A Review on Basic Mechanism of Polymer Electrolyte

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OVERVIEW

A general overview on Polymer electrolyte including ionic conductors, their classification, how polymer electrolytes are made (i.e from salt and polymer), their preparation, interaction between polymer and salt (ion solvation), their properties, characterization techniques and application.

Key words: Ionic Conductor, Polymer, Salt, Polymer Electrolyte.

1. INTRODUCTION

Ionic Conductors

Solid State Ionics is the field of materials science that deals with the preparation, characterization, theory and application of solids supporting ionic conduction. Although mass transport in solids has been recognized for some time as important to basic materials processes such as oxidation or sintering, the corresponding levels of ionic conductivity have been deemed to be low to be of interest for device applications. This changed dramatically in the late 1960’s, early 1970’s with reports of exceptionally high ionic conductivity in numerous solid electrolytes, including Na-β-Al₂O₃ and the development of the high energy density sodium buffer battery based on it. Earlier, most of the devices were based on motion of electrons (semiconductors). The discovery of transistors in 1950’s gave the new branch of science known as solid state electronics which had many applications like electronic devices, ICs, fiber optic technology etc. After that, in 1960s, a few devices were investigated based on ionic conduction but the devices had some problems like bulky in size, less rugged, corrosion by electrolyte [1-4]. To replace these electrolytes, researchers looked into some ion conducting solids like alkali halides and silver halides. Because of their low ionic conduction, they were unsatisfactory replacements. The reason of ion conductivity is the mobility of ions in crystals. It is caused by the existence of cavities, tunnels or other empty spaces in the matrix. In 1967, the discovery of β-alumina and MAg₄I₅ (where, M= Rb, K, NH₄) gave high Ag⁺ and Na⁺ ionic conduction, respectively [5-8]. After that, a large number of ion conducting solids have been investigated
having different types of charge species (cations and anions) H$^+$, Ag$^+$, Na$^+$, Li$^+$, Cu$^+$, F, O$_2^-$ etc. Such solids have various applications such as all solid state electrochemical devices (mini/macro batteries), fuel cells, supercapacitors, memory devices, electrochromic display panels [9-14]. Solid state ionic materials are also known as superionic solids or fast ion conductors.

1.2 Classification of Ionic Conductors

On the basis of microstructures, synthesis routes morphology and physical properties, classification of ionic conductors is shown in figure below amongst these, **polymer electrolyte** are of special interest because along with the ionic conductivity, they possess good properties such as chemical stability against corrosion, thin film forming, capacity, mouldability, flexibility and light weight [1].

![Figure 1.1 classification of ionic conductivity](image)

2. POLYMER ELECTROLYTE

These are ionically conducting phase which are made/formed by doping a sample salt in a solvating polymer matrix through direct interaction of the cation and electron pair. The complex material formed as a result of favourable competition between the solvation energy and the lattice energy of the salt becomes a good ionic conductor [1]. Polymer are usually formed by complexing polar polymers like PEO, PPO, PEG, PEMA e.t.c with ionic salts of monovalent alkali metal-divalent-transition metal ammonium salts[17]. Some salt-free polymer electrolytes have also been reported in which polymer like PVA and PVP have swollen lattices and anionic solute e.g H$_3$PO$_4$ is accommodated for ionic motion[18]. Whereas polysulphonic acid based polyelectrolyte, e.g Nafion, sodium polystyrene sulphate. Polymer thin film forming have good property, good processibility, flexibility, light weight, elasticity and transparency; polymer electrolytes have less mechanical strength, workability, time stability, ionic conductivity, e.t.c [18]. In synthesising polymer film the major requirement are the polymer ( which acts as the polymer host ) and the salt (which act as the ion donating salt) are keep in mind to as to make proper choice of them in other to have a good film having the necessary requirements.

Below we give a briefly highlight on polymer and salt for the synthesis of polymer film.
2.1 Polymer And Salt

2.1.1 Polymer

Polymers are substances formed by chemical reactions (polymerization) in which a large number of molecules called monomers are joined sequentially, forming a chain of polymers. Examples are a single monomer of ethylene combine to give polyethylene as shown below

![Polymerization](image)

Figure 2.1 polymerization

Other example are poly(ethylene oxide), polyether’s, poly(propylene oxide), poly(ethylene imine), e.t.c some important polymer are shown in the below table

Table 2.2: Some important polymer hosts along with their chemical formula

<table>
<thead>
<tr>
<th>Polymer Host</th>
<th>Repeat Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>-(CH(_2)_CH(_2)O(_n))^-</td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>-(CH(_2)CH(-CN)(_n))^-</td>
</tr>
<tr>
<td>Polyvinylidene chloride (PVC)</td>
<td>-(CH(_2)CH(_2)Cl(_n))^-</td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PVdF)</td>
<td>-(CH(_3)CF(_2))n^-</td>
</tr>
<tr>
<td>Polypropylene oxide (PPO)</td>
<td>-(CH(_3)(-CH(_2))CH(_2)O)n^-</td>
</tr>
</tbody>
</table>

Polymer Host

To act as a successful polymer host, a polymer or the active part of a copolymer should generally have a minimum of three essential characteristics:

1. Atoms or groups of atoms with sufficient electron donor power to form coordination bonds with cations
2. Low barriers to bond rotation so that segmental motion of the polymer chain can take place readily.
3. A suitable distance between coordinating centers because the formation of multiple intrapolymer ion bonds appear to be important[15].

2.1.2 Salt

Salts are ionic compounds that result from the neutralization reaction of an acid and a base. They are composed of related number of cations (positively charge ions) and anions (negatively charge ions) so that the product is electrically neutral (without a net charge). Also other salt can be made from metal & acid, metal & non metal, base & acid anhydride , Acid & basic anhydride. Examples of such salts in their equations (chemical reaction) are

A base and an acid, e.g., NH\(_3\) + HCl → NH\(_4\)Cl

A metal and an acid, e.g., Mg + H\(_2\)SO\(_4\) → MgSO\(_4\) + H\(_2\)
A metal and a non-metal, e.g., \( \text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}_2 \)

A base and an acid anhydride, e.g., \( 2 \text{NaOH} + \text{Cl}_2 \text{O} \rightarrow 2 \text{NaClO} + \text{H}_2 \text{O} \)

An acid and a basic anhydride, e.g., \( 2 \text{HNO}_3 + \text{Na}_2 \text{O} \rightarrow 2 \text{NaNO}_3 + \text{H}_2 \text{O} \)

Salts can also form if solutions of different salts are mixed, their ions recombine, and the new salt is insoluble and precipitates (see: solubility equilibrium), for example:

\[
Pb(\text{NO}_3)_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow Pb\text{SO}_4(\text{s}) + 2 \text{NaNO}_3(\text{aq})
\]

This salt can be monovalent, divalent or trivalent, but monovalent salts are more better used in polymer electrolyte because they have a less cation size to penetrate through the matrix of the polymer [16].

### 2.2 Preparation of Polymer Electrolyte

Mostly polymer electrolyte are prepared by

1. Solution-cast method (solvent casting method).
2. Solvothermal method.
3. Electrodeposition method
4. Sol-gel method

Let's have a brief explanation on the familiar method usually used in the polymer electrolyte community (solution cast method)

**solution-cast method** (solvent casting method); this is one of the used method of fabricating a polymer electrolyte thin film, in this process an appropriate solvent is chosen in which both the polymer and the salt are soluble in it (preferably completely soluble but if partially then heat is required also). In this process the polymer host and the salt are separately dissolved in the solvent for some time (depending on the polymer as well as the salt), it is then stirred until the solution of each solute in the solvent is homogenous, then the two solution are then mixed and further stirring is continuous using magnetic stirrer until the solution are homogenously mixed and viscous which is then poured in a Petri dish (glass or rubber), the solution is then allowed to dried, by drying the solvent of assume to evaporate (in some process vacuum dry is done) and at last a thin film of the chosen composition of the desired polymer electrolyte is obtained. Below is a flow chart showing the steps involve in synthesis of polymer electrolyte using solution cast method

![Flow Chart](image-url)

**Figure 2.1** schematic representation of different steps, in general involve in the solution casting technique.
2.3 Interaction Between Polymer and Salt; ion Solvation by the Polymer

Salt dissolve in a solvent only if the associated energy and entropy changes produce an overall reduction in free energy of the system. In polymer exist polar groups and it can be expected that polymers behave as solvents and dissolve salts to form stable ion-polymer complexes. It is possible when the interaction between the ionic species and the coordinating groups on the polymer chain compensate for the loss of salt lattice energy. Ion transport in polymer electrolytes is considered to take place by a combination of ion motion coupled to the local motion of polymer segments and inter- and intrapolymer transition between ion coordinating sites[15].

Intra polymer; 180° bond rotation at C-O bond A-B

![Schematic representation of the cation transport mechanism in a PEO-based polymer electrolyte.](image1)

While for inter polymer

![Schematic representation of the cation transport mechanism in a PEO-based polymer electrolyte.](image2)

Schematic representation of the cation transport mechanism in a PEO-based polymer electrolyte. (a) Lateral displacement of the cation brought about by 180° bond rotation at the C-O bond along the AB line; (b) the transfer of the cation between PEO chains, possibly along with anions as either an ion pair or an ion triplet (After Gray, 1991, copyright 1991 VCH Publishers.)

In a polymer electrolytes no low-molecular-weight solvent is present and ion transport relies on local relaxation process in the polymer chain which may provide liquidlike degree of freedom giving the polymer properties similar to those of molecular liquid[15].

As can be seen in Figure 2, the ionic mobility is closely correlated to the relaxation modes of the polymer host, which become effective above the polymerglass transition temperature, $T_g$ (e.g. -60°C for PEO). Indeed, polymer electrolytes have long been considered to transport charge only above $T_g$, and the relatively slow segmental motion of polymer chains has limited the hopping rate of cations, and hence the conductivity. For this reason, the highest room-temperature conductivity ($ca.10^{-4}$ S/cm) reported for PEO-LiX electrolytes [with X being a negative ion like Cl, ClO₄, AsF₆, CF₃SO₃ and N(SO₂CF₃)₂] is still several orders of magnitude less than the corresponding values of most inorganic solid-state ionics. In comparison with inorganic solid-state ionics, however, polymer electrolytes offer many advantages, including the
replacement of liquid electrolytes currently used in the lithium-battery technology, the versatility for fabrication of flexible solid-state devices free from seals, and the availability in various geometries[20]. Therefore for better practical utility, polymer electrolyte must meet few basic requirements, which are given as below [21,22]:

(a) **High ionic conductivity:** The high ionic conductivity with reduced thickness of the polymer electrolyte assures low internal resistance of the device and hence maximizes the output power obtained from the device. Therefore, the conductivity of the polymer electrolyte should be as high as possible.

(b) **High ionic transference number \( t_{\text{ion}} \) and low electronic transference number:** The polymer electrolyte must be pre-dominantly an ionic conductor and purely an electronic insulator. Most preferably, the movement of specific ion only is desired for the better performance of the electrolyte in the devices like fuel cell and batteries. For example, in fuel cell, only proton (H\(^+\)) ions are essential to pass through the electrolyte, which implies the polymer electrolyte must be exclusively proton conducting. In sensors and actuators, polymer electrolyte should exhibit conduction of a specific ion to obtain a measurable signal from the material.

(c) **High Electrochemical stability window:** The polymer electrolyte should be stable for wider working voltage range as high as ~ 4 V. In the energy storage systems like batteries and supercapacitors, it is a fundamental requirement.

(d) **Durability:** In order to maintain longer time durability of the device, the polymer electrolyte must be capable of maintaining its performance for a sufficiently long time within the operating conditions of the specific device. For this, polymer electrolyte should have high chemical and thermal stability. Any undesirable reaction at electrode/electrolyte interface or between electrolyte and other components of the device may result into its performance degradation. Further, the polymer electrolyte should be thermally stable over a wide temperature range [22].

(e) **Cost:** In order to maximize the use of the polymer electrolytes in various devices, the cost of the polymer electrolytes should be as low as possible.

### 2.4 Characterization of Polymer Electrolyte

After successfully synthesis of the polymer electrolyte many techniques are incorporated to the polymer film so as to make sure that the polymer can be used to put as an ionic conductor in various application, this techniques are

1. Impedance Spectroscopy
2. Scanning Electron Microscope (SEM)
3. Transmission Electron Microscope (TEM)
4. X-ray Diffraction (XRD)
5. Fourier Transform Infrared Spectroscopy (FTIR)
6. Raman Spectroscopy
7 Differentially Scanning Calorimetry (DSC)
8 Thermo Gravimetric Analysis (TGA)
9 Number of Charge Carriers. e.t.c

**Successful polymer electrolyte should possess the following properties**

1. Ionic conductivity should be very high (approximately $10^{-1}$-$10^{-4}$ Scm$^{-1}$) and electronic conductivity should be negligibly ($<10^{-6}$Scm$^{-1}$)
2. The activation energy should be very low (<0.3eV)
3. The sole charge carrier should be ion only i.e ionic transference number, $t_{ion} \approx 1$[15].

**Application of Polymer Electrolytes are**

1. Electrochromic devices
2. Modified electrodes/sensors
3. Electrochemical switching
4. Thermoelectric generators
5. Supercapacitors
6. high-vacuum electrochemistry e.t.c[15].

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