2.4.4 Summary to: Ionic Conductors

Electrical current can conducted by *ions* in

- Liquid electrolytes (like H_2SO_4 in your "lead - acid" car battery); including gels
- Solid electrolytes (= ion-conducting crystals). Mandatory for fuel cells and sensors
- Ion beams. Used in (expensive) machinery for "nanoprocessing".

Challenge: Find / design a material with a "good" ion conductivity at room temperature

Basic principle

- *Diffusion current* j_{diff} driven by concentration gradients **grad(*c*)** of the charged particles (= ions here) equilibrates with the
- *Field current* j_{field} caused by the internal field always associated to concentration gradients of charged particles plus the field coming from the outside
- Diffusion coefficient ***D*** and mobility **μ** are linked via theEinstein relation; concentration ***c*(*x*)** and potential ***U*(*x*)** or field ***E*(*x*) = –d*U*/d*x***by the Poisson equation.

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

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

$$\mu = eD/kT$$

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

Immediate results of the equations from above are:

- In equilibrium we find a preserved quantity, i.e. a quantity independent of ***x*** - the electrochemical potential V_{ec}:

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

- If you rewrite the equaiton for ***c*(*x*)**, it simply asserts that the particles are distributed on the energy scale according to the Boltzmann distrubution:

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

- Electrical field *gradients* and concentration *gradients* at "contacts" are coupled and non-zero on a length scale given by the **Debye length** d_{Debye}
- The Debye length is an extremely important material parameter in "**ionics**" (akin to the space charge region width in semiconductors); it depends on temperature ***T*** and in particular on the (bulk) concentration c_0 of the (ionic) carriers.
- The Debye length is not an important material parameter in metals since it is so small that it doesn't matter much.

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

The potential difference between two materials (her ionic conductors) in close contact thus...

- ... extends over a length given (approximately) by :

$$d_{Debye}(1) + d_{Debye}(2)$$

- ... is directly given by the Boltzmann distribution written for the energy:
(with the c_i =equilibrium conc. far away from the contact.

- The famous *Nernst equation*, fundamental to ionics, is thus just the Boltzmann distribution in disguise!

$$\frac{c_1}{c_2} = \exp - \frac{e \cdot \Delta U}{kT}$$	**Boltz-mann**
$$\Delta U = - \frac{kT}{e} \cdot \ln \frac{c_1}{c_2}$$	**Nernst's equation**

"Ionic" sensors (most famous the $\mathbf{ZrO_2}$ - based $\mathbf{O_2}$ sensor in your car exhaust system) produce a voltage according to the Nernst equation because the concentration of ions on the exposed side depends somehow on the concentration of the species to be measured.

Questionaire
Multiple Choice questions to all of 2.4