CHAPTER I

POLYMER ELECTROLYTES

1.1. INTRODUCTION

Solid polymer electrolytes have attracted a great deal of interest. The major motivation for this interest is a technological application – rechargeable and high energy-density power sources. They are also experimented upon for a variety of other applications such as sensors, electrochromic devices and photoelectrochemical cells. Research and development efforts of the last fifteen years have contributed significantly towards the identification and definition of issues for further development in the area of solid polymer electrolytes. Indeed concerted efforts have yielded polymer electrolytes which are not only compatible with lithium, but also possess room temperature conductivities of the order of $10^{-4}$ S cm$^{-1}$ or better. With the available technology, some Japanese companies launched commercial polymer electrolyte cells in January 1999. However, problems in ion transport, ion-ion, ion-polymer and ion-solvent interactions in polymer electrolytes and charge-transfer reactions at the electrode-electrolyte interface continue to interest researchers.

A large variety of conductive polymers have been discovered. Those that acquire high electronic conductivities upon reversible electrochemical doping are classified as electronically conducting polymers. Those characterized by electrical transport principally due to ions have come to be known as polymer electrolytes. Polymer electrolytes are solid solutions of salts in polymer hosts and should not be confused with polyelectrolyte in which either the cation or the anion is covalently bonded to the polymer repeat units. Polymer-salt compositions as in polymer electrolytes have often been termed complexes.
The term complex has, however, been used rather loosely and is meant to designate the homogeneous polymer-salt phase formed when a polymer host interacts with a salt.

1.2. POLYMER ELECTROLYTES

Ionically conducting polymers or polymer electrolytes are generally described as ion-co-ordinating macromolecular solids in which a salt has been dissolved. Polymer electrolytes offer several advantages over conventional liquid electrolytes and solid crystalline electrolytes in applications [1] like in advanced high energy density lithium batteries, fuel cells, electrochromic display devices, smart windows, photovoltaic cells etc. Polymer electrolytes possess several desirable properties like

1. Good electrical conductivity at ambient temperature
2. Adequate flexibility for fabricating complex shape
3. Adequate mechanical strength in order to make free, self-supporting films
4. Necessary dimensional stability to function as separators in batteries and to provide electrical insulator between cathode and anode.
5. Good thermal stability in the -40°C to 70°C range.
6. Chemical compatibility with both the lithium anode and the cathode over the whole ambient temperature range.
7. An ability to afford lithium cycling at an efficiency of greater than 99%

The ambient temperature operation of devices could require appreciable conductivities. High electrolytic conductivity could dictate the rate at which a solid-state device can be operated, for instance, how fast energy from a lithium battery can be drained, or the speed with which the colour of an electrochromic window can be switched. Ionic conductivity
must be complemented by good dimensional stability since the polymer electrolyte will also function as a separator in the battery providing electrical insulation between the anode and cathode. This means that it must be possible to process the electrolyte into free-standing thin films having mechanical strength adequate for withstanding the physical dynamics of the electrodes during cycling of secondary polymer batteries. In this respect, the mechanical strength of polymer electrolytes should be comparable to that of conventional, non-aqueous liquid electrolyte battery separators such as porous polyethylene and polypropylene membranes. On the other hand, to expect an ionic conductivity similar to that of highly conductive liquid electrolytes and a dimensional stability reminiscent of solids in a single polymer electrolyte is to expect the coexistence of two properties which are probably mutually exclusive, especially in view of the fact that mechanism by which ions are transported in polymer electrolytes is significantly different from that involved in liquid electrolytes.

1.2.1. Classification of Polymer Electrolytes

Polymer electrolytes may be classified into three broad types: (a) dry polymer electrolytes, (b) gelled polymer electrolytes and (c) porous polymer electrolytes.

1.2.1.1. Dry Polymer Electrolytes

All the early work was on dry polymer electrolyte in which polymers, either singly or in combination with another, are complexed with suitable salts. Such materials were first investigated by Wright as early as 1973 [2, 3]. Later Armand [4, 5] proposed their use in batteries as such electrolytes combine the advantages of solid-state electrochemistry with
the ease of processing inherent to plastic materials. Their low conductivities, typically in the \(10^{-9} - 10^{-8}\) S cm\(^{-1}\) were sought to be improved upon by several means: (i) suppression of crystallization in order to enhance chain mobility and (ii) increase in charge-carrier concentration \([6-9]\). Suppression of crystallization has been attempted through polymer cross-linking \([10]\) co-polymerization, development of comb structure along the main chain through side chains \([11]\) and dendritic polymers \([12]\), polymer alloying through networking more than one polymer, and addition of fine ceramic particles. One off-shoot of high salt concentration electrolyte is the polymer-in-salt type systems which has been demonstrated to give as much as \(10^{-3}\) S cm\(^{-1}\) at 25°C \([7, 8]\). In the polymer host modification approach room temperature conductivities in the range of \(10^{-4}\) S cm\(^{-1}\) have been realized \([10-14]\). Such systems based on polysiloxanes with poly (ethylene oxide) (PEO) side chains were liquids at room temperature with LiClO\(_4\) as the complexing salt. Spindler \([12]\) studied comb-branched systems based on poly(phospazene) (MEEP) backbones and PEO side chains which are completely amorphous with glass transition temperature \(T_g\) around -80°C. However, conductivities of electrolytes based on such systems were only in the \(10^{-5}\) S cm\(^{-1}\) range \([15]\). Later interest turned to polymer alloying or blends of two or more polymers. For example, a relatively fluid polymer host such as MEEP (poly [bis-((methoxyethoxy)ethoxy) phosphazene]) which can facilitate ion transport is blended with a rigid polymer such as PEGDA (poly[(ethylene glycol) diacrylate]) to produce a mechanically stable film \([16]\). Such electrolytes gave room temperature conductivities of the order of \(10^{-4}\) S cm\(^{-1}\); these electrolytes are, however, more appropriate for applications at temperatures above 50°C.
1.2.1.2. Gelled Polymer Electrolytes

Dimensionally stable polymer electrolytes with conductivities of the order of $10^{-3}$ S cm$^{-1}$ at room temperature may be prepared by (i) incorporating a liquid plasticizer, or by (ii) cross-linking or by (iii) chemical cross-linking. In the first approach, a liquid of low volatility and high dielectric constant has been used [17-20]. These gel-polymer electrolytes show promise as an optimum material for application in electrochemical devices. However, the high conductivities of such electrolytes are dependent on considerable amounts of organic liquids. The electrochemical stability of some of these plasticizing liquids are insufficient for application such as lithium power sources. Physical cross-linking was first researched upon by Fenillade et al. [21] for PAN based systems in 1975. In 1983 Tsuchida et al. [22] and Iijima et al. [23] demonstrated room temperature conductivities of the order of $10^{-3}$ S cm$^{-1}$ for PVdF and PMMA based systems. In 1975 Fenillade et al. [21] began investigations on poly (vinylidene fluoride-hexafluoropropylene). Morita et al. [24] demonstrated a conductivity of $10^{-3}$ S cm$^{-1}$ at 25°C for PEO system. Chemically cross-linked electrolytes seem thermally stable over time, while physically cross-linked ones tend to swell and dissolve with heat and leaks solution from the structure with time.

1.2.1.3. Porous Polymer Electrolytes

In 1995 Gozdz et al. [25] realized a room temperature conductivity of $10^{-3}$S cm$^{-1}$ with a PVdF-HFP copolymer. Further scope in this area is the development of micro-phase separated electrolytes that is an intermediate stage between chemically cross-linked electrolyte and porous polymer electrolytes.
1.2.2. Thermodynamics of Polymer –salt complex formation

Polymer electrolytes are essentially solutions of inorganic salts in a polymer. The stability of a salt in a particular solvent is determined by the energy and entropy changes associated with the transfer of its constituent ions from the crystal lattice to their equilibrium positions in solution. A thermodynamic treatment of such changes requires a knowledge of the following [26]

1. Energy of cavity formation within the solvent host.
2. Short-range specific interactions between the ions and the solvent molecules or solvating groups within their immediate neighborhood, for example hydrogen bonding, coordinate bond formation, etc.
3. Long range electrostatic forces.

In polymer electrolytes the solvent is a macromolecular array of Lewis bases of low polarity. These are commonly based on hetero atoms like O, N, etc., in the polymer backbone, and is highly facilitated when the geometry of the ligand is pre-arranged to form cyclic structures where the ion is part of a five, or more rarely six membered ring. This has been obtained in analogy with host-guest chemistry [27] of general alkali metal-organic ligands. Interaction with both cations and anions with the polymer host must be considered.

Unlike in polar protic media, specific anion solvation is absent. The stability of anions in the polymer matrix is related to their charge density and basicity, and follows the order:

\[ \text{BF}_4^- > \text{ClO}_4^- > \text{SCN}^- , \text{I}^- > \text{Br}^- > \text{CH}_3\text{COO}^- \]
Thus the most suitable anions for polymer electrolytes will be large, soft ions such as BF\textsubscript{4}\textsuperscript{-} or ClO\textsubscript{4}\textsuperscript{-}. Such ions have low ion-dipole stabilization energies, but the ion-solvent interaction due to mutual polarizability is relatively large.

Cations on the other hand get solvated in the polymer through simple electrostatic interaction between the positive charge on the ion and the negative end of a dipole, or by the partial sharing of a lone pair of electrons leading to the formation of a coordinate bond.

The steps involved in cation solvation are shown in fig (1.1) with PEO as an example. Since the solvent-free complex is thermodynamically stable, ΔG for step (5) must be negative. The enthalpy associated with step (3), a gas phase interaction of the cation with four ether oxygen repeat units of the polymer, is important in understanding the mechanism of ion transport.

In a nutshell the criteria for the formation of salt-polymer complexes may be summarized as follows [28, 29].

(a) The salt should have relatively small lattice energy; this will be aided by choosing anion, to be large and the conjugate base of a strong acid.

(b) The polymer should have a low cohesive energy density; this will be favoured by a low glass transition temperature.

(c) The polymer should have a high concentration of polar groups.

(d) The polymer chain should be flexible to provide effective solvation of cations and to provide favourable solvation entropy.

The effect of (a) is reflected in the fact that the salts of strongly solvated ions like Li\textsuperscript{+} with small anions like Cl\textsuperscript{-} can also form complexes. Stiff-chain polymers such as
Scheme 1. Thermodynamic cycle for cation solvation in poly(ethylene oxide) with a 4:1 oxygen:cation mol ratio

\[ [M^+(g) + X^-(g)] + -(CH_2CH_2O)_4(g) \rightarrow M - (CH_2CH_2O)^+ \quad (3) \]

\[
\begin{align*}
(1) & \uparrow 3H_2 \\
MX(c) & + -(CH_2CH_2O)_4(s) \rightarrow M-(CH_2CH_2O)^+X^-(s) \\
(5) \end{align*}
\]

\[
\begin{align*}
\downarrow \text{solvent} & \quad \downarrow \text{solvent} & \uparrow \text{dry} \\
M^+(\text{soln}) + X^-(\text{soln}) + -(CH_2CH_2O)_4(\text{soln}) & \rightarrow M-(CH_2CH_2O)^+ \quad (6) \\
\end{align*}
\]

Scheme 2 Ion transport process in poly(ethylene oxide), gas phase

Dissociative process

\[ \Delta H_1 \\
M-(CH_2CH_2O)^+ \leftrightarrow M-(CH_2CH_2O)^+3(g) \]

Associative process

\[ \Delta H_2 \\
M-(CH_2CH_2O)-^+ \leftrightarrow M-(CH_2CH_2O)^+3(g) \]

Fig. 1.1. Thermodynamic Cycle of Complex Formation
aramides or polyoxymethylene which violate condition (b) do not form complexes. The condition (c), however, is not always followed as single polysiloxanes and polyphosphazenes (with Si and P, respectively) do not form very good electrolytes. Condition (d) is generally followed, an examples of which is PEO.

1.3. POLYMER ELECTROLYTE DYNAMICS

1.3.1. Glass transition temperature ($T_g$) and melting temperature ($T_m$)

An important physical quantity which is characteristic of polymers is the glass transition temperature $T_g$. It may be noted in a thermogram as a small magnitude asymmetric endothermic event, associated with a somewhat abrupt increase of heat capacity. However crystalline polymers exhibit an endothermic feature at higher temperatures corresponding to their melting. Both features are observed in partially crystalline polymers, although crystallization exotherms are rarely clear evidenced in polymers of large molecular weight.

Glass transition is an incompletely understood phenomena. There have been several theories of glass transition. Notable are the free volume theories (Cohen and Turnbull [30]), entropy theory (Gibbs and Dimarzio [31, 32] and more recently mode coupling theories [33-36]. Aspects of glass transition phenomenon have been reviewed extensively in literature. The glass transition temperature ($T_g$) and melting temperature ($T_m$) help in the right choice of processing temperature for various techniques like moulding extrusion, casting, etc.. In polymers $T_g$ marks a temperature below which the polymer is hard and above which it is soft. The hard-brittle state is the glassy state and the soft-flexible state is
known as the rubbery state or viscoelastic state. The change of states is illustrated in fig. (1.2).

1.3.2. Polymer motion

Variation in temperature causes polymer chains to follow continuous zig-zag random movement similar to ‘Brownian motion’ obeying no specific path. Two types of motion are ascribed to such behaviour. They are ‘segmental motion’ and ‘molecular motion’.

Segmental motion is described as a localized mobility of monomeric species present in the polymer chain. The movement gives rise to internal or micro Brownian motion (IBM). The movement of a molecule as a whole contributes to molecular motion and leads to external or macro Brownian motion (EBM). On increasing the temperature, IBM is followed by EBM. At very high temperature both types of movements are operative and the polymer chains in the polymer move independent of one another.

For a polymer which exists in highly crystalline, amorphous or partially crystalline state, the functional behaviour of specific volumes as a function of temperature can be very different as shown in fig. (1.2). For highly crystalline polymers, there is reasonably an abrupt change in specific volume at the melting temperature (T_m). For partially crystalline polymers this temperature is not so well defined. In the case of truly amorphous phase, there is not even a change of slope in this temperature range. The ‘abrupt’ part of the change in specific volume in crystalline and partly crystalline polymers occurs over a range of temperature often known as the melting range of the polymer. This range depends on the
Fig. 1.2. Plots showing variation of specific volume with temperature for

(A) highly crystalline, (B) amorphous and (C) partially crystalline polymers.
degree of polydispersivity - the broader the molecular weight distribution the wider the range. Beyond $T_m$, both IBM and EBM coexist.

1.3.3. Ionic Conduction in Polymer Electrolytes

Ionic conductivity $\sigma$, may be expressed as

$$\sigma = ne\mu$$

where $n$ is the effective number of mobile ions, $e$ the electronic charge, and $\mu$ the ionic mobility. Since the fraction of 'free' ions that can be effectively transported is an important parameter, a high degree of dissociation of the salt in the polymer is a pre-requisite for high ionic conductivity. The degree of dissociation depends on the concentration of the salt. It has been observed that usually the fraction of the free ions is maximum at around $[\text{Li}]/[\text{O}] = 0.04$ in PEO, for example, where $[\text{Li}]$ is the molar ratio of the lithium salt and $[\text{O}]$ that of the repeating units.

Ionic conduction is again a function of the transference number. The transference number of ion 'i' in an electrolyte is defined as

$$t_i = \frac{\sigma_i}{\sigma}$$

where $\sigma_i$ is the conductivity due to the ion $i$, and $\sigma$ that of the electrolyte including any contribution from electronic conductivity, $\sigma_e$. Thus $\sigma$ may be defined as

$$\sigma = \sigma_i + \sigma_e + \sum \sigma_j (j \neq i)$$

where the last term is the sum of the conductivity due to all mobile ions other than $i$. Because an ideal electrolyte possess no electronic current, $\sigma_e = 0$. Mobile ions other than
the working ion i encounter blocking ions resulting in an ion pile-up at the
electrode/electrolyte interface lowering the voltage across the electrolyte of the cell.
Ideally, therefore, the working species should alone contribute to conductivity, leaving
\[ \sum \sigma_i = 0. \] Thus \( t_i = \frac{\sigma}{\sigma_{i}} \) for ideal electrolytes. The influence of ion-ion and ion-polymer as
well as ion-plasticizer interactions on the ion transport in solid polymer electrolytes has
been an important subject of study in recent years [37, 38].

When different polymer electrolytes are derived from the same family of polymer
hosts, such as polyethers, the permittivity of the medium does not change significantly from
one host to another. In other words, the concentration of ionic charge carriers does not
change with the type of host. Thus for hosts of similar permittivity values, room
temperature conductivity of the electrolyte can be increased only by increasing the ionic
mobility of the charge carriers. This may be accomplished by providing a fluid
environment for ionic motion in the polymer matrix. The coupling of high ionic
conductivity to polymer fluidity is reflected in the description of the temperature
dependence of ionic conductivity of polymer electrolytes by the Vogel-Tamman-Fulcher
(VTF) equation:

\[
\sigma = AT^{-\nu_s}e^{-B(T-T_0)}
\]

where \( A \) is a constant related to the number of carrier ions, \( B \) another constant but related to
energy, and \( T_0 \) is the temperatures at which the configurational entropy of the polymer
becomes zero and is close to the glass transition temperature, \( T_g \).
The VTF equation is an adaptation of the relationship developed to explain the temperature dependence of such polymer properties as viscosity, dielectric relaxation and magnetic relaxation rate. The VTF equation relating viscosity, $\eta$ and $T$ is

$$T = \eta A e^{B(T-T)}$$

The fact that equation (1.4) can be applied to conductivity implies that, as with viscosity, ionic conductivity in polymers is strongly coupled to the flow behaviour of polymers. Lower $T_g$ and a fully amorphous morphology produce greater polymer flow and ionic diffusivity. That is to say that ionic conductivity is obtained in amorphous polymers having highly flexible backbones and low $T_g$.

Often the $\sigma$ vs $T$ behaviour of polymer electrolytes seems to follow the simple Arrhenius relation

$$\sigma = \sigma_0 e^{E_a/kT}$$

where $k$ is the Boltzmann constant. In general, however the conductivity vs temperature behaviour of the salt-polymer complexes may be described by any of the following types

(a) VTF behavior throughout the temperature range available

(b) Arrhenius behaviour at lower temperature and VTF behaviour at high temperatures.

(c) Arrhenius behaviour throughout, but with two different activation energies high $E_a$ close to $T_g$ and a smaller $E_a$ at higher temperatures.

(d) VTF behaviour in the temperature range slightly above $T_g$, but Arrhenius behaviour at high temperatures.

(e) Behaviour which is unlike either Arrhenius or VTF at all temperatures.
1.3.4 Additional Requirement for Polymer Electrolytes

Apart from exhibiting good ionic conductivity and such other features like processability, polymer electrolytes should possess the following characteristics.

1.3.4.1 Film forming Ability

Electrochemical devices are low voltage devices. Therefore, high power (IxV) requirements necessitate high currents which call for low IR losses. Polymer electrolyte films should hence offer very small resistance, 'R', to charge flow. R can be expressed as

\[ R = \frac{d}{\sigma A} \]

where \( d \) is the thickness of the film and \( A \) its area. It is thus obvious that polymer electrolyte should be amenable to be formed as thin, large-area films. Moreover, they should be impervious to the reactants and must maintain mechanical and chemical integrity.

1.3.4.2 Chemical, Electrochemical and Thermal Stability

In order that polymer electrolyte, which also acts as a separator in such applications as batteries, it is essential that they remain compatible with the other constituents of the system such as anodes and cathodes. Further, they should not be oxidized or reduced within the voltage limits in which the system works. They also should be thermally stable in the temperature range of operation so as to function effectively without deterioration.

1.3.4.3 Low Interfacial Ion Transfer Resistance

The properties of the electrode-electrolyte interface are of paramount importance in the design of electrochemical systems. In power cells, for example, ions are transported
across this interface. Any resistance to charge transfer across the interface can contribute to overvoltage or cell polarization, defined as the difference between the open-circuit voltage and voltage under given current, \( I \). In a power cell, overvoltage results in a loss in cell voltage while in an electrolyte cell, it leads to increased cell voltage.

1.4. POLY ELECTROLYTES

While in polymer electrolytes both the cations and anions may contribute to ionic conductivity [39], it is possible to restrict the movement of either of the ions by chemically bonding it to the polymer backbone so that the transference number of the unbonded ion becomes unity. Such polymer structures are called 'single-ion' conductors or polyelectrolytes in which only one ion is mobile. Several kinds of single-ion conductors have been proposed [40], but the conductivities of such systems turned out to be about 1% that of ordinary solid polymer electrolytes. This is mainly attributed to the insufficient dissolution of such polymer-ion matrixes [41].
1.5. REFERENCES


