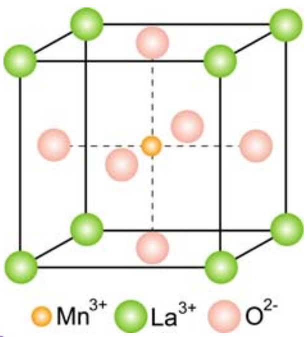
Class 2: Introduction to Ceramics



PRIME Modules
Project-based Resources for Introduction to Materials Engineering

A ceramic is a ionic compound of metals with non metals

Most generally, a compound of metals with non-metals.

The bonding is either totally or predominantly ionic.

This bonding gives the following properties:
- •Brittle
- •High melting temperature
- •Poor conductor of electricity
- •Poor conductor of heat.

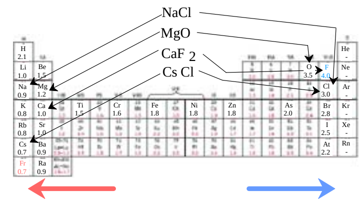
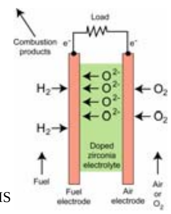


Figure from Callister

There are a wide range of ceramic compounds and applications

Some Examples:
- Carbides: SiC, TiC, TaC, WC, B_4C
- Oxides: ZrO_2, SiO_2, TiO_2, MgO, Al_2O_3, $CaTiO_3$, Al_2SiO_5
- Borides: TiB_2
- Chlorides: NaCl, CsCl
- Fluorides: CaF_2, $KLiBeF_4$, $CsBeF_4$, Li_2NiF_4, BeF_4, $CsNaInF_6$
- Sulfides: ZnS, FeS_2, Ba_2TiS_4, $ZnCr_2S_4$, $MnAl_2S_4$
- Nitrides: Si_3N_4, Al_3O_3N
- Iodides, Bromides, Selenides, Tellurides

Some Applications:
- Traditional ceramics
- Insulators and packaging in microelectronics and MEMS
- Fiber optics
- Fuel cells

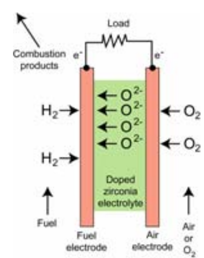


SOFC use ceramics for ionic diffusion and their high melting temperature

The electrolyte in a SOFC must be a ceramic to allow for oxygen ions to diffuse through them.

The diffusion of the oxygen ions requires a very high temperature

The anode and cathode must also be ceramics to withstand this high temperature. (Refractory metals can also be used but they are a lot more expensive.)

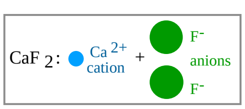


The structure type is determined by the coordination number and the stoichiometry

- Charge Neutrality:
  --Net charge in the structure should be zero.

  --General form: $A_m X_p$

  m, p determined by charge neutrality



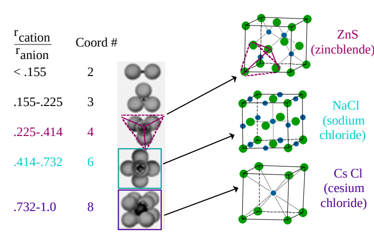
Adapted From Callister

The coordination number is the number of nearest neighbors bonded to an atom.

The coordination number is the number of nearest neighbor atoms bonded to an atom.

In ionic materials the anion (negatively charged ion) and cation (positively charged ion) bond together.

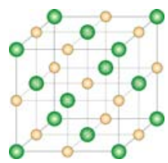
The relative size of the cation (r_c) and anion (r_a) determines the coordination number.

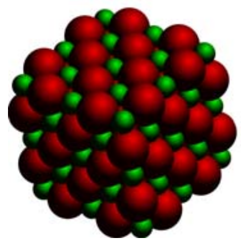


Rock salt is an FCC lattice with 2 atoms per basis

Crystal structure with a 1:1 stoichiometry (AX) and a coordination number of 6 have the rock salt structure

NaCl is a common example

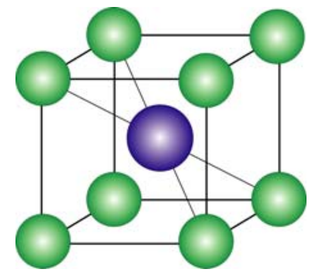




http://cimesg1.epfl.ch/CIOL/ems.html

CsCl is an SC lattice with 2 atoms per basis

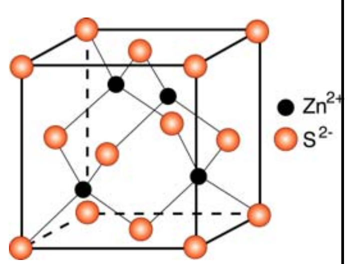
Crystal structure with a 1:1 stoichiometry (AX) and a coordination number of 8 have the cesium chloride structure



A Zinc blende structure is an FCC lattice with 2 atoms per basis

Crystal structure with a 1:1 stoichiometry (AX) and a coordination number of 4 have the zinc blende structure

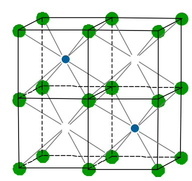
ZnS, SiC, and GaAs are common examples



Fluorite's structure is determined by r_c/r_a and stoichiometry

AX_2 Structure: CaF_2 : $\frac{r_{cation}}{r_{anion}} = \frac{0.100}{0.133} \approx 0.8$

Based on this ratio, coord # = 8 and structure = CsCl.
Result: CsCl structure w/only half the cation sites occupied.



Only half the cation sites are occupied since $\#Ca^{2+}$ ions = 1/2 $\# F^{-}$ ions.

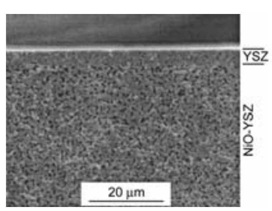
Adapted from Fig. 12.5, *Callister 6e.*

Ceramics are needed to allow for the ionic conduction

The most common electrolyte material is ZrO_2 (zirconia), which is doped with small amounts of Y_2O_3 (yttria). This material is known as yttria-stabilized zirconia (YSZ). This is a ceramic material - a compound of a metal with a non-metal.

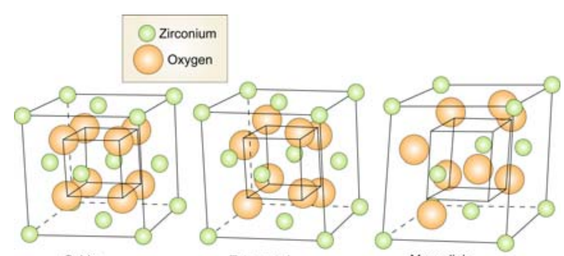
Ni/YSZ cermet (ceramic-metal composite) is used as the anode material because of its low cost. It is also chemically stable at high temperatures and its thermal expansion coefficient is close to that of the YSZ electrolyte.

The cathode is based on a $(La_{1-y}Sr_y)MnO_{3-\delta}$ (LSM) perovskite material.



J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, and L.J. Gauckler, "Fabrication of thin electrolytes for second-generation solid oxide fuel cells," *Solid State Ionics*, **131** (2000) 79-96.

Zirconia is used in the electrolyte and anode of SOFC



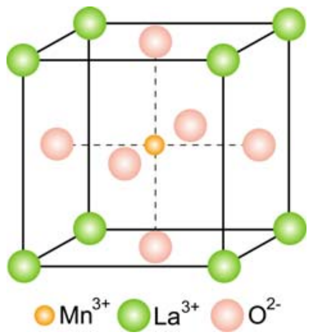
Cubic - stable above 2700°C

Tetragonal - stable above 1000°C

Monoclinic - stable at room temperature

Perovskite is used in the cathode of SOFC

The cathode in SOFC's is based on a $LaMnO_3$ perovskite material.

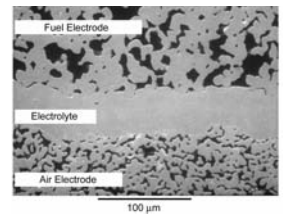


The anode, cathode, and electrolyte are manufactured from ceramic nanoparticles

Nanoparticles of each layer are made separately

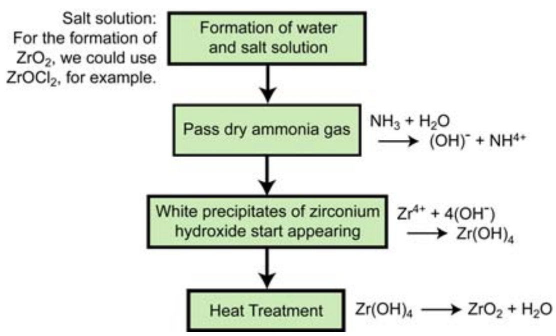
Nanoparticles are the then synthesized into solid layers stacked on top of each other

The 3 layer structure is annealed (baked at high temperature) to create a porous anode and cathode and a dense electrolyte

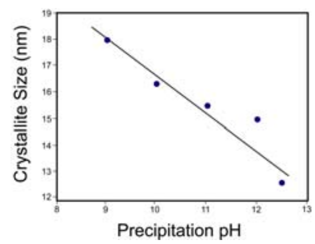


S.C. Singhal, "Advances in solid oxide fuel cell technology," *Solid State Ionics*, **135** (2000) 305-313

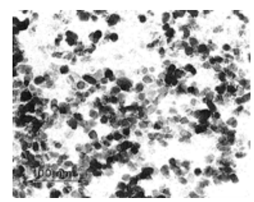
The nanoparticles precipitate out from solution



The size of the resulting nanoparticles of ceramics has to do with the chemistry of the starting solution.



The pH is increased by adding more NH_3.



Nanocrystalline ZrO_2-3 mol%Y_2O_3
Average Particle Diameter = 13 nm

M.J. Mayo, D.C. Hague, and D.-J. Chen, "Processing nanocrystalline ceramics for applications in superplasticity," *Materials Science and Engineering A*, **166** (1993) 145-159.

EVD was first used to turn the nanoparticles into SOFC layers

Initially cell construction was completed by depositing powders in order to produce thick films of the cathode $LaMnO_3$, electrolyte YSZ (35 mm thick) and anode Ni-YSZ, using electrochemical vapor deposition (EVD).

This allowed good quality components to be produced. However, the capital and labor costs associated with EVD are high.

Tape casting, screen printing, and possibly thermal spray technologies are all preferred methodologies, and are replacing EVD, due to lower costs associated with them.

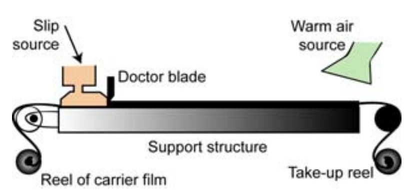
B.C.H. Steele, "Material science and engineering: the enabling technology for the commercialization of fuel cell systems," *Journal of Materials Science*, **36** (2001) 1053-1068.

F. Tietz, H.-P. Buchkremer, and D. Stöver, "Components manufacturing for solid oxide fuel cells," *Solid State Ionics*, **152-153** (2002) 373-381.

Tape Casting Process can be used to turn the nanoparticles into layers

The technique consists of casting a slurry (containing the nanoparticles of ceramics) onto a moving carrier surface and spreading the slurry to a controlled thickness with the edge of a long, smooth blade.

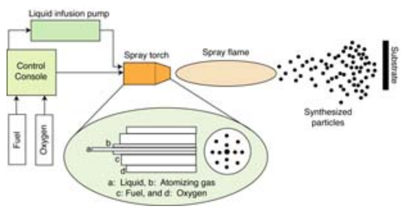
The slurry contains a binder system dissolved in a solvent; enough binder is present so that a flexible tape will result when the solvent is removed.



Flame Spraying can be used to turn nanoparticles into layers

Flame spraying refers to a technique of spraying molten ceramic droplets onto a surface. This molten particle deposition is commonly referred to as flame spray – plasma spray.

The advantages of this process are the flame spray versatility and the wide range of sizes and shapes of substrates that can be coated.



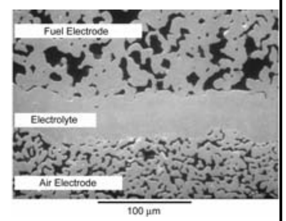
J. Karthikeyan, C.C. Berndt, J. Tikkanen, J.Y. Wang, A.H. King, and H. Herman, "Nanomaterial powders and deposits prepared by flame spray processing of liquid precursors," *Nanostructured Materials*, **8** [1] 61-74 (1997).

In summary, SOFC use ceramic nanomaterials for their high melting temperature and ionic diffusion.

The ionic bonding in ceramic materials allow for the high melting temperature and ionic diffusion needed in SOFC

In making SOFC, the anode, cathode, and electrode are made from ceramic nanoparticles.

The nanoparticles are precipitated out of solution and then tape casted or flame sprayed onto layers.



S.C. Singhal, "Advances in solid oxide fuel cell technology," *Solid State Ionics*, **135** (2000) 305-313