ELECTROLYTES

An *electrolyte* is a substance containing ions that are able to move under the influence of an electric field. By far the most common example of an electrolyte is a solution of an ionic compound (or *salt*) in water. In an aqueous environment the positive and negative ions become dissociated from one another to some extent and are therefore able to migrate in response to an applied electric field. In most cases the electrolyte contains both mobile positive ions (*cations*) and negative ions (*anions*), and the current that flows in response to the field is therefore made up of a combination of positive- and negative-ion fluxes in opposite directions. The extent to which the electric field produces a flux of ions is described by the intrinsic quantity *conductivity* σ (SI units $\mathrm{S \cdot m^{-1}}$, where the quantity siemens, S, is the reciprocal of the resistance in Ω). The conductivity is formally the inverse of the resistivity of the material and the ion conduction process will normally obey Ohm's law. The application of electrolytes in devices utilizes this ionic mobility to carry current in an electrochemical device (as described in the following section) and the conductivity is therefore one of the key properties.

Electrolytes can take many forms other than the aqueous solution. Conceptually these forms can be grouped into:

1. Those systems with a solvent host for the ions, the solvent being either liquid or polymeric
2. Crystalline or amorphous solid state ion conductors, in which ion motion takes place in a largely static matrix
3. Molten salts

Mixtures of these three groups are possible and are the subject of much current research. Some of these are summarized graphically in Fig. 1.

APPLICATIONS

Batteries

The traditional application of electrolyte solutions has been the battery, examples of which were in use in the nineteenth century. Until very recently battery electrolytes were based almost entirely on aqueous electrolyte systems, such as concentrated sulfuric acid solutions in the lead acid battery. However, the commercialization of the lithium cell and the prospects for this cell to have important applications in vehicle traction have created the need for nonaqueous electrolyte systems that are compatible with lithium metal. This has created a surge of interest in new electrolyte systems. The lithium cell (1) requires a wide operating voltage range, particularly in the stability of the electrolyte against reduction since lithium metal is one of the most powerful reductants known. Electrolytes containing water, alcohols, or other sources of reducible hydrogen atoms must therefore be strictly avoided. Thus research has sprung up in the areas of aprotic (i.e., nonproton-containing) liquids, polymers, and molten salts and also lithium-conducting ceramic/glass electrolytes and their composites with other types of electrolytes. Most types other than the aprotic liquids, for example, ethylene carbonate-based mixtures, do not attain the minimum 10^{-3} S/cm lithium ion conductivity required by most of the high-discharge-rate (i.e., high-power) applications of these cells. It has been suggested that a pure lithium anode is more stable against dendrite formation in secondary (i.e., rechargeable) lithium cells in which a polymer electrolyte is used; however, the safety concerns generated by such dendrite formation have caused

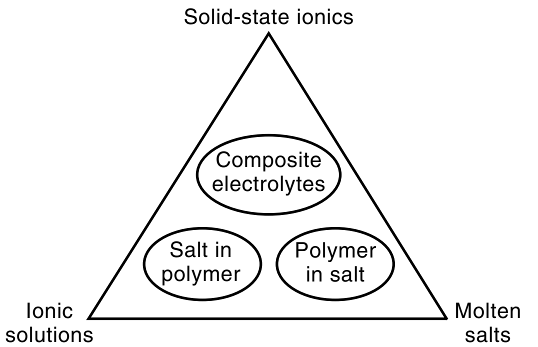


Figure 1. Types of electrolyte systems and their combinations.

J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*. Copyright © 1999 John Wiley & Sons, Inc.

attention to shift to some extent to the lithium ion battery in which the lithium electrode is replaced by an intercalation compound of lithium. The electrolyte requirements of such a battery are nonetheless similar to those of the lithium battery.

Capacitors

Traditional aluminium electrolytic capacitor technology was based on an electrolyte composed of boric acid and its salts. This electrolyte is usually impregnated into a rolled-form assembly of the anodized aluminium. More recently, in an effort to curb the volatility of water from such an electrolyte, boric acid was dissolved in ethylene glycol, and in some cases reacted (by esterification) into this solvent by heating and removal of water. Similar electrolytes are used in wet tantalum electrolytic capacitors. In the past decade solid electrolytic capacitors have begun to appear (2); these are based either on a polymer electrolyte or on an inorganic ion conductor.

Electrochemical double-layer capacitors have also recently found increasing application. This device is based on the exceptionally high capacitance that appears at the surface of a charged electrode in an electrolyte solution, at potentials below that at which electrochemical reactions begin at the electrode. In some cases capacitances in excess of 1 F/g of active material are possible if very-high-surface-area electrodes are used. Typical low-voltage supercapacitors contain sulfuric acid; up to 2.75 volts can be obtained by use of aprotic electrolytes such as dimethylene chloride.

Fuel Cells

Fuel cells, in which a chemical fuel, for example, methane, is directly oxidized at a catalytic electrode to produce an electron flow in the electrode, have been the subject of intense research for many years. Practical devices operating at room temperatures using aqueous electrolytes have been developed. For high efficiency, attention has shifted to high-temperature cells operating at temperatures in the region 700 to 1000°C. The electrolytes used in these high-temperature cells are usually oxide conducting ceramics such as stabilized zirconias. Such cells are intended for the direct oxidation of natural gas and use a solid-state inorganic oxide anion conductor as the electrolyte. A schematic diagram of a typical solid oxide fuel cell is shown in Fig. 2. Many such cells are connected in series via interconnects as shown.

Electrochromics and Smart Windows

The phenomenon of electrochromism, that is, when an electroactive material changes color on oxidation or reduction, has led to a number of practical devices being manufactured that utilize this principle. In all cases a thin, transparent layer, usually less than 1 μm, of the electrochromic material is deposited on a conductive glass substrate. Several transition-metal oxides exhibit electrochromism; however, WO_3 is one of the most commonly used. The electrochemical cell is then completed by combination with an electrolyte (3), usually a polymer or inorganic solid type, and a counterelectrode, which may itself be transparent. In the latter case an electrochromic window can be produced as shown in Fig. 3. The device shown is colorless in its uncharged state, but on passage of 10 to 20 mC/cm^2 of charge, the WO_3 is partially reduced to form a blue film that has lower transmission in the red end of the visible spectrum and in the near-infrared region. Such windows thus allow reflection or absorption of a substantial fraction of the incident solar energy on a window while continuing to pass a controllable amount of daylighting. A similar device is used in antiglare rear-vision mirrors. The role of the electrolyte is similar to that in the lithium ion battery, transporting lithium ions from the source (the counterelectrode) to the sink (WO_3) of lithium ions during the charging (coloring) process. Aprotic liquid electrolytes have been widely used but are problematic to seal in large-area devices and especially in vertically mounted window designs. Polymer electrolytes are therefore favored.

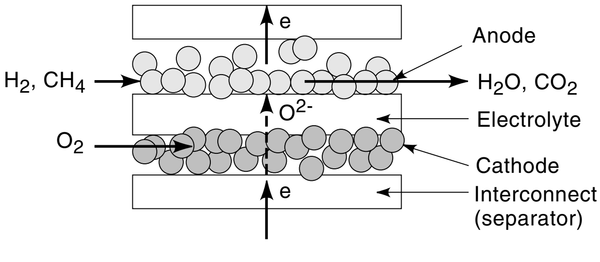


Figure 2. Schematic representation of a typical solid oxide fuel cell. Many of these are connected in series via interconnects as shown.

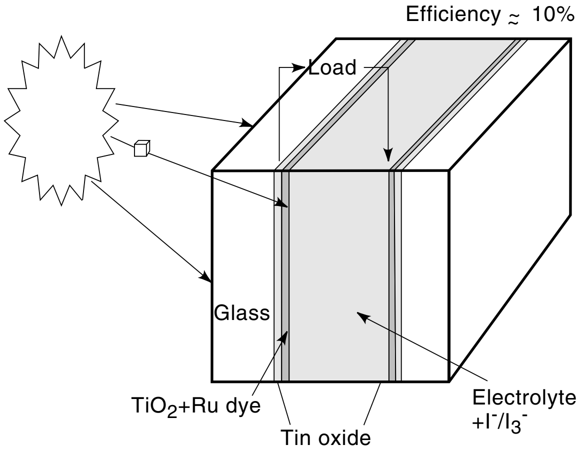


Figure 3. Schematic diagram of an electrochromic window that uses a polymer electrolyte to separate and laminate the electrode-coated glass sheets.

Photoelectrochemical Cells

There has long been interest in photovoltaic cells, which operate by harvesting light in a photoelectrochemical cell. These cells include a photoelectrode, which absorbs the incident photon, thus initiating an electrochemical cycle that delivers a fraction of the photon energy to the external circuit. In a typical cell (4), the photoelectrode is a semitransparent layer of a semiconductor (TiO_2) onto which has been adsorbed a monolayer of a photosensitive dye. The dye absorbs strongly in the 500 to 650 nm region of the visible spectrum, and on absorbing photons of this wavelength, the excited electron created in the dye molecule is able to inject with high efficiency into the conduction band of the semiconductor. The dye molecule thus becomes oxidized and is returned to its reduced form by an electrolyte solution phase reductant, in this case iodine. The tri-iodide ion formed in this process migrates to the counterelectrode where it recombines with the electron, which has traveled through the external circuit, to regenerate the iodide ion. The electrolytes needed for this device are usually of the aprotic liquid form because of the relatively high-ion-mobility requirement of the device when operating under full sun conditions (typically 20 mA/cm^2). Some applications may, however, be better suited for molten salt electrolytes.

THEORY

In a solvent of sufficiently high relative permittivity (dielectric constant, ϵ_r), for example, water, an ionic compound of general formula MX may exhibit *strong electrolyte* behavior:

$$\mathrm{MX} \rightarrow \mathrm{M}^+ + \mathrm{X}^-$$

Such a salt is called a 1 : 1 salt since the ratio of anion to cation is 1 : 1 and the ions are singly charged. In strong electrolytes such solutes dissociate completely into ions in the solvent since the electrostatic force of attraction at distance r between the separated ions (each of charge q coulombs)

$$F(r) = \frac{q^2}{4\pi\epsilon_0\epsilon_r r^2}$$

is screened (*Coulomb screening*). In such solutions the immediate environment of the ions is several layers of solvent molecules. Application of an electric field to the electrolyte causes motion of not only the ions, but also some of the immediately adjacent solvent molecules. In describing the effective contribution of each ion to the whole conductivity of the solution, it is customary to define the molar conductivity Λ given by

$$\Lambda\ (\mathrm{S \cdot mol^{-1} \cdot m^2}) = \frac{\sigma\ (\mathrm{S/m})}{c\ (\mathrm{mol/m^3})}$$

where c is the concentration of the salt in the solution. This quantity therefore provides a way of measuring the average conductivity *per ion* (or mole of ions) in the solution and therefore of understanding the influence of chemical makeup and structure on the individual motion of the ions. The molar conductivity of such a solution is observed to be only weakly dependent on salt concentration between 0 and 0.1 mol $\cdot$ dm^{-3}. The slight dependence on c is nonetheless observed to be well described by the Kohlrausch equation:

$$\Lambda = \Lambda^0 - Kc^{1/2}$$

where Λ^0 is the molar conductivity at infinite dilution ($c \rightarrow 0$) and K is a constant. Λ^0 for a 1 : 1 salt can be expressed as a sum of individual ion components:

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0$$

where λ_+^0 (λ_-^0) is the molar conductivity of the cation (anion) at infinite dilution.

Weak electrolytes are formed from salts that only undergo dissociation from dissolved neutral species to a minor extent:

$$\mathrm{MX} \leftrightharpoons \mathrm{M}^+ + \mathrm{X}^-$$

The fraction of ions dissociating is a strong function of concentration, and the molar conductivity drops markedly with increasing concentration. The same dissociation equilibrium has an influence also on the strong electrolytes at sufficiently high concentrations (> 0.1 mol $\cdot$ dm^{-3}) at which the concentration of associated species becomes significant. The terms *ion association* and *ion pairing* are used to describe this phenomenon.

Ion Mobility

When an electric potential difference $\Delta\phi$ is applied across a pair of electrodes in an electrolyte, a force is experienced by each ion according to

$$F = -q\Delta\phi/L$$

where L is the electrode separation.

The effect of this field is often described in terms of a simple model corresponding to a charged macroscopic sphere moving in a viscous fluid. In this description the electric field E is thought of as accelerating the ion to some limiting, drift velocity v at which the force of frictional drag balances the electric force. By applying the Stokes equation describing the viscous drag on a spherical object moving in a fluid medium, the drift velocity can thus be estimated from

$$v \approx \frac{qE}{6\pi a\eta}$$

where η is the viscosity of the medium and a is the effective, or hydrodynamic, radius of the ion. The combination of system constants relating the perturbation, E, to its effect, v, is called the *mobility* of the ion, u, and hence:

$$v = uE$$

Typical ionic mobilities in aqueous solutions lie in the region of 5×10^{-5} m$^2 \cdot$ s$^{-1} \cdot$ V^{-1} such that a voltage drop of 1 V across a pair of electrodes 1 cm apart produces a drift velocity of 5×10^{-5} m $\cdot$ s^{-1}.

A more sophisticated picture of the conduction process recognizes that the ions and solvent molecules are in constant random motion, even in the absence of the electric field, by virtue of the constant, thermally activated collisions by which they are buffetted. The imposition of a realistic electric field (e.g., 1 V/m) produces only a slight perturbation to this constant ionic motion, biasing the movements very slightly in the direction of the field such that the ionic drift velocity is established.

The mobilities are directly related to molar conductivity via $\Lambda = \mathscr{F}(u_+ + u_-)$ for a 1 : 1 salt (where $\mathscr{F}$ is Faraday's constant). The ionic mobility is also related to the *diffusion coefficient* D for each ion via the well-known Einstein relation

$$D = \frac{ukT}{q}$$

where T is the Kelvin temperature and k is Boltzmann's constant. Combining these two relationships provides a relationship between Λ and D,

$$\Lambda = \frac{\mathscr{F}^2}{RT}(D_+ + D_-)$$

which is known as the Nernst–Einstein relationship and R is the ideal-gas constant. Combining the Einstein relationship with the Stokes equation for mobility provides a further linking equation between the motional properties of the electrolyte (the Stokes-Einstein equation):

$$D = \frac{kT}{6\pi\eta a}$$

The temperature dependence of all of these motional properties (i.e., γ, Λ, u, D) is usually well described by the Arrhenius expression, for example,

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right)$$

where D_0 is the diffusion coefficient at infinite temperature and E_a is the *activation energy* for the process. In some electrolyte systems that do not easily form crystalline phases during cooling, the Arrhenius expression is found to apply no longer; however, a modified form, known as the Vogel-Tamman-Fulcher (VTF) equation, provides a better description of the data:

$$D = A \exp\left(\frac{-B}{T - T_0}\right)$$

where A and B are constants and T_0 is a temperature at which the diffusion coefficient appears to approach zero. This behavior is typically observed between the glass transition temperature T_g and approximately $2T_g$. Many polymer and nonaqueous electrolytes are well described by the VTF equation over limited temperature ranges.

A detailed review of the interpretation of conductivity phenomena in electrolytes can be found in the book by Smedley (see the Reading List).

METHODS OF CHARACTERIZATION OF ELECTROLYTES

Impedance and Conductivity

One of the most important properties of an electrolyte in most applications is its conductivity. Conductivity is measured in a cell consisting of a pair of electrodes in direct contact with the material. For a liquid, the electrodes are encased in a container; for a solid, the electrodes are applied to or coated onto the solid. The conductance G of the material is then measured, usually by an ac method, and is related to the material conductivity by

$$\sigma\ (\mathrm{S \cdot cm^{-1}}) = [b\ (\mathrm{cm^{-1}})][G\ (\mathrm{S})]$$

where b is the cell constant of the conductance cell. The cell constant is usually obtained by calibration using a solution of accurately known conductivity or by measurement of the empty cell capacitance.

The ac measurement method usually involves an ac bridge or impedance meter. The frequency of the measurement is of critical importance in obtaining meaningful results. The preferred method involves carrying out measurements of impedance over a broad frequency range, for example, 10 Hz to 1 MHz. This is often described as impedance spectroscopy. A typical data set is shown in Fig. 4 where the various features are modeled by the equivalent electrical circuit shown in the figure. In a simple conductivity cell the electrodes will operate capacitively (*blocking electrodes*) at all but low frequencies. In this case the desired conductance is obtained from the resistance measured, as indicated, in Fig. 4. At higher frequencies capacitive effects associated with the relative permittivity of the sample, the leads, and the electrodes produce an arc connecting R_s to the origin. The electrode capacitance (mostly double-layer capacitance C_{DL}) is, however, a factor that can become significant if its series contribution to the total complex impedance

$$Z_T = R_s - j/\omega C_{DL}$$

becomes significant, for example, because of changes in temperature or if the sample is of intrinsically very high conductance. In measurements involving liquid electrolytes of conductivity $>10^{-4}$ S/cm, platinized platinum electrodes are commonly used to increase dramatically the active surface area of the electrodes (and thereby the capacitance) over their geometric surface area. Nonetheless, electrode capacitance remains a commonly observed feature at the lower frequencies. At very low frequencies it is possible for the electrode process to become limited by a diffusion process in the electrolyte near the electrode.

Transport Number

In many applications, in particular the battery, fuel cell, and electrochromic devices mentioned previously, it is not sufficient simply to characterize the electrolyte in terms of its conductivity to assess how it will perform in the device. Whereas only one of the mobile ions is involved in the electrochemical

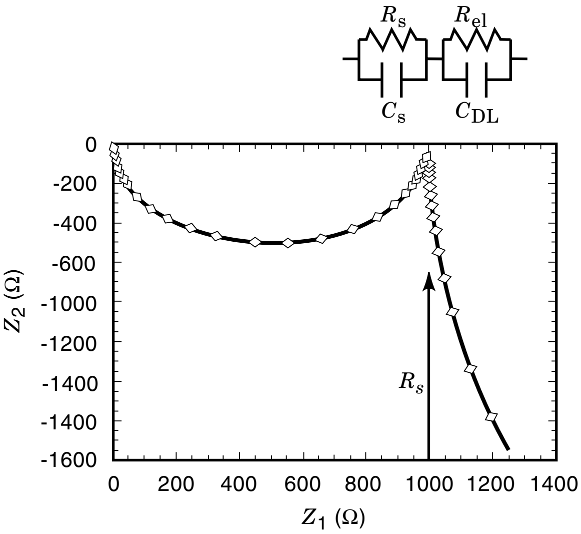


Figure 4. Typical impedance plot of the imaginary part of impedance (Z_1) versus the real part of impedance (Z_2) measured as a function of frequency for a sample of conductivity $\sigma = 10^{-3}\ \mathrm{S \cdot cm^{-1}}$ in a cell of cell constant 1.0 $\mathrm{cm^{-1}}$. The resistance of the sample in the cell is determined from the cusp point arrowed. Frequency decreases from left to right in the plot. The low-frequency spur is caused by the electrodes. These are assumed to be identical and therefore act in the equivalent circuit as a single resistor/capacitor parallel element.

reactions at the electrodes, both are involved in the transport process, it is possible that the actual current-carrying capacity of the electrolyte will fall below that expected from ac measurements. In the case of the lithium battery based on a polymer electrolyte, the lithium ion may account for only approximately 20% of the current flow in the electrolyte. The *transport number* is defined as the fraction of current carried by a single species. In this case the cation transport number is 0.2. There are many methods of measuring transport numbers; details can be found in standard texts.

Potential Window

In many applications of electrolytes it is of importance that the electrolyte, or at least the base constituents, be completely unreactive electrochemically. The voltage range over which the electrode is inert is described as its *electrochemical* or *potential window.* For example, many aqueous electrolytes are stable over a range of 1.2 V. This range is determined for most salts by hydrogen evolution at the reduction edge and oxygen evolution at the oxidation edge. There are many methods of determining these limits, perhaps the simplest of which is the standard cyclic voltammetry technique, using an appropriate *reference electrode* and noting that some electrode materials, for example, Pt, may catalyze some solvent oxidation-reduction reactions more than others (e.g., carbon).

ELECTROLYTE TYPES

Liquid Electrolytes

Protic Electrolytes. These systems include all of those involving solvents or solutes that can release an active proton. This proton is usually relatively easily reduced and the production of hydrogen is usually the limiting electrochemical process in the electrolyte at negative potentials. Aqueous (i.e., water based) and some alcohol and glycol solvents make up the vast majority of the protic electrolytes of interest. Water in particular is an excellent solvent for salts. The strength of the solvent–cation and solvent–anion interactions is sufficient that, for most salts, ion pairing only becomes a significant effect at concentrations above ~0.1 (mol salt)/dm^3. The early analysis of the arrangement of dissolved ions in solution by Debye and Huckel provided a basis for a detailed theory of conduction in strong electrolytes, in water or other high relative permittivity constant solvents. As described by the theories of Fuoss and Onsager, the motion of an individual ion is seen to cause two consequential effects on the surrounding ions (the *ionic atmosphere*): (1) the *relaxation effect,* which arises from the need of the ionic atmosphere to adjust to the new position of the central ion as it travels in the electric field, and (2) the *electrophoretic effect,* which describes the influence of the motion of neighboring ions and solvent molecules on the motion of the central ion.

The combination of these two effects produces a theoretical functional form for conductivity as a function of concentration as follows:

$$\sigma = \Lambda^0 c - Sc^{3/2} + (E_1\Lambda^0 - E_2)c^2 \ln(c) + J_1 c^2 + J_2 c^{5/2}$$

where S, E_1, E_2, J_1, and J_2 are combinations of constants. This form is found to fit experimental data for dilute aqueous solutions very well; for example, the conductivity of an aqueous potassium chloride solution is well described by

$$\sigma\ (\mathrm{S\cdot m^{-1}}) = 14.994c - 9.488c^{3/2} + 2.58c^2 \log c + 22.10c^2 - 22.90c^{5/2}$$

where c is the salt concentration in mol · dm^{-3}. The linear term dominates at low concentrations. Extensive tabulations of conductivity and other physical properties of aqueous electrolyte solutions can be found in the *CRC Handbook of Physics and Chemistry* (see, e.g., the 77th edition, 1996).

In aqueous solutions of strong acids or bases, the conductivity is found to be higher than that of an equivalent salt. The H$^+$ and OH$^-$ mobilities in such solutions are substantially higher than the mobilities of other ions. This is the result of a special process by which these ions can be transported through the medium, known as the Grotthus mechanism. In this mode of ion transport a mobile hydrogen ion can join a cluster of water molecules at one edge and, by a rearrangement of the hydrogen–oxygen bonding within the cluster, a different hydrogen ion can depart from an opposite, down-field, edge of the cluster.

Aprotic Electrolytes. These liquid-based electrolytes have long been of interest in applications of electrochemistry requiring electrolyte stability beyond the ~1.2 V available with aqueous systems. The surge of interest in Li batteries, requiring electrolyte stability versus lithium metal, has generated a large investigative effort worldwide involving suitable electrolytes. Some typical systems and their properties are summarized in Table 1 (5,6). Aprotic electrolytes characteristically have lower conductivities at equivalent concentration compared with an aqueous electrolyte; this reflects a number of factors:

1. The viscosity of the solvent is often substantially higher than an aqueous system.
2. The dielectric constant of the solvent is usually only 75% or less than that of water, this factor influencing the Coulomb screening of ions from one another.
3. Specific ion-solvent interactions are in many cases weaker than those observed in aqueous electrolytes, in particular anion–solvent interactions. This produces a much greater degree of ion pairing in the electrolyte and therefore a relatively smaller fraction of charged and mobile species.

Despite this limitation, other properties can be substantially improved over aqueous-based systems, for example, temperature range of stability, volatility, and electrochemical range of stability. A very useful discussion of properties of aprotic electrolytes as used in electrochemical applications can be found in the article by Mann (5).

Polymer Electrolytes

Polymer electrolytes have been intensively investigated over the last two decades since P. V. Wright first discovered that complexation of alkali-metal salts with polyethylene oxide (PEO) resulted in ionically conductive materials (7). Armand, Chabagno, and Duclot (8) later envisaged the importance of these complexes as solid electrolytes in high-energy-density, all-solid lithium-battery applications, and hence research and

Table 1. Properties of Various Nonaqueous Solvents

Solvent	Boiling Point,[a] °C	Melting Point, °C	Vapor Pressure,[b] mm	Density,[b] g/cm³	Viscosity,[b] cP	Dielectric Constant[b]
Nitriles						
Acetonitrile	81.6	−45.7	$91.4_{25.5}$	0.77683_{25}	0.325_{30}	37.45_{20}
Benzonitrile	191.1	−13.5	$1_{28.2}$	0.99628_{30}	1.111_{30}	25.58_{20}
Butyronitrile	117	111.9	18.6_{25}	0.7817_{30}	0.515_{30}	20.31_{21}
Phenylacetonitrile	233.5	−23.8	1_{60}	1.0125_{25}	1.93_{25}	18.7_{27}
Propionitrile	97.2	−91.6	$46.7_{24.55}$	0.7770_{25}	0.389_{30}	27.2_{20}
Amides						
Formamide	210.5	2.55	$1_{70.5}$	1.12918_{25}	3.302_{25}	109.5_{25}
Dimethylacetamide	165	−20		0.9366_{25}	0.92_{25}	38.93_{20}
Dimethylformamide	153.0	−61		0.9445_{25}	0.796_{25}	36.7_{25}
N-Methylacetamide	206	28.0		0.9571_{25}	3.019_{40}	178.9_{30}
N-Methylformamide	180	−5.4		0.9961_{25}	1.65_{25}	182.4_{25}
Amines						
Ethylenediamine	117.0	11.0	$10_{21.5}$	0.895_{25}	1.54_{25}	12.5_{25}
Morpholine	128.9	−4.9	6.6_{20}	1.002_{20}	2.23_{20}	7.33_{25}
Pyridine	115.5	−41.6	$10_{13.2}$	0.97281_{30}	0.878_{25}	13.24_{20}
Ethers						
1,2-Dimethoxyethane	85	−58		0.8665_{20}		4.265_{25}
1,4-Dioxane	101.3	11.8	$40_{25.2}$	1.02687_{25}	1.087_{30}	2.23_{25}
Tetrahydrofuran	64	108.5		0.8892_{20}		7.39_{25}
Acids						
Acetic acid	118	16.6	15.4_{25}	1.04365_{25}	1.040_{30}	6.195_{25}
Formic acid	100.5	8.3	33.55_{20}	1.214_{25}	1.966_{25}	57.9_{20}
Alcohols						
1-Butanol	118	−89.8	6_{24}	0.80206_{30}	2.271_{30}	17.1_{25}
Ethanol	78.32	114.5	40_{19}	0.78506_{25}	1.08_{25}	24.30_{25}
Ethylene glycol	197.8	−12.6	1_{53}	1.10664_{30}	13.55_{30}	37.7_{25}
Glycerol	290	17.9	$1_{125.5}$	1.2552_{30}	5.87_{30}	42.98_{25}
Methanol	64.51	97.49	$200_{34.8}$	0.78675_{25}	0.445_{25}	32.6_{25}
1-Pentanol	138	78.85	10_{45}	0.80764_{30}	3.347_{25}	15.27_{20}
1-Propanol	97.2	126.1	27.6_{30}	0.79950_{25}	2.004_{25}	19.7_{25}
Sulfur Compounds						
Dimethylsulfone	233.5_{750}	110.8		1.1702_{110}		37
Dimethylsulfoxide	189.0	18.55	0.6_{25}	1.096_{25}	2.003_{30}	46.7_{25}
Sulfolane	285	28.86		1.2615_{30}	9.87_{30}	44_{30}
Miscellaneous						
Acetone	56.2	−94.8	180_{20}	0.7846_{25}	0.2954	21.26_{20}
Methylene chloride	39.95	−96.7	$400_{24.1}$	1.30777_{30}	0.393_{30}	8.93_{25}
Nitromethane	101	−28.6	$7.1_{25.3}$	1.13118_{25}	0.627_{25}	36.67_{25}
Propylene carbonate	241.7	−49.2	75_{160}	1.0257_{20}		64.4_{25}

[a] Bp 760 mm unless given as subscript.
[b] Subscript gives temperature in °C.

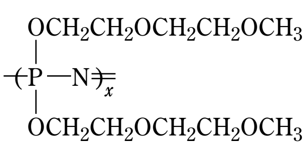
development in this field has been intense. A polymer electrolyte can be described as a material that comprises a host polymer (the solvent), usually containing polar atoms or groups [such as in poly(ethers) (I); poly(ethylene imine) (II); poly(acrylates) and poly(esters)]

$-\!(CH_2CH_2O)_x\!-$

I

$-\!(CH_2CH_2NH)_x\!-$

II



$$-\!\!\left(\overset{OCH_2CH_2OCH_2CH_2OCH_3}{\underset{OCH_2CH_2OCH_2CH_2OCH_3}{P}}\!=\!N\right)_{\!x}\!-$$

III

into which a low-*lattice-energy* salt is dissolved. These low-lattice-energy salts typically include the lithium or sodium salts of the triflate ($CF_3SO_3^-$), perchlorate (ClO_4^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) and more recently, bis(trifluoromethane sulfonyl)imide [$N^-(O_2SCF_3)_2$] anions. In the case of linear PEO-based polymer electrolytes, quite complex phase behavior can be observed due to the semicrystalline nature of the polymer and the formation of high-melting-point compounds (9). Since conductivity has been shown to occur primarily in the amorphous (i.e., noncrystalline) phase, the presence of crystallinity is detrimental to high conductivities. Recent work has focused on developing completely amorphous polymers, for example, by preparing random copolymers of ethylene oxide units with propylene oxide or methylene oxide groups. Copolymerization of short ethylene oxide units onto siloxane (10) or phosphazene backbones (11) [e.g. poly(methoxyethoxyethoxy phosphazene) MEEP (III)] also yields amorphous polymers. This has the added advantage of a flexible backbone that decreases the glass transition temperature of the electrolyte and hence produces higher conductivity (10^{-4} S/cm at 25°C) through higher ionic mobility.

Other amorphous polymer electrolyte systems have been obtained, for example, by addition of an inert filler such as alumina (12).

For some applications, it is favorable for the conductivity to be dominated by a single ionic species, for example, lithium in the case of a lithium battery, in order to avoid polarization of the electrodes. In most traditional polymer electrolytes, such as those based on the previously mentioned polymers, both ionic species contribute to the conductivity. Single-ion conductors can be achieved, however, by anchoring the counterion so that it is relatively immobile, as in the case of a polyelectrolyte (see, e.g., Ref. 13) in which the anion or cation is attached to the polymer backbone. Alternatively, large bulky counterions can be used that have significantly lower mobilities. Unfortunately, these routes to single-ion conductors result in low conductivities ($\sim 10^{-6}$ S/cm) because of a high degree of anion-cation association in the electrolyte. In fact, due to the low dielectric constant of most available host polymers, ionic association is a limiting factor in achieving high-conductivity polymer electrolytes since Coulomb screening cannot occur efficiently. The addition of chemical species such as cryptands or cryptates (14), which can encapsulate the cation, results in significant enhancement of conductivities due to decreased ion association.

Higher conductivities can be obtained in polymer electrolytes by adding a low-molecular-weight cosolvent or plasticizer (15). This can have the dual effect of improving ion mobility by decreasing the overall glass transition temperature of the polymer system and of providing better Coulomb screening between ions by increasing the number of ionic charge carriers. Typical plasticizers include propylene carbonate (PC), ethylene carbonate (EC), ethylene glycol (EG), and tetraglyme. These can increase the conductivity by up to two orders of magnitude. These electrolytes are often termed *gel electrolytes,* particularly when the plasticizer content is greater than 50 wt% and the polymer itself is not an ion conductor. Examples of the latter systems are poly(methylmethacrylate)/PC, poly(acrylonitrile)/PC/EC, and poly(hydroxyethylmethacrylate)/EG. In these cases, the ionic transport occurs predominantly in the liquid (or plasticizer) microphase with the polymer providing the mechanical integrity. Ion transport is more complex in plasticized systems where the polymer also contributes to the conductivity. In these cases, the conduction mechanism will change from being polymer governed, to some combination of polymer and cosolvent, to predominantly liquidlike as the concentration of plasticizer is increased.

Proton-conducting polymer electrolytes based on the Nafion structure (Dow Chemical) (16) are used in low-temperature fuel cells. These electrolytes conduct protons through domains of water (in which the acidic groups are dissolved) in an otherwise hydrophobic, fluorinated polymer backbone. Other proton conductors that have been investigated include poly(ethers), poly(amides), and poly(vinyl alcohol) reacted with strong phosphoric or sulfuric acid. The conductivities in these systems are between 10^{-2} and 10^{-5} S/cm at room temperature. The conduction mechanism in these cases involves proton hopping between polymer sites or, in the case of water-containing systems, via a Grotthus-type mechanism.

Molten Salts

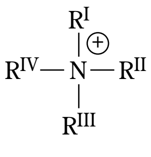
Molten salts consist simply of the molten phase of an ionic substance. For example, sodium nitrate melts to form a clear, stable liquid at 306°C. Molten salts contain dissociated ions that are free to move under the influence of an applied electric field. They are therefore able to behave in every sense the same as solvent-based electrolytes. There are several high-temperature electrochemical processes that use molten salts as the electrolyte; for example, molten cryolite, Na_3AlF_6, is used in the electrodeposition of aluminum from its oxide minerals.

Many molten-salt systems based on single compounds or multicomponent mixtures are known and described in various handbooks (17). Most of these molten-salt systems are molten at elevated temperatures (i.e., $>200°C$). In order to lower the melting point and improve the liquid-state temperature range it is common to use binary, ternary, and sometimes higher-order mixtures of salts. The phase diagrams of these multicomponent systems often contain deep eutectics such that at particular binary compositions a stable liquid can be obtained at temperatures far below the melting point of the pure components.

Examples include

1. The LiCl/KCl binary system in which molten salts are obtainable in the region of 400 to 500°C.
2. Alkali-metal nitrate binaries and ternaries, for example, 50 mol% $NaNO_3$–50 mol% KNO_3 and alkali-metal nitrate/alkaline-earth nitrate binaries and ternaries such as the $NaNO_3/Ca(NO_3)_2$ system. Silver nitrate and ammonium nitrate also form important binary mixtures with the alkali-metal nitrates.
3. Multicomponent fluoride systems such as the Zr/Ba/Na/Al fluoride quarternary, which is a fluid melt over a range of temperatures above 500°C for various compositions in the quaternary system.

In recent developments room-temperature molten salts based on organic cations, such as the ammonium, pyridinium, or imidazolium cations, and mixtures of these with $AlCl_3$ have been described. Some of these systems, in particular those based on the imidazolium bis(trifluoromethane sulfonyl)imide family are stable with respect to crystallization over a range of subambient temperatures down to their glass transition temperatures near $-90°C$ (18). Typical conductivities at room temperature are of the order of 1 mS/cm.



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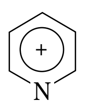

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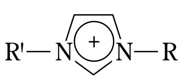

VI

The mechanism of charge transport in an applied electric field in molten salts has a number of important similarities with and differences in the mechanism describing ion transport in solvent-based systems. Both systems in general provide ions of both positive and negative charge that will migrate in opposite directions in an electric field. In the solvent-based electrolyte these motions are screened to some extent by the solvent molecules, which, in all but the most concentrated solutions, can be viewed as a stationary medium in which the migration takes place. In fact, in some binary salt-solvent systems it is possible to achieve a continuous set of liquid states with compositions varying from dilute salt in solvent at one extreme, through a region of concentrated salt-solvent mixtures, to almost pure molten salt. The transition from solvent-based electrolyte behavior to molten-salt behavior across this set of compositions has been investigated (17). The transition appears to be associated with the disappearance of bulk solvent with increasing salt concentration, leaving only solvent molecules that are intimately associated with the ions and ion clusters.

Solid Electrolytes

Ceramic Conductors—General Background. Certain classes of crystalline solids, in which a one-, two-, or three-dimensional *sublattice* of mobile ions is intertwined through a rigid framework lattice, show moderately high ionic conductivities at temperatures well below their melting point. Such electrolytes are often termed fast ion conductors or superionic conductors. The conduction mechanism of such electrolytes is usually one of rapid ion hopping from one equivalent or near-equivalent site to another. This hopping can occur either via *vacancy* or *interstitial* migration, where the vacancies could be formed, for example, via the presence of charged "impurities." Interstitial atoms are those atoms (usually smaller than the framework lattice atoms) that occupy otherwise empty sites in an ideal structure.

One method of creating a significant number of vacancies in a lattice is by doping with ions of higher or lower charge (*aliovalent dopants*) so that defects are created within the lattice, for example, calcia-stabilized zirconia $Zr_{1-x}Ca_xO_{2-x}$, which is an oxygen conductor due to the presence of oxygen vacancies. Some solid electrolytes, such as α-AgI, and their related compounds, show high conductivities due to the intrinsically mobile silver ions. These occupy random interstitial positions in a rigid framework of I^- ions and can easily move between sites. Figure 5 gives an example of the inverse-temperature dependence of conductivity for a number of crystalline electrolytes. The slope of these curves is proportional to the activation energy for the conduction process (i.e., the energy required to overcome, for example, the barrier to hopping from one site to another through a so-called "bottleneck"). α-AgI has an extremely low activation energy ($E_a \sim 3$ kJ/mol) as compared with most other solid electrolytes and, in general, the more densely packed the structure and the smaller the tunnels through which ions move from one site to another, the higher the activation energy. An additional contribution to the activation energy of crystalline conductors can occur via the association of vacancies with aliovalent dopants. This is termed *ion trapping* and is present in many oxide conductors, resulting in activation energies greater than 80 kJ/mol. When the dopant ionic radius is similar to the host ion, such association effects can be minimized and improved conductivity is obtained.

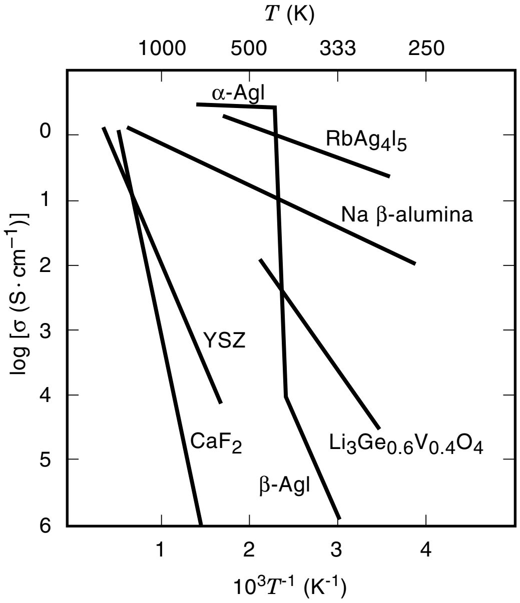

Figure 5. Conductivity trends for typical electrolyte systems. YSZ refers to yttrium-stabilized zirconia (ZrO_2).

Apart from the silver conductors, which show by far the highest conductivity, the other major compounds in this class of electrolytes conduct either Na^+, Li^+, O^{2-}, or F^-. Some of the more common types are discussed later.

***β*-Aluminas.** There are two main types of β-aluminas, termed β or β″. Both phases are based on a mixture of soda (Na_2O) and alumina (Al_2O_3), with the latter phase being richer in soda (19). The β″ phase is thermodynamically unstable and requires the addition of further components such as lithium or magnesium oxides to achieve stability. The resultant compound has a *spinel* structure, and conduction occurs via the motion of Na^+ ions in the two-dimensional conduction planes that separate "impenetrable" dense spinel blocks. Slight crystallographic differences in the β-alumina structure compared with the β″ lead to differences in the nature of the sites that are occupied by the conducting species (Na^+). The mechanism of conduction for the two materials is therefore distinctly different, leading to distinctly different temperature dependences for the conductivity. Substituted β-aluminas, in which divalent or trivalent cations are substituted into the crystals, are also known to have relatively high ionic conductivities. Typical conductivities in these materials is 10^{-2} S/cm at 25°C and $>10^{-1}$ S/cm at 200°C.

Nasicon and Lisicon. LISICON and NASICON are the acronyms for Li and Na super ionic conductors, respectively. These materials have distinctly different chemical frameworks, with the NASICON based on a zirconophosphosilicate framework $[Na_{1+x}Zr_2(P_{1-x}Si_xO_4)_3]$. LISICON (e.g., Fig. 6), on the other hand, can refer to a number of different lithium conductors, for example, those based on the phases γ-$Li_3(PO_4)$, Li_3AsO_4, or Li_3VO_4 with some excess interstitial lithium ions being introduced by substituting aliovalent ions (e.g., Zn, Al, Si) for the main framework cation (20). In NASICON the conduction mechanism probably involves random Na^+ hops in contrast to LISICON structures, where there is significant evidence to suggest that lithium ions cluster and ion transport involves the rearrangement of these clusters. The highest room-temperature conductivity in these phases is about 10^{-4} S/cm.

Oxide Conductors. Aliovalent doping of oxides such as ZrO_2, Bi_2O_3, $Ce^{IV}O_2$, and ThO_2 can lead to the formation of oxygen vacancies in the crystal lattice and hence high anion

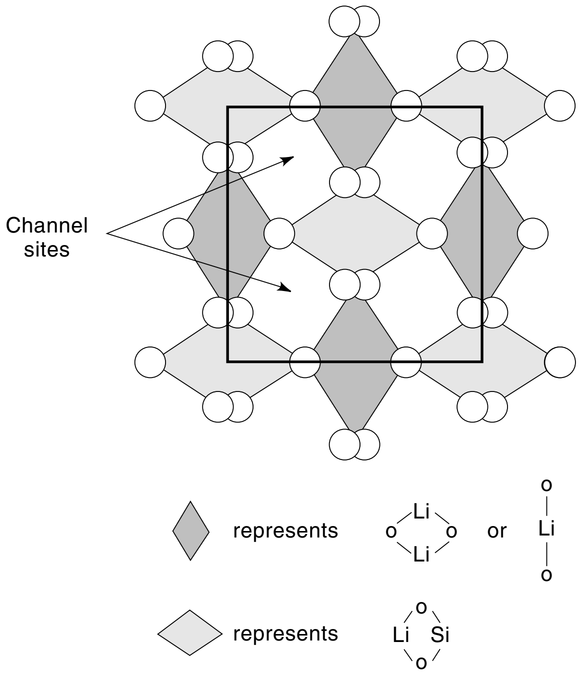

Figure 6. Structure of a LISICON lithium-ion conductor. The channel sites form continuous channels in the direction perpendicular to the plane of the page.

conductivities. There is, however, an optimum dopant concentration above which conductivity starts to decrease. Electrolytes that have exclusively oxygen anion transport can be utilized in the oxygen fuel cells described earlier (21). The crystal structure of the conducting oxides is based on the cubic fluorite structure shown in Fig. 7; however, ZrO_2 requires addition of dopants such as yttria (approximately 8 mol%) to stabilize this structure below 2300°C (known as YSZ or yttria-stabilized zirconia). The conductivity of these materials is of the order of 10^{-1} S/cm at 1000°C. With activation energies around 80 kJ/mol, these oxides are practically insulators at room temperature and so these fuel cells are designed to operate at very high temperatures to maximize efficiency. Partially stabilized zirconia (PSZ with only 3 mol% yttria added) may also be considered a candidate electrolyte for fuel-cell applications, particularly if better mechanical properties are required, which may be important if the electrolyte is designed to be self-supporting. However, PSZ has a lower chemical stability than YSZ, which results in conductivity degradation with use.

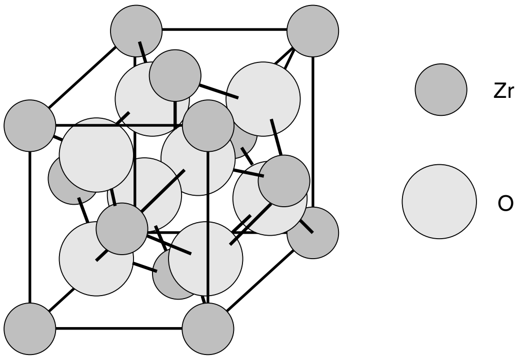

Figure 7. Cubic fluorite structure of ZrO_2.

For lower operating temperatures, oxide conductors with higher conductivities are required, for example, CeO_2-based oxides or oxides that have a *perovskite* structure. The latter often suffer from high electronic conductivities. A requirement of these oxide electrolytes in practical applications is that the electronic transport numbers are negligible so as to avoid electronic short circuits, i.e., the electronic conductivity should be at least three orders of magnitude lower than the ionic conductivity. This is true in the case of YSZ, however, some of the other oxides can easily react in air, which generates mobile electrons by reactions such as $2O^{2-} = O_2 + 4e^-$.

Ionic Glasses

Ionically conductive glasses are disordered solids in which at least one ion is mobile in an otherwise rigid matrix (22). The composition of such electrolytes usually contains a network former (i.e., a compound such as common silica glass, SiO_2, which consists of relatively strong covalent bonds), a network modifier (i.e., oxides such as Li_2O that interact strongly with the network former structure, breaking some of the covalent bonds and introducing ionic bonds), and an ionic salt (generally Cl^-, I^-, or F^- salts). The addition of an ionic salt greatly increases the conductivity of the glass. The highest conductivity in these electrolytes occurs for silver and lithium conductors with the best room-temperature conductivity approaching 10^{-2} S/cm. The temperature dependence of conductivity is fairly linear below the glass transition temperature, and activation energies for these materials vary with the nature of the conducting ion and composition but are usually between 20 and 100 kJ/mol. Since most inorganic salts have low dielectric constants (between 5 and 15) these electrolytes tend to follow weak electrolyte theory with the presence of significant ion association.

Composites and Mixtures

A composite electrolyte is one that contains two or more phases, one of which is usually an insulator and modifies the properties of the conducting phase when added in sufficient quantity. An example of this is the addition of γ-alumina to poly(ethylene oxide)-based electrolytes (12). This has the major effect of suppressing polymer crystallinity and hence increasing the fraction of the conductive amorphous polymer phase. More complex systems are based on two inorganic solids, one of which is an insulator, whose addition results in a conductive boundary phase (called a space-charge layer) due to polarization of the interphases (23). Recently, composites based on a conducting ceramic together with a polymer electrolyte have been investigated. These are proposed to give improved lithium ion conduction (due to the ceramic) and improved mechanical properties, without the need for high temperatures or pressure to ensure a compact ceramic electrolyte.

In a similar vein, recent work has developed polymer in molten-salt electrolytes in which the (minor) polymer component provides mechanical properties and, in some cases, solvent-type interactions with the molten salt. In one case involving poly(vinyl alcohol) (24) the polymer provides a glassy host within which the ions of the molten salt are able to move.

Computer Simulations

Computer simulations of electrolyte systems are used in attempts to understand the link between structure and transport properties in these materials. These simulations have to date been limited to regular crystalline conductors such as β-alumina (25) and a number of its derivatives, simple solvent-based electrolytes in the case of amorphous systems (26,27), and, more recently, to PEO/NaI complexes (both crystalline and amorphous) (28,29). Ab initio calculations of low-molecular-weight ethers complexed to a variety of cations have also been performed (30). These have described the nature of the cation–solvent complexes and have been useful in developing a picture of the local ionic structure in polyether electrolytes. The greatest limitation in computer simulation experiments is having confidence in the form of the interaction potentials used to describe the evolution of the molecular system with time. An additional limitation is the computer time required to simulate even small ensembles of "real" systems. These limitations have hindered the use of computer simulations as a predictive tool. However, the information obtained from current simulations is nevertheless of great interest and has been valuable in obtaining a molecular picture of structure and conduction in simple nonaqueous electrolytes, crystalline and glassy fast ion conductors, and to a lesser extent in polymers.

Methods. There are two major computer simulation techniques that can be used to study electrolytes: *molecular dynamics* (MD) and *Monte Carlo* (MC) methods. Monte Carlo simulations are often more useful for the determination of equilibrium properties and structure, being able to sample over a larger ensemble of atoms with less computational intensity as compared with MD. The general technique is well described in a number of publications (31). The simple lattice-gas model assumes that mobile particles occupy sites on a lattice and diffuse by hopping between nearest-neighbour sites, say, i and j. The probability W_{i-j} (based on the Metropolis transition probability) is given by

$$W_{i-j} = \begin{cases} \exp(-\Delta H_{ij}/kT) & \text{if } \Delta H_{ij} \geq 0 \\ 1 & \text{if } \Delta H_{ij} < 0 \\ 0 & \text{if } n_j \neq 0 \end{cases}$$

where ΔH_{ij} is the enthalpy change associated with the hop and n_j is an occupation number equal to -1, 0, or 1 for an anion, a vacancy, and a cation site, respectively, that is, a move is not allowed if a site is already occupied.

The system is allowed to evolve from some arbitrary starting point until equilibrium is reached, that is, the total energy begins to fluctuate about some mean value. Further evolution of the system with time (in this case time is in arbitrary units and is related to the number of steps) can lead to structural and dynamic information.

In molecular dynamics simulations, Newton's classical equations of motion are solved and the system can evolve in real time. Hence appropriate diffusion coefficients and conductivities can be calculated and compared to laboratory measurements. Due to the enormous number of calculations that are needed, MD simulations are often simplified by decreasing the size of the simulated system, called the simulation box, and extending this system out to infinite dimensions by using the periodic boundary conditions, that is, the same simulation box is repeated periodically in space so that if one atom or molecule should leave the confines of the box it reenters another one and in this way the number of atoms are conserved. Simulations are usually run at constant number, volume, and temperature (NVT) although other ensembles are possible (31). The time step in MD simulations is usually of the order of 1 to 5 femtoseconds (fs) and, due to time constraints, simulations rarely last longer than 100 ps to 1 ns. This presents a problem for simulating the longer-time behavior of a system, in particular, relaxation properties associated with polymeric systems.

Although many researchers in this field have produced individual computer codes for MD simulations of electrolytes, a number of commercial packages now exist, such as BIOSYM and CERIUS, which include relatively user-friendly front ends. These, in theory, allow even the nonspecialist to perform computer simulations on any number of systems including electrolytes. One must however be aware that the results of any simulation are only as good as the interatomic potential functions that are used to describe the molecular system and hence these packages must be used with some care.

Ab initio calculations are usually performed using the Hartree–Fock self-consistent field molecular orbital calculation methodology. In these simulations, suitable geometries are usually selected from experimental structures. Energy minimization is then performed, with structural and energetic information provided as output. Most recently these quantum-mechanical calculations have been extended to model simple Li ion transport.

Outcomes. Computer modeling thus far has provided some interpretation of experimental findings in electrolytes (27,32). For example, MD simulations have suggested that in low-dielectric solvents, significant ion pairing and clustering are present and the mechanism of conduction is likely to involve the collective motion of ions rather than simply "free" ions. Higher-dielectric solvents, on the other hand, will have less clustering due to the improved Coulomb screening. In all cases, simulations suggest that increasing temperatures will increase ion association and hence clustering, thereby decreasing the effective number of charge carriers. Similar results are obtained from MC simulations and dynamically disordered hopping models. The latter model has been used to describe the frequency and temperature dependence of conductivity in polymer electrolytes successfully. Other simple lattice models have shown that changes in the glass transition temperature T_g of a polymer electrolyte system are mainly responsible for changes in conductivity.

The work by Nyertz et al. on PEO/NaI systems has also confirmed the effect of salt concentration on ion association, with significant competition being indicated between the iodide ion and the ether oxygen to coordinate the sodium cation. Ion diffusion in these systems is clearly difficult to simulate since diffusiuon coefficients of the order of 10^{-6} cm^2/s to 10^{-7} cm^2/s are beyond the time scale range currently accessible (nanoseconds). However, the dynamics of ligand exchange have been nicely described in this work, with correlations to the rate of exchange and polymer flexibility being observed.

MD simulations of Na β''-Al$_2$O$_3$, a sodium cation conductor, have produced good agreement with experimental observations that either excess or deficiencies in sodium amounts are needed to obtain high ionic conductivities. Other structural and transport experimental properties were also reproduced and the simulation was run at higher temperatures for which it is predicted that diffusion mechanisms change from hopping to liquidlike. Simulations of β-Al_2O_3 and its isomorphs have also been used with mixed success to explain the compositional effects on conductivity (33). For example, cation ordering was observed in a barium-substituted β-alumina, which explained the decreasing ionic conductivity. However, even in such a regular system, an incorrect choice of interatomic potentials can lead to inconsistencies between simulation and experiment.

In the case of crystalline and glassy conductors, the jump relaxation model has also been used to interpret frequency and temperature behavior of conductivity (34). This model suggests nonrandom hopping of ions due to the repulsive Coulombic interaction among mobile ions, that is, each ion will "feel" a time-dependent potential from its mobile neighbors as well as the static periodic lattice potential. The analytical expressions developed can be used to show that the frequency (and hence time and temperature) dependence of the transport properties obey Kohlrausch–Williams–Watts behavior.

BIBLIOGRAPHY

1. O. Yamamoto, in P. G. Bruce (ed.), *Solid State Electrochemistry.* Cambridge, UK: Cambridge University Press, 1995; see also the many papers in *Electrochem. Soc. Prepr.,* Fall, 1996.
2. Crosslinked electrolyte capacitors and methods of making the same, Specialised Conductives P/L, U.S. Patent 5153,820, 1991.
3. D. R. MacFarlane et al., Polymer electrolytes for electrochromic window applications, *Solid State Ionics,* **86-88**: 959–964, 1996.
4. B. O'Regan and M. Grätzel, A low cost, high efficiency solar cell based on dye sensitized colloidal TiO_2 films, *Nature (London),* **335**: 737–739, 1991.
5. C. K. Mann, in A. J. Bard (ed.), *Electroanalytical Chemistry,* New York: Dekker, 1969.
6. A. Abbot, Electrochemistry in media of low dielectric constant, *Chem. Soc. Rev.* **22**: 435–440, 1993.
7. P. V. Wright, Electrical conductivity in ionic complexes of polyethylene oxide, *Br. Polym. J.,* **7**: 319–327, 1975.
8. M. B. Armand, J. M. Chabagno, and J. M. Duclot, in P. Vashishta, J. N. Mundy, and G. K. Shenoy (eds.), *Fast Ion Transport in Solids,* Amsterdam: North-Holland, 1979.
9. A. Vallee, S. Besner, and J. Prud'homme, Electrolytes mode with lithium trifluoromethanesulfonate and lithium perchlorate: Thermal properties and conductivity behaviour, *Electrochim. Acta,* **37-9**: 1579–1583, 1992.
10. K. Nagoka et al., High ionic conductivity in poly(dimethyl siloxane-co-ethylene oxide) dissolving lithium perchlorate, *J. Polym. Sci. Polym. Lett. Ed.,* **22**: 659–663, 1984.
11. P. M. Blonsky et al., Polyphosphazene solid electrolytes, *J. Am. Chem. Soc.,* **106**: 6854–6855, 1984.
12. W. Wieczorek, Z. Florjarczyk, and J. R. Stevens, Composite polyether based solid electrolytes, *Electrochim. Acta,* **13-14**: 2251–2258, 1995.
13. D. J. Bannister et al., Ionic conductivities for poly(ethylene oxide) complexes with lithium salts of monobasic and dibasic acids and blends of poly(ethylene oxide) with lithium salts of anionic polymers, *Polymer,* **25**: 1291–1296, 1984.
14. K. Chen et al., Influence of macrocyclic ligands on ion transport in solid polyelectrolytes, *Proc. Mater. Res. Soc. Symp. Solid State Ionics II,* **210**: 211–214, 1991.
15. K. M. Abraham and M. Alamgir, Li^+ conductive solid polymer electrolytes with liquid-like conductivity, *J. Electrochem. Soc.,* **137**: 1657, 1990.
16. M. Faulk, An infrared study of water in perfluorosulfonate (nafion) membranes, *Can. J. Chem.,* **58**: 1495–1501, 1980.
17. D. Inman and D. G. Lovering, *Ionic Liquids,* New York: Plenum, 1981.
18. P. Bonhote et al., Hydrophobic, highly conductive ambient temperature molten salts, *Inorg. Chem.,* **35**: 1168–1178, 1996.
19. J. H. Kennedy, in S. Gellar (ed.), *Solid Electrolytes,* Berlin: Springer-Verlag, 1977, p. 105.
20. A. R. West, in P. G. Bruce (ed.), *Solid State Electrochemistry,* Cambridge, UK: Cambridge University Press, 1995.
21. T. Kawada and H. Yokokawa, *Key Eng. Mater.,* **125-126**: 87, 1997.
22. P. G. Bruce (ed.), *Solid State Electrochemistry,* Cambridge, UK: Cambridge University Press, 1995.
23. J. Maier, *J. Phys. Chem. Solids,* **46** (3): 309–320, 1985.
24. M. Forsyth et al., Glassy PVOH-lithium salt electrolytes, *Proc. Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.,* **76**: 223, 1997.
25. M. L. Wolf, S. R. Walker, and C. R. A. Catlow, Structural and transport properties of β''-Al_2O_3, *Solid State Ionics,* **13**: 33–44, 1984.
26. M. Forsyth et al., Molecular dynamics simulations of highly concentrated salt solutions: Structural and transport effects in polymer electrolytes, *Solid State Ionics,* **53-56**: 1011–1026, 1992.
27. V. A. Payne et al., Simulations of structure and transport in polymer electrolytes, *Solid State Ionics,* **81**: 171–182, 1995.
28. S. Neyertz and D. Brown, *J. Chem. Phys.,* **104**: 3797–3809, 1996.
29. S. Neyertz, D. Brown, and J. Thomas, Molecular dynamics simulation of the crystalline phase of poly(ethylene oxide)-sodium iodide, PEO_3NaI, *Electrochim. Acta,* **40**: 2063–2069, 1995.
30. P. Johansson et al., Local coordination and conformation in polyether electrolytes: Geometries of M-triglyme complexes (M = Li, Na, K, Mg and Ca) from ab initio molecular orbital calculations, *Solid State Ionics,* **86-88**: 297–302, 1996.
31. M. P. Allen and D. J. Tildsley, *Computer Simulation of Liquids,* Oxford: Clarendon Press, 1989.
32. M. C. Lonergan et al., Monte Carlo investigations of coulombic correlations in lattice gas models, *J. Chem. Phys.,* **98**: 4937–4947, 1993.
33. C. L. Rohrer and G. C. Farrington, Composition dependent ionic conductivity in β''-alumina, *Proc. Mater. Res. Soc. Symp.,* **210**: 119–124, 1991.
34. K. Funke, Jump relaxation: Simple equations, relevant functions, and Kohlrausch-Williams-Watts behaviour, *Proc. Mater. Res. Soc. Symp.,* **210**: 97–108, 1991.

Reading List

M. P. Allan and D. J. Tildesley, *Computer Simulation of Liquids,* Oxford: Clarendon Press, 1990.

W. I. Archer and R. D. Armstrong, The application of ac impedance methods to solid electrolytes, *Electrochemistry,* **7**: 157–202, 1980.

P. G. Bruce (ed.), *Solid State Electrochemistry,* Cambridge, UK: Cambridge University Press, 1995.

P. G. Bruce and C. A. Vincent, Polymer electrolytes, *J. Chem. Soc., Faraday Trans.,* **89**: 3187, 1993.

F. M. Gray, *Solid Polymer Electrolytes: Fundamentals and Technological Applications,* New York: VCH, 1991.

R. A. Robinson and R. H. Stokes, *Electrolyte Solutions,* London: Butterworth, 1959. A classic account of aqueous electrolytes.

S. I. Smedley, *The Interpretation of Ionic Conductivity in Liquids,* New York: Plenum, 1980.

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