2.5 Ionic Conductors

2.5.1 General Remarks

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.

In contrast to purely electronic current transport, there is *always* a chemical reaction tied to the *current flow* that takes place wherever the ionic current is converted to an electronic current - i.e. at the contacts or electrodes. There may be, however, a measurable potential difference *without* current flow in ionic systems, and therefore applications *not* involving chemical reactions.

- This is a big difference to current flow with electrons (or holes), where no chemical reaction is needed for current flow across contacts since "chemical reactions " simply means that the system changes with time.

If we look at the conductivity of solid ionic conductors, we look at the movement of ions in the crstal lattice - e.g. the movement (= diffusion) of O^- or H^+ ions either as interstitials or as lattice ions.

- In other words, we look at the diffusion of (ionized) atoms in some crstal lattice, described by a diffusion coefficient *D*.
- 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*.

Ionics is the topic of dedicated lecture courses, here we will only deal with two of the fundamental properties and equations - the **Debye** length and the **Nernst** equation - in a very simplified way.

- The most general and most simple situation that we have to consider is a contact between two materials, at least one of which is a *solid ionic conductor* or solid electrolyte. Junctions with liquid electrolytes, while somewhat more complicated, essentially follow the same line of reasoning.

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**

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

- 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.

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

With μ = **mobility** of the particle.

Both driving forces may be present *simultaneously*; the total current flow or voltage drop then results from the combined action of the two driving forces.

Note that in one equation the current is proportional to the *gradient* of the concentration whereas in the other equation the proportionality is to the concentration *directly*. This has immediate and far reaching consequences for all cases where in equilibrium the two components must cancel each other as we will see in the next sub-chapter.

In general, the two partial currents will not be zero and some *net* current flow is observed. Under equilibrium conditions, however, there is no net current, this requires that the partial currents either are all zero, or that they must have the same magnitude (and opposite signs), so that they *cancel each other*.

The equilibrium condition thus is

$$q \cdot j_{diff} = j_{field}$$

The importance of this equation cannot be over emphasized. It imposes some general conditions on the *steady state concentration profile* of the diffusing ion and thus the charge density. Knowing the charge density distribution, the potential distribution can be obtained with the **Poisson** equation, and this leads to the *Debye length* and *Nernsts law* which we will discuss in the next paragraphs.

Questionaire
Multiple Choice questions to all of 2.4