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Stoichiometry-dependent conductivity in framework ionic conductors

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Stochastic Langevin dynamics simulation of a one-dimensional model for framework ionic conductors shows competing effects of static lattice potential and ion interactions. For commensurate cases, repulsions decrease the conductivity, whereas for incommensurate systems, Coulomb repulsion partly overcomes lattice potential localization, leading to increased conductivity. A new explanation is offered for the observed behavior of NASICON ($Na_3^{\dagger}Zn_2PSi_2O_{12}$), based on the important interparticle correlations.

Framework solid electrolytes are of considerable current interest for applications in high-power-density cells.[1] In these systems the charge carriers diffuse through a rigid (skeleton) counterion sublattice. Hence, the size and density of moble ions can be varied over a wide range, while the geometry of the skeleton structure is maintained. For example, in the pyrochlore system $M_{1+x}Ta_{1+x}W_{1-x}O_6$ (M =Na, K, Tl), x can be varied from 0 to 1.

Goodenough et al.[2] completed a systemic study of several such framework systems. $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, $0 \leq x \leq 3$ (when $x=2$ the material is referred to as NASICON), exhibited the highest ionic conductivity. Further, the experiments of Kafalas et al.[3] and Ref. 2 demonstrate that ionic conductivity in these materials is strongly affected by mobile-ion concentration. Kafalas attributes this behavior to changes in bottleneck diameter with variation in x. The geometry changes are in fact very small and do not seem sufficient to produce the observed variation. In this paper we present an attractive alternative explanation based on correlated ionic motion.

Recent important work by Geisel[4] has studied the role of carrier correlations in determining the conductivity in one-dimensional solid electrolytes. Using a nearest-neighbor harmonic repulsion model, he found oscillations in the conductivity as a function of mobile-ion density. We focus here on the effects of variable mobile-ion density on the conductivity in systems with Coulombic interactions. We employ stochastic Langevin dynamics[5] to calculate transport properties of several one-dimensional-model systems in order to deduce some of the principles of ionic diffusion through a skeleton sublattice, to understand the competing effects of static lattice potentials and realistic interparticle repulsions, and, in particular, to understand the reported stoichiometry dependence of the NASICON system. In framework solid electrolytes the interaction between mobile ions and the skeleton lattice can be represented by viscous and stochastic forces due to thermal motion on the lattice ions, and a periodic force due to the equilibrium positions of counterion sublattice. The dynamics of the mobile ions are described by the following set of coupled Langevin equations[6,7]:

$$m\ddot{X}_i = -m\Gamma\dot{X}_i - \frac{A\pi}{a}\sin\left(\frac{2\pi}{a}X_i\right) + \phi(i)_{\rm int} + R(t), \tag{1}$$

$$\phi(i)_{\rm int} = \sum_j \left(\frac{7C}{r_{ij}^8} + \frac{(qe)^2}{r_{ij}^2}\right),$$

where Γ is the damping constant, A is the height of the periodic potential due to the static framework, $\phi(i)_{\rm int}$ is the ion-ion interaction force (a sum of repulsive short-range and Coulombic interactions), and $R(t)$ is a δ-correlated Gaussian random variable

$$\langle R(0)R(t)\rangle = \delta(t)2m\Gamma k_B T.$$

Typical values of these parameters are given[6,7] in Table I. Equation (1) is solved numerically with periodic boundary conditions, yielding stochastic trajectories from which the desired observables are calculated. A detailed description of the stochastic Langevin dynamics techniques as applied to framework solid electrolytes has been presented in an earlier paper.[6]

The diffusion coefficient is calculated via the definition

$$D = \lim_{t\to\infty}\langle r(t)^2\rangle/2t, \tag{2}$$

where $r(t)$ is the particle displacement. The conductivity was calculated using the following relations:

$$\mu = qeD/k_B T, \tag{3}$$

$$\sigma = qe\mu\rho,$$

where ρ is the mobile-ion density and μ is the mobility. These are the data we report here. The conductivity obtained in this way agrees closely with results obtained from a Fourier analysis of the velocity correlation function.[6]

Interionic forces have an important role in fast-ion transport. The stochastic trajectories (position versus time) show that when interionic forces are present, ionic motion is highly correlated. If no periodic barrier is present, stochastic forces tend to disorder the mobile ions, while the repulsive Coulombic force with periodic boundary conditions tends to order them. When the mobile ions are equidistant, the Coulombic potential energy is minimum. As the strength of the interionic forces increases, ionic motion becomes more correlated, but the bulk conductivity remains constant.[8]

In a periodic potential where the average separation of the charge carriers is equal to a multiple of the lattice constant of the potential [that is, $1/\rho = na$, where ρ is the number of particles per unit length, n is an integer, and a is the lattice constant (commensurate case)], the bulk and tracer dc conductivities decrease as q is increased. The periodic barrier keeps the ions separated so local motion of the ions in the bottom of the potential wells is largely uncorrelated, but when a mobile ion has enough thermal energy to approach the top of the periodic barrier, Coulomb repulsions take over, inducing either backward correlations (the mobile ion migrates back to its original lattice site) or forward correlations (the mobile ion migrates to a vacancy inducing migration of its neighbors). Comparison of stochastic trajectories with and without Coulombic forces indicates that back correlation is most frequent, hence σ is decreased.

When the mobile-ion density is incommensurate with the periodic of the lattice, calculated values of σ (Table II; we have also included for comparison the bare particle $A = 0$ and noninteraction $q = 0$ limits) indicate that a very different mechanism is dominant. In contrast to the commensurate systems, the dc conductivity is strongly enhanced when interionic forces are present; for example, when Eq. (1) is solved using the parameters in Table I with $A = 0.2$ eV, $\rho = 0.75$, the calculated σ increases by a factor of ~8 as q varies from 0.4 to 1.0 (Table II). When $q = 1.0$ and $A = 0.1$ eV the calculated conductivity is comparable to the value obtained with no barrier. When A is changed from 0 to 0.1 eV for a system with incommensurate mobile-ion density ($q = 0.6$, $\rho = 0.75$) the conductivity drops by 30%; however, σ drops by a factor of 40 when a similar change is imposed on systems with commensurate density. Thus, in all of these model systems the periodic barrier keeps the mobile ions separated, but this effect is much greater when the mobile-ion density is commensurate with the period of the lattice.

TABLE I. Parameters used in stochastic dynamic studies.

Temperature	453 K
Damping coefficient (Γ)	1.35×10^{12} sec^{-1}
Distance between sites (a)	3.1 Å
Mass	1.776×10^{-22} g
Barrier height (A)	0.1–0.3 eV
Effective charge	0.4–1.0
Ratio of mobile ions to total sites (ρ)	0.94–0.30
Short-range repulsive potential strength (C)	$0.56\times10^{17}\frac{g\,Å^{8a}}{sec^2}$

[a] Reference 10.

Our numerical studies here (and previous numerical and formal work[4,9]) indicate a conflict between the Coulombic repulsive forces which drive the mobile ions to equidistant positions and the periodic potential which, being incommensurate with the number of mobile ions, groups them into arrays separated by vacancies. The Coulomb forces push the mobile ions up the crystal framework potential well, lowering the effective potential barrier, and increasing the conductivity. When the lattice potential is dominant [$A/a > \langle \phi_{int}(i) \rangle$, $q = 0.4$, Table II] the ions will tend to be localized at the bottom of the periodic potential. When Coulombic repulsions are dominant ($A/a < \langle \phi_{int} \rangle$), the minimum-potential configuration

TABLE II. Calculated conductivity for incommensurate systems, $\rho = 0.75$.

A (eV)	q	σ (relative units)
0.2	0.0	0.35
0.2	0.4	1.75
0.2	0.6	6.1
0.2	0.8	11.25
0.2	1.0	14.3
0.0	0.0	19.5
0.0	0.6	19.1

These are relative conductivities. Using densities relevant for NASICON, our computed conductivity for $\rho = 0.75$ is 4.9 Ω^{-1} cm^{-1} (for $q = 0.4$), compared to the reported value of 0.27 Ω^{-1} cm^{-1}. Raising the A value to 0.3 eV drops the calculated σ by roughly 10, putting it close to experiment.

is mostly determined by Coulombic forces and not by the lattice potential, the mobile ions will be only slightly affected by the barrier, and the conductivity will be of order comparable to the zero-potential case. Qualitatively similar behavior occurs for harmonic nearest-neighbor repulsions.[4]

Figure 1 presents σ as a function of ρ. Curve (a) is the result obtained for independent charge carriers ($A=0.1$). Here D is independent of ρ and a linear function is obtained [Eq. (3)]. In contrast, curves (b), (c), and (d) result when interionic forces are present. Consider curve (b): $A=0.1$, $q=0.6$; when the mobile-ion density is commensurate with the period of the lattice, $\rho=0.5$ or 0.33, the conductivity is minimum; however, a sharp enhancement of σ results when ρ deviates from commensurate values; for $\rho=0.52$ σ changes by a factor of 20. Moreover, as ρ varies from 0.6 to 0.9 the enhancement of σ is increased. This can be attributed to the fact that Coulombic interactions become stronger as the charge carriers become closer together. When $\rho>0.91$ σ decreases sharply due to a lack of available sites. The density ρ_m for which σ attains its maximum depends on the particle-particle interaction and on the periodic barrier. For example, when the height of the periodic barrier is 0.2 eV, curve (d), $\rho_m=0.83$. As the charge carriers become localized, ionic motion exhibits hopping behavior, which is strongly dependent on the number of available sites. Thus site-availability effects will become more important as the periodic barrier is increased or as $\langle \phi_{\mathrm{int}} \rangle$ is decreased.

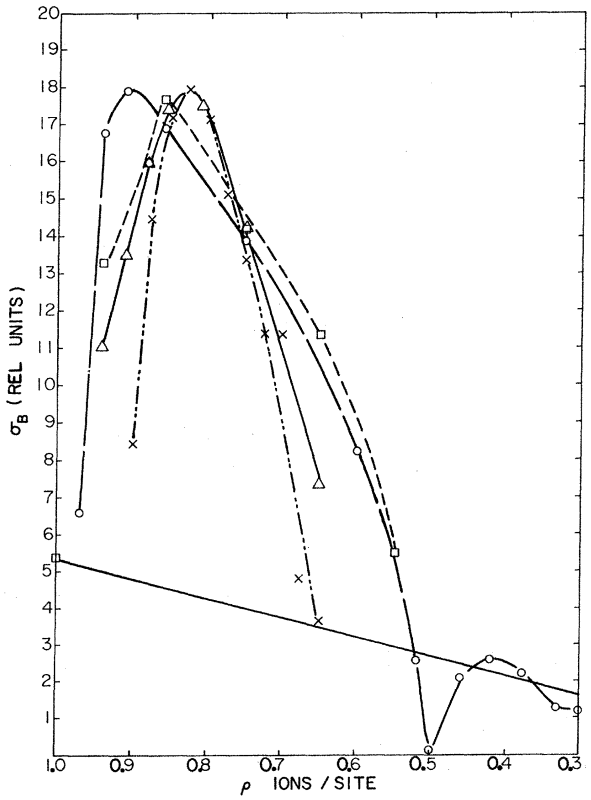

FIG. 1. Computed relative conductivities. (a)——, free carriers; (b) -O—O-, $A=0.1$ eV, $q=0.6$; (c) --□--□--, $A=0.2$ eV, $q=1.0$; (d) -Δ—Δ-, $2.4\sigma_B$, $A=0.2$ eV, $q=0.6$; (e) — --×— --, experiment (Ref. 9).

These observations explain some of the experimental data obtained for framework solid electrolytes. In $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, $0\leq x\leq 3$, a rigid skeleton is constructed from SiO_4 and PO_4 tetrahedra corner shared with ZrO_6 octahedra such that the mobile Na^+ ions diffuse through a network of intersecting tunnels. The dynamics of the mobile ions at these intersections is not represented in the present model; however, the conductivity in these materials is characterized by diffusion of charge carriers through tunnels with periodic barriers, hence our model is qualitatively correct. Kafalas *et al.* measured the conductivity at several incommensurate mobile-ion densities, $0.65<\rho<0.90$. Their data[3] show that σ is increased as ρ increases from 0.65 to 0.83, followed by a sharp decrease in σ for $\rho>0.83$. This behavior is similar to that obtained from the results of the stochastic dynamics simulations presented in Fig. 1 curve (d).

We have included the (replotted) NASICON data of Kafalas *et al.* in Fig. 1, curve (e), where its qualitative agreement with the present model calculations is clear. It would be very interesting to extend the measurements downward in mobile-ion density to see if the correlation-induced minimum at $\rho=0.5$ can be observed experimentally. Extension of the measurements down to $\rho=0.4$ would serve to differentiate this explanation from the bottleneck enlargement originally invoked.[3]

In summary, these calculations indicate large differences between the transport properties of commensurate and incommensurate framework solid electrolytes. Enhancement of the conductivity is obtained when the mobile-ion density is incommensurate with the period of the lattice. Moreover, there is an optimum density for which enhancement is maximum, as evidenced both from these stochastic trajectory calculations and the experimental data of Kafalas.[9]

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