Chapter 2: Metal materials - 3

Ionic Conductors

- In **ionic conductors**, the current is transported by *ions* moving around (and possibly electrons and holes, too). Electrical current transport via **ions**, or *ions and electrons/holes*, is found in:
  - Conducting *liquids* called **electrolytes**.
  - **Ion conducting solids**, also called **solid electrolytes**.
- **Ionic conductivity** is important for many products:
  - Type **I** and type **II batteries** (i.e. regular and rechargeable).
  - **Fuel cells**.
  - **Electrochromic** windows and displays.
  - Solid state **sensors**, especially for reactive gases.

- Since a diffusion coefficient ***D*** and a mobility **μ** describe essentially the same thing, it is small wonder that they are closely correlated - by the **Einstein-Smoluchowski relation** (the link leads you to the semiconductor Hyperscript with a derivation of the equation).

$$\mu = \frac{e \cdot D}{kT}$$

- The conductivity of a solid-state ionic conductor thus becomes

$$\sigma = e \cdot c \cdot \mu = \frac{e^2 \cdot c \cdot D}{kT} = \frac{e^2 \cdot c \cdot D_0}{kT} \cdot \exp - \frac{H^m}{kT}$$

- with the normal Arrhenius behaviour of the diffusion coefficient and H^m = migration enthalpy of an ion, carrying one elementary charge. In other words: we must expect complex and strongly temperature dependent behaviour; in particular if ***c*** is also a strong function of ***T***.

Since this involves that some kind of ion can move, or, in other words, *diffuse* in the solid electrolyte, the *local concentration* **c** of the mobile ion can respond to two types of driving forces:

- **1.** *Concentration gradients*, leading to particle currents j_{diff} (and, for particles with charge q, automatically to an electrical current $j_{elect} = q \cdot j_{diff}$) given by **Ficks laws**

$$\boxed{j_{diff} = -D \cdot \mathrm{grad}(c)}$$

- With D = **diffusion coefficient** of the diffusing particle.
- **2.** *Electrical fields* **E**, inducing electrical current according to *Ohms law* (or whatever current - voltage - characteristics applies to the particular case), e.g.

$$\boxed{j_{field} = \sigma \cdot E = q \cdot c \cdot \mu \cdot E}$$

- With μ = mobility of the particle.

Debye Length

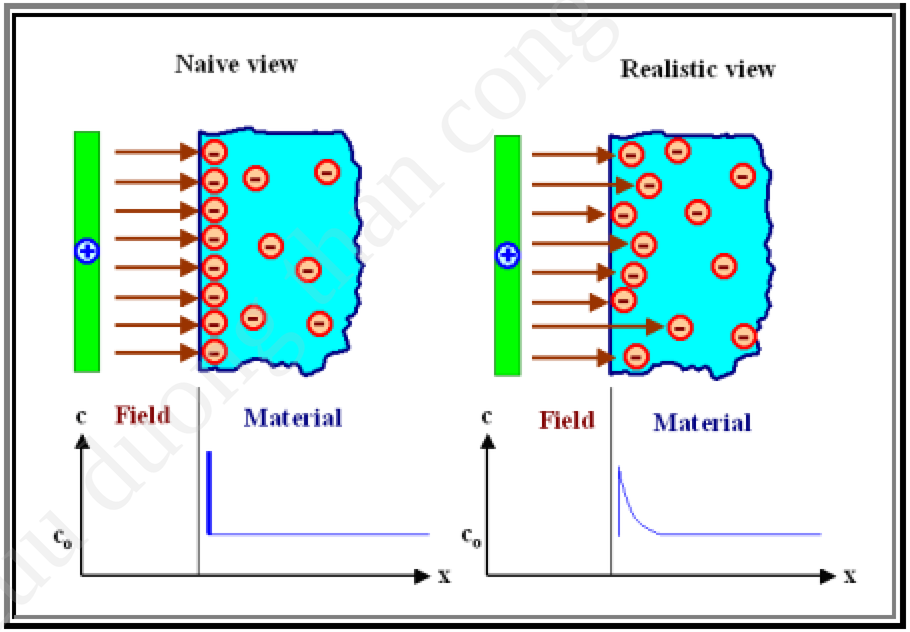
Equilibrium of Diffusion and Field Currents

- *Nernst law* is a special answer to the general and important question:

> How do *charged* and *mobile* particles redistribute themselves in an *electrical potential*
> if there are some restrictions to the obvious solution
> that they all move to one or the other pole of the field?

- It is the answer to this question that governs not only **pn**-junctions, but also batteries, fuel cells, or gas sensors, and, if you like, simply *all junctions*.

- Let us consider a material that essentially contains mobile carriers of only *one* kind, i.e. a metal (electrons) , a (doped) semiconductor (electrons *or* holes, depending on doping), or a suitable ionic conductor (one kind of mobile ion).
  - We imagine that we hold a positively charged plate at some (small) distance to the surface of a material having mobile negative charges (a metal, a suitable ionic conductor, a n-doped semiconductor, ...). In other words, the positively charged plate and the material are *insulated*, and no currents of any kind can flow between the two. However, there will be an electrical field, with field lines starting at the positive charges on the plate and ending on the negative charges inside the material. We have the following situation:



- In a *naive* (and *wrong*) view, enough negatively charged carriers in the material would move to the surface to screen the field completely, i.e. prevent its penetration into the material. "Enough", to be more precise, means just the right number so that every field line originating from some charge in the positively charged plate ends on a negatively charged carrier inside the material.
  - But that would mean that the concentration of carriers at the surface would be pretty much a δ- function, or at least a function with a very steep slope. That does not seem to be physically sensible. We certainly would expect that the concentration varies smoothly within a certain distance, and this distance we call **Debye length** right away.
  - As you might know, the Debye length is a crucial material parameter not only in all questions concerning ionic conducitvity (the field of "**Ionics**"), but whenever the carrier concentration is not extremely large (i.e. comparable to the concenetration of atoms, i.e in metals).

- If all (necessarily mobile) carriers would pile up at the interface, we would have a large concentration gradient and **Ficks law** would induce a very large *particle* current *away* from the interface, and, since the particles are charged, an *electrical* current at the same time! Since this **electrical *diffusion* current $j_{\text{el, Diff}}$** is proportional to the concentration *gradient* **–grad ($c(x)$)**, we have:

$$\boxed{j_{\text{el, Diff}}(x) = -q \cdot D \cdot \text{grad}\,(c(x))}$$

  - With D = diffusion coefficient. Be clear about the fact that whenever you have a concentration gradient of mobile carriers, you will always have an electrical current by necessity. You may not notice that current because it might be cancelled by some other current, but it exists nevertheless.

- The *electrical field* **$E(x)$**, that caused the concentration gradient in the first place, however, will also induce an electrical ***field* current** (also called **drift current**) $j_{\text{field}}(x)$, obeying Ohms law in the most simple case, which flows in the *opposite* direction of the electrical diffusion current. We have:

$$\boxed{j_{\text{field}}(x) = q \cdot c \cdot \mu \cdot E(x)}$$

  - With μ = mobility, q = charge of the particle (usually a multiple of the elementary charge **e** of either sign); $q \cdot c \cdot \mu$, of course, is just the conductivity σ
  - The *total* electrical current will then be the *sum* of the electrical field and diffusion current.

- In *equilibrium*, both electrical currents obviously must be *identical* in magnitude and *opposite* in sign for every x, leading for one dimension to

$$\boxed{q \cdot c(x) \cdot \mu \cdot E(x) = q \cdot D \cdot \frac{dc(x)}{dx}}$$

$$\boxed{\mu = e \cdot D/kT}$$

- We also can substitute the electrical Field $E(x)$ by $-\,dU(x)/dx$, with $U(x)$ = potential (or, if you like, voltage) across the system. After some reshuffling we obtain

$$\boxed{-e\,\frac{dU(x)}{dx} = \frac{kT}{c(x)} \cdot \frac{dc(x)}{dx} = kT \cdot \frac{d\,[\ln c(x)]}{dx}}$$

- Integrating this simple differential equation once gives

$$\boxed{U(x) + \frac{kT}{e} \cdot \ln c(x) = \text{const.}}$$

- That's why we give it a name and call it the **electrochemical potential V_{ec}** (after muliplying with **e** so we have energy dimensions). While its two factors will be functions of the coordinates, its total value for any **(x,y,z)** coordinate in equilibrium is a *constant* (the three dimensional generalization is trivial). In other words we have

$$\boxed{V_{ec} = V(x) + kT \cdot \ln c(x)}$$

- with **$V(x) = e \cdot U(x)$ =** electrostatic potential energy.
- The electrochemical potential thus is a real energy like the potential energy or kinetic energy.

- Obviously, *in equilibrium* (which means that nowhere in the material do we have a *net* current flow) the *electrochemical potential must have the same value anywhere in the material*.
- This is easy to see: Just rewriting the equation from above for **c(x)** yields

$$\boxed{c(x) = \exp - \frac{(Vx) - V_{ec}}{kT}}$$

Calculating the Debye Length

- First we realize that the voltage or potential distribution (voltage times **e**) in the interior of a material *in equilibrium* can only be caused by *concentration distributions of carriers that obey equilibrium statistics*, i.e. the Boltzmann or the Fermi distribution.
  - This is simply what the equation above tells us.
- What we still need in order to calculate the Debye length is a linkage between potentials $\mathbf{e} \cdot U(x) = V(x)$ and concentrations $c(x)$.
  - This is of course what the **Poisson equation**, the main equation for electrostatics, is all about. We will only look at the one-dimensional case here. The Poisson equation than states

$$\boxed{-\frac{d^2U}{dx^2} = \frac{dE}{dx} = \frac{\mathbf{e} \cdot c(x)}{\epsilon\epsilon_0}}$$

- We may thus assume within a very good approximation that the carrier density at any point is given by the constant volume density c_0 of the field free material, *plus* a rather small space dependent addition $c_1(x)$; i.e.

$$\boxed{c(x) = c_0 + c_1(x)}$$

  - Obviously, only $c_1(x)$ is important for Poissons equation.

- From Boltzmanns distribution we know that

$$\boxed{\frac{c(x)}{c_0} = 1 + \frac{c_1(x)}{c_0} = \exp\left(-\frac{\Delta(energy)}{kT}\right) = \exp\left(-\frac{V(x)}{kT}\right)}$$

- Since we assumed $c_1 << c_0$,

$$1 + \frac{c_1(x)}{c_0} \approx 1 + \frac{V(x)}{kT}$$

$$c_1(x) = c_0 \cdot \frac{V(x)}{kT}$$

- This is a simple trick, but important. Feeding the result back into Poissons equation yields:

$$\frac{d^2\,[c_1(x)]}{dx^2} = \frac{e^2 \cdot c_0 \cdot c_1(x)}{\epsilon \cdot \epsilon_0 \cdot kT}$$

- For a simple one-dimensional case with a surface at **$x = 0$** we obtain the final solution

$$\boxed{c_1(x) = c_1(x=0) \cdot \exp - \frac{x}{d}}$$

- The quantity ***d*** is the Debye length we were after, it is obviously given by

$$\boxed{d = \text{Debye length} = \left(\frac{\epsilon \cdot \epsilon_0 \cdot kT}{e^2 \cdot c_0}\right)^{1/2}}$$

- The *Debye length* is sometimes also called Debye-**Hückel** length (which is historically correct and just).
  - **$c_1(x = 0)$**, of course, is given by the boundary condition, which for our simple case is:

$$\boxed{c_1\,(x=0) = c_0 \cdot \frac{V\,(x=0)}{kT}}$$

Nernst's Equation

- **Nernst's equation** gives the *voltage* between two materials in close contact, i.e. the *potential difference* between the two materials.
- If the potential difference is ΔU, we thus, using the Boltzmann distribution, obtain for the concentration of the carriers c_1 in material **1**, and c_2 in material **2**:

$$\frac{c_1}{c_2} = \exp - \frac{e \cdot \Delta U}{kT}$$

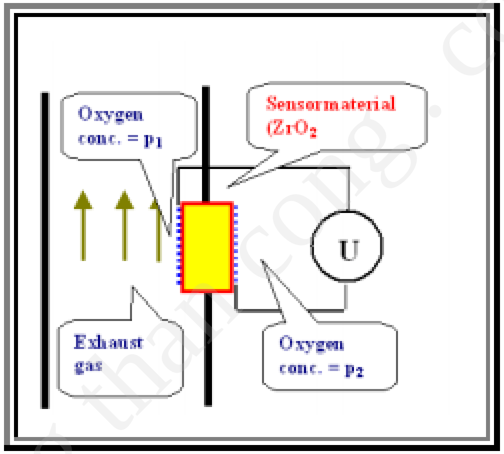
This is **Nernst's equation**

$$\Delta U = - \frac{kT}{e} \cdot \ln \frac{c_1}{c_2}$$

Nernsts law, being the Boltzmann distribution in disguise, is of course extremely general. It gives the potential difference and thus the voltage of *any* contact between two materials that have sufficiently large concentrations of mobile carriers so that an equilibrium distribution can develop. It describes, among other things

- The **contact voltage** (**Volta potential**) between two metals (i.e. **thermocouples**).
- The built-in potential in **pn-junctions**
- The voltage of any battery or accumulator.
- The voltage of fuel cells.
- The voltage produced by certain kinds of sensors.

- The last issue ***merits*** some brief explanation. Let's assume a material with a sufficiently large concentration of mobile **O^-** ions at interstitial sites (in other word, mobile interstitial point defects) at the working temperature - take **Y_2O_3** stabilized **ZrO_2** as an example (whatever that may be).
  - Use it to measure the amount of oxygen in a given gas mixture with the following **oxygen sensor** device:



- The sensor material experiences two different oxygen concentrations on its two surfaces, one of which is known (oxygen in air, a constant for all practical purposes), the other one is the concentration in the exhaust gas of a car which is supposed to be measured by the voltmeter
  - Two gas-permeable electrodes have been supplied which allow oxygen on both sides to react with the sensor material.

- In equilibrium, we will have some reaction between the oxygen in the gas and the oxygen in the crystal in the sense that oxygen will either come out, or diffuse into the material.
  - What we might expect is that the concentration of interstitial oxygen in the crystal will be larger near to the surface with the large oxygen gas concentration (air) compared to the surface exposed to a lower oxygen concentration (exhaust).
  - The gradient in the (negatively charged) oxygen concentration inside the material then will be determined by the **Debye length** of the system (in the real thing, which is **ZrO_2**, it will be just a few **nm**).
  - In total, the concentration **$[O]_S$** of mobile **O**-interstitials right at the surface will be *somehow* tied to the partial pressure **p_O** of the oxygen on both sides; lets say we have a general relation like

$$[O]_S = \left(\text{const.} \cdot p_O\right)^n$$

- Nernst's law then tells us immediately, how the voltage between the two electrodes depends on the oxygen concentration or partial pressure in the exhaust: For the assumed relation we have

$$\Delta U = -\frac{kT}{e} \cdot \ln \frac{c_1}{c_2}$$

$$\Delta U = -\frac{kT}{e} \cdot \ln \frac{(p_1)^n}{(p_2)^n}$$

$$\Delta U = -\frac{n \cdot kT}{e} \cdot \ln \frac{p_1}{p_2}$$