1. Materials and Energy

1.1 Storage and Conversion

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Electrochemical energy conversion

What is electrochemistry?

Electrochemistry deals with the relation between electrical phenomena and chemical reactions. It is important for a large part of the metallurgical industry in which electrical energy is used to produce metals by electrolysis. Moreover, it is important for energy technology and in particular clean, sustainable energy: fuel cells, electrolyzers for hydrogen production, and batteries.

A more precise definition of electrochemistry follows: Electrochemistry is reduction and oxidation processes where reduction and oxidation takes place on different locations. That means we must have transport of electrons and ions between these locations; in electronically and ionically conducting phases. If these phases are split into separate electronic and ionic pathways we have the possibility to convert chemical energy to electrical and vice versa.

In electrochemistry it is, as in red-ox-chemistry in general, useful to write the reduction and oxidation as separate half-cell reactions, like the following general example:

\[
\text{Reduction: } A + xe^- = A^{x-} \quad \text{l y} \\
\text{Oxidation: } B = B^{y+} + ye^- \quad \text{l x} \\
\text{Total: } yA + xB = yA^{x-} + xB^{y+}
\] (9.16)

In general electrochemistry we often represent cells like this by a diagram of the type

\[
B \mid B^{y+} || A^{x-} \mid A
\] (9.17)

Here the phase borders are marked by single lines, while the double line mark the division between the half cells – by an electrolyte, salt bridge, or ion-conducting diaphragma.

The electrode where oxidation takes place is called the anode. The electrode where a reduction takes place is called the cathode:

Anode Oxidation (both start with vocals)  
Cathode Reduction (both start with consonants)

The definition of anode and cathode is thus in general not defined by the sign of the voltage of the electrode.

Current may pass in the ionic and electronic pathways – driven by electrical or chemical gradients. Michael Faraday managed 200 years ago to find the relation between the magnitude of the current and the amount of chemical entities reacting. He took into use the constant we today call Faraday’s constant, namely the amount of
charge per mole of electrons: $F = 96485 \text{ C/mol}$, where C is one coulomb, the charge carried by one ampere in one second ($C = \text{As}$).

A cell driven by a spontaneous electrical total reaction can deliver electrical current – it converts chemical energy to electrical. We call them *galvanic cells*. A cell in which the chemically energetic reactants are installed during manufacture and that are designed for only one discharge cycle are called primary batteries, most often simply batteries. If they can be recharged by reversing the discharge reaction, they are called secondary batteries, or accumulators. If they can accept a continuous supply of chemicals – usually fuel and oxidant such as air – they are called ternary batteries, or fuel cells.

If the cell is reversed by forcing the chemical reaction backwards – producing chemicals of higher energy level - we call it an *electrolytic cell* - we do electrolysis or charging. This is what happens when we charge an accumulator or produce metals from ore or hydrogen from water with electrical energy.

### Cell voltage

In an electrochemical cell we can do electrical work, $w_{el}$. It can be shown that the electrical work we do reversibly on an electrolytic cell is equal to the increase in Gibbs energy of the cell system (strictly speaking at constant pressure and temperature). Similarly, the electrical work a galvanic cell does on the surroundings equals the reduction in the cell system’s Gibbs energy. Generally, we have

$$\Delta G = w_{el} \quad (9.18)$$

The electrical work for each electron taking part in the reaction is given by its charge $e$ times the potential difference between positive and negative electrode, i.e. the cell voltage $E$. The electrical work for the reaction is thus obtained by multiplication with the number of electrons. The work for a mole of reactions is similarly obtained by multiplying with Avogadro’s number:

$$w_{el} = \Delta G = -neE \quad \text{(for a reaction with } n \text{ electrons)} \quad (9.19)$$

$$w_{el} = \Delta G = -nN_AeE = -nFE \quad \text{(for } n \text{ mole electrons)} \quad (9.20)$$

From this, the cell voltage $E$ will, like $-\Delta G$, express how much the reaction tends to go forward:

$$\Delta G = -nFE \quad (9.21)$$

The standard Gibbs energy change, $\Delta G^0$, corresponding to the change in Gibbs energy when all reactants and products are present in standard state (unit activity) at 1 bar pressure, has a corresponding standard cell voltage $E^0$:

$$\Delta G^0 = -nFE^0 \quad (9.22)$$

From the relation between the Gibbs energy change and the reaction quotient $Q$:

$$\Delta G = \Delta G^0 + RT \ln Q \quad (9.23)$$

we can by combination of the above equations obtain
9. Conversion and storage of energy

\[ E = E^0 - \frac{RT}{nF} \ln Q \]  \hspace{1cm} (9.24)

This widely applied equation is called the \textit{Nernst-equation}.

Equilibrium means that the Gibbs energy sum of the products and that of the reactants are equal. At equilibrium we thus have \( \Delta G = 0 \), so that also \( E = 0 \):

\[ E = E^0 - \frac{RT}{nF} \ln Q_{\text{equilibrium}} = 0 \]  \hspace{1cm} (9.25)

e.

\[ E^0 = \frac{RT}{nF} \ln Q_{\text{equilibrium}} = \frac{RT}{nF} \ln K \]  \hspace{1cm} (9.26)

All in all, we can give the standard data for a reaction in terms of \( \Delta G^0 \), \( E^0 \), or \( K \):

\[ \Delta G^0 = -nFE^0 = -RT \ln K \]  \hspace{1cm} (9.27)

Gibbs energy change for a total reaction is the sum of the change for each half cell reaction:

\[ \Delta G_{\text{total}} = y\Delta G_{\text{red}} + x\Delta G_{\text{oks}} \]  \hspace{1cm} (9.28)

or, if we use reduction data for both reactions:

\[ \Delta G_{\text{total}} = y\Delta G_{\text{red}1} - x\Delta G_{\text{red}2} \]  \hspace{1cm} (9.29)

Vi see from this that

\[ E_{\text{total}} = \frac{\Delta G_{\text{total}}}{-nF} = \frac{\Delta G_{\text{total}}}{-xyF} = \frac{y(-xFE_{\text{red}}) + x(-yFE_{\text{oks}})}{-xyF} = E_{\text{red}} + E_{\text{oks}} \]  \hspace{1cm} (9.30)

or

\[ E_{\text{total}} = E_{\text{red1}} - E_{\text{red2}} \]  \hspace{1cm} (9.31)

We can measure the total cell voltage over an electrochemical cell. But we cannot measure the voltage of a half cell alone, because we would need two electrodes to do the measurement. The absolute potential of one half cell van thus not be known, only the difference to other half cells. To obtain a system of relative half cell voltages, we need a reference half cell. The half cell

\[ 2H^+(\text{aq, 1M}) + 2e^- = H_2(\text{g, 1 bar}) \]  \hspace{1cm} (9.32)

where we use platinum as inert electrode, is much used as reference in aqueous electrochemistry. It is called the Standard Hydrogen Electrode (SHE) and is defined to have have a half cell voltage of 0 V.
9. Conversion and storage of energy

Figure 9-10. Electrochemical cell with standard hydrogen electrode (SHE), salt bridge, and a Cu⁺/Cu-electrode at standard conditions.

Other, more practical reference electrodes are also in use in aqueous electrochemistry, such as the standard calomel electrode (SCE).

For non-aqueous, and particularly solid electrolytes, there are no standard electrodes defined. Half-cell electrode potentials are then not used, only full cell potentials.

Even if a total reaction does not indicate electron transfer, and thus also can be done without an electrochemical cell, we can still represent its thermodynamics by a cell voltage. The relation between Gibbs energy and the cell voltage then requires knowledge of the number of electrons n transferred in the reaction. As example, the total reaction between yA and xB above involves \( n = x^*y \) electrons.

The reaction between hydrogen and oxygen:

\[
\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \quad (9.33)
\]

has standard Gibbs energy of \(-228.7 \text{ kJ/mol}\) at ambient temperatures. We can utilise this in a fuel cell, but what is the standard cell voltage? We may assume that the process involves \( \text{O}^2^- \) or \( \text{H}^+ \) as ionic charge carrier in the electrolyte, and thus that we get two electrons (\( n = 2 \)) per reaction unit (i.e. per hydrogen or water molecule):

\[
E^0 = \frac{\Delta G^0}{-2F} = +1.185 \text{ V} \quad (9.34)
\]

It may be useful to note that Gibbs energy is an extensive property. If we consider, the double of the reaction above,

\[
2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{H}_2\text{O}(\text{g}) \quad (9.35)
\]
then Gibbs energy is twice as big; \(2\times-228.7 = -457.4 \text{ kJ/mol}\). But the number of electrons is also doubled, so the cell voltage remains constant, it is an intensive property:

\[
E^0 = \frac{-457400}{-4F} = +1.185 \text{ V}
\]  

(9.36)

It may also be useful to emphasise that an electrochemical cell is not at equilibrium as long as the cell voltage is different from 0. Only at \(E = 0\) is the system at equilibrium and has reached a minimum in Gibbs energy, so that \(\Delta G = 0\). Only then is \(Q = K\).

**Fuel cells**

A fuel cell is a galvanic cell in which the chemicals (fuel and oxidant) are continuously supplied to the electrodes.

The fuel can be of fossil origin or come from renewable energy. With fossil origin we think primarily of gases produced from natural gas, oil, or coal. They comprise hydrogen, CO, methanol or propane, methanol, gasoline or diesel, or mixtures such as syngas or coal gas (both mainly \(H_2 + CO\)). Fuels from renewables comprise primarily hydrogen, but also a number of what we may call hydrogen carriers; methanol, ammonia, etc. Recently, focus has been put on biofuels; carbonaceous fuels (alcohols, biodiesel) from organic harvest of sunlight.

Fuel cells offer potential advantages in efficiency and environment-friendly operation for all types of fuels. The choice of fuel has nevertheless influence on which type of fuel cell it is most reasonable to use.

All fuel cells can use hydrogen as fuel, but hydrogen is not easy to store and transport, and there is thus a desire to use other fuels. As a general rule, the higher the operating temperature of the fuel cell, the better does the cell tolerate variation and non-hydrogen elements of the fuel. CO and many other compounds poison electrodes at low temperatures, so that organic fuels, that often contain traces of CO or form CO as intermediate combustion product, for the most part is excluded from use with low temperature fuel cells. Some poisons such as sulfur affect also high temperature cells, but the critical contents are usually higher the higher the temperature. Direct use of kinetically inert molecules such as \(CH_4\) can only be imagined in high temperature cells. Water soluble fuels can be used below 100 °C because they can then be supplied in an aqueous phase. Fossil fuels, forming the acidic product \(CO_2\), can not be used in alkaline fuel cells because \(CO_2\) will react with the electrolyte. Conversely, ammonia, which is a basic gas, can not be used in phosphoric acid fuel cells or other fuel cells with an acidic electrolyte.

The discovery of the fuel cell has been attributed to Sir William Grove, who filled small containers with hydrogen and oxygen and used sulfuric acid as electrolyte and platinum for electrodes. He described that when he connected several such cells in series the voltage of the end terminals became increasingly painful to touch. He also showed that a number of such cells connected to two electrodes standing in sulfuric acid led to the production of hydrogen and oxygen over those two electrodes (electrolysis).
9. Conversion and storage of energy

(see figure below). Grove published his findings in 1839 – thus usually considered the year of the discovery of the fuel cell.

Figure 9-11. Grove’s illustration of his fuel cell, consisting of four individual cells in series, and using the electrical power to electrolyse sulfuric acid.

**General principle of operation and requirements of materials for fuel cells**

A fuel cell consists of 4 central elements: Electrolyte, anode, cathode, and interconnect. In addition one may say that the medium of the fuel and oxidant makes up a fifth element. Each element has individual tasks and requirements.

The electrolyte must be an ionic conductor, being able to transport ions of fuel or oxidant elements to the opposite side. The ionic transport number (fraction of the total conductivity) is considered to have to be 0.99 or more, because any electronic conductivity will cause loss by partial electrical shortcircuit. The electrolyte moreover has to be very redox-stable, i.e. withstand the oxidising conditions of the oxidant as well as the reducing conditions of the fuel. The electrolyte must furthermore not react with the electrodes or have any degree of mutual solubility. If the electrolyte is solid one must furthermore appreciate the chemical potential gradient it faces. This causes the fast ions to migrate, but it also puts a similar force on the stationary ions in the material; if the metal cations of a solid electrolyte have non-negligible mobilities, the whole electrolyte membrane may move. Thus, there is a requirement on small diffusivities for stationary components.

The cathode must be an electronic conductor, being able to transport electrons from the electrochemical reaction site to the current collector. It should also be catalytic to the electron transfer and other reaction steps. The cathode stands in the oxidant and must tolerate oxidising conditions. For this reason, metals except the most noble ones such as Pt, Au, and Au, are excluded from use here. Instead one tends to use graphite at low temperatures and oxidic materials at higher temperatures. The cathode must not react with the electrolyte or with the interconnect (current collector). Finally, the cathode must be porous so as to allow the fuel medium to react the reaction site and the products to diffuse away.

The anode must similarly be an electronic conductor, stable under reducing conditions. In addition to noble metals, some additional metals may be stable here, like Ni and Cu. Like the cathode the anode must not react with the electrolyte and interconnect.
9. Conversion and storage of energy

Figure 9-12. General principle of fuel cells with H⁺ (upper) or O²⁻ (lower) conducting solid electrolytes, running H₂ and O₂ (air). For each cell is shown a schematic anode and cathode electrode grain. For each of these the electrode reaction on the top of the grain is the normal three-phase-boundary reaction, while the lower part depicts extended reaction possibilities if the electrode conducts also ions or is permeable to atomic species.

One cell is usually series connected to a next cell in order to increase the overall voltage. The material that makes this connection is called an interconnect or bipolar plate and is thus placed between one cathode and the next anode. It must thus be an electronic conductor, and in this case have no mixed conduction; any transport of ions will lead to chemical short-circuit; loss of fuel by permeation. The interconnect must obviously also not react with either of the electrodes it contacts. Moreover, the interconnect separates the oxidant of one cell from the fuel in the next. This requires that it is redox stable and gas tight (and as said above also diffusion tight).

Especially in ceramic fuel cells, the thermal expansion coefficient must match between the various materials, or else delamination, bending, and cracking may result from startups, shutdowns, thermal cycling, and even load variations. This is hard, because ceramic materials usually have smaller expansion coefficients than metals. In addition to the thermal expansion, many materials also suffer from chemical expansion. One example is the swelling of polymers during water uptake. In ceramic cells, some materials similarly expand upon stoichiometry changes. Even metals may be affected: A metal serving as interconnect may for instance dissolve hydrogen and carbon at the fuel...
side, and dissolve oxygen or oxidise at the air side. This may lead to expansion, stresses and bending of the interconnect and eventually cracking of the cells and stack.

**Three-phase boundaries of electrodes and ways to expand them**

Both anode and cathode are in principle rate limited by the length of the three-phase boundary, i.e. the place where electrons, ions, and reacting neutral species in gas or liquid phases can all meet. The width of the reaction zone can be increased by diffusion of adsorbed species on the surface of the electrode or electrolyte, as shown in two of the cases in the figure below.

![Figure 9-13. Schematic showing four ways of expanding the reaction area from a pure three-phase boundary line in solid oxide fuel cell cathodes: Cathode surface diffusion of adsorbed oxide ions or atoms; cathode volume diffusion of oxygen atoms; electrolyte surface diffusion of oxygen atoms; mixed ionic-electronic conduction in the cathode.](image)

Diffusion of reactant atoms or molecules in the volume of the electrode increases the reaction zone inwards under the electrode. Finally, one may apply electrode materials that are mixed ionic and electronic conductors. The two latter cases are also illustrated in the figure.

From being a one-dimensional three-phase boundary line, these extra transport paths make the reaction zone transform into an area.
9. Conversion and storage of energy

Composite electrodes

In order to increase further the number of reaction sites one usually makes the electrode a porous structure of the electron conductor in which a percolating ionically conducting network is embedded and the fuel or oxidant medium can flow. With liquid electrolytes one lets the electrolyte and reactants penetrate a porous electrode. With solid electrolytes one makes a porous composite of the electron and ion conductors. This composite must have three percolating phases: the pores, the electron conductor and the ion conductor (electrolyte).

In polymer fuel cells these electrodes are called gas diffusion electrodes, made of a porous nanograinned carbon-polymer composite.

![Figure 9-14. Gas diffusion electrode for polymer fuel cells: Electrolyte, finely distributed mixture of electrolyte, electrolyte and carbon+catalyst (A), The gas diffusion layer (B) is a mixture of pores.](image)

In solid oxide fuel cell anodes one uses a cermet – a porous mixture of electrolyte ceramic and Ni metal.

Needless to say, a composite electrode gets even better if one of the two conductors exhibits more or less mixed conduction or volume diffusion of reactants. One may for instance expect that in a Ni anode cermet, hydrogen dissolves in the Ni metal and diffuses to the reaction interphases.

Overview of fuel cell types

In the sulfuric acid fuel cell the electrolyte – sulfuric acid - works by transporting protons or more precisely H$_3$O$^+$ ions. The sulfuric acid fuel cell is not persued today. The figure below shows the main types of fuel cells considered for general energy production, classified according to the type of ionic charge carrier of the electrolyte.
9. Conversion and storage of energy

In the following, we look at the various types in more detail.

Proton conducting fuel cell - PCFC

A fuel cell with a purely proton conducting electrolyte is the simplest thinkable if we want to combust pure hydrogen, and can thus be our starting point for a tour of the different fuel cell types. Pure proton conductors work at elevated temperatures (e.g. CsHSO$_4$ and imidazole based water-free polymers; ca 200 °C) or high temperatures (e.g. Y-doped BaCeO$_3$; 6-800 °C). The product water will thus be gaseous. The figure below shows how the PCFC is particularly simple since water is formed on the oxidant (cathode) side and no circulation of fuel is required.
9. Conversion and storage of energy

PCFC with basic electrolytes like BaCeO$_3$ can in principle use also ammonia as fuel. Fossil fuels must be pre-reformed or at least have added water vapour in order to deliver hydrogen to the anode without sooting. PCFCs are not commercialised, but there is per 2007 an American initiative of developing solid acid fuel cells (SAFC) based on CsHSO$_4$-type materials (http://www.superprotonic.com/).

**Phosphoric acid fuel cell – PAFC**

The phosphoric acid fuel cell (PAFC) uses concentrated phosphoric acid H$_3$PO$_4$ as electrolyte. As electrodes are used porous carbon with platinum as catalyst.

PAFC operates at what we may call intermediate temperatures (160-220 °C). This enables the use of synthesis gas (reformed fossil fuels) as fuel without catalyst poisoning. Moreover, the dissipated heat is valuable for distributed heat.
As in other cells using synthesis gas, \( \text{H}_2 \) is the main electroactive reactant while \( \text{CO} \) is oxidised to \( \text{CO}_2 \) via the water shift reaction. In contrast to PCFC, the mobile ion in PAFC is \( \text{H}_3\text{O}^+ \).

Some of the world’s largest installed fuel cell power plants are of PAFC type, but it is being delivered also for small demo units, including autonomous hydrogen-based energy systems. The technology is in other words proven, but the efficiency considered modest (40-45 \%) and problems with corrosion of containers and current collectors to some extent still unresolved.

**Polymer electrolyte fuel cell - PEFC**

This type uses the so-called proton-exchange membranes (PEM) like Nafion® as electrolyte and are often abbreviated PEMFC. PEFC is used normally below 100 °C (normally 50-85 °C) and in presence of liquid water. The water makes the polymer swell and form zones with liquid water inside – zones in which protons can move in. As in PAFC the mobile ions are not protons but \( \text{H}_3\text{O}^+ \) ions. Each of these in turn drags another 5-6 water molecules. These will partly diffuse backwards in the polymer and partly have to be recirculated externally.

Also PEFC uses porous carbon as electrodes, with Pt as catalyst. The low temperature makes the catalyst sensitive to CO (adsors on and blocks the catalyst surface) and \( \text{H}_2\text{S} \) (PtS is very stable). The fuel must thus be clean hydrogen, with small tolerances for CO and \( \text{H}_2\text{S} \).

The electrodes make up an interface between”solid” electrolyte and liquid water. The reactants are gases and must also reach this interface. The progress in PEFC development has for a large part reflected mastering of fine porous carbon electrodes, where the electrolyte is infiltrated in the electrode and Pt-catalyst distributed finely as nanoparticles. A number of alloying elements and additional catalysts (e.g. RuO\(_2\)) are in use.

The value of the dissipated heat is lower for PEFC than for PAFC since it is difficult to exchange the heat from so low temperatures.
9. Conversion and storage of energy

We will use the PEFC for illustrating how cells are stacked in series to obtain higher voltage. The individual cells (membrane-electrode-assemblies, MEAs) are connected together with so-called bipolar plates ("interconnects") that make electrical series contact and keep hydrogen and air separated. They contain grooves to guide the gas flow.

![Series connection of PEFC elements in a stack. An element consists of one electrolyte membrane with electrodes and half a bipolar plate ("interconnect").](image)

Each cell consists of several components, as shown below.

![Components in a PEFC cell. The layer in the middle is the electrolyte (PEM), while the next layers on either side contain the critical gas diffusion layer.](image)

**Direct methanol fuel cell (DMFC)**

This is a kind of PEFC, but with methanol as fuel. Normally one would think that methanol needs pre-reforming to form $\text{H}_2$, and that CO must be separated out before
poisoning the anode. However, it is possible to send methanol directly to the anode when the anode is prepared for it, e.g. by using ruthenium as catalyst.

Figure 9-21. Direct-methanol fuel cell (DMFC).

The DMFC electrochemistry is aided by methanol fuel dissolving in the electrolyte. On the other hand, methanol dissolved in the electrolyte may diffuse to the cathode to be combusted there (chemical short circuit). Despite this, the cells are simple and have higher energy density than accumulators.

Alkaline fuel cell (AFC)

In an alkaline fuel cell, a strong solution of KOH is used as electrolyte, while the electrodes again can be porous carbon with fine spread platinum as catalyst. AFCs operate below the boiling point of water and have thus the same demands for fuel purity to avoid poisoning, as in PEFC systems. carbon-containing (fossil) fuels must be avoided, as CO₂ in the exhaust will react with the alkaline electrolyte. On the other hand, AFC can be operated with basic fuels like ammonia and hydrazine (N₂H₄). As for the methanol cell there are advantages and disadvantages of these fuels dissolving in the aqueous electrolyte.

Alkaline fuel cells are among the oldest technologies and have been used for a few decades onboard spacecrafts, where they are essential. They have also been tested in numerous fuel cell cars, e.g. London cabs.
9. Conversion and storage of energy

**Molten carbonate fuel cell (MCFC)**

MCFC and SOFC make up the so-called high temperature fuel cell technologies. They are the ones best suited for fossil fuels. MCFC utilises a melt of Li$_2$CO$_3$, Na$_2$CO$_3$ or K$_2$CO$_3$ impregnated in a porous carrier made of lithium aluminate, LiAlO$_2$. The anode is nickel, Ni, while the cathode is Li-doped NiO, which is a good p-type conductor. As the CO$_3^{2-}$ ion is the charge carrier in the electrolyte, CO$_2$ must be recirculated in the cell, from the anode back to the cathode.

MCFC is well-proven technology, installed in several large plants. However, as for the PAFC systems, the operation and lifetime is troubled by large corrosion problems at the high temperature in and around the very aggressive molten salt melt.

**Solid oxide fuel cell (SOFC)**

The SOFC technology has for the most part based itself on yttrium stabilised (kubic) zirconia (YSZ) as oxide ion conducting electrolyte. The cathode is typically Sr-
doped LaMnO$_3$ (lanthanum manganite) or similar perovskites. As anode is most often used a cermet of nickel and YSZ. The cells operate typically at 700-1000 °C depending on the thickness of the electrolyte and quality of the electrodes.

The SOFC can, like other fuel cells run pure H$_2$ as fuel. Compared with the purely proton conducting fuel cell, the SOFC is characterised by by forming water at the anode (fuel) side.

The figure shows an SOFC that uses CH$_4$ as fuel: CH$_4$ reacts (is reformed) with H$_2$O over the anode whereby the H$_2$ is oxidised electrochemically to H$_2$O. This is used in its turn to reform more CH$_4$ and to shift CO to CO$_2$ + H$_2$. In practice we must add H$_2$O (steam) to the CH$_4$ before the cell, because we otherwise get too reducing conditions with too high carbon activities, giving sooting in the fuel inlet.

SOFCs can in principle be used with all kinds of fossil fuels, because the fuel is reformed on its way to and over the anode. In reality we have as mentioned some problems with sooting in the fuel inlets. Moreover, the reforming reaction is endothermic. This may cool the cells anode too much at the inlet and we may get cracks because of the thermal stresses. One may design the cell such that the cooling from the reforming just balances the heating from the ohmic losses, but usually chooses to do the reforming in a separate reactor before the cell.

It has been speculated and tested whether one can oxidise the CH$_4$ molecule directly on the anode (without reforming). However, such a process from CH$_4$ to CO$_2$+2H$_2$O is an 8-electron process – a very unlikely pathway. Thus, intermediate reforming and shift by the formed water and subsequent oxidation of H$_2$ and possibly CO is probably inevitably the reaction path in operation on an SOFC anode.

The materials and ways of assembling them in SOFC concepts are many and challenging. As electrolyte is used Y- or Sc-doped ZrO$_2$, or other oxide ion conductors (based e.g. on CeO$_2$ or LaGaO$_3$). These must be sintered gastight, typically at 1400 °C, and in as thin layers as possible.

As anode is used Ni-YSZ-cermet. These are fabricated as a fine grained mixture of NiO and YSZ powders that is sintered onto the YSZ electrolyte at high temperture (typically 1400 °C). NiO is then reduced to Ni metal under the reducing conditions at the anode, at around 800 °C. Ni is a very good catalyst for reforming of methane and for
electrochemical oxidation of hydrogen. Because the Ni metal has higher thermal expansion coefficient than YSZ it is a challenge to fabricate constructions of YSZ+Ni/YSZ that can be cycled in temperature without cracking.

Figure 9-25. Cross section of SOFC single cell with self-supported gastight YSZ electrolyte in the middle, porous LaMnO$_3$ based cathode (top) and porous Ni/YSZ cermet anode (bottom). The magnifications to the right show the interfaces between electrolyte and electrodes, the critical place for mechanical strength and adhesion and electrochemical kinetics (E. Ivers-Tiffee et al., Universität Karlsruhe).

As cathode is used LaMnO$_3$ and similar perovskites, doped with acceptors to give high electronoc p-type conductivity. LaMnO$_3$ has a thermal expansion similar to that of YSZ.

SOFC, like other fuel cells, need interconnects to connect single cells in stacks and to separate the gases. LaCrO$_3$ doped with an acceptor is a perovskite material with a high electronic (p-type) conductivity from reducing to oxidising conditions and it has TEC similar to that of YSZ. The problems with it is the cost; it is expensive to sinter dense and to machine. It has limited stability and low heat conduction. One thus seeks to develop metallic interconnects for SOFCs: With that one can achieve better electrical and thermal conduction and the materials have in principle easier and cheaper machining. But the metals (except noble metals) that can withstand 800-1000 °C without oxidising – and where the protective oxide layer is conducting – are Cr-rich Fe-Cr-superalloys, that form Cr$_2$O$_3$ as protective layer. These are expensive and very hard. Moreover, chromium compounds evaporate and deposit on and poison the LaMnO$_3$-cathode. To solve the problem with the hardness one have to form the parts using powder metallurgy. To reduce evaporation one covers them with a a layer of LaCrO$_3$. Today the temperature for SOFC is sought brought down to 600°C. If that succeeds we can imagine using ordinary stainless steel qualities as interconnects. These then have sufficiently low corrosion rates, and are machinable and more affordable in every sense than the superalloys. The desire for lower temperatures (often referred to as intermediate temperature SOFCs) does however put severe demands on the conductivity of electrolytes and the kinetics of electrodes.
SOFC-modules can be built along various design classes. The first with any success was the tubular design, introduced by Westinghouse (now Siemens-Westinghouse). Here, carrier tubes are made of a porous cathode material, closed in one end. Electrolyte is deposited as a thin layer by chemical vapour deposition (CVD), whereafter the anode is sprayed on as a slurry and sintered. A stripe is left without electrolyte and anode and instead covered with an interconnect. The tubes are stacked so that the cathode has contact to the next anode through the interconnect stripe. This makes the series connection that builds voltage. At the same time the tubes are placed in parallel to increase the current, see figure.

The figure below shows how a stack like this is operated. Notice how some used fuel is recirculated for use in reforming of new fuel, and how rest air and rest fuel are mixed and burned after the fuel cell to provide heat to preheating of ingoing air and fuel. In the tubular design sealing and manifolding is relatively unproblematic, but the packing density of cells is poor.

Figure 9-26. The construction of SOFC tube (left) and stacking (right) in series (upwards) and parallel (sideways). From Siemens-Westinghouse.

Figure 9-27. Schematic illustration of how a stack of tubular SOFC can be operated. From Siemens-Westinghouse.
In the so-called planar concept thin plates of cathode-electrolyte-anode are stacked, connected and separated by bipolar interconnect plates. The packing density becomes very good, while the challenge is the sealing between the layers. The sealing can be for instance glass, glass-ceramic, or a noble metal such as gold or silver.


Most SOFC development projects today work within planar concepts. Some apply variations over planar and tubular concepts. Siemens-Westinghouse has flattened their tubes so that they can be packed better. Rolls Royce additionally uses short and flat tube segments with bipolar connecting between each segment.

Figure 9-29. Fabrication of Rolls Royce SOFC stacks. From Rolls Royce.
9. Conversion and storage of energy

One of the problems with today’s SOFC-technology is the use of nickel. If we run the cell too hard and oxidise the fuel too much, Ni oxidises to NiO. Moreover, Ni is a (too) good catalyst for reforming reactions, leading to spot cooling. It is also a good catalyst for carbon deposition (sooting). Therefore we are looking for new anode materials. Candidates are oxides with high conductivity under reducing conditions, so far with limited success, however.

**Losses**

There are many sources of loss of energy in the fuel cell process:

The first is the so-called IR-loss, from the current running in the cell, an that is proportional to the resistivity and thickness of the electrolyte. It is inversely proportional to the membrane area. $U_{IR} = IR$ and $R = \rho d / A$.

There may also be ohmic resistances to electronic flow in the electrodes or current collectors, not easily distinguishable from the electrolyte resistance.

Next come the overpotential losses. These arise from the limiting kinetics at the electrodes. They can be represented as electrochemical resistances. They are non-linear except at low currents.

Another source of loss is the change in Nernst voltage that arises from production of products, and thus changing the reaction quotient. This is usually seen as a change in cell voltage (and seemingly a high resistance) at small currents.

Finally, we have the mass transport limitations, that restricts the supply of fuel and oxidant and the transport away of the products. This eventually limits the current of the cell; the limiting current.

**Potential and current; loss and effect**

There are many ways of displaying the performance of a fuel cell. The most fundamental and scientific is the potential vs current plot. We shall use the plot in the figure below to illustrate this. It shows cell voltage falling with increasing current, from open circuit voltage of close to 1.1 V (the Nernst voltage), to 0 V at the short circuit current close to 450 mA/cm$^2$. The slope is given by the total resistance in the cell. The figure shows also the potential drop over the cathode – its overpotential – which increases with increasing current, due to the limiting kinetics for reduction of oxygen gas. Likewise, there is an anode overpotential for hydrogen oxidation. A third loss is the so-called IR-loss given by the resistance to ionic transport in the electrolyte. In the experiment plotted in the figure, the anode overpotential and IR drop were measured together. The two overpotentials and the IR loss come out as heating.
How much effect can we extract from the cell? The effect is given by the cell voltage \( U \) that we can apply to the external load, multiplied with the current: \( P = I \times U \). The plot shows an effect curve (area specific). It starts at zero at zero current. It then rises to a maximum, typically at halved cell voltage. Then it decreases again as the cell voltage approaches zero, at the short circuit current.

When we extract relatively little current, the cell is very efficient; most of the energy is extracted as electrical effect. When we reach the maximum in effect, we lose half the energy as heat. At short circuit, we lose everything as heat. From this it is clear that it is not optimal to run the cell at maximum power; half the energy would be lost. The operation point is a compromise between efficiency and investment in more or bigger cells: Usually one operates around 2/3 of the open circuit voltage, or ca. 0.7 V for a \( \text{H}_2 - \text{O}_2 \) fuel cell.

**Fuel utilisation**

The fuel cell plotted in the figure above can look OK, but the plot itself says less about the overall efficiency than we might have pretended; It does not say what the fuel utilisation is. Often such tests are carried out with a large surplus of fuel, meaning that most of it is wasted. In order to properly characterise a fuel cell, the fuel utilisation \( u_f \) (a unitless ratio) must be specified. The fuel utilisation can in most cases not be drawn towards 1 (\( = 100\% \)), because if products dilute the fuel, the cell voltage at the outlet is close to zero, and this dramatically lowers the electrical output. Instead a practical compromise has to be chosen, and the remaining fuel must be burnt in an afterburner. This restriction is not applicable to purely proton conducting fuel cells running on pure hydrogen; here the fuel utilisation can in principle be 100\%. 

Efficiency

The electrical efficiency $P_e$ we can get is given by

$$P_e = \eta_G \ u_f \ P_{in}$$ \hspace{1cm} (9.37)

where $\eta_G$ is the Nernst efficiency, $u_f$ is fuel utilisation, and $P_{in}$ is the effect in the fuel and oxidant supplied that we supply (energy per time unit).

The Nernst efficiency is electrical energy divided by used chemical energy. The chemical energy is close to equal to the enthalpy (heat value) that the reactants would have delivered if they reacted with other in a simple combustion process. The electrical energy is on the other hand equal to the electrical work that the cell does on the surroundings, in turn equal to the Gibbs energy change for the process. Dependent on the entropy change, the Gibbs change can be larger or smaller than the enthalpy change and the Nernst efficiency thus smaller or bigger than 100%.

The overall efficiency for the cell is $P_e/P_{in} = \eta_G u_f$. This is the number that should be referenced and that typically ends up around 50% - because of electrical loss and because of finite fuel utilisation. When fuel cells offer superior efficiency it is usually after taking the heat value also into account, and using afterburners or a gas turbine + generator running on the rest fuel. The heat can be utilised in remote heat systems, in steam turbines, etc.

The figure below estimates and compares the overall electrical efficiency of various power technologies.

![Figure 9-31. Estimate of overall electrical efficiency ($P_e/P_{in}$) for various power technologies as a function of produced effect. From Bellona.](image)

For use of pure hydrogen as fuel, the fuel cells are clearly competitive (gas turbinides and engines do not tolerate well pure hydrogen) so that fuel cell cars will probably eventually become dominating. But for the fossil and biological fuels the fuel cells so far has difficulty to compete with engines for large scale as well as mobile power. Also rechargeable batteries is a hard competitor for mobile applications. Fuel
cells have their potential in the near future perhaps mostly for auxiliary power units (APUs) and small distributed power applications.

*From DC to AC*

Fuel cells produce direct current (DC). In many applications it needs to be converted to alternating power. This is done by inverters. This is power electronics that reverses the current, smooths it into a sine curve, and synchronises it to the grid.
11. Materials for fuel cells and electrolyzers

Electrochemical energy conversion devices that we include in this chapter comprise fuel cells and electrolyzers. They convert chemical energy to electricity and vice versa. Other electrochemical energy conversion devices comprise photoelectrochemical cells, which we treat under solar cells, and batteries, which we treat in a separate chapter.

Fuel cells and electrolyzers come in a variety of types, the main difference being the electrolyte – the ionic conductor that allows ions to pass between fuel and oxidant but denies passage of electrons so that these go through an external path – our electrical circuit. The electrolyte may be as different as an aqueous solution, a molten salt, a solid polymer, or a metal oxide. Their ionic conduction can be utilised at widely different conditions, especially concerning temperature. For this reason, it is common to classify these devices according to the type of electrolyte, because the construction and all other materials involved will mainly depend on this.

Fuel cells and electrolyzers within one type of electrolyte will for a large part contain the same kind of materials and face many of the same problems and challenges. We will in our treatment concentrate on fuel cells.

Materials for polymer electrolyte fuel cells

This kind of fuel cells traditionally uses the so-called Proton-Exchange Membrane (PEM) like Nafion® as electrolyte. The term PEM is nowadays also used as abbreviation for Polymer Electrolyte Membrane. A fuel cell based on PEMs is here called polymer electrolyte fuel cell (PEFC) but can obviously also be abbreviated PEMFC.

PEFCs are used below 100 °C (normally 50-85 °C) and in the presence of semi-liquid water. The water absorbs in the polymer and makes it swell. The swelling leads to formation of regions (channels) of liquid or liquid-like water in which the proton transport takes place in a manner similar to that of aqueous electrolytes. Correspondingly, the charge carrier is not protons, but H$_3$O$^+$-ions. These are hydrated, so that each of them drag an additional number (typically 5) of water molecules. Since these can not be recirculated by convection in the polymer, the water molecules must return by diffusion. In addition, PEFCs require normally an external recirculation of water. Despite the fact that proton conducting polymers like these conduct protons by means of semi-liquid water inside it, the polymer has the appearance of a solid that can be handled conveniently in thin sheets, like we are used to with other polymer materials.

A second class of polymers are not based on transport of water by means of water, but by protons jumping as such between stationary sites in the polymer, notably N-atoms in aromatic N-containing rings. Such polymers are thus “dry” and can be heated to above 100 °C, and this is also required in order to get sufficient proton mobility, and
desired to avoid condensation of product water. We will treat this class of polymers separately later, but now concentrate on the standard – low temperature - types.

**Polymer electrolytes**

Polymer electrolytes are based on a suitably branched backbone of a chemically robust polymer. The branching can be done by so-called grafting of a long-chained polymer, or it can be branched during initial synthesis.

The polymer is then reacted with an oxidic group that will form an anion bonded to carbon in the polymer, usually terminating branches. These branch structures are therefore called ionomers. Mobile protons will eventually charge compensate these stationary anions.

The ionomers reorganise to form polar regions, while the backbones form non-polar regions. In contact with water, the polymer swells as water is absorbed into and fills channels of hydrophilic – polar – character. The protons on the sulfonate groups are now released to the water to form mobile $\text{H}_3\text{O}^+$ ions. The figure below indicates the composition of two such polymers, Nafion® and PEEK.


The standard proton conducting polymers can best be described as co-polymers of tetrafluorethylene (TFE) and perfluorosulfonate (PFS) monomers. The latter are
11. Materials for fuel cells and electrolysers

terminated as perfluorocarbon-sulfonic acid (PSA) ionomers. The most well-known of these materials is the Nafion® manufactured by DuPont, but there are several similar formulations provided by other manufacturers.

We will now look a little closer at the details of producing the Nafion® polymer electrolyte. One starting material is tetrafluoroethylene which is reacted with $\text{SO}_3$ dissolved in sulfuric acid. The product is polymerised with hexafluoropropylene-epoxide:

$$\text{CF}_2=\text{CF}_2 + \text{SO}_3 \rightarrow \text{CF}_2=\text{CF}_2 + \text{FSO}_2\text{CF}_3\text{C}==\text{O}$$

This addition polymer is heated with $\text{Na}_2\text{CO}_3$ and then transforms into a polyvinyl ether. This is co-polymerised with more tetrafluoroethylene to a so-called XR-resin:

$$\text{FSO}_2\text{CF}_2\text{CF}_2(\text{OC}\text{CFCF}_2)_n\text{OC}==\text{CF}_2 + \text{CF}_2==\text{CF}_2 \rightarrow$$

$$\text{CF}_3$$

$$-(\text{CF}_2\text{CF}_2)_n\text{C}==\text{O}(\text{CF}_2=\text{CFO})_m\text{CF}_2\text{CF}_2\text{SO}_2\text{F} \quad \text{(XR resin)}$$

The XR-resin is molten and cast into thin plates, tubes, etc. These are now hydrolysed with $\text{NaOH}$ to a polymer sodium perfluorosulfonate (Nafion®):

$$\text{XR resin} + \text{NaOH} \rightarrow$$

$$-(\text{CF}_2\text{CF}_2)_n\text{C}==\text{O}(\text{CF}_2=\text{CFO})_m\text{CF}_2\text{CF}_2\text{SO}_3\text{Na}$$

Before use as proton conductor, the material is ion exchanged with an aqueous acid.

The polymer hydrates in two stages in contact with water. The first involves solvation of the ions, i.e. providing each $-\text{SO}_3\text{H}$ group with up to 5-6 water molecules. In the second step additional water is taken up to fill the hydrophilic channels and swelling the material, and we end up with a total of typically 14-15 water molecules per $-\text{SO}_3\text{H}$ group.

Nafion for proton-conducting membranes for are made by extrusion and have designations such as Nafion® N117, where the two first digits in the number refer to the equivalent weight (EW) of the polymer divided by 100, and the remaining digits refer to the thickness number in mills (1 mill = 1/1000 inch = 0.0254 mm). The N117 thus has EW = 1100 and a thickness of 7 mills = 0.18 mm.

The membrane swells typically 10 % by immersion in water and an additional 5 % by soaking in boiling water.

From the above it is easy to understand why nafion is expensive in production. In addition the product is well protected by patents, increasing the price further. It is this, together with the price of platinum catalyst, that makes PEFC too expensive today. It is
thus of great interest to develop alternative proton conducting polymers, with production simpler and cheaper than for Nafion. Typical routes have the following steps: Polymerisation of a suitable monomer that is preferably non-perfluorinated for price and patent conflict reasons. Grafting is done e.g. by radiating the polymer with electrons in order to get many defects (broken chains). When the fragments recombine we get a polymer with more branches that may be used for sulfonation. Sulfonation comes next and consists of a heat treatment with SO\(_3\) or concentrated sulfuric acid to bond (-SO\(_3\)H) to the polymer. By swelling the hydrophilic parts take up water and liberate the protons. The process is thus similar to what is done for Nafion\(^8\), but is supposedly simpler and cheaper. So far, though, at the expense of conductivity.

The essential properties of the proton conducting polymer are proton conductivity and permeability of gases. The proton conductivity increases with temperature and water content. The water content itself decreases with increasing temperature at constant activity of liquid water. Thus, the proton conductivity becomes a fairly weak and complex function of temperature: It increases weakly towards the boiling point of water, goes through a maximum and decreases more steeply. The conductivity of various polymer electrolytes soaked in liquid water is around 0.1 S/cm at room temperature, increasing to around 0.2 S/cm at 60 °C.

The proton conduction process drags up to 5-6 molecules of water per proton. To some extent these water molecules diffuse back in the opposite direction due to the buildup of a water activity gradient. For thin electrolyte membranes this counterflow ensures that the water content stays high enough at the anode that the proton conduction remains independent of the current. For thicker electrolytes the effective proton conductivity may decrease somewhat with increasing current because of drying out near the anode. External circulation of water to the anode may then ease the situation.

Permeation of gases in the polymer is advantageous in terms of electrode kinetics, since it helps the reactants find electrolyte-electron conductor reaction sites in the electrode composite. However, it is disadvantageous in terms of chemical shortcircuit. Permeability is the product of diffusivity and solubility (concentration):

\[
P = D \cdot c \tag{11.4}
\]

The two gases of main interest in this context are hydrogen and oxygen. Dissolution and diffusion of these take place as molecular species.

Diffusivity is in all cases an exponential function of temperature. In Nafion, we have

\[
D_{H2} (\text{cm}^2/\text{s}) = 0.0041 \exp(-21.63(\text{kJ/mol})/RT) \tag{11.5}
\]

\[
D_{O2} (\text{cm}^2/\text{s}) = 0.0031 \exp(-23.01(\text{kJ/mol})/RT) \tag{11.6}
\]

The concentrations \(c\) are proportional to the partial pressure of the gas, and may thus have units of, for instance, m\(^3\).Pa\(^{-1}\) or cm\(^3\).Pa\(^{-1}\) or mol.cm\(^{-3}\).Pa\(^{-1}\). The solubility of H\(_2\) in Nafion is around \(2.2 \cdot 10^{-10}\) mol.cm\(^{-3}\).Pa\(^{-1}\) and fairly independent of temperature, while for O\(_2\) we have

\[
c_{O2} (\text{mol}.\text{cm}^{-3}.\text{Pa}^{-1}) = 7.43 \cdot 10^{-12} \exp(5.54(\text{kJ/mol})/RT) \tag{11.7}
\]

On this basis, permeability gets units of, for instance, mol.s\(^{-1}\).cm\(^{-1}\).Pa\(^{-1}\). The overall permeability of hydrogen is around one order of magnitude higher than that of oxygen under normal operating conditions, and so-called hydrogen cross-over is thus a
main factor for the overall fuel efficiency of the PEFC, and oxygen transport in the polymer at the cathode may be limiting for kinetics.

Regardless of type, polymers have advantages and drawbacks compared with other solid electrolytes. They are currently too expensive, but this is shared with the other solid electrolytes. The polymers are robust and flexible, and they tolerate fast startups. The around 5 water molecules each proton drags require a water handling system. Moreover, the materials and cell operation do not tolerate overheating above ca. 100 °C, that would lead to dehydration and possibly irreversible mechanical failure and electrolyte deterioration.

Electrodes for PEFCs

Today, standard electrode structures for PEFCs comprise two layers. The layer facing the electrolyte is a fine-structured composite electrode consisting of graphite and the electrolyte, giving many reaction sites for electrons, ions, and reactants dissolved in the electrolyte. Nanoscopic and finely distributed platinum catalyst particles are embedded in the composite. A number of alloying elements and other catalysts (e.g., RuO$_2$) are in use as additions to the Pt. Moreover, carbon nanoparticles of various kinds are in use to enhance the effective reaction interface area and provide novel catalytic properties over traditional graphite materials.

The second layer – the so-called gas diffusion layer - may be composed much like the first, but has relatively large pores for reactant gases to diffuse into – shortening their path to the reaction sites. The same pores however also serve to let water out of the cathode electrode and – when required – water into the anode electrode. In addition the gas-diffusion layer conveys the current of electrons to or from the interconnect, so that electronic conductivity is essential. It should finally exhibit good heat conduction.

The gas diffusion layer provide mechanical support to the electrolyte membrane. During stack mounting a high mechanical force is applied to ensure good contact between all cell components, the compressibility of the gas diffusion layer is a key property here.

The gas-diffusion layer is made usually of graphite structures and often contains pore-formers, i.e., material that evaporate or melt during baking, leaving open pore structures. The materials are often treated with a hydrophobic surface coating to prevent that pores are entirely flooded with water. Many gas diffusion materials are available commercially, such as the Toray carbon fiber paper.

It may be noted that graphite – actually similar to the PEM electrolyte itself – is not thermodynamically stable in air, it survives well due to the low kinetics of oxidation of the carbon at temperatures as low as for PEFCs (and even HTPEFCs).
11. Materials for fuel cells and electrolysers

The low temperature of operation leads to poisoning of the Pt catalysts by CO(g) and other reactive species, like H$_2$S: CO is absorbed preferentially on the catalyst surface and prevents other reactions. H$_2$S leads to formation of the very stable platinum sulfide PtS. The fuel must for these reasons be pure hydrogen, with very low tolerances for CO and H$_2$S.

*Interconnects and seals*

In a practical fuel cell, single PEFC cells, so-called membrane electrode assemblies (MEAs) are stacked in order to achieve a higher cell voltage and power output (proportional to the number of single cells) at the same current. The single cells are connected using so-called bipolar plates (interconnects) that ensure electrical series contact from cathode of one cell to anode of the next (series connection). It also keeps fuel and oxidant separate.

Interconnects must be gas-tight, provide high electrical and thermal conduction, be conformable to provide gas flow channels, and preferably light-weight. They must be mechanically strong and chemically stable. Two types of interconnect materials are in use; graphite plates and metallic plates. Graphite is lighter and more chemically stable, while metallic materials have better electrical and heat conduction. Composite solutions are often applied; graphite is inherently somewhat porous and may thus be impregnated with a polymer to close the pores. Metallic interconnects may suffer from corrosion by the acidic membrane polymer material, and may be covered by graphite, e.g. in the form of plates.

Other components include gas seals and electrical insulation. These can be made of, for instance, Teflon.
11. Materials for fuel cells and electrolyzers

Figure 11-3. Components in a typical PEFC cell. The layer in the middle is the electrolyte membrane (PEM) with the two electrodes containing catalysts (MEA). The two layers on each side next to the MEA are the gas diffusion layers (porous conducting material, usually a graphite structure). Next follow seals and finally interconnects.

Figure 11-4. Series connection of PEFC-elements to form a stack.

**High temperature polymer electrolytes**

The problem of temperature limitations by using water as vehicle in traditional PEMs is sought solved by various means. Replacement of sulfonic anions with phosphonic ones plus addition of additional phases into composites can enable use of temperatures somewhat above 100 °C. These are still reliant on remaining water as proton vehicles, though.

A more radically different approach is to remove water entirely, and to introduce nitrogen as host and donor/acceptor for the protons. In particular, polymers containing imidazole is found a good candidate; imidazole is an organic ring compound with
11. Materials for fuel cells and electrolysers

formula $C_3N_2H_4$. One nitrogen atom has a hydrogen bonded to it, and both nitrogen atoms have lone electron pairs. Imidazole can be protonated into an ion where the positive charge is delocalised between the two nitrogens:

This allows uptake of one proton to the vacant nitrogen in imidazole, and that the hydrogen on the other nitrogen leaves as a proton. This allows imidazole to transfer protons from one donor to another if the geometrical arrangement is suitable. The imidazole molecules can be dissolved in a suitable polymer, or bonded to polymer chains. By adjusting e.g. the length of these chains it is possible to optimise the dynamics and spacial conditions so that the imidazole molecules can donate and accept protons between themselves and thus constitute a proton conducting network. Polybenzimidazole (PBI) is such a proton conducting polymer and is marketed by BASF. These polymers operate without water and are stable for operation up to around 200 °C, but the proton conductivity is so far considerably smaller than for the best ordinary polymers.
Materials for solid oxide fuel cells (SOFCs)

SOFCs with oxide-ion conducting electrolytes

Oxide ion conductors

Already at the end of the 1800s the German scientists Walther H. Nernst discovered that ZrO$_2$ with additions of other (lower-valent) metal oxides became well conducting at high temperatures. He developed the so-called Nernst-glower, in which a bar of Y-doped ZrO$_2$ was preheated and subjected to a voltage. The current through the material heated it further, making it even more conductive, and it ended up white-glowing. Edison’s lamps based on coal and later tungsten needed vacuum or inert atmospheres in order not to burn, while Nernst’s ZrO$_2$ was already an oxide stable in air and with very high melting point and hardly any evaporation. Nernst himself hardly realised the mechanism of conduction in ZrO$_2$ – only well into the 1900s did one begin to understand defects in crystalline solids and that the Nernst glower was based on lowervalent $\text{Y}^{3+}$ ions in the ZrO$_2$ structure compensated by mobile oxygen vacancies. Later it was proposed that doped ZrO$_2$ could be used as a solid electrolyte in electrochemical energy conversion processes. Only in the last quarter of the 1900s did this begin to approach reality. Doped ZrO$_2$ has been and is still the dominating electrolyte in the development of solid oxide solid oxide fuel cells (SOFCs).

Undoped ZrO$_2$ is monoclinic. At higher temperature it transforms into more symmetric tetragonal and cubic modifications (see figure). The cubic polymorph is the fluorite structure (named after fluorite, CaF$_2$). Lowervalent cations, like $\text{Ca}^{2+}$ or $\text{Y}^{3+}$ lead to charge compensation by oxygen vacancies. These vacancies stabilise the more symmetrical high temperature modifications so that 3 mol% $\text{Y}_2\text{O}_3$ may stabilise the tetragonal polymorph to room temperature (metastable). 8-10 mol% $\text{Y}_2\text{O}_3$ or more can stabilise the cubic structure. The latter type of materials is abbreviated YSZ (yttria stabilized zirconia).
11. Materials for fuel cells and electrolyzers

Figure 11-11. Sketch of temperature (°C) vs composition (mol% YO$_{1.5}$) in the ZrO$_2$-rich part of the ZrO$_2$-YO$_{1.5}$-phase diagram. ss=solid solution. Beneath a certain temperature equilibrium is in practice frozen out, and the lines near room temperature indicate the phase one gets. From Phase Diagrams for Ceramists (VI-6504), The American Ceramic Society.

The defect reaction of dissolution of Y$_2$O$_3$ in ZrO$_2$ can be written

\[ Y_2O_4(s) = 2Y^{\prime}_{Zr} + V^{\ast\ast}_O + 3O^{\prime}_O \]

and the concentration of vacancies is thus fixed by the concentration of yttrium substituents:

\[ 2[V^{\ast\ast}_O] = [Y^{\prime}_{Zr}] = \text{constant} \]

The conductivity, given by the charge, concentration, and charge mobility, then becomes

\[ \sigma_{\nu^{\ast\ast}} = 2e[Y^{\prime}_{Zr}]\mu_{\nu^{\ast\ast}} = e[Y^{\prime}_{Zr}]\mu_{\nu^{\ast\ast}}T^{-1}\exp\left(-\frac{\Delta H^{m,\nu^{\ast\ast}}}{RT}\right) \]

At temperatures around 1000 °C YSZ has sufficient mobility of oxygen vacancies and thereby sufficient oxide ion conductivity that we can make a working fuel cell with 100 µm thick YSZ electrolyte.

There has been considerable optimism around such cells; the high temperature enables use of fossil fuels and the heat loss is easy to heat exchange and utilise. One early on identified cathode (LaMnO$_3$-based) and anode (Ni+YSZ cermet) and the interconnect (LaCrO$_3$-based) which all had thermal expansion sufficiently similar to that of YSZ so that cells could be constructed and assembled. But it has turned out that degradation is too fast at this temperature. The LaCrO$_3$ interconnect is too expensive to buy and machine. Thus, the operation temperature must be brought down so that the life time can be improved and we can use a cheap and machineable metal as interconnect. The development of better electrolytes has therefore been going on continuously the last decades.
Firstly, one has been able to reduce the thickness of the electrolyte. Early, one used self-supported sheets of 100-200 µm thickness, made by tape-casting (in which ceramic powder is dispersed in a plastic medium, cast to a thin film on a glass plate by a doctor’s blade, dried to a foil, and burned and sintered at high temperature). Today is used typically 10 µm thick films supported on a porous substrate of anode or cathode material, so that we can have an order of magnitude lower conductivity and thus temperatures lowered to 7-800 °C.

One may in principle add more dopant to get more oxygen vacancies, but the conductivity goes through a maximum as a function of concentration; at higher concentration, vacancy-vacancy and vacancy-dopant association becomes dominant, immobilising the vacancies. Moreover, vacancy ordering and overstructure formation sets in. Computer simulations of the lattice may give insight into e.g. dopants with lower association to the vacancies. It turned out from such simulations that scandium, Sc$^{3+}$, should fit better in ZrO$_2$ than Y$^{3+}$, and thus give less association. Scandia-stabilised zirconia (ScSZ) was developed based on this, and has higher conductivity than YSZ by typically half an order of magnitude. The combination of thin films and use of ScSZ enables so-called intermediate temperature SOFC (ITSOFC) down towards 600 °C.

![Figure 11-12. Conductivity of some oxide ion conductors. Fra P.G. Bruce: Solid State Electrochemistry.](image)

A number of other oxides also exhibit high oxide ion conductivity. CeO$_2$ is similar to ZrO$_2$ and has higher ionic conductivity when acceptor doped, in this case optimally by Sm$^{3+}$ or Gd$^{3+}$. It can thus be used at lower temperatures. But it also has a higher tendency of reduction:

11.23
11. Materials for fuel cells and electrolysers

\[ O_2^e = v_0^e + 2e^+ + \frac{1}{2}O_2(g) \]
\[ \frac{K_{\text{red}}}{v_0^e} = \left[ \frac{v_0^e}{p_{O_2}^{1/2}} \right] \]  

(11.45)

and accordingly exhibit higher n-type electronic conductivity as well as some chemical expansion due to the extra oxygen vacancies.

Bismuth oxide, Bi\textsubscript{2}O\textsubscript{3}, has several structure polymorphs. One of these, \( \delta \)-Bi\textsubscript{2}O\textsubscript{3} has a cubic fluorite structure similar to ZrO\textsubscript{2}. It lacks \( \frac{1}{4} \) of the oxide ions, but without doping; it has inherent deficiency and disorder. It thus has a high oxide ion conductivity. However, the cubic, disordered polymorph is stable only over a limited temperature window and it reduces easily. It can thus not be used in fuel cells it seems, but has been employed in e.g. oxygen pumps for medical oxygen generators. The \( \delta \)-Bi\textsubscript{2}O\textsubscript{3} phase can be stabilised by certain dopants, such as WO\textsubscript{3} (see figure above).

New oxide ion conductors are continuously being discovered. After numerous attempts at the end of the 1990s one finally succeeded in making a good perovskite-structured oxide ion conductor based on LaGaO\textsubscript{3}. A combination of Sr\textsuperscript{2+} and Mg\textsuperscript{2+} as acceptor-substituents for La\textsuperscript{3+} and Ga\textsuperscript{3+} was necessary to give mutually high solubility and a high concentration of oxygen vacancies. Sr+Mg-doped LaGaO\textsubscript{3} (LSGM) has higher conductivity than ZrO\textsubscript{2}-based electrolytes at low temperature and are therefore promising, except for a problem with Ga evaporation under reducing conditions.

Among other new oxide ion conductors we find materials based on La\textsubscript{10}Ge\textsubscript{6}O\textsubscript{27} and La\textsubscript{2}Mo\textsubscript{2}O\textsubscript{9}, both with interstitial oxide ions as defects.

SOFC anodes

Only two non-noble metals are stable in typical fuel gas conditions; nickel (Ni) and copper (Cu). Nickel is the common choice for SOFC, because of its good catalytic properties for anode reactions involving hydrogen, and its mechanical stability at high temperatures. Ni is applied in a composite with the electrolyte, e.g. a Ni-YSZ cermet. This must be porous to allow gas access, and both the Ni and YSZ phases should percolate. It is often applied in a fine-grained microstructure close to the electrolyte (to optimise catalytic area) and in a courser version towards the interconnect to optimise electronic conduction and current collection.

Nickel is applied during fabrication and sintering of the anode as NiO, which is subsequently reduced to Ni during the first operation when fuel is introduced.

Ni cermet anodes have the disadvantages that they are catalytic not only to the electrochemical reaction, but also to reforming

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

(11.46)

This means that this exothermic reaction takes place quickly as soon any unreformed fossil fuel and water meets at the anode inlet, and this part of the stack may get too cold. Internal reforming (by supplied water or by water from the anode reaction) may thus be possible and advantageous to consume joule heat from the stack, but requires very difficult control of many parameters to avoid large temperature gradients and resulting cracks.

The other reaction Ni catalyses is coking:

\[ \text{CH}_4 = \text{C(s)} + 2\text{H}_2 \]  

(11.47)
11. Materials for fuel cells and electrolysers

which takes place quickly unless counteracted by a supply of an oxidant, such as oxygen ions or water from the anode, or steam in the fuel stream.

Finally, Ni has a problem in a cell which is running at too high current and anode overpotential: The oxygen activity may be too high, and Ni oxidises to NiO. This has a low electronic conductivity and the overpotential gets even higher, locking the cell (which may be only one detrimental cell in a whole stack) in an "off" state.

The problems altogether with Ni anodes has led some to try to develop alternative anodes, especially to achieve direct introduction of fossil fuels, hoping to avoid coking and instead have direct oxidation on the anode, e.g.

\[
\text{CH}_4 + 4\text{O}^2^- = \text{CO}_2 + 2\text{H}_2\text{O} + 8e^- \tag{11.48}
\]

Formulations for such anodes are mainly either to replace Ni with Cu (troubled by Cu’s lower melting point and thus higher tendency to creep and sinter) or to have an oxide with high electronic conductivity. The latter can be achieved by donor-doping, for instance by substituting \(\text{Sr}^{2+}\) in \(\text{SrTiO}_3\) with \(\text{Y}^{3+}\) which is then compensated by conduction band electrons. Such materials do work, but are troubled by limiting electronic conductivity and catalytic activity.

\[SOFC\text{ cathodes}\]

For cathodes, we cannot use any metals except the noble ones (Pt, Au, Ag). They are mainly considered too expensive. Silver, Ag, is thinkable, and it has a beneficial oxygen diffusivity so that this would spread out the reaction zone considerably. However, it smelting point is close to the operating temperatures, and it has a considerable evaporation.

Thus, oxides is the common choice, and in particular \(\text{LaMO}_3\) perovsklites where M is Mn, Fe or Co are much studied. We will here use LaMnO\(_3\) as example. It has a favourable thermal expansion match with YSZ.

The first thing we need to do is to give it a high electronic conductivity. The material itself has a relatively low band gap such that the formation of electrons and holes according to

\[0 = e^* + h^* \tag{11.49}\]

\[K_g' = [e^*] [h^*] = np = K_{g,0} \exp\left(-\frac{E_g}{RT}\right) \tag{11.50}\]

is considerable. The states \(e^*\) and \(h^*\) can be seen as representing \(\text{Mn}^{4+}\) and \(\text{Mn}^{2+}\), respectively, in in \(\text{LaMnO}_3\) which otherwise nominally contains \(\text{Mn}^{3+}\).

We use an acceptor dopant that will enhance the concentration of holes. A suitable dopant is \(\text{Sr}^{2+}\) substituting \(\text{La}^{3+}\) and the resulting electroneutrality becomes

\[ [h^*] = [\text{Sr}^{2+}] = \text{constant} \tag{11.51}\]

We note that this oxide chooses to compensate the acceptors with holes instead of oxygen vacancies (as in \(\text{ZrO}_2\)) – a result of the lower bandgap. The \(\text{Sr}\)-doped \(\text{LaMnO}_3\) is abbreviated LSM or LSMO.

The lack of oxygen vacancies means LSMO has little mixed conduction and little spreading of the reaction three-phase boundary. Additions of Co and Fe on the B site
increase the oxygen vacancy concentration and thus the reactive area and also the catalytic activity.

LSMO tends to form reaction layers of La$_2$Zr$_2$O$_7$ and SrZrO$_3$ in contact with YSZ. This is fortunately counteracted by stabilisation of the perovskite structure by the Sr dopants in LSMO. Despite these reactions, cathode performance is often increase by making porous "cercer” composites of YSZ and LSMO.

**SOFC interconnects**

Finally, the SOFC interconnect presents a challenge. Early on it was common to use Sr-substituted LaCrO$_3$ (here called LSCrO). Its defect structure is much like that of LSMO, but LSCrO has a lower p-type conductivity – especially in hydrogen. Its essential advantage is that it is stable in hydrogen, contrary to LSMO. Problems of LSCrO comprise chemical expansion and some permeation due to mixed conduction from a certain concentration of oxygen vacancies.

As an alternative one can use metallic interconnects. These are alloys which form Cr$_2$O$_3$ on the surface during oxidation. This provides oxidation protection while being electronically conductive. The problem is that Fe-Cr superalloys with sufficient Cr content to form a protective Cr$_2$O$_3$ layer at high temperature are very hard and difficult to machine and end up very expensive. There is thus a driving force to develop intermediate temperature ITSOFCs where normal chromia-forming stainless steels are protective enough. Temperatures of 600 °C or less are probably required.

Metallic interconnect have much higher electronic and thermal conductivity than ceramic ones, and give easier design of stacks and more robust stacks. However, the corrosion problem is always there, and in addition, evaporation of chromium in the form of gaseous Cr$^{6+}$ oxyhydroxides from the interconnect’s protective Cr$_2$O$_3$ layer to the cathode is detrimental – it settles as Cr$_2$O$_3$ and blocks the reactive sites. To avoid this, the alloy is often covered with a more stable Cr compound, like LaCrO$_3$ or a Cr spinel like MnCr$_2$O$_4$.

**SOFCs with high temperature proton conducting electrolytes**

Proton conducting hydrates, solid acids, and hydroxides may conduct by defects or disorder among their protons. However, they tend to decompose at relatively low temperatures.

*Proton conducting oxides*

Oxides and other nominally water-free materials may still contain a few protons in equilibrium with surrounding water vapour. With acceptor-doping the proton concentration may be further increased. Oxide ions are hosts for the protons, so that the protons can be seen as present as hydroxide groups occupying oxide ion lattice sites; $OH^*_i$. When they migrate, the protons jump from oxide ion to oxide ion, and the defect is thus often also denoted as interstitial protons, $H^*_i$. The protons are bonded rather strongly, so that the activation energy for the jump is quite high, and relatively high
temperatures are required for conductivity. The best high temperature proton conductors are perovskites with large and basic A-site cations, like BaCeO$_3$, BaZrO$_3$, and SrCeO$_3$, doped with a suitably small lower-valent cation like Y$^{3+}$ on the B-site. We can write the acceptor-doping of BaCeO$_3$ in wet atmospheres as

$$\text{BaO}(s) + \frac{1}{2} Y_2 O_3 (s) + \frac{1}{2} H_2 O(g) = \text{Ba}^{\text{III}}_{\text{Ba}} + Y^{3+}_{\text{Ce}} + 2O^{2-}_{\text{O}} + OH^{\ast}_{\text{O}}$$

We see that we get one proton per Y$^{3+}$ acceptor. High temperature proton conductors have a tendency to revert the uptake of water at higher temperatures, as the hydration reaction

$$H_2 O(g) + v^{2+}_{\text{O}} + O^{1+}_{\text{O}} = 2OH^{\ast}_{\text{O}}$$

is exothermic, driven to the left at increasing temperatures. We then replace the effective charge of the protons with those of the oxygen vacancy. Proton conduction in these materials is thus a battle and compromise at increasing temperature between sufficient proton mobility and loss of protons from dehydration. Most materials thus exhibit a maximum in proton conductivity with temperature.

The proton conductivity in the best Ba-based perovskites is superior to the oxide ion conduction in ZrO$_2$-based materials at low and intermediate temperatures, but ends up lower by an order of magnitude, typically 0.01 S/cm, at high temperatures due to the loss of protons.

The best Ba- or Sr-based perovskites have the disadvantage of reactivity with acidic gases, notably CO$_2$ to form alkali earth carbonates (like BaCO$_3$). The reaction prevents use with reformed fossil or biological fuels and also in some cases with normal air. The formation of BaCO$_3$ markedly weakens grain boundaries and the overall mechanical properties. Alternative materials without the most basic alkali earths comprise acceptor-doped Gd$_2$O$_3$, LaScO$_3$, LaPO$_4$, and LaNbO$_4$. The proton conductivity of these is an order of magnitude less than in the Ba-based perovskites, and thinner films, in the micrometer-range, need to be developed.

Proton conducting solid oxide fuel cells have some advantages over standard SOFCs, as mentioned earlier, but thinner electrolytes need to be implemented. In addition, new sets of anode, cathode, and interconnects may need to be developed.