

Materials for Electrochemical Energy Conversion and Storage

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Preface

This text is being written in the first round to serve as curriculum for parts of the course MEF3200/MEF4200 Energy Materials at the University of Oslo.

The text is partly based on and an expansion of parts of the broader introductory course MENA1000 Materialer, energi og nanoteknologi (Materials, Energy and Nanotechnology).

Truls Norby, October 2013

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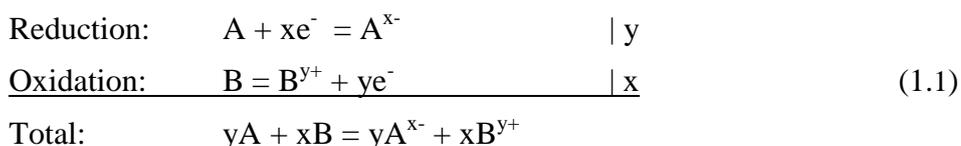
1. Electrochemical cells

What is Electrochemistry?

Electrochemistry deals with the relation between chemical reactions and electrical phenomena – mainly potential and current of electrons. 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 production of hydrogen and other fuels, and batteries.

A more precise definition of electrochemistry states that *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:



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



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

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

Anode *Oxidation* (both start with **vowels**)

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, but on whether the process releases or consumes electrons.

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 established 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 the coulomb, the charge carried by one ampere in one second ($1 \text{ C} = 1 \text{ A}\cdot\text{s}$).

A cell driven by a spontaneous chemical redox 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* (although today they are so common that we tend to call also them simply batteries, like in “battery cars”). If the cells 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 by supplying electrical current – 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. The latter is an *electrolyser* – a reverse fuel cell.

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*. Thus, generally, we have

$$\Delta G = w_{el} \quad (1.3)$$

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:

$$w_{el} = \Delta G = -neE \quad (\text{for a reaction with } n \text{ electrons}) \quad (1.4)$$

$$w_{el} = \Delta G = -nN_A eE = -nFE \quad (\text{for } n \text{ mole electrons}) \quad (1.5)$$

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

$$\Delta G = -nFE \quad \text{or} \quad E = \frac{-\Delta G}{nF} \quad (1.6)$$

The *standard* Gibbs energy change, ΔG^0 , corresponding to the change in Gibbs energy when all reactants and products are present in standard state (unit activity, e.g. at 1 bar pressure or 1 M concentration, or as a pure condensed phase) has a corresponding standard cell voltage E^0 :

$$\Delta G^0 = -nFE^0 \quad (1.7)$$

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

$$\Delta G = \Delta G^0 + RT \ln Q \quad (1.8)$$

we can by combination of the above equations obtain

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (1.9)$$

This widely applied and important equation is called the *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 $E = 0$:

$$E = E^0 - \frac{RT}{nF} \ln Q_{\text{equilibrium}} = 0 \quad (1.10)$$

i.e.,

$$E^0 = \frac{RT}{nF} \ln Q_{\text{equilibrium}} = \frac{RT}{nF} \ln K \quad (1.11)$$

All in all, we can give the standard data for a reaction in terms of ΔG^0 , E^0 , or K :

$$\Delta G^0 = -nFE^0 = -RT \ln K \quad (1.12)$$

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

$$\Delta G_{\text{total}} = y\Delta G_{\text{red}} + x\Delta G_{\text{oks}} \quad (1.13)$$

or, if we use reduction data for both reactions:

$$\Delta G_{\text{total}} = y\Delta G_{\text{red1}} - x\Delta G_{\text{red2}} \quad (1.14)$$

Vi see from this that

$$E_{\text{total}} = \frac{\Delta G_{\text{total}}}{-nF} = \frac{\Delta G_{\text{total}}}{-xyF} = \frac{y(-xFE_{\text{red}}) + x(-yFE_{\text{oks}})}{-xyF} = E_{\text{red}} + E_{\text{oks}} \quad (1.15)$$

or

$$E_{\text{total}} = E_{\text{red1}} - E_{\text{red2}} \quad (1.16)$$

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



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 a half cell voltage of 0 V.

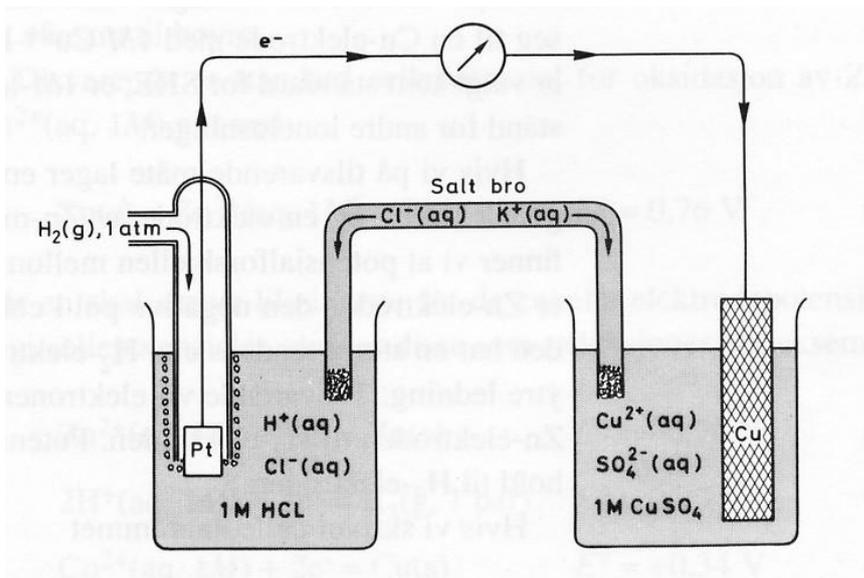


Figure 1-1. Electrochemical cell with standard hydrogen electrode (SHE), salt bridge, and a Cu^{2+}/Cu -electrode at standard conditions.

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.

A total red-ox reaction does not indicate electron transfer, it does not specify the number n of electrons exchanged and can be done without an electrochemical cell. Nevertheless, 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 $y\text{A}$ and $x\text{B}$ above involves $n = x \cdot y$ electrons.

The reaction between hydrogen and oxygen:



has standard Gibbs energy of -228.7 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 O^{2-} or 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):

$$E^0 = \frac{\Delta_r G^0}{-2F} = +1.185 \text{ V} \quad (1.19)$$

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



then Gibbs energy is twice as big; $2 \times -228.7 = -457.4$ kJ/mol. But the number of electrons is also doubled, so the cell voltage remains constant, it is an *intensive* property:

$$E^0 = \frac{-457400}{-4F} = +1.185 \text{ V} \quad (1.21)$$

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 the quotient Q equal to the equilibrium coefficient K for the overall reaction.

It is worth noting that the above reaction and associated standard cell voltage refers to formation of water vapour (steam). Often – especially for processes at room temperature and up to 100°C – it is more relevant to consider formation of liquid water,



which has a standard potential of 1.23 V.

As discussed earlier, the voltage of an electrochemical galvanic cell changes from the standard voltage if the activities of reactants deviate from unity, calculated simply using the Nernst equation (eq. 1.9). Thus, we can increase the voltage of galvanic cells such as fuel cells by increasing the pressure or concentrations of the reactants, or decrease the pressure or concentrations of products. And the voltage naturally falls if the supply of reactants is obstructed or if products cannot be removed fast enough.

In an electrolyser, we apply a voltage - calculated according to the same equations - that is needed to produce the products at the required activity. For instance, to split liquid water into 1 bar H_2 and 1 bar O_2 , we need in principle to apply 1.23 V.

Batteries have voltages along the same principles as fuel cells and electrolyses. A typical voltage resulting from the reaction between zinc metal and MnO_2 in a dry alkaline cell,



is around 1.5 V. Rechargeable lithium ion batteries have much larger voltages, mainly arising from the half cell reaction



with standard half-cell voltages in the range of 3 V depending of the state of the Li ions and elemental lithium. The total cell voltage depends somewhat on the other half cell, where Li^+ ions are intercalated into an oxide structure. Recharging the battery requires in principle simply the reverse voltage.

Current and overvoltage losses

The current running in a cell and its outer circuit can be expressed by ohm's law:

$$I = E_N / R_{tot} \quad (1.25)$$

where E_N is the Nernst equation and R_{tot} is the sum of all resistive terms in the circuit. For a galvanic cell this is normally limited to:

$$R_{tot} = R_{load} + R_{electrolyte} + R_{anode} + R_{cathode} \quad (1.26)$$

Of these, R_{load} is the electronic load resistance in the external circuit, $R_{electrolyte}$ is the ionic resistance of the electrolyte, and R_{anode} and $R_{cathode}$ are the resistances corresponding to the limited kinetics of the two half-cell reactions involving ions and electrons. $R_{electrolyte}$ is an ohmic (constant, current-independent) resistance; the voltage lost over it is linearly proportional to the current, and it is often referred to as IR loss. R_{anode} and $R_{cathode}$ on the other hand can be complex functions of the current. They involve charge transfer processes and diffusion of ions and neutral species.

The output voltage of the entire cell, E_{cell} , is the voltage that lies over the load resistance:

$$E_{cell} = I \cdot R_{load} = E_N - I \cdot (R_{electrolyte} + R_{anode} + R_{cathode}) \quad (1.27)$$

i.e., the Nernst voltage minus all the overpotentials.

For electrolytic cells (electrolysers and charging batteries) the same sum of resistances applies, now only with the current having the opposite sign, whereby the overpotentials serve to increase the applied voltage.

Obviously, the goal of materials research on electrochemical energy conversion and storage devices is to lower the ohmic and kinetic resistances as much as possible, until they become small compared with the external load.

The resistance of an electrolyte is inversely proportional to its specific conductivity, proportional to its thickness, and inversely proportional to its area. Also the resistance attributed to electrode kinetics is inversely proportional to the area of the electrode. So, in principle – besides increasing conductivity and thinning the electrolyte and improving electrode kinetics – one may reduce losses by simply increasing the area of the cell and running small currents – it is all set by the current to area ratio. In rechargeable batteries this is set for low losses, one reason being simply that the system cannot tolerate too much heat developing. A battery is therefore by necessity quite efficient. A fuel cell or electrolyser could be equally efficient, but instead of having a large expensive and heavy device with small losses, the overall economy usually calls for a smaller cheaper device designed for giving losses in the range of for instance 40%. This is tolerable in such systems since they often operate at higher temperatures where heat is more easily removed, and since products can carry some of the heat off.

2. 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 – with very different operational modes and requirements - comprise photo-electrochemical 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.

Fuel cells

General aspects

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, methane 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 (alcohols, bio-diesel, etc.) 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 sulphur 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 such as methanol can be used below 100 °C because they can then be supplied in an aqueous phase. Fossil fuels, forming the acidic product CO₂, can not be used in alkaline fuel cells because CO₂ 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 sulphuric 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 sulphuric acid led to the production of hydrogen and oxygen over those two electrodes (electrolysis) (see figure below). Grove published his findings in 1839 – thus usually considered the year of the discovery of the fuel cell.

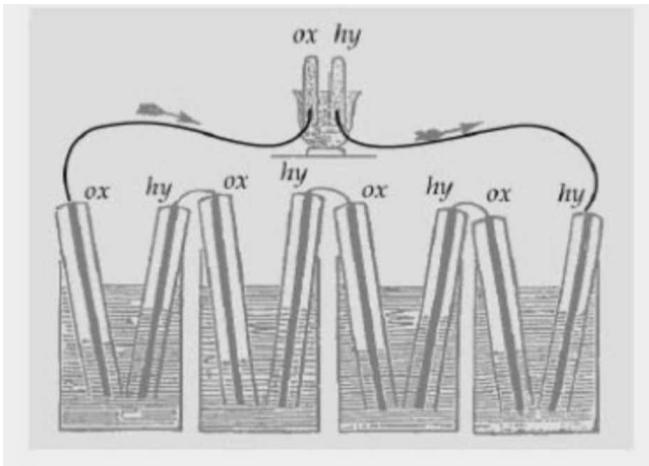


Figure 2-1. Grove's illustration of his fuel cell, consisting of four individual cells in series, and using the electrical power to electrolyse sulphuric acid.

General principle of operation and requirements of materials for fuel cells

A fuel cell consists of 4 central elements: Electrolyte, anode, cathode, and the interconnect that links stacked cells. 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 short circuit. 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 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.

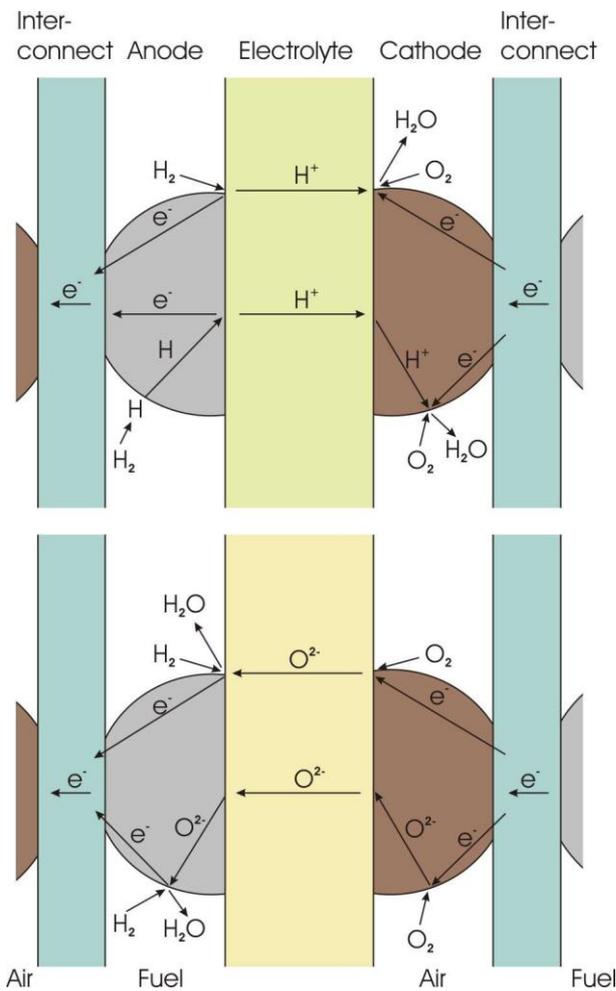


Figure 2-2. General principle of fuel cells with H^+ (upper) or O^{2-} (lower) conducting solid electrolytes, running H_2 and O_2 (air). For each cell is shown a schematic anode and cathode electrode grain. For each of these the electrode reaction on the top of the grain is the normal three-phase-boundary 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 start-ups, 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.

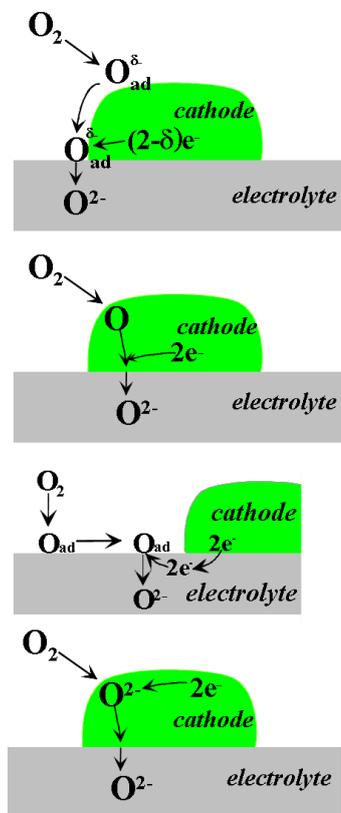


Figure 2-3. Schematic showing four ways of expanding the reaction area from a pure three-phase boundary line in solid oxide fuel cell cathodes: Cathode surface diffusion of adsorbed oxide ions or atoms; cathode volume diffusion of oxygen atoms; electrolyte surface diffusion of oxygen atoms; mixed ionic-electronic conduction in the cathode.

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.

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 nano grained carbon-polymer composite.

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 interfaces.

Overview of fuel cell types

In the sulphuric acid fuel cell the electrolyte – sulphuric acid - works by transporting protons or more precisely H_3O^+ ions. The sulphuric acid fuel cell is not pursued 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.

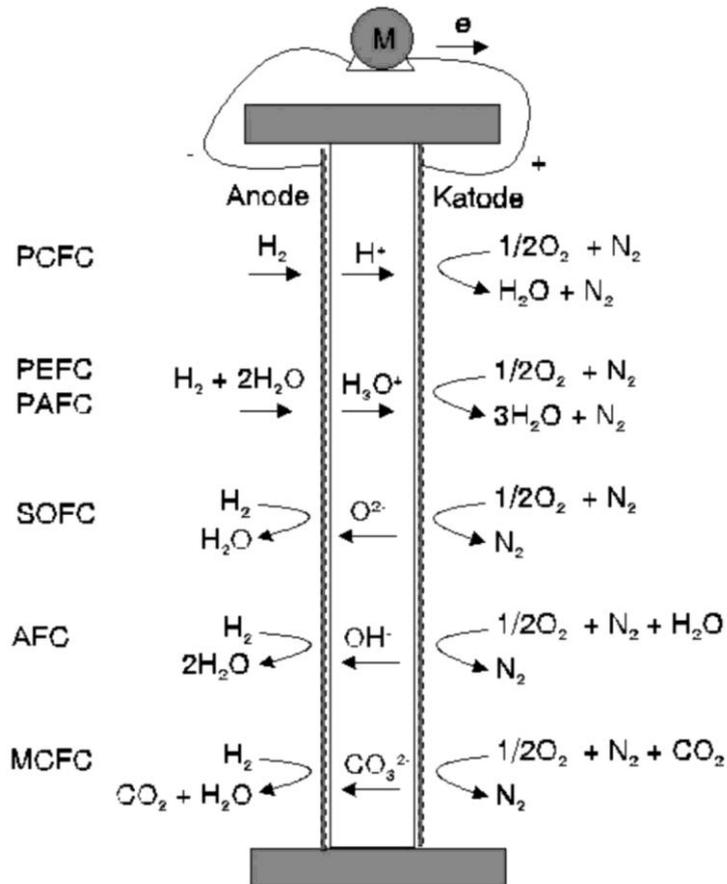


Figure 2-4. Various types of fuel cells, here in use with hydrogen as fuel and air as oxidant. PCFC = Proton Conducting Fuel Cell, PEFC = Polymer Electrolyte Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, SOFC = Solid Oxide Fuel Cell, AFC = Alkaline Fuel Cell, MCFC = Molten Carbonate Fuel Cell.

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. CsH_2PO_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.

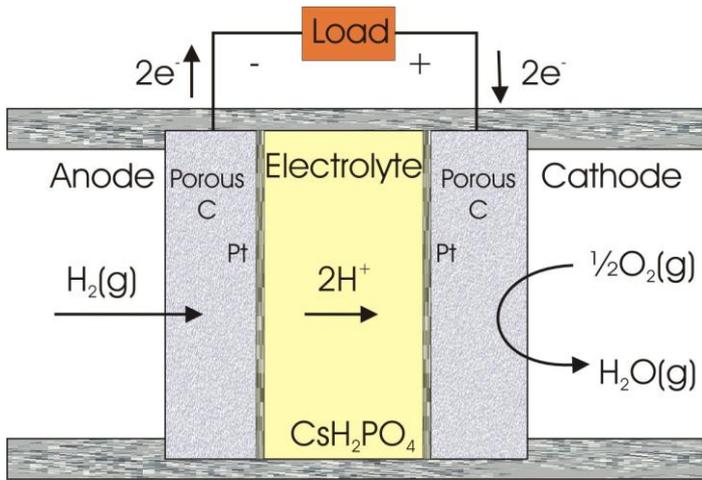


Figure 2-5. Proton conducting fuel cell (PCFC). CsH_2PO_4 as example electrolyte; Pt-activated graphite as electrode materials.

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 an American initiative of developing solid acid fuel cells (SAFC) based on CsH_2PO_4 -type materials).

Phosphoric acid fuel cell – PAFC

The phosphoric acid fuel cell (PAFC) uses concentrated phosphoric acid H_3PO_4 as electrolyte. As electrodes are used porous carbon with platinum as catalyst.

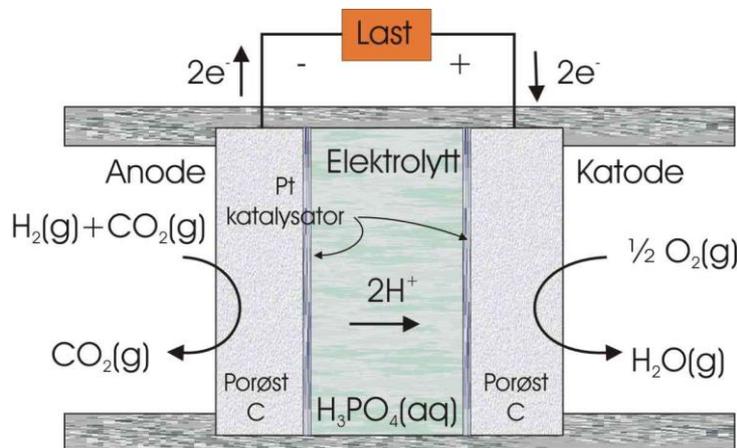


Figure 2-6. Phosphoric acid fuel cell (PAFC), drawn with H^+ transport for simplicity, but in reality with H_3O^+ as the mobile charge carrying ion..

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, H_2 is the main electro-active reactant while CO is oxidised to CO_2 via the water shift reaction. In contrast to PCFC, the mobile ion in PAFC is H_3O^+ .

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 H_3O^+ 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.

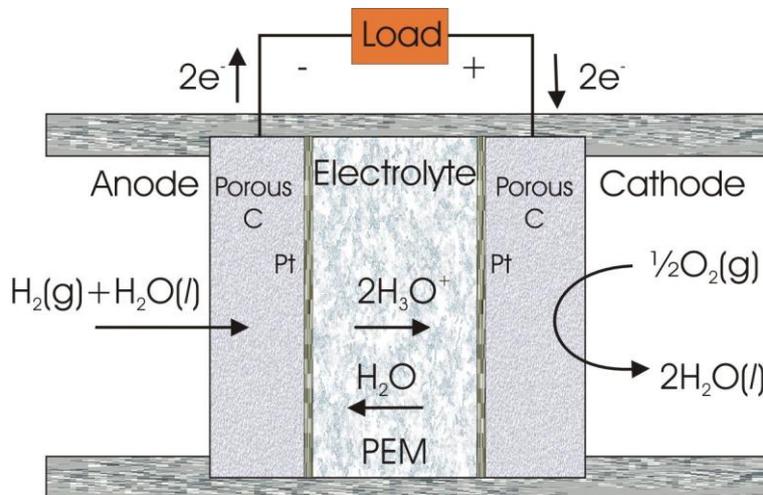


Figure 2-7. Polymer electrolyte fuel cell (PEFC, PEMFC). Each H_3O^+ ion drags another 5-6 water molecules.

Also PEFC uses porous carbon as electrodes, with Pt as catalyst. The low temperature makes the catalyst sensitive to CO (adsorbs on and blocks the catalyst surface) and H_2S (PtS is very stable). The fuel must thus be clean hydrogen, with small tolerances for CO and H_2S .

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.

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.

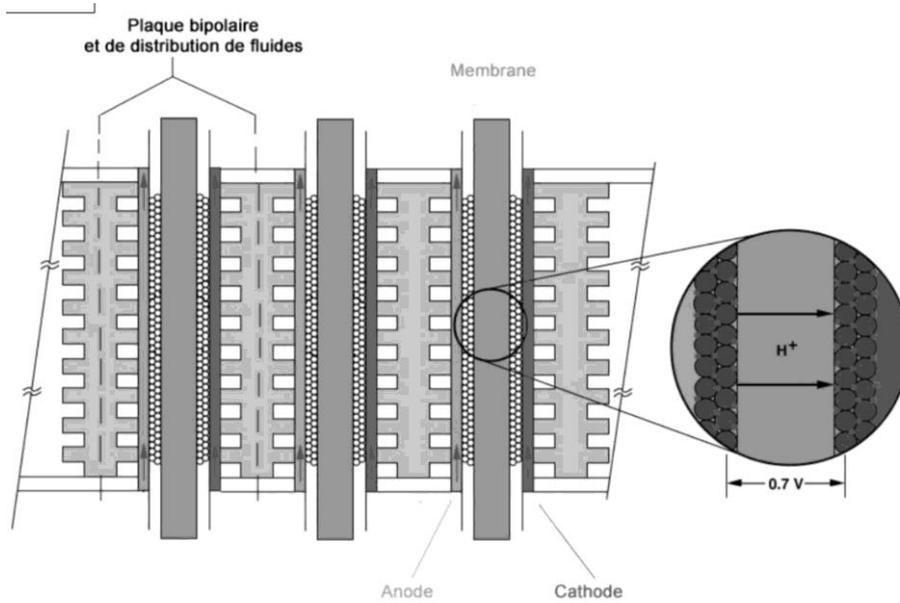


Figure 2-8. Series connection of PEFC elements into a stack. An element consists of one electrolyte membrane with electrodes and half a bipolar plate ("interconnect").

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 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.

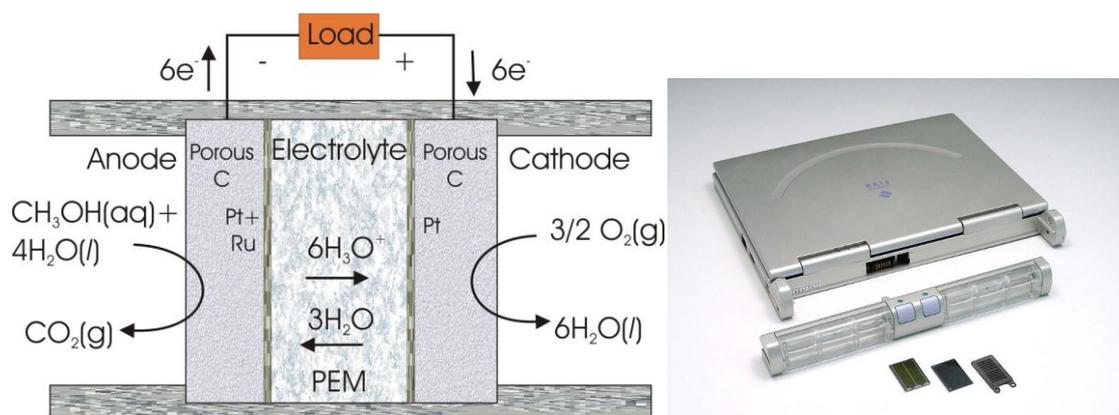


Figure 2-9. Direct-methanol fuel cell (DMFC).

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.

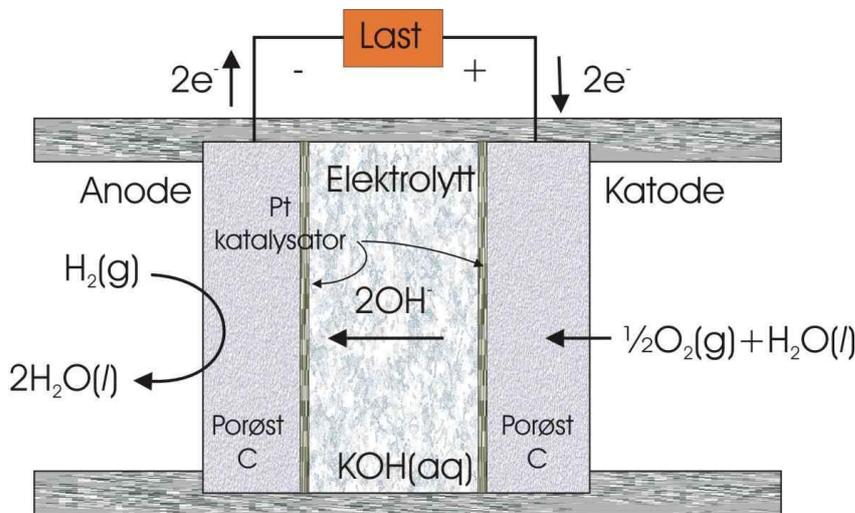


Figure 2-10. Alkaline fuel cell (AFC). The temperature of operation is 60-90 °C.

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 Li₂CO₃, Na₂CO₃ or K₂CO₃ impregnated in a porous carrier made of lithium aluminate, LiAlO₂. The anode is nickel, Ni, while the cathode is Li-doped NiO, which is a good p-type conductor. As the CO₃²⁻ ion is the charge carrier in the electrolyte, CO₂ must be re-circulated 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.

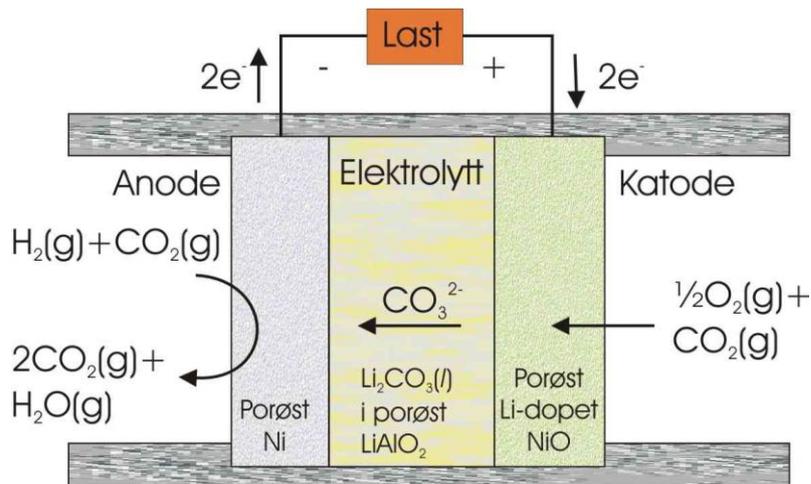


Figure 2-11. Molten carbonate fuel cell (MCFC).

Solid oxide fuel cell (SOFC)

The SOFC technology has for the most part based itself on yttrium stabilised (cubic) 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 forming water at the anode (fuel) side.

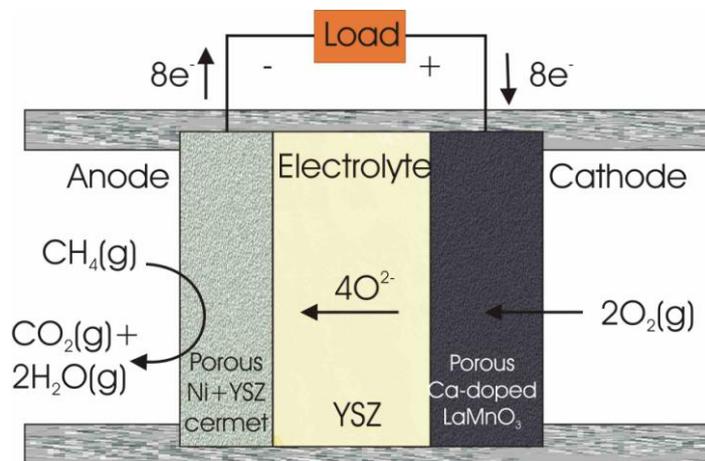


Figure 2-12. SOFC with methane as fuel and internal reforming over the anode.

The figure shows an SOFC that uses CH_4 as fuel: CH_4 reacts (is reformed) with H_2O over the anode whereby the H_2 is oxidised electrochemically to H_2O . This is used in its turn to reform more CH_4 and to shift CO to $\text{CO}_2 + \text{H}_2$. In practice we must add H_2O (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 one usually chooses to do the reforming in a separate reactor *before* the cell.

It has been speculated and tested whether one can oxidise the CH₄ molecule *directly* on the anode (without reforming). However, such a process from CH₄ to CO₂+2H₂O is an 8-electron process – a very unlikely pathway. Thus, intermediate reforming and shift by the formed water and subsequent oxidation of H₂ and possibly CO is probably inevitably the reaction path in operation on an SOFC anode.

Losses and efficiency of fuel cells

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, and 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/cm². 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.

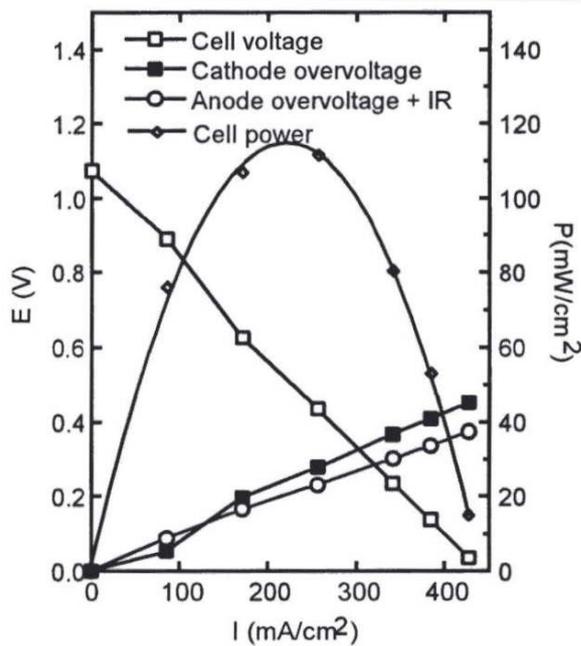


Figure 2-13. Potential (left axis) and power density (right axis) vs current density for a cell with 1 mm thick YSZ electrolyte and Ca-doped LaCrO₃ as anode and cathode. Fuel: H₂, oxidant: air. T=1000°C. T. Norby et al., *Proc. 1st European SOFC Forum*, Oct. 1994 (U. Bossel, ed.) (1994) 217-26.

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: $P = I \cdot U$. 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 H₂-O₂ 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 unit-less 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 effect P_e we can get is given by

$$P_e = \eta_G u_f P_{in} \quad (1.28)$$

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

The Nernst efficiency is electrical energy delivered by the cell divided by consumed chemical energy. The chemical energy is close to equal to the enthalpy (heat value) that the reactants would have delivered if they reacted with each 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 as heat 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.

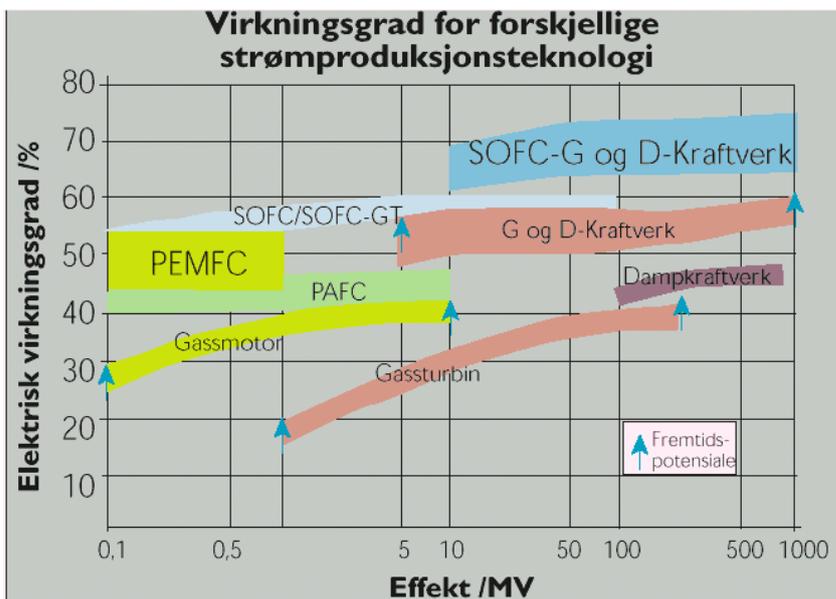


Figure 2-14. Estimate of overall electrical efficiency (P_e/P_{in}) for various power technologies as a function of produced effect. From Bellona.

For use of pure hydrogen as fuel, the fuel cells are clearly competitive (gas turbines 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 – such as load by AC motors in electrical vehicles or application to a distributed AC electricity grid, it needs to be converted to alternating current (AC). This is done by so-called inverters. This is power electronics that alternately reverses the current and smoothes it into a sine curve. If applied to a grid it needs to be synchronised with the grid before application to it.

Materials for polymer electrolyte fuel cells (PEFCs)

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_3O^+ -ions. These are hydrated, so that each of them drag an additional number (typically 5) of water molecules. Since these can not be re-circulated 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 sulphonate groups are now released to the water to form mobile H_3O^+ ions. The figure below indicates the composition of two such polymers, Nafion® and PEEK.

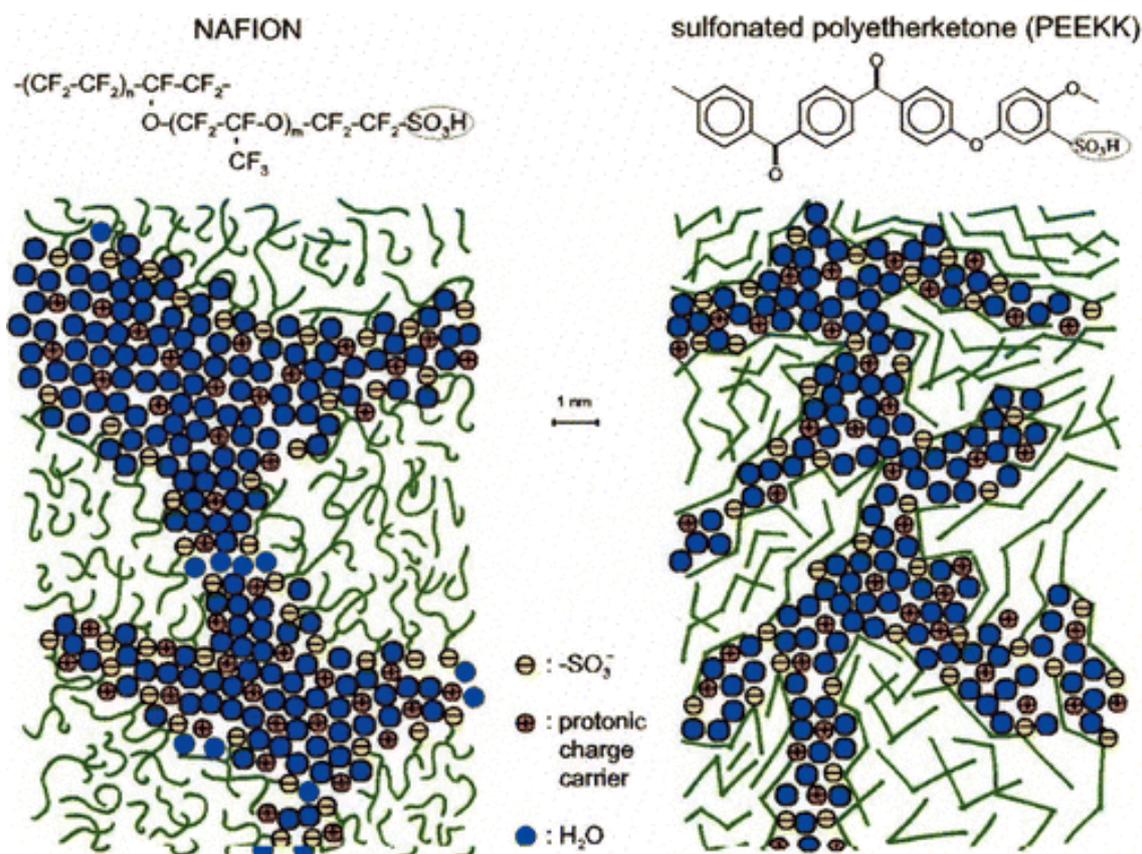


Figure 2-1. Schematic representation of the microstructure in water-containing (swelled) polymer electrolytes; Nafion® and sulfonated PEEK. From S.J. Paddison, *Ann. Rev. Mater. Res.*, 33 (2003) 289.

The standard proton conducting polymers can best be described as co-polymers of tetrafluoroethylene (TFE) and perfluorosulphonate (PFS) monomers. The latter are terminated as perfluorocarbon-sulphonic 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 SO_3 dissolved in sulphuric acid. The product is polymerised with hexafluoropropylene-epoxide:

liberate the protons. The process is thus similar to what is done for Nafion[®], 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 build-up of a water activity gradient. For thin electrolyte membranes this counter-flow 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 short-circuit. Permeability is the product of diffusivity and solubility (concentration):

$$P_i = D_i \cdot c_i \quad (1.4)$$

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

$$D_{\text{H}_2} \text{ (cm}^2\text{/s)} = 0.0041 \exp(-21.63(\text{kJ/mol})/RT) \quad (1.5)$$

$$D_{\text{O}_2} \text{ (cm}^2\text{/s)} = 0.0031 \exp(-23.01(\text{kJ/mol})/RT). \quad (1.6)$$

The concentrations c_i are proportional to the partial pressure of the gas, and may thus have units of, for instance, $\text{m}^{-3} \cdot \text{Pa}^{-1}$ or $\text{cm}^{-3} \cdot \text{Pa}^{-1}$ or $\text{mol} \cdot \text{cm}^{-3} \cdot \text{Pa}^{-1}$. The solubility of H_2 in Nafion is around $2.2 \cdot 10^{-10} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{Pa}^{-1}$ and fairly independent of temperature, while for O_2 we have

$$c_{\text{O}_2} \text{ (mol} \cdot \text{cm}^{-3} \cdot \text{Pa}^{-1}) = 7.43 \cdot 10^{-12} \exp(5.54(\text{kJ/mol})/RT). \quad (1.7)$$

On this basis, permeability gets units of, for instance, $\text{mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-1} \cdot \text{Pa}^{-1}$. 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 start-ups. 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., RuO₂) are in use as additions to the Pt. Moreover, carbon nano-particles 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 fibre 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).

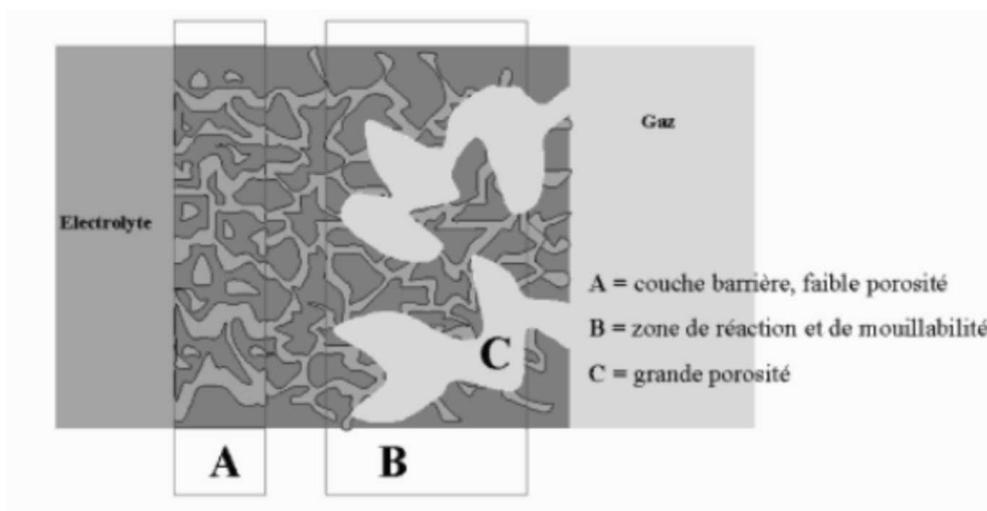


Figure 2-2. PEFC-electrode: Electrolyte, finely distributed mixture of electrolyte and carbon plus catalyst (A), gas diffusion layer (B) as a mixture of pores (C) and the structure in (A), and outermost the gas channel.

The low temperature of operation leads to poisoning of the Pt catalysts by CO(g) and other reactive species, like H₂S: CO is absorbed preferentially on the catalyst surface and prevents other reactions. H₂S leads to formation of the very stable platinum sulphide PtS. The fuel must for these reasons be pure hydrogen, with very low tolerances for CO and H₂S.

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.

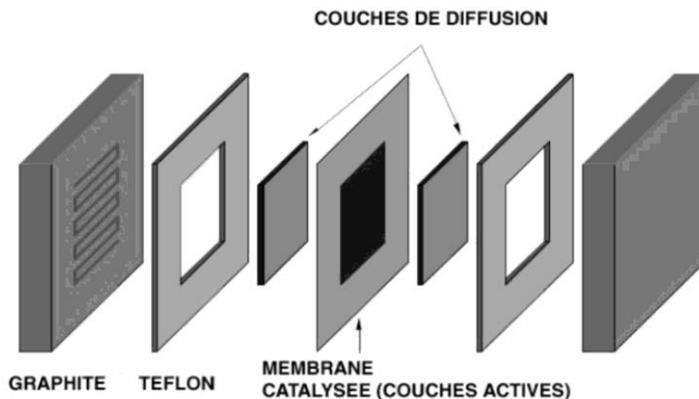
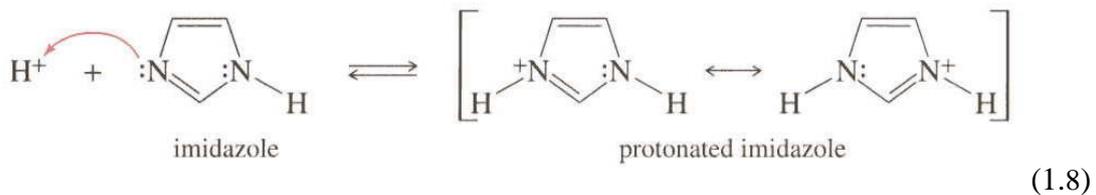


Figure 2-3. Components in a typical PEFC cell. The layer in the middle is the electrolyte membrane (PEM) with the two electrodes containing catalysts (MEA). The two layers on each side next to the MEA are the gas diffusion layers (porous conducting material, usually a graphite structure). Next follow seals and finally interconnects..

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 sulphonic 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 formula C₃N₂H₄. 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 nitrogen atoms:



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 spatial 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.

Defects and transport in crystalline solids

In processing and use of some materials it is important to avoid defects. In other cases the possibility to fabricate and form the material and its functional property may be dependent on defects in a sufficient concentration. In a perfect lattice no long-range transport can take place, all species are restricted to a lattice site. Defects are necessary for transport of atoms, ions, and – in many cases – electrons. For this reason understanding and control of defects are essential for fabrication and use of materials. In addition to transport, defects can also determine e.g. optical or catalytic properties.

In crystalline materials certain atoms (or ions) are expected to occupy certain sites in the structure, because this configuration gives lowest total energy. We attribute normally this energy lowering to bonding energy. At $T = 0$ K, absolute zero, there are no defects in the perfect crystalline material. As temperature increases the entropy gain leads to formation of defects in order to minimize Gibbs energy. Defects can also be introduced by doping or as a result of synthesis or fabrication. Many defects will be

present not because they have reached an equilibrium, but because they have had no practical possibility to escape or annihilate – they are "frozen in".

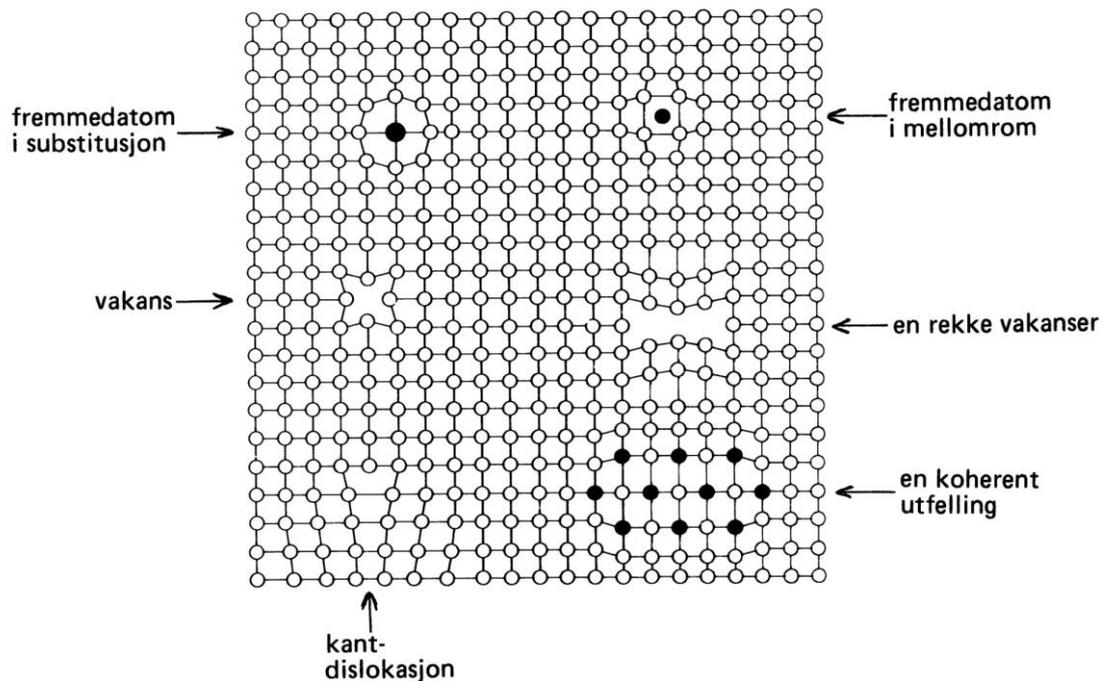


Figure 2-4. Types of defects in a metal lattice. From A. Almar-Næss; "Metalliske materialer".

We have various ways to classify defects. We may describe them as zero-dimensional (a point), one-dimensional (a row of defects), two-dimensional (a plane of defects) and three-dimensional (a foreign body in the structure). As a rule of thumb one may say that high dimension of the defects gives relatively little disorder, i.e. large enthalpy over entropy, and is stable at low temperatures, while low-dimensional defects are stable at high temperatures.

One-dimensional defects comprise primarily dislocations, of primary importance for mechanical properties. Two-dimensional defects comprise grain boundaries and surfaces. When objects or grains become nanoscopic these interfaces come very close to each other and we enter the area of nanotechnology.

We shall here focus on zero-dimensional defects – point defects. We will see them as chemical species and touch upon defect chemistry. We shall also look at the relation between these defects and transport (diffusion and electrical conductivity).

Zero-dimensional defects

Classification

Zero-dimensional defects comprise three types:

Point defects, which are atomic defects limited to one structural position:

- *vacancies*; empty positions where the structure predicts the occupancy of a regular atom,

- *interstitials*; atoms on interstitial position, where the structure predicts that there should no occupancy, and
- *substitution*; presence of one type of atom on a position predicted to be occupied by another type of ion.

Electronic defects, which may be subdivided into two types:

- *delocalised or itinerant electronic defects*, comprising *defect electrons* (or conduction electrons; in the conduction band) and *electron holes* (in the valence band),
- *localised or valence defects*; atoms or ions with a different formal charge than the structure predicts; the extra or lacking electrons are here considered localised at the atom.

Cluster defects; two or more defects are associated into a pair or larger cluster.

Defect chemical reactions and Kröger-Vink nomenclature

The formation of defects and other reactions involving defects follow two criteria in common with other chemical reactions; conservation of mass and conservation of charge (maintaining mass and charge balance). In addition, specific for defect chemistry, we must have *conservation of the structure*. This means that if structural positions are formed or annihilated, this must be done so that the ratio of positions in the structure is maintained.

In modern defect chemistry we use so-called Kröger-Vink notation, A_s^c , where A is the chemical species (or v for vacancy) and s denotes a lattice position (or i for interstitial). c denotes the *effective charge*, which is the real charge of the defect minus the charge the same position would have in the perfect structure. Positive effective charge is denoted \cdot and negative effective charge is denoted $'$. Neutral effective charge can be denoted with \times (but is often omitted).

Point defects in metals

We shall use nickel metal as an example. A regular Ni atom on a regular Ni structural site is denoted Ni_{Ni} or Ni_{Ni}^\times according to the above. A vacancy in nickel metal is denoted v_{Ni} while an interstitial Ni atom is denoted Ni_i . If we heat Ni metal, these defects will form, in principle independent of each other. The nickel vacancy is formed by a Ni atom leaving its site and forming a new structural site at the crystal's surface:



The equilibrium constant K_v is from the reaction equation simply the equilibrium activity of nickel vacancies. This is expressed as the site fraction X of vacancies:

$$K_v = a_{v_{Ni}} = X_{v_{Ni}} = \exp\left(\frac{\Delta S_v}{R} - \frac{\Delta H_v}{RT}\right) \quad (1.10)$$

and the concentration of vacancies as a function of temperature is this given by the standard entropy and enthalpy changes for the reaction.

A nickel interstitial is formed by an atom leaving the surface (annihilating that structural site) and entering an interstitial position in the structure:

$$Ni_{Ni} = Ni_i \quad (1.11)$$

Control shows that both defect chemical reactions we have introduced here obey the criteria for defect chemical reactions equations stated above. (In a simple metal we can freely make or remove structural sites, because there is no ratio between different lattice positions to maintain.)

Electronic defects and dopants in semiconductors

Defect chemistry is very important in ceramic materials – semiconductors and ionic materials alike – where the defects become charged. A non-metallic material has an electronic band gap between the energy band of the valence electrons (the valence band) and next available energy band (the conduction band). An electron in the valence band can be excited to the conduction band. If we describe a valence electron as effectively neutral, we have

$$e^x = e' + h^\bullet \quad (1.12)$$

but the equation is most often written without the valence band electron, since it is effectively neutral and we neglect the mass and mass balance of electronic species:

$$0 = e' + h^\bullet \quad (1.13)$$

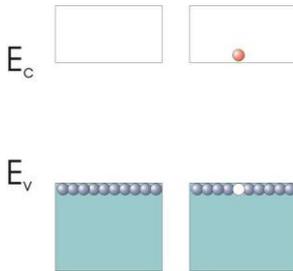


Figure 2-5. Schematic representation of the valence and conduction band of a semiconductor, and the intrinsic ionisation.

If we consider this a chemical equilibrium, the equilibrium constant can be expressed as

$$K'_g = [e'] [h^\bullet] = np = K'_{g,0} \exp\left(\frac{-E_g}{RT}\right) \quad (1.14)$$

where we by tradition use the notation n and p for the concentrations of electrons and holes, respectively. In this equilibrium we do not operate with place fraction and entropies because the electrons normally do not follow statistical thermodynamics. (The equilibrium constant does not relate to standard conditions for all defects – notably the electronic defects – and we thus here denote it with prime " ' ".) The energy E_g , that corresponds to a Gibbs energy change in a normal chemical reaction, is the *band gap*.

Foreign atoms or native point defects make local energy levels in the band gap. A defect which contains an easily ionised electron is a *donor* and is placed high in the band gap. A phosphorus atom in silicon, P_{Si} , has 5 valence electrons, but donates one to

the crystal in order to fit better into electronic structure of the Si host atoms with four valence electrons:



Phosphorus is thus a donor dopant in silicon and makes it an n-type conductor.

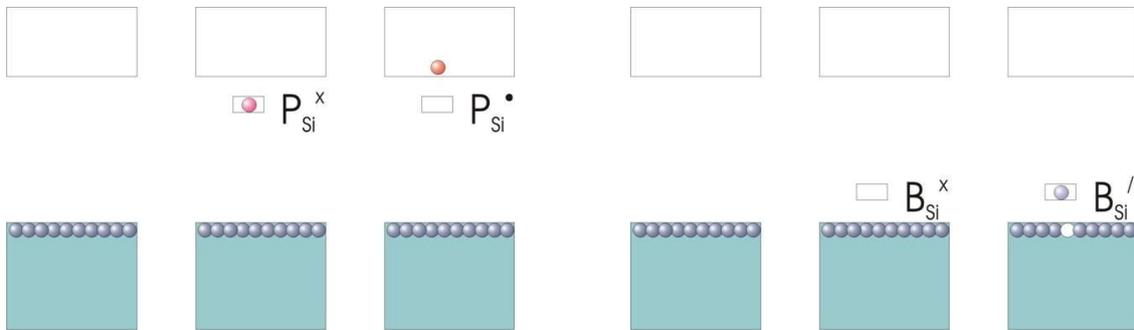


Figure 2-6. Band gap of Si, showing schematically P-doping (left) and B-doping (right).

A defect that easily accepts an extra electron from the crystal (ending up low in the band gap) is called an *acceptor*. Boron has only three valence electrons and readily takes up an extra in order to dissolve in silicone, making boron-doped silicon a p-type conductor.



Intrinsic defect disorder in ionic compounds

As a first example of an ionic material, let us use nickel oxide, NiO. Here, a metal ion vacancy will be denoted $v_{Ni}^{//}$, while an interstitial nickel ion is denoted $Ni_i^{\bullet\bullet}$. An oxide ion vacancy is denoted $v_o^{\bullet\bullet}$. Heating of an ionic compound will create disorder in the form of charge compensating defect pairs. In the case of NiO these may be Frenkel pairs (vacancies and interstitials) on the cation sublattice;



or Schottky pairs (vacancies of both cations and anions):



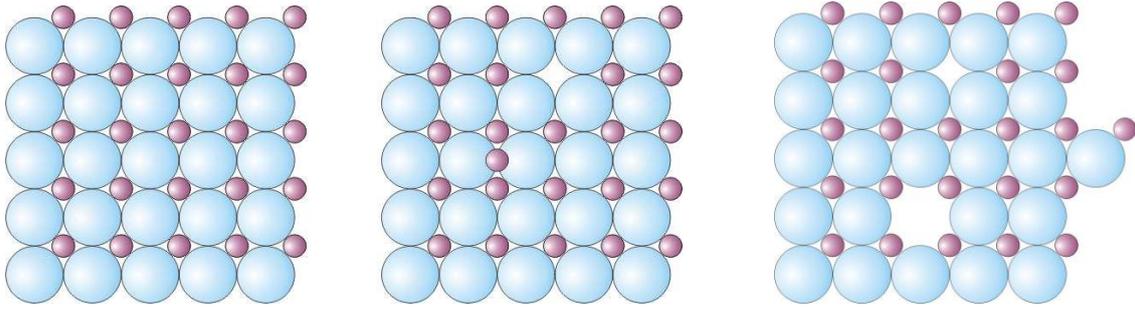


Figure 2-7. Left: Schematic perfect MO structure. Middle: Frenkel defect pair. Right: Schottky defect pair.

We have in both cases formed two defects and maintained electroneutrality, conserved mass and maintained the ratio between the two types of positions. We can in the latter reaction eliminate the effectively neutral species on both sides of the equation and instead write

$$0 = v_{Ni}'' + v_O^{\bullet\bullet} \quad K_S = X_{v_{Ni}''} X_{v_O^{\bullet\bullet}} \quad \text{or} \quad K_S' = [v_{Ni}''][v_O^{\bullet\bullet}] \quad (1.19)$$

The equilibrium constant K_S is written using site fractions, but is commonly replaced by constants where concentrations are used.

Non-stoichiometry in ionic compounds

The reactions we have considered do not change the ratio between cations and anions, and the oxide thus remains *stoichiometric*. Under oxidising conditions (high oxygen partial pressures) the oxide has a tendency to increase the average valence of nickel and increase the oxygen content, which might be thought of as:



But the structure is close-packed and does not easily accommodate oxygen interstitials. Instead it prefers to remove cations and creating extra lattice sites:



The defect chemical reaction for this and its equilibrium constant are written

$$\frac{1}{2} O_2(g) = v_{Ni}'' + O_O^x + 2h^{\bullet} \quad K_{ox}' = [v_{Ni}''][O_O^x] p^2 p_{O_2}^{-1/2} \quad (1.22)$$

At high oxygen partial pressures the oxide gets a deficiency of metal, it becomes non-stoichiometric, and it becomes a p-type electronic conductor. The oxide's ability to take up extra oxygen or make metal deficiency reflects its tendency of stability of more positive formal oxidation states (Ni^{3+} and/or O^-) than the stoichiometric oxide has (Ni^{2+} and O^{2-}).

ZrO_2 is an oxide that has a tendency to become reduced and oxygen deficient at low oxygen activities, thus being represented as ZrO_{2-y} :

$$O_O^x = v_O^{\bullet\bullet} + 2e' + \frac{1}{2} O_2(g) \quad K_{red}' = \frac{[v_O^{\bullet\bullet}]^2 p_{O_2}^{1/2}}{[O_O^x]} \quad (1.23)$$

We may use this latter reaction to illustrate that point defects such as the cation vacancies in $Ni_{1-x}O$ and oxygen vacancies in ZrO_{2-y} are in fact acceptors and donors.

Figure 2-8 shows how an oxygen vacancy can be seen first to be formed with the two electrons left localised at the vacancy. They are then placed at high donor levels in the band gap and are easily ionised in two steps until all electrons are delocalised in the conduction band according to

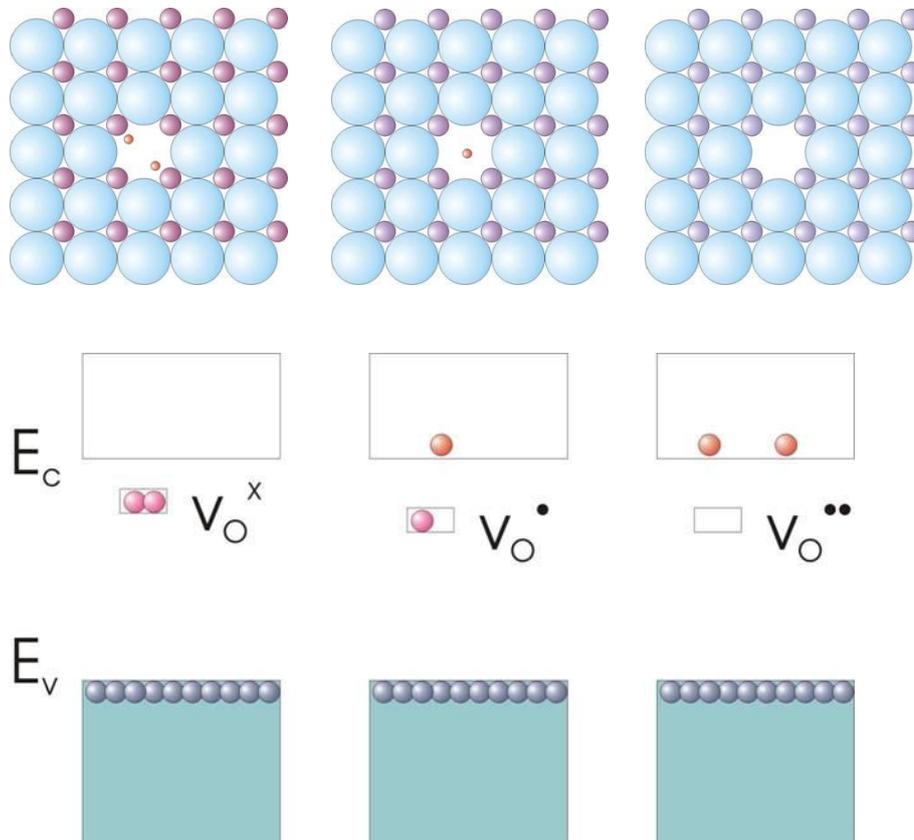


Figure 2-8. Schematic representation of the ionization of oxygen vacancy donors in two steps to the fully ionized defect, in which small spheres in the top figures represent electrons.

Doping of ionic compounds

We may affect the concentration of native defects by adding aliovalent dopants. Electron-poor dopants act as electron acceptors, and the negative charge thus obtained is charge compensated by increasing the concentration of positive defects. Donors correspondingly increase the concentration of negative defects.

Non-stoichiometric nickel oxide $Ni_{1-x}O$ as discussed above can be acceptor-doped with lithium: Li^+ dissolves on Ni^{2+} sites to form Li_{Ni}^{\prime} . This is compensated by an increase in the major positive defect – electron holes – and in this way Li-doped NiO becomes a good p-type electronic conductor that can be used as electrode on the air-side (cathode) of certain types of fuel cells.

In zirconia ZrO_{2-y} the acceptor dopant is typically yttrium, Y^{3+} , or some other rare earth, substituting the Zr^{4+} . In this case, the concentration of oxygen vacancies is enhanced while the concentration of electrons is suppressed, such that the material becomes an oxide ion conductor – a solid state electrolyte.

Defect associates and clusters

Defects have a tendency of association to each other. This may be due to electrostatic attraction between defects of opposite charge, e.g. defect-dopant pairs. But it may also be due to reduction of total elastic strain and comprise defects of the same charge. In the latter case defects – e.g. oxygen vacancies – order in lines or planes and form new structure polymorphs where the former defects are no longer defects but parts of the new structure. Formation of defect associates and ordered structures involve gain in enthalpy, but loss of entropy. It is thus typical of low temperatures, while dissociated separate defects are typical of high temperatures. An important consequence of defect association is suppression of mobility.

Of particular importance for solid electrolytes is the association between the mobile charge carrying defect and the dopant added for enhancing the concentration of that defect. In rare-earth (RE) doped MO_2 (ZrO_2 , CeO_2) electrolytes the oxygen vacancies are associated with the dopants (in nearest or next-nearest neighbour position) according to



whereby the associated vacancies are immobilised. The ionic conductivity increases with dopant content, but eventually goes through a maximum and decreases as the free oxygen vacancies are effectively trapped.

Electroneutrality and defect structure

The identities and concentrations of all defects are called the defect structure (even if it has no resemblance with the periodic crystal structure). In order to find the concentrations we use approaches equivalent to those used in aqueous solutions. This comprises expressions for the equilibrium constant and the electroneutrality, and in some cases mass balances. In crystalline compounds we may also employ site balances.

One usually applies simplifications in order to express analytical solutions to a limiting case of a smallest number of defects. This is analogue to simplified situations such as "weak acid", "pure ampholyte", "buffer", etc in aqueous acid-base-chemistry.

The full electroneutrality for NiO, with all defects we have mentioned above, would be

$$2[Ni_i^{\bullet\bullet}] + p = 2[v_{Ni}^{\prime\prime}] + [Li'_{Ni}] + n \quad (1.26)$$

In order to analyse how the concentrations of defects vary, we may for instance first assume that the material is undoped and that the partial pressure of oxygen is high so that electron holes and nickel vacancies are the dominating defects, and the electroneutrality can be approximated to

$$p = 2[v_{Ni}^{\prime\prime}] \gg 2[Ni_i^{\bullet\bullet}], [Li'_{Ni}], n \quad (1.27)$$

This limits the problem to two unknowns, and we only need two equations; the electroneutrality (Eq. 1.27) and the equilibrium constant K'_{ox} connecting the two defects (Eq. 1.22):

$$K'_{ox} = [v''_{Ni}] [O^x] p^2 p_{O_2}^{-1/2} = 4[v''_{Ni}]^3 [O^x] p_{O_2}^{-1/2} \quad (1.28)$$

We solve with respect to $[v''_{Ni}]$ and find that

$$[v''_{Ni}] = (\frac{1}{4} K'_{ox})^{1/3} [O^x]^{-1/3} p_{O_2}^{1/6} \quad (1.29)$$

Thus, the concentration of nickel vacancies $[v''_{Ni}]$ increases with the oxygen activity; it is proportional to $p_{O_2}^{1/6}$. The same thus goes for the nonstoichiometry x in $Ni_{1-x}O$, the concentration p of electron holes, and the p-type electronic conductivity.

As long as the simplified electroneutrality condition applies, we may find how minority defect vary by inserting the expression for the dominating defect, here Eq. (1.29), into appropriate equilibria linking it to the minority defect.

Transport

Defect diffusion

Point defects enable diffusion, most commonly via the vacancy mechanism or the interstitial mechanism, see Figure 2-9.

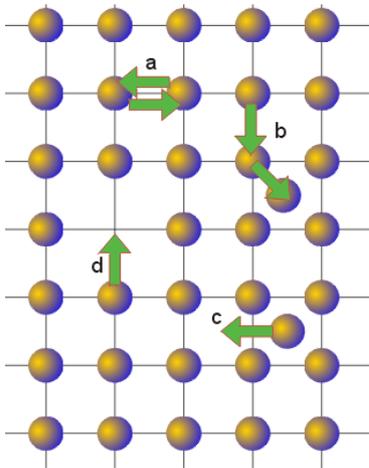


Figure 2-9. Diffusion mechanisms: Exchange (a), interstitialcy (b), interstitial (c), vacancy (d). From Shriver and Atkins: Inorganic Chemistry, 3rd ed.

Even in the absence of a driving force for transport there will be random jumps whenever there are defects that allow it, caused by the thermal energy ($=kT$). This is termed *random diffusion* or *self diffusion*. The diffusion coefficient D_r is a kind of measure of the extension of movement of the atoms in the crystal. The diffusion coefficient of an atom species is proportional to the concentration of enabling defects (vacancies or interstitials). It is furthermore proportional to the vibrating frequency of the atom and to the probability that a vibration will have sufficient thermal energy to overcome the activation energy barrier into the new position. This probability is proportional to $\exp(-Q_a/kT)$, where Q_a is the activation energy (barrier) for the jump. There are thus in principle two temperature dependent terms entering the self diffusion

coefficient; the enthalpy involved in the formation of defects and the activation energy for jumps. In general, therefore, D_r is an exponential function of temperature:

$$D_r = D_r^0 e^{-Q_D/RT} \quad (1.30)$$

where Q_D is the sum of the activation energy Q_a and an enthalpy for defect formation. In doped materials the latter may be zero because the defect concentration is fixed by the concentration of dopants. In addition we have seen that the defect concentrations may depend on doping level as such and for instance on p_{O_2} , entering in the pre-exponential factor D_r^0 .

In self diffusion the defects (and thus atoms) move far, but randomly, see Figure 2-10. It may be shown that for a cubic isotropic structure the total travelled distance is

$$s_{r,total} = \frac{6D_r t}{s} \quad (1.31)$$

where t is the time and s is the distance of each jump. An oxygen vacancy in an oxide may at high temperature have a diffusion coefficient of typically $D_r = 10^{-6} \text{ cm}^2/\text{s}$. If the jump distance s is 2.8 \AA , the vacancy will in one hour (3600 seconds) travel ca. 8 000 m (8 km) inside the crystal! It travels in other words far, but gets essentially nowhere because of the randomness in the motion. On average the radial distance from the starting point can be shown to be

$$r_{r,radial} = \sqrt{6D_r t} \quad (1.32)$$

In the example above this amounts to only 0.15 mm. If we observe how far the vacancy gets in only one predetermined direction x the distance is even shorter:

$$r_{r,x} = \sqrt{2D_r t} \quad (1.33)$$

In the example above this reduces to 0.085 mm. (Remember that the direction of this displacement is random such that the most probable place for the vacancy after an hour is still the point it started from!)

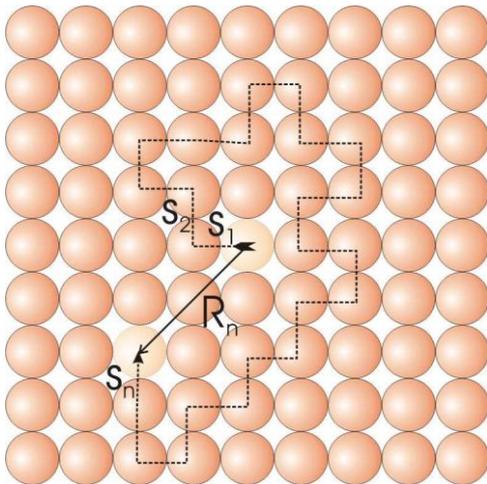


Figure 2-10. Schematic illustration of random diffusion via e.g. a vacancy mechanism. Individual jump distances s_1, s_2, \dots, s_n all sum up to a large total travelled distance ns . However, the displacement R_n is much shorter.

Imagine a structure where you have mobile vacancies diffusing randomly. Now follow one vacancy; it jumps all the time because there is (almost) always a neighbouring atom to jump to when it wants. Next choose instead an atom to follow: It rests motionless most of the time; it cannot jump except when a vacancy comes by. The diffusivity of the defect – here vacancies – is much higher than the diffusivity of the atoms. The ratio is given by the ratio of the concentrations of atoms and defects:

$$\frac{D_{r,defect}}{D_{r,atom}} = \frac{[atom]}{[defect]} \quad \text{or} \quad D_{r,defect}[defect] = D_{r,atom}[atom] \quad (1.34)$$

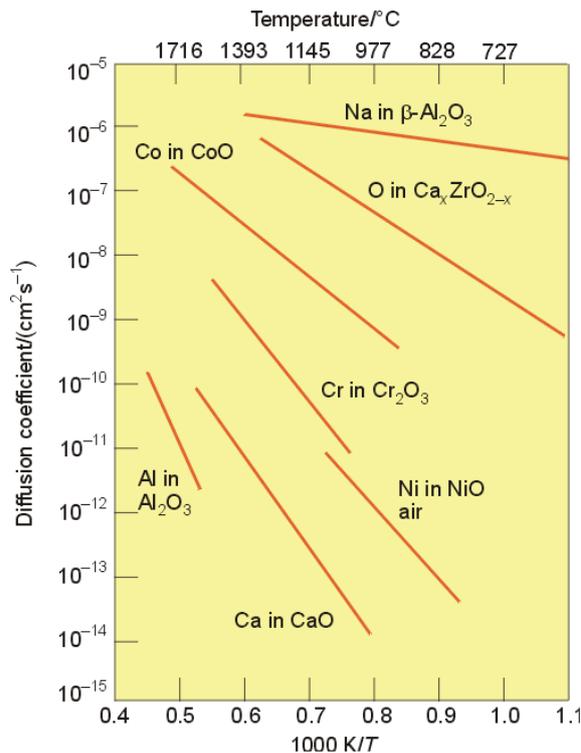


Figure 2-11. Arrhenius plot of the self diffusion in selected oxides. Note the large span in values, reflecting the difference in activation energies. From Shriver and Atkins: Inorganic Chemistry, 3rd ed.

Transport in a force field; flux and current; mobility and conductivity

In self diffusion as we have described it above the diffusing species (defects, atoms, ions, electrons) have no net displacement. If, on the other hand, they feel a force F from a field they will move by a net drift velocity v :

$$\vec{v} = B\vec{F} \quad (1.35)$$

The proportionality coefficient B is called *mechanical mobility* or just *mobility*. If the force acting on the diffusing particles is small compared to the thermal energy the net number of jumps in the direction of the force is small compared to the total number of random jumps. This is the normal case in volume diffusion since the forces are acting over considerable distances so that the field strength becomes modest. In this case the mobility is constant (independent of the force); we have a *linear* transport process and transport coefficient, and it can then be related to the random self diffusion coefficient via the *Nernst-Einstein relation*:

$$D_r = kTB \quad (1.36)$$

The relation states that random self diffusivity is equal to thermal energy multiplied with mechanical mobility.

The *flux density* (number of particles passing unit area per second) of the diffusing species equals the drift velocity times the volume concentration c , and together with the Nernst-Einstein relation we obtain:

$$\vec{j} = c\vec{v} = cB\vec{F} = \frac{cD_r}{kT}\vec{F} \quad (1.37)$$

The *force* may stem from gradients in *chemical potential*, μ , for the species in question. If the species is charged (with z elementary charges e) we also get a force from an electrical field E – i.e. a gradient in the electrical potential ϕ . In one dimension we obtain

$$F = -\left(\frac{d\mu}{dx} + ze\frac{d\phi}{dx}\right) = -\left(\frac{d\mu}{dx} + zeE\right) = -\frac{d\eta}{dx} \quad (1.38)$$

Here η represents the combination of chemical and electrical potential and is called the *electrochemical potential*. The minus sign in front of the expressions arise from forces acting *downhill* in potential gradients.

We have described mechanical mobility B and self diffusivity D_r as two measures of self diffusion and which can give us the net velocity and flux density of the species in force field gradients. For charged species it is furthermore useful to introduce also a *charge mobility*, u :

$$u = zeB \quad (1.39)$$

The *current density* i for a charged species equals the flux density times the charge. If the driving force for this current is only electrical – as in a measurement of electrical conductivity – we obtain from the equations above:

$$i = zej = cuF = zecuE \quad (1.40)$$

The product of charge, concentration, and charge mobility is called electrical conductivity:

$$\sigma = zecu \quad (1.41)$$

and we then obtain

$$i = \sigma E \quad (1.42)$$

This is a version of Ohm's law. It represents an example of macroscopic transport (flux of charged particles, i.e. electrical current) as a result of the particles' conductivity (charge, mobility, concentration) and a driving force (the electrical field). We can via the above set of equations track the conductivity and its variations back to the concentration and self diffusion of defects. More general, the equations we have used provide the basis for derivation of current, voltage, and mass transport in materials in batteries, fuel cells, membranes, etc.

Many situations can involve transport of more than one species or of more than one type of defect for one and the same atomic species. All these contribute to flux and current and one must sum as necessary in order to obtain the total conductivity or total current density. The *transport number* or *transference number* describes the fraction of

an electrical current that is transported by a particular species. It can normally be related to the ratio of the conductivity of a particular charge carrier s to the total conductivity:

$$t_s = \frac{\sigma_s}{\sigma_{total}} \quad (1.43)$$

We must also remember that real components and materials are not always homogeneous, but may contain several *parallel* transport paths, in bulk, along dislocations and grain boundaries, along pore walls, and outer surfaces. Likewise, transport may be restricted by several *serial* elements: through bulk, over grain and over electrode interfaces and surfaces.

Chemical diffusion, Fick's 1. law

We shall briefly return to the chemical potential μ , which enter directly in the driving force for transport. The chemical potential can under assumptions of ideality be expressed as

$$\mu = \mu_0 + kT \ln c \quad (1.44)$$

such that, at constant temperature,

$$\frac{d\mu}{dx} = kT \frac{d \ln c}{dx} = kT \frac{1}{c} \frac{dc}{dx} \quad (1.45)$$

The chemical potential and its gradient are thus not directly related to the concentration and the concentration gradient of the species, but we *can* obtain the relationship by using the expression above and applying the appropriate mathematics. We can thus treat situations involving concentration gradients by help of coefficients derived from random self diffusion.

Often it is still required or useful to relate flux densities directly to concentration, without going via chemical potential. For this purpose, we utilise a phenomenological law, *Fick's 1. law*:

$$j = -\tilde{D} \frac{dc}{dx} \quad (1.46)$$

where the proportionality factor \tilde{D} is a so-called chemical diffusion coefficient. This is however in general a phenomenological coefficient and not connected to a particular defect diffusion mechanism. Only in particular cases, where the particles we consider are electrically neutral and non-interacting is $\tilde{D} = D_r$, otherwise is \tilde{D} a figure that can vary over orders of magnitude with the concentration and concentration gradients.

Mobility and conductivity of electrons and electron holes

Localised electronic valence defects diffuse by hopping between atoms with available valence states. The process is characterised by a considerable activation energy.

Delocalised electrons and holes, on the other hand, behave more like waves in the lattice – they have access to all or large areas of the conduction and valence bands. We

can split transport from more or less delocalised electronic defects into three main types:

At very low temperatures (below the critical temperature, T_c) the materials are *superconducting* – they have zero electrical resistance; migration of a superconducting electron takes place without friction. The mechanisms involved in various classes of superconductors are not all understood and in any case beyond the scope here. A common picture is nevertheless that electrons move pair-wise and mutually alleviates obstructions.

Above T_c the electrons still move relatively fast – but they collide with defects and faults and impurities in the lattice. At temperatures near ambient and above the lattice vibrations become severe enough that electrons start colliding with them. the mobility then decreases weakly with increasing temperature. This is often referred to as as "metallic" behaviour. The mobility u of conduction band electrons is proportional to the mean free path L_m between collisions and can be expressed

$$u_e = \frac{eL_m}{m_e v_F} \quad (1.47)$$

where m_e is the rest mass of the electron and v_F is the speed corresponding to the Fermi energy the electrons have.

In ionic materials electrons and holes – irrespective of temperature – have a tendency to be trapped in their own field; the structure is deformed around them. In order to diffuse further the defect must now drag this deformation with it. The electronic defect and the deformation is called a *polaron*. If the deformation is fairly shallow (flat) and extends beyond a unit cell, it is called a *large polaron*. If it is deeper and smaller, it is called a *small polaron*. The latter retards the mobility much more than the others and involves an activation energy to make the jump from trap to trap. The mobility then gets a mechanism, behaviour, and temperature dependency like for diffusion of ions and atoms.

Figure 2-12 shows schematic and typical conductivities vs temperature for classes of electronic conductors. For superconductors and metallic conductors the temperature dependencies reflect the transport mechanisms and their mobility. For semiconductors it is a combined effect of mobility and concentration of charge carrying defects and can vary over many orders of magnitude.

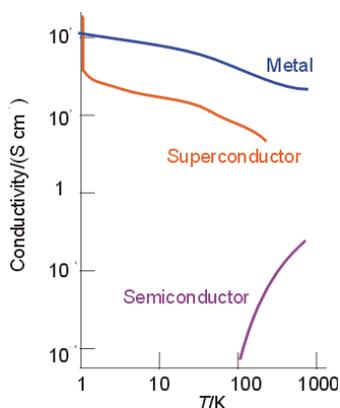


Figure 2-12. Based on how electronic conductivity varies with temperature, the conductors are divided into superconductors (infinitely high), metallic (decreases with increasing temperature) and semiconducting (low or moderate; usually increases with increasing temperature). From Shriver and Atkins: *Inorganic Chemistry*, 3rd ed.

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-glowler, 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 glowler was based on lower-valent 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). Lower-valent cations, like Ca^{2+} or Y^{3+} lead to charge compensation by oxygen vacancies. These vacancies stabilise the more symmetrical high temperature modifications so that 3 mol% Y_2O_3 may stabilise the tetragonal polymorph to room temperature (meta-stable). 8-10 mol% Y_2O_3 or more can stabilise the cubic structure. The latter type of materials is abbreviated YSZ (yttria stabilized zirconia).

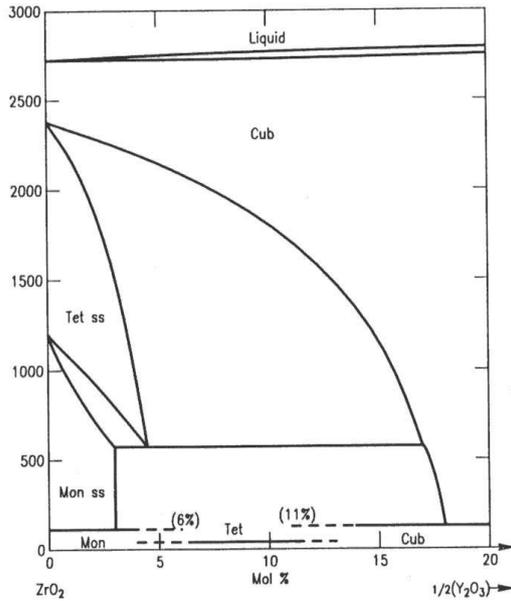


Figure 2-15. Sketch of temperature ($^{\circ}\text{C}$) vs composition (mol% $\text{YO}_{1.5}$) in the ZrO_2 -rich part of the ZrO_2 - $\text{YO}_{1.5}$ -phase diagram. ss=solid solution. Beneath a certain temperature equilibrium is in practice frozen out, and the lines near room temperature indicate the phase one gets. From Phase Diagrams for Ceramists (VI-6504), The American Ceramic Society.

The defect reaction of dissolution of Y_2O_3 in ZrO_2 can be written



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

$$2[v_{\text{O}}^{\bullet\bullet}] = [\text{Y}'_{\text{Zr}}] = \text{constant} \quad (1.49)$$

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

$$\sigma_{v_{\text{O}}^{\bullet\bullet}} = 2e[v_{\text{O}}^{\bullet\bullet}]u_{v_{\text{O}}^{\bullet\bullet}} = e[\text{Y}'_{\text{Zr}}]u_{0,v_{\text{O}}^{\bullet\bullet}}T^{-1} \exp\left(\frac{-\Delta H_{m,v_{\text{O}}^{\bullet\bullet}}}{RT}\right) \quad (1.50)$$

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 $100 \mu\text{m}$ 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 ($\text{Ni}+\text{YSZ}$ 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 superstructure formation set 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.

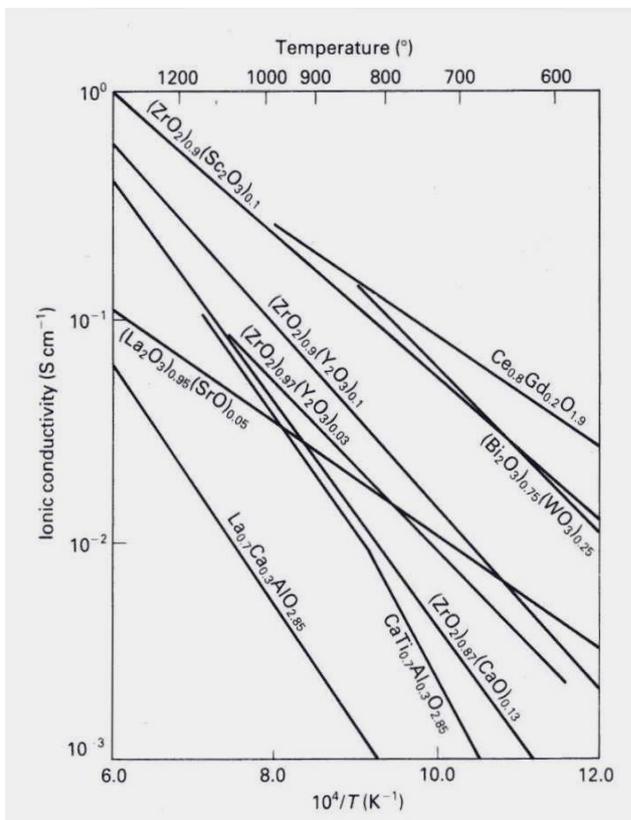
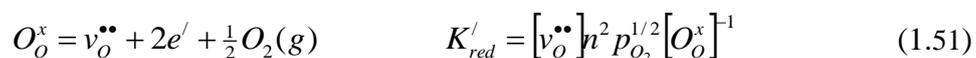


Figure 2-16. Conductivity of some oxide ion conductors. From P.G. Bruce: Solid State Electrochemistry.

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:



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

Bismuth oxide, Bi_2O_3 , has several structure polymorphs. One of these, $\delta\text{-Bi}_2\text{O}_3$ has a cubic fluorite structure similar to ZrO_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 $\delta\text{-Bi}_2\text{O}_3$ phase can be stabilised by certain dopants, such as WO_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_3 . A combination of Sr^{2+} and Mg^{2+} as acceptor-substituents for La^{3+} and Ga^{3+} was necessary to give mutually high solubility and a high concentration of oxygen vacancies. Sr+Mg-doped LaGaO_3 (LSGM) has higher conductivity than ZrO_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 $\text{La}_{10}\text{Ge}_6\text{O}_{27}$ and $\text{La}_2\text{Mo}_2\text{O}_9$, 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



This means that this endothermic 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 which is catalysed by Ni is coking:



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.



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 Sr^{2+} in SrTiO_3 with 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 cathodes

For cathodes, we can not 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, its melting point is close to the operating temperatures, and it has a considerable evaporation.

Thus, oxides is the common choice, and in particular LaMO_3 perovskites 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

$$0 = e' + h^\bullet \quad (1.55)$$

$$K'_g = [e'] [h^\bullet] = np = K'_{g,0} \exp\left(\frac{-E_g}{RT}\right) \quad (1.56)$$

is considerable. The states e' and h^\bullet can be seen as representing Mn^{4+} and Mn^{2+} , respectively, in LaMnO_3 which otherwise nominally contains Mn^{3+} .

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

$$[h^\bullet] = [\text{Sr}'_{\text{La}}] = \text{constant} \quad (1.57)$$

We note that this oxide chooses to compensate the acceptors with holes instead of oxygen vacancies (as in ZrO_2) – a result of the lower bandgap. The Sr-doped 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 $\text{La}_2\text{Zr}_2\text{O}_7$ 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 increased 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_2O_3 on the surface during oxidation. This provides oxidation protection while being electronically conductive. The problem is that Fe-Cr super-alloys with sufficient Cr content to form a protective Cr_2O_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 interconnects 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+} oxohydroxides from the interconnect's protective Cr_2O_3 layer to the cathode is detrimental – it settles as Cr_2O_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_2O_4 .

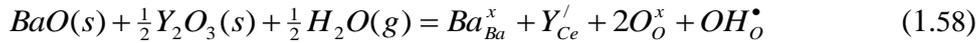
SOFCs with high temperature proton conducting electrolytes

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_o^\bullet . 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^\bullet . 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



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



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_2O_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. These should be mixed electron proton conductors or permeable to hydrogen or water vapour. This is well taken care of for the anode by a cermet of e.g. Ni and the electrolyte, aided by the solubility and transport of atomic hydrogen in Ni. For the cathode, no material with good mixed proton and electrons (electron holes) conduction is identified yet, and one must probably resort to ceramic-ceramic (cercer) composites of the electrolyte and some electronically conducting oxide, similar to the ones used for oxygen ion conducting SOFCs.

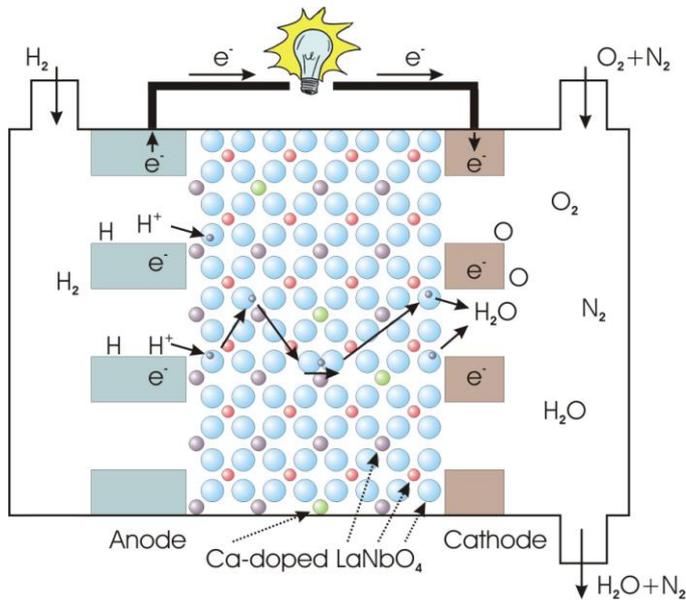


Figure 2-13. Proton conducting solid oxide fuel cell, based on Ca-doped LaNbO_4 . Note how H_2 fuel can be utilized fully as no water is produced to dilute it on the anode side.

SOFC geometries and assembly

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 $1400\text{ }^\circ\text{C}$, 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 temperature (typically $1400\text{ }^\circ\text{C}$). NiO is then reduced to Ni metal under the reducing conditions at the anode, at around $800\text{ }^\circ\text{C}$. 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.

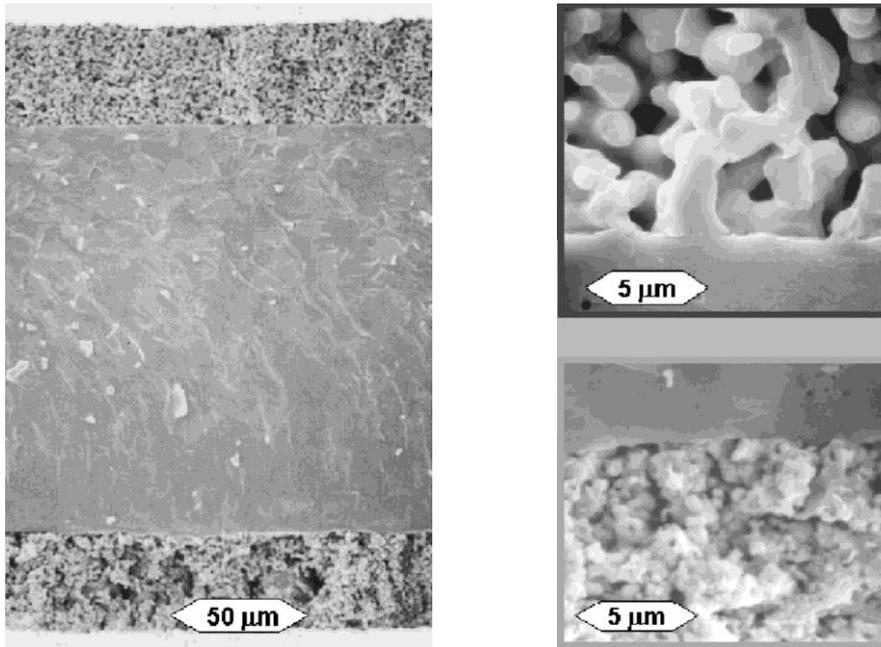


Figure 2-17. Cross section of SOFC single cell with self-supported gastight YSZ electrolyte in the middle, porous LaMnO_3 based cathode (top) and porous Ni/YSZ cermet anode (bottom). The magnifications to the right show the interfaces between electrolyte and electrodes, the critical place for mechanical strength and adhesion and electrochemical kinetics (E. Ivers-Tiffée *et al.*, Universität Karlsruhe).

As cathode is used LaMnO_3 and similar perovskites, doped with acceptors to give high electronic 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_2O_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 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 machineable 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),

where after 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, se figure.

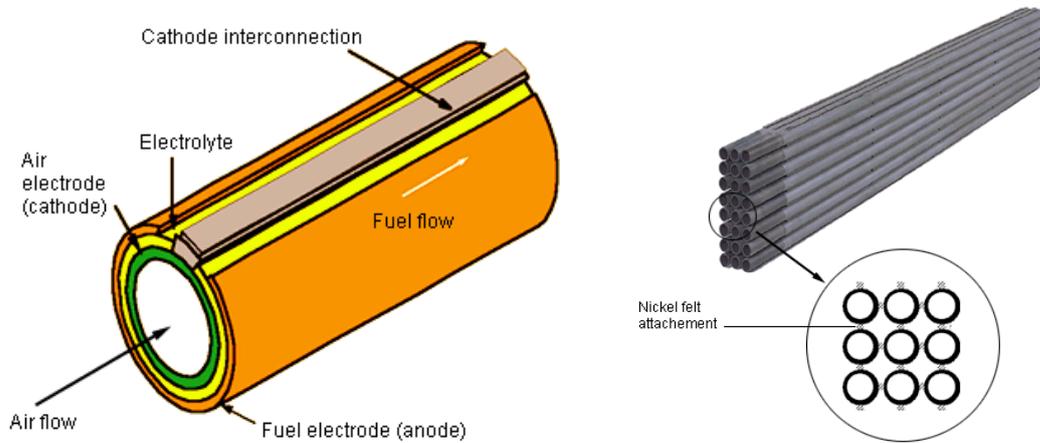


Figure 2-18. The construction of SOFC tube (left) and stacking (right) in series (upwards) and parallel (sideways). From Siemens-Westinghouse.

The figure below shows how a stack like this is operated. Notice how some used fuel is re-circulated 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.

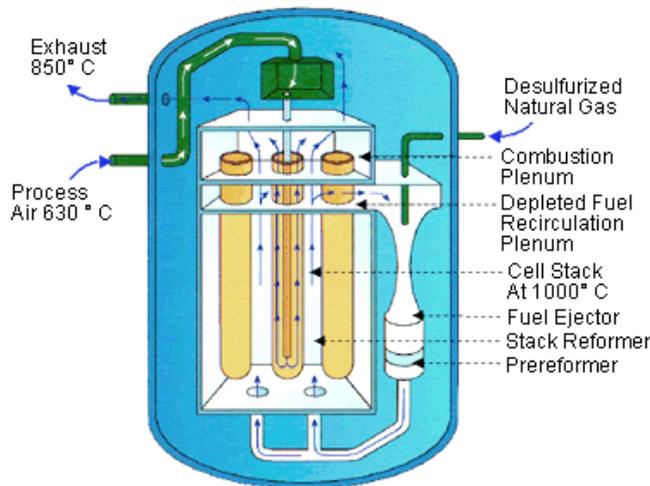


Figure 2-19. Schematic illustration of how a stack of tubular SOFC can be operated. From Siemens-Westinghouse.

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.

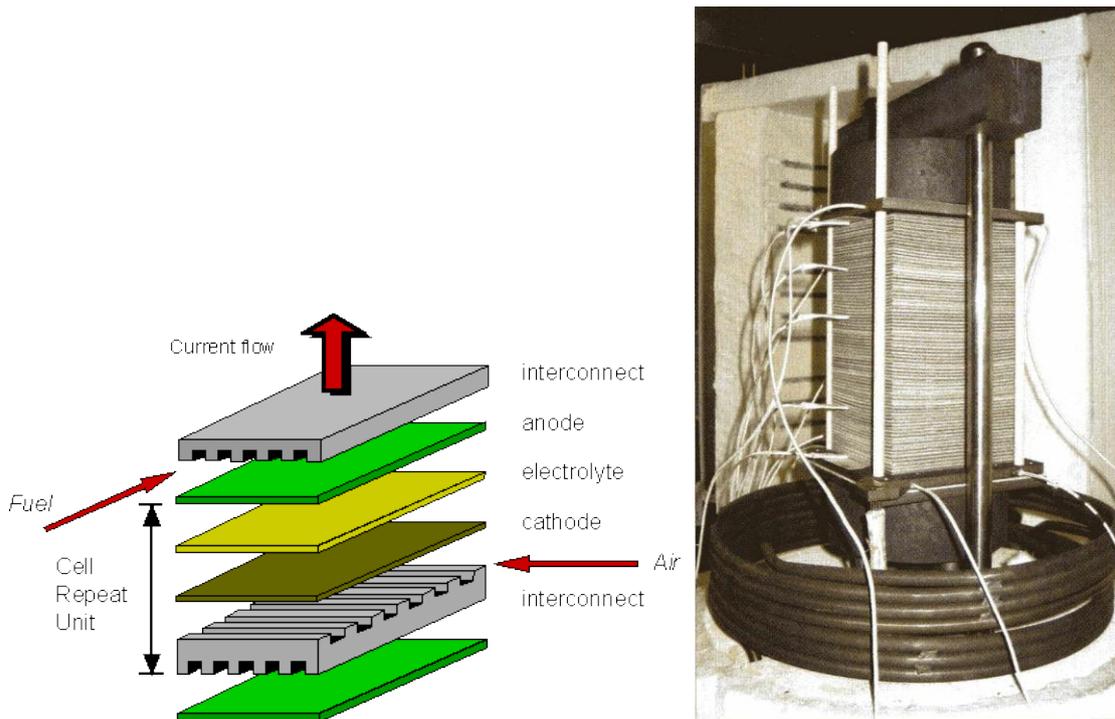


Figure 2-20. Left: Schematic principle of planar SOFC stack. Right: SOFC stack under mounting at Haldor Topsøe AS, Denmark. From S. Harris, *Fuel Cell Review*, 1[1] (2004) 31-32.

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 2-21. Fabrication of Rolls Royce SOFC stacks. From Rolls Royce.

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.

3. Lithium ion batteries

General features

Ternary batteries – rechargeable batteries or accumulators – contain, like all electrochemical energy conversion devices, three components: an electrolyte (ion conductor) and two electrodes (electron conductors).

In general, the negative electrode of batteries contains a relatively non-inert metal (Pb, Cd, Zn, Li) or hydrogen (H). During discharge this is oxidised to cations (Pb^{2+} , Cd^{2+} , Zn^{2+} , Li^+ , H^+) in the form of stable products (e.g. $\text{PbSO}_4(\text{s})$, $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, LiMn_2O_4 , NiOOH). The reaction is forced to go via ions in the electrolyte and electrons in the external circuit.

In a lithium ion battery, the negative electrode is lithium metal intercalated into a matrix like graphite that prevents it from explosion in contact with air in case of rupture of the battery. The electrolyte is a Li^+ ion conductor – usually a liquid contained in a gel or porous matrix. The positive electrode is a reducible oxide in which the Li^+ ions are intercalated. The figure below shows a battery with graphite (C) as one (left hand side) electrode. This can intercalate Li atoms. The other (right hand side) electrode is made of MnO_2 and can intercalate Li^+ ions to form spinel LiMn_2O_4 .

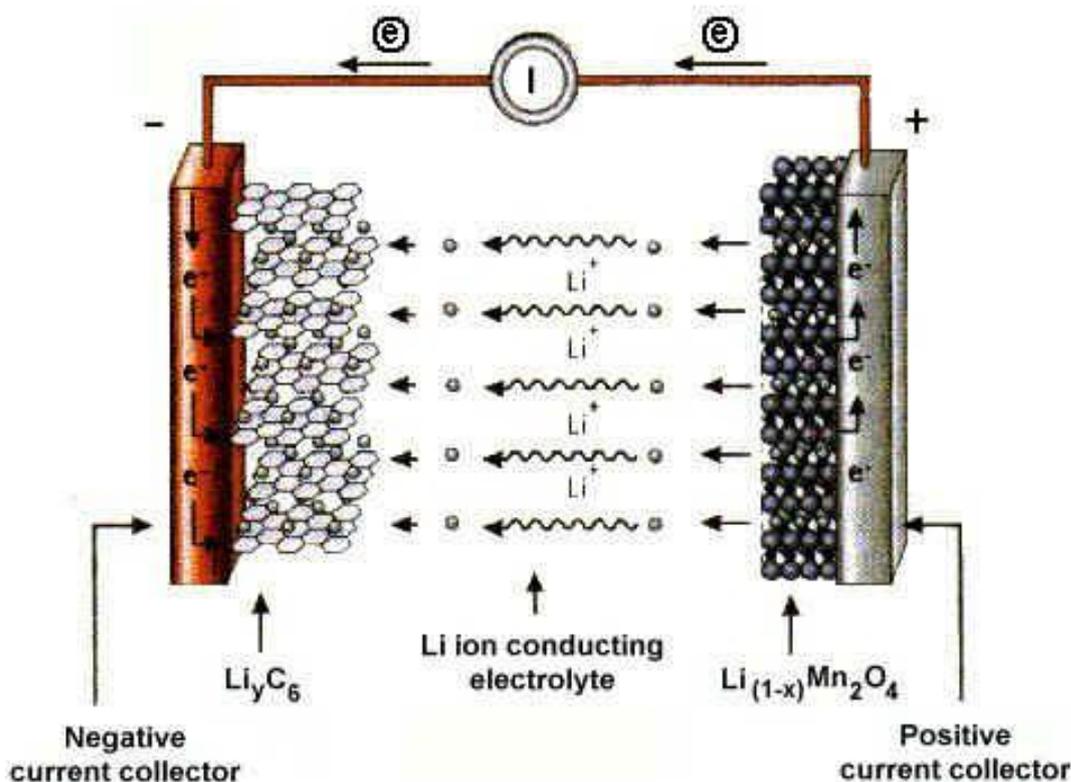


Figure 3-1. Example schematic of Li ion battery with graphite (C) and MnO_2 electrodes. The direction of the current is shown for the case of charging.

The two electrodes conduct electrons, but also store lithium in two forms – reduced Li^0 or oxidised Li^+ . The electrodes must therefore transport and hold these species: They are typically mixed electronic ionic conductors.

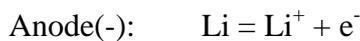
The graphite and Li electrode is negative during charging, as shown in the figure: A negative voltage is applied to the electrode and Li^+ ions are attracted to it; electrons are supplied to reduce Li^+ to form atomic Li. The MnO_2 electrode is positive during charging: It forces the Li^+ ions away and pulls the electrons left behind into the electrical circuit. In the process, Mn^{3+} is oxidised to Mn^{4+} . The chemical process of extracting Li^+ ions from the spinel and forcing them as Li atoms into the graphite is not spontaneous; it requires energy – here supplied by electrical energy. The electricity does work on the cell.

During discharge the reaction goes in the other – spontaneous – direction. Now the chemical energy is released and creates a voltage and drives a current. The cell does work on the load.

The two electrodes keep the sign of voltage from charging when they discharge; the graphite Li electrode is negative as it supplies electrons during oxidation of Li to Li^+ . And the MnO_2 electrode is positive; Li^+ ions arrive and get intercalated, and Mn^{4+} takes the electrons and are reduced. So – as said the voltage sign is the same, but the voltage during discharge is smaller than the voltage used during charging.

The negative electrode is an anode during discharge, and a cathode during charging. By tradition, we call it the anode, referring to the oxidation during discharge. Correspondingly, the positive electrode is called the cathode, referring to the reduction during discharge.

The electrochemical reactions in the Li ion battery above can during discharge be written:



The anode reaction has a half-cell potential of around 3 V. With additional voltage of the cathode reaction the total Li-ion cell typically gives 3.2 – 3.7 V, depending on the materials Li and Li^+ are intercalated into. During discharge, the voltage drops somewhat due to ohmic and kinetic losses, and because of changes in the electrodes (stoichiometry, structure, phase relationships) with changing content of Li and Li^+ in the anode and cathode, respectively. The voltage is used by the control circuitry to monitor the state of charge (SOC), see for example the figure blow.

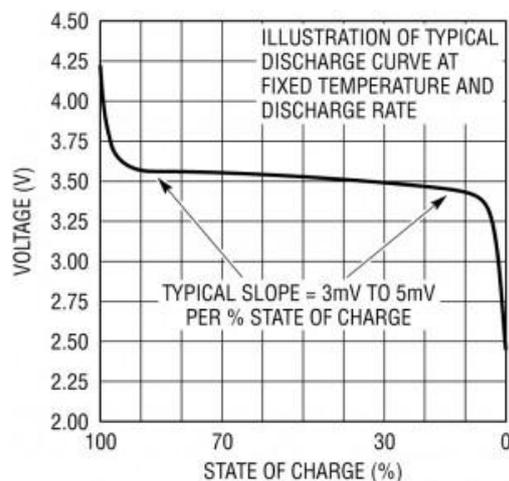
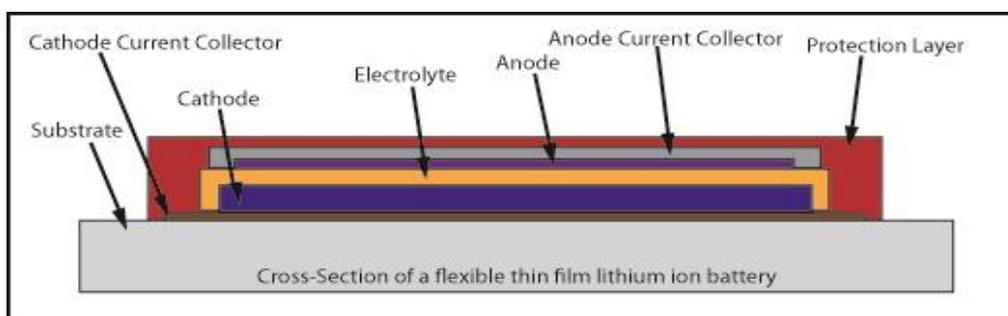


Figure 3-2. Typical discharge curve showing voltage vs state of charge (SOC). (From <http://johndayautomotiveelectronics.com>)

The electrolyte has to withstand voltages above 4 V, since higher voltages than the reversible potential are applied to charge the battery. This means that the electrolyte must be very redox-stable. Water as solvent is excluded, since it would split already well below half this voltage. Instead, one uses Li salts of very stable anions dissolved in polymers or ionic liquids. The electrolyte must be as thin as possible to reduce the ohmic resistance to ionic transport. On the other hand, it must be thick enough to keep the electrodes from contacting each other, which could cause a catastrophic short-circuit. Whiskers growing between the electrodes during charge-discharge cycles are one of the problems faced. Various strategies for reducing the effect of local short-circuits and overheating due to ohmic resistance are important parts of the development of high energy and high power Li ion batteries.

The amount of energy stored in the battery lies in the capacity of the anode to hold Li atoms and of the cathode to hold Li^+ ions. Essential factors are the capacity per weight and per volume of electrode materials, as well as the price of the materials involved.

Similar to other electrochemical devices, losses from kinetics (overpotentials) are unavoidable in batteries. The losses are proportional to the current drawn or applied during charging. Thus, the efficiency is high at low power and slow charging, while the loss and heat evolved are high with burst loads or rapid charging. In order to improve kinetics and reduce overpotentials, the number of contacts between electrolyte and electrode must be maximised. Furthermore, the diffusion lengths of atoms and ions in the electrode must be minimised. All this points towards the use of nanograined electrode materials, and this is indeed essential in the advances of batteries recently. Thin film batteries offer another way to increase interface areas and shorten diffusion lengths.



A major problem in rechargeable batteries is the volume change involved in the uptake of Li and Li^+ in the anode and cathode, respectively, during charge and discharge. This causes morphological changes in the electrode materials – typically coarsening of the nanograins – and loss of contacts to the current collectors and electrolyte. This reduces the kinetics (power) and useable volume (energy) of the battery for each charge-discharge cycle – especially deep ones. Advanced materials and interfaces combined with specialised charging procedures and control circuitry is part of the development of reliable high performance batteries with long lifetime.

Li ion batteries are today in widespread use in hand-held power-tools and portable electronic equipment, notably mobile phones and laptop computers, where their superior energy-to-weight and -volume ratios are essential. The same reason makes

them also mobilise the most advanced fully electrical cars, as well as a variety of hybrid and plug-in hybrid cars.



Figure 3-3. In 2013, Nissan Leaf (left) and Tesla S (right) are two of the most successful fully electrical cars, with driving ranges of, respectively, around 200 and 400 km. Middle picture shows the Nissan Leaf battery package.

Li-ion batteries have typically specific (gravimetric) energy densities of 150-250 W·h/kg (540-900 kJ/kg), volumetric energy densities of 250-620 W·h/l (900-1900 J/cm³), and specific power densities of 300-1500 W/kg.¹

More on chemistry and materials for Li ion batteries

Electrolytes

The original electrolytes for Li-ion batteries have been liquid, based on stable salts of Li⁺ dissolved in non-aqueous solvents. The better packing and reliable separation offered by a solid electrolyte brings the development of composite polymer Li-ion conductors. Truly solid Li⁺ ion conductors may offer the ultimate solution, but are difficult to realise in terms of all requirements (redox stability, mechanical stability, conductivity).

Lithium salts traditionally used comprise LiPF₆, LiBF₄, LiClO₄, and LiCF₃SO₃ (lithium triflate). They are dissolved in e.g. ethylene carbonate or dimethyl carbonate. Typical conductivities are 0.01 S/cm at room temperature, increasing somewhat by increasing temperature. The stability of organic solvents during charging is increased by its decomposition into a so-called solid electrolyte interphase (SEI) at the anode during the first charging. Many ionic liquids are under investigation for use in Li ion electrolytes with improved stability. Polymers like polyoxyethylene (POE) in a composite with the Li ion salt makes the electrolyte more solid (polymer Li-ion batteries).

Solid Li ion conductors comprise a range of glasses and crystalline compounds, like the layered perovskite-related Li_{3x}La_{0.67-x}TiO₃ where Li⁺ ions diffuse via vacancies on the partially filled A-site sublattice.

¹ Wikipedia 2013, based on references from 2010-2011.

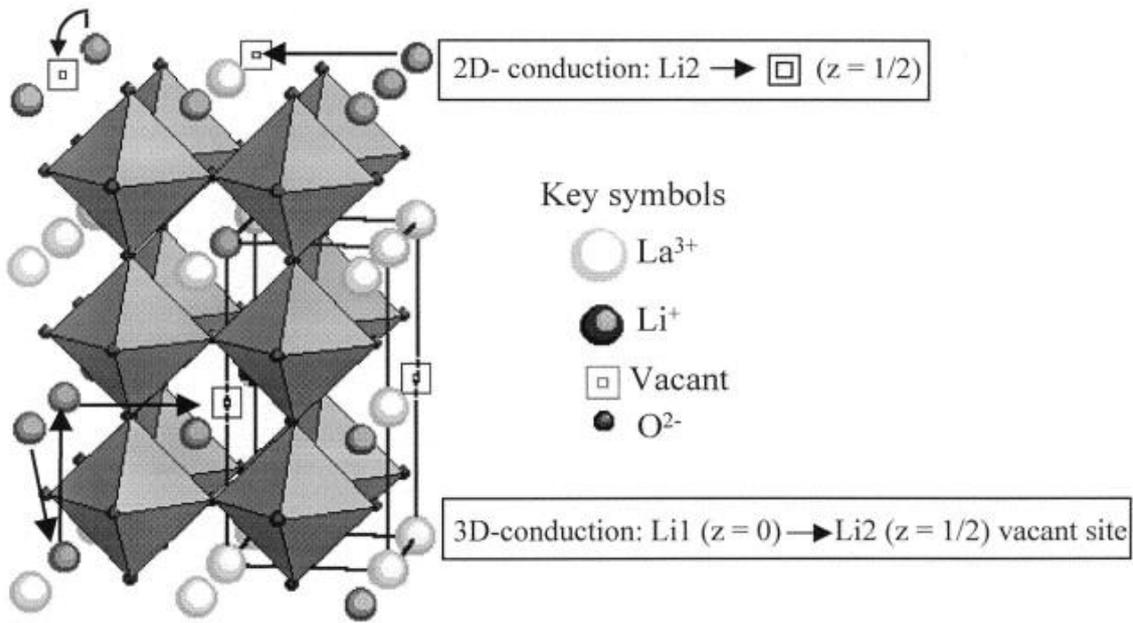


Figure 3-4. Conductivity pathways in $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ ²

As evident from the figure below, the conductivities at room temperature are considerably lower for this materials class than the 10^{-2} S/cm for the best liquid Li ion conductors.

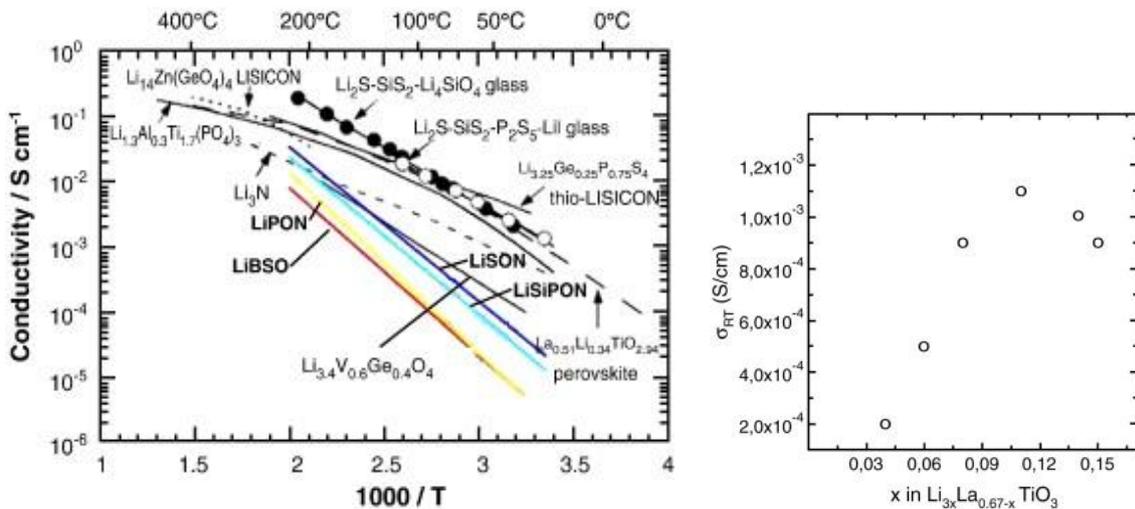


Figure 3-5. Left: Conductivity of some solid-state Li ion conductors vs $1/T$. Right: Conductivity of $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ vs x .³

Anodes

The very first Li-ion batteries had metallic Li anodes, but safety problems soon introduced carbon materials, notably graphite, for intercalation of the Li atoms. Graphite is still the most used anode material.

² A.I. Ruiz et al., *Solid State Ionics*, 112 (1998) 291.

³ Ph. Knauth, *Solid State Ionics*, 180 (2009) 911.

Other elements in the carbon group can also be used for intercalation of Li. Silicon anodes are thus under study and development. The volume expansion upon intercalation is substantial, but this is solved by using porous Si that has enough internal volume to take up the expansion internally. Recently there is interest also in tin as anode material.

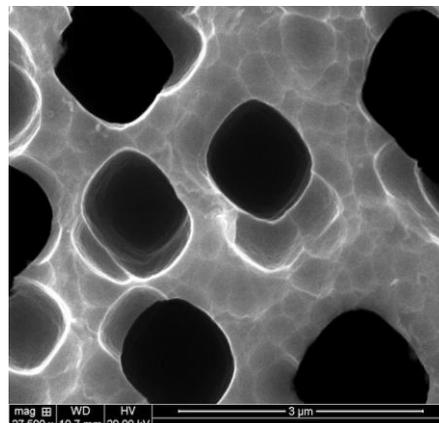
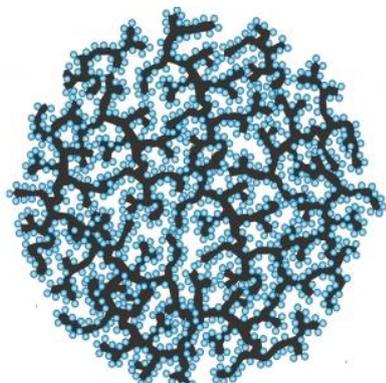


Figure 3-6. Left: Nanocomposite of Si backbone and C nanoparticles. Right: Porous Si structure.

Cathodes

The cathodes are generally a transition metal oxide that can have a variable content of Li^+ , compensated by a variable oxidation state of the transition metal: Some of these are spinels like LiMn_2O_4 , layered oxides like LiCoO_2 , or metal oxyacid (polyanion) salts such LiFePO_4 . The latter material has good structural stability during charge cycles and contains no rare or hazardous elements, contrary to the majority of other cathode materials.

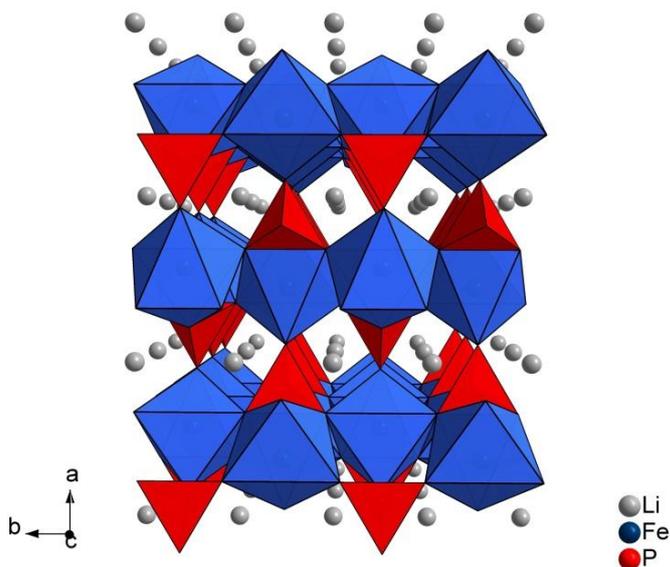


Figure 3-7. Left: LiFePO_4 . The FePO_4 olivine structure with FeO_6 octahedra and PO_4 tetrahedra remains intact while accommodating Li interstitially. Right: John B. Goodenough (1922 -) was central in inventing early 4 V Li ion batteries through use of LiCoO_2 cathodes and the more recent LiFePO_4 .

