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BRIEF COMMUNICATION

Ion Trapping and Its Effect on the Conductivity of LISICON and Other Solid Electrolytes

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Conductivity data for the lithium ion conducting solid electrolyte, LISICON, $Li_{2+2x}Zn_{1-x}GeO_4$ over a particularly wide composition range, $0.15 < x < 0.85$, and over the temperature range ~25 to 150°C show that both the activation energy and preexponential factor pass through maxima around $x \sim 0.4$ to 0.5, at which the preexponential factor exhibits anomalously high values, $\sim 10^{13}$ ohm^{-1} cm^{-1} K. An explanation is offered which involves the trapping of mobile Li^+ ions by the immobile sublattice at lower temperatures. This model also accounts for ageing effects observed at lower temperatures in which the conductivity decreases slowly with time. In the isostructural Li^+ electrolytes, $Li_{3+x}Si_xY_{1-x}O_4$ (Y = P, As, V), the compositional dependence of both the preexponential factor and activation energy is less marked and no evidence for ion trapping effects is observed.

Conductivity data on systems which have a low concentration of charge carriers, such as doped alkali halide crystals, are reasonably well characterized and can be readily interpreted in terms of point defect models (*1, 2*). By contrast, systems with large carrier concentrations cannot be understood in terms of simple point defect models (*3, 4*). Often such systems exhibit linear log σT vs T^{-1} plots and attention has focused on correlating changes in activation energy with variations in mobility associated with structural effects such as variations in bottleneck size (*5*). Recently, the importance, in nonstoichiometric conductors, of interactions between mobile ions and the immobile sublattice, which lead to the trapping of potentially mobile ions, has been appreciated (*6*) particularly in the F^- and O^{2-} ion conductors with the fluorite structure (*7, 8*). Such systems show unusual variations in the activation energy and preexponential factor with composition (*9*) but they can be studied over only limited ranges of solid solution composition, e.g., ~9 to 19 mole% dopant.

In Li^+ ion conducting solids, few detailed studies of the compositional dependence of ion migration have been carried out. One system that exhibits a particularly wide

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compositional range is the LISICON solid electrolyte system, $Li_{2+2x}Zn_{1-x}GeO_4$ where x can vary from ~0.15 to 0.87 (*10*). High ionic conductivity in this system is attributed to the presence of interstitial Li^+ ions (*11*). The conductivity data show marked variations in both activation energy and preexponential factor with composition; the latter exhibits anomalously large values for compositions around $x = 0.5$. The LISICON system therefore offers considerable scope for investigating the compositional dependence of conductivity in nonstoichiometric materials.

Conductivity data (*11*) for the LISICON system over the temperature range, 25 to 150°C are reproduced in Fig. 1. Activation energies, E and preexponential factors, A, extracted from Fig. 1 are given in Fig. 2. Both E and log A show a similar compositional dependence in which two linear regions are observed. In region 1 with $x \leq 0.4$, E and log A increase with increasing x. In region 2 with $x \gtrsim 0.55$, E and log A decrease with increasing x. The similar compositional dependences of E and log A (Fig. 2) imply that linear relationships exist between them and this is found on plotting log A vs E.

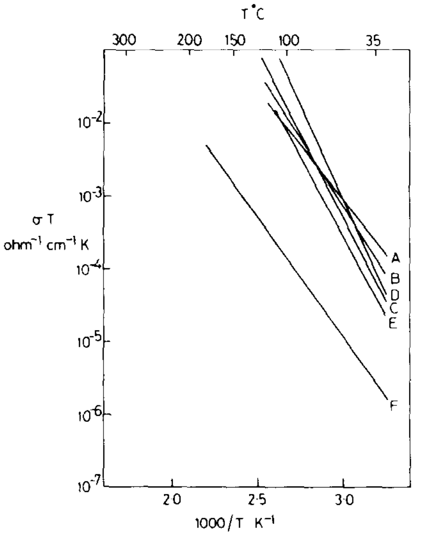

FIG. 1. Intracrystalline conductivities of LISICON solid solutions $Li_{2+2x}Zn_{1-x}GeO_4$. The x values are A(0.85), B(0.75), C(0.55), D(0.40), E(0.30), F(0.15), see Ref. (*11*).

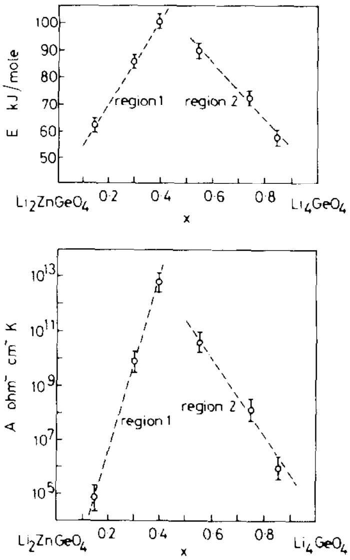

FIG. 2. Variation of (a) activation energy, E and (b) preexponential factor, A with composition for the data given in Fig. 1.

From Fig. 2, the preexponential factor attains very high values, ~10^{13} ohm^{-1} cm^{-1} K, at intermediate x values. Such high A values cannot be rationalized in terms of a model in which all of the interstitial Li^+ ions are mobile. In this model, the preexponential factor is given by (*12*)

$$A = g\nu_0 d^2 q^2 c k^{-1} \exp(\Delta S/k) \qquad (1)$$

where g—geometrical factor, depends on lattice geometry, d—jump distance, q—charge on the mobile ion, c—concentration of mobile ions, ν_0—attempt frequency, ΔS—entropy of migration, k—Boltzman constant. If realistic values for the above parameters are chosen, a value for the prefactor of ~10^4 ohm^{-1} cm^{-1} K is obtained. This varies by a factor of 2 to 3 over the compositional range of interest, in marked contrast to the observed variation of ~10^8 with composition (Fig. 2).

In order to explain the observed trends, an alternative model involving the trapping of mobile ions by the formation of defect clusters is proposed. It is noteworthy that similar effects to those found in region 1 have been reported by Hohnke in doped ZrO_2 (*9*). He found that both log A and E increased with dopant concentration over the range $x = 0.08$ to 0.16 in $Zr_{1-2x}\, In_{2x}\, O_{2-x}$ and that A reached a value of 10^8 ohm^{-1} cm^{-1} K at $x = 0.16$. He also showed that the results could not be explained by a model in which all of the potentially mobile species are free to migrate.

The LISICON solid electrolytes may be regarded as interstitial solid solutions based on γ_{II}-Li_2ZnGeO_4 (*10*) in which each Zn^{2+} ion is replaced by two Li^+ ions. One of these occupies the tetrahedral zinc site in the framework $[Li_{2+x}\, Zn_{1-x}\, GeO_4]^{x-}$. The other occupies a distorted octahedral interstitial site, the fractional occupancy of which is equal to x. These octahedral sites are therefore half-occupied at $x = 0.5$. Conduction may be regarded as arising from interstitial Li^+ ions for $x < 0.5$ and from Li^+ vacancies for $x > 0.5$.

Possible origins of the observed behavior can be understood by considering the effects of compositional variations starting from both $x = 0$ and $x = 1$. For $x = 0$, $Li_2\,Zn\,GeO_4$, partial substitution of Zn^{2+} by Li^+ gives rise to substitutional Li^- ions, which carry an effective charge of 1− and interstitial Li^+ ions with a net charge of 1+. Dipoles may therefore form between the two types of Li^+ ion which effectively trap the interstitial Li^+ ion. Freely mobile Li^+ ions are able to form by dissociation of such dipoles for which a quasichemical equilibrium may be written

$$(Li_{Zn}\, Li_i)^X \rightleftharpoons Li_{Zn}' + Li_i^{\cdot} \qquad (2)$$

where subscripts, *Zn*, *i*, indicate the sites that are occupied and superscripts, *X*, /, ·, represent the effective charges, 0, 1−, 1+, respectively. The enthalpy, ΔH_d^0 and entropy, ΔS_d^0 of dissociation contribute to the overall activation energy and preexponential factor for conduction. As x increases, the dipoles may aggregate to form dimers, trimers, and larger clusters for which both ΔH_d^0 and ΔS_d^0 increase with cluster size.

Starting on the other hand, from $x = 1.0$, Li_4GeO_4 with a hypothetical γ_{II} structure, the effect of partly replacing Li^+ ions by Zn^{2+} ions is to create Li^+ ion vacancies. These carry a net charge of 1− and the substitutional Zn^{2+} ions have an effective charge of 1+. The concentration of these two species increases with decreasing x. Again, dipoles may form. These associate into larger clusters and ΔH_d^0, ΔS_d^0 increase with increasing cluster size and hence with decreasing x.

In both regions 1 and 2, therefore, an increased cluster size may be associated with increased activation energy and preexponential factor. These ion trapping effects are maximized as the composition $x \sim 0.5$ is approached from either direction.

Additional features of the LISICON conductivity data that are consistent with a model of ion trapping at low temperatures are that (i) curvature of the Arrhenius conductivity plots occur at higher temperatures with a reduced activation energy and preexponential factor (*11*). This is because at higher temperatures, the majority of the Li^+ interstitials are freely mobile and the dissociation enthalpy and entropy terms contribute little to the overall activation energy and preexponential factor and (ii) ageing effects are observed, even at room temperature, in which the conductivity decreases slowly over a period of several weeks. This is presumed to be associated with the gradual formation of clusters that are larger than in material that is prepared at 1200°C and quenched. Since this process involves the migration of ions in the immobile sublattice, it occurs only slowly.

It is relevant to note that qualitative information on the compositional dependence of the free energy of the solid solutions may be obtained from the equilibrium phase diagram of the LISICON-containing system Li_4GeO_4–Zn_2GeO_4 (*10*). The phase diagram shows that although a very wide range of γ_{II} LISICON solid solutions is stable at high temperatures, from $x \simeq -0.3$ to $+0.87$, only a very limited range of solid solutions, $x \sim 0.45$ to 0.55, is thermodynamically stable at lower temperatures, e.g., 300°C. The solid solutions therefore have a minimum free energy and hence greatest stability at compositions around $x = 0.5$. This is in accord with our proposition that defect clustering exhibits its maximum effect at these compositions.

Although the phase diagram shows that only a limited range of compositions near to $x = 0.5$ is thermodynamically stable at low temperatures, a much wider range of solid solutions is kinetically stable. Thus, compositions in the entire range $x \sim 0.15$ to 0.87 can be quenched from high temperature as single-phase solid solutions. Most of these solid solutions should decompose on either slow cooling or on prolonged annealing at low temperatures. It is possible, therefore, that the defect clusters that have been proposed to explain the conductivity results, are associated with the initial stages of decomposition or precipitation. Since the defect clustering appears to be maximized at $x \sim 0.4$ to 0.5, the defect clusters that format other x values may also have a composition near to $x = 0.40$ to 0.50.

LISICON is just one member of a new class of Li^+ ion conducting solid electrolytes that results on forming solid solutions between either Li_4SiO_4 or Li_4GeO_4 and either Li_2MXO_4 (M = Zn,Mg,etc; X = Si,Ge) or Li_3YO_4 (Y = P,As,V). In each case, isostructural γ solid solution series are formed. Systematic studies on the systems Li_4SiO_4–Li_3YO_4 (Y = P,As,V) have shown rather different behavior (*13–15*) to that in Figs. 1 and 2. In particular, the activation energy passes through a minimum for intermediate x values, in contrast to Fig. 2 and the preexponential factor, while passing through a maximum, attains values of only 10^6 ohm^{-1} cm^{-1} K and varies by less than one order of magnitude for $x > 0.1$.

In these systems, solid solutions form by the mechanism

$$Y^{5+} \rightleftharpoons Si^{4+} + Li^+.$$

It is anticipated that ion trapping, through the formation of defect clusters is unimportant in these systems. This is because large departures from electroneutrality are not introduced into the immobile sublattice by substitution of essentially covalently bonded Y by Si. In the LISICON system, however, the replacement of Zn^{2+} by Li^+ in the immobile sublattice does cause a large change in the charge distribution in what must be a more ionic environment. In the Li_4SiO_4–Li_3YO_4 electrolytes, there was no evidence of either curvature in the Arrhenius plots at high temperatures or ageing effects at low temperatures. This is consistent with the supposed absence of defect interactions in these systems.

As yet, the precise nature of the defect clusters in LISICON remains undetermined. The results reported here do, however, indicate the significance of possible defect interactions in solid electrolytes. In particular, the importance of minimizing ion trapping effects is shown especially for materials that are to be used at relatively low temperatures. This is illustrated by a comparison between two isostructural, γ_{II} solid electrolytes: LISICON, $x = 0.55$ and $Li_{3+x}Si_xV_{1-x}O_4 : x = 0.4$. These have a similar conductivity at high temperatures, e.g., 300°C. At room temperature, however, LISICON has a conductivity of only 4×10^{-8} ohm^{-1} cm^{-1} (*11*) whereas that of $Li_{3.4}Si_{0.4}V_{0.6}O_4$ is 1×10^{-5} ohm^{-1} cm^{-1} (*15*). Ion trapping effects in LISICON have therefore reduced the conductivity by more than 2 orders of magnitude in comparison with

$Li_{3.4}Si_{0.4}V_{0.6}O_4$ in which ion trapping is minimized.

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References

1. A. B. Lidiard "Handbuch der Physik" (S. Flugge, Ed.), Vol. 20, p. 246, Springer, Berlin (1957).
2. L. A. Acuña and P. W. M. Jacobs, *J. Phys. Chem. Solids* **41**, 595 (1980).
3. M. S. Whittingham, *Electrochim. Acta* **20**, 575 (1975).
4. Da Yu Wang, D. S. Park, J. Griffith, and A. S. Nowick, *Solid State Ionics* **2**, 95 (1981).
5. H. U. Beyeler and T. Hibma, *Solid State Commun.* **27**, 641 (1978).
6. D. Wolf, *J. Phys. Chem. Solids* **40**, 757 (1979).
7. K. E. D. Wapenaar and J. Schoonman, *J. Electrochem. Soc.* **126**, 667 (1979).
8. A. S. Nowick and D. S. Park, *in* "Superionic Conductors" (G. D. Mahan and W. L. Roth, Eds.), Plenum, New York (1976).
9. D. K. Hohnke, *J. Phys. Chem. Solids* **41**, 777 (1980).
10. P. G. Bruce and A. R. West, *Mater. Res. Bull.* **13**, 117 (1978).
11. P. G. Bruce and A. R. West, *J. Solid State Chem.* **44**, 354 (1982).
12. F. K. Fong, *in* "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 3, p. 135, Pergamon, Elmsford, N.Y. (1967).
13. Y-W. Hu, I. D. Raistrick, and R. A. Huggins, *J. Electrochem. Soc.* **124**, 1240 (1977).
14. A. Khorassani and A. R. West, *Solid State Ionics* **7**, 1 (1982).
15. A. Khorassani and A. R. West, *J. Solid State Chem.* **53**, 369 (1984).