

A Critical Review on Charge Transport Mechanism in Composite Polymer Gel Electrolytes from Micro to Nano

Neelesh Rai* and Lovely Ranjta

Department of Physics, AKS University, Satna, (M.P.) 485001, India.

*Corresponding author E-mail address: neeleshssi@gmail.com (Neelesh Rai)

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Abstract: In this review, we present the progress and recent advances in composite polymer electrolytes (CPEs) containing micro and nano-sized materials with due attention paid to the role of multi-phases on the charge transport properties of the electrolytes. Mainly, attention is focused to provide information on the theoretical developments in the field of underlying charge transport mechanism of polymeric materials pertaining to this review article. Thus, few theoretical models relevant to present work in regards to ionic conduction in polymer electrolytes, composite polymer electrolytes and nanocomposite polymer gel electrolytes has been dealt in detail. The paradigm shift from composite polymer electrolytes to nanocomposite polymer gel electrolytes (NCPGEs) is highlighted and the possible improvement and future directions in NCPGEs are discussed. The need of the polymer electrolyte composites along with active and passive fillers is well explained. The preparation of NCPGEs by dispersing the various semiconducting, ceramic, insulating particles and various nanotubes in the nano range are overviewed. The different types of models like Semiempirical model, Effective medium theory and percolation model are well subjected. Arrhenius, Vogel-Tamman-Fulcher (VTF) and Williams, Landel and Ferry (WLF) equation studies and interprets their conductivities data. Effective medium theory model 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 dispersoid in the CPEs. Importance on addition of nanofillers in CPEs has been discussed well by using Tanaka's and Tsagaropoulos' models.

Keywords: Polymer Electrolytes; Gel Polymer Electrolytes; composite polymer electrolytes; Nanocomposite Polymer Gel Electrolytes; Charge Transport Mechanism; Ionic Conductivity

1. Introduction

Surrounded by the vast array of materials, ionic materials in the past few decades have added a new dimension for the growth of science and technology termed as "Polymer Electrolytes" (PEs). Within this framework, the study of polymer electrolytes was launched by Fenton et al.^[1] in 1973 but their technological significance was not appreciated until the research undertaken by Armand et al.^[2] It is the result of these advances that in the world of today, polymer electrolytes are dominating in ionic materials. Continuous efforts have been devoted to develop newer ion conducting materials and their distinctive properties have brought to vanguard their applications for electrochemical devices such as electrochromic windows, supercapacitors, high energy density batteries, micro/nano electrochemical sensors etc.^[3] but the ion conducting polymers called polymer electrolytes are receiving remarkable attention because of their immense potential applications.^[4] Although, liquid electrolytes (LEs) show excellent electrochemical performance but suffer from limitations resulting them to be conveniently replaced with PEs such as low operating temperature range,^[5] liquid oozing,

internal short circuiting and the encapsulation of a liquid^[6] is difficult which restricts the shape and size of electrochemical devices. On the other hand, solid polymer electrolytes (SPEs) are stable at higher temperatures but they are limited by their conformality^[7] and have relatively lower conductivity. Currently, there is no such electrolyte that meets all the qualifications but gel polymer electrolytes (GPEs) are attractive candidates for such a system.^[8] In recent years, there has been growing demand of gel polymer electrolytes due to their immense potential applications in solid state batteries, fuel cells, dye sensitized solar cells and supercapacitors etc.^[9-11] Also, gel polymer electrolytes can provide high reliability with minimum electrolyte leakage and evaporation which can be used in conformal, flexible batteries^[11] and as physical barriers separator-free devices.^[12] Past few years, considerable progress has been made to enhance the electrical conductivity, electrochemical and mechanical stability of these polymer electrolyte materials through various modification techniques creating new dimensions to expand their potential applications. The development of novel gel polymer electrolytes with good interface stability and better manufacturability is important for the development of the next generation electrochemical devices.^[13] Therefore, gel polymer electrolytes are the potential candidate to

overcome the above mentioned drawbacks and to meet the desired requirements.^[14,15] However, gel polymer electrolytes are also limited by their ionic conductivity^[16] and poor mechanical, thermal and electrochemical stability for developing high performance devices.^[17] An effort to improve the above drawbacks associated with the gel polymer electrolytes, addition of nanosized inorganic fillers have become an ever increasing attractive approach which leads to enhanced ionic conductivity, improved mechanical and thermal stability with electrode-electrolyte interface stability by forming filler network into the polymer host, inhibiting crystallization, reorganization of polymer chains, which have altered crystallinity^[18] and stabilized the conductive amorphous phase^[19] is adopted. These types of materials are termed as nanocomposite polymer gel electrolyte (NCPGE) and are the main focus of the present study. Thus, a new class emerged as nanocomposite polymer gel electrolytes (NCPGEs), which is a compromised option that combines the liquid phase conductivity of gel polymer electrolytes (GPEs) and improves mechanical properties of GPEs.^[20,21] The formation of nanocomposite polymer gel electrolyte membranes through the reinforcement by nanofillers results into the excellent thermal and mechanical properties making them ideal candidate for reinforcing a polymer matrix.^[22] The main challenge in this case lies in the fact of increased specific surface area due to small size of the dispersing fillers and consequently forces per unit mass resulting from interactions between these surfaces and surrounding area become more pronounced. As a result, dispersion of nanofiller into the gel polymer matrix with different surface energy is quite tedious. However, a strong interface between the reinforcing phase and the polymer matrix is always required in order to achieve desirable properties. Keeping these facts in mind the present review article is focused on details studies of charge transport mechanism in various types of nanocomposite polymer gel electrolytes materials.

2. Polymer Electrolytes (PEs)

Few decades ago, extensive studies have been carried out on ion conducting behaviour of array of ion-containing polymers. These ioncontaining polymers show a relatively high ionic conductivity which renders their application potentiality as possible solid electrolytes. They are easy to make as soft membranes with thickness bringing down to a few microns and their flexibility permits good interfaces with solid electrodes. Also they remain intact, when utilized in ionic devices.^[1,4,23] Essentially in solid polymer electrolytes, high molecular weight polar polymer host acts as solvent in which ionic salt is dissolved/complexed. Polymeric host dissociates salt into cations and anions and both become mobile giving rise to high ionic conductivity. The ionic salts with large anions are intentionally chosen for complexation/dissolution in polymer matrix in order to achieve faster cation transport which is more relevant as far as battery performance is concerned. For the purpose of reliable all-solid-state electrochemical device applications, polymer electrolyte materials should essentially possess the following properties:^[3,4,6,8]

i) Ionic conductivity at room temperature ($\sigma \geq 10^{-4} \text{ S cm}^{-1}$): This enables us to achieve a performance level close to that of the liquid electrolyte-based devices. The ionic conductivity should be $\sigma \geq 10^{-4} \text{ S cm}^{-1}$ at room temperature.

- ii) Ionic transference number ($t_{ion} \sim 1$): Polymer electrolyte should preferably be a single-ion (namely cation) conducting system. For battery applications, the polymer electrolyte should perfectly act as an ion conducting medium and as an electronic separator. However, the majority of the polymer electrolytes reported so far, although exhibiting negligible electronic conduction showing the cationic transference number ~ 0.5 . This is in-line with the fact that at the maximum only half of the potential transporting ions move in the polymer electrolytes.^[24] Obviously, the larger the cationic transference number (\sim unity), the smaller would be the concentration polarization effect in the electrolytes during charge–discharge steps, and hence, the higher would be the power density possible to achieve in the battery.
- iii) High chemical, thermal and electrochemical stabilities: The solid state electrochemical devices are fabricated by sandwiching the polymer electrolyte membranes between appropriate cathode and anode materials. In order to avoid undesired chemical reactions proceeding at the electrode/electrolyte interfaces, the polymer electrolytes should possess a high chemical stability. In order to have a wider temperature range, polymer electrolytes should be thermally stable. They should also have good electrochemical stability domain extending from 0–5V.
- iv) High mechanical strength: The polymer electrolytes should be mechanically stable, so that the scaling up and large-scale manufacturing of the devices could be realized.
- v) Compatibility with the electrode materials: Finally, the polymer electrolytes should be compatible with the variety of electrode materials. Hence, adequate and possibly non-toxic anode/cathode materials should be identified. Presently, major effort has been emphasized to explore such active electrode materials which would sufficiently improve the performance level of the electrochemical devices.

3. Gel Polymer Electrolytes (GPEs)

Some solvents (aqueous/non-aqueous) swell the basic polymer host like polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP), polyvinyl difluoride (PVdF), polymethyl methacrylate (PMMA), carbomethyl cellulose (CMC) and the dopant ionic solute like H_3PO_4 or NH_4SCN are accommodated in this swollen lattice, which permit ionic motion in solvent rich swollen region of the polymer host.^[24,25] These materials are in general unstable as their conductivity depends on the ambient temperature and the concentration of the solvent in the swollen region. Even though the gel polymer electrolyte exhibits high ionic conductivity, its thermal and mechanical stability are poor and it has higher reactivity towards the electrode. Gel electrolytes may undergo solvent exudation upon long storage, especially under open atmospheric conditions. Gel polymer electrolyte consists of the three terms polymer, gel and electrolyte. The term “polymer” stands for the substances having high molecular weight which are formed by the union of the small molecular groups called monomer units joined through the covalent bond. The term “gel” stands for the solid like network which is swelled by the continuous dispersion of liquid phase. The role of the liquid is swelling in the solid frame network while solid network helps in preventing the liquid from flowing away. Due to this property, gel is a compromise between solid state and

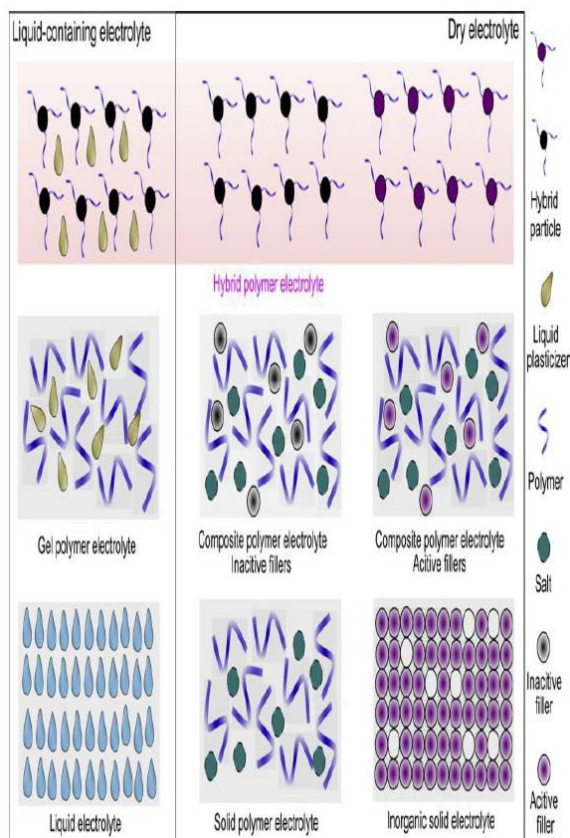


Fig. 1. Classification of gel polymer electrolytes for electrochemical device applications.

liquid state. At high temperature, it behaves like behaviour and at the low temperatures it shows the rubbery properties of solid. The third term “electrolyte” stands for salt in dissociable form in ions in some solvent.^[14] The choice in regards to polymer hosts for gel polymer electrolyte basically depends upon the presence of polar groups with large power of electron donor to get easily coordinate with cations and less hindrance to their bond rotation.^[15] A tentative classification of electrolytes is depicted in Fig. 1, where the two main categories liquid containing and gel electrolytes are sorted out.

4. Composite Polymer Electrolytes (CPEs): General Overview

Composite polymer electrolytes are essentially analogous to the usual two-phase composite electrolyte system. They are usually prepared by dispersing a small fraction of micro/nanosized inorganic (ceramics)/organic filler particles into the conventional PE host.^[25] PEs acts as phase-I, while filler materials are as phase-II dispersoid. As consequence of dispersal, ionic conductivity, mechanical, thermal, electrochemical stability and interfacial activity of PEs usually get substantially enhanced.

CPEs are also called heterogeneously doped dispersed phase electrolyte. Conductivity enhancement in two phase composite system has been known for more than 90 years,^[26] however the research activity in this field got thrust only after the work of C.C. Liang in 1973 when he reported approximately ~50 times

enhancement in Li⁺ ion conduction at room temperature simply by dispersing ultrafine (size around 4 μ m) particle Al₂O₃ in LiI.^[26,27] It is well recognized that ion transport in polymer electrolytes basically occurs in the amorphous regions and is strongly attached to chain segmental mobility of the polymer backbone. Since long, over the years, noble efforts have been made over the years to overcome this limitation of polymer electrolytes without sacrificing the mechanical integrity. In this direction one of the approaches is the introduction of a third component in the host electrolyte to form a new class of modified polymer electrolyte termed as Composite Polymer Electrolytes (CPEs) has been outshined.^[28-30] The addition of third component inorganic/organic filler is reckoned to improve ionic conductivity by lowering electrolyte crystallinity besides improving electrochemical stability. An analysis of different routes followed for the preparation of composites show that the best results can be achieved by mixing the host and dispersoids in the molten state of the host material. This increases the contact surface area and provides more uniform distribution of dispersoids. The general representation of composite polymer electrolyte with fillers is depicted in Fig. 1.

5. Composite Polymer Electrolytes: Micro to Nano

Composite polymer electrolytes possess properties that are superior to conventional polymer electrolytes and have been synthesized by using simple and inexpensive techniques. Dispersal of micro-ceramic filler particles in polymer electrolyte host improves the morphological, electrochemical, electrical and thermal properties of the membranes.^[31,32] It has been observed that the particle size and the physical nature of the dispersoid particles play a significant role in the design of composite polymer electrolytes. During the studies on composite polymer electrolytes, Wiczorek et al.^[33] observed that the size of the filler particle plays a pivotal role and demonstrated a significant increase in the conductivity of PEO-Na:Al₂O₃ system when the size of the Al₂O₃ particles was kept smaller than 4 μ m. They suggested that the surface groups of the ceramic particles play quite active role in promoting local structural modifications. Wiczorek et al.^[34] applied the Lewis acid-base theory to analyze the structure and the ionic conductivity of a number of CPEs complexed with alkali metal salts.

A comprehensive review on the state-of-art modifications in ionic conductivity, transference number and electrode-electrolyte interfacial activity of the composite polymer electrolytes has been studied by Kumar & Scanlon.^[35] According to them, dispersion of nano-sized filler particle leads to better electrode-electrolyte compatibility as compared to micron-sized particles. On the basis of DSC analysis, Kumar & Rodrigues^[36] explained the effect of particle size on the crystalline-amorphous transition of polymer electrolyte PEO:LiBF₄ dispersed with inorganic filler namely, Al₂O₃, SiO₂ etc. The nano-sized inorganic filler was found to be very effective in reducing the crystallinity in PEO based polymeric host. Kumar & co-workers^[37] also carried out similar DSC studies on PEO-LiBF₄ dispersed with nano-sized ceramic filler particles of materials with a high dielectric constant, namely, TiO₂ and ZrO₂ and identified that interactions between polymer chain and high dielectric constant inorganic fillers are influenced by the size and mass of the particles which lead to a

better improvement in the ionic conductivity. The nature of the interaction has been supposed to be dipole-dipole type driven by a dielectric constant gradient. Comparable results have also been presented by Krawiec et al.^[38] during the use of active fillers LiAlO₂ and Li₃N of nanometric dimensions. According to them nano-sized particles suppress the growth of resistive passivation layers at electrode/electrolyte boundary which in turn more effective than micro-sized particles. This effect may be caused by the layer itself being disordered, possibly by a scavenging effect of the ceramic powder. The mechanism by which ceramic or glass powders can provide the interface more stable is not completely understood. Hence, dispersal of nano-sized filler particles has been found to be more efficient in the composite polymer electrolyte systems, particularly in terms of improvement in the physical, mechanical and electrochemical properties. This new class of materials has been referred to as Nanocomposite Polymer Gel Electrolytes (NCPGEs).^[4,39-41] As a result of dispersal of nanodimension ceramic filler particles in conventional polymer electrolytes host, an enhancement of 1–2 orders of magnitude in room temperature conductivity from that of the undispersed system could be achieved along with a substantial improvement in the mechanical integrity of the electrolyte membrane as well as electrode/electrolyte interfacial activity.^[4,40]

6. Nanocomposite Polymer Gel Electrolytes (NCPGEs): An Overview

Nanocomposite Polymer Gel Electrolytes are synthesized by the addition of high surface inorganic nanosized powders such as Al₂O₃, SiO₂, MgO, TiO₂, BaTiO₃, ZnO₂, ferrites (Zn, Al-Zn, Ba, Mg-Zn) etc. or nanotubes (SWCNTs, MWCNTs, BNNT) or nano muds/clays (MMTs). The mechanical strength and stiffness of the complex systems were found to improve noticeably when these nano scale fillers are incorporated into the polymer matrix.^[18] Though main advantages of NCPGEs are the enhancements in ionic conductivity at room temperature and an improved stability at the electrode-electrolyte interfaces. Inert fillers due to their large surface area avoid the local chain reorganization which results in ambient temperatures, a high degree of disorder characteristics of amorphous phase—a feature favorable for high ion-transport.^[41]

Nanocomposite polymer gel electrolytes (NCPGEs) are also multiphase systems but their macroscopic properties are dominated by interfacial interactions. These NCPGE systems have obtained special attention because of the New Physics of the two phase hetero junctions leading to improvement in electrical and mechanical properties like hardness, fracture strength and toughness. Nanocomposite polymer gel electrolytes can be defined as the distribution of second or even third phase of nanometric dimension in a matrix electrolyte which can be amorphous or crystalline. Based on this criterion different types of nanocomposites have been envisaged like solid-solid, solid-liquid, solid-polymer etc.^[42,43] According to Maier,^[44] the physical addition of coexisting second phases of dispersed nanometric particles to ionic conducting matrix (or solid electrolyte) is now commonly referred to heterogeneous doping and valid for almost all different types of nanocomposite polymer electrolyte systems.^[45,46] In these nanocomposite polymer

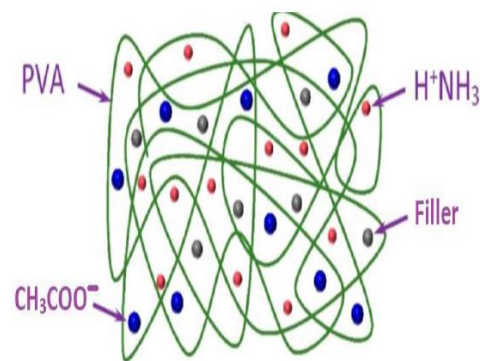


Fig. 2. Proposed pictorial diagram of NCPGE membrane with various Fillers like as ZnO; Al₂O₃; BiNiFeO₃; BNNT & MWCNT with NH₄CH₃COO salt.

Table 1. Nanocomposite Polymer Electrolytes (NCPGEs) with ionic conductivity.

Materials	Ionic Conductivity (S cm ⁻¹)	Temp. (K)	Ref.
PEO-LiClO ₄ -CNT	2 × 10 ⁻⁵	300	47
PEO-LiBF ₄ -MMT	6.2 × 10 ⁻⁵	300	48
PEO-NaClO ₄ -MMT	10 ⁻⁶	301	49
PEO-NH ₄ SCN-Al-Zn	1.23 × 10 ⁻⁴	295	50
PEO-NH ₄ SCN-SiO ₂	× 10 ⁻⁴	298	51
PVA-NH ₄ SCN-Al ₂ O ₃	5 × 10 ⁻⁴	298	52
PVA-NH ₄ SCN-MWNT	~5.8 × 10 ⁻⁴	300	53
PEO-LiI-AlO ₃	~5 × 10 ⁻⁴	298	54
PEO-LiClO ₄ -TiO ₂	~10 ⁻⁶	298	55
PEO-LiBOB-Al ₂ O ₃	2 × 10 ⁻⁵	298	56
MEEP-LiBF ₄ -TiO ₂	4 × 10 ⁻⁴	298	57
MEEP-LiBF ₄ -Al ₂ O ₃	5 × 10 ⁻⁴	298	57
PEG-EC/PC-LiClO ₄ -SiO ₂	3.5 × 10 ⁻⁵	298	57
PEO-LiClO ₄ -MMT	5 × 10 ⁻⁵	298	58
PEG × LiBr-SiO ₂	6.5 × 10 ⁻⁵	298	59
PMMA-NaClO ₄ -SiO ₂	1.5 × 10 ⁻³	298	60
PEO-LiCF ₃ SO ₃ -Al ₂ O ₃	6 × 10 ⁻⁴	298	57
PEO-EC-LiCF ₃ SO ₃ -Al ₂ O ₃	3 × 10 ⁻⁴	298	57
PEO-Nal-DMMT-PEG	8 × 10 ⁻⁶	298	57
PEO-LiClO ₄ -PbTiO ₃	~10 ⁻⁷ - 10 ⁻⁶	298	61
PEO-LiClO ₄ -Fe ₂ O ₃	~10 ⁻⁶	298	61
PEO-NH ₄ I-PbS	~10 ⁻⁶	298	62
PEO-NaClO ₄ -DMMT-PEG	2.5 × 10 ⁻⁵	298	63
PVA-LiOH-Fe ₃ O ₄	1.81 × 10 ⁻⁴	295	64
PEO-LiBOB-Al ₂ O ₃	2.0 × 10 ⁻⁵	298	65
PVA-LiAc.-LiFe ₅ O ₈	2.0 × 10 ⁻⁷	298	66
PVA-LiAc.-TiO ₂	4.5 × 10 ⁻⁶	298	67
PS-LiCF ₃ SO ₃ -Al ₂ O ₃	~10 ⁻⁴	298	68
PEO-KNO ₃ -SiO ₂	~1.07 × 10 ⁻⁶	300	69
PEO-LiPF ₆ -EC-CNT	1.30 × 10 ⁻⁴	298	70

electrolytes, introduction of new interfaces into the host matrix leads to the formation of continuous network of space charge layers and redistribution of the ions in the space-charge regions. This is likely to support improvement in ionic conductivity of the composite systems based on the supposition that surface groups of the ceramic nano particle could play an active role in influencing the re-crystallization kinetics of the host polymer chains thus promoting salt dissociation and improving ion mobility of conducting species. Various nanocomposite polymer electrolyte systems have been investigated in recent past. Fig. 2 shows a proposed pictorial diagram of NCPGE membrane with various fillers like as ZnO; Al₂O₃; BiNiFeO₃; BNNT & MWCNT with NH₄CH₃COO salt. Few examples of this category of electrolytes with their ionic conductivity are shown in Table 1.

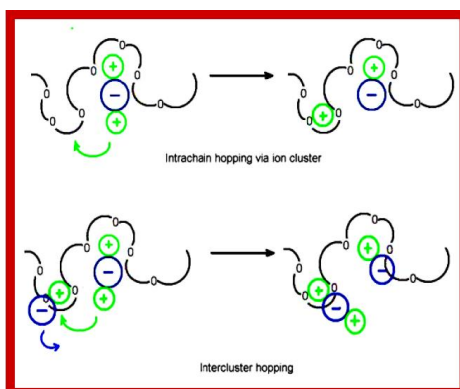


Fig. 3. Cation motion in a polymer electrolyte assisted by polymer chains only.

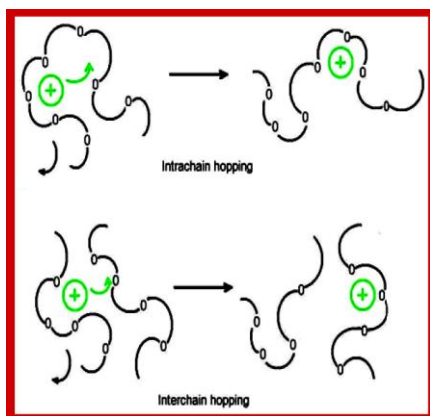


Fig. 4. Cations motion in a polymer electrolyte facilitated by the ionic cluster.

7. Theoretical Concepts

This section deals with the charge transport mechanism and many theories associated to conduction mechanism in polymer electrolyte, composite polymer electrolyte and nanocomposite polymer electrolyte systems.

7.1. Charge transport mechanism in polymer gel electrolytes

Although an intensive research towards understanding different phenomenon occurring in polymeric gel electrolytes, the mechanism of ion transport is still a matter of prime concern. Difficulties occur in interpretation of the conduction behaviour on account of complicated phase structure of polymer electrolytes which typically consists of several crystalline and amorphous phase. In addition, since polymeric electrolytes are weak ionic conductors, ion association, leading to the formation of contact ion pairs, triplets and higher multiples, normally observed in polymer electrolytes seem to play a crucial role.^[4,25] Ion association of this further complicates the understanding of ion conducting property of selected electrolytes. Fig. 3 and Fig. 4 depict the cation motion in the polymer electrolyte.

Since the beginning of studies on polymer electrolytes, a number of ideas concerning ionic transport were introduced. In a systematic investigation it has been revealed that the temperature dependence of conductivity for most of the polymer electrolytes must exhibit one of the following behaviours:

- Vogel-Tamman-Fulcher (VTF) behaviour.
- Arrhenius behaviour for low temperatures and VTF behaviour at higher temperatures.
- Arrhenius behaviour throughout but different activation energies in different temperature ranges.
- VTF behaviour for temperatures slightly greater than T_g , but Arrhenius behaviour at higher temperature.
- Behaviour which neither follow Arrhenius nor VTF in any temperature range.

The first three forms of behaviour are most commonly observed. Behaviour four has been rationalized by arguing that the two behaviours VTF and Arrhenius should merge when temperature sufficiently exceeds the reference temperature in the argument of VTF relation. Behaviour five has been rarely observed and difficult to understand.

It is important to understand these behaviours which have been empirically developed to describe the dynamical and mechanical properties of the polymer itself. Arrhenius behaviour of ionic transport stems from thermally activated hopping process. The thermal variation of conductivity (σ) for such a process can be simply expressed as:

$$\sigma = \sigma_0 T^{-1} \exp(-E_a/KT) \quad (1)$$

where σ_0 is called the pre-exponential factor of conductivity and E_a is the activation energy. This behaviour is usually observed for crystalline materials. In many polymer electrolytes, the temperature dependence of conductivity does not follow eq (1) rather it is better described by the empirical relation as:

$$\sigma = \sigma_0 T^{-1/2} \exp[-B/(T - T_0)] \quad (2)$$

where $T_0 \approx T_g - 60$ is the equilibrium glass transition temperature. This eq (2) is known as VTF equation.

Historically Vogel,^[71] Tamman and Hesse,^[72] Fulcher^[73] developed VTF equation independently not for just ion transport rather to study viscosity (η) of supercooled liquids. The empirical relationship for viscosity is given as:

$$\eta = C \exp[-B/(T - T_0)] \quad (3)$$

with $C \propto T^{1/2}$

This viscosity is further related to diffusion coefficient (D) by the well-known Stokes-Einstein relation:

$$D = KT/6\pi r_i \eta \quad (4)$$

where K is the Boltzman constant and r_i is the radius for diffusion. Combination of eq (3) and (4) enables to describe temperature dependence of D as:

$$D = C_1 T^{1/2} \exp[-B/(T - T_0)] \quad (5)$$

Conductivity of mobile ions is related to this diffusion coefficient through the relation:

$$(D/\sigma) = (KT/Nq) \quad (6)$$

Combination of eqs (5) and (6) results in eq (2). Using the Nernst-Einstein relation, in eq (5), the VTF relation eq (2) for conductivity is obtained.

Williams, Landel and Ferry (WLF)^[74] considered viscosity as well as the relaxation processes while developing their theory to understand the mechanism of ion transport in polymer electrolytes. They considered a quantity a_T , (often called the shift factor), which is simply the ratio of any mechanical relaxation process at any temperature T to its value at some reference temperature T_s and expressed it as a function of $(T-T_s)$. The functional form of a_T turns out to be nearly universal for all polymers i.e. variation of $\log a_T$ versus $(T-T_s)$ gives a master curve for all polymers. To derive analytical form of a_T , WLF first adopted the VTF eq (2) and defined a_T in terms of viscosity as:

$$\log a_T = \text{constant} + \log[\eta(T)/\eta(T_s)] \quad (7)$$

Using the following parameter transformations:

$$C_1 = B/(T_s - T_0); C_2 = T_s - T_0$$

within an additive constant yields as:

$$a_T = \log[\eta(T)/\eta(T_s)] = [C_1(T - T_s)]/[C_2 + (T - T_s)] \quad (8)$$

where C_1 and C_2 are "universal" constants. Eq (8) is often called the WLF relationship. The merit of this equation is that it can be used to compare the properties (η , D , σ) in a large range of temperatures with those measured at a reference temperature T_s , which may be chosen anywhere between T_g and T_g+150 according to experimental convenience. Thus a property can be specified over a wide temperature range by tuning C_1 and C_2 to give the best-fit data. Eq (8) can be further coupled to eqs. (3) and (4) to have a relation describing temperature dependence of conductivity in WLF form as:

$$\log[\sigma(T)/\sigma(T_s)] = [C_1(T - T_s)/(C_2 + T - T_s)] \quad (9)$$

The above discussed WLF eq (9) and VTF eq (2) equations are essentially empirical generalizations, rather than the result of any theoretical approach. In an attempt to understand the conduction mechanism in polymer electrolytes, quasi-thermodynamic theories^[75] originally developed to deal with molten salts and pure polymers, have in fact been applied with some success. These theories are based on considerations involving the critical role of glass transition temperature (T_g) and equilibrium glass transition temperature (T_0). Above T_g , the polymeric material becomes macroscopically rubbery and mechanistically understood by considering that a local environment on any given polymer chain becomes liquid like at the glass transition. Hence Arrhenius behaviour involving the term $1/T$ merges with the VTF relation containing the term $1/(T-T_0)$ at temperature well in excess of T_0 . The concept of T_0 is based on the kinetic feature of T_g and can be idealized as the temperature at which all "free volume" vanishes or at which all polymer segmental motion disappears or at which the

excess configurational entropy of the material vanishes. The theoretical scheme which treats T_0 in terms of free volume is called the free volume theory and the one describing in terms of entropies is called the configurational entropy model.^[75,76]

The free volume model states that as the temperature increases, the expansion of the material produces local empty space, the "free volume", into which ionic carriers, solvated molecules or polymer segments themselves can move. The overall mobility of the material, is then, determined by the amount of free volume present in the material. The free volume is calculated by the usual statistical argument of maximizing the number of ways in which the volume can be distributed. Thus, mobility/diffusion is not thermally activated rather occurs as a result of redistribution of free volume within a liquid like amorphous phase. The molecules are assumed to be confined within their cages except when a hole is opened which is large enough for the molecule to diffuse through. The contribution of a molecule with thermal velocity (u) to the diffusion coefficient (D) is then:

$$D(V) = g \cdot a \cdot (V) \cdot u \quad (10)$$

$$D = \int_{v^*}^{\infty} D(V)\rho(v)dv \quad (11)$$

where $\rho(v)$ is the probability of observing the free volume v . Maximizing the number of ways of distribution of free volume (i.e. maximizing the entropy) subject to conservation of total free volume and of the number of molecules leads to

$$\rho(v) = \gamma/V_f \exp(-\gamma V/V_f) \quad (12)$$

where γ is a Lagrangian parameter. Using eqns. (11) and (12) we get

$$D = g a^* u \exp(-\gamma V^*/v_t) \quad (13)$$

where, a^* is the molecule diameter. The above relations imply that if solute molecules (ions or ion pairs) are far smaller than the solvent (polymer) specie, their diffusion rate will be fixed and same as the solvent since the solute can move only when solvent cage hole appears. Expanding v_f around the temperature at which free volume disappears, we get

$$v_f = \alpha \bar{V}_m (T - T_0) \quad (14)$$

Where m is the mean molecular volume over the range $(T - T_0)$ and α is the difference in the thermal expansion coefficients between liquid and glass phase over the same range. Expanding v_g about a more realistic temperature T_g instead of T_0 (temperature where free volume vanishes) gives:

$$v_f = v_g [0.025 + \alpha(T - T_g)] \quad (15)$$

Where v_g is the molar volume at T_g and the factor 0.025 comes from WLF treatment. When eqn. (14) is substituted in eq (13) the free volume expression for the diffusion coefficient takes the form as:

$$D = g a^* u \exp[-\gamma V^* / \alpha \bar{V}_m (T - T_0)] \quad (16)$$

Though the model is successful in rationalizing many of the properties of polymer electrolytes in particular temperature dependence of conductivity, it is inadequate for several reasons. The major weakness is that the model ignores the kinetic effects associated with macromolecules. When the free-volume model is corrected for kinetic effects it becomes very similar to the configurational entropy model of Gibbs and di-Marizo^[75] described below.

The model was originally developed as a lattice model by Gibbs and di-Marizo^[75] who replaced the single parameter of free volume theory with two parameters: one simply counting the number of lattice sites and the other number of distorted bonds. Adam and Gibbs^[76] have analyzed WLF-type behavior in terms of configurational entropy using few simplified arguments. They constructed a partition function of the overall system which may or may not undergo a configurational transition and then evaluated the overall entropy in terms of configurational entropy of oligomer subunits. Considering the mass transport mechanism to be group co-operative rearrangements of the chain they have expressed the average probability \bar{W} of a rearrangement as:

$$\bar{W} = \bar{A} \exp(-\Delta\mu S^*_c / kT S_c) \quad (17)$$

Where S^*_c is the minimum configurational entropy required for rearrangement (often taken as $S^*_c = k \ln 2$). S_c is the configurational entropy at temperature T and $\Delta\mu$ is the free energy barrier per mole that opposes the rearrangement. Using the thermodynamic definition of entropy, one can write

$$S_c(T) - S_c(T - T_0) = \int_{T_0}^T (\Delta C_p / T) dt \quad (18)$$

The probability W, related to the inverse relaxation time and ΔC_p , the heat capacity difference between the liquid and glass state have been assumed to be temperature independent. So one obtain as:

$$\bar{W}(T) = \bar{A} \exp[-\Delta\mu S^*_c / kT \Delta C_p \ln(T - T_0)] \quad (19)$$

On account of definition of a_T from eqn. (6) they have finally obtained WLF type relation

$$-\log a_T = a_1(T - T_s) / [a_2 + (T - T_s)] \quad (20)$$

Where the constants a_1 and a_2 correspond to

$$a_1 = 2.303 \Delta\mu S^*_c / \Delta C_p k T_s \ln(T_s / T_0) \\ a_2 = T_s \ln(T_s / T_0) / [1 + \ln(T_s / T_0)]$$

With a_2 as slightly temperature dependent. In eq (19) one can write as:

$\ln(T/T_0) \approx (T - T_0)/T_0$; $T/T_0 \approx 1$, Then eqn. (19) can be written in VTF form as:

$$\bar{W} = \bar{A} \exp[-k\sigma / (T - T_0)] \quad (21)$$

With $k\sigma = \Delta\mu S^*_c / k \Delta C_p$

Shriver and co-workers^[77] applied the configurational entropy model to polymer electrolytes. They used the assumption $\Delta C_p = B/T$ (as a fair consequence of experimental data) where B is a constant and shown that:

$$\sigma(T) = A \exp[-k_\sigma / (T - T_0)] \quad (22)$$

where $k_\sigma = \Delta\mu S^*_c T_0 / kB$

It may be concluded from the above that the assumption of temperature independent ΔC_p yields the WLF form (eq. 20) and if $[(T - T_0)/T_0] \ll 1$, the VTF form (eqs. 21 and 22) and the two VTF forms differ slightly in the values of apparent activation energy k_σ . Therefore, the configurational entropy model for the polymer, like the free volume model, permits derivation of a VTF like form for the rate of polymer rearrangement or equivalent for the polymer viscosity or fluidity ($\phi = \eta^{-1}$). The approach appears to have merit and analysis several polymer electrolyte systems.^[78] It gives reasonable values of $(T_g - T_0)$ close to 50K. Certain aspects of conductivity are also implied by configurational entropy approach for example; fall in conductivity with increasing pressure, the molecular weight independence of conductivity in amorphous polymer above a certain molecular weight and the fact that if T_0 is lowered, the conductivity at fixed reduced temperature $(T - T_0)$ should increase.

7.2. Charge transport mechanism in CPE: Micro to Nano

The theoretical progress to know about the charge transport in composite polymer electrolytes (CPEs) must consider that CPEs as multiphase system and reveals crystalline as well as amorphous structure. Therefore, all recently discussed models basically dealing with two phase mixture only. Raleigh^[78] in his model conceptualized the second phase material in the form of spheres/cylinders embedded in the first phase to constitute a rectangular array. In this model, he further assumed that the current flow through first phase material leading to only dominant contribution of first phase in the overall conductivity of composite even if the volume of both phases are equal. Such a model is applicable when the volume of second phase is quite small compared to first phase material in such a way that the first phase envelops the second phase material. Since such a physical arrangement is not possible practically this model can be treated as ideal.

Subsequently, Lichtnecker^[79] tried to explain the conductivity of composite system by considering both phases as active metallic mixture. Based on this assumption an expression for resistivity ρ_m was obtained as:

$$\rho_m = \rho_1^{X1} \rho_2^{X2} \quad (23)$$

Where ρ_1 and ρ_2 resistivities of first and second phase respectively and $X1$ and $X2$ are their respective volume fractions. Validity of this model extends in the range where the conductivity of the two phases is comparable.

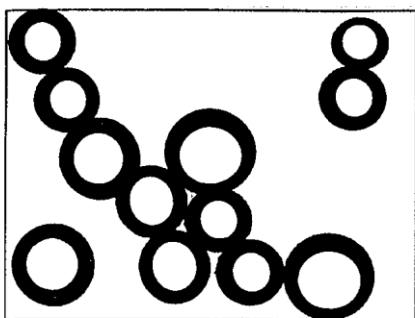


Fig. 5(a). Schematic morphology of quasi-two phase composite electrolyte.

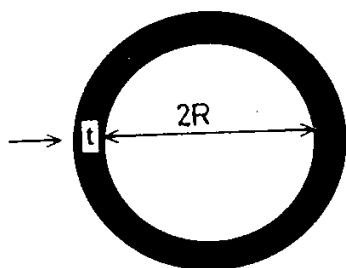


Fig. 5(b). Composite grain unit comprising of insulating and interface layer: (t) thickness of surface layer and (R) radius of insulating grain.

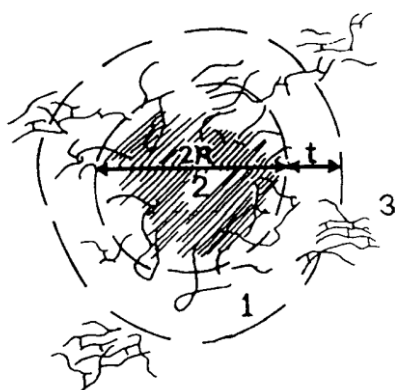


Fig. 5(c). Schematic representation of composite polymer electrolyte: 1, 2, 3 depicts the three phase present in CPE.

Landauer^[80] proposed Effective Medium Theory (EMT) by considering layered arrangement of phases in the composite system and of low resistance. However, currents can't be ignored in highly resistive regions as in case of random mixtures.

Wagner^[81] made an effort to explain the conductivity behaviour of bi-phasic metal semiconductor mixtures by introducing the concept of presence of interfacial space charge region (the double layer) at the phase boundary between the two phases. Existence of such a region originates from charge density gradient on account of non-passive nature of constituent phases at the interface. Few additional models for conductivity were reported in subsequent years.

However, all these theories and models failed to explain several experimental results on composite polymer electrolytes and hence were abandoned owing to the basic fact that these models were essentially developed for electron conducting biphasic systems. Despite this fact, all these models in general and Wagner's model^[81] in particular, served the basis for future developments i.e. the

possible existence of a space charge region propounded by Wagner became the basis for forthcoming models. Most of these models focus on the calculation of compositional dependence of conductivity. They differ only in the method of calculation and in the assumption concerning the distribution of dispersoid particles in the composite system. The theoretical developments involving these assumptions are listed below:

- i) Space-Charge Models
 - a) Jow and Wagner's Model
 - b) Discrete Shell and Screening Layer Models
 - c) Pack's Model
- ii) Absorption/Desorption Model
- iii) Resistor-Network Model
- iv) Percolation Model
- v) Concentration Gradient Model
- vi) Morphological Model
- vii) Improved Effective Medium Theory
- viii) Mobility Enhancement Model

It should be noted that the mechanism of defect generation in this space-charge layer and its topological and structural behaviour have been renewed/rectified from time to time to either explain a particular set of composites or to provide a general theoretical basis for the conductivity behaviour with second phase concentration.

7.3. Effective Medium Theory for Composite Polymer Electrolytes:

This model has been based on the effective medium approach of Landauer^[80] originally proposed for multi-phase solid systems for evaluating the average material parameters which were developed to explain conductivity enhancement in composite polymer electrolytes by Nan & Smith.^[82] It has been successfully applied to describe electrical properties of various heterogeneous systems including polymer electrolytes. It can also explain very well, the effect of insulating fillers and consequent enhancement in the conductivity in composite electrolytes. The conductivity improvement is attributed to high defect concentration on the surface of the filler grains due to the formation of 'space charge' layers. EMT approach for composite polymer electrolytes supposes that there are three phases present in the composite polymer electrolyte as shown in Fig. 5(a-c). Each phase has different electrical properties. Phase (ia) represents part of the amorphous shell formed on the grain surface. Phase (ib) is the highly conductive interfacial layer covered on the surface of the grain. Phase (ii) is the insulating grain dispersed in the matrix of polymer ion conductor and phase (iii) is polymer electrolyte host matrix. Further, the highly conducting interface layer covered on the surface of grains overlap or contacts each other resulting into high conducting pathways. However, the extent of σ -enhancement in composite polymer electrolytes depends on the conductivity of interface layers, dispersoid particle distribution and their size. A higher conductivity augmentation is expected at relatively smaller volume fraction with smaller particle size. This basic EMT model was accordingly modified by Wiczorek et al.^[33] and successfully applied by Agrawal et al.^[39] to explain conductivity enhancement in PVA:NH₄SCN electrolyte in the presence of nano aluminium oxide (Al₂O₃) used as third component.

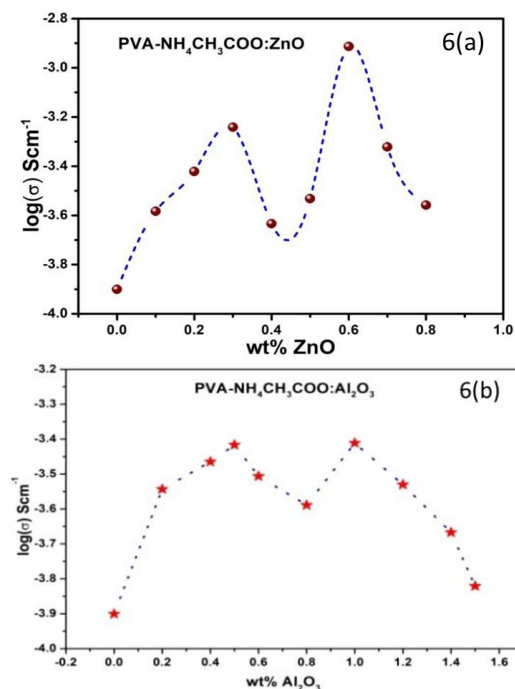


Fig. 6. DC conductivity of nanocomposite polymer gel electrolyte membranes with varying concentrations of (a) ZnO and (b) Al₂O₃ nanoparticles.

In the modified model effect of T_g has been considered along with thickness of interfacial layer of electrolyte covering insulating grain and grain size to understand compositional dependence of the conductivity of composite system.

7.4. Percolation Model

The conductivity of nanocomposite electrolytes shows a marked initial increase with dispersoid concentration (p) attaining a maxima followed by rapid drop (Fig. 6) and were reported earlier.^[83,84] Bunde et al. 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.^[85]

The composites are considered to be three component systems consisting of matrix of bonds which can be normally conducting with conductivity σ_b , insulating or high conducting with conductivity $\sigma_a \gg \sigma_b$. The dispersoids are randomly distributed in the conducting matrix with a high conducting interface between them. Bunde and coworkers^[85] 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.

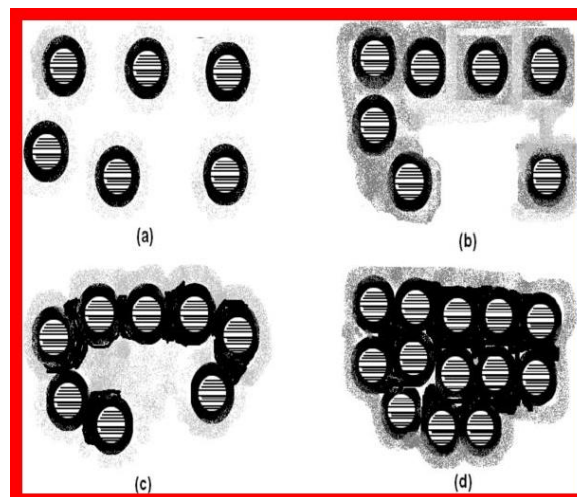


Fig. 7. Tsagaropoulos model for polymer nanocomposite.

7.5. Tsagaropoulos and Tanaka's models for analyzing the electrical properties of nanocomposite polymer electrolytes

In recent times, researchers have tried to improve properties of conventional polymer electrolytes by adding small particles (nanoparticles) into the polymer matrix. Dispersal of such particles create large interfacial region which play an important role in affecting different electrical, mechanical and thermal properties. A number of models and theories have been propounded to understand nanocomposite materials and the most interesting two models that have been developed with respect to the interpretation of some of the electrical properties and/or electrical phenomena in nanocomposites are:

- (i) Tsagaropoulos' model.^[86]
- (ii) Tanaka's model.^[87]

Tsagaropoulos' model which is focused on glass transition behaviour in different polymer nanocomposites assumes two basic layers around a nanoparticle, an inner tightly bound layer in which polymer motion is severely restricted, and another intermediate layer of restricted mobility which is more loosely bound.^[86] In the first layer which exists at a distance of $2-19 \text{ \AA}$ from the nanoparticle surface, the polymer is physically (if not chemically) adsorbed and its dynamics is slowed down. As a consequence of this it is generally thought to be tightly bound. At larger distances of about $30-80 \text{ \AA}$ from the nanoparticle surface, the polymer is assumed to be less tight and performs an intermediate dynamics; this layer is more loosely bound. A third layer is also believed, that of the unrestricted bulk polymer. With this assumption, this model intends to explain the effect of nanoparticle concentration on layer morphology and consequently on glass transition. In Fig. 7, the morphology of the polymer around filler particles and the sequence of events accompanying the incorporation of increasing amounts of nano particles in the polymer are observed. Ultimately, when the nanoparticle content exceeds to the extent that average inter-particle distance becomes much smaller than critical inter-particle distance described above nearly all polymer chains are immobilized.

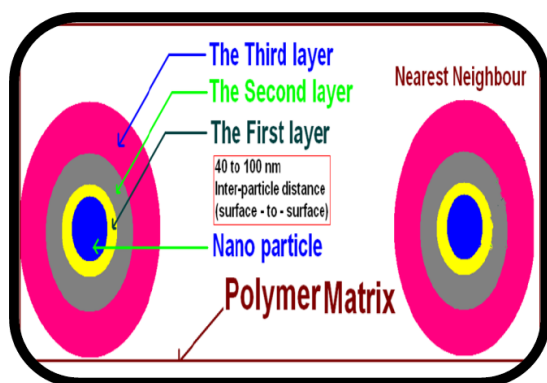


Fig. 8. Tanaka's multi-core model for polymer nanocomposite.

At extremely low concentrations the inter-particle distances are large enough to affect the mobility of the polymer next to tightly bound layers. In other words, at lower filler content the amount of the immobilized polymer around the particles is small allowing for adequately strong interactions between the loosely bound polymer and the particles. As a consequence these regions do not give rise to second glass transition though the temperature of first glass transition may decrease. On increasing filler concentration the inter-particle distances decrease while the loosely bound layer around the particle augments. As the amount of immobile polymer increases at higher nanoparticle contents, such interactions will become weaker. Subsequently, as the immobile polymer does not restrict the chain mobility as efficiently as the nanoparticles do; the second T_g decreases. The moment this loosely bound layer extends to the limit that they start overlapping, a critical inter-particle distance is achieved. These regions can now exhibit their own glass transition. On further enhancement of filler concentration polymer regions with reduced mobility decreases while the immobilized ones will increase. Thus as the inter-particle distance decreases, it is the most restricted regions of loosely bound polymer which are transformed first into tightly bound polymer. The regions with the highest T_g will be eliminated earliest as filler content increases resulting in an actual decrease of the second T_g .

In such situations due to smaller inter-particle distances, the volume fraction of the loose polymer layer reduces and the nanoparticles themselves start acting as barriers to the flow of current between the electrodes.

Tanaka's model is a multicore model^[87] describing the chemical and electrical features of interfaces. It bears also the name 'multicore' model since it considers more than two layers. According to this model when a spherical nanoparticle is embedded in polymer matrix, three layers are formed. There is a bonded layer around the nanoparticle (first layer), a bound layer (second layer), and a loose layer (third layer) and an electric double layer overlapping the above three layers. A sketch of Tanaka's model is shown in Fig. 8. The first layer corresponds to a transition layer tightly bonded to both inorganic (nanoparticle) and organic substances (polymer) by coupling agent. Its thickness is postulated to be of about 1nm. The first layer is tied by ionic, covalent, hydrogen and Vander Waals bonding. This bonding hinders the polymer chain mobility outside the monolayer. The second layer or the bound layer is an interfacial region consisting of a layer of polymer chains strongly bound or

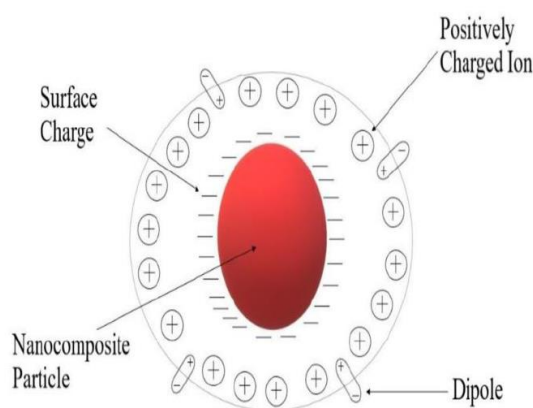


Fig. 9. Schematic representation of the space charge and local electric field formation around a nanocomposite particle.

interacted to the first layer and the surface of the inorganic particle. The thickness of this layer is between 2-9 nm. The chain mobility characterizing this region affects glass transition temperature. These values depend on the strength of the polymer-particle interaction. Clearly, stronger the interaction is, larger the polymer fraction. Thus, chain mobility and crystallinity are deeply involved. The average chain conformation can be altered and the type and degree of crystallinity may change. The third layer is a region loosely coupled/interacted to the second layer. The loose layer has different chain conformation, chain mobility and even free volume compared to polymer matrix. This layer is having several tens of nanometre thickness. The fourth layer, the electric double layer, forms a long distance dipole. This will affect electrical conduction and dielectric properties in the low frequency region.

The role of fillers has been shown to be of great importance. These nanocomposites can form space-charge regions and induce a local electric field. This phenomenon was first approached by Kumar who revealed the electric charge and area associated with the particle interact with the structure of the liquid electrolyte, provoking the space-charge region.^[88] It can be described as containing free electrons at the surface of the nanocomposite, and cations along with dipoles at the adjacent double-layer balance the surface electronic charge (Fig. 9). Magnesium oxide is known to be slightly electronegative in nature.

8. Conclusions

An overview of the state-of-the-art of composite polymer electrolytes and nanocomposite polymer gel electrolytes (CPEs and NCPEGs, respectively) with the main focus dedicated to the impact of challenges and possible remedies. The polymer electrolyte has been classified in different categories and their concept has been understood. An attempt has been made to review the polymer electrolytes with the different material like gel polymer electrolytes, composite polymer electrolytes and nanocomposite polymer gel electrolytes. The ultimate aim is to review and serve the composite 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 introduction of inorganic phase in polymer

electrolytes tends to improve the charge transport properties of cationic species (e.g. ionic conductivities, cation transference number etc.) as well as the chemical and electrochemical stability of electrode/electrolyte interphase. The ion conduction through the polymer chain has been expressed by various types of models like Semi empirical model, Effective medium theory, Percolation model, Tsagaropoulos' model and Tanaka's model etc. However, several impediments have to be addressed in the future work to bring one step further the composites and nanocomposites concept to reality, balancing the properties of CPEs and NCPGE according to the requirement of each category, and gaining a deeper understanding on the transport properties in particular of CPEs with various salts and fillers. Believing that, with continuous efforts on aforementioned aspects, the CPEs and NCPGEs would certainly be promising candidates for developing better electrochemical devices.

Conflicts of Interest

The authors declare no conflict of interest.

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