

## 7. IONIC CONDUCTION

In this lecture we give an overview of the basic concepts concerning ionic conduction in solids. We treat mainly the case where electrical transport is dominated by ionic movements, but also describe how to distinguish ionic from electronic conduction.

Ionic conduction can occur in both crystalline and amorphous materials. Both anions and cations can carry the current. In amorphous solids cation motion is the most common, but also anions such as  $F^-$  or  $O^{2-}$  can be of importance. The highest ionic conductivities are obtained in cases where small ions like  $H^+$  and  $Li^+$ , or very deformable ones like  $Ag^+$  are present. Ionic conductivities can be as high as above  $10^{-2}$  S/cm at room temperature in so called “superionic materials”. Ion conductors have various technological applications in for example fuel cells, batteries and electrochromic devices.

The ionic conduction is usually thermally activated below the glass transition temperature. It is due to thermally activated hopping of ions over an energy barrier between equivalent sites in the structure. In the strong electrolyte model, all the ions are considered to be active in the conduction process. The energy barrier is due to an electrostatic term due to Coulomb interactions and a strain energy term, because the ion has to push on other atoms in order to pass from one site to another. Both terms depend on the length of a single hop. In the weak electrolyte model, ions are trapped and have to be excited to a transport state in order to participate in the transport process. This model has mainly been developed by using thermodynamic concepts. For more reading, see Elliott Ch. 4.5 .

In mixed conductors, we have both ionic and electronic contributions to the conductivity. In order to distinguish them one can use different electrodes when measuring the conductivity. In the case of ion blocking contacts (most metals), the conductivity at sufficiently long times will be due only to the electrons. The opposite holds for electron blocking contacts, for example electrolytes. In addition the diffusion coefficient of the blocked species can be obtained from the transient behaviour. Some methods (transient currents and impedance spectroscopy in the frequency range of electrode polarisation) can be used to determine both the concentration of ions participating in the conduction process, as well as their mobility. Regrettably they have been little used.

We discuss the ac conductivity of ionic conductors. By so called Broadband Dielectric Spectroscopy, it is possible to study the dynamics of the ion transport on time scales from picoseconds to thousands of seconds. Starting at the low frequency end, one observes electrode polarisation, dc conductivity, a power-law ( $\omega^n$ ) frequency response, and a high-frequency relaxation crossing over to the response of the vibrational modes at infrared frequencies. A multitude of mechanisms have been proposed for the power-law response, but the theoretical situation is far from clear.

Percolation models can be used for ionic conduction in several cases, specifically when the high ionic conductivity is due to doping of a glass with a compound containing a very mobile ion, or when the material contains two or more mobile ions. We conclude with two examples: 1. The ac conductivity of AgI-silver borate glass shows a behaviour consistent with fractal dynamics and a power-law exponent close to the one expected for percolation. In this case the ionic conduction is almost entirely due to the AgI component. 2. When there are two mobile ions, the “mixed mobile-ion effect” is observed. The conductivity exhibits a minimum when there are an equal number of the two ions. They seem to hinder each others movement. This

behaviour can be qualitatively understood from a three-component percolation model, employing A and B sites occupied by the two types of ion as well as empty C sites.