MODELLING OF IMPEDANCE SPECTROSCOPIC DATA AS A MEANS OF DETERMINING THE ELECTRICAL PROPERTIES OF MULTIPLE PHASES IN SOLID STATE IONIC CONDUCTORS

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Introduction

Impedance spectroscopy is a characterisation technique that has been extensively employed for the measurement of the conductivity of solid-state ionic conductors [1, 2]. The electrical properties of the material under study are calculated by analysing the high-frequency branch of the spectrum. In case of multiple phases being present in the material, the high-frequency branch consists of multiple circular arcs [1, 3], that are not always clearly resolved in the spectrum's Nyquist plot. In such a case, modelling of the impedance spectrum by an equivalent circuit is a necessary means of extracting the electrical properties of the distinct material phases.

Experimental

The sample chosen to exemplify the modelling procedure is a lithium fast-ion conductor, 4.5 Li_2O – B_2O_3, in the form of a thin slab, 610 μm thick. Lithiated boron oxides are a class of vitreous solid-state ionic conductors that exhibit high lithium-ion conductivity, which increases as the lithium content in the material increases [2]. At high lithium content a second, crystalline, phase appears besides the vitreous one, in the form of crystallite islands against the glassy background [4]. Details on the preparation of the sample have been given elsewhere [4]. Ohmic contacts on both sides of the sample slab were provided by thermal evaporation of gold.

Results and Discussion

The Nyquist plot of the impedance spectrum of the sample at 132 ^{o}C temperature is shown in Fig.1. The frequency range of the measurements is 1 Hz to 100 kHz. Two different fits to the experimental data are presented. As a first approach, the high-frequency branch of the spectrum is treated as a single semi-circular arc. According to a refined fitting approach, the same branch is considered to be a combination of two overlapping semi-circular arcs. The electrical equivalent circuit, whose frequency response in Nyquist representation turns out a semi-circular arc, is a resistor parallel to a constant phase element, which is sometimes termed the Voigt element [1]. Therefore, the first fitting approach models the material bulk properties as a single Voigt element, while the second approach as two Voigt elements in series.

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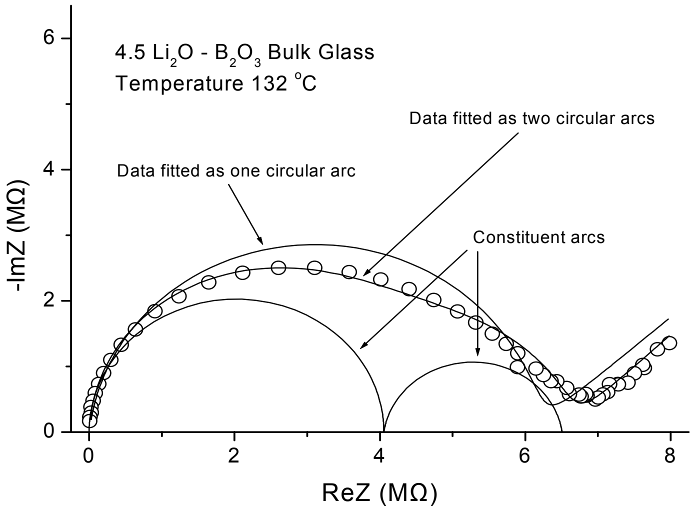

Fig.1 *Nyquist plot of the impedance spectrum of the sample at 132 °C, fitted with the high-frequency branch modelled as one or two circular arcs. The constituent arcs in the latter case are also shown.*

It is clear from Fig.1 that the data is not fitted very well when modelled as a single arc. The result that the high-frequency branch of the spectrum actually consists of two arcs indicates the presence of two phases in the sample, a fact that can be verified by Scanning Electron Microscopy (SEM) measurements [1, 4]. However, the equivalent circuit, consisting of two Voigt elements in series, implies that the two phases within the material microstructure are distinctly separated and stacked in consecutive parallel layers. Another equivalent circuit, whose frequency response is similar to that of the two Voigt elements and in practice provides a better fit to the data, is shown in Fig.2. The resistors R_1 and R_2 model the DC resistance that the vitreous and crystalline phases, respectively, present to the ionic current. The constant phase element Q_2 in parallel to the resistor R_2 suggests that the ionic charge is partly blocked at the boundaries between the vitreous and crystalline phase.

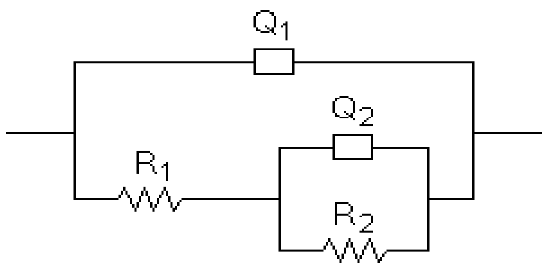

Fig.2 *Equivalent circuit modelling the material bulk properties.*

After a series of impedance spectra had been recorded at various temperatures and the high-frequency branch data fitted to the model circuit of Fig.2, the Arrhenius plot Fig.3 was used to extract the activation energy of the ionic conductivity for the two phases (Fig.3). The temperature range of the impedance measurements was 95 °C to 175 °C. The calculations turned out different activation energies for the two phases, 0.67 eV and 0.79 eV for the vitreous and crystalline phase, respectively.

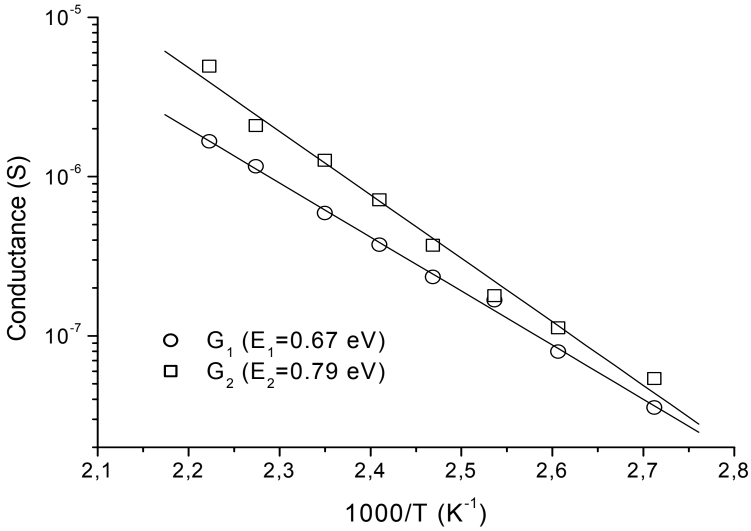

Fig. 3 *Arrhenius plot of the conductance corresponding to the vitreous (G_1) and crystalline (G_2) phases present in the sample.*

Conclusions

The presence of multiple phases in an ionically conducting solid is reflected in the impedance spectrum and, more specifically, in the high-frequency branch being constructed out of multiple semi-circular arcs. Fitting of the experimental data to an appropriate equivalent circuit, related to the material microstructure, can yield the electrical properties of the individual phases making up the material. The above process was exemplified by analysing the impedance spectra of a sample slab of 4.5 Li_2O – B_2O_3 lithium-ion conductor obtained over a range of temperatures.

References

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