CHAPTER 2

LITERATURE SURVEY
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2.1 Solid Polymer Electrolytes

In the polymer electrolyte concept, the macromolecule itself acts as a solvent for a salt which becomes partially dissociated in the matrix, leading to ionic conductivity (Armand and Gauthier, 1989; Gray, 1991; Samllman and Bishop, 1995).

There are 3 desired properties which polymer electrolytes should exhibit:

(i) The availability of atoms or groups of atoms in the polymer that have sufficient electron donating power to form coordinate bonds with the cation of the doping salt. For example, N, O, S or Cl in the polymer.

(ii) A completely amorphous morphology and;

(iii) A highly flexible polymer backbone resulting in a low glass transition temperature. Segmental motion of the polymer chain should take place readily and the polymer chain should be flexible to ensure effective solvation of cations and to provide favourable solvation entropy.
Nuclear Magnetic Resonance (NMR) studies carried out by Berthier et al have shown conclusively that ionic motion in polymer electrolytes is predominant through the amorphous phase (Gray, 1991). The greater ease with which ions may be reasonably expected to move through amorphous regions, as compared with crystalline regions ties in with the general fall in conductivity with crystallinity observed in most polymers (Blythe, 1979).

The electrolyte properties can be improved by modifications to the polymer host and changing the salt. The influence of the nature and concentration of the incorporate salt on the electrolyte is complex. Essentially, polymer electrolytes form when the salt consists of a polarizing cation and a large anion of delocalized charge to minimize the lattice energy. The salt affects the conductivity through crystalline complex formation, intramolecular crosslinking of the polymer chains, and the degree of salt dissociation (the number of charge carriers). When a salt is dissolved in a polymer matrix, the conductivity increases as a result of the addition of charge carriers, however, as the salt concentration increased above a certain limit, the conductivity reaches a maximum and then falls. It has been suggested that at high salt concentrations, formation of immobile aggregated species will contribute to the fall in conductivity (Gray, 1991). As the salt concentration in a solution is increased, the interionic distance decreases and ion-ion interactions become progressively more significant.
Complexation means the material formed when the polymer host interacts with the salt to form a new polymeric system. At high enough temperatures or in systems where crystallization is prevented, the ions are solvated by the polymer to form a homogeneous polymer-salt solution.

The disadvantage of a predominantly crystalline phase at room temperature which impedes high ionic conductivity has stimulated new directions in the search for systems that are relatively amorphous at ambient temperature. There are several approaches including:

1. Modification on the polymer host by
   a. using new synthesized amorphous polymer;
   b. enhanced chain flexibility by cross linking two polymers, copolymerisation. This involves addition of another polymer host with lower $T_g$ to the original polymer host; irradiate polymer with gamma-irradiation to initiate crosslinking (Kronfli et al., 1988; Koksbang et al., 1994);
   c. blending two polymers (Wieczorek et al., 1992; Koksbang et al., 1994);
   d. adding plasticizers to polymer. A plasticizer is a substance incorporated in a material to increase the flexibility. In plasticized polymer electrolytes, the salt solvating power and the sufficient mobility of ion necessary for ionic conduction are imparted by incorporated plasticizers. The plasticizers assist in the dissolution
and dissociation of salts and therefore increase the number of mobile charges (Sukeshini et al., 1998; Frech and Chintapalli, 1996; Koksbang et al., 1994). The plasticizer will reduce local viscosity and thereby facilitating the mobile ion to move faster within the medium which in turn enhances mobility and hence conductivity (Souquet et al., 1996);

e. adding fillers to make composite polymer electrolytes. Composite solid electrolytes typically consists of a solid electrolyte matrix containing well dispersed submicron sized second phase particles such as \( \gamma \)-Al\(_2\)O\(_3\) (Khandkar and Wagner, 1986). Other second phase materials such as NiO, CeO\(_2\), Bi\(_2\)O\(_3\), Cu, Ni and Ni\(_3\)S\(_2\) have been added as dispersoids (Wen et al., 1983; Tare and Wagner, 1983). The addition of the finely dispersed powder improves the morphological and electrochemical properties of the electrolytes. Chandra et al. (1992) reported that addition of Al\(_2\)O\(_3\) to PEO system marginally decrease the conductivity of the system, but its mechanical stability increases. This is due to the increase in the degree of crystallinity of the system due to absorption of H\(^+\) and I\(^-\) ions, which saturate the free bonds on the activated alumina surface, resulting an increase in the crystallinity. Another example is the dispersion of Al\(_2\)O\(_3\) in LiI where conduction is believed to take place in the thin interfacial region surrounding the dispersed particles (Radhakrishnan, 1991).
f. incorporate 'anion trapping' groups into the polymer host (Mehta and Fujinami, 1998).

2. Complexation using different salts. Salts having low lattice energies are expected to promote greater dissociation of the salt, thereby providing higher concentrations of ions (Armand, 1996).

When the cation-polymer interaction is insufficient, the salt deposits out on surface of the film. This is a particular problem with PEO_n:RbX electrolytes. Often, this type of phase separation (sometimes called 'salting-out') occurs at elevated temperatures only (Linford, 1991).

2.2 Conductivity Mechanism

The two important variables in the case of polymers are the degree of crystallinity and the glass transition temperature (Baril et al., 1997). Polymer salt complexes are either semicrystalline or amorphous. Up to now, no evidence of conductivity has been found in crystalline complexes, as checked by NMR (Berthier et al., 1983; Ward et al., 1994) nor in sub-T_g glassy materials (Baril et al., 1997).

Conductivities are usually temperature dependent for all materials, except metals, conductivity increases with increasing temperature (West, 1992). According to Gray (Gray, 1991), Cheradame and co-workers analyzed
conductivity data for network polymers by considering the electrolyte species as predominantly associated. Quartets and ion pairs were assumed to coexist, and continuous ion pair transfer through the matrix was envisaged as resulting from exchange conformations assisted by segmental motion of the polymer.

The quantitative description of ionic conductivity in polymers requires the use of empirical equations. There are a few approaches in understanding conductance behaviour:

1. Arrhenius equation

If conductivity ($\sigma$) follows an activated law as follows:

$$\sigma T = A \exp\left(-\frac{B}{RT}\right)$$  \hspace{1cm} (2.1)

where $A, B =$ calculated parameter

$R =$ ideal gas constant

then below $T_g$, the Arrhenius behaviour is explained by the dissociation of ionic pairs, leading to the formation of interstitial defects migrating by an indirect interstitial mechanism. Above $T_g$, the ionic transport involves a cooperative mechanism of the neighbouring atoms or the macromolecular chains.
2. **VTF (Vogel-Tamman-Fulcher) equation** (Kudo and Fueki, 1990; MacCallum and Vincent, 1987; Kumar and March, 1991)

The temperature dependence of the ionic conductivity in polymers has been often represented by the empirical VTF equation, originally developed to describe the viscosity of supercooled liquids (Kumar and March, 1991).

\[ \sigma = \sigma_0 \exp\left[ -\frac{B}{(T - T_o)} \right] \]  

(2.2)

where B and To are activation energy and fitting parameter respectively (Kumar and March, 1991). The formula was initially derived from a free volume model of a glassy body, in which T_o is a parameter corresponding to an ideal glass transition temperature assuming the thermodynamic equilibrium, while the actual T_g is considerably higher than T_o (usually T_g-T_o = 50°C) (Kudo and Fueki, 1990)

The functional dependence can be described by a model in which the motion of the polymer chain is crucial for ion transport.

Souquet et al. (1996) showed that salt-polymer complexes can be considered as weak electrolytes from the discrepancies between the experimental determination of the V.T.F parameter. Charge carrier formation would remain a thermally activated mechanism and the observed V.T.F.
behavior for ionic conductivity result from a free volume mechanism for
their mobility.

Often, the temperature dependence of the conductivity follows the
VTF form. According to Ratner (1987), the $\sigma(T)$ curves for most polymer
electrolytes show one of five patterns of behavior:

(a) VTF behavior throughout the available thermal range;
(b) Arrhenius behavior for low temperatures and VTF behavior at higher $T$;
(c) Arrhenius behavior throughout, but with two different activation
energies, high $E_A$ closer to $T_g$ and a smaller $E_A$ at higher temperatures;
(d) VTF behavior for temperatures slightly greater than $T_g$, but Arrhenius
behavior at higher temperatures;
(e) behavior which is very unlike either Arrhenius or VTF at all temperatures

3. WLF (from Williams, Landel & Ferry).

This is a similar semi-empirical relation based on the free volume
model, which was developed to explain the fluidity of hydrocarbon liquids
(Kumar and March, 1991). William, Landel and Ferry (WLF) developed the
idea further to characterize relaxation processes in polymers and other glass
forming liquids. They defined a shift ratio, $a_T$ as a ratio of any relaxation
process (viscosity, diffusion, conductivity) at temperature $T$ to its value at
some reference temperature, $T_s$. An appropriate choice of $T_s$ yields a universal plot of $\log(a_T)$ as a function of $(T-T_s)$ (Kumar and March, 1991).

$$a_T = a_r \exp \left( \frac{C_1(T-T_s)}{C_2 + (T-T_s)} \right)$$  \hspace{1cm} (2.3)

Here $C_1$ and $C_2$ are constants. This formula is often used to express the temperature dependency of the relaxation time in relation to the major chain’s motion in polymers. The temperature dependency suggests that ionic conduction in amorphous composites results from the local motion of the polymer chains (Kudo and Fueki, 1990).

The VTF and WLF are in fact equivalent where

$$C_1 = \frac{B}{T-T_s} , \quad C_2 = T_s - T_o$$

The application of free-volume ideas to polymer electrolytes consists largely of using the WLF relationship for the physical properties (viscosity, storage modulus) and VTF for conductivity (Ratner, 1987)

4. **Free Volume Theory and Configurational Entropy Models**

This is another approach to describe ion transport in polymeric electrolytes. In this model, the polymer above $T_o$ behaves like a liquid. Below $T_o$ the structure is frozen and no further entropy can be lost. Above $T_o$ a high density of configurational states exists which gives rise to increased entropy (Kumar and March, 1991).
Cohen and Turnbull considered an assembly of identical atoms without electrical interaction, each of them trapped in a cage formed by its nearest neighbours. In case of a salt polymer complex, both cationic and anionic species are supposed completely dissociated, not interact with each other and solvated by the polymer chains. Salt polymer electrolytes are considered strong electrolytes (Souquet et al., 1996). The local displacement of a solvated ion around its equilibrium position in the polymer chain network defines a cell of volume $V$ which expands with increasing temperature. Above a critical temperature $T_c$, at $V$ equal to $V_c$, the excess volume $V_f = V - V_c$ is considered free, that is distributable without any enthalpic contribution (Souquet et al., 1996; Miyamoto and Shibayama, 1973). The ions which are free to move in a volume fraction (voids), which is called free volume. Following the Cohen and Turnbull treatment, the diffusion $D$ is

$$D = g au \exp \left[ \frac{-\gamma v}{\alpha v_m (T - T_c)} \right]$$

(2.4)

where $g$ is geometrical factor, $a$ is molecular dimension, $u$ is thermal velocity, $v_m$ is mean molecular volume, $\gamma$ is Lagrange parameter, and, $v$ is critical volume.

This theory explains some properties of polymer electrolytes via VTF equation. It considers the motion of polymer hosts. Free volume theory is realistic only for rigid molecules. When the free volume model is corrected for the treatment of flexible molecules, it becomes similar to configurational
entropy model given by Gibbs and coworkers. The WLF behaviour has been derived using configurational entropy model by Adam and Gibbs.

According to Kumar et al (1991), the derivation of a conductivity expression based on the configurational entropy model envisions a physical mechanism of cooperative motion of conducting ions and polymer chain segments. In an electric field the cooperative motion gives rise to a flow of current. In the absence of an electric field, these cooperative motions are random and there is no net flow of charge and current. The electric field on the cation perturbs its random thermal motion and increases the probability of a transition in the direction of the field. The transition is assisted by the thermally induced motion of chain segments.

The cation migration by a free volume mechanism is shown in figure 2.1. while figure 2.2 shows the cationic displacement in a salt-polymer complex.
Figure 2.1. Cationic migration by a free volume mechanism (Souquet et al., 1996). (a) the local displacement of two solvated cations define two similar cells in which the grey colour represents the free volume; (b) local free volume transfer allowing a displacement to an available neighbouring solvating site; (c) after a cationic displacement and free volume redistribution.
Figure 2.2. A schematic representation of a cationic displacement in a salt-polymer complex: (a) an interstitial cationic pair formation by dissociation of a neutral ionic pair; (b) and (c) the interstitial pair migration with a cooperative displacement of the macromolecular chain by a local free volume redistribution as depicted in figure 2.1. (Souquet et al., 1996)

5. Dynamic Bond Percolation theory

The WLF and VTF equations, free volume theory and configurational entropy models describe some broad physical properties of polymer electrolytes such as temperature dependence of conductivity, diffusivity and viscosity. These models only describe the hosts, not the ionic motion in
polymer-salt complexes. Percolation theory is useful in understanding transport processes in disordered media, and has been recently used in the interpretation of the free-volume behavior of transport properties of several disordered materials such as polymers and molten salts (Druguer et al., 1983).

In polymer electrolytes above the glass transition, the ionic motion is due to ionic transitional motion/hopping and dynamic segmental motion of the polymer hosts which assist the ionic motion. This model is able to describe the various physical properties of polymer electrolytes such as dependence of conductivity on chain length or the polymers, molecular weight, effect of host polymer change, frequency dependence of conductivity, etc.

Static percolation theory describes transport in systems in which hops between sites are either forbidden or allowed with specific fixed probabilities. In the Dynamic Bond Percolation model, these probabilities change with time because of the structural evolution of the host (Druguer et al., 1983).

Conduction may occur when there is:

1. Transfer of anions between Lewis acid (attract anion) sites (Fujinami et al., 1996)
2. Lowering of the crystallinity of the electrolytes (Wieczorek et al., 1992)
3. Presence of high flexible amorphous phases (Wieczorek et al., 1992), or
4. Cooperative effect of polar groups on ionic transport (Wieczorek et al., 1992)