further reaction.

Molten Carbonate Fuel Cells (MCFC)

Molten carbonate fuel cells use an electrolyte that conducts carbonate ions from the cathode to the anode. This is the opposite of many other types of fuel cells, which conduct hydrogen ions from the anode to the cathode.

The electrolyte is composed of a molten mixture of lithium and potassium carbonates.

This mixture is retained by capillary forces within a ceramic support matrix of lithium aluminate.

At the fuel cell operating temperature, the electrolyte structure is a thick paste, and the paste provides gas seals at the cell edges.

Molten carbonate fuel cells operate at about 650ºC (1.200 ºF) and a pressure of 1 to 10 bar (15 to 150 psi). Each cell can produce up to between 0.7 and 1.0 VDC.

Molten carbonate fuel cells can operate using pure hydrogen or light hydrocarbon fuels. When a hydrocarbon, such as methane, is introduced to the anode in the presence of water,

it absorbs heat and undergoes a steam reforming reaction. When using other light hydrocarbon fuels, the number of hydrogen and carbon monoxide molecules may change but in principle the same products result.

The carbon oxide ions draw through the electrolyte from the cathode to the anode by the reactive attraction of hydrogen and carbon monoxide to oxygen, while electrons are forced

through an external circuit from the anode to the cathode.

Advantages and Disadvantages

The advantages of molten carbonate fuel cells are that they:

- support spontaneous internal reforming of light hydrocarbon fuels
- generate high-grade waste heat
- have fast reaction kinetics (react quickly)
- have high efficiency
- do not need noble metal catalysts

The disadvantages are that they:

- require the development of suitable materials that are resistant to

corrosion, are dimensionally stable, have high endurance and lend

themselves to fabrication.

Corrosion is a particular problem and can cause nickel oxide from the cathode to dissolve into the electrolyte, loss of electrolyte, deterioration of separator plates, and dehydration or flooding of the electrodes. All of these corrosion effects result in a decline in performance, limit cell life, and can culminate in cell failure. Use of a platinum catalyst overcomes some of these problems, but eliminates an important cost-saving advantage.

Dimensional instability can cause electrode deformation that alters the active surface area and may cause loss of contact and high resistances between components.

- have a high intolerance to sulphur. The anode in particular can not

tolerate more than 1-5 ppm of sulphur compounds (primarily H_2S and

COS) in the fuel gas without suffering a significant performance loss.

- have a liquid electrolyte, which introduces liquid handling problems
- require a considerable warm up period
- the fuel cell produces water, regardless of fuel, and carbon dioxide if using

a hydrocarbon fuel. Both products water and carbon dioxide must be

continually removed from the cathode to facilitate further reaction.

- each start up reduces the expected lifetime at 10%

Solid Oxide Fuel Cells (SOFC)

Solid oxide fuel cells use an electrolyte that conducts oxide ions from the cathode to the anode. This is the opposite of most types of fuel cells, which conduct hydrogen ions from

the anode to the cathode.

The electrolyte is composed of a solid oxide, usually zirconia (stabilized with other rare earth element oxides like yttrium), and takes the form of a ceramic.

Solid oxide fuel cells are built like computer chips through sequential deposition of various layers of material. Common configurations include tubular and flat (planar) designs. The

designs differ in the extent of dissipative losses within cells, in the manner of sealing between the fuel and oxidant channels, and in the manner that cell-to-cell electrical connections are made in a stack of cells. Metals such as nickel and cobalt can be used as electrode materials.

Solid oxide fuel cells operate at about 1,000 ºC (1,830 ºF) and a pressure of 1 bar (15 psi) . Each cell can produce between 0.8 and 1.0 VDC.

Solid oxide fuel cells can operate using pure hydrogen or hydrocarbon fuels, just like molten carbonate fuel cells. This results in an inlet fuel stream comprised of hydrogen with or without carbon monoxide.

Advantages and Disadvantages

The advantages of solid oxide fuel cells are that they:

- support spontaneous internal reforming of hydrocarbon fuels. Since oxide ions - rather than hydrogen ions - travel through the electrolyte, the fuel cells can in principle be used to oxidize any gaseous fuel.
- operate equally well using wet or dry fuels
- generate high-grade waste heat
- have fast reaction kinetics
- have very high efficiency
- can operate at higher current densities than molten carbonate fuel cells
- have a solid electrolyte, avoiding problems associated with handling liquids
- can be fabricated in a variety of self-supporting shapes and configurations
- do not need noble metal catalysts

The disadvantages are that they:

- require the development of suitable materials that have the required conductivity, remain solid at high temperatures, are chemically compatible with other cell components, are dimensionally stable, have high endurance and lend themselves to fabrication.

Few materials can operate at high temperatures and remain solid over long periods of time. Furthermore, the selected materials must be dense to prevent mixing of the fuel and oxidant gases, and must have closely matched thermal expansion characteristics to avoid delamination and cracking during thermal cycles.

- have a moderate intolerance to sulphur. Solid oxide fuel cells are more tolerant to sulphur compounds than are molten carbonate fuel cells, but overall levels must still be limited to 50 ppm. This increased sulphur tolerance makes these fuel cells attractive for heavy fuels. Excess sulphur in the fuel decreases performance.

- do not yet have practical fabrication processes
- the technology is not yet mature

- start up takes up to 100 hours
- each start up reduces the expected lifetime at 10%
- the fuel cell produces water - regardless of fuel - and carbon dioxide if

using a hydrocarbon fuel. Both products water and carbon dioxide must

be continually removed from the cathode to facilitate further reaction.

Summary

Fuel cell systems suitable for automotive applications operate at low temperatures (typically less than 100 ºC / 212 ºF. This is an advantage in that the fuel cells require little warm up time, high temperature hazards are reduced, and the thermodynamic efficiency of the electrochemical reaction is inherently better.

This is a disadvantage in that medium-grade waste heat is harder to expel (especially in hot climates) so that cooling systems must be larger, and the electrochemical reaction proceeds more slowly than at high temperatures.

Reformers used in conjunction with fuel cells operate at high temperatures and therefore may require prolonged warm up periods.

Fuel cell systems can be used in co-generation applications. In addition to electrical power, fuel cells generate pure hot water and medium-grade heat, both of it can potentially be used in association with domestic or industrial applications, which increases the overall efficiency.

Disadvantages of Fuel Cells

Fuel cell systems suffer the following disadvantages:

Fuel cells require relatively pure fuel, free of specific contaminants.

These contaminants include sulphur and carbon compounds, and residual liquid fuels (depending on the type of fuel cell) that can deactivate the fuel cell catalyst effectively and can destroy its ability to operate.

Fuel cells suitable for automotive applications typically require the use of a platinum catalyst to promote the power generation reaction. Platinum is a rare metal and very expensive.

Fuel cells must not freeze with water inside. Fuel cells generate pure water during the power generating reaction and most fuel cells suitable for automotive applications use wet reactant gases. Any residual water within the fuel cells can cause irreversible expansion damage if permitted to freeze. During operation, fuel cell systems generate sufficient heat to prevent freezing over normal ambient temperatures, but when shut down in cold weather the fuel cells must be kept warm or the residual water must be removed before freezing.

Fuel cells that use proton exchange membranes must not dry out during use and must remain moist during storage. Attempts to start or operate these fuel cells under dry conditions can lead to membrane damage.

Fuel cells require complex support and control systems.

Fuel cells themselves are solid state devices, but the systems required to support fuel cell operation are not. Of particular note is the requirement for compressed air; this necessitates a high-speed compressor that imposes a large parasitic load on the overall system. System complexity increases significantly when the fuel cells are operated in conjunction with an on-board reformer.

Fuel cell systems are heavy. Fuel cells themselves are not excessively heavy, but the combined weight of the fuel cells, their support systems and their fuel storage is presently greater than for a comparable internal combustion engine system.

System weight will likely continue to decrease as the technology develops.

Fuel cells are an emerging technology. As with any new technology, reductions in cost, weight and size concurrent with increases in reliability and lifetime remain primary engineering goals.