CHAPTER 2

LITERATURE REVIEW

2 LITERATURE REVIEW

2.1 Background

Broadly speaking there are two types of electrolytes, solid electrolytes and liquid electrolytes. Aqueous electrolytes normally comprise inorganic salts dissolved in a suitable solvent. The modern electrolyte theory is based on Arhennius proposal [2]. According to this theory, the dissociated ions are free to move in the solution when an electric field is applied. The anion will move towards the positive terminal (anode) while the cation moves to the negative terminal (cathode). The degree of dissociation into ions varies with concentration of the salt. The degree of dissociation in a dilute solution is thus the ratio of the corresponding equivalent conductivity to the conductivity at infinite dilution. If the salt is fully dissociated, the solution is called a strong electrolyte. In the case of partial dissociation, the solution is called a weak electrolyte [3,4]. For instance, NaCl or KCl will form strong electrolytes when dissolved in water giving high electrical conductivity. However, in the solid state these salts being crystalline have very low electrical conductivity as low as 10^{-12} Scm^{-1}. Liquid electrolytes have higher electrical conductivity. Their applications in devices are however limited especially when the devices are very sensitive to water [4] and require miniaturization for use in limited spaces.

Since the seventies, tremendous advances have taken place in the development of organic and polymeric conducting materials that are of great scientific and commercial interests. Usually polymeric materials exist in the solid state and are insulators. With proper innovative engineering, these insulating polymers can be turned into ion conducting polymers. Apart from the polymers, other solids can also conduct ions. These solids can exist as crystals or glasses. These solids have high ionic and low electronic conductivity. In polymers, the electronic conduction can be considered negligible [5] but the ionic conductivity is contributed by cations and anions. In glasses however the ionic conductivity is attributed to cations [7].

2.2 Ionic Conductivity

In nearly perfect crystals, ionic diffusion is always connected to the existence of lattice defects. The transport of ions through an ionic crystal depends on the presence of defects. The mechanism of the ionic transport process can be summarized as follows [8,9],

a) the vacancy mechanism: exchange of a vacancy with a neighboring ion in a normal lattice,
b) the interstitial mechanism: displacement of ion in a normal lattice site to an interstitial site by a neighboring interstitial ion and,
c) the interstitialcy mechanism: transport of an interstitial ion to a neighboring equivalent interstitial site

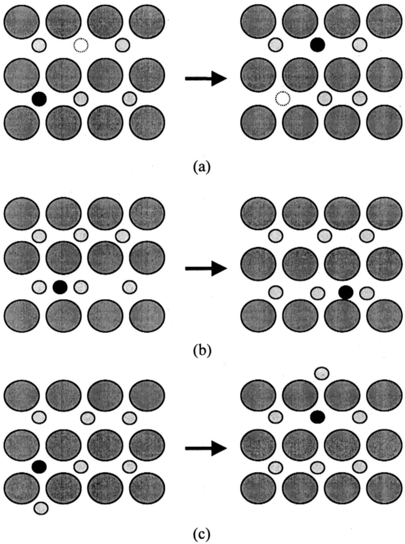


Figure 2.1: Mechanism of ionic transport in crystals: (a) the vacancy mechanism, (b) the interstitial mechanism, (c) the interstitialcy mechanism. Small circle represent cations, large circle represent anions.

The mechanisms in the above processes occur through either hopping or diffusion. Normally ion transport in crystals depends on the diffusion or migration of ions. The common diffusion is vacancy diffusion and interstitial diffusion. In ionic crystals, the motion of ions under the perturbation of an external field gives a net ionic current. The ionic conductivity σ is generally described by an Arrhenius equation

$$\sigma = (C/kT)\exp(-u/kT) \qquad (2.1)$$

where u is the activation energy of ion motion, k is the Boltzmann constant, T is the temperature and C is given by

$$C=(1/3)(Ze)^2nd^2\omega_o \qquad (2.2)$$

where Ze is the charge of the conducting ion, n is the density of defects, d is the unit jumps distance of the ion and ω_o is the attempt frequency. The corresponding diffusion coefficient D is defined by

$$D=D_o\exp(-u/kT) \qquad (2.3)$$

with

$$D_o=C/(Z^2e^2n) \qquad (2.4)$$

and hence

$$\sigma=n(Ze)^2D/(kT) \qquad (2.5)$$

This equation is called the Nernst-Einstein relation. The derivation of these relations can readily be made by the application of the random walk theory based on the assumption that n is small [9-12].

In order to have a large ionic conductivity in vacancy diffusion; the number of vacancies must be large enough so that the effective number of ions contributing to the diffusion is large. This means that the crystal must have a large number of available sites or defects and the number must be greater than the number of diffusing ions. The ions can be easily distributed over these available sites. In interstitial diffusion, ions occupying positions between lattice sites can be formed intrinsically due to temperature effect or extrinsically due to accidental impurity dopants. The ions located at lattice sites characterized by deep potential energy wells and ionic motion take place by a hopping mechanism between adjacent sites. The diffusion of these ions relatively depends on the variation of temperature. Increasing the temperature will result in increasing ionic diffusion. However, diffusion cannot occur if the lattice is perfectly ordered.

2.3 Cooperative Motions of Ions

The common explanation of ionic diffusion or conduction is based on ion hopping in the lattice in terms of the random walk theory. It is however, very difficult to give reasonable explanations of extremely fast conduction with extremely low activation energies within the framework of the random walk theory.

Cooperative motions of ions [11] are effective in reducing the activation energy of the ions especially in solids with highly disordered lattices. In disordered lattice, due to the availability of extra interstitial sites the location of all the conducting ions are not necessarily in the regular periodic potential well of the lattice. Therefore, in a cooperative motion of ions with a fixed interionic distance, not all the ions follow the path in phase with the period of the potential. The relation is shown schematically in Figure 2.2 (a) for two ions where one ion sits in a potential well while the neighboring ion sits on top of the potential barrier (see ions marked with asterisks). If these two ions move keeping the interionic distance fixed, a situation arise in which one ion is moving up the potential barrier while the other ion is moving down. As a result, the height of the potential barrier for the cooperative motion is cancelled out and the effective activation energy is zero. Considering the disorderliness of the lattice and the possibility of ions being at different heights of the potential barrier, the overall effect of cooperative motion of the ions leads to a decrease in activation energy and hence to an increase in conductivity.

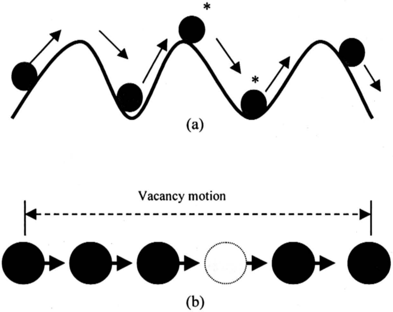


Figure 2.2 : a) Cooperative motion of ions with effect of reducing activation energy and, b) Caterpillar mechanism of ionic motion

A similar model known as the caterpillar mechanism is shown in Figure 2.2 (b). This mechanism has been proposed for high ionic conductors [11,13]. This mechanism is based on vacancy motion and involves a larger number of ions. In this model, a row of ions moves cooperatively by one atomic distance each through a vacancy, so that as a result, the vacancy moves a long distance nd where n is the number of ions involved in the row and d is the atomic distance. It is apparent that the caterpillar mechanism has a distinct advantage of increasing the jump distance.

2.4 Free Volume Theory

Generally, the polymer electrolytes are characterized by a glass transition temperature T_g. This means that below this temperature the chain segments are essentially immobile. This is due to the rigidity of the polymer structure or total polycrystallinity. As a result, the ions are trapped in between the polymer chains, making ions immobile [14-16].

Above the glass transition temperature, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighbors and create a small amount of space surrounding its own volume in which the vibrational motion can occur. This extra space is called the free volume per segment, V_f and varies randomly about a mean value $<V_{f.}>$. According to the free volume theory, the transport of the ions depends upon the formation of holes large enough for hopping or diffusion to occur. Hole formation is caused by the statistical redistribution of the volume and probability as given by the Cohen and Turnbull equation [17]

$$D = gdv \exp.(-\gamma V^*/V_f) \qquad (2.6)$$

where $g \approx 1/6$, d is the distance through which the particle are transported effectively (a molecular diameter), v is the velocity of the particle (proportional to $T^{1/2}$), V_f is the free volume of the medium, V^* is the critical volume required for migration of the particle and γ is a factor to allow for overlap of free volume. V_f in equation (2.6) increases with temperature above T_g and can be expressed as follows:

$$V_f = V_g \{f_g + \alpha(T-T_g)\} \qquad (2.7)$$

where V_g is the specific volume at T_g, f_g is free volume fraction at T_g and α is the coefficient of expansion of the free volume. From these two equations, one useful relationship can be obtained, i.e.

$$\ln \frac{D(T)}{D(T_g)} = \frac{(\gamma V^*/V_g f_g)(T-T_g)}{(f_g/\alpha)+(T-T_g)} \qquad (2.8)$$

Using the Nernst-Einstein relation of equation (2.5), an expression for the conductivity can be obtained as

$$\sigma = \frac{n(Ze)^2}{kT} gdv \ \exp\left[\frac{-\gamma V^*}{V_g \{f_g + \alpha (T-T_g)\}}\right] \qquad (2.9)$$

Here n, e, d, v, k and T have units of cm^{-3}, C, cm, cms^{-1}, JK^{-1} and K respectively, which rounds up to Scm^{-1}. Since γ and f_g has no units, V^* and V_g are both volume and α has unit of K^{-1} the exponential form does not have any units as it should be. Rewriting $n(Ze)^2 gdv / kT$ as σ_o equation (2.9) can be written as

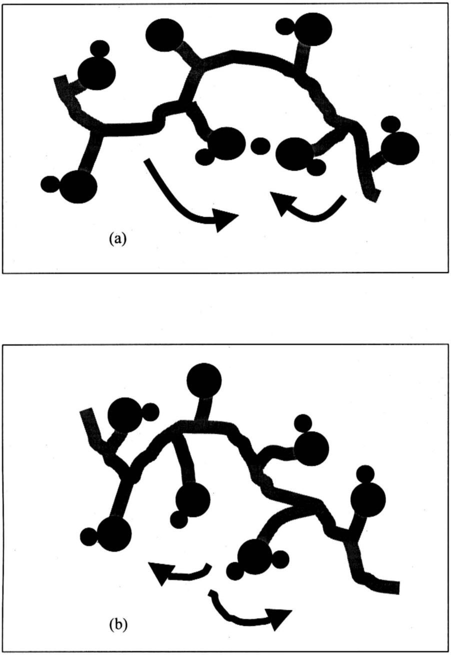


Figure 2.3 : (a) and (b) Segmental motion of the polymer chain leading to the transfer of charge [18]

$$\sigma = \sigma_o \exp\left[\frac{-\gamma V^*}{V_g\{f_g + \alpha(T-T_g)\}}\right] \qquad (2.10)$$

The free volume produced as a result of segmental motion (figure 2.3) in polymer electrolytes enables the ion to move together in relation with the motion of polymeric chain.

2.5 Solid Polymer Electrolytes

Polymer-based solid electrolytes are of growing importance in solid state electrochemistry. Most polymer materials, on their own, are insulators, but certain polymers can act as immobile solvents for ionic salts and behave as polymer electrolytes [19,20]. Polymer electrolytes are thin solid films consisting of ionic salts dissolved in an appropriate polymer. A number of monovalent [21], divalent [21] and trivalent [21] salts have been solvated in the polymer.

Polymer electrolytes generally suffer from low conductivity at and below room temperature [22]. Polymer electrolytes such as polyphosphazenes and polysiloxanes ethoxy-ethoxy-ethoxy-vinyl ether polymers (PEEEVE) have conductivity below 0.1 $mScm^{-1}$ at room temperature. Although this is a considerable improvement compared to the conductivity of the originally proposed PEO complexes, the conductivity is insufficient for the power required by lithium batteries used in many applications such as cellular phones [22].

Table 2.1: Comparison of electrochemical properties of lithium ion conducting electrolyte [22].

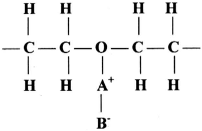
No	Electrolyte composition	Temperature (° C)	Conduction (mS cm^{-1})
Liquid electrolyte			
1	1M $LiAsF_6$/PC *	20	5.28
2	1M $LiCF_3SO_3$/PC*	20	1.75
Ceramic electrolyte			
3	Li_3N	25	0.3
4	Li-ß alumina	25	0.13
Polymer electrolyte			
5	$(PEO)_8LiClO_4$	30	$1.0X10^{-5}$
6	$(PEO)_{10}LiClO_4$	40	$6.0X10^{-3}$
7	$PEO/LiCF_3SO_4$	30	$1.1X10^{-3}$

* propylene carbonate

The viscosities of some of these electrolytes are low [23]. Some polymer electrolytes crystallize at room temperature, e.g. $(PEO)_9LiCF_3SO_3$ reducing the conductivity. Ionic conduction in polymer electrolytes is associated with the amorphous regions of the polymers. The greater the amorphous region, the higher the conductivity. Several attempts have been made to preserve the amorphous nature of PEO based electrolytes at room temperature by radiation crosslinking of the polymer [24]. While conductivity improvement has been achieved in several cases, high conductivity at and below room temperature has not been observed [25].

2.6 Complex Formation in Polymer Electrolytes

Polymeric materials that can be successful polymer hosts for the solvation of inorganic salts have to abide certain criteria. Amongst the important criteria is the existence of electron donor atoms in the structure of the polymer. For example, polyethylene oxide (PEO) with the general formula $(—CH_2CH_2O—)_n$ has oxygen as the electron-donating atom. The cation of the inorganic salt will form a dative bond with the oxygen and hence a PEO-salt complex is formed. Thus, in choosing a polymer to act as a host in which ions are the main conductors such electron donating atom must be present in the polymer. When such complexes are formed the cation and anion can be depicted as follows;



$$\begin{array}{ccccccccccc} & H & & H & & & & H & & H & \\ & | & & | & & & & | & & | & \\ - & C & - & C & - & O & - & C & - & C & - \\ & | & & | & & | & & | & & | & \\ & H & & H & & A^+ & & H & & H & \\ & & & & & | & & & & & \\ & & & & & B^- & & & & & \end{array}$$

Figure 2.4: Ions coordination onto the host polymer

The anion can be observed to be jutting out of the polymer plane and does not interact or interact very weakly with the polymer. Here A^+ is the cation and B^- is the anion of the salt AB. As in solids, the attached salt and oxygen will vibrate due to thermal energy. When the complexed site is in close proximity with an uncomplexed oxygen atom during the thermally assisted vibration, with sufficient activation energy the cation will be able to jump to the uncomplexed site and bonds with the uncomplexed oxygen atom. Hence, migration of the cation takes place. As can be observed in Figure 2.4, the anion interacts very weakly with the polymer. In polymers, both anion and cation contribute to the conductivity. The anionic mobility is almost equal to the cationic mobility. A second important criterion that a polymer should have to behave as a good polymer host is low glass transition temperature (T_g). A low T_g implies that the polymer has a soft backbone and the polymer can exhibit segmental motion as can be observed in the movement of worms and such annelids. However, the addition of salt to a polymer can increase T_g. When the salt content is too high such that segmental motion is reduced, the conductivity will again decrease. However with the appropriate salt content, segmental motion can help in enhancing conductivity. Thus, a low T_g would be a favorable property for a polymer salt complex to exhibit high ionic conductivity.

2.7 Some Characteristics of Chitosan

The term, chitosan currently refers to a deacetylation product obtained from chitin, where most of the acetyl groups have been removed. Chitosan was first obtained by Hoppe-Seyler in 1894 where chitin was fused by potassium hydroxide at 180°C. In nature, chitosan is rarely found but sometimes reported as a compound secretion from the spermatophore stalk of *Podura aquatica*. It can also be found in the Chlorella cell [26].

2.7.1 Solubility of Chitosan

Chitosan is insoluble in water and in organic solvents [27]. It is also insoluble in alkali and in mineral acids except under certain conditions. In the presence of a limited amount of acid, it is soluble in water-methanol, water-ethanol, water-acetone and other mixtures. Chitosan is solube in formic and acetic acids and in 10% citric acid. Chitosan is also soluble in pyruvic and lactic acids.

2.7.2 Optical Properties of Chitosan

Chitin and chitosan can be distinguished based on their functional group in the structure. The functional group in chitin is $NHCOCH_3$ amide and differs from the functional group in chitosan i.e. $-NH_2$ or the amine group [28]. Due to the stability of the amide group, it is used as reference for optical characterization. An FTIR spectrum shows absorbance of nitrogen containing functional groups at 1665, 1555 and 1313 cm^{-1}. The stretching of double bond, C=O occur at 1665 cm^{-1} and 1555 cm^{-1} show the deformation of N-H in the CONH plane. The absorbance at wavenumber 1313 cm^{-1} is assigned to CN bond and NH_2 wagging. When chitosan has chelated with a metal salt, all bands will shift to a new wavenumber. According to Muzarrelli [28], the chitosan spectrum differs from that of chitin in that the new band at 1590 cm^{-1} predominates over the one at 1665 cm^{-1} which could be an RN-C=O and the band at 1555 cm^{-1} which could be an NH_3^+ band may or may not be present due to the degree of deacytelation.

2.7.3 Complexation With Metal Salt

The lone pair electron of the nitrogen atoms and possibly those of the oxygen atom in the hydroxyl group can chelate with numerous metal or metallic salts. There are many papers [27] reporting the interaction of chitin and chitosan with metals to form polymer-salt complexes. The nitrogen atom in the amine group of chitosan acts as an electron donor to form a coordinate bond with cations. In this work we will have to show that complexation will occur between chitosan and the silver salt.

2.7.4 Thermal Degradation of Chitosan

Chitosan cannot withstand high temperatures even in air. It cannot withstand temperature higher than 100°C [28]. However, the glass transition temperature T_g of chitosan has been reported to be 203°C [29]. The source of chitosan is from the chitin of crabs which has a molecular weight of 90,000 g/mole.

2.8 Applications

The applications of solid electrolytes have been well established. Today super ionic conductors are used for many different applications [30] such as solid electrolytes rechargeable batteries [31], supercapacitors i.e. high-power energy storage devices [32], electrochromic display devices [33-34], gas sensors [35]. They are ideal for replacing liquid or paste electrolytes in conventional dry cell batteries

[36] and fuel cell [37]. The present energy situation has encouraged close scrutiny of all types of electrochemical power sources; solid electrolyte systems are particularly exciting because they are inherently robust, compact and spill-proof.

2.8.1 Solid State Polymer Cell

A solid-state polymer cell or solid state battery has three active components, Figure 2.5. The first is an ion source (IS), lithium metal for example. The second is a fast-ion conductor (FIC) which should be a good electronic insulator. This is to avoid electrical leakage when the battery is not in use and which would shorten its lifetime. The third component is a charge exchanger formed from an insertion material into which the positive charges, the lithium ions, and the negative charges, the electrons, penetrate via electrolytes and through the external circuit during the discharge, respectively. The cathode is therefore a mixed ionic-electronic conductor (MIC) and its performance will depend on the mobility of both ions and electrons.

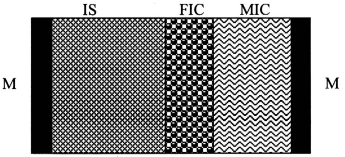


Figure 2.5: Schematizing showing the active component of a solid state battery with M=metal, IS=ion source, FIC=fast ion conductor, MIC=mixed ionic conductor. The metal electrodes are blocking the ions and transporting electron through the external circuit [38]

There are two types of electrochemical cells; the primary and secondary cell. The primary cell cannot be charged unlike the secondary cell. This dissertation is concerned with silver cells of the primary type.

2.8.2 Cell Performance Characteristics

2.8.2.1 Open Circuit Voltage (OCV)

This is the voltage generated between the anode and cathode components of a cell incorporating a solid electrolyte and such auxiliary components as are necessary, under conditions where negligible current passes. The electrode components contain the active materials that participate in the cell reaction, often together with electronic and/or ionic carriers which facilitate transport to and from the charge transfer interface. OCV is usually measured by connecting a high impedance voltmeter to the battery.

$$V_{oc} = E_{(+)} - E_{(-)}$$

The OCV value is always positive. This value depends on the characteristics of electrode-electrolytes and the structure or sizes of the cell were used [39].

The cell can be assembled as M / MX / X or to be exact Ag/chitosan-$AgCF_3SO_3$/AgI. The M^+ ion will move along the solid electrolyte. The oxidation reaction at the anode is given as

$$M \longrightarrow M^+ + e^-$$

The reduction reaction at cathode is

$$X + e^{-} \longrightarrow X^{-}$$

Thus total reaction is

$$M^{+} + X^{-} \longrightarrow MX$$

2.8.2.2 Discharge Characteristics

In simplest terms, these are plots of the voltage, V, obtained from a battery as a function of time, t, when a finite constant resistive load is used in place of an infinite load. Under such loads, they usually take the form of a plateau region (where V is independent of t) followed by step descent as the limiting cell reactants approach depletion. If the cell product is very sensitive the potential difference between the two working electrodes is decreased by an increasing IR drop across the electrode and can approximately be given by the relationship

$$V_{\mathrm{actual}} = V(t)_{\mathrm{measured}} + IR(t) \qquad (2.11)$$

where $I = V_{ocv} / R_L$, and R (t), the internal electrolyte resistance is much less than R_L, the external load. Hence, the discharge curve plateau will have a gentle downward slope.

Several technological parameters can be obtained from the discharge curve. It is most unusual for all the chemical reactants to be consumed within the useful lifetime of the cell. The efficiency of the cell can be calculated from an integration of the V-t plot, usually from t=0 to the time at which $V=0.6V_{ocv}$. This enable the total charge passed, Q, to be found since

$$Q = \int I(t)dt = (1/R_L) \int V(t)\, dt \qquad (2.12)$$

And the efficiency is

$$E = M_e/M_a \qquad (2.13)$$

Here M_e is the amount of the cell reactant, M_a is the amount available. When determining the efficiency, it is usual to use either anode-limiting or cathode-limiting cells so that the electrode from which M_a is calculated is known [40]. Some of the performance parameters are commonly defined as follows

Mass efficiency = $Q_{obtained} / Q_{obtainable}$

$$\text{Energy density} = 1/M \int VdQ$$

$$\text{Power density} = V^2 / (RM)$$

Here M is the mass of the system including electrodes, electrolytes and auxiliary components.

If a second plateau region is found in a discharge curve, it can be assumed that the initial available reactants have been consumed and a different cell reaction is proceeding. Short plateau regions, corresponding to low efficiencies, can indicate a chemical reaction that consumes only some of the active material or alternatively a surface oxidation or similar reaction that blocks up some of the electrode materials [41].

2.8.2.3 Self-Discharge in Electrode Limited System

Self-discharge can be estimated from electronic conductivity data or measured directly by high-precision microcalorimetry. It is also possible to determine this parameter by studying the discharge curves of several anodes or cathode limited systems under infinite external load. If the electrolyte is not an electronic insulator, there will be an internal short circuit within the cell and the voltage will fall after the cell reactants have been consumed. Practical considerations have recently been reviewed [42].