Conductivity Spectroscopy on Ionic Materials with Disordered Structures

Klaus Funke,* Radha D. Banhatti

Westfälische Wilhelms-Universität Münster, Institut für Physikalische Chemie und Sonderforschungsbereich 458, Corrensstraße 30, D - 48149 Münster, Germany

E-Mail: k.funke@uni-muenster.de

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Conductivity spectroscopy spans more than 17 decades on the frequency scale, ranging from a fraction of a mHz up to about 100 THz. It provides a time-resolved view of the dynamics of the mobile ions in materials with disordered structures, acting as a "microscope in time". It thus has the potential to elucidate the development from an individual ionic displacement or hop to macroscopic transport of mass and charge, *i.e.*, from less than a picosecond up to minutes and hours.

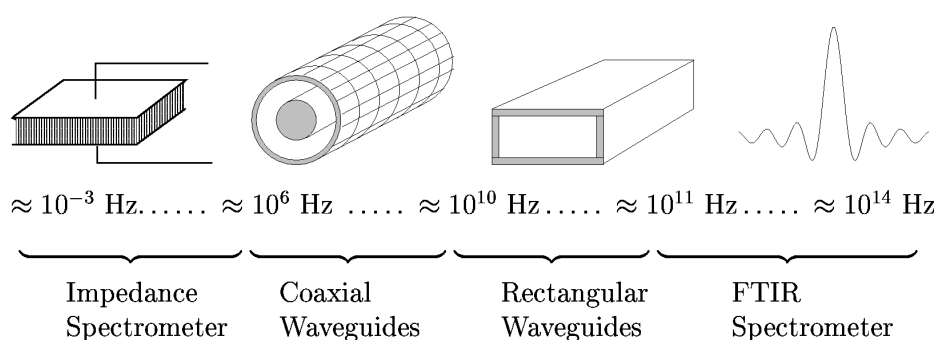The experimental set-ups required to cover the entire frequency range are sketched in Fig. 1.

$$\approx 10^{-3} \text{ Hz.} \ldots \ldots \approx 10^{6} \text{ Hz } \ldots \ldots \approx 10^{10} \text{ Hz} \ldots \ldots \approx 10^{11} \text{ Hz} \ldots \ldots \approx 10^{14} \text{ Hz}$$

| Impedance Spectrometer | Coaxial Waveguides | Rectangular Waveguides | FTIR Spectrometer |

Fig. 1 Schematic overview of techniques for the measurement of frequency-dependent conductivities.

Linear response theory is essential for relating conductivity spectra to time-correlation functions, which reflect the basic aspects of the ion dynamics in the sample. As it turns out, it is possible to sketch the dynamics in terms of a set of rules which, at the same time, reproduce the experimental spectra. We present such rules, written in the form of simple rate equations. The rules constitute the so-called MIGRATION concept [1].

Recently, this model treatment has been successfully applied to reproduce and explain the "universal" properties displayed by conductivity spectra of ion-conducting materials with disordered structures. These properties include scaling and, even more importantly, those ubiquitous features that have come to be known as "first" and "second" universality, to be outlined below.

As long as the conduction mechanism does not change with temperature, the low-frequency part of the conductivity spectrum of a disordered ion-conducting material is found to *scale*, which means that a "master curve" can be created by suitably superimposing spectra taken at different temperatures. Surprisingly, virtually the same "master curve" is obtained for materials with quite different structures, *viz.*, crystals, glasses, polymers and even ionic liquids. This unexpected finding is called the *"first" universality*. A universal function providing the correct relationship between scaled conductivities and scaled frequencies has indeed been derived from the MIGRATION concept.

Figure 2 (a) is a log-log plot of frequency-dependent conductivity isotherms of a glassy ion conductor. In the figure, the shape of the "first"-universality function clearly determines the spectra at temperatures above, say, 0 °C.

At low temperatures, however, with the 4 K and 125 K isotherms hardly differing from each other, the *"second" universality* [2] comes into view. The phenomenon is usually called "Nearly Constant Loss (NCL)" effect, since the loss function, which is proportional to conductivity divided by frequency, appears to become independent of both temperature and frequency.

While Fig. 2 (a) does not provide a clue for identifying a crossover from the "first" to the "second" universality, this is easily achieved, if the data are plotted versus temperature, as in Fig. 2 (b). Here, the solid lines represent the conductivity component due to regular hopping. The lines result from the high-temperature data in Fig. 2 (a) by reproducing them in terms of the MIGRATION concept and by using the scaling property for the transformation into Fig. 2 (b). Subtracting the solid lines from the experimental data yields the dashed horizontal lines which, at conductivities proportional to frequency, represent the "second" universality [3].

On the basis of the MIGRATION concept, a model is proposed for the physical origin of the NCL phenomenon. The effect is traced back to a large number of interacting ions, each of them moving locally. The key aspect is the Coulomb interaction between these ions which causes a "see-saw-type" time dependence of their individual single-particle double-well potentials [3].
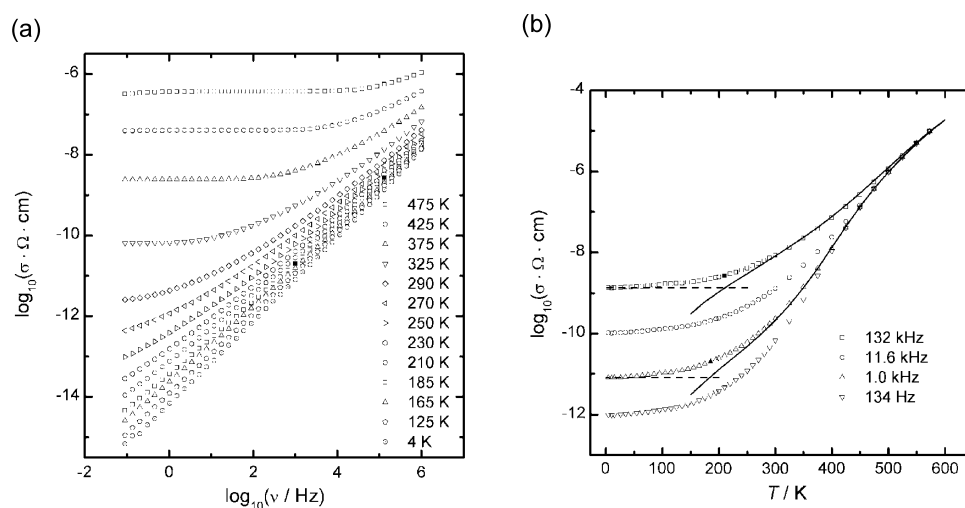

Fig. 2 (a) Log-log plot of the frequency-dependent conductivity of glassy $0.3\,Na_2O \cdot 0.7\,B_2O_3$ at different temperatures. (b) Semi-log plot of the temperature-dependent conductivity of this glass at four frequencies. In (a) and (b), darkened data points indicate the crossover from the "first" to the "second" universality.

References

[1]   K. Funke, R. D. Banhatti, Solid State Ionics 169 (2004) 1.
[2]   W.-K. Lee, J. F. Liu, A. S. Nowick, Phys. Rev. Lett. 67 (1991) 1559.
[3]   D. L. Laughman, R. D. Banhatti, K. Funke, Phys. Chem. Chem. Phys. 11 (2009) 3158.