

# 11. Materials for fuel cells and electrolyzers

Electrochemical energy conversion devices that we include in this chapter comprise fuel cells and electrolyzers. They convert chemical energy to electricity and vice versa. Other electrochemical energy conversion devices – 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.

## 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  $\text{H}_3\text{O}^+$ -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

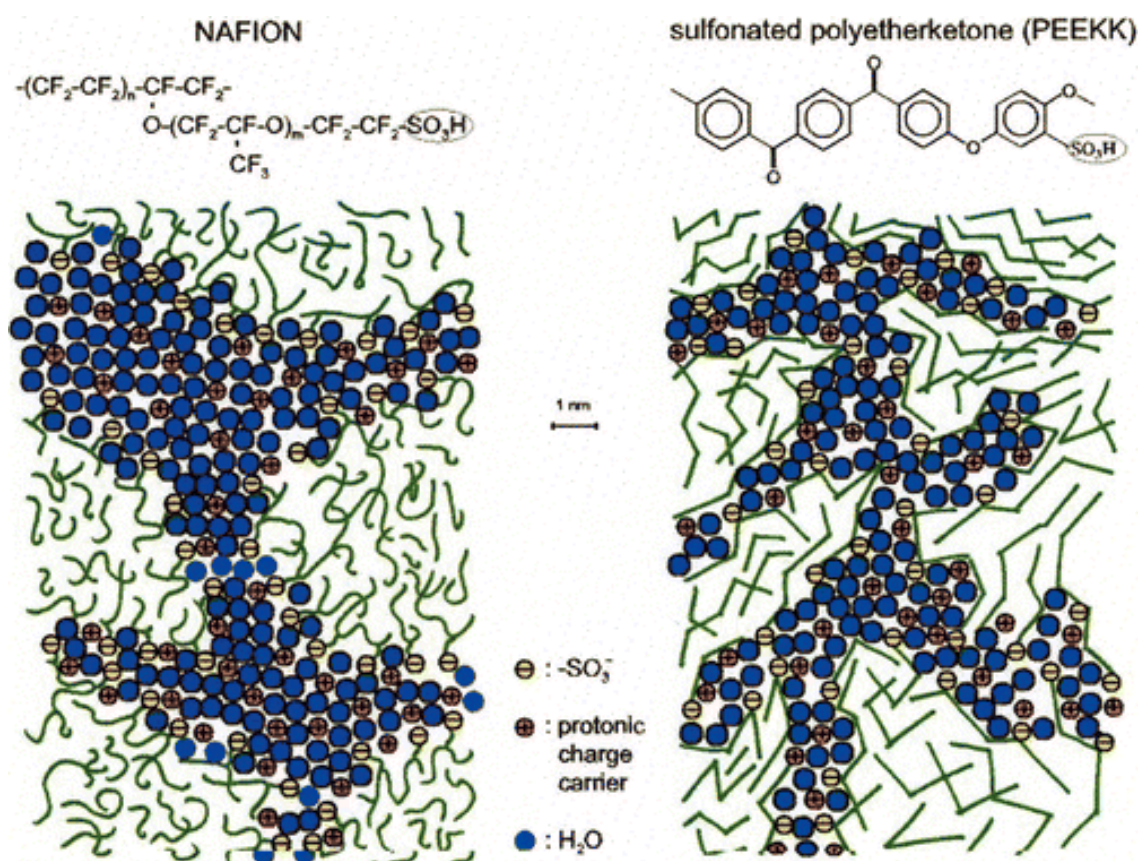
desired to avoid condensation of product water. We will treat this class of polymers separately later, but now concentrate on the standard – low temperature - types.

### *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.

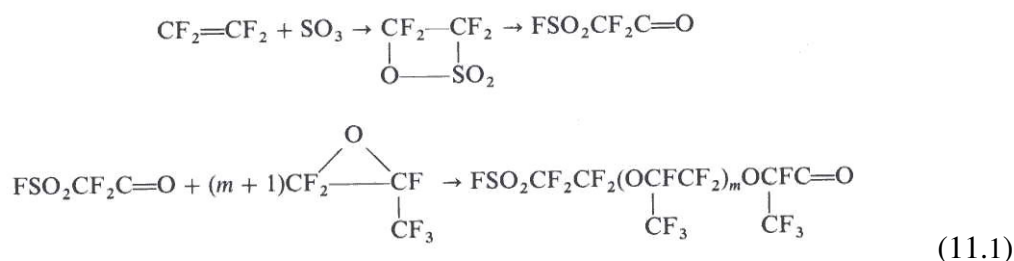
The ionomers reorganise to form polar regions, while the backbones form non-polar regions. In contact with water, the polymer swells as water is absorbed into and fills channels of hydrophilic – polar – character. The protons on the sulfonate groups are now released to the water to form mobile  $\text{H}_3\text{O}^+$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



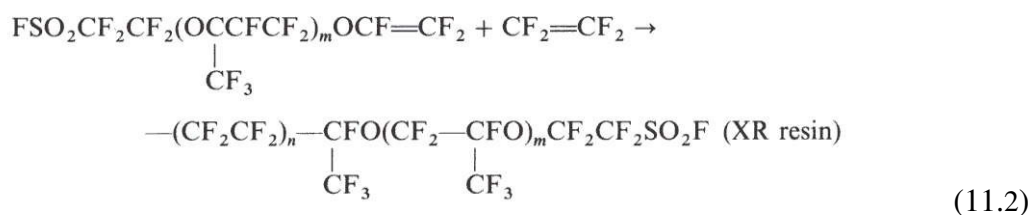
**Figure 11-1.** Schematic representation of the microstructure in water-containing (swelled) polymer electrolytes; Nafion® and sulfonated PEEK. From S.J. Paddison, *Ann. Rev. Mater. Res.*, 33 (2003) 289.

The standard proton conducting polymers can best be described as co-polymers of tetrafluoroethylene (TFE) and perfluorosulfonate (PFS) monomers. The latter are terminated as perfluorocarbon-sulfonic acid (PSA) ionomers. The most well-known of these materials is the Nafion® manufactured by DuPont, but there are several similar formulations provided by other manufacturers.

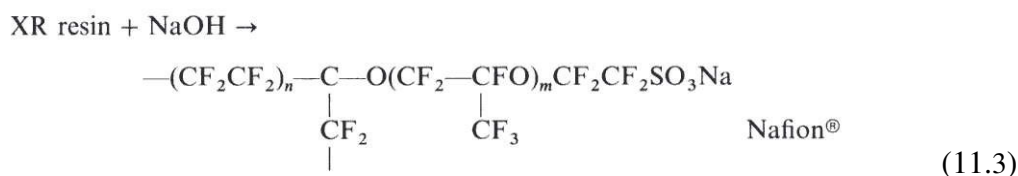
We will now look a little closer at the details of producing the Nafion® polymer electrolyte. One starting material is tetrafluoroethylene which is reacted with SO<sub>3</sub> dissolved in sulfuric acid. The product is polymerised with hexafluoropropylene-epoxide:



This addition polymer is heated with Na<sub>2</sub>CO<sub>3</sub> and then transforms into a polyvinyl ether. This is co-polymerised with more tetrafluoroethylene to a so-called XR-resin:



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



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

The polymer hydrates in two stages in contact with water. The first involves solvation of the ions, i.e. providing each -SO<sub>3</sub>H group with up to 5-6 water molecules. In the second step additional water is taken up to fill the hydrophilic channels and swelling the material, and we end up with a total of typically 14-15 water molecules per -SO<sub>3</sub>H group.

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

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

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

$$P_i = D_i \cdot c_i \quad (11.4)$$

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

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

$$D_{\text{H}_2} (\text{cm}^2/\text{s}) = 0.0041 \exp(-21.63(\text{kJ/mol})/RT) \quad (11.5)$$

$$D_{\text{O}_2} (\text{cm}^2/\text{s}) = 0.0031 \exp(-23.01(\text{kJ/mol})/RT). \quad (11.6)$$

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  $\text{H}_2$  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  $\text{O}_2$  we have

$$c_{\text{O}_2} (\text{mol} \cdot \text{cm}^{-3} \cdot \text{Pa}^{-1}) = 7.43 \cdot 10^{-12} \exp(5.54(\text{kJ/mol})/RT). \quad (11.7)$$

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 startups. The around 5 water molecules each proton drags require a water handling system. Moreover, the materials and cell operation do not tolerate overheating above ca. 100 °C, that would lead to dehydration and possibly irreversible mechanical failure and electrolyte deterioration.

### *Electrodes for PEFCs*

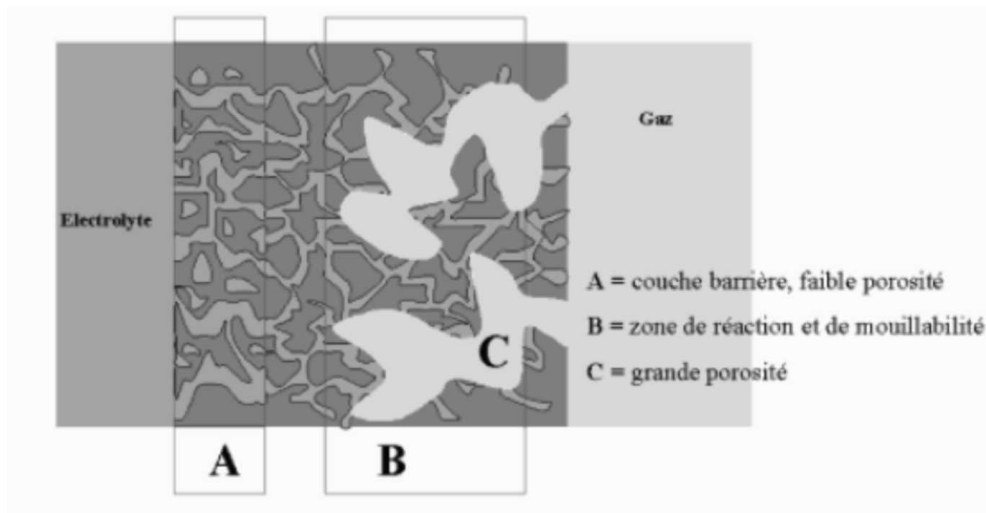
Today, standard electrode structures for PEFCs comprise two layers. The layer facing the electrolyte is a fine-structured composite electrode consisting of graphite and the electrolyte, giving many reaction sites for electrons, ions, and reactants dissolved in the electrolyte. Nanoscopic and finely distributed platinum catalyst particles are embedded in the composite. A number of alloying elements and other catalysts (e.g.,  $\text{RuO}_2$ ) 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 11-2.** 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.

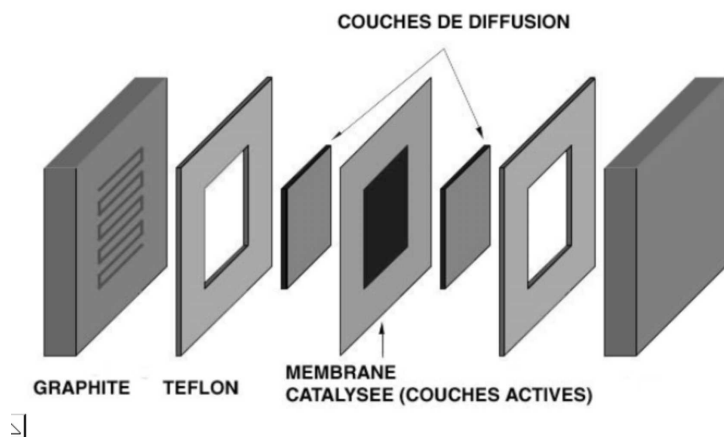
The low temperature of operation leads to poisoning of the Pt catalysts by CO(g) and other reactive species, like H<sub>2</sub>S: CO is absorbed preferentially on the catalyst surface and prevents other reactions. H<sub>2</sub>S leads to formation of the very stable platinum sulfide PtS. The fuel must for these reasons be pure hydrogen, with very low tolerances for CO and H<sub>2</sub>S.

#### *Interconnects and seals*

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

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

Other components include gas seals and electrical insulation. These can be made of, for instance, Teflon.

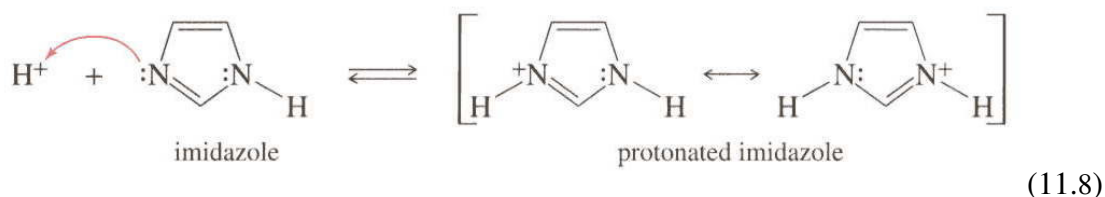


**Figure 11-3.** Components in a typical PEFC cell. The layer in the middle is the electrolyte membrane (PEM) with the two electrodes containing catalysts (MEA). The two layers on each side next to the MEA are the gas diffusion layers (porous conducting material, usually a graphite structure). Next follow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

### *High temperature polymer electrolytes*

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

A more radically different approach is to remove water entirely, and to introduce nitrogen as host and donor/acceptor for the protons. In particular, polymers containing imidazole is found a good candidate; imidazole is an organic ring compound with formula  $C_3N_2H_4$ . One nitrogen atom has a hydrogen bonded to it, and both nitrogen atoms have lone electron pairs. Imidazole can be protonated into an ion where the positive charge is delocalised between the two nitrogens:



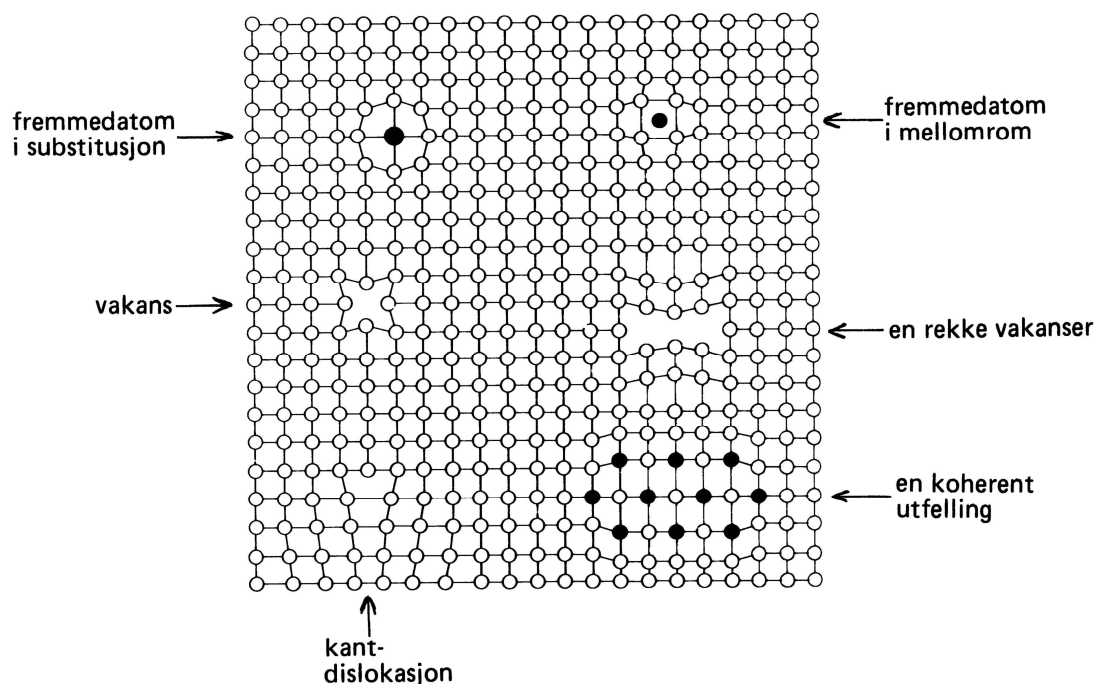
This allows uptake of one proton to the vacant nitrogen in imidazole, and that the hydrogen on the other nitrogen leaves as a proton. This allows imidazole to transfer protons from one donor to another if the geometrical arrangement is suitable. The imidazole molecules can be dissolved in a suitable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



## 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 11-4.** 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  $Ni_{Ni}^x$  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:

$$K_v = a_{v_{Ni}} = X_{v_{Ni}} = \exp\left(\frac{\Delta S_v}{R} - \frac{\Delta H_v}{RT}\right) \quad (11.10)$$

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:



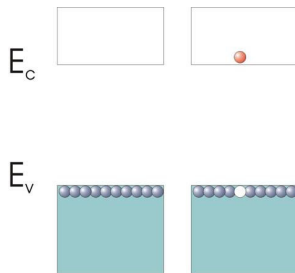
Control shows that both defect chemical reactions we have introduced here obey the criteria for defect chemical reactions equations stated above. (In a simple metal we can freely make or remove structural sites, because there is no ratio between different lattice positions to maintain.)

*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



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:



**Figure 11-5. 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

$$K'_g = [e'] [h^\bullet] = np = K'_{g,0} \exp\left(\frac{-E_g}{RT}\right) \quad (11.14)$$

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.

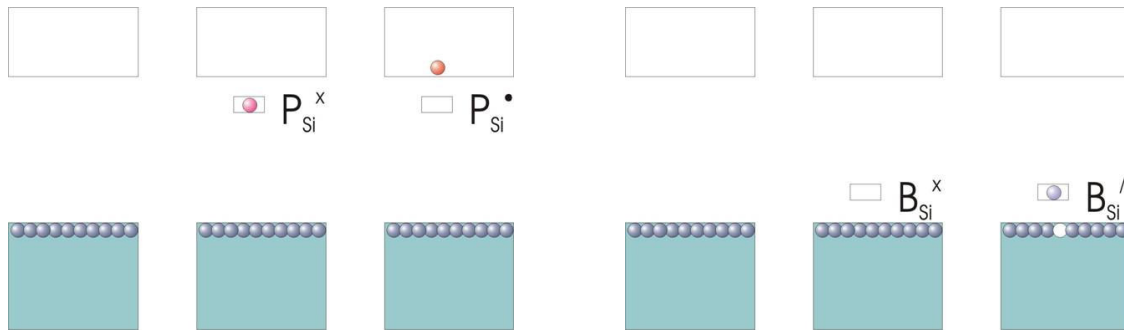


Figure 11-6. Band gap of Si, showing schematically P-doping (left) and B-doping (right).

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.



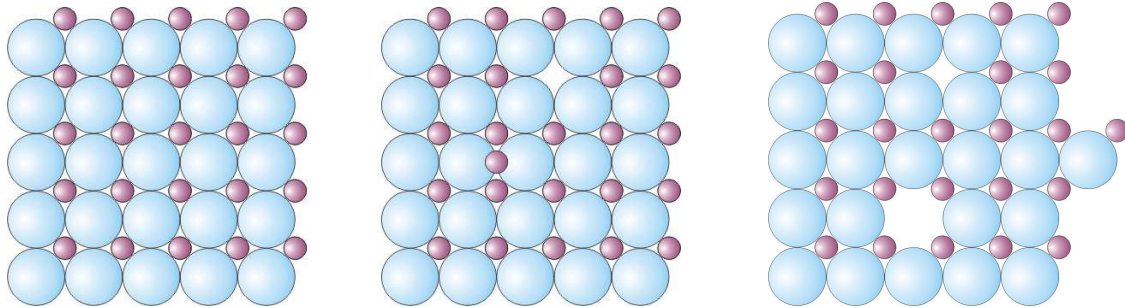
#### *Intrinsic defect disorder in ionic compounds*

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;

$$Ni_{Ni}^x = v_{Ni}'' + Ni_i^{\bullet\bullet} \quad (11.17)$$

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

$$Ni_{Ni}^x + O_O^x = v_{Ni}'' + v_O^{\bullet\bullet} + Ni_{Ni}^x + O_O^x \quad (11.18)$$



**Figure 11-7. 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

$$0 = v_{Ni}'' + v_O^{\bullet\bullet} \quad K_S = X_{v_{Ni}''} X_{v_O^{\bullet\bullet}} \quad \text{or} \quad K_S' = [v_{Ni}''][v_O^{\bullet\bullet}] \quad (11.19)$$

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

$$\frac{1}{2} O_2(g) = v_{Ni}'' + O_O^x + 2h^{\bullet} \quad K_{ox}' = [v_{Ni}''][O_O^x] p_{O_2}^{-1/2} \quad (11.22)$$

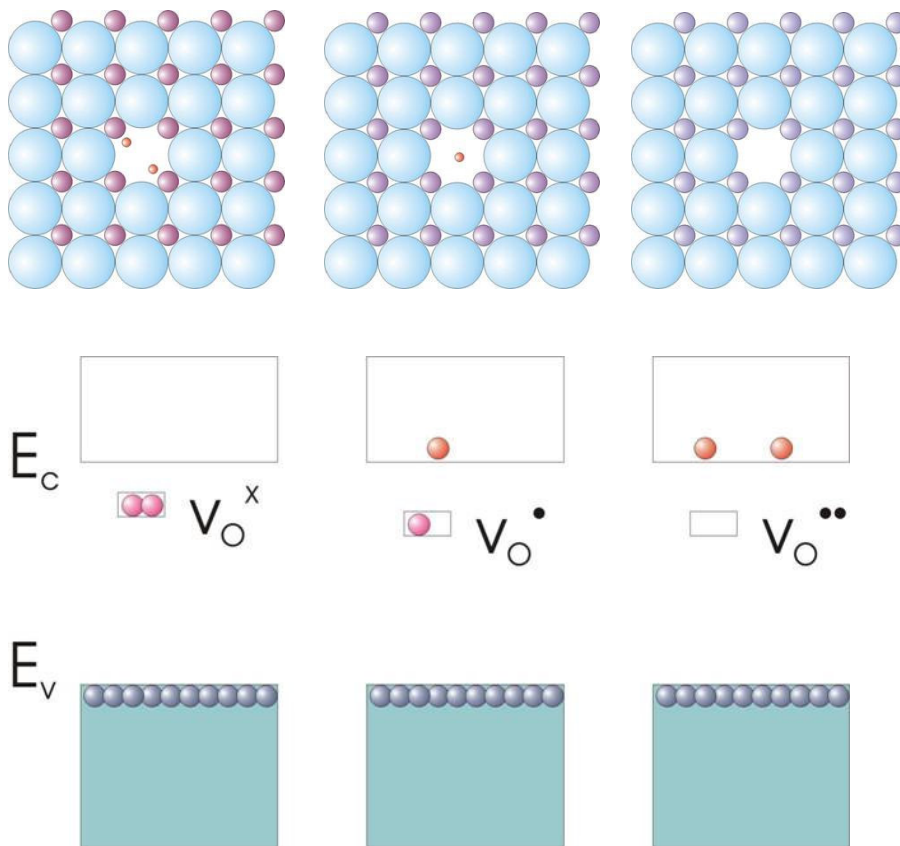
At high oxygen partial pressures the oxide gets a deficiency of metal, it becomes non-stoichiometric, and it becomes a p-type electronic conductor. The oxide's ability to take up extra oxygen or make metal deficiency reflects its tendency of stability of more positive formal oxidation states ( $Ni^{3+}$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

$\text{ZrO}_2$  is an oxide that has a tendency to become reduced and oxygen deficient at low oxygen activities, thus being represented as  $\text{ZrO}_{2-y}$ :

$$O_o^x = v_o^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g) \quad K_{red}' = \frac{[v_o^{\bullet\bullet}]n^2 p_{O_2}^{1/2}}{[O_o^x]} \quad (11.23)$$

We may use this latter reaction to illustrate that point defects such as the cation vacancies in  $\text{Ni}_{1-x}\text{O}$  and oxygen vacancies in  $\text{ZrO}_{2-y}$  are in fact acceptors and donors. Figure 11-8 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

$$v_o^x = v_o^\bullet + e' = v_o^{\bullet\bullet} + 2e' \quad (11.24)$$



**Figure 11-8.** 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  $\text{Ni}_{1-x}\text{O}$  as discussed above can be acceptor-doped with lithium:  $\text{Li}^+$  dissolves on  $\text{Ni}^{2+}$  sites to form  $\text{Li}_{\text{Ni}}'$ . 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  $\text{ZrO}_{2-y}$  the acceptor dopant is typically yttrium,  $\text{Y}^{3+}$ , or some other rare earth, substituting the  $\text{Zr}^{4+}$ . 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  $\text{MO}_2$  ( $\text{ZrO}_2$ ,  $\text{CeO}_2$ ) 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

$$2[\text{Ni}_i^{\bullet\bullet}] + p = 2[v_{\text{Ni}}^{\prime\prime}] + [\text{Li}'_{\text{Ni}}] + n \quad (11.26)$$

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

$$p = 2[v_{Ni}^{//}] \gg 2[Ni_i^{\bullet\bullet}], [Li_{Ni}^{' }], n \quad (11.27)$$

This limits the problem to two unknowns, and we only need two equations; the electroneutrality (Eq. 11.27) and the equilibrium constant  $K'_{ox}$  connecting the two defects (Eq. 11.22):

$$K'_{ox} = [v_{Ni}^{//}][O_o^x]p^2 p_{O_2}^{-1/2} = 4[v_{Ni}^{//}]^3 [O_o^x] p_{O_2}^{-1/2} \quad (11.28)$$

We solve with respect to  $[v_{Ni}^{//}]$  and find that

$$[v_{Ni}^{//}] = (\frac{1}{4} K'_{ox})^{1/3} [O_o^x]^{-1/3} p_{O_2}^{1/6} \quad (11.29)$$

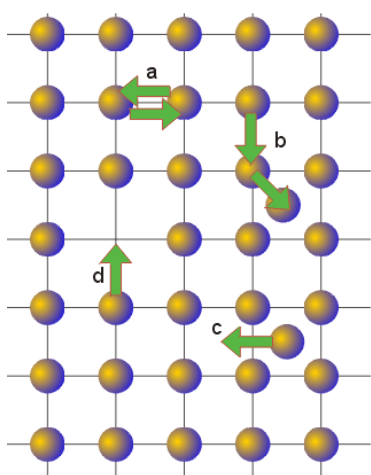
Thus, the concentration of nickel vacancies  $[v_{Ni}^{//}]$  increases with the oxygen activity; it is proportional to  $p_{O_2}^{1/6}$ . The same thus goes for the nonstoichiometry  $x$  in  $Ni_{1-x}O$ , the concentration  $p$  of electron holes, and the p-type electronic conductivity.

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. (11.29), 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 11-9.



**Figure 11-9.** Diffusion mechanisms: Exchange (a), interstitialcy (b), interstitial (c), vacancy (d). From Shriver and Atkins: Inorganic Chemistry, 3<sup>rd</sup> 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:

$$D_r = D_r^0 e^{-Q_D/RT} \quad (11.30)$$

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 11-10. It may be shown that for a cubic isotropic structure the total travelled distance is

$$s_{r,total} = \frac{6D_r t}{s} \quad (11.31)$$

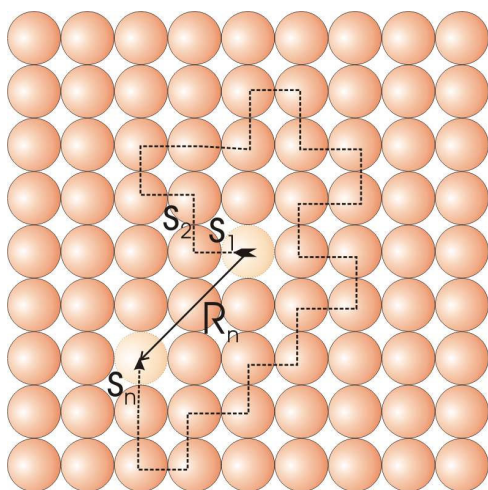
where  $t$  is the time and  $s$  is the distance of each jump. An oxygen vacancy in an oxide may at high temperature have a diffusion coefficient of typically  $D_r = 10^{-6} \text{ cm}^2/\text{s}$ . If the jump distance  $s$  is  $2.8 \text{ \AA}$ , the vacancy will in one hour (3600 seconds) travel 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

$$r_{r,radial} = \sqrt{6D_r t} \quad (11.32)$$

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:

$$r_{r,x} = \sqrt{2D_r t} \quad (11.33)$$

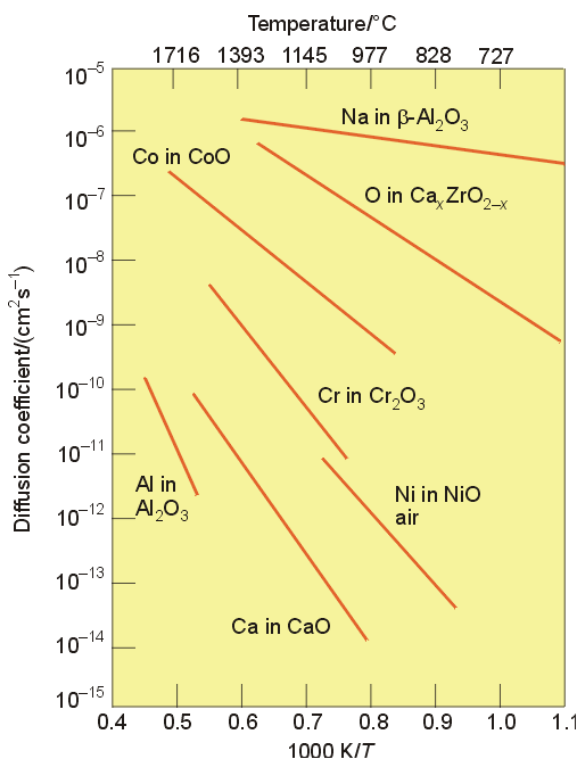
In the example above this reduces to 0.085 mm. (Remember that the direction of this displacement is random such that the most probable place for the vacancy after an hour is still the point it started from!)



**Figure 11-10.** 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:

$$\frac{D_{r,defect}}{D_{r,atom}} = \frac{[atom]}{[defect]} \quad \text{or} \quad D_{r,defect}[defect] = D_{r,atom}[atom] \quad (11.34)$$



**Figure 11-11.** 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, 3<sup>rd</sup> 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  $v$ :

$$\vec{v} = B\vec{F} \quad (11.35)$$

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*:

$$D_r = kTB \quad (11.36)$$

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:

$$\vec{j} = c\vec{v} = cB\vec{F} = \frac{cD_r}{kT} \vec{F} \quad (11.37)$$

The *force* may stem from gradients in *chemical potential*,  $\mu$ , 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  $\phi$ . In one dimension we obtain

$$F = -\left(\frac{d\mu}{dx} + ze\frac{d\phi}{dx}\right) = -\left(\frac{d\mu}{dx} + zeE\right) = -\frac{d\eta}{dx} \quad (11.38)$$

Here  $\eta$  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*,  $u$ :

$$u = zeB \quad (11.39)$$

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:

$$i = zej = cuF = zecuE \quad (11.40)$$

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

$$\sigma = zecu \quad (11.41)$$

and we then obtain

$$i = \sigma E \quad (11.42)$$

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:

$$t_s = \frac{\sigma_s}{\sigma_{total}} \quad (11.43)$$

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  $\mu$ , which enter directly in the driving force for transport. The chemical potential can under assumptions of ideality be expressed as

$$\mu = \mu_0 + kT \ln c \quad (11.44)$$

such that, at constant temperature,

$$\frac{d\mu}{dx} = kT \frac{d \ln c}{dx} = kT \frac{1}{c} \frac{dc}{dx} \quad (11.45)$$

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, *Ficks 1. lov*:

$$j = -\tilde{D} \frac{dc}{dx} \quad (11.46)$$

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

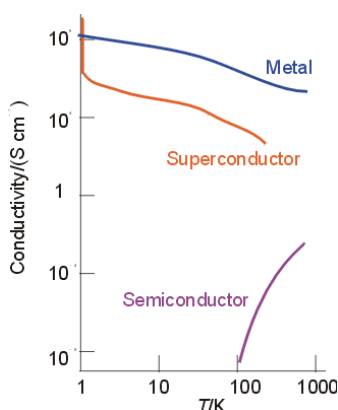
$$u_e = \frac{eL_m}{m_e v_F} \quad (11.47)$$

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 11-12 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 11-12.** 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*, 3<sup>rd</sup> 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  $\text{ZrO}_2$  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  $\text{ZrO}_2$  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  $\text{ZrO}_2$  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  $\text{ZrO}_2$  – only well into the 1900s did one begin to understand defects in crystalline solids and that the Nernst glowler was based on lower-valent  $\text{Y}^{3+}$  ions in the  $\text{ZrO}_2$  structure compensated by mobile oxygen vacancies. Later it was proposed that doped  $\text{ZrO}_2$  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  $\text{ZrO}_2$  has been and is still the dominating electrolyte in the development of solid oxide solid oxide fuel cells (SOFCs).

Undoped  $\text{ZrO}_2$  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,  $\text{CaF}_2$ ). Lower-valent cations, like  $\text{Ca}^{2+}$  or  $\text{Y}^{3+}$  lead to charge compensation by oxygen vacancies. These vacancies stabilise the more symmetrical high temperature modifications so that 3 mol%  $\text{Y}_2\text{O}_3$  may stabilise the

tetragonal polymorph to room temperature (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).

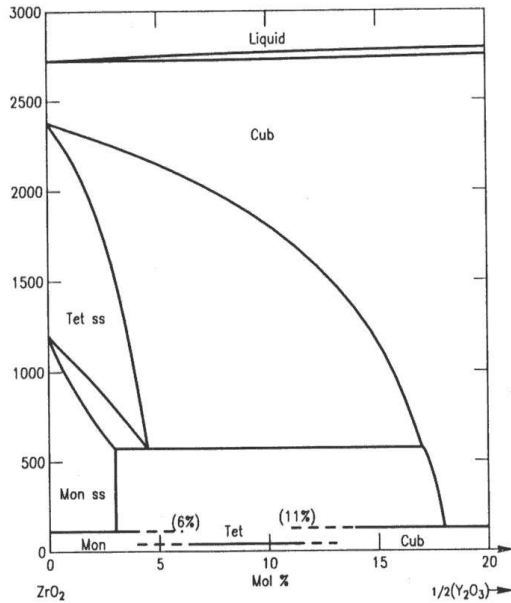


Figure 11-1. Sketch of temperature (°C) vs composition (mol%  $YO_{1.5}$ ) in the  $ZrO_2$ -rich part of the  $ZrO_2$ - $YO_{1.5}$ -phase diagram. ss=solid solution. Beneath a certain temperature equilibrium is in practice frozen out, and the lines near room temperature indicate the phase one gets. From Phase Diagrams for Ceramists (VI-6504), The American Ceramic Society.

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



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

$$2[v_{O}^{\bullet\bullet}] = [Y'_{Zr}] = \text{constant} \quad (11.49)$$

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

$$\sigma_{v_{O}^{\bullet\bullet}} = 2e[v_{O}^{\bullet\bullet}]u_{v_{O}^{\bullet\bullet}} = e[Y'_{Zr}]u_{0,v_{O}^{\bullet\bullet}}T^{-1} \exp\left(\frac{-\Delta H_{m,v_{O}^{\bullet\bullet}}}{RT}\right) \quad (11.50)$$

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 ( $Ni+YSZ$  cermet) and the interconnect ( $LaCrO_3$ -based) which all had thermal expansion sufficiently similar to that of YSZ so that cells could be constructed and assembled. But it has turned out that degradation is too fast at this temperature. The  $LaCrO_3$  interconnect is too expensive to buy and machine. Thus, the operation temperature must be brought down so that the life



time can be improved and we can use a cheap and machineable metal as interconnect. The development of better electrolytes has therefore been going on continuously the last decades.

Firstly, one has been able to reduce the thickness of the electrolyte. Early, one used self-supported sheets of 100-200  $\mu\text{m}$  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  $\mu\text{m}$  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  $^{\circ}\text{C}$ .

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,  $\text{Sc}^{3+}$ , should fit better in  $\text{ZrO}_2$  than  $\text{Y}^{3+}$ , 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  $^{\circ}\text{C}$ .

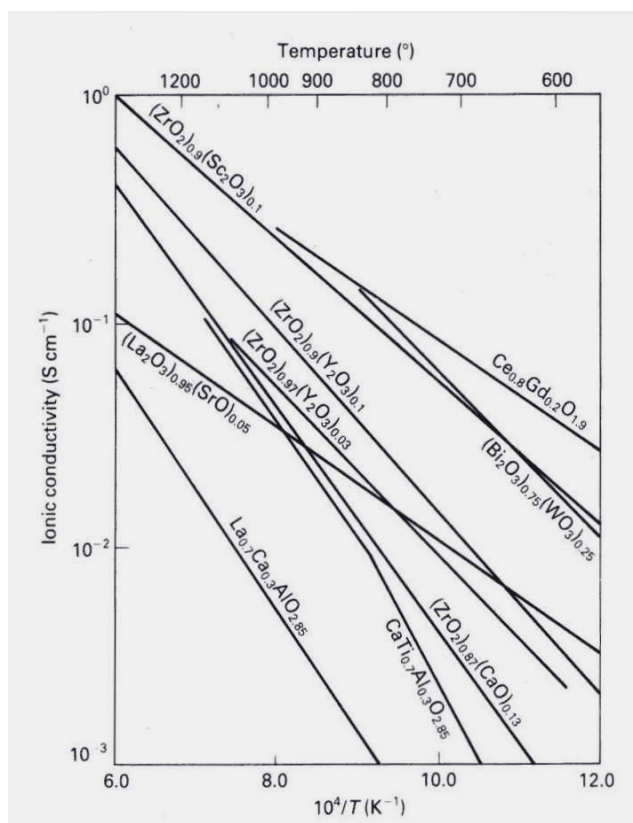


Figure 11-2. Conductivity of some oxide ion conductors. Fra P.G. Bruce: Solid State Electrochemistry.

A number of other oxides also exhibit high oxide ion conductivity.  $\text{CeO}_2$  is similar to  $\text{ZrO}_2$  and has higher ionic conductivity when acceptor doped, in this case optimally

by  $\text{Sm}^{3+}$  or  $\text{Gd}^{3+}$ . It can thus be used at lower temperatures. But it also has a higher tendency of reduction:

$$O_o^x = v_o^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g) \quad K'_{red} = [v_o^{\bullet\bullet}]n^2 p_{O_2}^{1/2} [O_o^x]^{-1} \quad (11.51)$$

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

Bismuth oxide,  $\text{Bi}_2\text{O}_3$ , has several structure polymorphs. One of these,  $\delta\text{-Bi}_2\text{O}_3$  has a cubic fluorite structure similar to  $\text{ZrO}_2$ . 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  $\text{WO}_3$  (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  $\text{LaGaO}_3$ . A combination of  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  as acceptor-substituents for  $\text{La}^{3+}$  and  $\text{Ga}^{3+}$  was necessary to give mutually high solubility and a high concentration of oxygen vacancies. Sr+Mg-doped  $\text{LaGaO}_3$  (LSGM) has higher conductivity than  $\text{ZrO}_2$ -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  $\text{Sr}^{2+}$  in  $\text{SrTiO}_3$  with  $\text{Y}^{3+}$  which is then compensated by conduction band electrons. Such materials do work, but are troubled by limiting electronic conductivity and catalytic activity.

### *SOFc 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  $\text{LaMO}_3$  perovskites where M is Mn, Fe or Co are much studied. We will here use  $\text{LaMnO}_3$  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

$$0 = \text{e}' + \text{h}^\bullet \quad (11.55)$$

$$K'_g = [\text{e}'] [\text{h}^\bullet] = np = K'_{g,0} \exp\left(\frac{-E_g}{RT}\right) \quad (11.56)$$

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

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

$$[\text{h}^\bullet] = [\text{Sr}'_{\text{La}}] = \text{constant} \quad (11.57)$$

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

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

LSMO tends to form reaction layers of  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$  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  $\text{LaCrO}_3$  (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  $\text{Cr}_2\text{O}_3$  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  $\text{Cr}_2\text{O}_3$  layer at high temperature are very hard and difficult to machine and end up very expensive. There is thus a driving force to develop intermediate temperature ITSOFCs where normal chromia-forming stainless steels are protective enough. Temperatures of 600 °C or less are probably required.

Metallic 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  $\text{Cr}^{6+}$  oxohydroxides from the interconnect's protective  $\text{Cr}_2\text{O}_3$  layer to the cathode is detrimental – it settles as  $\text{Cr}_2\text{O}_3$  and blocks the reactive sites. To avoid this, the alloy is often covered with a more stable Cr compound, like  $\text{LaCrO}_3$  or a Cr spinel like  $\text{MnCr}_2\text{O}_4$ .

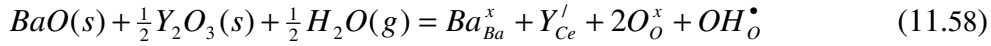
## **SOFCs with high temperature proton conducting electrolytes**

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

### *Proton conducting oxides*

Oxides and other nominally water-free materials may still contain a few protons in equilibrium with surrounding water vapour. With acceptor-doping the proton concentration may be further increased. Oxide ions are hosts for the protons, so that the protons can be seen as present as hydroxide groups occupying oxide ion lattice sites;  $\text{OH}_\text{O}^\bullet$ . 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  $\text{BaCeO}_3$ ,  $\text{BaZrO}_3$ , and  $\text{SrCeO}_3$ , doped with a suitably small lower-valent cation like  $\text{Y}^{3+}$  on the B-site. We can write the acceptor-doping of  $\text{BaCeO}_3$  in wet atmospheres as



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

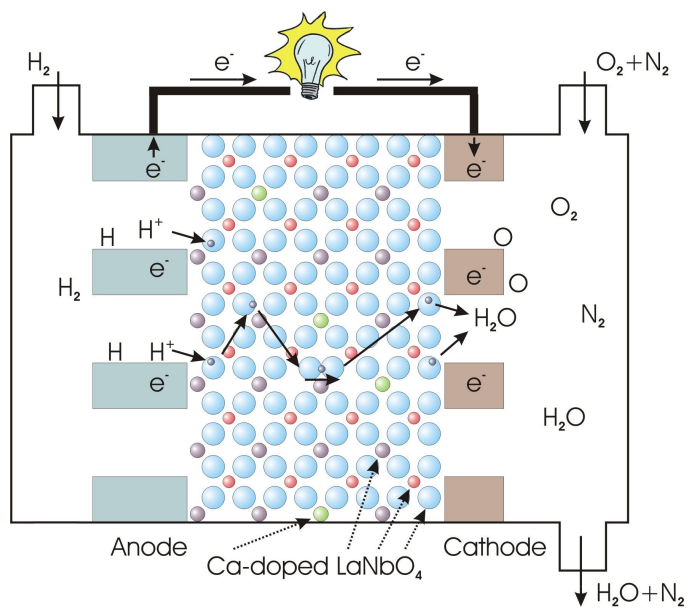


is exothermic, driven to the left at increasing temperatures. We then replace the effective charge of the protons with those of the oxygen vacancy. Proton conduction in these materials is thus a battle and compromise at increasing temperature between sufficient proton mobility and loss of protons from 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  $\text{ZrO}_2$ -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  $\text{CO}_2$  to form alkali earth carbonates (like  $\text{BaCO}_3$ ). The reaction prevents use with reformed fossil or biological fuels and also in some cases with normal air. The formation of  $\text{BaCO}_3$  markedly weakens grain boundaries and the overall mechanical properties. Alternative materials without the most basic alkali earths comprise acceptor-doped  $\text{Gd}_2\text{O}_3$ ,  $\text{LaScO}_3$ ,  $\text{LaPO}_4$ , and  $\text{LaNbO}_4$ . 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 11-13. Proton conducting solid oxide fuel cell, based on Ca-doped LaNbO<sub>4</sub>. Note how H<sub>2</sub> fuel can be utilized fully as no water is produced to dilute it on the anode side.**