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Review
Superionic solids: composite electrolyte phase – an overview

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A general overview on the field of solid state ionics, including materials and transport property, is presented. Superionic systems in the composite electrolyte phase are discussed in great detail. Possible theoretical models suggested to understand the ion-transport mechanism in these systems are reviewed extensively. © *1999 Kluwer Academic Publishers*

1. Superionic solids: general aspects

Historically, human endeavours to search for new materials along with their applications in devices, have been the story behind the scientific and technological advancements of mankind. Prior to the 1960s, most of devices were based on electron conducting materials, namely semiconductors. In fact, the discovery of transistors in the 1950s revolutionized the field of semiconductor electronics further and a new branch of science, termed *solid state electronics*, emerged. This branch of science mainly deals with the physics, engineering and technological aspects of electronic materials and has made tremendous strides, since then, especially in the area of integrated electronics. Until the late 1960s, very few devices based on ion-conducting materials, were available. Out of the known devices, the majority of them were liquid–aqueous electrolyte-based devices, namely aqueous batteries. These batteries were reported to suffer from a number of major shortcomings such as: limited temperature range of operation, device failure due to electrode corrosion by electrolytic solution, bulky in size, less rugged, etc. [1–4]. Hence, to eliminate these discrepancies, a need to replace the liquid–aqueous electrolytes with some suitable ion-conducting solids was strongly felt. As an early attempt, the then known ion-conducting solids such as: alkali halides, silver halides, etc., were used, but owing to the fact that these solids were poor conductors (ionic conductivity, σ approximately 10^{-7}–10^{-12} S cm^{-1}), they remained unsatisfactory choices as replacement. However, the search for solids exhibiting high ionic conductivity continued rigorously. Eventually, the situation took a dramatic turn in the year 1967 when two new kinds of solid systems: MAg_4I_5 (where M = Rb, K, NH_4) [5–7] and Na-β-alumina [8], exhibiting exceptionally high Ag^+ and Na^+ ion conduction (σ approximately 10^{-1} S cm^{-1}) at room and at moderately high temperature, respectively, were discovered. A large number of fast ion-conducting solids with various mobile ion species, namely H^+, Li^+, Na^+, K^+, Ag^+, Cu^+, F^-, O^{-2} etc., have been reported, since then. In fact the year 1967 has been marked as the beginning of a new era in the field of *materials science*, which currently bears the name *solid state ionics*, a terminology parallel to solid state electronics. Solid state ionics mainly deals with the physics, chemistry and technological aspects of high ionic conduction in solids and has become a major thrust area of research worldwide. The solids, exhibiting high ionic conductivity, are termed *superionic solids* or *solid electrolytes* or *fast ion conductors* or *hyperionic solids*. Table I compares room temperature values of some basic transport parameters of electron and ion conducting solids. It can be noted that superionic solids, which can be thought to be ideal electronic insulators, have extremely high ionic conductivity. Fig. 1 shows the temperature variation of electrical conductivity of some normal-ionic and superionic solids along with two aqueous electrolyte systems for direct comparison. One can clearly see that the conductivity values of a number of superionic systems are not only close to those of liquid electrolytes but remain stable over a fairly wide range of temperatures. Superionic solids show immense technological promise, especially in the development of solid state electrochemical devices such as high–low solid state power sources (batteries), sensors, fuel cells, electrochromic display devices, memory devices, supercapacitors, etc. In addition to overcoming several limitations of liquid–aqueous electrolyte based devices, as mentioned above, the major advantages of solid electrolyte based devices are: their utility over a wide range of temperatures, i.e. below 0 °C and above 100 °C, where devices with liquid electrolytes normally cease to work and there is a possibility of miniaturization. In fact, a wide variety of solid state electrochemical devices are already available commercially. The implantable heart-pace-maker

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TABLE I Room temperature values of conductivity, mobility and carrier concentration of electronic and ionic solids [9, 10]

Materials		Conductivity, $\sigma_{27\,^\circ\mathrm{C}}$ (S cm^{-1})	Mobility, $\mu_{27\,^\circ\mathrm{C}}$ (cm^2 V^{-1} s^{-1})	Carrier concentration, $n_{27\,^\circ\mathrm{C}}$ (cm^{-3})
Electronic conductors	Metals	$\sim 10^5$	$\sim 10^2$	$\sim 10^{22}$
	Semiconductors	$\sim 10^{-5}$–10^0	$\sim 10^3$	$\sim 10^{10}$–10^{13}
Ionic conductors	Superionic solids	$\sim 10^{-1}$–10^{-4}	$\leq 10^0$	$\leq 10^{22}$
	Normal-ionic solids	$\sim 10^{-5}$–10^{-10}		
	Poor-ionic solids	$<10^{-10}$		

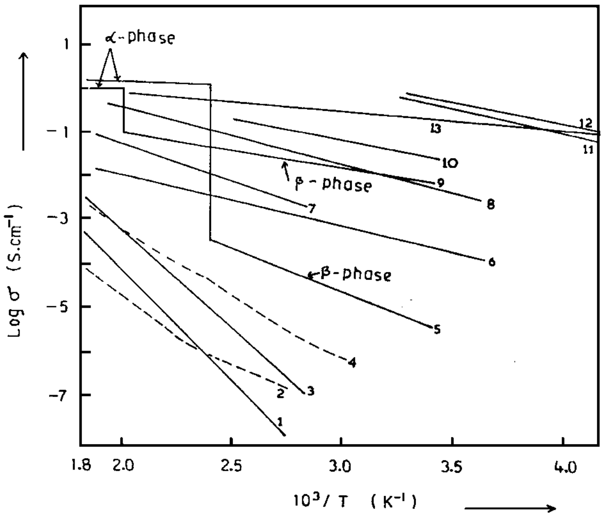

Figure 1 A plot of electrical conductivity versus temperature of some normal-ionic and superionic solids: (1) AgCl, (2) CuI, (3) AgBr, (4) β–PbF$_2$, (5) AgI, (6) Li$_4$B$_7$O$_{12}$Cl, (7) RbBiF$_4$, (8) β–alumina, (9) β–Ag$_3$SI, (10) Ag$_{13}$(Mo$_4$N)$_2$I$_{15}$, (11) 34% KOH (aqueous solution), (12) 35% H$_2$SO$_4$ (aqueous solution), (13) RbAg$_4$I$_5$ [10].

is one such device, which gives highly reliable performance as Li$^+$ ion conducting battery.

For electrochemical device applications, solid electrolyte systems should possess the following ideal properties [10]:

- Ionic conductivity should be very high (approximately 10^{-1}–10^{-4} S cm^{-1}) and electronic conductivity should be negligibly small ($<10^{-6}$ S cm^{-1}).
- The activation energy should be very low (<0.3 eV).
- The sole charge carriers should be ions only, i.e. ionic transference number, $t_{\mathrm{ion}} \simeq 1$.

Various structural and non-structural factors are responsible for the above characteristic properties of superionic solids [11]. Some important factors include: the crystal structure, high degree of lattice disorder, structure-free volume, high mobile ion concentration, size of mobile ions, ionic polarizibility, ion–ion interactions; bonding characteristics, vibrational amplitudes or rotational motion of neighbouring ions, number and accessibility of occupancy sites, intersite window or bottleneck size, presence of high conducting pathways, etc. In crystalline–polycrystalline solid systems, the structure is probably the main controlling factor for high ionic conduction. Significant progress has been made recently to synthesize fast ion-conducting solids in different phases adopting various preparatory routes. These developments have renewed the research activity in the field of solid state ionics tremendously [2, 10, 12–31]. The mechanism governing the ion transport property can be conveniently understood in crystalline–polycrystalline solid systems. The basic transport mechanism is dealt with for these solids in Section 2. Section 3 discusses some important theoretical aspects appropriately explaining fast ion conduction in these systems. A detail classification of these solids into various phases such as crystalline–polycrystalline, glassy–amorphous, composite, polymeric, etc., is presented in Sections 4 and 5 along with some important theoretical models suggested by different workers to explain transport phenomenon in these phases. The composite electrolyte phase, which is the main theme of this article, has been reviewed extensively in Section 5.

2. Transport mechanisms in ionic–superionic solids: basic notions

A perfect ionic crystal has no defects, hence, it behaves like an insulator. Point defects, namely Frenkel or Schottky defects, are necessary for ion transport in these solids. Fig. 2a, b schematically shows Frenkel and Schottky defects, respectively. Due to the thermal vibrations, ions sometimes receive enough energy to be pushed into an interstitial site or to a nearby vacant lattice site, this leads to ion conduction. When an electric field gradient exists across the sample (see Fig. 2c), the

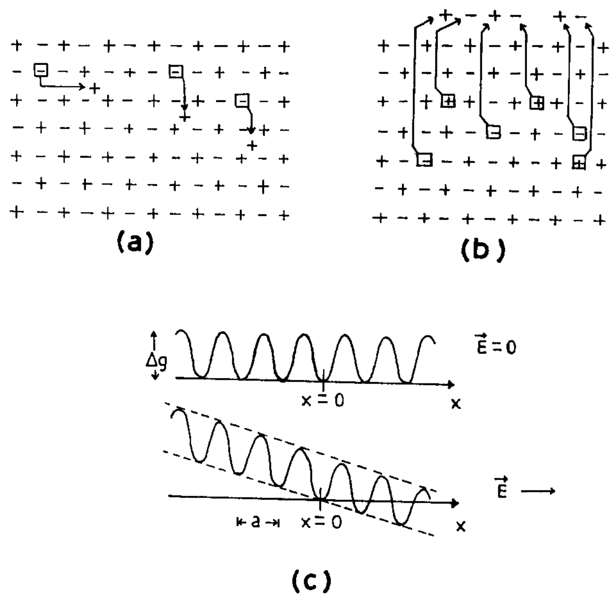

Figure 2 Schematic representation of (a) Frenkel defects and (b) Schottky defects. (c) Potential barrier for an ion with and without electric field, *E*, gradient. *a* is the interatomic space.

resulting electrical conductivity can be expressed by the following well known general equation

$$\sigma = \sum_i n_i q_i \mu_i \tag{1}$$

where n_i, q_i and μ_i are concentration, charge and mobility, respectively, of ith species of the carrier ions. The charge carriers are predominantly thermally generated Frenkel or Schottky defect pairs. At an equilibrium state, the number of defects is given by [10, 32, 33]

$$n_{\mathrm{f}} = (NN')^{1/2} \exp(-g_{\mathrm{f}}/2kT) \tag{2}$$

$$n_{\mathrm{s}} = N \exp(-g_{\mathrm{s}}/2kT) \tag{3}$$

Where the subscripts f and s stand for Frenkel and Schottky defects; g is the energy of formation; N and N' are the number of normal lattice and interstitial sites, respectively; k is the Boltzmann constant; and T the temperature.

Ion transport in ionic systems takes place by the jump mechanism (vacancy, interstitial or interstitialcy). Following the Einstein model, the probability, P (per unit time), for a given ion to jump from one site to another is governed by

$$P = \nu_{\mathrm{o}} \exp(-\Delta g/kT) \tag{4}$$

where ν_{o} is the vibrational frequency of the ions around their mean position in a potential well of barrier height Δg. Δg, termed as the Gibbs' free energy for migration of ions, is expressed as

$$\Delta g = \Delta h - T\Delta S \tag{5}$$

where Δh and ΔS are the enthalpy and entropy of migration, respectively. In the absence of an external electric field gradient this equation represents an equal number of ion jumps both in left and right directions at thermodynamic equilibrium.

As the electric field, E, is applied along the x-direction, as shown in Fig. 2c, the jump probabilities of the ions in and against the direction of the field are altered as follows. In the direction of the field

$$P' = \nu_{\mathrm{o}} \exp\{-[\Delta g - (qaE/2)]/kT\} \tag{6}$$

Against the direction of the field

$$P'' = \nu_{\mathrm{o}} \exp\{-[\Delta g + (qaE/2)]/kT\} \tag{7}$$

Hence, the number of ions per unit volume moving in the direction of the field is

$$\begin{aligned} n' &= n(P' - P'') \\ &\simeq n(qaE/kT)P \end{aligned} \tag{8}$$

where it is assumed that $qaE \ll kT$. Here n is the number of charge carriers per unit volume. So, the current density, j, defined as the amount of charge passing through per unit area per unit time, can be given by

$$\begin{aligned} j &= n'qa \\ &= nq^2a^2(PE/kT) \end{aligned} \tag{9}$$

Hence, the ionic conductivity, σ, can be expressed as

$$\begin{aligned} \sigma &= j/E \\ &= n(a^2q^2/kT)\nu_{\mathrm{o}} \exp(-\Delta g/kT) \end{aligned} \tag{10}$$

In case of Frenkel defect solids

$$\sigma = (NN')^{1/2}(a^2q^2/kT)\nu_{\mathrm{o}} \exp\{-[(g_{\mathrm{f}}/2) + \Delta g]/kT\} \tag{11}$$

In case of Schottky defect solids

$$\sigma = N(a^2q^2/kT)\nu_{\mathrm{o}} \exp\{-[(g_{\mathrm{s}}/2) + \Delta g]/kT\} \tag{12}$$

Apart from the above conduction mechanism governed by the thermally generated Frenkel and Schottky defect pairs, defect concentration and, hence, the conductivity of the ionic solids can also be altered by impurity doping [34–37]. However, in superionic solids, the number of mobile charge carriers is extremely large, therefore, the energy of formation of the defects, i.e. g_{f} or g_{s}, is negligibly small. Hence, for superionic solids, the Equations 11 and 12 are slightly modified and can be generalized to the following Arrhenius-type equation

$$\sigma = \sigma_{\mathrm{o}} \exp(-E_{\mathrm{a}}/kT) \tag{13}$$

where σ_{o} is the preexponential factor ($\equiv (NN')^{1/2}(a^2q^2/kT)\nu_{\mathrm{o}}$), for Frenkel defects; $\equiv N(a^2q^2/kT)\nu_{\mathrm{o}}$, for Schottky defects), and $E_{\mathrm{a}}(\equiv \Delta g)$ is called the activation energy.

The ionic transport parameters σ, μ and n in Equation 1, are temperature-dependent parameters, in general. Hence, for superionic systems with single mobile ion species, the equation can be written as

$$\sigma(T) = n(T)q\mu(T) \tag{14}$$

and variations of n and μ with temperature can be expressed by following the Arrhenius-type equations

$$n(T) = n_{\mathrm{o}} \exp(\mp E_{\mathrm{f}}/kT) \tag{15}$$

$$\mu(T) = \mu_{\mathrm{o}} \exp(\mp E_{\mathrm{m}}/kT) \tag{16}$$

where n_{o} and μ_{o} are the preexponential factors and E_{f} and E_{m} can be designated as energy of formation and energy of migration, respectively, for the mobile charge carriers. The negative and positive signs in the argument of the exponentials indicate the increase and decrease, respectively, of the factors on the left-hand side of Equations 15 and 16 with increasing temperature. The energy values (E_{a}, E_{f} and E_{m}) involved in the above thermally activated processes, Equations 13, 15 and 16, can be related to each other by following energy equation [38, 39]

$$E_{\mathrm{a}} = \pm E_{\mathrm{f}} \pm E_{\mathrm{m}} \tag{17}$$

It is well known that the current density, j, can be expressed in terms of drift velocity, v_{d}, in the following way

$$j\,(=I/A) = nqv_{\mathrm{d}} \tag{18}$$

Hence

$$\begin{aligned}\sigma &= j/E \\ &= nqv_{\mathrm{d}}/E \\ &= nq\mu \qquad (19)\end{aligned}$$

where I is the current passing through the cross-sectional area, A, and $v_{\mathrm{d}} = \mu E$. At a fixed value of E, v_{d} is directly proportional to μ. If μ is a temperature-dependent parameter, v_{d} will also vary with temperature. The temperature dependence of v_{d} would follow an Arrhenius-type equation similar to Equation 16 and can be written as

$$v_{\mathrm{d}} = v_{\mathrm{d_o}} \exp(\mp E_{\mathrm{d}}/kT) \qquad (20)$$

where E_{d} is the energy involved in this thermally activated process, which would be identical to E_{m} of Equation 16, if the electric field, E, is held constant.

Another way to understand the ion dynamics in solids is in terms of the diffusion coefficient, D^*. From Fick's first law, the flux, J (i.e. the amount of charge flowing in unit time through unit surface), is related to the concentration gradient, $\mathrm{d}N/\mathrm{d}x$, as follows

$$J = -D^*(\mathrm{d}N/\mathrm{d}x) \qquad (21)$$

The diffusion coefficient, D, can be related to the ionic conductivity, σ, by the well known Nernst–Einstein equation

$$(D/\sigma) = (kT/Nq^2) \qquad (22)$$

3. Superionic solids: theoretical aspects

Several theoretical models, based on various structural and non-structural factors, have been suggested to explain the fast ion conduction in superionic solids. There are certain specific models proposed for superionic solids in glass, polymer and composite phases, which will be discussed later in Sections 4 and 5. However, no unified theory exists as yet that can explain all the essential common features of different superionic systems. This section describes some of the earlier models proposed by various workers for superionic solids in crystalline–polycrystalline phases [10, 20, 33, 40].

3.1. Single-particle hopping and continuous diffusion models

This is the simplest approach to explain the ionic conduction [33]. In this model, it is assumed that an ion resides on a well defined site for an average time, t_{R}, then jumps to another site by crossing a potential barrier in a flight time, t_{F}, where $t_{\mathrm{F}} \ll t_{\mathrm{R}}$. The conductivity of the mobile ion is governed by Equation 1. The correlation function, relating the number, $n_{\mathrm{i}}(t)$, of ions at the ith site at time, t, is given by following rate equation

$$[n(\psi, t)\, n(-\psi, 0)] = \exp[-\Gamma(\psi)|\psi|] \qquad (23)$$

where ψ is the wave vector and $\Gamma(\psi) = (1/t_{\mathrm{R}})\ (1 - \cos a\psi)$ is the decay rate. In the limit $\psi \to 0$

$$\Gamma(\psi) \approx (1/2)a^2\psi^2/t_{\mathrm{R}} = D\psi^2 \qquad (24)$$

where D is the diffusion coefficient. In some solids t_{F} is comparable to t_{R}, hence, the motion between sites becomes important. Also, the oscillation in the potential well must be taken into account. Expecting the potential barrier to be very shallow and anharmonic, a continuous diffusion model can describe both the oscillatory and diffusion motion of the ions.

A Langevin equation takes into account the interaction with the *cage ions*, the effect of lattice vibrations on the mobile ions appears as a friction and a random force. Introducing a memory function into the Langevin equation, which accounts for lattice distortion, that is carried on with the particle as it moves with it. The equation simulates the coupling between the moving particles and the rigid framework.

3.2. Phenomenological models

Phenomenological models well explain the slow, discontinuous or abrupt changes in conductivity on the basis of change in the number of charge carriers due to mutual interactions between the thermally generated defects. These models only differ from each other by the manner in which the defect interactions are introduced. Huberman [41] assumed an attractive interaction, between the interstitial ion and vacancy, proportional to the square of the defect concentration, c, as being responsible for the superionic phase transition. The free energy, F, is a function of c. Rice, Strassler and Toombs (RST) [42] assumed that the transition to the superionic state is due to the defects interacting with the strain field, u. However, Welch and Dienes [43] have written a general equation that incorporates both Huberman's and RST's models. The thermally generated defect concentration and their free energy can be related as

$$\begin{aligned}F(c) = E(c) - kT[&-2c\ln c - (1-c)\ln(1-c) \\ &- (\alpha - c)\ln(\alpha - c) + \alpha \ln\alpha] - TS_{\mathrm{vib}}(c)\end{aligned} \qquad (25)$$

where $E(c)$ is the concentration-dependent energy involved in promoting an atom (or ion) into an interstitial site, α is the ratio of the number of interstitial cells to the number of ions, S_{vib} is the vibrational entropy. Both $E(c)$ and S_{vib} vary quadratically with c as follows

$$E(c) = E_1 c - E_2 c^2$$

and

$$S_{\mathrm{vib}}(c) = \Delta S_1 c - \Delta S_2 c^2 \qquad (26)$$

Welch and Dienes have shown that the Humberman and RST models are the special cases of their model. The equilibrium defect concentration can be obtained by minimizing $F(c)$ with respect to c. Based on their calculation for defect carrier concentration as a function of temperature for the three basic jump mechanisms described earlier, they explained the slow, discontinuous and abrupt changes in the conductivity. The above models are analytical rather than empirical. However, O'Reilly [44], later on, proposed a theory and derived an expression for $F(c)$ taking into account the energy term due to nearest neighbour interaction and the degeneracy of sites available to the mobile ions. Applying the model, he calculated ionic conductivity for a number of superionic crystals. The conductivity values obtained by him were in reasonably good agreement with the experimental results. Phillips [45] adopted rather a new approach to explain the phenomenon of phase transition by postulating the idea of the presence of microdomains in these systems. He assumed that if there are no microdomains at high temperatures, they start nucleating as temperature decreases, resulting in arresting of the phase transition by strain interactions between nuclei. On the basis of microdomains formation with temperature, he explained first-/second-order phase transitions *vis-à-vis* conductivity–specific heat capacity behaviour in AgI, Ag_2S and $RbAg_4I_5$. However, to test the correctness of the hypothesis near phase transition temperature, electron-microscope study is warranted. Kharkats [46] proposed a thermodynamic theory of domain formation in superionic crystals. He assumed that along with the homogeneous states of crystals with equal concentrations of interstitial-cations and cation-vacancies at every point, thermodynamically stable non-homogeneous states with increased–lowered concentrations of interstitial-cations–cation-vacancies are also possible. In the former case, the crystal possesses *local electroneutrality* at every point, while it has a *integral electroneutrality* in the latter. The non-homogeneous states, which correspond to the separation of a crystal into domain regions, are mainly responsible for any abrupt changes in the magnitude of defect-concentration–conductivity at the phase transition temperature.

These models clearly pointed out the importance of defect interaction; however, other significant features like mobility and availability of conduction path in the structure were not considered.

3.3. Lattice-gas models

The theoretical models described above are based on the random-walk hopping motion of mobile ions. However, there are several features namely: (i) correlation effects in the diffusion processes, i.e. the Haven ratio $(H, = D^*/D)$ has sometimes low value; (ii) structural effects, i.e. the static structure factor, $S(\psi)$, is indicative of short-range order interaction; (iii) co-operative effects, which result in a phase transition that cannot be explained by the hopping models. These many-body effects are taken into account in the lattice-gas model [47–54]. In the lattice-gas approach, it is assumed that a large number of mobile ions, comparable to or less than the number of their sites, are available and a *molten sublattice*-like situation exists. The mobile ions while hopping from one site to another, can interact with each other and modify the diffusion or transport activation energy. Sato and Kikuchi [47] used the *path probability method* (PPM) in place of the more common random-walk approach for the first time to explain Na^+ ion diffusion in β- and β''-alumina represented by a two-dimensional honeycomb network. They introduced a physical correlation factor, f, and wrote the expression for the diffusion coefficient, D, and ionic conductivity, σ, as

$$D = a^2\theta \exp(-\mu/kT)VWf \tag{27}$$

and

$$\begin{aligned}\sigma &= [a^2\theta \exp(-\mu/kT)VW](e^2 n_{\mathrm{Na}}/kT)\\ &= (D/f)(e^2 n_{\mathrm{Na}}/kT)\end{aligned} \tag{28}$$

where a is the perpendicular distance between two lattice arrays of Na^+ and O^{-2} ions in the honeycomb lattice structure of β-alumina; θ is the vibrational contribution to the jump frequency; μ is the activation energy for a jump of a cation into a vacant site; V is the vacancy available factor (i.e. probability of finding a vacancy next to Na^+); W is the effective jump frequency factor, which involves pair interaction, thus, expressing the many-body effect; e is the electronic charge; and n_{Na} is the density of Na^+ ions per unit volume. The above expression was derived using irreversible statistical mechanics assuming a short-range order interaction. This is a rigorous equation as far as the linear approximation can be rationalized. Furthermore, inappropriate values for tracer correlation factors, the lack of percolation thresholds, etc., are also observed. These results lead to incorrect frequency-dependent conduction at $\omega \to 0$. Hence, some amendments have recently been made [50–54] assuming a generalized interaction lattice-gas system by the pair-approximation of the PPM corrected for the time averaging in binary interacting gases (i.e. attractive as well as repulsive interaction). It has also been shown that hopping ionic conduction involves a non-Debye type relaxation processes. Sato *et al*'s [52] approach has common statistical features to the jump-relaxation model of Funke [55]. This model predicts the frequency-dependent conductivity even at $\omega \to 0$ in ordered as well as disordered ionic materials. However, it shows a limit of application at $\omega \to \infty$, where the conductivity approaches saturation. This limitation arose by neglecting the inertia of the particles.

A computer simulation procedure based on the Monto Carlo method (MCM) was employed by Murch and Thorn [56, 57] linking the random-walk hopping motion and statistical mechanics. MCM [58] is essentially a technique of computational statistical mechanics in which an ensemble of configurations is generated by a succession of random moves with an acceptance criterion, which depends on the Boltzmann factor, k. The values of V and W, obtained by MCM, were almost similar to those obtained by Sato and Kikuchi [47], however, f differed strikingly. This is probably due to the reason that Sato and Kikuchi overestimated f by assuming its contributions only to nearest neighbours. The MCM simulation approach has recently been extended for explicitly dealing with many-body interactions. Maass *et al.* [59] have shown by MCM that structure disorder and Coulomb interaction between the mobile ions mutually enhance each other in producing the fractional power laws in the dynamic response.

Dieterich [60] suggested the *discrete lattice-gas model* in which the mobile ions are well localized over most of the time. They are allowed to move only when the nearest neighbouring site is vacant. Due to pair interaction between the mobile ion and the vacant site, the jump probability depends upon the instantaneous configuration. Hence, these factors and the chemical potential decide the average occupation, $\langle n \rangle$, of the mobile ions.

A lattice-gas model, based on the improved MCM procedure [61] has also been proposed by Nachev and coworkers [62, 63] to describe Li^+ ion transport across the material interface of fast ion-conducting glasses and intercalations. This model explicitly takes into account the influence of Coulomb correlations, the site-blocking effect and the boundary conditions on the ion kinetics.

Pardee and Mahan [64, 65] suggested the *ionic polaron theory* in which they treated the problem of ionic lattice-gas hopping, similar to *Ising model* for antiferromagnetism with spin *up* and *down* equivalent to the ion *on* or *off* the site. They assumed a network of sites for the mobile ions, which is greater in number as compared with the number of mobile ions. A repulsive interaction exists between the nearest neighbours. The most important feature of this theory is the interaction of the mobile (hopping) ions with the lattice. As the ion moves, it polarizes the host crystal and carries the polarization cloud with it. Interaction between hopping ions and lattice vibrations, mediated via optical phonon (also called polarons), provides a sink or source of energy, which is coupled to the mobile ions, and hence contributes an activation energy to the conductivity. According to Pardee and Mahan, expressions for the conductivity and activation energy are given as

$$\sigma(\omega) = \sum_{n=1-z}^{Z-1} P_n(\hbar\omega + nU - \Delta) \tag{29}$$

and

$$(\Delta E)_p \simeq (e^2/\pi a)[(1/\epsilon_\infty) - (1/\epsilon_o)] \tag{30}$$

where P_n is the probability of finding an ion in a configuration where a hop changes its energy by nU, Z is the co-ordination number of the lattice, Δ is the site energy difference, U is the ion–ion nearest-neighbour interaction energy, ϵ_o and ϵ_∞ are the static and high-frequency dielectric constants. They wrote the expression for direct current (d.c.) conductivity at low and high temperature regions and concluded that conductivity at the low temperature region is lattice-gas dominated whereas the high temperature region is phonon-assisted hopping.

3.4. Free-ion model

A free-ion model, a microscopic theory, was proposed by Rice and Roth [66, 67] to explain the ion dynamics in superionic solids. In this model, it is assumed that an ion is thermally excited from a localized state across an energy gap, E_σ, to a free-ion-like state in which it moves translationally throughout the solid with energy, $E_o\,[=(1/2)mv^2]$. The free-ions have a finite life time, τ. According to Rice and Roth, the expression giving the d.c. conductivity, σ, and thermoelectric power, θ, can be written as

$$\sigma = (2/3)[(Ze)^2/kTm]n_\mathrm{I} E_\sigma \tau_o \exp(-E_\sigma/kT) \tag{31}$$

$$\theta = (k/Ze)(E_\sigma/kT) \tag{32}$$

and the frequency-dependent conductivity as

$$\sigma(\omega) = \sigma/(1 - i\omega\tau_o) \tag{33}$$

where $\tau_o = \tau(t_o)$, n_I is the number of available conducting ions per unit volume, Ze is the charge of each mobile ion, and E_σ is the activation energy. From the equation for θ we get

$$ZeT\theta = E_\sigma \tag{34}$$

This can be taken as a direct experimental test of the free-ion model by comparing E_σ, evaluated from log σ versus $1/T$ plot with the energy (q^*, termed as heat of ion transport) obtained from thermoelectric power studies. It has been reported by several workers [68–72] including us [73, 74] that the agreement between the two is fairly good. Rice and Roth's equation for conductivity, Equation 31, resembles the equation following the simple hopping model, which is of the form

$$\sigma = (1/3)[(Ze^2)/kT]na_o^2\nu_o \exp(-E/T) \tag{35}$$

where a_o is the hopping distance, ν_o is the ionic oscillator frequency, E is the migration activation energy. Rice and Roth also derived an expression for ionic oscillator frequency by connecting their free-ion model to the conventional hopping model. However, Haas [75] argued that the oscillator frequency can be obtained using a classical harmonic oscillator approximation and, hence, there is no need to invoke a free-ion model.

3.5. Jump-diffusion models

Another microscopic theory to understand the dynamics of ionic motion and the host lattice of solid systems was given by Huberman and Sen [76]. They assumed that the mobile ions have oscillatory motion in the potential well, as well as random-walk diffusion motion throughout the crystal. The two motions are uncorrelated and jump is assumed to occur instantaneously.

Several workers [77–79] considered the rigid periodic potential and studied the Brownian motion of particles in it, including the effects of polarizability of the lattice and correlated jumps. The approach involved three characteristic frequencies: (i) oscillatory (attempt) frequency, ω_o, of the particles in the potential well; (ii) frequency, $\omega_\mathrm{p}\,(=1/\tau_\mathrm{p})$, where τ_p is the time required for the lattice to relax after the particle jump; and (iii) jump frequency, $\omega_\mathrm{j}\,(=2/\tau_\mathrm{R})$, where τ_R is the residence time of the particle.

Zeller *et al.* [79] using a non-linear Langevin equation set up the equation of motion for the particle as

$$m\ddot{x} + m\Gamma\dot{x} + f(x) = K \tag{36}$$

This equation reduces to a simple diffusion equation at low frequencies while it represents a damped harmonic oscillator at high frequencies.

3.6. Jump-relaxation models

Direct information about ion dynamics can be obtained by the relaxation studies in terms of motional correlation time, τ, relating the microscopic processes. The crucial point, however, is to choose an adequate correlation function of the fluctuating local fields, which in turn reflects the ion dynamics [80].

The anomalous thermal and ultrasonic properties of disordered ionic solids at low temperatures are explained in the *two-level system model* [81, 82], where the concept of *localized low-energy excitations of disordered modes* is introduced. Here the microscopic origin of modes is unknown, however, it is believed that atoms or groups of atoms possess two or more configurations of linearly equal energy. These modes are also described in terms of an asymmetric double-well potential as a function of a configuration co-ordinate with a distribution of both the barrier height between the two wells and the difference of the two energy minima.

The *coupling model* developed by Ngai and coworkers [83–86] invoked the concept of *correlation states* whose excitations determine the dielectric and among others, the nuclear magnetic resonance (NMR) relaxation at low frequencies. This model leads to parametrized, but quantitative, description of the relaxation rate in complex correlated systems, where the motions of the basic relaxation units (primary species), such as some interacting ions in superionic conductors or a polymer chain, are correlated with each other. The primary species is coupled via some interactions (e.g. ionic) with its complex environment and with one another. Relaxation of the primary species involves a co-operative adjustment of its environment. This model yields a relation between the one particle energy barrier, E_a, and the activation energy, E_a^*, due to the presence of ion–ion interaction. They also derived an expression for relaxation rate at high temperatures.

Funke and coworkers [52, 55, 87–89] gave the *cage-effect jump-relaxation model* to surmount the number of unexplained experimental results like frequency-dependent conductivity, non-Debye type relaxation, quasi-elastic neutron scattering in superionic solids. The central idea is that the hop of a charged defect into a neighbouring vacant site may be either successful: i.e. the *defect cloud* comprised of all the defects present, relaxes with respect to the newly occupied site; or non-successful: i.e. the defect hops because of repulsive interaction between ions, this then is a correlated forward–backward hop. This model yields a frequency-dependent correlation function with the relaxation rate of limit $\omega\tau \gg 1$ as

$$1/T \propto \omega^{-(1+\beta)} \exp(-\beta \Delta_{\text{d.c.}}/kT). \qquad (37)$$

Here ω is the Larmer frequency, $\Delta_{\text{d.c.}}$ is the low frequency activation energy and factor β relates the $\Delta_{\text{d.c.}}$ to the apparent activation energy, Δ_{disp}, of the dispersive region by

$$\Delta_{\text{disp}} = \beta \Delta_{\text{d.c.}} \qquad (38)$$

The *counter-ion model* has also been proposed to explain mechanical relaxation [90–94]. This model is based on deformation potential coupling between elastic strains and a system of diffusing particles. The latter is described in terms of stochastic lattice gas that involves Coulomb interactions and structural disorder, so called *universal dynamic response* by using a lattice-gas Hamiltonian via Monto Carlo simulation technique. This model explains well the slow non-exponential relaxation detected by different spectroscopic techniques including dielectric spectroscopy, nuclear-spin relaxation, quasi-elastic neutron scattering, acoustic attenuation. The dynamic response observed in such experiments is often characterized by fractional power law or by a Kohlrausch–Williams–Watts (KWW) stretched exponential function, $\phi(t)$, in the time domain. This model is also useful to study the non-equilibrium processes, e.g. ion-exchange reaction, diffusion along and across interfaces or formation of intercalated compounds.

3.7. Molecular dynamics

Molecular dynamics (MD) computer simulation is a very powerful method to describe precisely in detail the ion dynamics in superionic solids, except for a limitation that it has not been possible to include a treatment of ionic polarization [95–100]. The MD method gives a numerical solution of the classical Newton equation of motion of an ensemble of particles, N, such as

$$m_i \ddot{r}_i = -\text{grad}_i V \qquad i = 1, \ldots, N \qquad (39)$$

where $\ddot{r}_i$ is the position vector of particle i having mass m_i, N may range from 300 to 500 and $V = V(r_1, \ldots, r_n)$ is the potential energy of the system. The particles are confined to a box of a given size, and periodic boundary conditions are applied. Here the initial positions and velocities of all particles are specified, the total momentum and total energy of the system are conserved such as the kinetic energy is given by (3/2) NkT. This method successfully predicted the ion dynamics in several ordered as well as disordered systems [58, 101–104].

4. Superionic solids: a classification

Superionic solids have different microstructure and physical properties, hence, fall in the domain of four types of phases:

1. framework crystalline materials,
2. amorphous–glassy electrolytes,
3. polymer electrolytes, and
4. composite electrolytes.

These phases belong to either ordered or disordered materials [33, 40, 90, 105]. Framework crystalline materials are ordered, whereas the rest of the three phases are disordered. Amorphous–glassy and polymer electrolytes are microscopically disordered, whereas composite electrolytes are macroscopically disordered materials. A brief review of the first three phases is given below, while the composite electrolyte phase is discussed extensively in a separate section, as the present article mainly concentrates on this phase.

4.1. Framework crystalline materials

Framework crystalline materials, as the name implies, consist of a crystalline skeleton of more or less rigid and mobile ions. They are further divided into two categories [33, 40]:

1. *Soft-framework crystals*. Such as AgI, CuI, $RbAg_4I_5$, Ag_2HgI_4, etc. They have the following characteristic properties: (i) the bonding is mostly ionic; (ii) the mobile ions are generally polarizable and heavy (e.g. Ag, Cu, etc.); (iii) the Debye temperature is low; (iv) a sharp ionic order–disorder phase transition appears between the low and high conducting phases (e.g. $\beta \rightarrow \alpha$ transition of AgI at 147 °C). Soft crystals–polycrystals are mostly solid solution of double salts (MX:xNY), where NY = AgI, CuCl, CuI, LiI, etc.; M = K, Rb, NH_4 or large ions; X = I, Br, Cl or radicals like S, P_2O_7, etc. The maximum conductivity generally results only for the higher value of x [10].

2. *Hard-framework crystals*. They are generally characterized by: (i) covalent bonds and consequently high frequency for local vibrations; (ii) high Debye temperatures; (iii) low polarizibility of mobile ions; and (iv) less sharp or absence of the order–disorder phase transition. They are usually oxides, e.g. β-aluminas, stabilized zirconias, Nasicons, montmorillonites, $LiAlSO_4$, etc., and generally referred to as a class of materials having similar structures and compositions.

Some epitomes of framework materials are listed in Table II. Framework crystalline–polycrystalline materials are the most extensively studied both in single-

TABLE II Some important framework crystalline materials with their electrical conductivities (figures in parenthesis refer to the temperature in degree celsius)

Material	Ionic conductivity (S cm^{-1})	Reference
Li^+ ion conductors		
LiAl SiO_4	1.4×10^{-5} (25)	[106]
$Li_4(Si_{0.7}Ge_{0.3})O_4$	6.0×10^{-4} (400)	[107]
$(Li_{2.8}Zn_{0.6})$ SiO_4	5.0×10^{-4} (400)	[108]
β-$LiTa_3O_8$	1.5×10^{-2} (400)	[109]
Li_4SiO_4 : $40mLi_3PO_4$	1.0×10^{-4} (100)	[110]
Li–β-alumina	1.3×10^{-4} (25)	[111]
Li–Na–β-alumina	5.0×10^{-3} (25)	[112]
$Li_{0.8}Zr_{1.8}Ta_{0.2}(PO_4)_3$	1.5×10^{-3} (200)	[113]
$Li_{1.4}Ti_{1.6}In_{0.4}P_3P_{12}$	5.5×10^{-2} (300)	[114]
Li_2CdI_4	1.0×10^{-1} (297)	[115]
$Li_{3.6}Ge_{0.8}S_{0.2}O_4$	1.0×10^{-5} (25)	[116]
$Ca_{0.95}Li_{0.1}WO_4$	3.0×10^{-4} (500)	[117]
$Li_{0.5}La_{0.5}TiO_3$	6.3×10^{-4} (20)	[118]
Na^+ ion conductors		
Na_2O–Ga_2O_3	3.0×10^{-2} (300)	[119]
Na–β-alumina	1.4×10^{-2} (25)	[8]
$NaTa_2O_5F$	4.0×10^{-5} (25)	[120]
$Na_2Ta_2O_5F$	6.7×10^{-3} (300)	[121]
$Na_{0.72}In_{0.72}Sn_{0.28}O_2$	$\sim 10^{-2}$ (227)	[122]
$Na_5GdSi_4O_{12}$	6.0×10^{-2} (200)	[123]
Nasicon–2mX($X = Mg^{2+}$; V^{5+}; Nb^{5+}; Tr^{5+})	$\sim 10^{-1}$ (300)	[124]
$Na_3Zr_{1.2}Yb_{0.8}Si_{1.2}P_{1.8}O_{12}$	1.4×10^{-1} (300)	[125]
$Na_{2.2}Al_{0.1}Yb_1Zr_{0.9}Si_{0.1}P_{2.9}O_{12}$	6.0×10^{-2} (400)	[126]
$Na_{1.9}Al_{0.3}Ti_{1.7}Si_{0.6}P_{2.4}O_{12}$	8.6×10^{-3} (25)	[127]
$Na_7M_3(X_2O_7)_4$(M = Al; Ga; Cr; Fe, X = P; As)	$10^{-3} - 10^{-2}$ (300)	[128]
K^+ ion conductors		
K_2O–Ga_2O_3	$\sim 10^{-3}$ (300)	[129]
K–β-alumina	6.5×10^{-5} (300)	[111]
$K_{0.9}Mg_{0.9}Al_{1.1}F_6$	1.2×10^{-3} (300)	[121]
$K_2O \cdot (6–x)Fe_2O_3 \cdot 0.8ZnO$	1.8×10^{-2} (300)	[130]
$K_{0.72}Se_{0.72}Hf_{0.28}O_2$	5.6×10^{-4} (225)	[122]
Ag^+ ion conductors		
α-AgI	~ 1 (150)	[131]
$RbAg_4I_5$	2.1×10^{-1} (22)	[6]
KAg_4I_5	2.1×10^{-1} (22)	[6]
N $H_4Ag_4I_5$	1.9×10^{-1} (22)	[6]
$(CH_3)_4NI$–6AgI	4.0×10^{-2} (22)	[132]
$(C_2H_5)_2NI$–6AgI	6.0×10^{-2} (22)	[133]
(Pyridinium)–3.5AgI	7.7×10^{-2} (22)	[134]
(C_7H_7I)–4AgI	5.8×10^{-3} (22)	[135]
β-Ag_3SI	1.0×10^{-2} (25)	[136]
$Ag_5I_3SO_4$	2.0×10^{-2} (25)	[137]
$Ag_7I_4PO_4$	1.9×10^{-2} (25)	[138]
$Ag_{19}I_{15}P_2O_7$	9.0×10^{-2} (25)	[138]
$Ag_7I_4VO_4$	7.0×10^{-3} (25)	[139]
KAg_4I_4CN	1.4×10^{-1} (25)	[140]
$Ag_{2.0}Hg_{0.25}S_{0.5}I_{1.5}$	1.4×10^{-1} (25)	[137]

TABLE II *Continued.*

Material	Ionic conductivity ($S\ cm^{-1}$)	Reference
Cu^+ ion conductors		
α-CuBr	5.0 (480)	[141]
α-CuI	9.0×10^{-2} (450)	[142]
KCu_4I_5	6.0×10^{-1} (280)	[143]
$C_6H_{12}N_{2.2}H$ Br–CuBr(87.5m)	4.9×10^{-2} (20)	[144]
$C_5H_{11}N \cdot CH_3Br$–CuBr	8.2×10^{-3} (20)	[145]
β-Cu_2Se	1.1×10^{-1} (150)	[146]
$RbCu_3Cl_4$	2.2×10^{-3} (20)	[147]
O^{-2} ion conductors		
ZrO_2–9mY_2O_3 (YSZ)	1.1×10^{-1} (1000)	[148]
ThO_2–8mYb_2O_3	4.8×10^{-3} (1000)	[148]
H fO_2–8mY_2O_3	2.9×10^{-2} (1000)	[148]
La_2O_3–15mCaO	2.4×10^{-2} (1000)	[148]
ZrO_2–8mSc_2O_3	3.0×10^{-1} (1000)	[149]
CeO_2–7mSrO	1.1×10^{-1} (1000)	[150]
BiO_3–22mWO_3	$\sim 10^{-1}$ (750)	[151]
$Bi_4\ V_2O_{11}$–M^{2+}(M = Cu; Co; Zr; Ca; Sr; Ge; Pb)	$\sim 10^{-3}$ (300)	[152]
$Bi_2Sr_2M'M''O_{11.5}$(M' = Nb; Ta, M'' = Al; Ga)	1.0×10^{-2} (800)	[153]
F^- ion conductors		
CaF_2	4.0×10^{-2} (700)	[154]
$La_{0.95}Sr_{0.05}F_{2.95}$	~ 3 (600)	[155]
$(CeF_3)_{0.95}(CaF_2)_{0.05}$	1.0×10^{-2} (200)	[156]
β-PbF_2	5.0×10^{-7} (25)	[157]
Proton conductors		
$HUO_2PO_4 \cdot 4H_2O$	4.0×10^{-3} (25)	[158]
$H_3P\ Mo_{12}O_4 \cdot 0.29\ H_2O$	1.8×10^{-1} (25)	[159]
Nafion	$\sim 10^{-2}$ (25)	[160]
$Al_2(SO_4)_3 \cdot 16H_2O$	7.0×10^{-5} (25)	[161]
H-mordenite	1.0×10^{-5} (25)	[162]
Silica gel film–$HClO_4$; $H_3PW_{12}O_4 \cdot 0.29H_2O$	$10^{-1} - 10^{-2}$ (25)	[163]
$BaCeO_3 \cdot 2.955H_2O$–10mGd_2O_3	2.4×10^{-7} (50)	[164]
$H_5O_2Ta(PO_4)_2$	1.0×10^{-3} (25)	[165]
$BaCe_{0.9}Nd_{0.1}O_3$	2.7×10^{-2} (750)	[166]

and polycrystalline form as evident from various available books, proceedings and reviews. However, polycrystalline materials are mostly used in technological applications simply because of ease and cost of preparation [167]. Now-a-days, efforts are directed to develop the materials in thin film form [10, 168–170].

4.2. Amorphous–glassy electrolytes

Ion-conducting glasses have several distinct advantages over their crystalline–polycrystalline counterparts, for instance: continuously variable compositions; high value of ionic conductivity with isotropic conduction; absence of grain boundaries; possibility of fabrication in thin-film form, etc. The first Ag^+ ion-conducting glass: AgI-Ag_2SeO_4 was reported by Kunze in 1973 [171]. Since then, a large number of glasses with various mobile ion species, namely Ag^+, Li^+, Cu^+, Na^+, F^-, have been discovered and studied [172–182]. These glasses are formed, in general, using the composition: ($MX{:}M_2O{:}A_xO_y$), where A_xO_y (e.g. B_2O_3, P_2O_5, SiO_2, MoO_3, etc.) is the oxide glass former, M_2O (e.g. Ag_2O, Li_2O, Cu_2O, Na_2O, etc.) is the network modifier and MX (e.g. silver halides, alkali halides, copper halides, etc.) is the dopant salt. Glasses can also be prepared by replacing oxygen in the above composition with anions such as S, Se [183–186]. All halide glasses as well as mixed network former–modifier glasses have also been reported [173, 185, 187–193]. Melt-quench techniques with various quenching rates (10^{-4}–10^{12} K s^{-1}) or sol–gel methods are used for the preparation of these glasses [181, 194]. Some important superionic solid systems in amorphous–glassy phase are listed in Table III.

Several theoretical models have been proposed to understand the ion transport mechanism in ion conducting glasses. Some of the models are briefly discussed below.

Anderson and Stuart [220] proposed the *A–S model* to explain the ion conduction in alkali silicate glasses. They assumed that measured activation energy, E_a, which corresponds to the energy barrier for cation migration, is the sum of an electrostatic binding energy, E_b (required to break the ion–oxygen bond and to move the ion halfway between neighbouring sites), and a strain energy, E_s (caused by deformation of the network due to ion movement). In their model, ionic mobility, μ, increases with increasing temperature rather than mobile ion concentration, n, which in turn results in increased conductivity, σ. This has been well supported by neutron and Brillouin scattering studies [221, 222].

Ravaine and Souquet [223] regarded the glasses as *weak electrolytes*, hence, proposed the *weak-electrolyte (WE) model*. The phrase weak electrolyte, means that the number of mobile ions is less than the stoichiometric concentration. It is also assumed that: (i) mobile and immobile ions are the carrier population, (ii) all the

TABLE III Some important amorphous–glassy electrolytes with their electrical conductivities (figures in parenthesis refer to the temperature in degrees celsius)

Material	Ionic conductivity (S cm^{-1})	Reference
Alkali ion conductors		
$LiI–Li_2O–B_2O_3$	3.2×10^{-3} (300)	[195]
$95LiI–37Li_2S–18P_2S_5$	1.0×10^{-3} (25)	[196]
$50LiI–20Li_2S–30GeS_2$	1.1×10^{-4} (25)	[188]
$Li_2S–GeS_2$	4.3×10^{-5} (25)	[189]
$LiCl–SiS_2–Li_2S$	1.9×10^{-3} (25)	[197]
$50Li_2S–50SiO_2$	$\sim 10^{-4}$ (250)	[198]
$50Li_2SO_4–15Li_2O–35P_2O_5$	6.8×10^{-3} (350)	[199]
$Li_3P_2O_4–Li_2S–SiS_2$	$\sim 10^{-3}$ (25)	[200]
$LiF–Li_2O–Al_2O_3–P_2O_5$	$\sim 10^{-6}$ (27)	[201]
$40Li_2O–8Al_2O_3–52B_2O_3$	6.1×10^{-5} (200)	[202]
$39.1Na_2O–7.5Y_2O_3–53.4SiO_2$	3.4×10^{-3} (300)	[203]
$Na_2S–SiS_2$	3.1×10^{-4} (100)	[187]
$Na_{3.75}Zr_{1.1}Si_{2.75}P_{0.25}O_{0.2}$	1.9×10^{-3} (300)	[204]
$90Na_2P_2O_6–10Na_2Te_2O_5$	2.4×10^{-6} (150)	[205]
Silver ion conductors		
$AgI–Ag_2SeO_4$	6.0×10^{-2} (25)	[171]
$AgI–Ag_2MoO_4$	6.0×10^{-2} (25)	[206]
$60AgI–30Ag_2O–10B_2O_3$	8.5×10^{-3} (25)	[183]
$45GeS_2–55Ag_2S$	1.4×10^{-3} (25)	[185]
$AgI–Ag_2O–B_2O_3–P_2O_5$	5.0×10^{-5} (25)	[190]
$73AgI–20Ag_2MoO_4–7Ag_2Mo_2O_7$	2.2×10^{-3} (25)	[173]
$35AgCl–45AgI–20CsCl$	4.7×10^{-2} (25)	[191]
$AgI–Ag_2Se–P_2Se_5$	$\sim 10^{-2}$ (25)	[183, 184]
$AgI–Ag_2O–WO_3$	3.1×10^{-2} (25)	[207]
$40AgI–18Ag_2O–42TeO_2$	4.8×10^{-4} (50)	[208]
$30CuI–46.66Ag_2O–23.33P_2O_5$	1.3×10^{-2} (31)	[209]
$60AgI–26.67Ag_2O–1.33SeO_2–12V_2O_5$	2.4×10^{-2} (25)	[193]
$60AgI–40(M\ Ag_2O–F[0.1SeO_2–0.9Cr_2O_3])$	2.4×10^{-2} (25)	[210]
$10PbF_2–90(2Ag_2O–V_2O_5)$	1.3×10^{-5} (28)	[211]
$80(Ag_{0.9}Cu_{0.1}I)–20(2Ag_2O–P_2O_5)$	8.6×10^{-3} (25)	[212]
Copper ion conductors		
$CuI–Cu_2O–P_2O_5$	1.0×10^{-2} (25)	[213]
$CuI–CuCl–RbCl$	1.0×10^{-2} (25)	[214]
$CuI–Cu_2O–P_2O_5–B_2O_3$	1.0×10^{-3} (25)	[215]
$CuI–Cu_2MoO_4–Cu_3PO_4$	1.0×10^{-2} (25)	[216]
$30CuI–30Cu_2O–30MoO_3–10WO_3$	3.0×10^{-4} (25)	[192]
$CuI–Cu_2WO_4–Cu_3PO_4$	$10^{-2}–10^{-4}$ (25)	[217]
Fluorine ion conductors		
$SiO_2–PbO–PbF_2$	2.2×10^{-5} (200)	[218]
$ZrF_4–BaF_2–CsF$	1.4×10^{-5} (200)	[219]
$35InF_3–30SnF_2–35PbF_2$	6.3×10^{-4} (150)	[186]

ions can move, (iii) the actual number of mobile carriers is small, and (iv) the mobility is independent of ion concentration in the glass composition. Based on these arguments, Isard *et al.* [224] proposed that the observed activation energy, E_a, is the sum of the enthalpy of reaction, ΔH, and true migration energy, E_m. If conductivity is dominated by the degree of dissociation of the oxide glass modifier and dopant salt then $(\Delta H/2) \gg E_m$, i.e. n increases with increasing temperature, which is espoused by quasi-elastic Raman scattering and NMR studies [225, 226]. Martin and Angell [227] argued that both the WE and A–S models are the same. The dissociation energy, $\Delta H/2$, and E_m of weak-electrolyte theory are identical to binding energy, E_b, and elastic strain energy, E_s, respectively, of the A–S model. Various thermodynamic analyses have been given to explain the mixed-alkali effect, conductivity enhancement by halide salts and mixed-anion effect [228, 229].

Glass and Nassau [230] developed the *random-site* (RS) model in which they made no distinction between the mobile and immobile ions and assumed that all the ions were potentially mobile. They also suggested, a wide distribution of mobile ion sites of differing free energy, hence, a wide distribution in activation energies for ion conduction.

Angell [172–174] introduced a decoupling index, R_τ, to define the disorderness in his *decoupling-index model*. R_τ, which is defined as the ratio of the structural relaxation time, τ_s, to the electrical relaxation time, τ_o, quantifies, how, as a function of temperature, the electrical process becomes decoupled from the viscous process. In highly conductive glasses, below the glass transition temperature, T_g, ion transport is decoupled from the structural dynamics and R_τ may be of the order of approximately 10^{12}.

Ingram *et al.* [202, 231] proposed the *cluster-bypass model* to explain the observed correlation in the conductivity at T_g with the E_a for Na^+ ion-conducting glasses. Ingram modified the continuous random network model in order to provide the preferred partial pathways for ion migration, which are located within the residual liquid surrounding ordered clusters (microdomains). The residual liquid accounts for the high conductivity at T_g and the larger R_τ. This model explained well the mixed-alkali effect and various transport phenomenon in AgI-based glasses. However, it failed to account for cluster formation in a wide range of glassy materials and to focus the co-ordination requirements of the mobile ions.

Recently, Bunde, Ingram and coworkers [232–236] proposed the *dynamic-structure model*, which is based on the experimental evidence that cations in glass create and maintain their own characteristic environments. They used the concept of fluctuating pathways within a dynamically determined structure. The key features of this model are: (i) the glass structure is not completely *frozen-in* until far below T_g, (ii) the mobile cations themselves are active in determining and creating the glass structure, and (iii) the transport is a hopping process. The combination of (i) and (ii) gives rise to various relaxation and site memory effects, which are characteristic of ion-conducting glasses and strongly influence the hopping process. This model quantitatively explains the occurrence of the mixed-alkali effect [237]. Also the anomalous dependence of conductivity on the modifier content in single alkali glasses follows a simple power law. However, the existence of site relaxation, cation memory effects and their link between ion transport and local structural relaxation remain to be proved. This model is, therefore, combined with the earlier *jump-relaxation model* of Funke and coworkers [55, 89], where the central feature is a *backward and forward* movement of mobile ions between neighbouring sites. This was seen as the origin of the memory effect as well as the mechanism whereby one kind of site is converted into another. This model is then termed the *unified site relaxation model* [238].

Shastry and coworkers proposed the *SUN model* to explain the Ag^+, Na^+, Li^+ ion conduction in various glasses [239, 240]. They introduced an index, called *structural unpinning number SUN* (S), based on the unscreened nuclear charge of mobile ion Z^*, the average electronegativity (anionic ψ_a or molecular ψ_b) and optical basicity of glasses, λ. They successfully explained the variation of T_g, σ and E_a as a function of dopant concentration in glasses using the expressions

$$\log \sigma = \log \sigma_o[1 + \exp(-aS)] \qquad (40)$$

and

$$-\ln E_a = aS - \{\ln RT + \ln[\ln(1/\sigma_o)]\} \qquad (41)$$

Shaju and Chandra [38, 241] proposed the *ion-association model* based on the cluster-bypass model in order to explain the experimentally observed phenomenon of $\mu(n)$ increasing (decreasing) with increasing temperature in silver borate glass systems. They proposed two type of ion-association mechanisms: (i) self-ion-association, and (ii) network association, which were responsible for the decrease in the number of mobile Ag^+ ions with increasing temperature.

4.3. Polymer electrolytes

Polymer electrolytes are a new class of solid ionic materials, which are usually formed by complexing polar polymers like PEO, PPO, PEG, etc., with ionic salts of monovalent alkali metal–divalent–transition metal–ammonium salts [40, 242–248]. Some salt-free polymer electrolytes have also been reported in which polymers like PVA and PVP have swollen lattices and an ionic solute, e.g. H_3PO_4 is accommodated for ionic motion [249]. Whereas polysulphonic acid based polyelectrolytes, e.g. Nafion, sodium polystyrene sulphate, poly[Na 2-(ω-methacryloyl oligo(oxyethylene) ethylsulfonates] have self-ion generating groups responsible for ion conduction [160, 250]. Polymer electrolytes are mostly prepared either by the solution-cast method, electrodeposition method or sol–gel method. Apart from several advantages, such as the thin-film forming property, good processibility, flexibility, light weight, elasticity and transparency; polymer electrolytes have less mechanical strength, workability, time stability, ionic conductivity, etc. [251]. Furthermore, both anions and cations may be mobile, in general, in polymer electrolytes [252]. To improve upon the electrical conductivity and mechanical stability of polymer electrolytes the following methods are adopted:

- *Copolymerization*. Adding a low T_g polymer into the host polymer [253–256].
- *Plasticization*. Adding a low molecular weight polymer, namely PEG, PEO, PC, EC, etc., into the host polymer [257, 258].
- *Dispersion of organic or inorganic fillers*. Dispersing a high T_g polymer, namely polystyrene, PMMA, PAA, PVA, etc., or an inorganic material such as Al_2O_3, SiO_2, $LiAlO_2$, Nasicon, β-alumina, Li_3N, glasses, etc., into the host polymer [259–262].
- *Radiation of γ-rays*. To introduce the cross-linking in polymer electrolytes [263–266].

Some typical polymer electrolytes are listed in Table IV.

The ion dynamics in polymer electrolytes are random as confirmed by their fractal growth [40, 300–302]. To understand the ion transport mechanism no well accepted theory is available. However, some of the proposed models are discussed briefly below [303, 304].

4.3.1. Phenomenological model

The polymer electrolytes are strongly coupled systems [305]. Consequently, the temperature dependence of σ is not the Arrhenius type but follows, in general, a Vogel–Tamman–Fulcher (VTF) type empirical relation:

$$\sigma = \sigma_o \exp[-B/(T - T_o)] \qquad (42)$$

The physics behind this equation is the *free-volume theory*, which assumes that conduction can proceed only when a sufficiently large void is created locally into which the charge carrier may jump. The constant B is proportional to a characteristic hard-sphere volume of the moving polymer chain segment, T_o is the temperature at which the free-volume vanishes.

TABLE IV Some important polymer electrolytes with their electrical conductivities (figures in parenthesis refer to the temperature in degrees celsius)

Material	Ionic conductivity ($S\ cm^{-1}$)	References
PEO–$LiClO_4$	$\sim 10^{-6}$ (25)	[267]
PEO–$LiCF_3SO_3$	$10^{-4} - 10^{-3}$ (100)	[268]
$(PEO)_5$–$LiBF_4$	$\sim 10^{-6}$ (25)	[269]
$(PEO)_8$–NaI	$\sim 10^{-5}$ (45)	[270]
PV Ac–LiSCN	$\sim 10^{-3}$ (100)	[271]
$(PPO)_8$–NaI	10^{-8} (25)	[272]
$(MEEP)_4$–$NaCF_3SO_3$	$\sim 10^{-5}$ (25)	[273]
MEEP–PEO–$(LiAsF_6)_{0.13}$	1.9×10^{-7} (25)	[274]
$(PMG)_8$–$LiSO_3CF_3$	$\sim 10^{-4}$ (60)	[255]
PMEEGE–$LiClO_4$	$\sim 10^{-4}$ (40)	[247]
$(PESc)_3$–$LiBF_4$	3.4×10^{-6} (65)	[275]
PEM–$LiSO_3CF_3$	2×10^{-5} (20)	[276]
$(PEO)_6$–$Cu(CF_3SO_3)_2$	5.0×10^{-7} (40)	[277]
$(PEO)_6$–$Cu(ClO_4)_2$	$\sim 10^{-6}$ (25)	[278]
PEO–CuI	1.2×10^{-6} (30)	[279]
PEO–$AgNO_3$	4.0×10^{-7} (30)	[280]
PEO–$RbAg_4I_5$/KAg_4I_5	2.0×10^{-3} (20)	[281]
$(PEO)_{16}$–ZnI_2/$MnBr_2$/$MgCl_2$/PbI_2	$10^{-4} - 10^{-6}$ (140)	[282]
PEG–M Br_2 (M = Ca; Co; Cd; Zn)	$\sim 10^{-5}$ (25)	[283]
PEG–NH_4ClO_4	1.0×10^{-6} (25)	[284]
(84PEO–16PPO)–10mNaI/LiI/$LiClO_4$	$\sim 10^{-5}$ (30)	[285]
PEO–PDMS–$LiCF_3SO_3$	3.0×10^{-5} (20)	[286]
PEO–MSA_2H_2(M = Li; Na; K; Rb; Cs)	1.7×10^{-5} (30)	[287]
POP–$(CF_3SO_2)_2$N Li	$\sim 10^{-6}$ (25)	[288]
PEO–PAA–NH_4SCN	$\sim 10^{-5}$ (25)	[289]
$(PEO)_{10}$–$CsBF_4$	1.7×10^{-7} (40)	[290]
PMMA–$LiClO_4$–PC	$10^{-3} - 10^{-5}$ (25)	[291]
PEO–$Pb(ClO_4)_2$	$\sim 10^{-4}$ (25)	[292]
PEO–$LiClO_4$	3.8×10^{-5} (25)	[293]
PAN–PC/EC/BL–$LiClO_4$/$LiAsF_6$/$LiN(CF_3SO_2)_2$	$\sim 10^{-3}$ (25)	[294]
PAN–EC–BL–$LiClO_4$	$\sim 10^{-3}$ (25)	[295]
PAN–EC–BL–SL/DL–$LiClO_4$	$\sim 10^{-3}$ (25)	[295]
PAN–PC–$NaClO_4$	$\sim 10^{-3}$ (25)	[296]
PVA–H_3PO_4	$\sim 10^{-5}$ (25)	[249]
PEO–NH_4HSO_4	2.0×10^{-4} (20)	[297]
PEO–PPO–H_3PO_4	1.8×10^{-3} (25)	[298]
PVP–H_2SO_4	3.9×10^{-3} (27)	[299]
poly[Na 2-(w-methacryloyl oligo(oxyethylene) ethylsul fonates]	3.5×10^{-6} (25)	[250]

4.3.2. Dynamic bond percolation model

This is a microscopic model given by Druger *et al.* [253, 306, 307]. They assumed that the local segmental mobility of the polymer host controls the conductivity, diffusion, etc. This motion together with independent carrier hopping causes conductivity. The time-scale of the hopping is much smaller than the time-scale of the polymer chain reorganization. The ionic motion may be described by percolation theory where the hopping rates, between any two sites, are either finite or zero depending on whether the jump routes (bonds) are mutually accessible or not for the static condition. For $T > T_o$, however, the disorder in the polymer is dynamic rather than static. The segmental motion can be sufficiently rapid in order to require assignment of the *bonds* as open or closed. This model also explain the frequency-dependent conductivity and viscosity associated with long-range carrier motion in polymer electrolytes.

5. Composite electrolytes: an overview

Composite electrolytes are multiphase (mostly two-phase) solid systems in which two or more materials are mixed together to achieve some desirable material properties, namely an enhancement in the ionic conductivity at room temperature. Composite electrolytes are also called *heterogeneously doped materials* or *dispersed solid electrolytes*. Conductivity enhancement in two-phase composite systems was known for about 75 years [308], however, the research activity in this area gained impetus only after 1973, when C. C. Liang [309] reported approximately 50 times enhancement in Li^+ ion conduction at room temperature simply by dispersing ultrafine particles of inert Al_2O_3 in LiI. Since then, a large number of two-phase composite systems have been investigated with the conductivity enhancement of about one to three orders of magnitude compared with those of constituent phases [260, 261, 310-321]. Two-phase composite electrolyte systems are prepared, in general, by dispersing submicrometre-size particles of insulating and chemically inert materials (called second phase dispersoids) into a moderate-ionic conducting solid (called first phase host-matrix). On the basis of the nature of the host-matrix and dispersoid, these systems are broadly classified into the following categories [313, 319]:

1. *Crystal–crystal composites*. They are the most extensively studied dispersed solid electrolyte systems

TABLE V Crystal–crystal composite electrolyte systems (figures in parenthesis and square brackets, respectively, refer to the temperature in degrees celsius and the size of the dispersoid particle in micrometres. DE, detrimental effect; NE, no enhancement; m, mole %; v, vol %; w, wt %)

Material	Ionic conductivity ($S\ cm^{-1}$)	Enhancement	Reference
LiI–40m γ-Al_2O_3	1.2×10^{-5} (25)	~50	[309]
LiI–40m γ-Al_2O_3[10]	3.7×10^{-5} (25)	~1300	[329]
(LiI–35m γ-Al_2O_3)–1.3m PI_3	1.5×10^{-4} (25)	~5300	[330]
LiI–50v SiO_2	2.0×10^{-4} (220)	~10	[331]
LiI–10w zeolite	3.3×10^{-6} (30)	~10	[332]
LiI–18m PLZT	—	—	[333]
LiI–25m LiBr	5.0×10^{-7} (25)	~75	[334]
LiI–30m Li_3N	3.5×10^{-7} (25)	DE	[335]
$LiI \cdot H_2O$–60m silica gel [150]	2.0×10^{-2} (25)	~1000	[336]
$LiI \cdot H_2O$–60m SiO_2 fumed [0.007]	2.0×10^{-3} (25)	~100	[336]
$LiI \cdot H_2O$–60m α-quartz [6]	6.0×10^{-7} (25)	DE	[336]
$LiI \cdot H_2O$–Al_2O_3	—	—	[337]
(LiI–LiOH)–Al_2O_3	—	—	[338]
LiI–NH_4I	—	—	[339]
$LiBr \cdot H_2O$–30m Al_2O_3	6.3×10^{-7} (25)	~10	[340]
$LiBr \cdot H_2O$–SiO_2	—	~10	[340]
LiBr–porous Al_2O_3	—	~1000	[341]
LiBr–SiO_2	—	NE	[341]
LiCl–25m α-Al_2O_3	1.0×10^{-6} (182)	~7	[313]
LiCl–25m γ-Al_2O_3 [0.7]	4.8×10^{-6} (182)	~30	[313]
LiCl–25m η-Al_2O_3 [1]	2.5×10^{-5} (182)	~150	[313]
LiCl–25m SiO_2	2.2×10^{-6} (182)	~13	[313]
LiF–50m Al_2O_3	3.6×10^{-8} (300)	DE	[320]
Li_2S–70m LiBr	4.7×10^{-5} (282)	~10	[342]
Li_2S–40m LiI	1.6×10^{-3} (227)	~300	[342]
Li_2SO_4–50m γ-Al_2O_3	4.3×10^{-5} (253)	~1000	[343]
Li_2SO_4–40m CeO_2; Y_2O_3; Yb_2O_3, LaO_3 [~15]	~10^{-6} (300)	NE	[320]
Li_2SO_4–40m ZrO_2 [0.008–0.02]	~10^{-6} (300)	NE	[320]
Li_2SO_4–40m $BaTiO_3$ [~8]	~10^{-6} (300)	NE	[320]
Li_2SO_4–10m LiCl	3.6×10^{-1} (500)	~100	[344]
Li_2SO_4–10m LiBr	3.3×10^{-2} (500)	~10	[344]
Li_2SO_4–55m Ag_2SO_4	1.17 (530)	~2	[345]
Li_2SO_4–90m Na_2SO_4	~10^{-4} (300)	~1000	[346]
Li_2SO_4–K_2SO_4	7.0×10^{-4} (530)	—	[347]
Li_2SO_4–70m Li_2WO_4	1.0×10^{-4} (400)	~50	[348]
Li_2SO_4–30m Li_3PO_4	1.0×10^{-4} (300)	~1000	[349]
Li_2SO_4–10m $Sm_2(PO_4)_3$	3.4×10^{-6} (300)	~10	[350]
Li_2SO_4–17.5m $CaSO_4$	2.1×10^{-3} (500)	~10	[351]
Li_2SO_4–22m $MgSO_4$	3.6×10^{-3} (500)	~10	[351]
Li_2SO_4–40m–Li_2CO_3	5.6×10^{-7} (220)	~10	[352]
(Li_2SO_4–MSO_4)–Al_2O_3(M = Zn; Ag; Na)	~10^{-2} (400)	—	[353]
Li_2SO_4–10m LiOH	1.0×10^{-3} (217)	~1000	[354]
Li_2SO_4–$Fe_2(SO_4)_3$	—	—	[355]
Li_2SO_4–Li_3VO_4	—	—	[356]
Li_2SO_4–$Ce_2(SO_4)_3$	—	—	[357]
Li_2SO_4–$LiNbO_3$	—	—	[358]
($60Li_2SO_4$–$40Li_2CO_3$)–1m Li_2MoO_4	~10^{-5} (180)	~20	[359]
($60Li_2SO_4$–$40Li_2CO_3$)–0.5m Li_2WO_4	3.1×10^{-5} (180)	~20	[359]
($60Li_2SO_4$–$40Li_2CO_3$)–3m LiCl	2.0×10^{-5} (180)	~10	[360]
($60Li_2SO_4$–$40Li_2CO_3$)–γ-Al_2O_3 [0.06]	—	—	[361]
$60Li_2SO_4$–$40Li_2CO_3$–CeO_2	—	—	[361]
(Li_2SO_4–Na_2SO_4)–50m Al_2O_3	10^{-2}–10^{-1} (500)	—	[353]
$LiNaSO_4$–Na_2XO_4 (X = Mo; W)	—	—	[362]
($LiNaSO_4$–Ag_2SO_4–AgI/P_2O_5/B_2O_3	—	—	[363]
Li_2MnClO_4–α-Al_2O_3; SiO_2; TiO_2	—	NE	[364]
Li_2MnClO_4–20m CeO_2	4.0×10^{-5}(27)	~10	[365]
Li_2PO_4–50m Al_2O_3 [0.003–0.03]	1.0×10^{-6} (300)	~100	[320]
Li_2CO_3–50m Al_2O_3 [0.003–0.03]	2.6×10^{-7} (300)	DE	[320]
Li_2CO_3–20w Al_2O_3	5.6×10^{-8} (150)	~80	[366]
Li_2CO_3–50w $BaTiO_3$ [<45]	1.4×10^{-7} (150)	~200	[366]
Li_2CO_3–30w $LiNbO_3$ [<45]	5.1×10^{-9} (150)	~7	[366]
Li_2CO_3–30w $KTiO_3$ [<45]	5.6×10^{-8} (150)	~80	[366]
Li_2CO_3–10w Na_2CO_3	—	—	[367]
Li_2CO_3–10w K_2CO_3	—	—	[367]
$LiNO_3$–50m Al_2O_3 [0.01]	~10^{-2} (140)	~10^{3}	[368]
$NaNO_3$–50m Al_2O_3 [0.01]	~10^{-2} (200)	~10^{4}	[368]
NaCl–30m γ-Al_2O_3 [0.05]	~10^{-4} (300)	~10	[369]
Na_2SO_4–20m $MgSO_4$	5.0×10^{-2} (540)	~6	[370]
Na_2SO_4–CeO_2	—	—	[371]

TABLE V *Continued.*

Material	Ionic conductivity ($S\ cm^{-1}$)	Enhancement	References
$Na_4Zr_2Si_3O_{12}$ (NZS)–40m PZT	8.0×10^{-7} (100)	$\sim$100	[372]
NZS–5m $BaTiO_3$ [0.9]	1.6×10^{-5} (130)	$\sim$100	[373]
NZS–70m SO_4^{2-}/ZrO_4	$\sim 10^{-5}$ (100)	$\sim$10	[374]
NZS–70m $Sb_5/(SiO_2–Al_2O_3)$	1.6×10^{-4} (100)	$\sim$200	[375]
NZS–70m $Sb_5/(SiO_2–ZrO_2)$	1.3×10^{-5} (100)	$\sim$10	[375]
NZS–70m $Sb_5/(TiO_2–ZrO_2)$	1.3×10^{-5} (100)	$\sim$10	[375]
$Na_2Zr_{1.5}Mg_{0.9}(PO_4)_3–Al_2O_3$	—	—	[376]
Nasicon–Al_2O_3	—	—	[377]
Nasicon–SiC; aluminium silicate fibre	—	—	[378]
KNO_3–50m Al_2O_3 [0.01]	$\sim 10^{-3}$ (200)	$\sim 10^3$	[368]
KCl–45m γ-Al_2O_3 [0.05]	$\sim 10^{-3}$ (500)	$\sim$30	[379]
$(KNO_3–NaNO_3)–Al_2O_3$	10^{-2}–10^{-1} (300)	—	[353]
$(KNO_3–NaNO_3–LiNO_3)–Al_2O_3$	10^{-2}–10^{-1} (300)	—	[353]
$(K_2SO_4–Na_2SO_4)–Al_2O_3$	$\sim 10^{-2}$ (400)	—	[353]
($KHSO_4$–70m KH_2PO_4)–SiO_2	$\sim 10^{-5}$ (20)	$\sim$100	[380]
$RbNO_3$–70m Al_2O_3	—	—	[381]
$CsNO_3$–70m Al_2O_3	—	—	[381]
$CsHSO_4–SiO_2$	—	—	[382]
CsCl–γ-Al_2O_3 [0.05]	—	—	[383]
CuCl–20m γ-Al_2O_3 [0.06]	5.0×10^{-6} (25)	$\sim$100	[322]
AgI–30m γ-Al_2O_3 [0.06]	6.0×10^{-4} (27)	$\sim$2500	[323]
AgI–30m α-Al_2O_3 [0.06]	1.2×10^{-5} (27)	$\sim$50	[323]
AgI–50m η-Al_2O_3 [1]	7.0×10^{-4} (27)	$\sim$230	[384]
AgI–10m SiO_2 fumed [0.007]	1.1×10^{-5} (27)	$\sim$45	[385]
AgI–13.5m fly-ash [5]	7.2×10^{-5} (27)	$\sim$50	[385]
AgI–40m α-Fe_2O_3	8.1×10^{-5} (27)	$\sim$25	[384]
AgI–20m γ-Fe_2O_3 [1–2]	8.3×10^{-5} (27)	$\sim$83	[386]
AgI–30m ZrO_2 [0.7]	1.1×10^{-4} (27)	$\sim$210	[386]
AgI–30m CeO_2 [1–2]	8.6×10^{-5} (27)	$\sim$86	[386]
AgI–10m MoO_3 [1–2]	4.4×10^{-5} (27)	DE	[386]
AgI–10m WO_3 [1–2]	4.0×10^{-5} (27)	DE	[386]
AgI–30m TiO_2 [0.08]	1.6×10^{-5} (27)	$\sim$30	[387]
AgI–25m AgBr	3.2×10^{-4} (27)	$\sim$1310	[388]
AgI–25m AgCl	8.0×10^{-5} (27)	$\sim$125	[389]
AgI–25m AgCl	3.1×10^{-5} (27)	$\sim$30	[390]
AgCl–25m AgBr	3.0×10^{-5} (27)	$\sim$25	[391]
AgCl–10m γ-Al_2O_3 [0.06]	4.6×10^{-6} (60)	$\sim$10	[392]
AgCl–13v α-Al_2O_3 [0.3]	$\sim 10^{-6}$ (27)	$\sim$10	[393, 394]
AgCl–4v Al_2O_3 fibre [3]	2.1×10^{-7} (27)	$\sim$2–5	[395]
AgCl–11v SiO_2 fumed [0.007]	1.0×10^{-6} (27)	$\sim$10	[396]
AgBr–15v γ-Al_2O_3 [0.06]	1.0×10^{-5} (27)	$\sim$25	[397]
AgBr–20m ZrO_2	7.4×10^{-5} (100)	$\sim$10	[398]
Ag_2SO_4–10m K_2SO_4	1.0×10^{-1} (260)	$\sim$316	[399]
Ag_2SO_4–20m $BaSO_4$	5.6×10^{-4} (300)	—	[400]
CaF_2–10m Al_2O_3 [0.06]	$\sim 10^{-5}$ (500)	$\sim$10	[401]
CaF_2–2m CeO_2 [0.01]	2.5×10^{-4} (390)	$\sim$1000	[402]
CaF_2–5m ZrO_2 [1.5]	4.8×10^{-7} (282)	$\sim$10	[403]
$CaHSO_4$–25m $Al_2O_3;SiO_2;TiO_2$	$\sim 10^{-3}$ (103)	$\sim$1000	[404]
$SrCl_2$–30m Al_2O_3 [0.3]	$\sim 10^{-3}$ (500)	$\sim$10	[405]
$Sr(NO_3)_2$–29.5m γ-Al_2O_3 [37]	2.5×10^{-4} (330)	$\sim$250	[406]
BaF_2–20m Al_2O_3 [0.3]	–(500)	$\sim$20	[401]
α–$Zr(HPO_4) \cdot H_2O$(ZrP)–Al_2O_3	—	NE	[341]
HgI_2–30m γ-Al_2O_3 [0.06]	–(202)	$\sim$10	[407]
α-Al_2O_3 (porous)–AgI	1.4×10^{-5} (40)	$\sim$10	[324, 325]
α-Al_2O_3 (porous)–AgCl	4.0×10^{-7} (25)	—	[326]
α-Al_2O_3 (porous)–AgI–AgCl	3.3×10^{-5} (25)	—	[326]
α-Al_2O_3 (porous)–Li_3PO_4	1.9×10^{-6} (347)	$\sim$10	[327]
α-Al_2O_3 (porous)–PbF_2	$\sim 10^{-6}$ (27)	—	[328]
TlCl–10v γ-Al_2O_3 [0.06]	$\sim 10^{-8}$ (25)	$\sim$10	[408]
MSZ–$Al_2O_3;TiO_2$	10^{-6} (500)	NE	[409]
YSZ–20w Al_2O_3	1.0×10^{-1} (1000)	DE	[410]
SnF_2–5m Al_2O_3	4.0×10^{-5} (100)	$\sim$2	[411]
SnF_2–5m SiO_2 [0.014]	1.0×10^{-5} (100)	$\sim$6	[411]
PbF_2–10m SiO_2 [0.014]	–(27)	$\sim$100	[412]
$NH_4ClO_4–Al_2O_3$	—	—	[413]

among the various others groups. In these systems the first phase host-matrices are moderate ionic solids, like silver halides, copper halides, etc.; whereas, the second phase dispersoid is either another ionic solid (such as AgCl or AgBr in AgI) or an inert and insulating material (such as Al_2O_3, SiO_2, ZrO_2, fly-ash, etc.). In case of dispersion of insulating and inert second phase material, it has been found that the smaller the particle size, the larger the conductivity enhancement [309, 322, 323]. The reason suggested for this effect is the increased surface area of the dispersoid particles. Nagai and Nishino [324–328] recently reported a novel electrodeposition technique to fabricate composite electrolyte systems following an entirely reverse approach, i.e. dispersing the ionic solid into the host-matrix of the insulating material. They used microporous Al_2O_3 as a host-matrix and ionic salts such as AgI, AgI–AgCl, Li_3PO_4 and PbF_2 as the dispersed phase and reported enhancements in the room temperature conductivity of the ionic solids.

Table V gives an extensive list of *crystal–crystal* composite electrolyte systems reported so far. The longest enhancement (approximately 2500 times) in room temperature conductivity has been achieved for the Ag^+ ion-conducting composite electrolyte system AgI–Al_2O_3 [323]. The majority of the fast-silver-ion-conducting two-phase composite electrolyte systems were prepared, in general, using AgI as a first phase host-matrix in order to stabilize the superionic α–AgI phase at room temperature. However, in a recent investigation, we suggested an alternate compound a *quenched–annealed* (0.75 AgI : 0.25 AgCl) *mixed system–solid solution* in place of AgI [414, 415]. The new host exhibited several transport properties superior to those of the conventional host AgI including identical $\beta \rightarrow \alpha$ like transition characteristics at a reduced temperature. Using the alternate salt as the first phase host-matrix, we investigated few new fast Ag^+ ion-conducting two-phase composite electrolytes by dispersing submicrometre-size particles of Al_2O_3, SnO_2, SiO_2 [73, 416–420]. Fig. 3 shows the compositional variation of room temperature conductivity for the composite electrolyte systems prepared using both the new and conventional host-salts. Table VI lists some important ionic transport parameters of the new as well as the conventional host-salts along with the values for the composite electrolyte systems prepared using both the host-salts. It can be noted from the figure–table that the new host yields better composite electrolyte systems.

2. *Crystal–glass composites*. These systems emerged recently as a new class of composite electrolytes. The conductivity enhancements have been reported either by freezing a thermodynamically unstable superionic phase of a fast ion-conducting crystalline solid (e.g. α-AgI) or dispersing a second phase insulating and inert material (e.g. Al_2O_3, SiO_2, SnO_2, etc.) or eutectic system (e.g. $60Li_2SO_4$–$40Li_2CO_3$) into an ion-conducting glass system. Tatsumisago and coworkers [423–425] reported approximately three orders of enhancement in Ag^+ ion conduction in a composite system in which α-AgI was frozen into glass-matrix of Ag_2O–A_xO_y ($A_xO_y = B_2O_3$, CeO_2, WO_3, P_2O_5, V_2O_5, MoO_3) at a particular compositional range with very high quenching rate (approximately 10^5 K s^{-1}). X-ray diffraction (XRD) studies showed the characteristic patterns of α-AgI reflections. There are several systems reported in the literature, which exhibited significant enhancements in conductivity. Table VII lists some important crystal–glass composite systems.

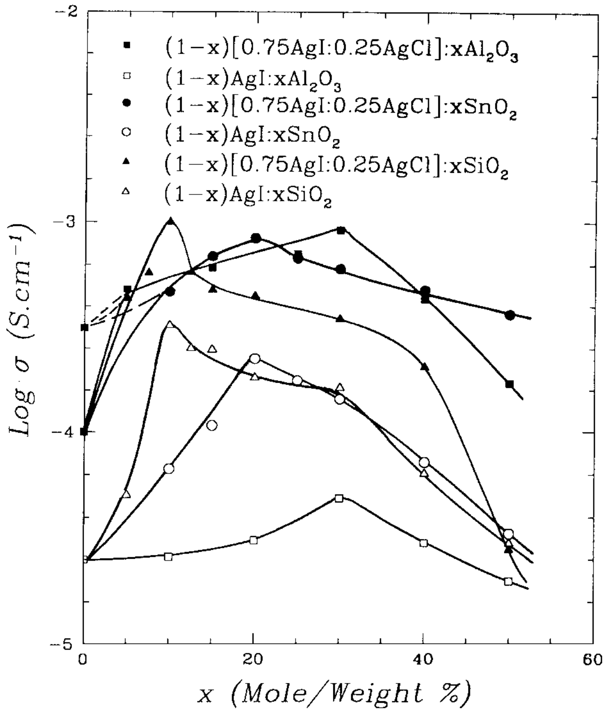

Figure 3 Compositional plots of room temperature conductivity for composite systems prepared with conventional host AgI and new host [0.75 AgI–0.25 AgCl].

3. *Glass–polymer composites*. Polymer electrolytes have several advantages over other solid electrolytes, as discussed earlier in Section 4.3. However, these systems exhibit less mechanical stability and low ionic conductivity at room temperature. Hence, in order to improve the electrical and mechanical properties high ion-conducting glasses can be dispersed into polymer electrolytes during sample preparation. There are very few systems of this class, listed in Table VII, in which dispersion has improved the mechanical stability alone [260, 321].

4. *Crystal–polymer composites*. Another way to improve the electrical and mechanical properties of polymer electrolytes is by dispersing an organic or inorganic filler, like PEO–PMMA, Al_2O_3, SiO_2, Nasicon, β-alumina, $LiAlO_2$, $LiClO_4$, etc., into polymer electrolytes [260, 321]. There are several crystal–polymer composite systems reported in the literature in which the dispersion of fillers has not only improved the mechanical stability of the polymer electrolytes but a significant enhancement in ionic conductivity has also been achieved. This class of solid electrolytes has attracted considerable attention as compared with glass–polymer composites. Some typical examples of crystal–polymer solid electrolytes are listed in Table VIII.

Composite electrolyte systems have several characteristic features. Some important features and theoretical understanding of the ion transport mechanism in these systems are described below.

TABLE VI Some important ionic transport parameters of conventional host AgI, new host: annealed and quenched [0.75 AgI: 0.25 AgCl] and some new composite electrolyte systems. Two energy values correspond to the region below and above the transition region.

Materials	$\sigma_{27\,^\circ\mathrm{C}}$ (S cm^{-1})	$\mu_{27\,^\circ\mathrm{C}}$ (cm^2 V^{-1} s^{-1})	$n_{27\,^\circ\mathrm{C}}$ (cm^{-3})	t_{ion}	$v_{d,27\,^\circ\mathrm{C}}$ (cm s^{-1})	E_a (eV)	E$_\mathrm{m}$ (eV)	E_f (eV)	E_d (eV)	q^* (eV)	Reference
Host compounds											
AgI	2.5×10^{-5}	$(2.5 \pm 1) \times 10^{-2}$	6.0×10^{15}	~1	2.4×10^{-3}	0.290	0.140	0.150			[421, 422]
						0.050	0.050	0.006			
[0.75 AgI–0.25 AgCl]	1.0×10^{-4}	$(1.5 \pm 1) \times 10^{-2}$	4.0×10^{16}	~1		0.243					[414, 415]
(annealed)						0.025					
[0.75 AgI–0.25 AgCl]	3.1×10^{-4}	$(2.4 \pm 1) \times 10^{-2}$	8.0×10^{16}	~1	2.4×10^{-3}	0.234	0.170	0.070	0.186		[414, 415]
(quenched)						0.050	−0.180	0.240	−0.189		
Composite systems											
0.7[0.75 AgI–0.25 AgCl]–0.3Al_2O_3	9.2×10^{-4}	$(2.4 \pm 1) \times 10^{-2}$	2.4×10^{17}	~1	1.2×10^{-3}	0.074	0.220	−0.145	0.230	0.070	[73, 416]
						0.024	−0.129	0.154	−0.142	0.020	
0.7 AgI–0.3 Al_2O_3	4.9×10^{-5}			~1							[73]
0.8[0.75 AgI–0.25 AgCl]–0.2SnO_2	8.4×10^{-4}	$(1.4 \pm 1) \times 10^{-1}$	3.7×10^{16}	~1	3.0×10^{-2}	0.147	0.111	0.036	0.126	0.148	[417, 418]
						0.052	0.010	0.042	0.008	0.048	
0.8 AgI–0.2 SnO_2	2.2×10^{-4}	$(1.5 \pm 1) \times 10^{-1}$	5.7×10^{15}	~1		0.223					[419]
						0.064					
0.9[0.75 AgI–0.25 AgCl]–0.1SiO_2	1.0×10^{-3}	$(1.4 \pm 1) \times 10^{-1}$	4.4×10^{16}	~1		0.096	0.037	0.053	0.040		[420]
						0.152	−0.083	0.253	−0.082		
0.9 AgI–0.1 SiO_2	3.2×10^{-4}	$(6.4 \pm 1) \times 10^{-2}$	7.1×10^{16}	~1		0.186					[420]
						0.086					

TABLE VII Some important crystal–glass and glass–polymer composite electrolyte systems (figures in parentheses and square brackets, respectively, refer to the temperature in degree celsius and the size of the dispersoid particle in micrometres). NE, no enhancement

Material	Ionic conductivity ($S\ cm^{-1}$)	Enhancement	Reference
Crystal–glass composites			
82α-AgI–(13.5 Ag_2O–4.5 B_2O_3)	4.0×10^{-2} (27)	~1000	[423]
82α-AgI–(13.3 Ag_2O–6.7 GeO_2)	−(27)	—	[423]
(60 Li_2SO_4–40Li_2CO_3) –20w (50.4Li_2O–39.6B_2O_3–10ZrO_2)	6.5×10^{-6} (220)	~10	[426]
(60 Li_2SO_4–40Li_2CO_3)–20w (42.5 Li_2O–57.5 B_2O_3)	6.6×10^{-6} (220)	~10	[426]
Li_2CO_3–10w (45.5 Li_2O–54.5 B_2O_3)	7.0×10^{-6} (150)	~1000	[427]
(55.5 AgI–22.25 Ag_2O–22.25 B_2O_3)–30w SnO_2 [~10]	1.0×10^{-2} (27)	~2	[428]
(66.67 AgI–14.29 Ag_2O–19.04 MoO_3)–10.5w Al_2O_3	7.0×10^{-3} (27)	~2	[429]
(41.5 Li_2O–24.5 LiCl–34P_2O_5)–60w Al_2O_3 [1]	1.4×10^{-4} (27)	—	[430]
(B_2O_3–0.7 Li_2O–0.7 LiCl)–0.1m Al_2O_3	~10^{-5} (227)	—	[313]
(90 $LiNaSO_4$–5 LiCl–5Na_2MoO_4)	3.6×10^{-4} (370)	—	[431]
SiO_2–PbO–PbF_2	3.1×10^{-6} (100)	—	[432]
Li_2O–Al_2O_3–4SiO_4–borosilicate	—	—	[433]
Bi_2O_3–In_2O_3–CuO–B_2O_3	—	—	[434]
Glass–polymer composites			
PEO–(Li_2O–3B_2O_3)	—	—	[435]
[PEO–(Li_2O–3B_2O_3)]–$LiClO_4$; $LiBF_4$	—	—	[435]
PEO–(Na_2O–3B_2O_3)	~10^{-10} (33)	~5	[436]
(PEO–$LiBF_4$)–lithium borosulphate glass	~10^{-7} (27)	NE	[437]
PEO_{10}–$LiCF_3SO_3$)–91.2v (1.2 Li_2S–1.6 LiI–B_2S_3) [50]	3.5×10^{-5} (25)	—	[438]
(PE617)–88.5v (1.2 Li_2S–1.6 LiI–B_2S_3) [50]	3.2×10^{-5} (25)	—	[438]
(PE817)–89.1v (1.2 Li_2S–1.6 LiI–B_2S_3) [50]	8.7×10^{-5} (25)	—	[438]

5.1. Characteristic features

5.1.1. *Concentration of the dispersoid plays a crucial role in conductivity enhancement in composite systems*

The conductivity increases with increasing dispersoid concentration, attains a peak value, then decreases. The peak is generally sharp, except for few systems, such as HgI_2–Al_2O_3, AgI–predried Al_2O_3 [323, 407]. Furthermore, the conductivity maxima may be different in different composite systems and depends on the nature of the second phase dispersoid [385]. In some composite systems, dispersion has not altered/increased the conductivity of the host-matrix [336, 341, 386, 437].

5.1.2. *The nature of dispersoid decides the order of enhancement in composite electrolyte systems*

For instance, highest conductivity enhancements were reported in AgI–Al_2O_3 and LiCl–Al_2O_3 systems with η-Al_2O_3 dispersoid [313, 323, 464]. In general, larger enhancements are reported with Al_2O_3 in many composite electrolyte systems as compared with other dispersoids [385, 386, 411]. It is also noteworthy that wet dispersoid results in better enhancement compared to dry in the same composite system [312, 323, 336, 407]. Ferroelectric materials of high dielectric constant and solid superacid of high surface area can also be used as dispersoids for conductivity enhancement in some composite electrolyte systems [387, 465, 466]. Conductivity enhancement was also observed in systems treated with Lewis acid, like SbF_5 [467].

5.1.3. *The conductivity enhancement in composite electrolyte systems is strongly particle-size dependent of the dispersoid*

It has been found that the conductivity of the composite system increases with decreasing particle size [261, 322, 336, 385]. Surface area determination showed that the surface area increased linearly with decreasing particle size [322, 335, 385]. Hence, porous materials having large surface areas, irrespective of the large particle size, are reported to exhibit better enhancements in ionic conductivity [341, 375, 428].

5.1.4. *Temperature influences conductivity enhancement in composite electrolyte systems*

The enhancement is highest only at low temperatures. As the temperature increases the enhancement decreases. This in turn lowers the activation energy as compared with the host-matrix. A detrimental effect is observed at high temperatures.

5.1.5. *Preparation route is another significant factor that controls conductivity enhancement in composite electrolyte systems*

An analysis of various methods, used for the preparation of the composites, shows that the best results can be achieved by mixing the host and dispersoid in the molten state of the host material [315, 319, 320, 386, 468]. This increases the contact surface area and provides more uniform distribution. Another important

TABLE VIII Some important crystal–polymer composite electrolyte systems (figures in parentheses and square brackets, respectively, refer to the temperature in degree celsius and size of dispersoid particle in micrometres). NE, no enhancement

Material	Ionic conductivity ($S\ cm^{-1}$)	Enhancement	Reference
$(PEO_{10}–LiI)–Al_2O_3$ [0.05]	$\sim10^{-4}$ (103)	~20	[439]
$(PEO_8–LiClO_4)$–10w γ-$LiAlO_2$ [1]	$\sim10^{-4}$ (60)	~10	[440]
$(PEO_{10}–LiClO_4)$–10v α-Al_2O_3 [40]	—	~2	[441]
$(PEO_{10}–LiClO_4)$–50w (PEO–PMMA)	5.1×10^{-5} (25)	~100	[261]
$(PEO_8–LiClO_4)$–10w β''-Al_2O_3 [5]	$\sim10^{-4}$ (60)	—	[442]
$(PEO_{16}–LiClO_4)$–5w SiC [1]	5.0×10^{-4} (100)	NE	[443]
(6PEO–4PMMA)–10m $LiClO_4$	1.0×10^{-5} (25)	~100	[261]
(8PEO–2PMMA)–10m NaI	2.0×10^{-7} (25)	~100	[261]
(7PEO–3IPMMA)–10m $LiClO_4$	9.0×10^{-5} (25)	~1000	[261]
(7PEO–3SPMMA)–10m $LiClO_4$	1.4×10^{-5} (25)	~100	[444]
(8PEO–2PMA)–10w $LiClO_4$	2.9×10^{-5} (25)	~40	[260]
(8PEO–2PAA)–10w $LiClO_4$	1.6×10^{-5} (25)	~20	[260]
(8PEO–2PAAM)–10w $LiClO_4$	6.3×10^{-5} (25)	~90	[260]
(8PEO–2PMMA)–10w $LiClO_4$	4.0×10^{-6} (25)	~6	[260]
(8PEO–2PAPG)–10w $LiClO_4$	1.6×10^{-4} (25)	~250	[260]
$(3PEG–LiCF_3SO_3)$–66w $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	1.9×10^{-4} (40)	~10	[445]
(PEO–DGEPEG–TGEG)–$LiClO_4$	$\sim10^{-5}$ (25)	~100	[250]
(PEO–12m PPG)–$NaClO_4$	1.8×10^{-4} (25)	~1000	[446]
(PEO–MEEP)–NaSCN	5.0×10^{-5} (25)	~100	[447]
$(PEO_{10}–NaI)$–10w θ-Al_2O_3 [2]	1.4×10^{-5} (25)	~100	[261]
$(PEO_{10}–NaI)$–10w α-Al_2O_3	6.5×10^{-5} (25)	~230	[448]
$(PEO_{10}–NaI)$–0.5w Nasicon	$\sim10^{-5}$ (25)	~35	[449]
$(PEO_{10}–NaI)–SiO_2$	5.0×10^{-6} (25)	~20	[450]
(PEO–NaSCN)–30w γ-Al_2O_3 [0.7]	$\sim10^{-5}$ (30)	~5	[313]
$(7PEO–3NH_4I)$–30w γ-Al_2O_3 [10]	5.1×10^{-4} (100)	~10	[451]
$(7PEO–8NH_4I)$–30w α-Al_2O_3	1.8×10^{-3} (100)	~100	[451]
(PEO–AgSCN)–10w Al_2O_3	8.8×10^{-4} (27)	—	[452]
(PEO–AgSCN)–SiO_2	—	—	[453]
(PEO–AgSCN)–Fe_2O_3	—	—	[454]
(PEO–PAA)–NH_4SCN	$\sim10^{-5}$ (25)	—	[289]
MEEP–13w (PEGDE–$LiClO_4$)	1.2×10^{-6} (25)	—	[455]
$(PEO–NaClO_4)–Na_2SiO_3$	—	—	[456]
LiOAc–LiTFSI–TEMAB	—	—	[457]
PVC–DOE/DBP–LiTFSI	$\sim10^{-4}$ (25)	—	[458]
(Chitosan + 1% acetic acid)–(NaI/$NaClO_4$)	5.0×10^{-5} (25)	~10	[459]
(PAN–AmMA)–2w I_2	1.0×10^{-3} (25)	~100	[460]
((PEO–PMMA)–30w (PC–$LiBF_4$))–0.1w $15Cr_5$	$\sim10^{-3}$ (25)	NE	[461]
$(0.5PEO + 0.5LiPEG)_{0.9}–LiCF_3SO_3$	$\sim10^{-5}$ (25)	—	[258]
(PEG–PMMA)–30v $LiCF_3SO_3$	10^{-4} – 10^{-5} (25)	—	[462]
(PVA–PVP)–NH_4SCN	—	—	[463]

factor that controls the conductivity enhancement is the duration (termed soaking time) for which the mixture is heated. Various other preparation methods, namely thermal decomposition of the precursors [320], preparation from eutectic [310], sol–gel technique, solution-cast method [369, 379, 451], and the electrochemical deposition technique [324–328], have also been attempted recently for fabrication of composite electrolyte systems. It has been reported that for composite electrolyte systems prepared by the solution-cast method, conductivity enhancement is about one order of magnitude higher than those prepared by conventional methods [369, 379].

5.1.6. In composite electrolyte systems, constituent phases coexist simultaneously and separately

Various techniques such as XRD, differential thermal analysis (DTA)/differential scanning calorimetre (DSC), and infrared (i.r.) analysis, are employed to identify the existence of separate phases. The presence of high conducting space-charge regions at host–dispersoid interfaces (which is responsible for the conductivity enhancement, to be discussed in detail later) has been indicated by nuclear magnetic resonance (NMR) studies. Scanning electron microscopy (SEM) is applied to determine the particle size of the dispersoid and their agglomeration during sample preparation.

5.2. Theoretical models

Several phenomenological theories have been proposed to understand the ion transport mechanism in composite electrolyte systems. No single unified model exists, as yet, which can explain uniquely various experimental results on different composite electrolyte systems. However, the central feature of the majority of the models, suggested to explain conductivity enhancement in two-phase composite systems, is the existence of a space-charge region (double-layer) at the interface between the host and dispersoid. Various experimental studies have been directed towards this theme, namely dependence of conductivity on the alumina surface area [322, 335, 385], apparent effect of surface hydration [312, 336, 385, 407, 469], etc. In addition to this, bulk interactions have also been suggested as a cause for conductivity enhancements in some composite systems [313, 470]. Most of these models focus on calculation of the compositional dependence of conductivity. They differ only in the methods of calculation and in the assumptions concerning the distribution of the dispersoid particles in the composite system. Some important models proposed for composite electrolyte systems are discussed below.

5.2.1. Earlier models (abandoned)

Some of the earlier models, attempted in the past, to explain the conductivity behaviour in two-phase mixtures, were put forth by Maxwell [471], Raleigh [472], Lichtenecker [473], Landauer [474], Wagner [475].

Maxwell [471] and Raleigh [472] have calculated the conductivity of two-phase mixtures in terms of the bulk conductivity of the individual phases. Raleigh assumed that material of the second phase in the form of spheres or cylinders is embedded in material of the first phase, forming a rectangular array. In this model, he assumed the current flow in this mixture is always through the first phase material only. Hence, the conductivity of the first phase material always dominates even if the volumes of both materials are equal. This model is applicable only when the volume of the second phase is much less than the first phase material, in such way that the first phase envelops the second phase material. However, this model is totally ideal since such physical arrangements never occur in real systems.

Lichtenecker [473] considered both the phases as non-passive metallic mixtures and expressed the resistivity, ρ_m, as

$$\rho_m = \rho_1^{x_1} \rho_2^{x_2} \tag{43}$$

where ρ_1 and ρ_2 are the resistivities of the first and second phase materials, respectively; x_1 and x_2 are their volume fractions. This model is valid only when ρ_1 and ρ_2 are of the same order of magnitude.

Landauer [474] proposed effective medium theory by considering the arrangement of materials in alternate layers. The flow of current is parallel to these layers, hence, the conductivity, σ_m, of the mixture can be expressed by

$$\sigma_m = x_1\sigma_1 + x_2\sigma_2 \tag{44}$$

This expression is adequate only for passive constituent phases, hence, the current can flow straight through the region of low resistance. However, in such a model, the current cannot avoid regions of high resistance, as it will do if the phases are randomly mixed.

Wagner [475] attempted to explain conduction behaviour of bi-phasic metal–semiconductor mixtures by introducing the concept of existence of an interfacial space-charge region at the boundary between the two phases, originating from the charge density (or potential) gradient due to the non-passive nature of the different constituent phases at the interface. He expressed the total conductivity, σ, of the system as

$$\sigma = 0.19(g\epsilon kT/q^2)\big(V_v/r_A^2\big)q\mu \tag{45}$$

where g is a structural factor; ϵ is the dielectric constant of the medium at temperature, T; k is the Boltzmann constant; V_v is the volume fraction of the dispersoid in the mixture; q is the fundamental charge; μ is the mobility of the charge carrier; and r_A is the radii of the dispersoid particle. Crosbie [476] modified the above expression to explain electrical conduction in a TiO_2–SiO_2 bi-phasic mixture and wrote the equation for total conductivity of the dispersed mixture as

$$\sigma = \sigma_b\big[1 + 0.83g|Z|V_v\big(\lambda/r_A^2\big)\big] \tag{46}$$

where σ_b is the conductivity of the host; Z is the effective charge on the defects created; and λ is the thickness of the double-layer, called the Debye length, which is given by

$$\lambda = [8\pi q^2 n(\infty)/\epsilon kT]^{-1/2} \tag{47}$$

where $n(\infty)$ is the defect concentration in the bulk. It is well known that the conductivity of lithium, silver and copper halide systems can be considerably influenced by homo- and alio-valent doping. If it is assumed that Al_2O_3 or SiO_2 were soluble at all in the halides, a few mole per cent would be sufficient to saturate the respective lattices with defects. Hence, a classical doping model can also be proposed to explain conductivity behaviour in the composite electrolyte systems. Jow and Wagner [322] attempted to explain the conductivity enhancement in the CuCl–Al_2O_3 composite system. However, as assumed by them in the model, dissolution of the dispersoid into the bulk lattice, creating copper vacancies, as well as an alternative explanation originating from severe lattice distortion of the phase boundaries resulting in conductivity enhancement, were ruled out by XRD results.

The above models failed to explain many experimental outcomes reported for composite electrolyte systems, hence, were eventually abandoned due to the reason that they were originally proposed for electron conducting bi-phasic systems. However, the possible existence of a space-charge region, which was ascribed as the major cause for conductivity enhancement by Wagner [475], became the basis for forthcoming models.

5.2.2. Space-charge models

5.2.2.1. Jow and Wagner's model. Kliewer [477] proposed the continuum model for the space-charge region near surfaces of Frenkel disorder type compounds (like CuCl) to describe the case of space-charge regions surrounding spherical inclusions in matrix material of Frenkel type. In order to explain conductivity enhancement in a CuCl–Al_2O_3 composite electrolyte system, Jow and Wagner [322] extended Kliewer's theory. They assumed that a space-charge region is created at the host–dispersoid interface boundary when a dispersoid phase (A) is introduced into the electrolyte host-matrix (MX). Fig. 4a shows a dispersoid particle embedded in an electrolyte host-matrix. A space-charge layer of thickness λ has been created around the dispersoid particle. Fig. 4b and c shows the idealized spherical particle and cross-sectional view for analytical calculation.

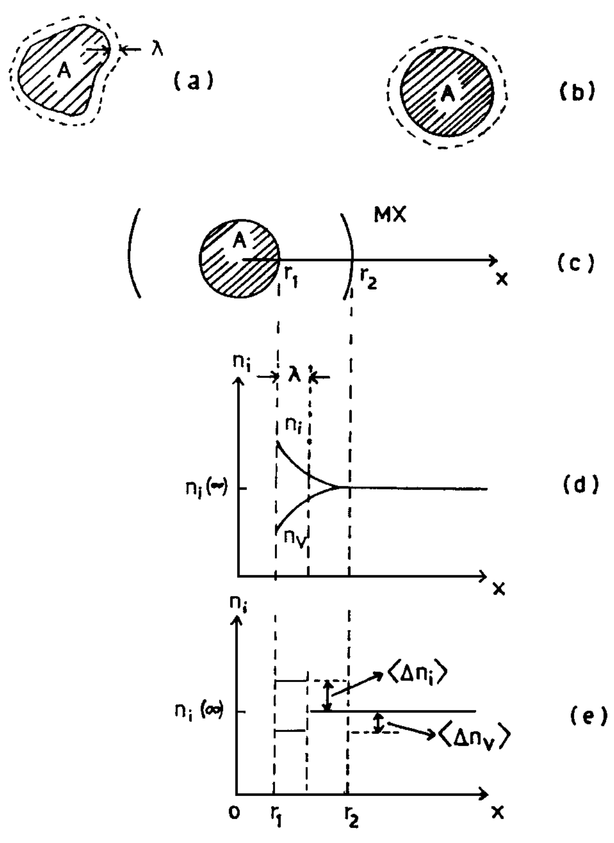

Figure 4 (a) Schematic diagram of a dispersoid particle (A) surrounded by a space-charge layer of thickness λ embedded in the host-matrix (MX); (b) an indealized spherical approximation of the dispersoid; (c) a cross-sectional view of A of radius, r_A, for analytical calculation; (d) defect concentration profile in the space-charge region where $F_I \ll F_V$; (e) average excess charge density, $\langle \Delta n_i \rangle$, in the space-charge region.

They proposed that the dispersoid particle has a charge, though the sign is not known, at/near the surface, which is compensated by the formation of oppositely charged defects in the diffused space-charge layer. As a result, an excess defect concentration in this region is formed. Fig. 4d and e shows the defect concentration profile and average excess charge density in the space-charge region. Hence, it is assumed that $F_I < F_V$, where F_I and F_V are the free energies of formation of interstitial and vacancy defects, respectively. Jow and Wagner attributed this as the main reason for conductivity enhancement, σ_{sc}, and wrote the expression for total conductivity, σ, of the composite electrolyte system as

$$\sigma = \sigma_b + \sigma_{sc} \tag{48}$$

$$= \sum_i n_i(\infty) q\mu_i + 3\sum_i q\mu_i \langle \Delta n_i \rangle (\lambda/r_A)[V_v/(1-V_v)] \tag{49}$$

where the conductivity contribution from the space-charge region is

$$\sigma_{sc} = \frac{\sum_i q\mu_i \left\{ \int_{r_1}^{r_2} \int_o^{\pi/2} \int_o^{2\pi} [n_i(r) - n_i(\infty)] r^2 \, dr \sin\theta \, d\theta \, d\phi \right\}}{\left\{ \int_{r_1}^{r_2} \int_o^{\pi/2} \int_o^{2\pi} r^2 \, dr \sin\theta \, d\theta \, d\phi \right\}} \tag{50}$$

$$= 3\sum_i q\mu_i \langle \Delta n_i \rangle (\lambda/r_A)[V_v/(1-V_v)] \tag{51}$$

The summation runs over all the different defect species. Other notations have their usual meaning as described in Section 5.2.1. $\langle \Delta n_i \rangle$ is the average excess charge density representing the excess defect concentration near the surface, for which $\lambda \ll r_A$. Here the conductivity contribution due to the dispersoid is neglected. Moreover, as μ and $\langle \Delta n \rangle$ increase with temperature, λ decreases with temperature. Hence, their combined effect is not easy to estimate in this treatment. This model has qualitatively explained the dependence of conductivity enhancement on temperature, particle size and volume fraction of the dispersoid, but with not much success. Jow and Wagner failed to predict a maxima in σ versus V_v experimental plots since the approximation used in their equation for σ_{sc} does not justify its application to composite systems containing high volume fractions of the dispersoid phase. The term $[V_v/(1 - V_v)]$ is an infinitely increasing term. It also failed to explain the mechanism leading to enrichment of the defect concentration in the space-charge region.

5.2.2.2. Discrete-shell and screening-layer models. Stoneham *et al.* [478] proposed the discrete-shell model and tried to explain the conduction mechanism in composite electrolytes (namely LiI–Al_2O_3) by considering the random distribution of non-conducting dispersoid particles within the host-matrix and high conducting boundary layers lying on the non-conducting core. This model is an extension of Landauer's effective medium model [474] discussed above, for the conductivity of a random mixture of two metallic media in good electrical contact and with differing conductivity. Fig. 5a shows the spatial distribution of conductivity, σ, in a bi-phasic metal mixture with dispersoid particle of radius r_A, in a host-matrix. In this mixture, the conductivity of the system will never go to zero as there is no insulating phase present. Landauer's approach cannot be applied directly to dispersed solid electrolyte systems, as pointed earlier, because of the basic difference in the nature of the two systems. If the thickness of the space-charge region is λ, Stoneham *et al.* [478] found that the conductivity of the composite electrolytes varies, as shown in Fig. 5b, near the insulating dispersoid particles. They further suggested that it would be appropriate to envisage a screening-layer model for two-phase composite electrolyte systems. In such a situation the conductivity varies as shown in Fig. 5c, which is more realistic. Although, this model successfully accounted for the decrease in conductivity with a larger concentration of dispersoid, it did not account for the influence of temperature on the conductivity of the system. Moreover, this model greatly underestimated the conductivity expected for less than about 10 vol % Al_2O_3 in LiI and shows strong deviations from the σ versus V_v plot.

5.2.2.3. Pack's model. In order to explain the conductivity enhancement in the HgI_2–Al_2O_3 composite system, Pack [407] developed a model and expressed the total conductivity by the following equation

$$\sigma = \sigma_b(1 - V_v) + GS(1 - V_v)^2 + \sigma_A V_v \tag{52}$$

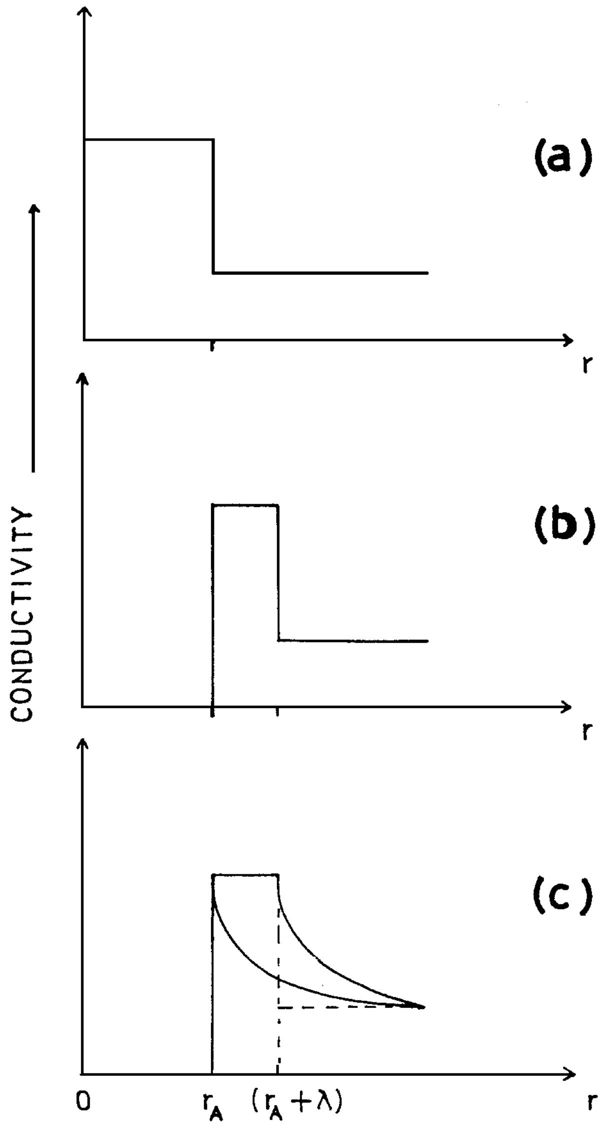

Figure 5 Spatial distribution of conductivity near the host–dispersoid interface boundary: (a) Landauer model of bi-metallic mixture, (b) discrete-shell, and (c) screening-layer models due to Stoneham *et al.* [478] for two-phase composite electrolyte systems.

where σ_b and σ_A are the conductivities of the host-matrix and dispersoid material, respectively; V_v is the volume fraction of the dispersoid; S is the surface area created by the dispersoid per unit volume of mixture. G is a factor that accounts for the number of excess charges per unit volume of mixture and can be expressed as

$$G = \sigma_{sc}/[S(1 - V_v)] \tag{53}$$

where σ_{sc} is the enhanced conductivity due to the space-charge effect.

This model not only describes the conductivity enhancement but also accounts for the decrease in conductivity value due to the blocking effect of the dispersoid particles.

The space-charge models, described above, qualitatively assumed a space-charge layer of high conductivity surrounding each dispersoid particle and the change in the conductivity as being proportional to the surface area of the dispersoid particles, i.e. for a fixed concentration of dispersoid, the smaller the particle size, the larger the surface area, hence, the larger the conductivity enhancement. However, there are a variety of complex behaviours observed for various composite electrolyte systems, namely effect of moisture on LiI–Al_2O_3, HgI_2–Al_2O_3, AgI–Al_2O_3; occurrence of a conductivity maxima at a particular concentration of the dispersoid; the mechanism of enrichment of defect concentration in the space-charge region, etc., that could not be explained.

5.2.3. Adsorption–desorption model

This is the most extensive quantitative model proposed by Maier [316–318, 390, 393, 394, 396, 397, 408, 479–483] giving a thorough treatment of the redistribution of mobile species at various types of interfaces and its consequences on ionic conduction parallel to the interfaces. He employed the principle of a parallel switching resistor and modified the space-charge model by considering the dispersoid phase not as an inactive insulator but as a driving force for the evolution of a space-charge region, which in turn causes an enrichment in defect concentration at the interfacial boundary. He treated the space-charge region as a separate phase and considered such a phase as a parallel resistor. He expressed the total conductivity of the two-phase dispersed solid electrolyte as

$$\sigma = \beta_A V_A \sigma_A + \beta_b V_b \sigma_b + \beta_{sc} V_{sc} \sigma_{sc} \tag{54}$$

where A, b and sc denote the dispersoid, the bulk (MX) and space-charge component respectively. V and σ are the volume fraction and conductivity of the respective phases, and β is the parameter describing the deviation from ideal parallel switching. Maier discussed a possible mechanism of enrichment of defect concentration at the interface boundary on the basis of defect chemistry of the dispersed solid electrolytes. The second phase dispersoid (A), which is chemically inert, affects defect equilibrium at the interface boundary. For a host-matrix (MX) with Frenkel defects, the metal ions (M^+) will be attracted from or repelled into the MX phase depending on the chemical (charged) species present on the surface of the dispersoid phase (A). The attraction or repulsion processes are discrete and only one of them occurs in a given system under specific conditions. Fig. 6a and b shows these phenomena for a Frenkel type MX–dispersoid A composite system. In the case of attractive interaction, the surface active dispersoid sucked out the cations from its regular sites and consequently enhanced the vacancy concentration (adsorption process), whereas in case of repulsive interaction, the dispersoid drives M^+ ions into interstitial sites and enhances the interstitial concentration (desorption process). Therefore, in this model, in both cases an extrinsic conductivity enhancement is assumed, as shown in Fig. 6c. Using Kroger–Vink notation, these mechanisms can be written as

For a free surface

$$\mathrm{M_M} + \mathrm{V_S} \rightleftharpoons \mathrm{M_S^{\bullet}} + \mathrm{V'_M} \qquad \text{Step 1}$$

$$\mathrm{M_S^{\bullet}} + \mathrm{V}_i \rightleftharpoons \mathrm{M}_i^{\bullet} + \mathrm{V_S} \qquad \text{Step 2}$$

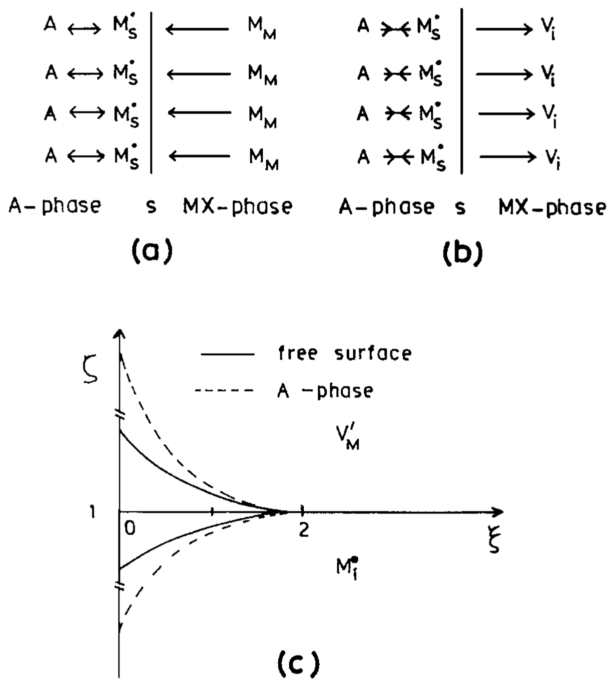

Figure 6 (a) Attraction and (b) repulsion mechanism by the surface of dispersoid A. (c) Concentration profiles for the cation vacancies, V_M', and the interstitial cations, M_i.

In the presence of dispersoid phase A

$$\begin{aligned} &M_M + V_S \rightleftharpoons M_S^{\bullet} + V_M' && \text{Step 1} \\ &M_S^{\bullet} + V_A \rightleftharpoons M_A^{\bullet} + V_S && \text{Step 2} \\ &M_A^{\bullet} + V_i \rightleftharpoons M_i^{\bullet} + V_A && \text{Step 3} \end{aligned}$$

where M denotes the cation or its regular site; V, a vacancy; S, surface; i, an interstitial site and "•" or "′" represent the charge of the defect (positive or negative) relative to the perfect lattice. Here, steps 1 and 2 indicate the adsorption process, whereas steps 1–3 indicate the desorption process. In the case of a Schottky defect ionic solid MX–dispersoid A composite system, both cation and anion compete for attractive and repulsive interaction of the dispersoid. Consequently, these two processes will be non-discrete in nature. Hence, it becomes too difficult to predict whether the dispersion of A into MX will enhance conductivity or not. The mechanism for the formation of cation and anion vacancy pairs in a Schottky ionic solid (MX)–dispersoid (A) composite system, can be visualized as

$$\begin{array}{c} M_M + V_S \rightleftharpoons V_M' + M_S^{\bullet} \\ X_X + V_S \rightleftharpoons X_S' + V_X^{\bullet} \\ \hline M_M + X_X + 2V_S \rightleftharpoons V_M' + V_X^{\bullet} + M_S^{\bullet} + X_S' \end{array}$$

Employing the principle of parallel switching, Maier calculated the conductivity contribution from the space-charge region by integrating Equation 50 in one–dimensional Cartesian co-ordinates using an exponential variation of the defect concentration and wrote the equation for conductivity enhancement as

$$\sigma_{sc} = q\mu_v(c_{vs}c_{vb})^{1/2} \qquad (55)$$

where μ_v is the mobility of vacancies; c_{vs} and c_{vb} are the concentration at the surface and the bulk, respectively. Here dispersoid particles are assumed to be spherical and surrounded by a spherical space-charge region of thickness 2λ. The volume fraction of the space-charge region can be obtained by subtracting the volume of the inner sphere from that of the outer sphere and is given by

$$V_{sc} = 3(2\lambda/r_A)V_A \qquad (56)$$

where r_A is the radius of the dispersoid particles. Neglecting the conductivity of the insulating dispersoid phase, Maier expressed the total conductivity finally as

$$\begin{aligned} \sigma &= (1 - V_A)\sigma_b + \beta_{sc}V_{sc}\sigma_{sc} \\ &= (1 - V_A)\sigma_b + 3q\beta_{sc}(2\lambda/r_A)V_A\mu_v(c_{vs}c_{vb})^{1/2} \end{aligned} \qquad (57)$$

By adjusting the ideal parallel-switching parameter, β_{sc}, in the range 0.2–0.7 depending upon distribution topology, it has been seen that the above equation explained experimental results such as larger conductivity enhancement at low temperatures, particle size dependence, effect of wet dispersoid, etc., for various solid electrolyte systems fairly well. The attractive feature of Maier's model is that it highlights the mechanism responsible for enrichment of surface defects in the space-charge region. Although, Maier's model explains many characteristic features of composite electrolyte systems well, it failed on several points such as: maxima in σ versus V_A plots; the assumption of an over-simplified distribution topology being characterized by a β-factor and resulting in quasi-parallel switching; the assumption of spatially constant values for mobility; the dielectric constant and the molar volume; neglecting the structural changes, polarization effect, elastic effects, etc.

5.2.4. Resistor-network model

Dudney [484] tried to explain the conductivity enhancements in composite electrolyte systems by considering random distribution of the dispersoid in the host-matrix and the role of the host–dispersoid particle sizes and the interface. Assuming the resistor-network, as shown in Fig. 7a, he calculated conductivity using

$$\begin{aligned} \sigma &= \\ &(1-x)\sigma_b + x\sigma_A + 2\{(1/r_b) + x[(1/r_A) - (1/r_b)]\} \\ &\times \frac{\sigma_{b/b}(1-x^2)r_A^2 + 2\sigma_{b/A}(1-x)xr_Ar_b + \sigma_{A/A}x^2r_b^2}{[(1-x)r_A + xr_b]^2} \end{aligned} \qquad (58)$$

where x is the volume fraction of the dispersoid; r_b and r_A are the grain size of the bulk and dispersoid, respectively; $\sigma_{b/b}$, $\sigma_{b/A}$ and $\sigma_{A/A}$ are the interfacial conductivities. This model predicts a peak in the σ versus x plot with the effect of the grain size of the bulk and

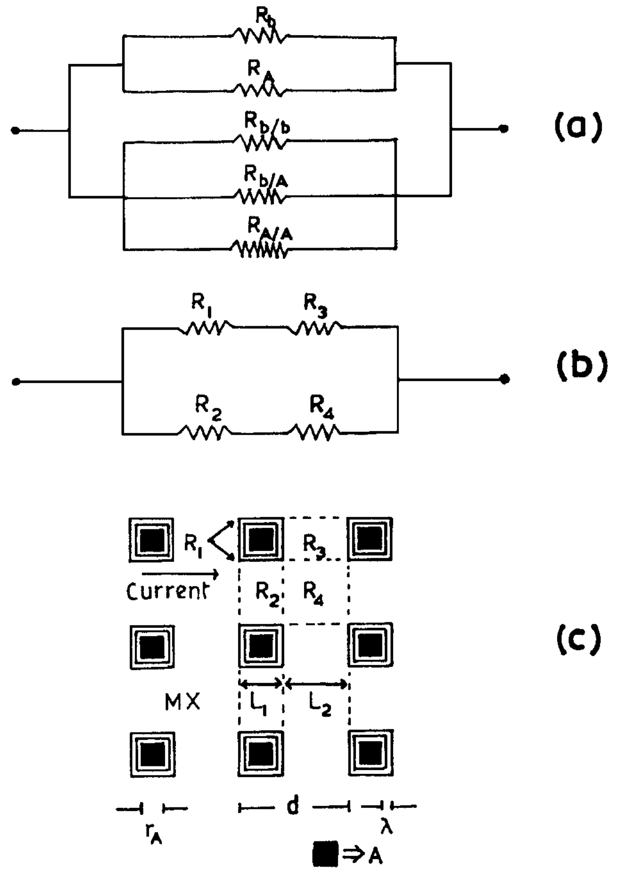

Figure 7 (a) A circuit network for analytical calculation of ionic conductivity [484], (b) a resistor network [485], and (c) schematic diagram showing the arrangement of cubic-dispersoid particles A on a simple-cubic lattice embedded in a conducting medium MX.

dispersoid. Wang and Dudney [485] modified the distribution topology of dispersoid A into the host-matrix. They used a resistor network to calculate the conductivity for a simple cubic-array of cubic insulating particles of dispersoid phase A embedded in the conducting host-matrix phase MX as shown in Fig. 7b and c. The total conductivity of the composite electrolyte system was expressed as

$$\sigma(x) = \sigma_b + \sigma_{sc}\{[x - (r_A/2)]/\lambda\}^m \qquad (a/2) < x < [(a/2) + \lambda] \quad (59)$$

$$\sigma(x) = \sigma_b + \sigma_{sc}\exp\{-[x - (r_A/2) - \lambda]/s\} \qquad x > [(a/2) + \lambda] \quad (60)$$

where x is the distance from the centre of the dispersoid, σ_b is the bulk conductivity, σ_{sc} is the conductivity of the high conducting layer of thickness λ, r_A is the size of the dispersoid; m and s are the parameters. The conductivity enhancement as a function of volume fraction and particle size of the dispersoid could very well be explained. The model also accounts for the effect of thickness of the double-layer and mobility in conductivity enhancement, however, temperature effects were not considered. As the model predicts the dependence of the maxima in σ *versus volume fraction* plot on λ and r_A, it is limited only to the LiI–Al_2O_3 composite electrolyte system. Moreover, the model suggests that grain boundaries or dislocations formed by plastic deformation, primary recrystallization of the host-matrix, defect mobilities, etc., are also the cause for large enhancements in conductivity along with enrichment of defect concentration in the space-charge region [395, 486].

5.2.5. Percolation model

Jow and Wagner's and Maier's models could not account for the typical conductivity variation in most composite electrolyte systems, which is marked by initial increases with increasing concentration of the dispersoid phase followed by rapid decrease. Bunde, Dieterich and coworkers [487–493] attempted to explain this behaviour through their percolation model. They assumed a two-dimensional percolation network, as shown in Fig. 8 in which insulating dispersoid and conducting host grains of identical size and shape are randomly distributed. An interfacial high conducting path is formed, as shown by the dark boundary line in the figure. Monto Carlo simulations for conduction in such a three-dimensional array identified two percolation threshold concentrations, p'_c and p''_c. p'_c $(0 < p'_c < 0.5)$ corresponds to the

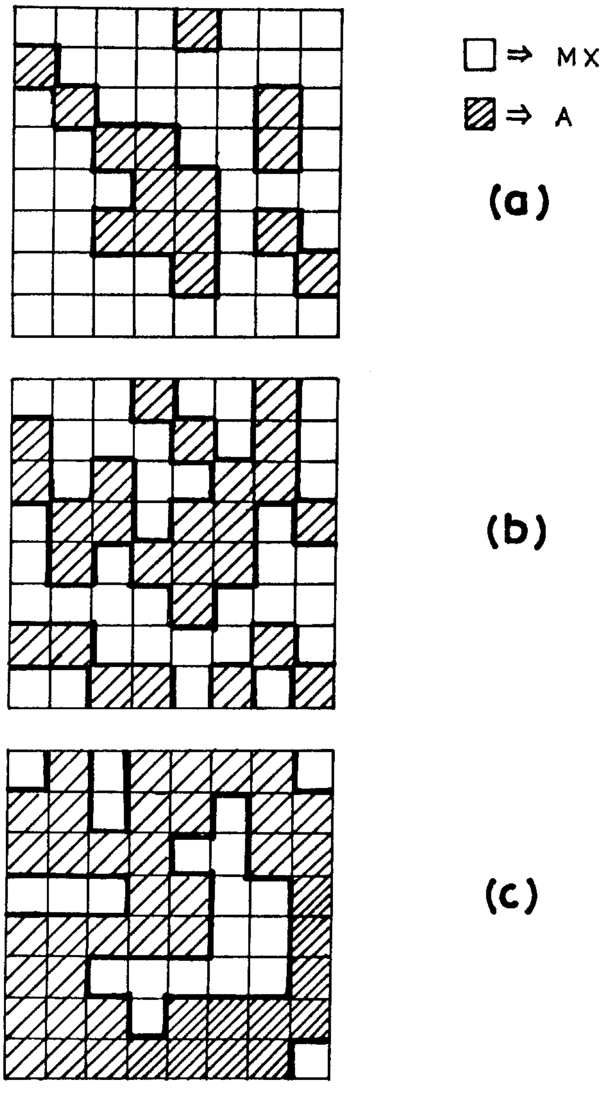

Figure 8 Two-phase mixture on a square lattice for different concentration, p, of dispersoid A. The highly conducting layers are marked by bold lines. (a) $p < p'_c$, (b) $p = p'_c$ onset of interface percolation, and (c) $p > p''_c$ for disruption of conducting paths.

onset of interface percolation and p''_c ($0.5 < p''_c < 1$) to conductor–insulator transition, where conductivity may approach to zero. Maximum enhancement in conductivity, σ, with concentration of dispersoid, p, is found to be between p'_c and p''_c. This model accounts well for effects of the physical nature (i.e. size and shape) of the dispersoid and bulk conductivity of the host-matrix in conductivity enhancement, however, only at $p \sim 50$ vol %.

5.2.6. Concentration gradient model

Rao and coworkers [386, 468] proposed that concentration caused by chemical interaction at the host (AgI)–dispersoid (oxide particles) interface is mainly responsible for conductivity enhancement in composite electrolyte systems. According to them, Ag^+–O^{-2} interaction, which occurs at the interface region, is stronger than Ag^+–I^- interaction. Therefore, Ag^+ ions that migrate towards the dispersoid surface are pinned down and an accumulation of Ag^+ ions thus occurs till the ions act as an effective barrier for further Ag^+ ion migration towards the dispersoid surface. As a consequence, a concentration gradient is formed at the interface region, as shown in Fig. 9. The size of the *valley* indicates the order of enhancement in conductivity of composite electrolyte systems. The depth of this valley depends on Ag^+ ion depletion, whereas the distance of the minimum to the dispersoid surface depends on the chemical force exerted by the dispersoid particles, which is a function of the concentration of AgI in the interparticle region, volume per cent and chemical nature (or partial charges) of the dispersoid.

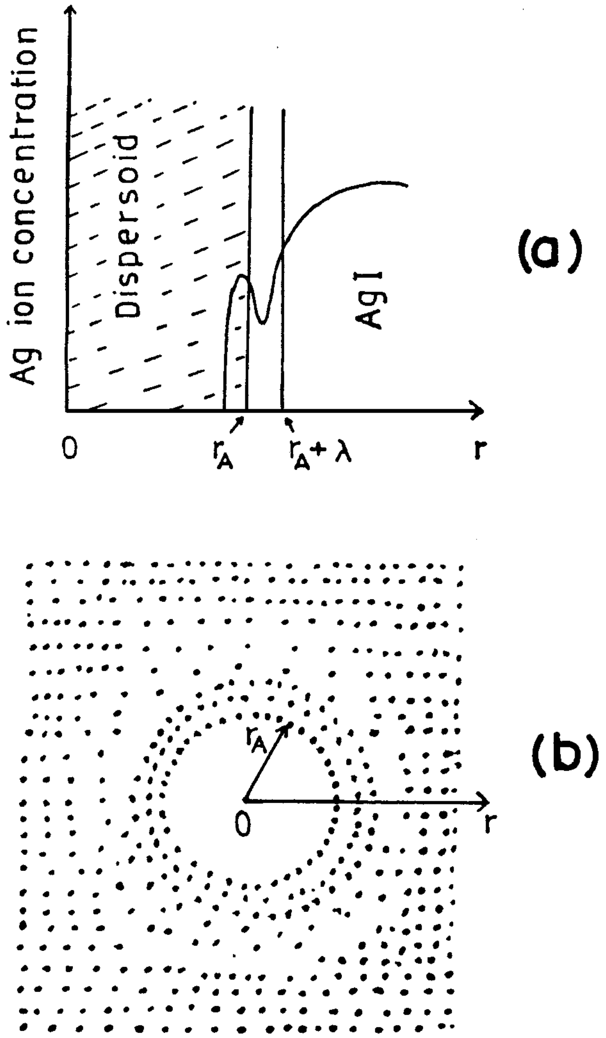

Figure 9 (a) Schematic representation of concentration profile of Ag^+ ions, and (b) microgradients of Ag^+ concentration at the AgI–dispersoid interface.

5.2.7. Morphological model

Recently, Uvarov *et al.* [320] proposed a morphological model that accounted for the effect of morphologies of MX–A composites as well as particle size on the conductivity of composite electrolyte systems. They studied the alternative current (a.c.) conductivity of a MX–A composite system prepared under two limiting conditions: (a) when the host-matrix contained as agglomerated dispersoid phase, as shown in Fig. 10a, the conductivity was expressed as:

$$\sigma_{\text{a.c.}} = \sigma_s(\lambda/r_b)(\beta/\gamma)(1-f)^2 + \sigma'_s(\lambda'/r_b)(\beta/\gamma)f(1-f) \qquad (61)$$

(b) when the host-matrix was homogeneously mixed with the dispersoid phase, as shown in Fig. 10b, the conductivity was given as

$$\sigma_{\text{a.c.}} = \sigma_s(\lambda/r_b)(\beta/\gamma)(1-f)^2 + \sigma'_s(\lambda'/r_A)(\beta'/\gamma')f(1-f) \qquad (62)$$

where σ_s and σ'_s are the conductivities of MX in the surface layer and at the MX–A interface; λ and λ' are the thicknesses of the surface layers of MX and the MX–A interface; r_b and r_A are the grain sizes of MX and the dispersoid A; $\beta, \beta', \gamma, \gamma'$ are dimensionless geometrical

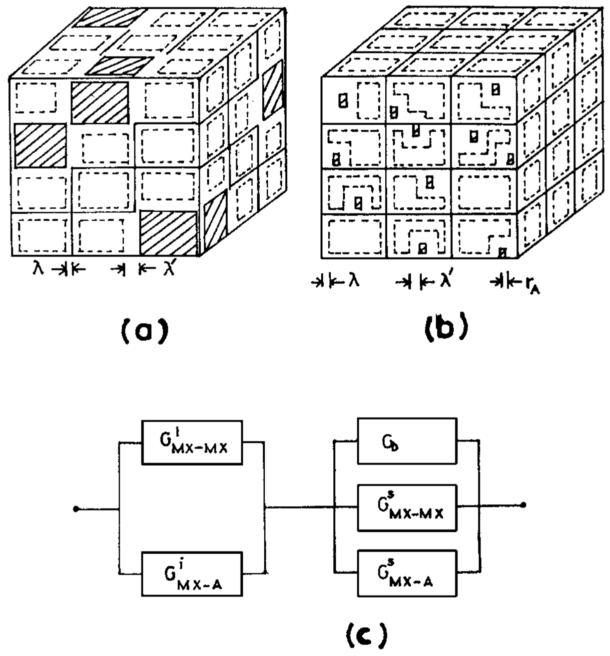

Figure 10 Representation of two limiting morphologies of MX–A composites: (a) A-particles are aggregated; (b) A particles are distributed uniformally; (c) an equivalent circuit for a two-phase composite system, where G^i_{MX-A} and G^s_{MX-A} are intergrain and surface conductance, respectively, due to MX–A contacts in the composites.

factors attributed to the morphology of the sample; f is the volume fraction of the dispersoid. To explain the conductivity behaviour, they used a circuit network, shown in Fig. 10c. They found that, in the first situation the volume of the dispersoid phase strongly dominated the surface conductivity, while in the second situation both the volume and morphology dictated the conductivity. This model suggests that the particle size of both the dispersoid and host affects ionic conductivity as well as the bulk properties of the host-matrix.

5.2.8. Improved effective medium theory

Nan and Smith [494] improved the effective medium theory proposed by Landauer [474], discussed earlier, and attempted to explain conductivity enhancements in composite electrolyte systems. They assumed that:

1. dispersoids of radius r_A are randomly distributed in the host-matrix;
2. space-charge layers of thickness λ are formed at the interface of the host and dispersoid;
3. the system is a quasi-two-phase mixture–the dispersoid along with the space-charge layer (assumed as amorphous) are considered as one phase, referred to as dispersoid or composite grains, while the host-matrix is considered as another phase;
4. three different volume fractions, V_1, V_2 and V_3, of dispersoid grains exist, which correspond to the volume when conductivity increases, attains a maximum value and then decreases, respectively–these volumes depend on the (λ/r_A) ratio;
5. enhancement is proportional to conductivity of the space-charge layer;
6. higher conductivity enhancement can be achieved by uniform distribution of the dispersoid grains in the host-matrix;
7. the smaller the dispersoid grains, i.e. λ/r_A ratio, the smaller the V values would be, and maximum conductivity would occur at a smaller volume fraction of dispersoid;
8. the a.c. behaviour of conductivity satisfies the universal power law.

This model qualitatively explained many features observed in composite electrolyte systems. However, it showed a slow response of conductivity for higher values of V_2. Hence, it was further modified by assuming that the conductivity of the amorphous shell, which is related to the glass transition temperature, T_g, is changed by changing the size and concentration of the dispersoid. Moreover, the a.c. behaviour of conductivity of composite electrolyte systems is also well predicted [260, 321, 495].

5.2.9. Mobility enhancement model

Shaju and Chandra [428] recently proposed a qualitative model to explain the observed conductivity enhancement in a *crystal–glass* composite electrolyte system (1–x) (55.5 AgI–22.25 Ag_2O–22.25 B_2O_3)–xSnO_2. According to them, the increase in ionic mobility rather than defect concentration is responsible for conductivity enhancement in the *crystal–glass* composite electrolyte system shown in Fig. 11a. They suggested that a concentration gradient is formed at/near the interfacial space-charge layer due to accumulation/adsorption of mobile ions (Fig. 11b). This in turn lowers the migration energy of mobile ions at/near the interfacial region (Fig. 11c). Hence, mobile ions find high conducting paths interconnecting the space-charge region, which result in enhanced mobility/conductivity.

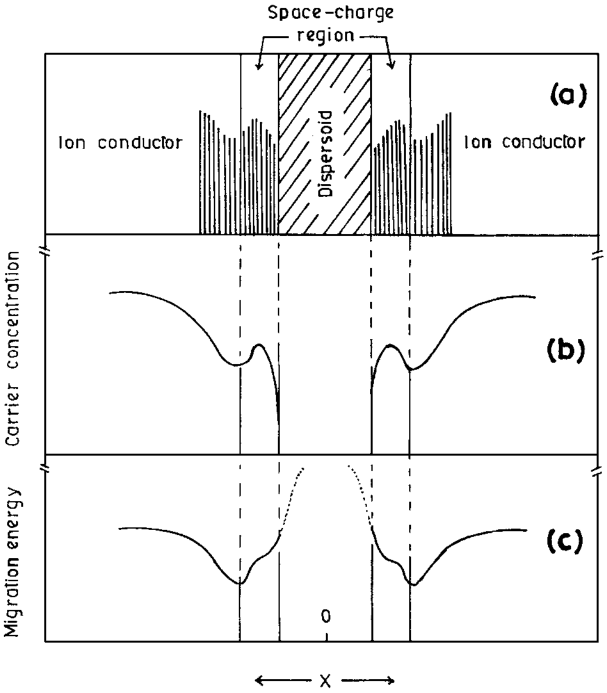

Figure 11 Schematic representations: (a) dispersoid embedded into ionic conductor; (b) mobile ion concentration profile; and (c) migration energy of mobile ions, near/at the interfacial space-charge region.

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