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## Polymer electrolyte and its transport phenomenon: A critical review

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## ABSTRACT

The polymer electrolytes along with importance and ion conduction mechanism are discussed. The various categories of polymer electrolyte are highlighted with their critical concepts. The role of the polar polymer chain (polar group) and types of ions in the polymer electrolyte are signified. The need of the polymer electrolyte composites along with active and passive fillers is well explained. The preparation of polymer nanocomposites by dispersing the various semiconducting, ceramic and insulating particles in the nano range are overviewed. The different types of models like Semi-empirical model, Effective medium theory and percolation model are well subjected. Vogel–Tamman–Fulcher (VTF) equation fits and interprets transport data and quasi thermodynamic data. Effective medium theorymodel relates the conductivity enhancement to the existence of a space-charge layer at the electrolyte/filler interface. The percolation model explains the presence of two peaks in the conductivity vs weight percentage of dispersoidin the polymer electrolyte composites.

**KEYWORDS:** Polymer electrolytes, Plasticized polymer electrolytes, Polymer electrolytes composites, Effective medium theory, Percolation model.

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## INTRODUCTION

Polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable with that of common liquid ionic solutions. This class of materials was first studied by Fenton et al. and Wright[1,2] who developed ion conducting polymers by doping polyethylene oxide (PEO) with $Li^+$ salts. Armanddiscussed the possibility of developing polymer which find immense potential application in solid state batteries fuel cells, supercapacitors, dye sensitized solar cells, sensors and electro chromic display and electrochemical devices[3]. Polymer electrolytes consist of salts in association with polymers such as polyethylene oxide (PEO), polypropylene oxide (PPO), polyacrylic acid (PAA), polyethylene imine (PEI), polyethylene glycol (PEG) etc. The most common examples concern complexes between polyethylene oxide (PEO) and alkali metal salt $(MX)$[4].
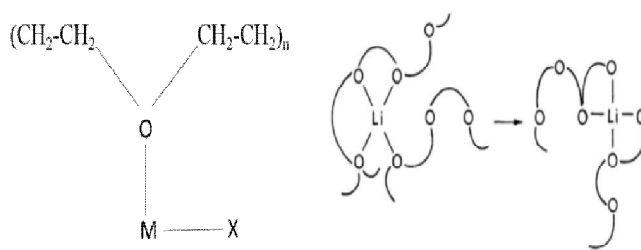


**Fig. 1:** Polymer electrolyte PEO-MX and ion motion in polymer chain

PEO is the most widely studied polymer system due to its solvating nature for a wide variety of ionic salts which together form solid electrolyte. In PEO based polymer electrolyte, the cations of the ionic salt are coordinated with the ether oxygen of PEO. The polymer electrolyte behaves as solvents for ions that exhibit a liquid-like degree of freedom. The ion conduction is due to the cation mobility in which the polymer chain motion plays a significant role as shown in figure 1. The concentration of charge carriers is important and it is function of salt concentration in the polymer. Polymer electrolytes have several advantages over other solid electrolytes because of properties like ease of preparation in thin film and other forms, good electrode-electrolyte contacts, wide range of composition and hence wider control of properties, mechanical stability and flexibility etc. A large number of solvent free polymer electrolytes based on the complexes of various metal and ammonium salts with different polymers are reported[5-7].

## CLASSIFICATION OF POLYMER ELECTROLYTE

Scrosati and Vincent [8] have divided polymer electrolyte into five categories/classes:

Class 1: ***Polymer salt complexes*** examples of which are lithium salts like $LiClO_4$ or $LiCF_3SO_3$ in a $Li^+$-coordinating polymer like polyethyleneoxide.

Class 2: ***Plasticized system*** in which small amount of liquid is added to class 1 electrolytes. Plasticized polymer electrolytes represent a compromise between polymer and liquid electrolytes. Liquid plasticizers, however, typically lead to worsening of mechanical properties of the electrolyte and increasing reactivity toward the metal electrode.

Class 3: ***Gel electrolytes*** formed by incorporating an electrolyte solution in the polymer matrix [9]. Since the electrolyte molecules can preferentially solvate ions, coordinating polymers like PEO are no longer necessary and may be replaced by more robust polymers like poly(vinylidene difluoride) (PVdF), polyacrylonitrile (PAN) and polymethyl methacrylate (PMMA). The electrolyte molecules form the network through which ion conduction occurs while the host polymer provides the structural support. Gel electrolytes offer high ambient conductivities but suffer the same disadvantages as the plasticized electrolytes-namely, release of volatile parts and increased reactivity toward metal electrode.

Class 4: ***Polymer-in-salt or rubbery electrolytes*** were discovered by Angell and coworkers[10]. The salt typically has low glass transition temperature so that a rubbery material is formed when the salt and polymer are mixed together. Although, high ambient conductivities have already been realized, the salts tend to crystallize at lower temperatures, preventing their practical use.

Class 5: ***Composite electrolytes*** in which inorganic (ceramic) particles are introduced into a polymer electrolyte. In addition to improvements in the conductivity, the mechanical stability and interfacial stability are also enhanced in the composites.

The PEO-MX membranes offer a series of unique advantages such as, good chemical and electrochemical stability and particularly ionic conductivity which is of the order of $10^{-4}$-$10^{-3}$ $Scm^{-1}$. However, the conductivity remains at these levels only above $70^0C$, typically in the $80$-$100^0C$ range, where the PEO retains its amorphous state. Hence, the low value conductivity of polymer electrolytes at room temperature is a major problem associated with solvent free polymer electrolytes which restrict their use in solid state devices[11].

## *Gel electrolyte*

Gel can be defined as a substance that contains a solid phase network swelled by continuous dispersion of a liquid phase. Liquid helps in swelling the solid network and the network prevents the liquid from flowing away. Due to this property, gels lie between solids and liquids and show liquid like behaviour at high temperature whereas at low temperature, they behave as rubbery solids. Ion conducting gels are becoming popular and increasingly useful materials for technological applications. The gels can be easily obtained into thin film as well as bulk form. They can be prepared in desired shapes and large areas can be deposited by dip, spin or spray coating methods. Sol-gel process is an innovative technique which has the advantages of versatility in fabricating systems with complex structures at ambient temperature with high ionic conductivity, homogeneity, purity, etc. Two routes that can be adopted for the gel preparation are: (i) inorganic route with metal salts in aqueous solutions and (ii) the metal organic route with metal alkoxides in organic solvents. In both the cases, the reaction is initiated via hydrolysis and gellation occurs by polymerization of monomeric units resulting in many forms like powders, films, fibres, monolithic glasses, etc.

Apart from the sol-gel route, another approach to obtain high conductivity is the polymeric gel electrolyte route in which a liquid electrolyte is immobilized in a highly viscous polymeric matrix. These gel electrolytes retain most of the high conductivity characteristics of liquid phase but are also mechanically stable[12,13].

## Composite electrolytes or dispersed phase system

Various techniques have been employed to enhance ionic conductivities of the ionic solids such as the addition of aliovalent impurities, stabilization of unique open channel structures and preparation of disordered glass phase. Another technique is to disperse in ionic conductors different materials like $Al_2O_3$, $SiO_2$, $Fe_2O_3$ etc. Ionic conductors containing such dispersed second phase are commonly known as "composite electrolytes". Composite electrolytes are generally two phase solid mixtures which are prepared by the addition of dispersoid (generally an insulator and chemically inert material) into low conducting solids. Most of the work reported in the literature has been done with the dispersions of insulators such as $Al_2O_3$, $SiO_2$, flyash etc. in ionic conductors (LiI, AgI, AgCl, AgBr etc.).

In 1973, it has been reported by Liang that the conductivity of LiI increases by two to three order of magnitude with the addition of $Al_2O_3$ [14]. After this, a lot of work has been reported by using different types of composite materials[15,16].

## *Polymer electrolyte composites*

Polymer electrolyte composites offer improved morphological and electrochemical properties of polymer electrolytes. Although, the concept of composite electrolytes was introduced in 1973 by Liang who studied LiI–$\alpha$-Al$_2$O$_3$[14], the first work on polymer-based materials was published only about 10 years later with the work of Weston and Steele[17]. The aim of this pioneering work was primarily to improve the mechanical properties of the PEO films. It was found that addition of 10 vol% of $\alpha$-Al$_2$O$_3$ to PEO–LiClO$_4$ resulted in a substantial improvement in the electrolyte's mechanical stability. On the other hand, it was already known at that time that introduction of fillers into a polymer matrix improves the mechanical stability of the host polymer and increases its temperature stability range[18].

Also, incorporation of solid nanometric fillers results in an increase of the ionic conductivity. This increase in ionic conductivity is explained by enhanced degree of amorphicity of the polymer or hindered re-crystallization[19]. In general, the ceramic fillers for the polymer matrix are broadly classified into two categories: active and passive. The active component materials participate in conduction process (such as Li$_2$N, LiAl$_2$O$_3$) while the passive fillers (such as Al$_2$O$_3$, SiO$_2$, MgO) do not participate in the transport process. The selection of fillers between active and passive components is quite arbitrary. The different types of polymer electrolytes composites including ceramic zeolites, ionites, and semiconductor particles as additives are reported[20,21].

## *Passive fillers*

Polymer electrolyte nanocomposites involve dispersion of small particle sized selected ceramic powders in the polymer matrix. It has been demonstrated that the ceramic additives, due to their large surface area, prevent PEO chain reorganization resulting in a high degree of disorder[22]. In addition, enhancement in conductivity is also favoured by preferred metal ion conducting pathways promoted by Lewis acid-base interactions between the ceramic surface states and the PEO segments[21].

## *Active fillers*

This polymer electrolyte composites deals with the incorporation of the semiconductor particles in the host polymer electrolyte. Semiconductor particles remain dispersed in the host and contribute in the increase of the conductivity of the composite. Such a composite is called semiconductor dispersed polymer electrolyte (SDPE) composite[23-24]. The other route for the above mentioned composite is in corporation of the electron conducting polymer in the ion conducting polymer matrix[25]. Polymers like

polyacetylene, polyaniline, polypyrrole, polythiophene etc. are electron conducting polymers. This is because of presence of conjugation (by aromatic, hetro aromatic and electron rich), which provide a great degree of delocalization of π- electrons in these molecules. The overlapping set of molecular orbitals gives a reasonable mobility to the charge carrier along the polymer chain. The electrical conductivity of these conjugated polymers can be controlled by the process of doping from insulator to semiconductor to metallic range. Due to the versatility in manipulation of their structure, conducting polymers have emerged as exciting materials for solid state technology and biotechnology[26-27]. The example of the electron conducting polymer is polyacetylene, polyaniline, polypyrrole, polythiophene etc. Out of which Polyaniline (PANI) has been studied extensively because of the ease in its synthesis in aqueous media, its environmental stability and special electrical properties. PANI has become a suitable candidate for variety of technological applications such as solar cells, electromagnetic shielding, electrodes for rechargeable batteries, sensors, etc. One way of making these composites involves synthesizing the conducting polymer inside the matrices of conventional polymers using chemical or electrochemical polymerization. The most preferred method for synthesis of PANI composites is to use either HCl or $H_2SO_4$ with ammonium peroxydisulfate as an oxidant. In these approaches, monomer is polymerized in the presence of commercially available inorganic acid particles which act as colloidal substrate for the precipitating polymer nuclei leading to the formation of conducting polymer–polymer (inorganic oxide) composites.

## *Models for conductivity in polymer composites*

The interpretation of conduction phenomena in polymer composites is difficult because of their complicated structures. Moreover, polymers are weak electrolytes and ion association leads to the formation of ion pairs, triplets and multiplets.

## *Macroscopic approaches*

Following Armand's original work[3], conductivity in polymer electrolytes is generally fitted in terms of the Vogel–Tamman–Fulcher (VTF) equation which is a phenomenological way to interpret transport data. Quasi thermodynamic models like free volume and configurational entropy leads to fitting the data in term of following equation. However, their applications is limited to simple monophase system where the salts are almost fully dissociated.

$$\sigma (T) = AT^{-0.5} e^{-(B/T-T_0)}$$

## *Microscopic approaches*

Microscopic models to describe ionic mobility in polymer electrolyte were earlier proposed by Armand and Wright and coworkers in terms of cation hopping motions along the PEO helix.

## *Semi-empirical model*

Generally, conductivity $\sigma(T)$ may display VTF or Arrheniousbehaviour, a mixture of the two or even more complex behaviours at all temperatures. For a wide range of fast ionic conductors (FIC), the conductivity is Arrhenious, the pre-exponential factor $\sigma_o$, and the activation energy $E_a$, are connected by the Meyer–Neldel (MN) rule (or Compensation Law):

$$\ln \sigma_0 = \alpha E + \beta = E_a/kT_D + \ln K\omega_0$$

The above equation was initially applied by Dienes[28] to atomic diffusion in metals. Here, $T_D$ is a characteristic temperature, K is the concentration term and $\omega_o$ is the ions attempt frequency. Almond and West[29] showed that, in the case of FICs, T is the temperature of an order/disorder transition. The general MN rule is valid for a number of blend-based and mixed-phase polymer electrolytes

## *Effective medium theory*

This model relates the conductivity enhancement to the existence of a space-charge layer at the electrolyte/filler interface. According to the model, the composite electrolyte can be treated as a quasi-two-phase system consisting of a ionically conducting polymer matrix with dispersed composite units. General Effective Medium (GEM) equation is

$$\frac{f(\sigma_1^{1/t} - \sigma_m^{1/t})}{\sigma_1^{1/t} + A\sigma_m^{1/t}} + \frac{(1-f)(\sigma_2^{1/t} - \sigma_m^{1/t})}{\sigma_2^{1/t} + A\sigma_m^{1/t}} = 0$$

Where, $\sigma_1$, $\sigma_2$ and $\sigma_m$ are the conductivities of the two phases and of the composite material, respectively, the constant *A* depends on the particular composite medium and the approach to the problem, *t* is an exponent related to the filler volume, PEO fraction *f* and to the grain shape.

For the microscopic view, composite electrolytes were studied as addition of the fillers improves both, transport and mechanical properties of electrolyte films. The maximum enhancement in $\sigma$ Vs filler concentration was found to be for 10-20 wt % of the ceramic additive.

*Percolation model*

The conductivity of composite electrolytes shows a marked initial increase with dispersoid concentration (p) attaining a maxima followed by rapid drop. Bundeet al.[30] showed the critical properties of both, random resistor network and a random superconducting network near threshold concentration at $p_c$ and (1- $p_c$), respectively.

The composites are considered to be three component systems consisting of matrix of bonds which can be normally conducting with conductivity $\sigma_b$, insulating or high conducting with conductivity $\sigma_a >> \sigma_b$. The dispersoids are randomly distributed in the conducting matrix with a high conducting interface between them.Bunde and coworkers assumed a two phase model for four different concentrations p of insulating material. The special feature of this model is the presence of two threshold concentrations $p_c'$ and $p_c''$. For the smaller values of p, very few high conducting bonds occur and the total conductivity is due to normally conducting bonds. For the larger p values, a critical concentration $p_c'$ $(0 < p_c' < 0.5$ ) exists corresponding to onset of interfacial percolation. For still higher values of p, conductivity is governed by high conducting bonds and hence, increases drastically. If p is increased further, then a second critical concentration $p_c''$ $(0.5 < p_c'' < 1)$ is attained where all conduction paths become disrupted and conductor-insulator transition takes place. Above $p_c''$, the conductivity drops to zero.

## CONCLUSION

The polymer electrolyte has been classified in the different categories and their concepts has been understood. An attempt has been made to design the polymer electrolytes with the different material like plasticized polymer electrolyte, gel polymer electrolyte, composite polymer electrolyte. The ultimate aim of the all above mentioned is to prepare the polymer electrolyte with high conductivity and good mechanical stability at the ambient condition. The role of the polymer backbone or polar group present on the polymer electrolyte has been explained. The ion conduction through the polymer chain has been expressed by various types of model like Semi-empirical model, Effective medium theory and Percolation model etc.

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