02D_Materials for Construction of SOFC

Topics

•The electrolyte (should have a high conductivity for oxygen ions)

Note: the nomenclature for a battery or a fuel cell is usually defined by the ion which is transported through the electrolyte.

•The anode

The anode is where the ion is oxidized, so in fuel cell it is where $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e$

Note that oxygen ion arrives from within the electrolyte, while the oxygen molecule is released to the fuel chamber (hydrogen and water), and the electrons are released to a metallic current collector.

Therefore the anode must have sites where these three species are brought together to achieve the oxidation reaction.

The anode in a fuel cell

•porous to allow H_2, H_2O, O_2 to access the electrolyte.

•Must have sites where the ion conductor and the metal are in contact. This structure is a composite of Ni metal and zirconia particle (zirconia is also the electrolyte). The Ni also serves as a catalyst for the oxidation reaction.

The anode is made by mixing powders of nickel and zirconia and partial sintering to a density of about 70%.

•The cathode

The cathode must be porous to provide access to air. $\frac{1}{2}O_2 + 2e \rightarrow O^{2-}$

The material is chosen to have both some ionic conductivity of oxygen ions but more importantly have electronic conductivity. The material must be different than for the anode because of the oxidizing environment (air) at the cathode.

The cathode materials always have a transition metal (Co), and rare earth (La) and it is an oxide.

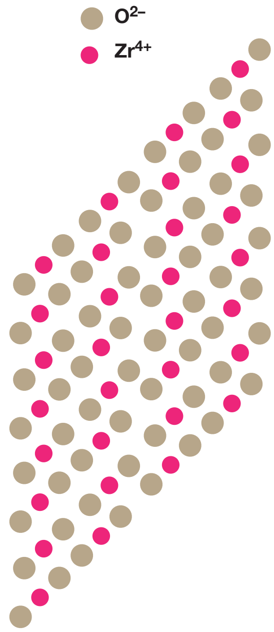
•The Electrolyte

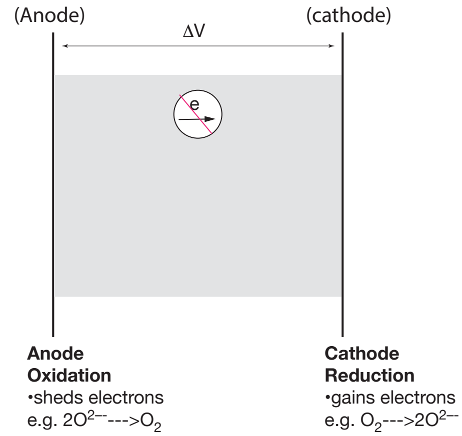
The electrolyte must have a high diffusivity for oxygen ions and negligible conductivity for electrons.

The standard material is zirconia doped with yttria.

The question is why doping with yttria leads to a high conductivity of oxygen ions.

We must now consider the mechanism of diffusion of oxygen ions in zirconia.





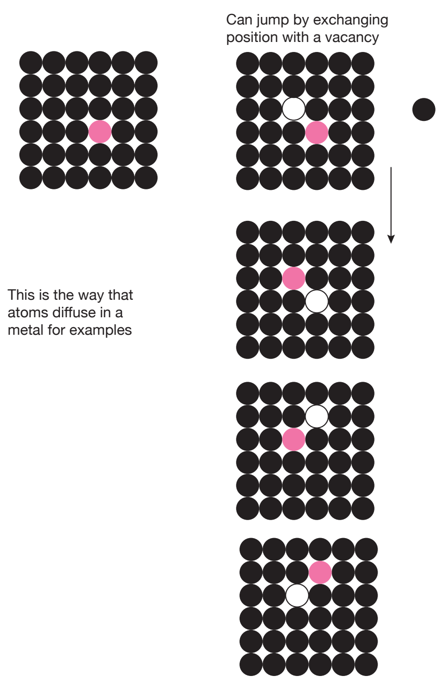
Notes:
Mass Balance: 2 O for one Zr
Charge Balance: 4+ on Zr balanced by two O^{2-}

Despite a large ionic radius oxygen diffuses faster than oxygen, partly because of oxygen vacancies induced by adding yttrium.

(i) Its chemical formula is ZrO_2 : must have two oxygens for one zirconium. That is the material is stoichiometric. Can become non-stoichiometric by doping.

(ii) If we dope to make non-stoichiometric, then we must enforce charge balance. The number of positive charges (Zr^{++++}), must be the same as the negative charges (O^{--}); thus ZrO_2 meets the charge balance criterion.

Let us consider diffusion of a species within the structure of a crystal



In a “packed” crystal atoms can jump more easily if they have a vacancy in an adjacent lattice site. Therefore the probability of jump (which is the fundamental mechanism of diffusion) is related to to the probability of finding a vacancy next to itself. This probability is equal to the molar concentration of vacancies.

Normally the concentration of vacancies of oxygen in zirconia are negligible. Therefor the diffusion of oxygen ions in pure zirconia is not enough to enable a fuel cell to function.

Dope with Y_2O_3

$ZrO_2 \rightarrow Zr_2O_4$

If two zirconia molecules are substituted by one molecule of yttria and the yttrium atoms occupy the zirconium sites then one oxygen site must be left vacant. Typically the zirconia is doped with 8 mol% yttrium oxide which produces 8 mol% of vacancies.. this is a huge number.

The Question of Charge Balance

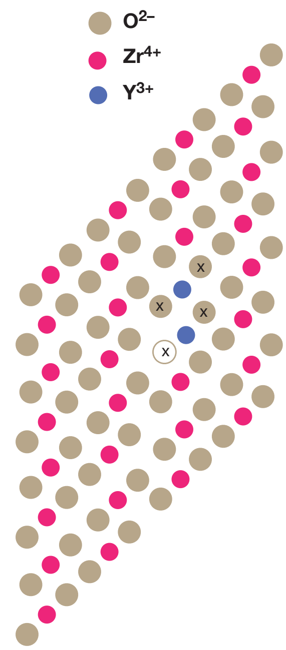
Vacancies are called point defects, or just defects. They are important for the diffusion of the host species as described just above.

Point defects in ionic materials must meet two criteria,

•Mass balance: $2ZrO_2$ equivalent to Zr_2O_4 then if replace Y_2O_3

•Charge balance

For example consider doping of ZrO_2 with Y_2O_3. Remember that Zr has a charge number of +4 and yttrium +3. Therefore we consider how charge balance is achieved.



First consider the mass balance:

The crystal has specific lattice sites for Zr and O.

Y ions replace the Zr ions.

Therefore Zr_2O_4 is equivalent to Y_2O_3,

Now only three of the four oxygen sites are occupied by the Y_2O_3

Therefore one oxygen site is left vacant when one molecule of yttria substitutes for two molecules of zirconia.

This leads to a "structural" introduction of vacancies by doping with yttria, thereby greatly enhancing the diffusion rate of oxygen ions, a very desirable property for the electrolyte in the solid oxide fuel cells.

Let us now consider the charge balance

Charge	(2)Zirconium	(3)Oxygen(full)	(1)Oxygen	(2)Yttrium
Before Doping	+4, +4	-2, -2, –2	–2	n/a
After Doping	n/a	-2, -2, -2	0 (vacancy	+3, +3
After-Before	-4, -4	0	+2 (vacancy)	+3, +3

Thus we see that (-4,-4) on Zr sites has been replaced by (+3,+3) of yttrium atoms. For charge balance the vacancy now has an effective charge of +2.

A simple way to think of it is that if and O^{2-} is removed then it leaves behind an effective charge of +2. Charge balance plays an important role in research on transport properties in ionic materials.