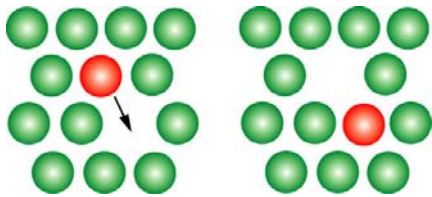


## Class 4: Diffusion Using Defects



PRIME Modules  
Project-based Resources for Introduction to Materials Engineering

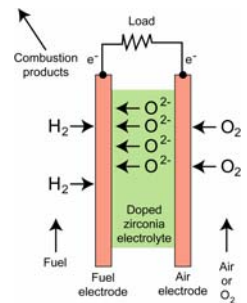
Diffusion is the movement of atoms due to a driving force

The most common driving force for diffusion is a concentration gradient

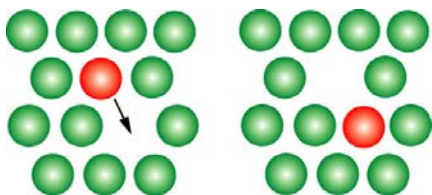
Atoms can diffuse via point defects or through fast diffusion paths (such as surfaces or grain boundaries)

In SOFC diffusion is needed in fabrication to form the dense electrolyte layer through sintering

Diffusion is critical in operation for the  $O^{2-}$  ion to move across the electrolyte



Substitutional/Vacancy diffusion is a motion of atoms along the lattice by exchanging places with a vacancy



In substitutional/vacancy diffusion, there is motion of substitutional atoms from one vacancy location to another. The diffusing atoms do not have to be of a different element (although that is what is shown in this diagram). This type of diffusion occurs during sintering.

Interstitial diffusion is the motion of atoms along the empty spaces in a crystal structure



An interstitial atom, can move from one interstitial position to another. Since most interstitial positions are not occupied, this type of diffusion is more common than substitutional diffusion, where a vacancy would be needed. This type of diffusion does not occur during sintering.

The diffusion rate increases with temperature

Temperature has a profound influence on diffusion rates. The temperature dependence of diffusion coefficients is related to temperature according to

$$D = D_0 \exp\left\{-\frac{Q_d}{RT}\right\}$$

$D_0$  = a temperature-independent preexponential ( $m^2/s$ ).

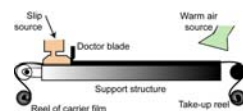
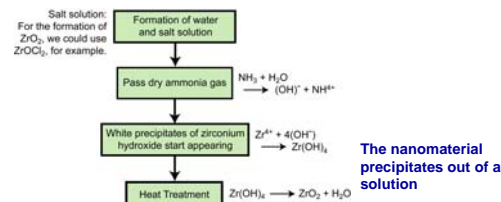
$Q_d$  = the activation energy for diffusion (J/mol, cal/mol, or eV/atom).

$R$  = the gas constant, 8.31 J/mol-K, or 1.987 cal/mol-K.

$k$  = the Boltzmann's constant,  $8.62 \times 10^{-5}$  eV/atom-K.

$T$  = absolute temperature (K).

SOFC fabrication involves creating nano powders and then using them to make a solid layer

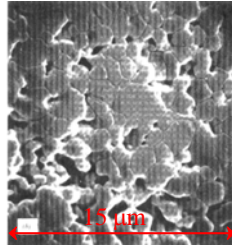


Tape casting can be used to turn those powders into a solid layer

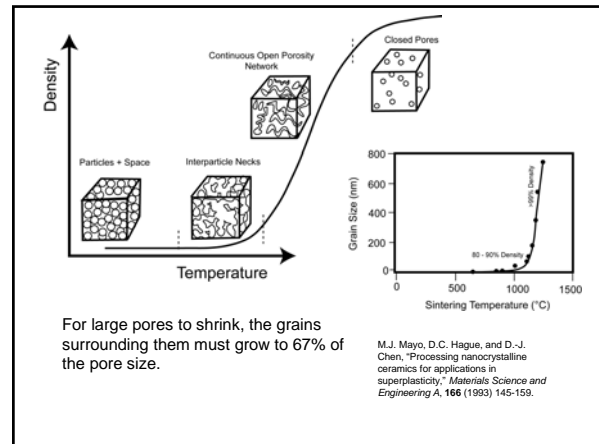
## Sintering is needed to densify the layers made of the nanomaterials

After deposition of powders using techniques such as tape-casting or flame spraying, a sintering step is necessary in order to remove and/or control porosity in the final component.

Sintering is the removal of pores between powders particles accompanied by shrinkage.

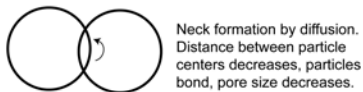


Adapted from Fig. 13.15, Callister 6e. (Fig. 13.15 is from W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, 2nd ed., John Wiley and Sons, Inc., 1976, p. 483.)



## Solid State Sintering takes place by a diffusion of atoms to form the neck

Involves material transport by volume diffusion. Diffusion can consist of movement of atoms or vacancies along a surface or grain boundary or through the volume of the material.



## The amount of sintering is greater for smaller particles and with faster diffusion

The driving force for solid-state sintering is the difference in energy between the free surfaces of particles and the points of contact between adjacent particles.

$$\frac{\Delta L}{L_0} = \left( \frac{K\gamma a^3 D^* t}{kT d^n} \right)^m$$

If the powder particle diameter,  $d$ , is smaller, the sintering rate will increase.

Hence, starting with nanocrystalline powders will promote sintering.

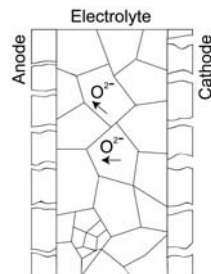
Diffusion is very important in order for sintering to occur.

where  
 $\Delta L/L_0$  = linear shrinkage (equivalent to the sintering rate)  
 $\gamma$  = surface energy  
 $a^3$  = atomic volume of the diffusing species  
 $D^*$  = self-diffusion coefficient  
 $k$  = Boltzmann constant  
 $T$  = temperature  
 $d$  = particle diameter  
 $t$  = time  
 $K$  = constant dependent on geometry  
 $n, m$  = constants independent

## Diffusion in the electrolyte takes place through oxygen vacancies and along grain boundaries

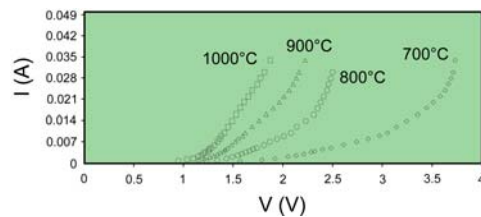
Diffusion is enhanced by:

- Adding more oxygen vacancies, so that oxygen ions can travel easily through the  $ZrO_2$  crystal. The number of vacancies can be increased by adding more yttrium.
- Adding more grain boundaries so that oxygen can travel through these high diffusion paths. Having nanostructured grains would be ideal for this.



**Note: The only way to obtain nanostructured grains, is to start with nanostructured powders.**

## Diffusion in the electrolyte is enhanced by the added driving force of the electric field



Diffusion increases with temperature (gets a large current at smaller applied voltages due to the increase in vacancy concentration and the increase in diffusion rate)

P. Mondal, A. Klein, W. Jaegermann, and H. Hahn, "Enhanced specific grain boundary conductivity in nanocrystalline  $Y_2O_3$ -stabilized zirconia," *Solid State Ionics*, 118 (1999) 331-339.

**In summary, diffusion is important for the fabrication and operation of SOFC**

The use of nanostructured powders for the manufacturing of SOFC's has several advantages:

- By using nanostructured powders, sintering can be enhanced and a fully dense electrolyte can be obtained in a shorter time.
- By using nanostructured powders, sintering can be controlled in order to obtain nanoporosity in the anode and cathode, which is necessary for transport of oxygen and hydrogen.
- By having nanostructured grains in the electrolyte, ionic conductivity can be enhanced, which enhances the efficiency of the SOFC device.

