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TECHNICAL NOTE

A chronopotentiometric determination of D_{Ag^+} in α-Li_2SO_4

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Kvist [1] has published an extensive series of papers on the electrochemical and other properties of α-Li_2SO_4 and solid solutions therein. Lithium sulphate exhibits a phase transformation around 585°C. Above this temperature, face-centred cubic α-Li_2SO_4 is the stable phase. The Li^+ ions are thought to be mainly distributed over the tetrahedral lattice positions; Li^+ ions in octahedral positions can be considered to be thermal defects. The silver ion is small enough to fit into octahedral positions but is too large for the tetrahedral positions. The conductivity of this phase is almost as high as that of the corresponding melt which exists above about 860°C. Thus techniques such as chronopotentiometry, which have proved particularly useful in the study of molten salt solutions, should be directly applicable to this solid. Kvist [2] has *inter alia* determined the diffusion coefficients of a series of univalent cations including Ag^+ in Li_2SO_4, using a radio-tracer technique to monitor the movements of the ions down a column of salt. Therefore to illustrate the usefulness of chronopotentiometry for electrochemical studies in this medium we have determined the diffusion coefficient of silver ion.

The experimental set-up was very simple. A platinum crucible contained the electrolyte and also served as the macro-counter electrode. The micro-cathode was a gold wire which was embedded in the surface of the electrolyte, concentric with the platinum crucible.

The appropriate quantity of silver sulphate was admixed with the solvent lithium sulphate which had been previously dried in an oven at 160°C. The mixture was then melted for a short time and the gold wire cathode immersed to the appropriate depth. The temperature was then reduced below the melting point to the desired temperature.

The input electrical signal, in this case applied between a macro-anode and a micro-cathode, is a square wave current pulse and the output signal a cathode potential vs. time profile which was recorded on a storage oscilloscope. The time which elapses between the application of the pulse and the appearance of a sharp inflection on the cathode potential/time profile (the transition time τ) is given by the expression (for semi-infinite linear diffusion conditions).

$$\tau = \frac{n^2 F^2 \pi D C^2}{4i^2}$$

where n is the number of electrons involved in the unit electrode process, F is the Faraday, D the diffusion coefficient, C the concentration of ions undergoing reduction and i the cathodic current density. In the present work, transition times were determined as a function of a series of applied current densities (see fig. 1). The linear nature of this plot and the lack of an intercept indicate that, at least with regard to the limiting condition, the process is diffusion-controlled. On this basis, D_{Ag^+} at 700°C has been calculated to be $2{\cdot}19 \times 10^{-5}$ cm^2 s^{-1}, which is in good agreement with the value previously published by Kvist ($2{\cdot}34 \times 10^{-5}$ cm^2 s^{-1}).

Chronopotentiometry thus appears to be a useful method for the rapid determination of diffusion coefficients in solid electrolytes, at least when the solid electrolytes behave like conventional molten salts. Some work in B_2O_3-Na_2O [3] glasses has indicated that diffusion coefficients as low as 10^{-9} cm^2 s^{-1} can be determined without special modifications

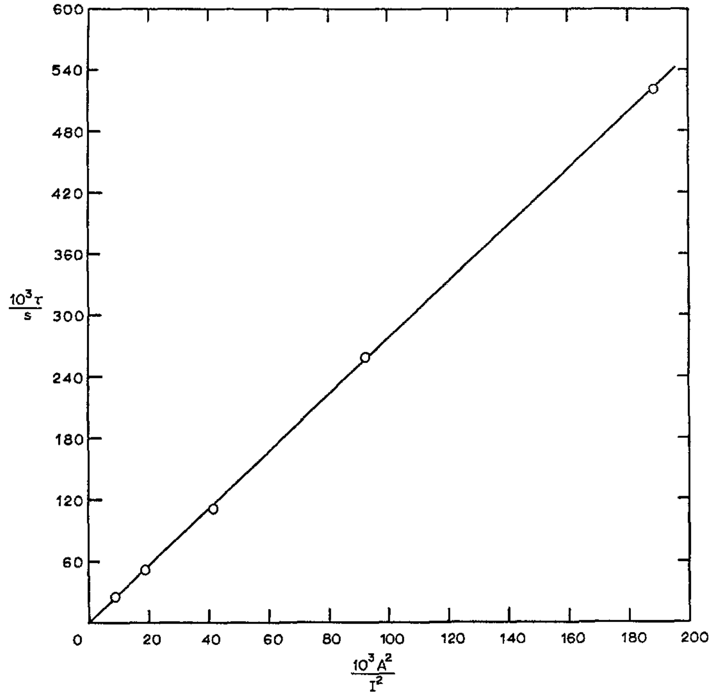

Fig. 1. τ v $1/I^2$ (τ, the transition time; s, seconds; I, the applied current; A, amperes).

to the equipment. Above all, however, chronopotentiometry enables rapid monitoring of diffusion coefficient-determining structural changes in the solid electrolytes as evidenced in an extension of the present work [4] at the $\alpha \rightarrow \beta$ phase transition.

References

[1] Series of papers in *Z. Naturforsch.* 1964 to date.
[2] A. Kvist and A. Bengtzelius, *Z. Naturforsch.*, **23a** (1967) 679.
[3] D. Inman and D. M. Wrench, to be published (see D. M. Wrench, Thesis, London, 1968).
[4] D. Inman and M. Johnson, to be published.