

Solid Electrolytes: Some Theoretical Approaches to Ionic Motion Mechanisms

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Solids may generally be distinguished from liquids by the strong restoring forces that are encountered when any atomic displacement occurs. There is a large and dispersed group of solids in which certain ionic displacements occur for which the restoring potentials are quite weak and highly anharmonic. These solids may then exhibit diffusion of ions at a rate ($D \sim 10^{-5}$ cm²/s) more characteristic of liquid electrolytes. These solids are called solid electrolytes, or fast-ion conductors, or superionic conductors, and include solids as common as silver bromide or as specialized as Na₅Gd-Si₃O₁₂, as soft as polymers or as hard as aluminas, as light as sodium sulfate or as heavy as lead fluoride.¹

The remarkable properties of solid electrolytes were first noted by Faraday,² who examined PbF₂. Some extensive work on a number of silver salts was reported in the early years of this century. The first modern studies were carried out by Ketelaar,³ who investigated the structures, phase transition, and ionic conduction of the ternary electrolyte Ag₂HgI₄. The burgeoning current interest in ionic conductors may be traced to the development of the β -alumina materials by the Ford group in the early 1960s. Since then, interest in the field has spread widely, partly because of the promise of widespread technical application (to sensors, water electrolyzers, fuel cells, and particularly high-energy-density batteries) and partly because of the intrinsic fascination of a material which exhibits some properties of a liquid (facile diffusion) while remaining a solid.

A helpful, though arbitrary and imperfect, classification of solid electrolytes is presented in Table I. Generally the framework materials conduct well at quite elevated temperatures (>300 °C for β -alumina, >800 °C for cerium-doped zirconia), while the sublattice, heavy-metal conductors melt or decompose at lower temperatures. Some of the newest and most exciting electrolytes, which are polymer based, do not fit the scheme at all. The temperature-dependent conductivity for four solid electrolytes is shown in Figure 1; note the rather different behavior of the materials and the pronounced phase transition in the Ag₂HgI₄.

It is the task of the theorist to attempt an explanation, in microscopic, mechanistic terms, of the conduction properties of solid electrolytes, to try to explain why some materials conduct well and others do not, and to provide correlations between response properties (spectra, diffusion, dielectric constant, thermal behavior) and the microscopic motions of the ions and the

lattice. From a theorist's viewpoint, the problem is a classical (the large particle masses assure that classical mechanics is valid) many-body problem of a special and difficult type: many of the atoms (the lattice) are really of little interest, but they profoundly influence those which are (mobile ions). From a practical viewpoint, theoretical interpretation is needed to correlate microscopic behavior with laboratory measurement, in order to understand the mechanistic processes in these solids. Our work at Northwestern has centered on some questions of chemical relevance, including electronic structure work,⁴ dynamics simulations,⁵⁻⁹ formal modelling, and, particularly and most importantly, mechanisms of transport.⁴⁻¹² These aspects will be stressed in this review.

Conductivity: Measurement and Theory

Since the fundamental property of fast-ion conductors is fast-ion conduction, the most important experimental measurements involve the conductivity as a function of temperature and frequency. Conductivity experiments are most often carried out by using the complex impedance or complex admittance techniques, which permit bulk conduction to be distinguished from grain boundary or surface contributions; because ion polarization is very rapid unless ion-reversible electrodes are available, simple DC conductivity measurements are less common for these materials. As the experimental frequency range increases, the shorter time motions of the ions can be sampled.

Thus, although the apparatus needed to measure the ionic motion may change from an infrared spectrometer

(1) Recent reviews may be found in (a) J. B. Bates and G. C. Farrington, Eds., "Fast-Ion Transport in Solids", North-Holland, Amsterdam, 1981; (b) P. Vashishta, J. N. Mundy, and G. K. Shenoy, Eds., "Fast Ion Transport in Solids", North-Holland, Amsterdam, 1979; (c) M. B. Salamon, Ed., "Physics of Superionic Conductors", Springer, Berlin, 1979. A recent theoretical review is given by W. Dieterich, P. Fulde, and I. Peschel, *Adv. Phys.*, **29**, 527-605 (1980).

(2) M. Faraday, "Experimental Researches in Electricity", B. Quaritch, London, 1839, 1340.

(3) J. A. A. Ketelaar, *Trans. Faraday Soc.*, **34**, 874 (1938).

(4) J. McOmber, S. Topiol, M. A. Ratner, D. F. Shriver, and J. W. Moskowitz, *J. Phys. Chem. Solids*, **41**, 447 (1980); J. McOmber, Thesis, Northwestern University, 1980.

(5) S. H. Jacobson, A. Nitzan, and M. A. Ratner, *J. Chem. Phys.*, **72**, 3712 (1980).

(6) S. H. Jacobson, M. A. Ratner, and A. Nitzan, *Phys. Rev. B: Condens. Matter*, **B15**, 1580 (1981). The commensurate notion in ionic conductors is stressed by T. Geisel, *Phys. Rev. B: Condens. Matter*, **B20**, 4294 (1979).

(7) S. H. Jacobson, M. A. Ratner, and A. Nitzan, *Solid State Ionics*, **5**, 125 (1981).

(8) S. H. Jacobson, Thesis, Northwestern University, 1981.

(9) S. H. Jacobson, A. Nitzan, and M. A. Ratner, to be published.

(10) A. Nitzan, M. A. Ratner, and D. F. Shriver, *J. Chem. Phys.*, **72**, 3320 (1980).

(11) S. H. Jacobson and M. A. Ratner, *Solid State Ionics*, **5**, 129 (1981); *J. Chem. Phys.*, submitted for publication.

(12) B. L. Papke, D. F. Shriver, and M. A. Ratner, *J. Electrochem. Soc.*, **129**, 1694-1701 (1982).

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Table I
Solid Electrolyte Classification

class	thermal properties; conduction	frequencies	examples
framework conductors (often covalent solids)	no sharp onset of conduction; Arrhenius form for $\sigma(T)$	$\omega_{\text{lattice}} \gg \omega_{\text{ion}}$	NaTaWO ₆ (Ag ₂ O) _x ·(Al ₂ O ₃) ₁₁
sublattice conductors (usually soft crystals)	often phase transition, above which $\sigma(T)$ is Arrhenius	$\omega_{\text{lattice}} \gtrsim \omega_{\text{ion}}$	AgBr Cu ₂ HgI ₄ LiI

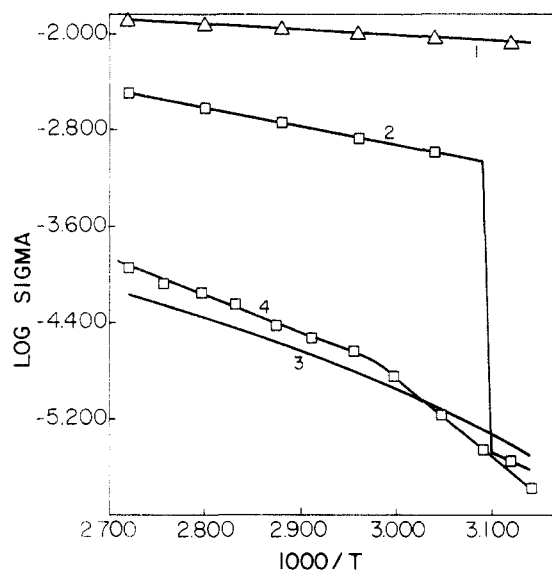


Figure 1. Arrhenius plots of cation conductivity for four solid electrolytes. Curve 1 is for Ag- β -alumina, which is simply activated in this range. Curve 2 is for Ag₂HgI₄, which undergoes a phase transition at 50 °C. Curve 3²² is for poly(propylene oxide)/NaCF₃SO₃ and shows typical curvature observed for highly disordered polymers. Curve 4²³ is for poly(ethylene oxide)/NaBF₄; the knee is due to melting of uncomplexed polymer.

(at 10¹³ s⁻¹) to a waveguide (at 10¹⁰ s⁻¹) to a vector impedance meter (at 10 s⁻¹), the essential property, the ion response to an electromagnetic field, is the same. Accordingly one expects that the theoretical expression for this response should be the same, and indeed the frequency-dependent conductivity is given, for classical particles moving in one dimension, by¹³

$$\sigma(\omega) \propto \int_0^{\infty} e^{i\omega t} \langle j(t)j(0) \rangle dt \quad (1)$$

where $j(t)$ is the current density at time t and the symbols $\langle \rangle$ means that the average is taken over an ensemble. If the particles indeed moved freely, the correlations would be constant in time since $j(t) = j(0)$, and thus $\sigma(\omega)$ would be a δ function at $\omega = 0$ (free carrier limit). The opposite limit is a carrier trapped in a harmonic well; then the current is just the momentum times the charge, and will vary (as does the momentum) as $e^{i\omega_0 t}$, where ω_0 is the harmonic frequency (since the carrier is trapped, it has no DC conduction). Then (1) will give a δ function at $\omega = \omega_0$. In any real system these responses are damped by interaction between ion motions and other motions; these two δ functions become Lorentzians, and we may write

$$\text{Re}[\sigma(\omega)] = C/[(\omega - \omega_0)^2 + \Gamma^2] \quad \text{harmonic well} \quad (2)$$

$$\text{Re}[\sigma(\omega)] = C/(\omega^2 + \Gamma^2) \quad \text{free ion} \quad (3)$$

We can then roughly speak of ionic motion as becoming

(13) E.g., R. Zwanzig, *Annu. Rev. Phys. Chem.*, 16, 67 (1965).

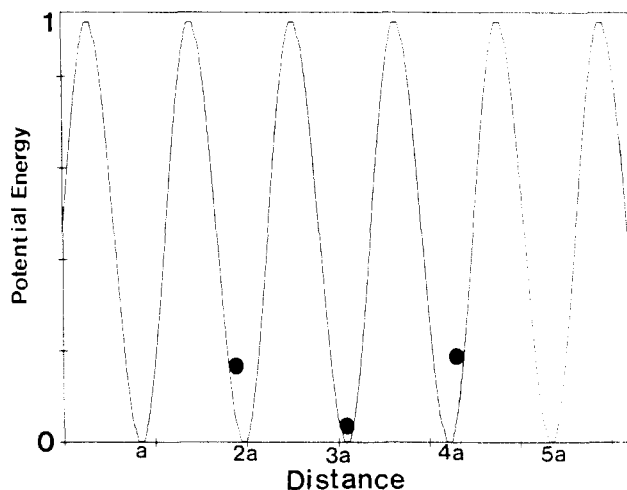


Figure 2. The potential $V_1(x)$ for the one-dimensional model of a framework solid electrolyte. The dots show calculated positions for reasonable choice of the parameters of V_1 and V_2 , when $\bar{x} = 1.33a$ (incommensurate).^{5,8}

more harmonic as the frequency maximum of $\sigma(\omega)$ approaches ω_0 and becoming more like free ions as the frequency of strongest response goes toward zero.

Since in most superionic conductors only one ion type is really highly mobile, we can to a good approximation regard the mobile ions as moving in a potential set up by the other ions—the picture is thus similar to, say, Ar diffusion on a metal surface. For a one-dimensional channel conductor then (such as hollandite), the potential for ion motion may be idealized as in Figure 2. The minima are the stable ion occupation sites that should be occupied at $T = 0$, while the maxima are the barrier tops for ion motion between cells. We write the potential as

$$V_1(x_i) = A \cos^2(\pi x_i/a) \quad (4)$$

where a is the lattice constant, $2A$ is the barrier height, and V_1 symbolizes the one-particle part of the full potential. These carriers are ions, however, and thus mutually interact. The interactions include both Coulomb and van der Waals components; simulations have shown the latter to be unimportant.^{5,8} Thus, to a good approximation we may write for the interaction potential

$$V_2(x_i, x_j) = q_i q_j / |x_i - x_j|, \quad (5)$$

for effective ion charges q_i and q_j .

Mobile Sublattice Conductors: Electronic Structure Effects

Ternary conductors of the Ag₂HgI₄ class usually undergo a phase transition of order-disorder type, and the ionic conduction is high in the (higher temperature) α phase. The monocations are generally found in tetrahedral sites at low temperature, and the crystal chem-

Table II
Conduction Data for Some Selected Heavy Metal Ionic Conductors^a

species	σ , $\Omega^{-1} \text{ cm}^{-1}$	activation energy, kJ/mol	ionic radius, ^b Å	dipole polarizability, ^c Å
α -AgI	1 at 150 °C	5	1.27	2.4
RbAg ₄ I ₅	0.2 at 20 °C	7	1.27	2.4
α -Ag ₂ HgI ₄	10 ⁻³ at 60 °C	36	1.27	2.4
α -Cu ₂ HgI ₄	10 ⁻⁵ at 67 °C	60	0.96	1.6
In ₂ ZnI ₄	1.5 × 10 ⁻⁴ at 220 °C	72	1.32	
Tl ₂ ZnI ₄	1.5 × 10 ⁻⁶ at 260 °C	84	1.54	5.2
Cs ₂ HgI ₄	10 ⁻⁶ at 250 °C	79	1.84	3.34

^a R. Ammlung, Thesis, Northwestern University, 1979. ^b F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, p 52. ^c J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).

istry suggests¹⁴ that the barrier site for passage between T_d sites is the threefold site in the planar face of the tetrahedron. One obvious chemical question then involves how the conductivity will vary with mobile ion: what causes the barrier height, and how will it differ with mobile ion species? Table II shows that the barrier height (roughly the same as activation energy for these materials) does not vary smoothly with ion radius or ion polarizability. In an attempt to find out which ion parameters were dominant, we carried out ab initio LCAO pseudopotential calculations on the MI_4^{3-} cluster (M = metal) and examined the changes in wave function and in energy when the mobile ion was moved from the T_d site to the face.⁴

From a local symmetry viewpoint, the barrier site is D_{3h} , while the stable site is T_d . Thus if the iodides are pictured as point charges, the electron cloud of the mobile ion should distort as the symmetry of the potential changes. The potential of the idealized D_{3h} site has no dipole component, so that, from a classical viewpoint, high quadrupolar (not dipolar) polarizability of the mobile ion should lower its energy in the transition state and therefore facilitate transport. Quantum mechanically, this means that in the barrier site there should be mixing of atomic levels whose l quantum number differs by two (s with d , p with f). Then we expect ions whose ground state permits $s \rightarrow d$ or $d \rightarrow s$ excitation to be more mobile than ions whose highest occupied orbital is a partly full p . Accordingly, our calculations favor the 1b metals Ag^+ and Cu^+ . If the d basis set is artificially frozen so that no $d \leftrightarrow s$ mixing is permitted, the calculated activation energy rises sharply for Ag^+ or Cu^+ , but much less so for In^+ (Table 3), for which there are no variable low-energy d states.

The Mulliken population changes upon transfer from the tetrahedral to the trigonal site confirm the qualitative notion of quadrupolar distortion. For the "good" mobile ions Ag^+ and Cu^+ , the major population shifts are from (p_x, p_y) to p_z and from $d_{x^2-y^2}$ to d_{z^2} and s levels. For In^+ , no significant changes occur in the d levels, because the potential cannot provide $p \leftrightarrow d$ or $s \leftrightarrow p$ mixing and the $s \leftrightarrow d$ promotion energy is far too large. The fact that silver is the best mobile ion in this group thus follows from its low $s \rightarrow d$ promotion energy and the orbital composition of three low states (s^2d^8, sd^9, d^{10}), which can all mix with each other in the potential field at the barrier site. As the silver moves from the tetrahedron center to the face, d^9s character mixes with the ground state, producing, in the facial site, a sort of "waist" in the xy plane, as density flows out of p_x, p_y ,

(14) K. Funke, *Prog. Solid State Chem.*, **11**, 345 (1976).

Table III
Calculated Activation Energies Using MI_4^{3-} Cluster Model⁴

species	I-I assumed distance, Å	ΔE_{calcd} , kJ/mol	
		all valence	frozen d ^a
NaI ₄ ³⁻	4.577	80.25	
KI ₄ ³⁻	4.996	85.08	
CuI ₄ ³⁻	4.320	72.38	106.36
AgI ₄ ³⁻	4.577	54.77	
AgI ₄ ³⁻	4.491	59.57	98.87
HgI ₄ ²⁻	4.577	94.18	
InI ₄ ³⁻	4.577	101.32	
InI ₄ ³⁻	4.675	71.66	75.90

^a In the calculations denoted frozen d, the s and d orbitals on the metal were not permitted to mix in going from T_d to D_{3h} site.

$d_{x^2-y^2}$ into p_z and d_{z^2} . The decreased electron density lowers Ag^+-I^- repulsions and more than balances the (small) promotion energy. For In^+ , by contrast, the ground state is $d^{10}s^2$ and the lowest excitation, to $d^{10}sp$, is not permitted by the quadrupolar field in the facial site. Similar problems occur for the alkali cations.

These ab initio electronic structure studies help understand why neither ion size nor (dipole) polarizability is a sufficient criterion for determining mobility in a given structure; they show that, in addition, covalent chemical bonding and valence-shell distortion are very important.

Framework Conductors: Langevin Dynamics

Framework ionic conductors are often hard, covalent oxide materials; even in the highest conduction regions ($\sigma \sim 0.1 \Omega^{-1} \text{ cm}^{-1}$), the mobile ion time to move from one lattice site to another is much longer than the typical vibration time of the oxide lattice. In the conducting region, these are nearly always disordered materials, in which X-ray studies show that the mobile ions exist not only at certain well-defined crystallographic symmetry sites but also, with variable probabilities, at other sites and between sites. From a theorist's viewpoint, this implies that site-to-site hopping models, while they may prove valuable for ascertaining certain qualitative properties such as the initial slope of $\sigma(\omega)$, cannot describe the full dynamics adequately. Then the ion dynamics should be reasonably described by a Langevin model,¹⁵ in which the ion dynamics is explicitly considered, while the framework lattice acts as a heat bath, exchanging momentum and energy with the mobile ions. This is very much like the Brownian

(15) S. A. Adelman, *J. Chem. Phys.*, **74**, 4646 (1981); S. A. Adelman and J. D. Doll, *ibid.*, **64**, 2375 (1976).

motion problem, except that the static potential V_1 due to the frozen equilibrium lattice remains, and the ion-ion interactions (eq 5) must be retained.

Experimentally it is found that most framework conductors show activated conductivities, with rather small activation energies ($E_A < 0.2$ eV). Theoretically, the total current density is a sum of contributions from each carrier:

$$j = \sum_i J_i = \sum_i q_i \dot{x}_i \quad (6)$$

with \dot{x}_i the velocity of the i th ion, of charge q_i .

We have carried out Langevin calculations⁵⁻⁹ on one-dimensional models of framework electrolytes. These are simply Newton's equations for the mobile ion array, generalized to include a damping term, with a damping frequency Γ , and a random force term $R(t)$; both of the latter arise from framework vibration. Cyclic boundary conditions are used. The equations are written

$$m\ddot{x}_i = -m\Gamma\dot{x}_i + R(t) - \frac{\partial}{\partial X_i} V_{\text{TOT}}(x) \quad (7)$$

where V_{TOT} is the sum of (4) and (5). After (7) is solved for x_i eq 1 and 6 yield $\sigma(\omega)$. The calculations were carried out with variable masses m , effective charges q , barrier heights A , temperatures T , mobile-ion densities ρ , and damping strengths Γ . These parameters were varied both to help interpret specific experiments and to understand the general mechanisms of ion motion in frameworks. Several interesting features emerge; we consider only four.

(1) Although to a first approximation the framework is rigid, conduction cannot in fact occur without vibrational motion of the lattice. Accordingly, experiments show low conductivity for temperatures much below 0 °C for framework conductors. This can be understood by considering the potential in Figure 2: without thermal activation, the diffusing particles cannot overcome the barriers in the periodic potential. Such a potential for electrons would lead to infinite conductivity at $T = 0$ because of the small mass and wavelike properties of the electron, but this cannot occur for nuclei. In the Langevin description, the random force term vanishes as $T \rightarrow 0$, so that there is no driving force for diffusion. Full molecular dynamics calculations on AgI show the same result: if the masses of the iodines are artificially set at a huge number, so that no I⁻ motions occur, no Ag⁺ diffusion is seen.¹⁶

(2) The qualitative effects of V_2 on the motion vary depending on whether the stoichiometry is commensurate. Commensurate densities are those for which

$$al = \bar{x} \quad (8)$$

where a is the cell length, \bar{x} the average ion-ion separation, and l an integer. For commensurate stoichiometries, both V_1 and V_2 are minimized when the ions sit at the local minima of Figure 2, with a length la between them. Then the effective barrier felt by any given ion if it tries to move will be increased by repulsion from other ions, the frequency ω_0 of eq 2 will increase compared to the noninteracting case, and the DC value $\sigma(0)$ will drop. Increasing the charge q or decreasing \bar{x} will

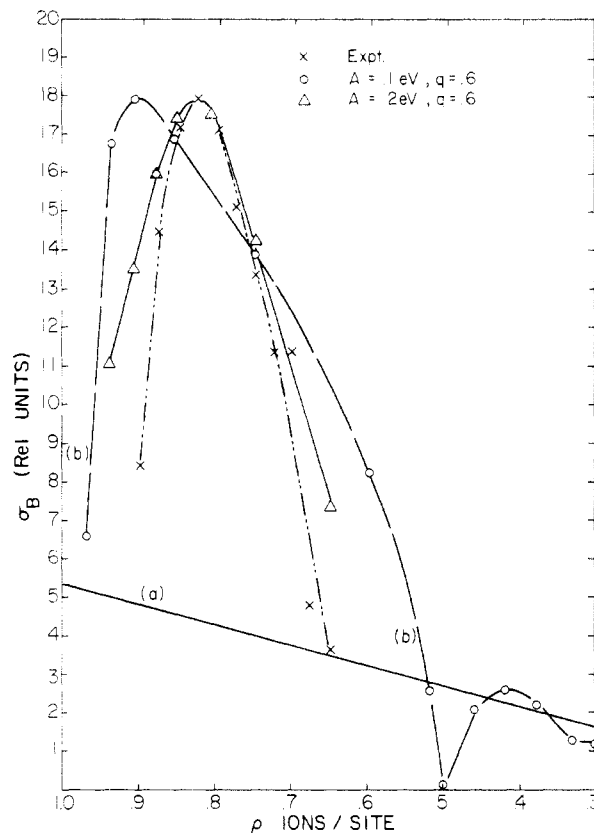


Figure 3. The calculated and observed conduction in NASICON as a function of Na⁺ concentration (from ref 6, 8, and 18).

amplify this effect. Thus for commensurate systems the interactions (5) decrease σ_{DC} .

(3) For incommensurate densities (l nonintegral in (8)) an entirely different result obtains. The minimum of V_1 still occurs with each ion at the bottom of its well, but the minimum of (5) occurs when the ions are equally spaced. The ground state will be determined from a competition between these two potential terms. The effect of V_2 is to cause some ions to climb up the walls (of the potential) to get away from their fellows; this means that they are closer to going over the top, and thus that the effective activation energy should be lowered and σ_{DC} raised. It also means that a sort of "clustering" should occur, as indicated in Figure 2 for $l = 0.75$; similar clustering has been observed experimentally by Beyeler,¹⁷ and our calculated cluster probabilities agree quite well with his X-ray results. Because the ions are no longer all in equivalent positions, they will respond at different frequencies to an applied field, and the calculations predict a split vibrational spectrum. This has not yet, to our knowledge, been observed.

The commensurability effect may explain the observations¹⁸ of the Lincoln Laboratory group on $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$. In this material a rigid skeleton is constructed from SiO_4 and PO_4 tetrahedra corner shared with ZrO_6 octahedra so that the Na^+ ions diffuse through a network of intersecting tunnels; our model does not treat the intersections, but since the motion is via diffusion in channels, the model is qualitatively valid. In Figure 3 we have plotted the observed con-

(17) H. U. Beyeler, *Phys. Rev. Lett.*, **29**, 1557 (1976).

(18) J. Goodenough, H. Hong, and J. Kafalas, *Mater. Res. Bull.* **11**, 203 (1976); J. Kafalas and R. J. Cava ref 1b, p 419.

(16) P. Vashishta and A. Rahman, *Phys. Rev. Lett.*, **40**, 1337 (1978).

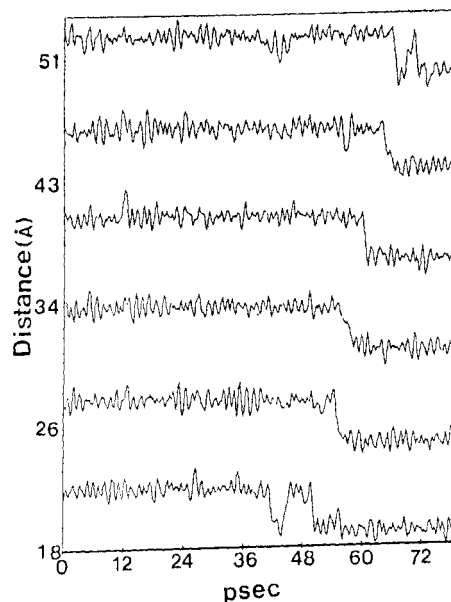


Figure 4. Displacement vs. time, calculated from Langevin dynamics. Charge is set at 0.4. This is typical behavior for correlated hopping, with long residence and short flight times. Incommensurate system ($\rho = 0.75$).

ductivity data compared with the Langevin simulations.⁶ The structure of the major peak is reproduced. The theoretical curve shows minima at the commensurate densities. The maximum is determined by the availability of vacancies as well as by the effective barrier heights.

(4) In nearly all framework conductors, the mobile ions are introduced by adding a salt; thus, counterions (extra oxides in Na- β -alumina) are present in the structure and can lead to trapping; this is the ionic conductor equivalent of Mott's exciton trapping in low-density compensated semiconductors.¹⁹ At very low density, this trapping should reduce the conduction markedly. The presence of many carriers should reduce the trapping for two reasons: the first is simple screening such as occurs for the analogous electronic problem; the second involves the ion-ion repulsions even more directly. Our simulations show⁹ that for commensurate systems, an off-axis trap (which we model by a negative point charge) actually can *increase* the conductivity, since it causes a bunching of cations near itself, rendering the ion array effectively incommensurate, and therefore decreasing the activation energy for ion motion. For incommensurate density, conversely, the trap lowers the conductivity by providing a local bottleneck.

The Langevin dynamics work not only correlates to experimental data such as σ_{DC} and vibrational spectra but also permits viewing the molecular details of the transport mechanism. For commensurate systems increases of the barrier height A cause decreases in both conductivity and correlation. When a mobile ion oscillates in its local well, the correlations are relatively unimportant, but when it reaches the barrier top, the dominant effect is back correlation (bounce back) due to Coulombic repulsion; this drives the ion back where it started. Only if $A \rightarrow 0$ is the correlated hop picture invalid for commensurate systems. Incommensurate

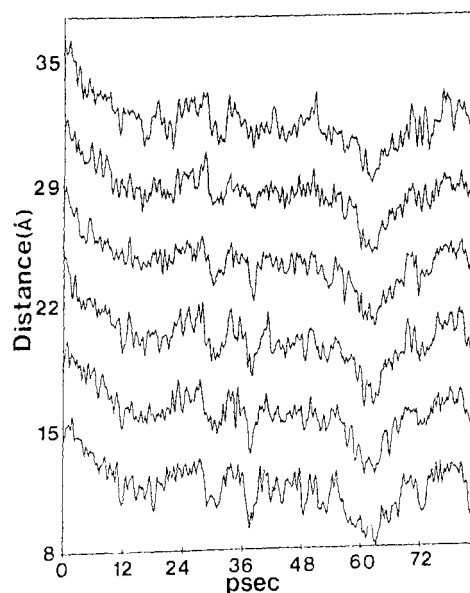


Figure 5. As in Figure 4, but charge is 0.4. The behavior is liquidlike, with very strong correlations, and no residence time (the Coulomb repulsion completely dominates V_1) (from ref 8 and 9).

systems are again more interesting;²⁰ for typical ones Figures 4 and 5 show displacement as a function of time. Increase of q significantly raises $\sigma(0)$; the only difference between Figures 4 and 5 is that the Coulomb interactions are four times as strong in (5) as in (4). The relative importances of V_1 and V_2 then invert between these two; when $q = 0.4$, the periodic potential largely determines the ion positions, and correlated hops occur between equilibrium positions. When $q = 0.8$, the relative positions of the ions are determined largely by their mutual repulsion, the density is not restricted to any special site, and the motion is liquidlike. The liquidlike behavior cannot occur for commensurate systems with finite A .

Many other interesting features of motion mechanism in frameworks may be deduced from these Langevin simulations. They also provide data against which to test approximate theories of ionic motion in these electrolytes. The overall behavior, as we have begun to see, results from a rich interplay of thermal, barrier, repulsion, and trapping energies. The actual prediction of $\sigma(\omega)$ for any given set of parameters is still an unsolved problem, both theoretically and experimentally.

Polymeric Electrolytes

Very recently a new class of solid electrolytes has been prepared in which the lattice, though covalent, exhibits large-scale motional freedom, softness, and disorder. These materials are prepared by solvation of alkali ion salts with poly(ethylene oxide), or PEO. The resulting solids do not fit either category of Table I very well, though they are more like the soft-lattice than the framework conductors. Recent work in England,²¹ France,²² Evanston,^{12, 23} and Philadelphia²⁴ has been

(20) Other workers have stressed the incommensurate behavior: A. Bunde, *Z. Phys. B*, **44**, 225 (1981), and T. Geisel, in ref 1b.

(21) P. V. Wright, *Br. Polym. J.* **7**, 319 (1975); D. E. Fenton, J. M. Parker, and P. V. Wright, *Polymer*, **14**, 589 (1973).

(22) M. B. Armand, J. M. Chabagno, and M. J. Duclot, Abstract C.5, Second International Meeting on Solid Electrolytes, St. Andrews, 1978; also ref 1b, p 131. J. M. Chabagno, Thesis, Grenoble, 1980.

(19) N. F. Mott, "Metal-Insulator Transitions", Taylor and Francis, London, 1974.

devoted to these electrolytes, which are very promising for battery applications because of their conformability, low-temperature conductivity, stability, lightness, and formability into thin films. Like most polymeric materials, these electrolytes require slightly different structural and transport models than are needed in crystalline solids or slightly disordered ones, such as framework electrolytes.

The Arrhenius-type curves in which $\log(\sigma T)$ is plotted against T^{-1} show straight-line behavior for activated processes such as conduction in frameworks. For the polymers, such curves can exhibit a variety of shapes. In highly crystalline polymeric conductors such as $(\text{PEO})_n\text{-NaSCN}$ ($n \sim 4$), they are Arrhenius-like, but for amorphous polymers like $(\text{PEO})_n\text{-LiNO}_3$, they are generally curved; partially crystalline substances like $(\text{PEO})_n\text{-NaBF}_4$ can exhibit knees or breaks in the plot; some of these typical features are shown in Figure 1. On the basis of earlier work by Armand²² and on vibrational spectroscopy,²⁵ conductivity, and thermal measurements in our own laboratories,²³ we have put forward a structural model¹² that rationalizes several of the properties of the PEO electrolytes. The cations are solvated in a tetrahedral or distorted tetrahedral cage of oxygens, which, in the crystalline polymer, are provided by four repeat units of the helical $(\text{CH}_2\text{-CH}_2\text{-O})_n$ chain. In the amorphous materials, and in the interlamellar regions of the ordered polymers, the fourfold solvation is retained, but the oxygens may come from differing polymer chains. Ionic motion then takes place by a cooperative process involving breaking of one $\text{Na}^+\text{-O}$ link and its replacement by another; if the second O differs from the first, ionic motion has occurred. The motion is determined largely by the solvent, whose motions permit the ions to sample different sorts of barriers as temperature changes. If solvent motions are impeded, as occurs in highly crystalline samples, the configurational entropy of the polymer chain is only very weakly temperature dependent, and thus Arrhenius behavior is found. When specific ion pairing occurs, as it does for $(\text{PEO})_n\text{-NaBH}_4$, the conduction drops, as the oxygen ligand-exchange process is impeded by the paired counterion.

Quantitative description of the conductivity behavior may be often obtained from the empirical Vogel-Tammann-Fulcher equation²⁶

$$\sigma(T) = A e^{-B/(T-T_0)} / T^{1/2} \quad (9)$$

A microscopic understanding of this form may be obtained from the conformational entropy model developed by Gibbs²⁷ and co-workers and extensively modified and applied by Angell.²⁸ In this model the liquid phase, which obtains above the glass transition temperature T_g , can lose configurational entropy rapidly

when temperature is lowered; this restricts the phase space sampled by the cations, raising the local Arrhenius activation energy (the slope of the curved line in Figure 1 decreases with increasing temperature) and lowering the conductivity. This suggests that in highly disordered polymer electrolytes above T_g the local structure should be thought of as liquidlike, and that the highest conduction should be achieved for the lowest T_g ; recent work by several groups^{22,23} supports this idea.

Remarks and Challenges

Theoretical understanding of ionic conduction in solids is uneven: in some areas, such as correlation effects in the hopping regime in AgI, quantitative statements are possible, whereas with polymer composites only rough qualitative notions are available. Nevertheless theory has a key role to play in any attempt to prepare new materials with given, desired properties: theoretical constructs can guide the difficult processes of solid-state synthesis and characterization. Generally, the low-frequency conduction is a complex many-body problem, but simple models and mechanistic concepts can lead to satisfactory interpretation of many experiments. The mechanisms differ considerably among the classes of materials: on the one hand, in the polymers the softer, more disordered, and more liquidlike the matrix, the better the conductivity seems to be. In the frameworks, a rigid structure to provide conductive channels is required.

These two simple mechanistic requirements lead naturally to two of the very newest solid electrolytes. One form of very high disorder is a glass, and recent experiments have demonstrated high conductivity in several glassy systems, notably Li/Ge/O glasses.²⁹ In the opposite limit, a solvated proton system may be assembled on a rigid framework conductor; in the case of $\text{H}_2\text{O}_2\text{PO}_4\cdot 4\text{H}_2\text{O}$ or of β -alumina, this leads to a two-dimensional hydrogen-bonded net, in which extremely rapid proton transport occurs (these are the best solid protonic conductors known),³⁰ probably by a two-dimensional variant of the Grotthus cooperative mechanism. Thus, the behaviors of a large number of quite different materials are all approachable with similar theoretical notions.

The theoretical questions to be addressed in solid electrolytes are of a rather special type: unlike, for instance, electronic-structure theory or bimolecular kinetics, fully quantitative, nearly exact solutions may be neither obtainable nor important. Mechanistic implications of structural and compositional variations, and the relationship of microscopic change and macroscopic behavior, are crucial areas of theoretical studies in these substances. Although presently more problems are confused than solved, this area of solid-state chemistry is one of the richest and most satisfying

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on which research is being conducted at present.

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Glycogen Phosphorylase Structures and Function

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The carbohydrate reserve of most metabolically active cells in the animal kingdom is glycogen, a polymer of glucose. The cellular demands to convert glycogen and orthophosphate (P_i) to glucose 1-phosphate (G-1-P) are met by glycogen phosphorylase, one of the most complex and finely regulated enzymes yet encountered. The observation by Cori and Cori^{1,2} that the catalytic activity of phosphorylase *b* could be triggered by AMP provided the first example of enzyme regulation by a ligand which is not a substrate. In their classic treatise defining the fundamental concepts of allostery, Monod, Jacob, and Changeux³ interpreted this phenomenon as a "concerted" transition between conformational states. Phosphorylase, like the archetypical allosteric protein hemoglobin, assumes at least two conformations, of which only one is catalytically active. It is accepted that the equilibrium among these is modulated by small molecules, "effectors", which, by interacting at specific sites on the protein, favor a particular conformation. Thus, the positive allosteric effectors of phosphorylase promote a catalytically active "R" state while negative effectors are inhibitors and bind to stabilize the inactive "T" conformation. In general, the effector is not a substrate nor is the effector site the active site, although substrates that are also effectors at the active site are common.

The complexity of phosphorylase admits a variety of allosteric mechanisms, involving both the catalytic site and specific loci elsewhere on the molecule. Phosphorylase is no exception to the general rule that allosteric proteins are multimeric, such that the binding of effectors and substrates is cooperative among the subunits. The best characterized and physiologically important species of phosphorylase is the dimer, although in the absence of its glycogen substrate, the "R" state enzyme tends to form tetramers.⁴ The activity of glycogen phosphorylase is promoted not only by effec-

tors but also by covalent modification: the addition of a phosphate at the hydroxyl group of a serine residue located near the N terminus of the molecule. Thus phosphorylase *b* (predominantly T) is converted to phosphorylase *a* (predominantly R) by phosphorylase kinase, a very complex enzyme, which is itself regulated by phosphorylation in response to nervous or hormonal regulation. The *dephosphorylation* of Ser-14-P, which inactivates phosphorylase, is catalyzed by yet another enzyme, phosphorylase phosphatase. This enzyme is regulated, at least in part, by phosphorylase itself. The system is designed such that a *functioning* phosphorylase, promoted by positive effector ligands or substrates at high concentration, inhibits the phosphatase, while an idling phosphorylase, resulting from a lack of substrate or high concentrations of negative effectors, is a phosphatase substrate.⁵ Conceptually, the covalent effector site is similar to the other effector sites. Functionally, the difference is that covalent modification allows a precise temporal control that is insensitive to short-term changes in effector fluxes. Even though the stoichiometric ratio of the kinases to their substrates is low, a relatively light hormonal signal can, by cascade amplification, effectively and rapidly activate phosphorylase. Figure 1 shows the relationship among the kinases, phosphatase, phosphorylase, and glycogen synthetase.

The phosphorylase molecule, then, can be imagined to be a molecular transducer that samples positive effector signals (nervous or hormonal stimulation, G-1-P, P_i , glycogen, AMP) and negative effector signals (insulin-induced signals, glucose, ATP, and some still unidentified ligands) and proceeds either to degrade glycogen for fuel or halt its degradation, allowing the cell to begin storing glucose as glycogen for a later time.

The details of this catalytic process have yet to be described at the molecular level although it is certain that the catalytic event requires the formation of a ternary enzyme-substrate complex⁶⁻⁸ comprising the

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