

2.4.4 Summary to: Ionic Conductors

Electrical current can be 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".

Basic principle

- **Diffusion current** j_{diff} driven by concentration gradients $\text{grad}(c)$ 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 the Einstein relation; concentration $c(x)$ and potential $U(x)$ or field $E(x) = -dU/dx$ by the Poisson equation.

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

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

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

$$\mu = eD/kT$$

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

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} :
- If you rewrite the equation for $c(x)$, it simply asserts that the particles are distributed on the energy scale according to the Boltzmann distribution:
- 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.

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

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

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

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

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

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

... is directly given by the Boltzmann distribution written for the energy:
(with the c_1 = equilibrium conc. far away from the contact.

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

"Ionic" sensors (most famous the ZrO_2 - based 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.

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

$$\Delta U = - \frac{kT}{e} \cdot \ln \frac{c_1}{c_2} \quad \text{Nernst's equation}$$

Questionnaire

Multiple Choice questions to all of 2.4