

Migration Losses in Single-Crystal Ionic Conductors: Sodium Beta Alumina and LiGaO₂

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Dispersions have been observed in the ac conductivity of 2 single-crystal ionic conductors, Na β -alumina and LiGaO₂. The results have been analyzed in the complex modulus formalism, M^* , where $M^* = (\epsilon^*)^{-1}$. It is suggested that these dispersions represent conductivity losses and are similar to those observed in glasses. The losses are related to the mechanism of ion migration and may be a characteristic feature of many ionically conducting crystalline materials.

I. Introduction

THE electrical properties of glasses and solid electrolytes are often studied by ac methods. The variable frequency effects which are observed arise from several causes. Glasses are generally simpler than polycrystalline solid electrolytes because intergranular effects are absent. They show mainly 2 dispersions caused by (1) electrode polarization (only if blocking electrodes are used) and (2) migration losses or conductivity relaxation. It has commonly been assumed that significant migration losses are a property of disordered materials such as glasses and (by implication) will not, therefore, be expected in crystalline materials. However, recent results from the present laboratory gave evidence of a frequency dispersion in polycrystalline Li₄SiO₄, which could result from migration losses¹; the uncertainty arose because anisotropic conductivity coupled with the polycrystallinity of the samples could also give the same effect.

In the present paper, we report the results of an investigation into the occurrence of migration losses in single crystals of 2 very different materials, i.e. Na β -alumina and LiGaO₂. We believe that the results will be of wide significance in the understanding of conduction mechanisms in both glassy and crystalline materials. A preliminary note on migration losses in β -alumina has been published.²

Associated with the recent increasing interest in solid electrolytes, there has been a diversification in the methods of analyzing conductivity data. Results can now be analyzed in any of 4 basic formalisms: the complex impedance, Z^* ; complex admittance, A^* or Y^* ; complex permittivity, ϵ^* ; and complex modulus, M^* . In the present work, we have used the complex modulus method, which is both suitable for the present problem and allows an easy comparison with literature results on glass. The theory of the complex modulus³ and its application to solid electrolytes⁴ has been covered adequately in the literature; only the main points will be summarized herein.

The complex electric modulus, M^* , is defined:

$$M^* = (\epsilon^*)^{-1} = (\epsilon' - j\epsilon'')^{-1} \quad (1)$$

The imaginary component M'' is given by:

$$M'' = \epsilon'' / [(\epsilon')^2 + (\epsilon'')^2] \quad (2)$$

For an equivalent circuit which consists of a resistance, R_p , and capacitance, C_p , in parallel, substituting for ϵ' and ϵ'' in Eq. (2) gives⁴

$$M'' = (C_0/C_p) \{ \omega R_p C_p / [1 + (\omega R_p C_p)^2] \} \quad (3)$$

where C_0 is the vacuum capacitance of the cell. Therefore, a plot of M'' vs angular frequency, ω , gives a Debye peak of height proportional to $1/C_p$.

Every parallel RC element in the equivalent circuit of a solid electrolyte or cell will give its own Debye peak, but an important feature of these "modulus spectra" is that RC elements corresponding to electrode double-layer or interfacial effects will give extremely small and generally nondetectable peaks because their C_p values are, relatively, much too large. Thus, the broadening of the modulus spectra reported and discussed here represents bulk crystal properties and is not caused by interfacial phenomena. Should one wish to study interfacial effects (which are generally detected at frequencies lower than bulk dispersions are), some other method of data analysis, e.g. complex impedance analysis, must be used.⁴

II. Experimental Procedures

For choosing materials suitable for study, the following criteria were adopted. The crystals should exhibit ionic conductivity at some temperature, preferably by migration of alkali cations. Electronic conductivity should be negligible compared with ionic conductivity. The crystal structure should be fairly complex, e.g. alkali halides were unsuitable for these experiments. Readily available to us in single-crystal form and satisfying these criteria were Na β -alumina from 2 sources and LiGaO₂. The β -alumina crystals used were (1) optically transparent, irregularly shaped, thin flakes with the crystallographic c axis perpendicular to the flakes¹ and (2)

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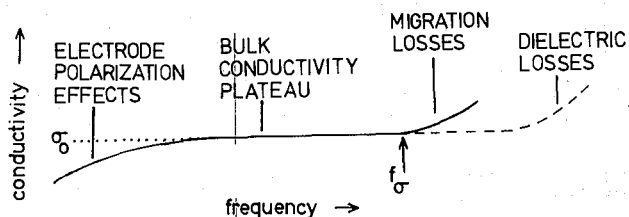


Fig. 1. Schematic frequency spectrum for single-crystal solid electrolyte showing possible conductivity dispersions which may occur.

cylindrical boules 0.5 in. in diameter with smooth, flat ends,* the conduction planes, which were perpendicular to c , were parallel to the cylinder axis. The crystals were not analyzed chemically, but single-crystal, X-ray rotation photographs of small fragments showed that both types of crystal were the 2-block, 22-Å, β -modification. Powder X-ray patterns of crushed fragments of the 2 crystals were also very similar. The LiGaO_2 crystals† were irregularly shaped blocks with 2 flat, opposite faces measuring ≈ 0.2 by ≈ 0.2 in. The crystals were slightly yellow, perhaps because they contained some residual lead borate flux. The X-ray powder diffraction analysis showed LiGaO_2 as the only crystalline phase present. The crystallographic orientation is not known.

The experimental setup and apparatus were similar to those used previously.^{1,4} Briefly, gold electrodes were formed from gold paste or evaporated gold. For the β -alumina flakes, opposite edges were embedded in Au paste in a 2-terminal arrangement. For the β -alumina boules, a thin layer of gold was evaporated onto opposite boule faces, and contact with the Pt leads was made via Au paste. A 3-terminal arrangement was used, i.e. one face of the boule was not completely covered with Au but was divided into a central spot and an outer ring, as used previously.¹ Only the conductivity of that part of the boule covered by the central spot was effectively measured, thus any possible surface effects were eliminated. A 3-terminal arrangement was also used for the LiGaO_2 crystals, but contact with the crystals was made directly via Au paste. The sample and jig were heated in a tube furnace (LiGaO_2) or cooled in slush baths (β -alumina), in all cases in an atmosphere of dried N_2 . Conductivities and capacitances were measured over the frequency range 10^2 to 10^7 Hz.

III. Theory

When migration losses are studied in crystals, conductivities must be measured over the appropriate frequency range. In Fig. 1, a schematic generalized frequency spectrum for a single-crystal solid electrolyte is given. The frequencies at which migration losses occur (if at all) are related to the value of the dc or plateau conductivity, σ_0 , which has an associated conductivity relaxation time, t_σ , given by

$$t_\sigma = RC = \epsilon_0 \epsilon' \infty / \sigma_0 \quad (4)$$

where R is the resistance, C the bulk or geometric capacitance, ϵ_0 the permittivity of free space ($8.854 \times 10^{-14} \text{ F cm}^{-1}$), and $\epsilon' \infty$ the relative permittivity of the sample at high frequencies. Also, t_σ has an associated frequency, f_σ , given by

$$f_\sigma = \omega / 2\pi = 1 / (2\pi t_\sigma) \quad (5)$$

and any migration losses will occur at frequencies around f_σ .‡ For most materials, $\epsilon' \infty \approx 5$ to 10 and, therefore, for f_σ to occur in the frequency range 10^2 to 10^7 Hz, σ_0 must be in the range 5×10^{-10} to $5 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$. Consequently, β -alumina (which at

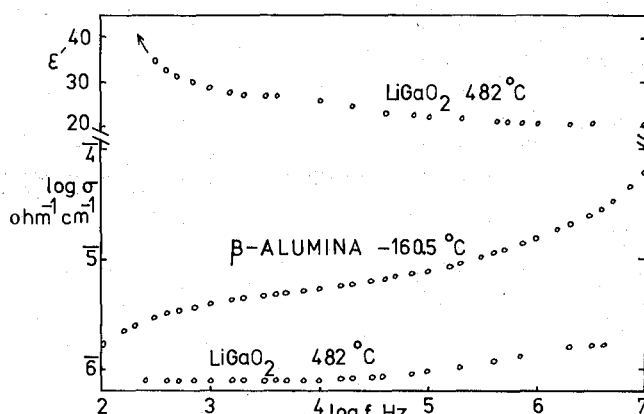


Fig. 2. Frequency dependence of conductivity and relative permittivity for LiGaO_2 and of conductivity for β -alumina single crystals. Error bars for σ and ϵ' represent $\pm 1\%$.

room temperature has a conductivity of $\approx 0.002 \Omega^{-1} \text{ cm}^{-1}$ (Ref. 5)) must be cooled to below room temperature if its migration losses are to be studied with conventional ac bridges. On the other hand, LiGaO_2 is a very poor ionic conductor and must be heated to 500°C to obtain appropriate conductivities.

IV. Results

Results are given in Fig. 2 for the frequency dependence of the conductivity, σ , at one temperature for LiGaO_2 and β -alumina. For LiGaO_2 at 482°C , the conductance dispersion begins at $\approx 10^4$ Hz, and below this temperature a good plateau is observed. For β -alumina at -160.5°C , only a rather poorly defined plateau with $\log \sigma_0 = 6.73 \Omega^{-1} \text{ cm}^{-1}$ is observed between electrode and bulk dispersion regions; similar results were obtained for both types of β -alumina crystal. Also shown in Fig. 2 are relative permittivity data for LiGaO_2 . Above 10^4 Hz, a small dispersion in ϵ' occurs which is associated with the corresponding conductivity dispersion; at lower frequencies, the tail end of a dispersion in ϵ' results from electrode polarization. Permittivity data for β -alumina are not shown since the two dispersions are not visibly separated.

The data which were selected for presentation in Fig. 2 were chosen because they contain the conductivity plateau, part of the electrode polarization dispersion, and part of the high-frequency bulk dispersion, all at the same temperature and in the frequency range available. An increase in the temperature causes both dispersions to move to higher frequencies.¹ Thus, at higher temperatures, less was seen of the high-frequency dispersion and more of the electrode polarization, and vice versa at lower temperatures. The temperature dependence of the high-frequency dispersion depends on the value of σ_0 and can be predicted using Eq. (5) (also see Fig. 4 later).

The high-frequency dispersions in σ and ϵ' which are shown in Fig. 2 can be interpreted in terms of a distribution of conductivity relaxation times. The nature of this distribution is better seen by analyzing the data in terms of the complex electric modulus, M^* . When a material is characterized by a single relaxation time (i.e. the equivalent circuit is a single, parallel RC element), the modulus spectrum (plot of imaginary component, M'' vs $\log f$) is a single Debye peak (Fig. 3, curve 1). A distribution of relaxation times (corresponding to a series array of parallel RC elements) gives either band broadening or multiple peaks, depending on the relative relaxation times of the constituent RC elements. Experimental modulus spectra are given in Fig. 3 for LiGaO_2 and β -alumina crystals; literature data for LiAlSiO_4 glass are included for comparison. The peaks are normalized so that the peak maxima coincide. The modulus spectra of all the single crystals are broader than Debye peaks, and it is especially notable that the spectra for β -alumina crystals are broader than those which have been reported previously for silicate glasses. The similarity in the modulus spectra

*Roditi Corp., London, England; grown by the Union Carbide Corp., New York, N.Y.

†Obtained from B. Wanklyn, Clarendon Laboratory, Oxford University, England.
‡It is, of course, possible that other phenomena such as intergranular effects, crystal misorientation coupled with anisotropic conductivity, and Maxwell-Wagner effects may also give losses at frequencies around f_σ . (The Maxwell-Wagner effect refers to the dispersion which may be observed in a system consisting of conducting droplets dispersed in a nonconducting medium.) However, these phenomena should all be absent from the present single-crystal materials.

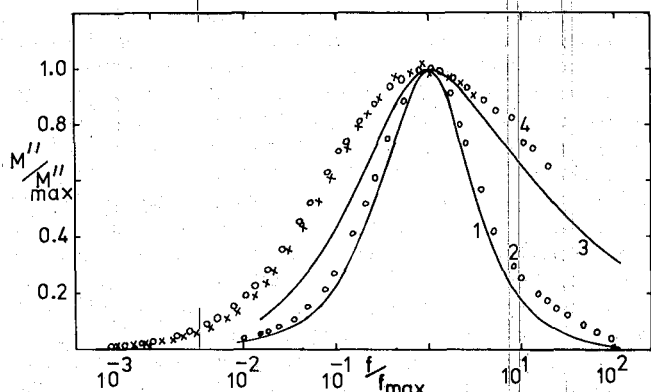


Fig. 3. Experimental modulus spectra (M'' vs $\log f$) for β -alumina and LiGaO_2 single crystals. Curve 1 represents Debye peak, curve 2 LiGaO_2 at 482°C , curve 3 LiAlSiO_4 glass (Ref. 6), curve 4 β -alumina at -160°C ; \times = cylindrical boules, \circ = flakes.

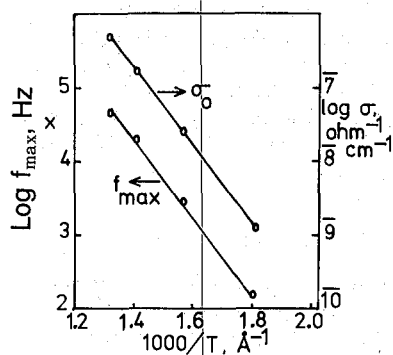


Fig. 4. Arrhenius plots for LiGaO_2 single crystal of plateau conductivity values ($E=24.2$ kcal mol $^{-1}$) and modulus peak maxima ($E=24.0$ kcal mol $^{-1}$).

of β -alumina crystals from different sources and modes of preparation provides very strong evidence that the observed dispersion is a fundamental property of the crystals.

A further indication that the conductivity plateau and its related high-frequency dispersion (Figs. 1 and 2) are in fact part of the same process is given in Fig. 4. Arrhenius plots of the σ_0 values and the frequencies of the modulus peak maxima for LiGaO_2 give essentially the same activation energy. If the dispersion were caused by localized dielectric losses, it might be expected to have a lower activation energy than that resulting from any long-range conduction losses occurring in the same sample. The dispersion is not caused by electrode or interfacial polarizations, because modulus spectra discriminate heavily against such high-capacitance effects^{3,4} and there is a good qualitative correlation between the size of the conductivity dispersions in Fig. 2 and the breadth of the corresponding modulus peaks in Fig. 3. The activation energy for conduction in β -alumina (3.10 kcal mol $^{-1}$ between -98° and -160°C), obtained from the σ_0 values or inflection points (Fig. 2), is in fair agreement with previous literature values (3.78 kcal mol $^{-1}$, Ref. 5) but data were obtained at insufficient temperatures to determine activation energies corresponding to the maximum of the modulus peak. The modulus peaks can be characterized both in terms of their width at half height (Table I) and their shape. For β -alumina, the peak is similar to that observed in glass, i.e. it is noticeably asymmetric with a high-frequency tail.

V. Discussion

For the reasons given earlier, the conductivity dispersions observed at high frequencies in β -alumina and LiGaO_2 single crystals can be associated with the processes of bulk conduction. The precise cause of the dispersions is at present uncertain although they may be related to various microscopic models of the conduction

Table I. Peak Shape Parameters for Modulus (M'' vs $\log f$) Spectra

Material tested	Peak width at half-height
Parallel RC element	1.15 (Debye peak)
LiGaO_2 single crystal	1.34 (1.17 Debye peaks)
Na β -alumina single crystal	≈ 4.5 (≈ 3 Debye peaks)
Li_4SiO_4 polycrystal (Ref. 15)	1.94 (1.69 Debye peaks)

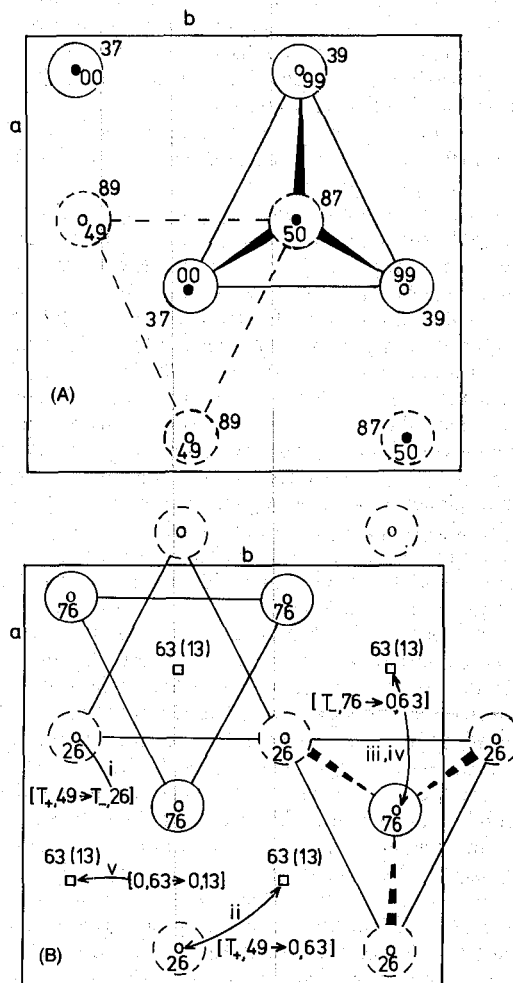


Fig. 5. (A) A (001) projection of LiGaO_2 crystal structure (Ref. 7). Atom heights are given as percents of c cell dimension. Oxygen atoms form close-packed layers at heights of ≈ 38 (large solid circles) and ≈ 88 (dashed circles); small filled circles represent Ga, small open circles Li. Tetrahedral coordination of one Ga at height 50 is shown; 3 oxygens at ≈ 38 form the base and 1 oxygen at 87 the apex. (B) Empty octahedral (squares) and tetrahedral (small circles) sites in LiGaO_2 .

mechanism. The explanations are based on 2 alternative approaches; the explanation is formulated in terms of a distribution of energy barriers for individual ion jumps or in terms of a short-range ion atmosphere relaxation related to the long-range Debye-Falkenhagen effect. These two possibilities will be discussed first for LiGaO_2 , whose crystal structure is well characterized.

(1) LiGaO_2

The LiGaO_2 has an ordered tetrahedral structure derived from the wurtzite (ZnS) structure.⁷ The oxygen atoms (or ions) form an approximately hexagonal close-packed array with the cations ordered over one set of tetrahedral sites (Fig. 5(A)). With this arrangement, the (LiO_4) and (GaO_4) tetrahedra all point in the same

direction, i.e. along the positive c axis in Fig. 5(A). The LiGaO_2 structure has many empty sites: for every occupied tetrahedral site (say T_+), there is an empty tetrahedral site (T_-) which points in the opposite direction and an empty octahedral site (O) (Fig. 5(B)). Conduction in LiGaO_2 is assumed to occur with the aid of the Frenkel disorder and involves the migration of Li^+ ions through interstitial sites, i.e. the normally empty T_- and O sites. This model has yet to be proven but there seems to be no other simple alternative mechanism.

Consideration of the structure and the ion jumps possible shows that long-range migration of Li^+ in any direction necessarily involves several types of jump and, therefore (according to the first model for the conductivity dispersion just discussed), several different activation energies. Thus, for Li^+ in a T_+ site, there are two possible first (or starter) jumps, i.e. $T_+ \rightarrow T_-(i)$ or $T_+ \rightarrow O(ii)$ (Fig. 5(B)). Subsequent jumps can then be (in addition to the reverse of the above two jumps which regain the status quo): $T_- \rightarrow O(iii)$, $O \rightarrow T_-(iv)$, or $O \rightarrow O(v)$.

All of these jumps occur between two adjacent polyhedra connected by a common face of 3 oxygens. Further differences in jump activation energies may arise because the windows are not all of the same size. For example, the window for $O(63) \rightarrow O(13)$ in Fig. 5(B) is of a different size than that for $O(63) \rightarrow O(113)$; in the former, the 3 window edges are also the edges of two (LiO_4) and one (GaO_4) tetrahedra, respectively, whereas in the latter, two (GaO_4) and one (LiO_4) tetrahedron edges comprise the window. Therefore, it could be argued that conduction involves a distribution of activation energies, with the highest activation energy in the series process controlling the dc conductivity. The conductivity dispersion arises as the higher activation energy jumps are gradually relaxed out with increasing frequency. A similar model involving a distribution of barrier heights or activation energies has been proposed to account for the migration losses in glass^{3,8} although in glass the actual sites involved cannot be specified.

The conductivity dispersion could also arise quite simply as a consequence of the conduction process. Conduction losses in glasses have been formulated in terms of the Debye-Falkenhagen effect,^{9,10} and more recently, the concept of screening charge has been introduced to account for both conduction and dipolar losses in a much wider range of materials.¹¹ These treatments differ in several ways but there are also important similarities. Thus, the mobile ion (or defect) imposes a coulomb-like potential on the surrounding medium, which tends to repel like charges and attract oppositely charged particles nearby. Every mobile ion, therefore, has its associated ion atmosphere or screening charge which decreases rapidly to zero outside a sphere several Debye lengths in diameter. Details of these theories may be obtained from the references cited; it is sufficient to note here that both can account qualitatively for an increase in conductivity with increasing frequency.

In lithium gallate, a very poor ionic conductor ($\sigma \approx 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 500°C), the concentration of mobile charges is probably low. It follows, therefore, that the coulomb interactions between these mobile ions must be long range in character and, hence, very weak. The relatively small magnitude of the conductivity dispersion and the almost Debye-like appearance of the modulus peak are in accord with this expectation.

(2) β -Alumina

Although two plausible explanations can be given for the conductivity dispersion in LiGaO_2 , the dispersion in β -alumina is much greater than that in LiGaO_2 . It seems unlikely that β -alumina, with its disordered sodium ions, would have a sufficiently large range of energy wells to account for the observed dispersion.* A model based on the second mechanism of "hindered ionic mobility" is therefore favored, and it is suggested that the conductivity dispersion arises from mutual interactions between the sodium ions themselves. In β -alumina, a significant percentage of the sodium

ions is thought to be mobile at any time (in marked contrast to LiGaO_2), thus the coulombic interactions between the sodium ions will be relatively short-range and strong. Some continuous reorganization of the surrounding ion atmosphere will, therefore, be required as long-range conduction continues. The extent of the conductivity dispersion in β -alumina (and hence the breadth of the modulus peak) can be associated with the large number of mobile Na^+ ions and the strength of the short-range, mutual interactions between them. It is emphasized that this model of hindered ionic mobility does not describe the mechanics of conduction (e.g. interstitialcy or otherwise) but rather describes how diffusive processes are involved in minimizing departures from local electroneutrality which occur as a consequence of the migration process.

There seems to be a qualitative correlation between the size of the conductivity dispersion and the complexity of the crystal structure. For single crystals, the dispersion increases in the order $\text{NaCl}^{14} < \text{LiGaO}_2 < \beta$ -alumina, and for polycrystalline materials, $\text{LiGaO}_2^{15} < \text{Li}_4\text{GeO}_4^1 \approx \text{Li}_4\text{SiO}_4^1 < \beta$ -alumina. This correlation could simply be a reflection of the number of mobile ions present in each. In the fast ion conductors, the ionic disorder (of either cations or anions) is presumably comparable with that in glasses but the number of mobile ions is probably much greater, since many of the cations in glass are probably trapped in relatively deep energy wells. This situation may account for the greater breadth in the modulus spectrum of β -alumina as compared with glass. There could also be a correlation between the breadth of the modulus peak and the reciprocal of the activation energy for conduction. Activation energies increase in the order β -alumina⁵ $< \text{Li}_4\text{SiO}_4^1 \approx \text{Li}_4\text{GeO}_4^1 < \text{LiGaO}_2 < \text{NaCl}^{14}$.

VI. Conclusions

Migration losses and broad modulus spectra, as found in single-crystal β -alumina and LiGaO_2 , are predicted to be common in ionically conducting solids and are probably associated with the effects of "hindered ionic mobility" on the conduction process.

A wide range of conductivity relaxation times appears to be a characteristic of the disordered state in crystalline as well as amorphous materials. The electrical properties of vitreous and crystalline electrolytes thus have more in common than has been supposed previously.

The equivalent circuit of a solid electrolyte in the absence of electrode and grain-boundary effects is sometimes given as a single, parallel RC element. Since conductivity and permittivity are frequency dependent quantities, this representation is obviously a gross simplification.

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*Recent NMR data (Ref. 12) suggest that, at low temperatures, β -alumina has a wide range of ion jump frequencies as well as 2 thermally activated migration processes. There is also evidence for the ordering of Na^+ ions at low temperatures (Ref. 12) and Na^+/Li^+ ordering, with very different mobilities of Na^+ and Li^+ , in mixed Li^+/Na^+ β -alumina (Ref. 13). These results could be variously interpreted so as to lend support to either or both of the models for migration losses already proposed.