Ch. 2: Theoretical Details

****

This chapter provides an insight regarding ion conduction mechanism in disordered systems viz. polymer electrolytes. Various theories/models and different formalisms of Impedance Spectroscopy are discussed to explain the ion dynamics herein.

****

2.1 Ionic Conductivity and Ion Conduction Mechanism

Long range migration of either electrons or ions contributes to the electrical conduction in a material. Electrons and ions respectively contribute in the conduction process taking place in crystalline as well as disordered solids. Interestingly, in *'Solid Electrolytes'*, both electrons as well as ions participate in the conduction process. However, in this case, the majority charge carriers leading to this process of conduction are ions, which hop through lattice via defects upon application of electric field. Electrons may also be mobile in such electrolytes and participate in the conduction process; but their contribution is quite negligible. Hence, as in such solid electrolytes, ions govern the conduction process and lead to *'Ionic Conductivity'*; these electrolytes are also termed as *'Superionic Conductors'* or *'Fast Ion Conductors'*. One such type of solid electrolyte is *'Polymer Electrolyte (PEs)'*. Ion transport mechanism in solid polymer electrolytes was firstly studied by **Armand et al.** [1].

In these electrolytes, ions experience potential energy landscapes. But as these landscapes are irregular, they contain distribution of barrier heights and depths. The ions are unable to overcome the energy barriers and to move to the next sites if they do not have enough energy to escape from their lattice sites. In such a case, these ions perform vibratory motion. But if the ions possess sufficient energy to overcome the barriers, they can easily escape from the energy site. However, in case of polymer electrolytes, this ion transport phenomenon is associated with structural relaxations of host polymer and occurs either by *'Liquid-Like Mechanism'* or *'Solid-Like Mechanism'*. In case of liquid-like mechanism, the ions get temporarily attached to the polymer chain and lead to the *'short range'* ionic motion in these polymer electrolytes. On the other hand, at times local matrix provides pathways or opportunities for the mobility of ions between suitable low lattice sites [2] thus, yielding ionic conductivity. Thus, in polymer electrolytes, the ionic conductivity can be expressed as:

$$\sigma_v = \frac{1}{\rho_v} = \frac{t}{R_v A} \qquad \ldots\ldots\ldots\ldots\ldots (2.1)$$

where, σ_v = conductivity of the sample in Siemens/cm or mho/cm, ρ_v = resistivity of the sample in Ohms, t = thickness of the sample in cm, R_v = resistance of the sample in ohms and A = area of the electrodes in cm^2, [3,4]. Hence, dc (ionic) conductivity depends mainly on the thickness of the polymer film and is mainly influenced by:

- Mobility of charge carriers i.e. the way they move through the solids
- Number of charge carriers
- Amount of charge on the charge carriers

On the other hand, in solid-like mechanism, the *'long range'* motion of cations takes place which is activated by thermal means. However, the cationic motion can occur only when the ions get solvated in low molecular weight polar molecules. Basically, here, the local segmental motion of the host polymer(s) aids in long range diffusion of these ions thus, yielding the ionic conductivity. This suggests that the ionic and segmental motion of the host polymer(s) are *'Coupled'* together. Hence, higher the segmental mobility, higher is the ionic conductivity [5-7].

2.2 Theories & Theoretical Models of Conductivity

Ion conduction mechanism and ionic conductivity in certain systems including polymer electrolytes can be understood by using various proposed models/theories described briefly as follows.

2.2.1 Temperature Dependent Arrhenius, VTF and WLF Theories of Conductivity

In polymer electrolytes, both ionic conductivity as well as ion transport mechanism mainly depends upon temperature. Such a temperature dependence of ionic conductivity and ion transport mechanism in a polymer matrix can be explained on the basis of three major empirical relations as explained.

♣ ***Arrhenius Type of Conductivity***

In case of some simple ionic conductors viz. polymer electrolytes, in the plot of logarithmic conductivity (log σ) vs. inverse of temperature, conductivity varies or increases linearly with temperature. This indicates that temperature dependent conductivity shows a straight line feature. Such type of behaviour of conductivity with respect to rise in temperature is termed to be of *'Arrhenius Type'*. Such a linear rise in conductivity with temperature following the Arrhenius relation suggests that conductivity is a thermally activated process of ion hopping. This phenomenon can be easily explained on the basis of *'Arrhenius Theory'* put forward by **Svante Arrhenius** in 1889 [8]. Though this theory was initially proposed for liquid electrolytes, it is used nowadays for solid electrolytes too. Suppose, a solid electrolyte like polymer electrolyte wherein, ions perform hop from one site to another. However, there are certain energy barriers (difference between free energy of ion at normal lattice point and that at the top) which the ions have to overcome for their successful hops from one site to another i.e., the ion can successfully hop from one site to the neighbouring available site and undergo the jump process only if it overcomes the energy barriers. To do so, the ion requires certain minimum amount of energy equal to *'Activation Energy (E_a)'* [9,10] which can be obtained from the slope of Arrhenius plot of 'logarithmic conductivity (log σ) vs. 1000/Temperature'. The temperature dependent conductivity of a polymer electrolyte in this case is given by the following equation [11-14]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \qquad \ldots\ldots\ldots\ldots\ldots (2.2)$$

where, $\sigma =$ dc conductivity, $\sigma_0 =$ pre-exponential factor, $k_B =$ Boltzmann constant, $T =$ absolute temperature and $E_a =$ activation energy for the migration of ions and creation of defects.

♣ ***Vogel-Tamman-Fulcher (VTF) Type of Conductivity***

Another type of temperature dependent conductivity is Vogel-Tamman-Fulcher (VTF) like. Basically, at a certain critical temperature 'T_c' known as *'Percolation Temperature'*, the Arrhenius (linear) behaviour of conductivity changes to VTF (non-linear or curve) like behaviour. According to VTF model, the random motion of small polymer chains provides the free volume wherein, the ions can diffuse upon application of electric field. In this way, segmental motion of polymer chains in an amorphous phase influences the migration of ions [15]. This suggests that in most of the cases, this VTF behaviour is a characteristic of strong coupling between ion motion and polymer segments in the host matrix which leads to the conduction process in polymer electrolytes. In this case, the temperature dependent conductivity of a polymer electrolyte is given by the following relation [13,14,16-22]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{(T - T_0)}\right) \qquad \ldots\ldots\ldots\ldots\ldots (2.3)$$

where, σ = dc conductivity, σ_0 = pre-exponential factor, k_B = Boltzmann constant, T = absolute temperature, T_0 = quasi-equilibrium glass transition (Vogel Scaling) temperature and E_a = pseudo activation energy of mobile ions related to segmental motion of the polymer chains above a particular temperature. But if ion-ion interaction takes place, then a significant deviation of conductivity from VTF form is likely to occur.

♣ ***William-Landel-Ferry (WLF) Type of Conductivity***

In a few polymer electrolytes, ionic conductivity is observed to enhance with reducing glass transition temperature 'T_g' and this can be successfully explained on the basis of William-Landel-Ferry (WLF) equation. Likewise, Arrhenius and VTF equation, this WLF equation also informs about the temperature dependence of ionic conductivity in polymer electrolytes. However, this WLF behaviour of conductivity is different from Arrhenius or VTF type. The WLF equation is given as [23,24]:

$$\log a_T = \left(\frac{C_1(T - T_g)}{C_2 + (T - T_g)}\right) \qquad \text{… … … … … (2.4)}$$

where, C_1 and $C_2 =$ universal constants for various polymers, $T_g =$ glass transition temperature, $T =$ absolute temperature, $a_T =$ temperature shift factor. If glass transition temperature 'T_g' is considered as some reference temperature 'T_r' then the above WLF equation can be written as:

$$\log a_T = \left(\frac{C_1(T - T_r)}{C_2 + (T - T_r)}\right) = \log\left(\frac{\sigma(T)}{\sigma(T_g)}\right) \qquad \text{… … … … … (2.5)}$$

where, $\sigma(T) =$ ionic conductivity at absolute temperature 'T' and $\sigma(T_g) =$ ionic conductivity at glass transition temperature 'T_g'. Usually, for various polymers, $C_1 = -17.44$ K and $C_2 = 51.6$ K. Hence, substituting these values of 'C_1' and 'C_2' in Eqs. 2.4 and 2.5 gives:

$$\log a_T = \left(\frac{-17.44\ (T - T_g)}{51.6 + (T - T_g)}\right) = \left(\frac{-17.44\ (T - T_r)}{51.6 + (T - T_r)}\right) \qquad \text{… … … … … (2.6)}$$

However, these values of 'C_1' and 'C_2' can only be used if the data of the polymer of interest is unavailable. In case, the data of these constants, 'C_1' and 'C_2' are available, then instead of $C_1 = -17.44$ K and $C_2 = 51.6$ K, the available data should be used to obtain the best results as these 'C_1' and 'C_2' constants may vary from polymer to polymer. Additionally, the WLF concept also explains certain essential phenomena such as *'relaxation processes'* in amorphous solids which are unable to be explained by VTF equation. Hence, this WLF behaviour of temperature dependent conductivity is said to be an *'extension'* of VTF equation. However, WLF equation is unable to explain ion transport mechanism taking place in the polymer electrolytes.

Generally, the temperature dependence of conductivity exhibits any one of the five following behaviours [25].

- Arrhenius behaviour is followed usually at low temperatures whereas, at high temperatures, VTF behaviour is depicted.
- The VTF behaviour is likely to occur at temperatures higher than glass transition temperature (T_g); but at further higher temperatures, the Arrhenius behaviour is seen.
- At times, throughout the temperature range, the Arrhenius behaviour can be seen but possessing two different activation energies.
- In most of the cases, VTF behaviour is likely to be exhibited throughout the available temperatures.
- At all the temperatures, behaviour of conductivity with temperature, different from Arrhenius or VTF-like (for instance WLF-like) may take place. However, this type of behaviour is quite rare.

2.2.2 Rouse Model

Rouse model is basically a theoretical model which efficiently explains various properties of polymer electrolytes [26]. It is well known that ionic conductivity of polymer electrolytes depends upon the concentration of free ions present therein. As the free ion concentration in the polymer electrolyte increases, the ionic conductivity of the electrolyte also enhances initially owing to the free motion of ions in the polymer matrix. However, after attaining a certain concentration of these free ions, the ionic conductivity reaches to a plateau. Beyond this free ion concentration, the ionic conductivity gradually drops down.

Basically, the ions form *'Temporary'* crosslinks with the oxygen atoms present at the backbones of a polar host polymer at short time scales. Owing to such an attachment of ions with the chains of the host polymer, a very limited area is available wherein, these ions can undergo motion. The unavailability of enough area thus, restricts the motion of ions through the polymer matrix. Hence, the crosslinking of ions with the oxygen atoms of the polymeric chains slows down the structural relaxation. However, as the time passes, structural relaxation of the polymer host occurs such that the old crosslinks between the ions and oxygen atoms break and new crosslinks are formed through which the ions can diffuse in the entire system. This phenomenon hence, leads to the conductivity enhancement. In this way, Rouse model explains conductivity dependence of polymer electrolyte viz. PEO based electrolytes, on the concentration of ions wherein, ions form *'temporary'* crosslinks with oxygen atoms of PEO's polymeric chains. However, Rouse model is also successfully applicable to explain polymer dynamics and ionic conductivity of PEO-NaI polymer electrolytes wherein, each Na-ion of the system is assumed to form a *'Permanent'* crosslink between two oxygen atoms of PEO backbone. However, this possibly happens but at temperatures > glass transition temperature. This discussion can also be expressed mathematically in terms of *'Rouse Matrix'* given as [27]:

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_0 & 0 & & & \cdots & 0 \\ 0 & \ddots & 0 & & & \vdots \\ & 0 & \mathbf{A}_0 & 0 & \cdots & \\ & & 0 & 1 & 0 & \\ \vdots & & & 0 & \ddots & 0 \\ 0 & \cdots & & & 0 & 1 \end{bmatrix} + \sum_{n=1}^{N_b} \mathbf{B}_n \qquad \ldots\ldots\ldots\ldots\ldots (2.7)$$

This Rouse matrix is basically sum of matrices containing crosslinks between the ions and atoms of the host polymer. This matrix contains 'N_1' free ions and 'N' linear and flexible polymeric chains with chain length 'M' made with 'n' completely flexible repeating units. Here, the total number of bonds between the ions and the polymers is represented by 'N_b', 'B_n' is the matrix representing n^{th} bond, where $B_{ij} = B_{ji} = -1$ and $B_{ii} = B_{jj} = 1$, but the rest of all elements = 0; $j \in [1 \ldots\ldots N^*M]$ & $i \in [N^*M+1 \ldots\ldots N^*M+N_i]$ which represents a bond between 'i' & 'j' particles and suggests that the actual location of these bonds affect the resulting matrix 'A'.

Using this Rouse matrix, the dependence of conductivity on the ion concentration can be successfully calculated provided the breaking of crosslinks is included in the calculation part. The hence, calculated part is in agreement with the experimental observations as per which the cooperative motions of polymer-ion complex mainly determines the conductivity on short time scales. But at longer time scales, the normal diffusion of ions possibly occurs through the electrolyte [27].

2.2.3 Amorphous Phase Model

Ionic conductivity in case of high molecular weight PEO based composite polymer electrolyte (CPE) with filler dispersed therein was found to be higher than that of undispersed PEO-salt complex. To explain such an enhancement of conductivity in the PEO based CPEs, the *'Amorphous Phase Model'* was developed [28,29]. In this case, filler particles such as α-Al_2O_3, incorporated in the high molecular weight crystalline PEO-salt complex, act as the nucleation centres and get attached to PEO segments via acid 'Al' surface centres. As there are certainly a large number of such nucleation centres, the nucleation rate also increases. This phenomenon leads to the higher level of disorder in a CPE system and disrupts the crystalline phase therein, thus, reducing the degree of crystallinity of the CPE matrix. As this degree of crystallinity of the filler incorporated PEO based CPE is lower than that of the undispersed crystalline PEO-salt complex, the PEO based CPE shows higher conductivity than that observed for the PEO-salt complex.

Another such example is of a polyether-CPE, the morphology of which consists of three portions which include (i) ionically conducting polymer matrix wherein, the filler grains are immersed, (ii) insulating filler grains dispersed in the polymeric matrix and (iii) highly conductive interfacial layer which coat the surfaces of the filler grains. In such a CPE system, the conductive pathways (composed of surface layers) are likely to occur which in turn lead to the conductivity enhancement [30]. In some cases of CPEs, these conductive pathways are formed all over the bulk of CPEs which further improve the conductivity.

2.2.4 Effective Medium Theory

The *'Effective Medium Theory'* proposed by **Nan & Smith** in 1994 [31,32] mainly explains the effect of fillers on conductivity (mainly conductivity enhancement) in composite polymer electrolytes (CPEs). When fillers are added in the CPEs, the space charge layers are formed which in turn create high defect concentrations on the surface of the filler grains and affect conductivity. According to the effective medium approach proposed by **Landauer** [33], the conductivity can be bifurcated into three different regions based on the filler concentrations.

I-Region: At low filler concentration, inspite of formation of composite grains, no percolation threshold is achieved. Hence, conductivity of CPE remains the same as that of the undispersed polymeric system.

II-Region: At a certain concentration of filler, the percolation threshold is achieved hence, providing the maximum of conductivity that is usually yielded by a purely amorphous phase.

III-Region: At excessive filler concentration, the inert isolative filler grains block the charge carrier transport and lead to the dilution effect. This further abruptly decays the percolation threshold and deteriorates the conductivity in the polymer matrix.

According to effective medium theory approach, the CPE comprises of three different *'Phases'* having different electrical properties.

I-Phase: In this phase, insulating filler particles/grains are dispersed in overall polymer electrolyte host matrix. Here, highly conducting interface layer coatings on the surfaces of the filler particles either touch each other or overlap. In both these cases, the highly conducting pathways are produced which facilitate the conduction of ions and lead to conductivity enhancement.

II-Phase: This is an ion conducting polymer host matrix wherein, insulating filler grains or particles are dispersed.

III(a)-Phase: Amorphous shell is formed on a filler grain surface that is dispersed in the polymer host matrix. This amorphous shell in turn enhances the amorphous phases and hence, reduces the stiffened/crystalline phase of the host matrix.

III(b)-Phase: Amorphous phase thus, formed creates coating of interface layer on the highly conductive surface of filler grain. This hence, formed layer is also highly conductive in nature. These amorphous phase and conductive interface layer altogether promote ionic conduction hence, leading to the conductivity enhancement.

Further, **Nan & Smith** [32] put forward the *'Improved Effective Medium Theory'* which, likewise Effective Medium theory, qualitatively explained various features in CPE systems. Another approach is the *'Dynamic Effective Medium Approach'* which aids in investigating the ionic motion in dynamically disordered systems [34].

2.2.5 Free Volume Theory

In case of polymers, there is a certain space or volume which remains unoccupied by the polymeric molecules. This unoccupied space or unfilled volume in a polymer is termed as *'Free Volume'* based on which **Cohen & Turnbull** [35-38] and **Kovacs et al.** [39,40] proposed *'Free Volume Theory'*.

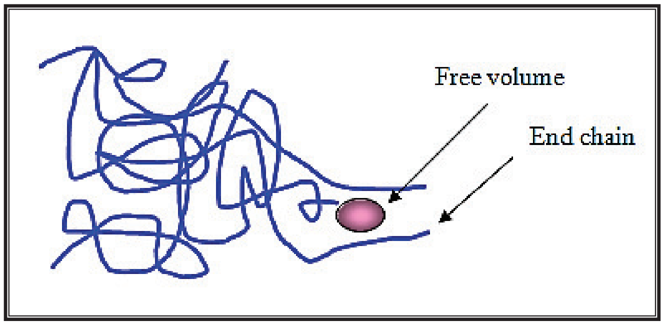


Fig. 2.1 Motion of polymeric chains around free volume

Even a small amount of this free volume in polymeric materials is associated with the ends as well as parts (segments) of polymeric chains as seen from Fig. 2.1. Hence, the amount of such a free volume for a given mass of polymer is said to depend upon the number of chain ends and polymer chain segments. According to **Cohen & Turnbull**, the matrix of polymeric molecules or chains consists of a free volume. But at low temperatures, the matrix of polymeric chains is considered to be hard sphere. Hence, the ions remain caged in the free volume present in between this matrix. However, as temperature increases, the polymer chains of the matrix relax gradually owing to which the free volume gets substantially larger. When these voids become appreciably large, the ions no longer remain caged and hence, are allowed to diffuse. This indicates that as temperature rises, the free volume of the polymer matrix also enhances due to finite expansion. This in turn reduces the caging of ions thus, favouring the ion diffusion process. Hence, with the rise in temperature, the overall mobility of ions into the polymeric system enhances which in turn improves the conductivity.

However, rather than independent motion, these ions firstly get attached to the polymer chain segments and then participate in the conduction process. As polymeric chains get gradually flexible with rising temperature, mobility of polymer chain segments also enhances. Thus, with the improvement in segmental mobility, the mobility of ions attached to these chain segments automatically increases hence, leading to conductivity enhancement. All this discussion suggests that in **Cohen & Turnbull** framework, there exists a relationship between free volume, temperature and conductivity wherein, as temperature increases, free volume also enhances thus, further improving the conductivity. In this way, the link between free volume and mobility of ions along with that of polymer chain segments can be easily understood. In polymeric systems, usually four types of free volume exist that are explained briefly as follows [41].

- ***Configurational Free Volume:*** It is the additional space created due to insufficient chain packing.
- ***Hole Free Volume:*** It is the free space existing between the polymer chains inspite of perfect alignment of these polymeric chains.

- ♣ ***Excess Free Volume:*** If a polymer is allowed to cool under the equilibrium conditions, then it usually has a volume greater than what it should possibly have. But this is likely to happen only at the temperatures below glass transition temperature. This difference between actual volume under quenched conditions and equilibrium free volume is known as *'Excess Free Volume'*.
- ♣ ***Dynamic (Fluctuation) Free Volume:*** Owing to thermal activation, the polymer main chains or side chains rather than remaining fixed; perform random rotational and vibrational motions, which in turn generate transient gaps and create extra free volume. The thus, produced free volume is called *'Dynamic Free Volume'*.

2.2.6 Configurational Entropy Model

In case of polymer electrolytes, the factors such as ion pairing, polymeric chain length, ion concentration, polarizability, ion size, etc., play a major role in affecting the conduction process. But all these factors are excluded in Free Volume theory. However, it was highly essential to understand these factors owing to which a new model termed as *'Configurational Entropy Model'* was put forward by **Gibbs & DiMarzio** [42,43]. This Configurational Entropy model is basically the modification of Free Volume theory and likewise Free Volume model, this Configurational Entropy model is also a quasi-thermodynamic representation.

In this model, entropy is considered to be more important parameter than free volume. Basically, here the changes taking place in entropy during the conduction process are considered. But this entropy vanishes with second order phase transition of temperature. Hence, the number of configurations that a system can possess gradually reduces upon cooling of the system and finally becomes zero at a certain lower temperature.

The highly important feature of this model is the group cooperative rearrangement of polymer chains taking place in the ion transport mechanism. Hence, this model mainly describes the motion but only of the host polymeric chains. This phenomenon makes this Configurational Entropy picture different from the Free Volume picture wherein, void to void jump motion of ions occurs. However, likewise Free Volume theory, this Configurational Entropy theory is also a macroscopic theory and remains unsuccessful in explaining the details at microscopic level which is a highly essential requirement for understanding the ion transport mechanism in polymer electrolytes.

2.2.7 Jump Relaxation Model

The hopping of ions in disordered solid materials may take place randomly and can be described in terms of *'Jump Diffusion of Ions'*. Such a phenomenon leads to the constant conductivity even upto a very high frequency of 100 GHz [44]. But experimentally, rather than remaining constant throughout the frequency range, the conductivity dispersion is attributed. Hence, in such a case, the experimental results contradict the theoretical results. Hence, there arose a need to propose a new model to overcome this limitation. **Funke** [45,46] satisfied this condition by proposing such a new model termed as *'Jump Relaxation Model (JRM)'*. According to this model, conductivity can be divided into dc type at low frequency region and ac type at high frequency region depending upon the respective successful and unsuccessful hops of ions taking place to the neighbouring available vacant sites. But such successful and unsuccessful jump of these ions into the next available site is mainly affected by the frequency of an applied alternating electric field. Basically, the successful hop of a mobile ion is said to be its jump into the new available vacant site in its neighbourhood (effective potential well). But in a disordered solid electrolyte, there are numerous such empty equivalent vacant sites available wherein, the ion can successfully jump. Moreover, the ion can hop into any of these vacant sites with equal probability [44,45,47]. However, such a successful jump of mobile ion into the next available vacant site is possible only if the frequency of applied electric field is quite low as at such a low frequency, the periodic reversal of alternating electric field is very slow.

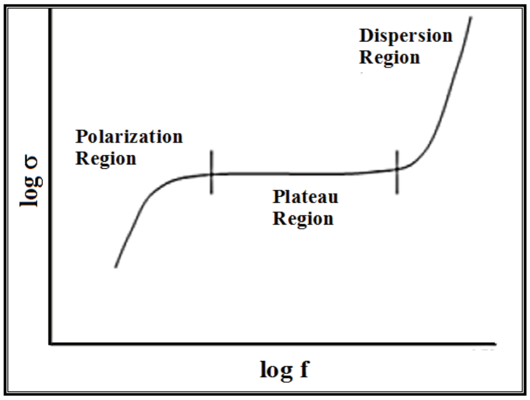


Fig. 2.2 Schematic representation of frequency dependent conductivity curve

Owing to such a slow reversibility of electric field, the ions of the opposite signs (anions and cations) can easily move to the respective electrode-electrolyte interfaces and get accumulated there thus, leading to polarization effect which in turn restricts the entry of other mobile ions therein. As the frequency reduces, more and more such free ions can get accumulated at the electrode-electrolyte interface. Due to this reason, the number of free ions contributing in conductivity drop down with the reducing frequency which in turn substantially deteriorate the conductivity as seen from Fig. 2.2. At the lowest frequency, as the *'maximum'* number of mobile ions gets accumulated at the electrode-electrolyte interface, the number of ions contributing in conductivity gets *'minimum'*. Hence, the conductivity is least at lowest frequency as clearly observed in the *'polarization region'* of Fig. 2.2.

However, as frequency increases beyond the polarization region, the ions possess enough energy to overcome the activation energy barrier. Hence, as the ions become free, they can diffuse in the medium and can travel larger distances before the electric field reverses. It is this long range transport of ions which yields a plateau occurring in the intermediate frequency region as seen from the Fig. 2.2. At the plateau region, the conductivity remains *'independent'* of frequency and is termed as *'dc Conductivity'*. Hence, the plateau region can be said to describe the dc conductivity of ions in a medium. However, such a long range diffusion of charge carriers can occur only till the applied electric field is below a certain characteristic frequency known as *‘Hopping Frequency’*.

Beyond the hopping frequency, the periodic reversal of electric field gets significantly rapid with increasing frequency. Hence, the polarity of the applied electric field reverses before the ion undergoes a successful hop to the next available vacant site. This is because, very short time periods are available for the ions to hop into the neighbouring vacant site. Thus, with the increasing frequency beyond the hopping frequency, instead of jumping to the next vacant site, the probability of the ion to go back to its initial site increases which refers to an unsuccessful hop. Such a phenomenon taking place at frequency > hopping frequency is termed as *‘Correlated Forward-Backward Hopping’* [48,49]. Thus, at frequency higher than hopping frequency, instead of long range transport of ions, the correlated forward-backward hopping or short range localised hopping of ions becomes a highly probable condition. However, according to the Jump Relaxation model, though the probability of ion to jump back (unsuccessful hop) to its original site is quite high; it can stay for some time in the new vacant site if its neighbourhood becomes relaxed with respect to its position. This suggests that the motion of ion deals with the strong correlation between its forward and backward jump. Such a correlated forward-backward hopping of ions thus, leads to conductivity dispersion at higher frequencies. Hence, beyond the hopping frequency, the conductivity becomes frequency *‘dependent’* and increases sharply with the increasing frequency as seen from the Fig. 2.2 at dispersion region. Such a phenomenon wherein, frequency *‘independent’* dc conductivity (σ_{dc}) switches to frequency *‘dependent’* ac conductivity (σ_{ac}) and in which the transition from *‘long range’* transport of ions to *‘short range’* localised hopping of charges (ions) takes place is termed as *‘Dispersion Phenomenon’* [50].

In this way, frequency dependent conductivity curve as seen from Fig. 2.2 consists of:

- Polarization region at lower frequency side.
- Plateau region representing frequency independent dc conductivity at mid or intermediate frequencies.
- Dispersion region indicating frequency dependent ac conductivity in the higher frequency region [51-54].

Such as discussed variation of conductivity with frequency indicates that conductivity follows the given equation [50,55,56]:

$$\sigma'(\omega) = \sigma_{dc} + A\omega^{n} \qquad \text{... ... ...} (2.8)$$

where, $\sigma'(\omega)$ = frequency dependent real part of conductivity, σ_{dc} = dc conductivity, A = pre-exponential constant, $\omega = 2\pi f$ = angular frequency ('f' is expressed in Hertz) and n = power law exponent or frequency exponent, usually $0 \leq n \leq 1$ [57]. However, according to **Papathanassiou et al.** [58] and various other researchers [59-61], there is no argument which restricts the 'n' value between 0 and 1. Rather, for some of the polymeric materials, this 'n' can possess values greater than unity such that $0 < n < 2$ [58,62,63]. Usually, $0 < n < 1$ if site relaxation is faster than backward hop and $n \geq 1$, if site relaxation is slower than the backward hop. Now, if the conductivity measured depends upon temperature 'T', then Eq. 2.8 can be written as [62].

$$\sigma'(\omega) = \sigma_{dc}(T) + A(T)\omega^{n} \qquad \text{... ... ...} (2.9)$$

where each term has its usual meaning. These Eqs. 2.8 and 2.9 of conductivity are termed as *'Jonscher's Power Law (JPL)'* equations which were put forward by **A.K. Jonscher** [55,56] in the year 1967 and can be further written in the form of *'Almond West Formalism'* proposed by **Almond & Co-workers** [63-71], given as:

$$\sigma'(\omega) = \sigma_{dc} + A\omega^{n} = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_h}\right)^{n}\right] \qquad \text{... ... ...} (2.10)$$

where, the terms have their usual meanings. However, the term 'ω_h' appearing in this Almond-West formalism is actually the hopping frequency which explains the onset of conductivity relaxation phenomenon and translation from the long range transport of ions to the short range localised hopping of ions [72]. This hopping frequency of the mobile ions 'depends' upon temperature no matter, the mobile ion concentration is temperature 'independent'.

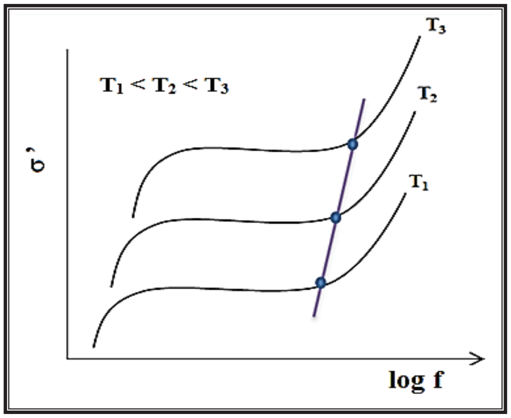


Fig. 2.3 Frequency dependent conductivity behaviour at different temperatures

Hence, as seen from Fig. 2.3, as the temperature increases, the hopping frequency shifts towards higher frequency side which suggests that hopping frequency is thermally activated. This hopping frequency informs about the 'mobility of charge carriers (ions)' and can be mathematically written as:

$$\omega_h = \left(\frac{\sigma_{dc}}{A}\right)^{1/n} \quad \ldots\ldots\ldots\ldots\ldots (2.11)$$

where the terms have their usual meanings. The previously discussed Almond-West formalism is actually the conductivity formalism which forms the basis of conductivity scaling. Such a scaling law compares ion dynamics of mobile ions in the conductivity spectra at different temperatures.

2.2.8 Percolation Model

In most of the composite electrolyte systems, the conductivity reduces rapidly with the increasing concentration of dispersoid phase therein. In order to explain this concept the *'Percolation Model'* was put forward which also deals with the transport of ions taking place in strongly inhomogeneous systems such as polymer electrolytes [73-78]. Percolation models are based on *'Percolation Theory'* which can be said as a general mathematical theory of *'transport and connectivity'* in geometrically complex systems. This percolation theory considers the idea of percolation processes. Generally, the motion of ions from one site to another neighbouring available site occurs by either *'Site Percolation'* process or by *'Bond Percolation'* process explained shortly as follows.

♣ ***<u>Site Percolation Process</u>***

In Site Percolation process, mobility of an ion from its actual site 'i' to the next available neighbouring site 'j' takes place only if site 'j' is not blocked. Suppose, in Fig. 2.4 (a), the black circles represent the 'sites' and the white circles represent the 'blocks'. The ion positioned on one site can diffuse successfully to the neighbouring available site only if it hops to the neighbouring 'black' circle. In this way, the ion positioned on black circle successfully diffuses even upto infinity provided it hops on neighbouring available black circles only.

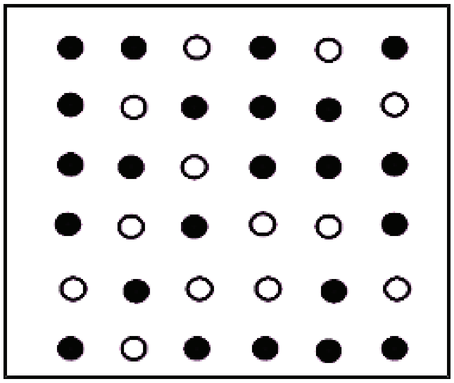


Fig. 2.4 (a) Site percolation model in 2-D square lattice

On the contrary, if the ion residing on the black circle jumps on the white circle, then this leads to unsuccessful hop of the ion as here, the white circle represents 'blocks' and not the vacant 'sites'. Owing to this unsuccessful hop, the probability of the ion to move back to its initial site denoted by black circle is quite possible. In this way, Site Percolation model deals with the description of connectivity of sites on the lattice.

♣ ***Bond Percolation Process***

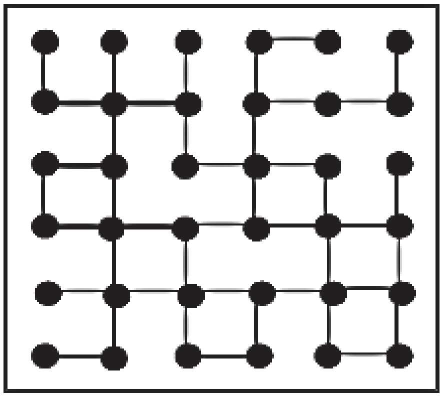


Fig. 2.4 (b) Bond percolation model in 2-D square lattice

Consider Fig. 2.4 (b) which represents Bond Percolation process wherein, the 'black' circles refer to 'sites' whereas; the 'solid lines' correspond to 'bonds' (different from chemical bonds) which act as the connecting pathways between the two sites (black circles). The mobile ions can undergo motion from one site to another through these bonds. Hence, as per this model, the hopper (ion) can be mainly located on the bonds rather than on the sites. This Bond Percolation model can be further subdivided into two major types described briefly as follows.

❖ **Static Bond Percolation (SBP) Model**

Static Bond Percolation (SBP) model aids in providing the microscopic explanation of (i) transport of ions occurring in the systems or electrolytes with rigid framework and (ii) ion conduction mechanism taking place in various polymer electrolytes through high degree of amorphous phases rather than crystalline phases [79-81]. Now, the bonds (different from chemical bonds) connect the localised sites and act as the pathways for the motion of ions between these sites which are actually the localisation positions of the mobile ions [80].

However, there are certain sites which are ‘mutually accessible’ (available) whereas; the rest are ‘mutually inaccessible’ (unavailable) sites [82]. Out of both these sites, the ions can jump into and hence, reside only on the mutually accessible sites. However, the jump of these ions from one site to the next accessible site is permitted or not depends upon the availability or unavailability of the ‘bonds’ connecting these sites. The motion of an ion in a given lattice can successfully take place from one site to the neighbouring available site only if the bonds connecting both these sites are available with a certain probability. Moreover, the ion usually hops between the two sites with a certain hopping rate which can be either finite or zero depending upon the availability or unavailability of the sites [82].

The theory of SBP model is successful in explaining the well-known experimentally observed property which indicates that crystalline phase has no conductivity whereas; the amorphous phase is completely responsible for the conduction of ions in the polymer electrolytes [13]. Hence, this model is based on one concept according to which the motion of ions between two sites for a fixed polymer configuration is described by percolation/hopping process [82].

❖ Dynamic Bond Percolation (DBP) Model

Dynamic Bond Percolation (DBP) model put forward by **Druger, Nitzan & Ratner** [79,82-88] is a microscopic model which explains the actual ionic motions (hopping/diffusion) taking place in a dynamically disordered medium of certain systems such as polymer electrolytes and their relationship with conductivity. For polymer electrolyte system, likewise the static bond percolation model, the dynamic bond percolation (DBP) model also considers ‘sites’ as the localization positions for mobile ions and ‘bonds’ as the pathways for the motion of these ions between the mutually accessible sites. Generally, the ions can jump from one site to the neighbouring available site and undergo a translational motion. But in certain cases, initially, the local environment at a given time does not permit the individual hopper (ion) to hop from its site to the next available site and hence, leads to a 'forbidden hop'. But after a certain waiting time, this local environment of the host polymer gets structurally evolved in such a way that the hop is allowed. Hence, the hopping of ion from one site to another available site it either allowed or forbidden depending upon the 'structural evolution' of the host polymer. But as the structure of host polymer continuously evolves with time, the probabilities of the allowed and/or forbidden hop of the ion also changes with time. However, the hopping of ions between the sites is either allowed or forbidden with specific fixed probabilities. This concept makes DBP model different from SBP model. Owing to this reason, the DBP model is said to be a *'Natural Extension'* of SBP model [82]. In case of a successful hop of an ion from one site to another, the free ions as well as the stable sites move together with respect to each other. Hence, such a translational motion of ions rather than occurring independently combines with the dynamic segmental motion of the host polymer chains. In such a process, the lattice no longer remains static; instead it undergoes various dynamic rearrangements that reassign available and unavailable bonds. Physically, these rearrangements corresponding to the oriental motion of lattice host polymer occur on a certain time scale, usually shorter than the observed time which makes ionic motion dynamic in nature instead of being static. However, this phenomenon occurs at a temperature (T) > glass transition temperature (T_g). In this way, DBP model successfully explains the dynamics of ionic as well as segmental motion of host polymeric chains in polymer electrolytes [82-84,89].

2.3 Complex Impedance Spectroscopy (CIS)

'Electrical Resistance' which is actually an ability of a circuit element to resist flow of electric current is written as the ratio of voltage (v) to current (i) as per Ohm's law, given as:

$$\mathrm{r} = \frac{\mathrm{v}}{\mathrm{i}} \qquad \ldots\ldots\ldots\ldots\ldots (2.12)$$

However, such a relation which is valid only for one circuit element such as *'Ideal Resistor'*, is abandoned in practical situations wherein, the circuits contain the elements having a quite complex behaviour. In such a case, concept of *'Impedance'* comes in picture.

Impedance measurements of a cell under consideration can be carried out over a wide range of frequencies and temperatures in a single experiment using a non-destructive technique called *'Complex Impedance Spectroscopy (CIS)'*. If a small monochromatic excitation voltage signal (v) as a function of time (t) is applied across a cell, the pseudo-linear response of this cell is measured in the form of a steady state current (i) as a function of time (t) and finally, impedance (Z) as a function of signal frequency (ω) (where, $\omega =$ angular frequency $= 2\pi f$; 'f' is the frequency expressed in Hertz) of such a system is obtained and is given as:

$$Z(\omega) = \frac{v(t)}{i(t)} \qquad \ldots\ldots\ldots\ldots\ldots (2.13)$$

This suggests that when an ac signal is applied to a system, likewise resistance, impedance also obeys Ohm's law and measures the flow of electric current and finally can be given as the *'ratio of voltage to current in the time domain'* [90]. In polar coordinates, impedance 'Z(ω)' can be written as:

$$Z(\omega) = Z' + j\,Z'' \qquad \ldots\ldots\ldots\ldots\ldots (2.14)$$

where, $Z' =$ real part of impedance, $Z'' =$ imaginary part of impedance and $j = \sqrt{-1} =$ imaginary number which indicates the anticlockwise rotation $\left(\frac{\pi}{2}\right)$ relative to the real axis. This concept of electrical impedance was put in terms of vector diagrams and complex representation by **Kennelly & Steinmetz** [91,92]. In this method, the instrument firstly measures both the real (Z') and imaginary (Z'') parts of impedance (Z) of the sample simultaneously at various applied frequencies. This suggests the frequency dependent nature of impedance. Later, Z' is projected on the X-axis and plotted against Z'' projected on the Yaxis to obtain a *'Complex Impedance Plane'* also termed as *'Nyquist Plot'* as shown in the Fig. 2.5 [13]. Each point on the Nyquist plot corresponds to the impedance at that particular frequency. Also, (Z′) represents the resistive character of the cell whereas; (Z″) indicates its capacitive or inductive character. If an electrolyte sample sandwiched between two electrodes of the cell is considered as 'resistor' (real resistance of a material to the flow of dc current) and geometrical capacitance of the cell with the electrodes as plates is considered as 'capacitor' then for such a case, R||C combination produces a semicircle in the Nyquist plot as shown in Fig. 2.6 (a) [13].

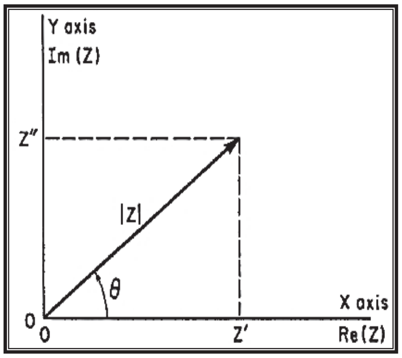
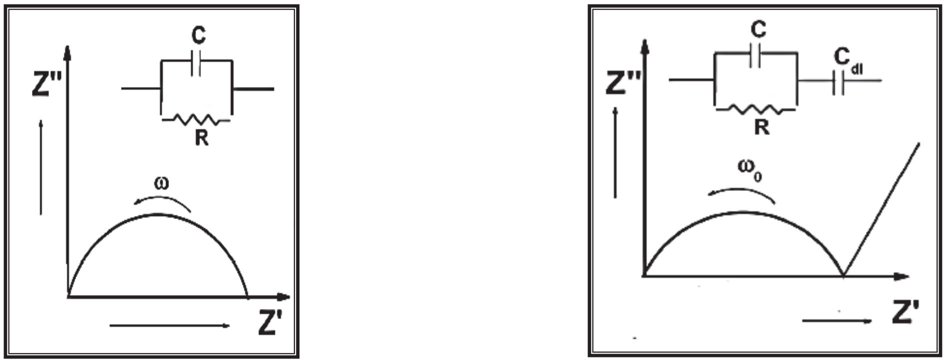


Fig. 2.5 Impedance 'Z' plotted as a planar vector



(a) **(b)**

Fig. 2.6 Nyquist plot consisting of **(a)** a semicircle and **(b)** a semicircle with a spike

For ideal cases, the Nyquist plot shows a semicircle having the centre exactly on the X-axis. But in case of real experiments, this Nyquist plot shows an arc of a circle with the centre at some distance below the X-axis. Such an imperfection may be due to surface layers on the electrodes, ion-ion interactions, non-uniform diffusion, fractal nature of the materials, rough electrode surfaces, inhomogeneities of polymer electrolytes, dielectric relaxation, etc. [91]. However, R || C combination of the semicircular arc at high frequency region appearing on the left hand side (LHS) is at times followed by a spike at low frequencies on right hand side (RHS) as shown in Fig. 2.6 (b) [13] and this corresponds to the motion of charge carriers in solid electrolyte material. For such a real case of practical solid electrolytes the procedure is equivalent of plotting the following equation given in terms of complex impedance (Z^*) rather than plotting the simple impedance ($Z(\omega) = Z' + j\,Z''$).

$$Z^*(\omega) = Z' - j\,Z'' \qquad \dots\dots\dots\dots\dots (2.15)$$

where, the superscript '∗' denotes the complex conjugation of the complex impedance. However, in this plotting of Nyquist format, the shape of the curve is highly essential factor as it informs about the possible mechanisms or phenomena taking place in these solid electrolytes thus, providing a complete overview of the data by which certain interpretations can be done. If the shape of the curve gets distorted, it is nearly difficult to make out the information obtained from this data. Hence, to prevent distortion of the shape of the curve, the real axis must be equal to the imaginary axis in the Nyquist plot. The thorough study of the Nyquist plot thus, provides an insight regarding ionic behaviour and ion transport mechanism taking place in the sample under consideration along with various electrical properties such as conductivity, modulus, dielectric constant and dielectric loss with respect to frequency of the applied electric field. In this way, complex impedance spectroscopy (CIS) acts as a tool for electrical characterization of solid electrolyte materials such as polymer electrolytes as well as of various other electrochemical systems [91,92,94].

2.4 Dielectric Formalism

'Dielectric Spectroscopy' is a highly efficient study which informs about relaxation phenomenon along with the dielectric response of an ion-conducting material viz. polymer

electrolyte [95-97]. The dielectric properties of this material are mainly associated with (i) storage of electrical energy and (ii) dissipation (loss) of electrical energy.

Suppose, a polymer electrolyte sandwiched between two electrodes is subjected to an ac electric field. When the frequency of applied electric field is low, along with the motion of free ions, the dipoles also possess sufficient time to reorient and align themselves in the direction of this applied electric field prior the polarity of the field reverses. Hence, the ions of the opposite signs move towards the respective electrode-electrolyte interfaces, get accumulated there and lead to the polarization phenomenon. In this way, the ions and dipoles altogether contribute in the process of *'Polarization'* in a polymer electrolyte. But when the electric field is removed, this polarization disappears. However, in the presence of electric field, such an existing polarization phenomenon opposes this applied electric field and draws ions onto the electrodes, hence, resulting in the storage of charges. If the ions present in an electrolytic material are easily polarizable, then this generates higher degree of these charges for the material to store in. Such an ability of a material to store charges (ions) or energy in each cycle from an externally applied electric field is termed as *'Dielectric Constant (ε′)'*.

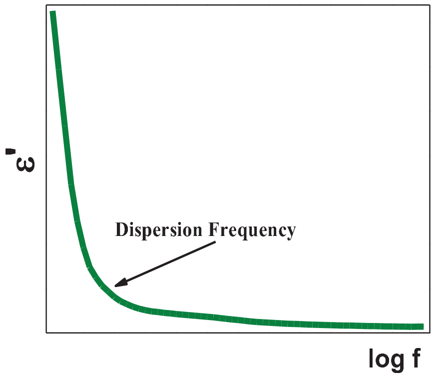


Fig. 2.7 (a) Variation in dielectric constant (ε′) with logarithmic frequency

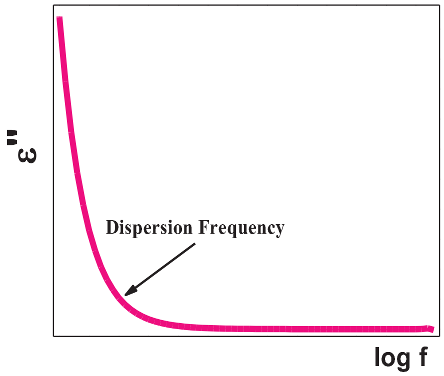


Fig. 2.7 (b) Variation in dielectric loss (ε″) with logarithmic frequency

This dielectric constant is also a measure of alignment of dipoles and it increases with the increasing dipolar orientation and alignment. This indicates that both mobile ions as well as dipoles of an electrolytic material altogether contribute in the dielectric constant (ε′) of that material. Hence, dielectric constant (ε′) of a material depends upon degree of polarization taking place in it. Higher the value of dielectric constant (ε′) of a material, better is its electrical conductivity (σ) [13,91]. Such a material is highly applicable in various applications. In this way, dielectric constant (ε′) plays a major role in deciding practical applicability of a given material.

On the contrary, when the ionic species conduct through a particular material under the influence of electric field of low frequency, certain amount of this electric energy is dissipated (usually, in the form of heat) inside the medium. Moreover, same phenomenon of energy loss occurs when work is done by dipoles in overcoming the damping forces during their reorientation. Such a loss of electrical energy in the form of heat energy during conduction process of mobile ions leading to polarization and reorientation/alignment of dipoles upon application of electric field is termed as *'Dielectric Loss (ε″)'* This parameter measures as to how much a material is dissipative under the influence of external electric field. Hence, higher the conduction of ions resulting in polarization and higher the reorientation/alignment of dipoles, higher is the dielectric loss (ε″). Generally, in the polymeric materials the polar groups of polymeric chains respond to the ac electric field and result in the dielectric loss [16,98,99].

On the other hand, as frequency increases beyond a certain frequency termed as *'Dispersion Frequency'*, the periodic reversal of the applied electric field occurs quite rapidly. Hence, the ions are unable to respond to such a fast changing electric field and fail in contributing to the polarization phenomenon. Moreover, dipoles also face difficulty in orienting themselves in the direction of such a rapidly changing electric field. This phenomenon creates a lag or a delayed response of the ions as well as dipoles in the time domain with respect to the applied electric field. Owing to all these factors, the polarization phenomenon gradually reduces with increasing frequency and finally disappears at a very high frequency hence, leading to a drop in dielectric constant (ε'). As the migration of ions as well as orientation of dipoles hardly take place with a rapidly changing electric field, a negligible amount of energy loss occurs which leads to the reduction in dielectric loss (ε'') with increasing frequency [100-104]. Such a variation of dielectric constant (ε') and dielectric loss (ε'') with logarithmic frequency is as shown in Figs. 2.7 (a) and 2.7 (b), respectively.

Dielectric constant (ε') and dielectric loss (ε'') altogether lead to complex dielectric function (ε^*), which is mathematically expressed as [105-107].

$$\varepsilon^* = \frac{1}{j\omega C_0}\left(\frac{1}{Z^*}\right) \qquad \dots\dots\dots\dots\dots (2.16)$$

$$\Rightarrow\ \varepsilon' - j\varepsilon'' = \frac{1}{j\omega C_0}\left(\frac{1}{Z' - jZ''}\right) \qquad \dots\dots\dots\dots\dots (2.17)$$

$$\Rightarrow\ \varepsilon' = \frac{Z''}{\omega C_0\left(Z'^2 + Z''^2\right)}\ \&\ \varepsilon'' = \frac{Z'}{\omega C_0\left(Z'^2 + Z''^2\right)} \qquad \dots\dots\dots\dots\dots (2.18)$$

where, $j = \sqrt{-1}$, $C_0 =$ capacitance with vacuum between the conducting parallel plates (electrodes) $= \varepsilon_0\left(\frac{A}{t}\right)$ where, $A =$ cross-sectional area of the sample, $t =$ thickness of the sample, $\varepsilon_0 =$ dielectric constant in vacuum (free space) also defined as a measure of influence of electric field in the absence of medium or material between the conducting parallel plates (electrodes) = 8.854×10^{-12} F/m = constant, $\varepsilon^* =$ complex dielectric permittivity, $\varepsilon' =$ real part of complex dielectric permittivity (dielectric constant), $\varepsilon'' =$ imaginary part of complex dielectric permittivity (dielectric loss), $Z^* =$ complex impedance, $Z' =$ real part of complex impedance, $Z'' =$ imaginary part of complex impedance.

2.5 Modulus Formalism

'Electric Modulus (M^*)' developed by **Macedo et al.** [108] in early 70s is basically an electric analog of dynamic mechanical modulus or mechanical shear modulus. This modulus formalism was mainly put forward to analyse the relaxation processes taking place in solids

wherein, modulus (M^*) is derived from complex impedance (Z^*) and hence, can be written as [91,108]:

$$M^* = (j\omega C_0)(Z^*) \qquad \text{… … … … … (2.19)}$$

$$\Rightarrow (M' + jM'') = (j\omega C_0)(Z' - jZ'') \qquad \text{… … … … … (2.20)}$$

$$\Rightarrow M' = j\omega C_0 Z' \;\&\; M'' = -j\omega C_0 Z'' \qquad \text{… … … … … (2.21)}$$

Here, M^* = complex modulus function, Z^* = complex impedance, M' = real part of complex modulus, M'' = imaginary part of complex modulus, Z' = real part of complex impedance and Z'' = imaginary part of complex impedance. Electric modulus (M^*) can also be related to dielectric permittivity (ε^*) and written as [91,108-112]:

$$M^* = \frac{1}{\varepsilon^*} \qquad \text{… … … … … (2.22)}$$

$$\Rightarrow (M' + jM'') = \frac{1}{(\varepsilon' - j\varepsilon'')} \qquad \text{… … … … … (2.23)}$$

Multiplying and dividing the above equation with '$(\varepsilon' + j\varepsilon'')$' gives:

$$\Rightarrow (M' + jM'') = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} + \frac{j\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} \qquad \text{… … … … … (2.24)}$$

$$\Rightarrow M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \;\&\; M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \qquad \text{… … … … … (2.25)}$$

Suppose, an ion conducting polymer electrolyte is placed between a pair of electrodes and ac electric field is applied across this assembly. At lower frequencies, as the electric field cycle changes its polarity slowly, enough time is available for the cations and anions (ions of the opposite signs) to get displaced from their regular lattices, to orient themselves in the direction of applied electric field and to undergo long range diffusion to the oppositely charged plates. These cations and anions finally get accumulated at the respective electrode-electrolyte interface thus, leading to the polarization phenomenon. Such a tendency of the ion to get polarized or to orient itself with respect to the externally applied electric field is termed as *'Ionic Relaxation'* or *'Dielectric Relaxation'* or at times *'Conductivity Relaxation'*.

However, as the interaction of charge takes place with the spin of the ion participating in this process of polarization, the ion stores some or the entire amount of energy of the applied electric field. But during this time of polarization, along with the ion, the surrounding charges/ions also reorient themselves in the direction of applied electric field so that the electrically neutral character can be retained in the local area with respect to the electrostatic considerations. Hence, the ion along with its surrounding environment relaxes simultaneously. However, ion takes certain time to reorient itself with respect to applied electric field and to get polarized and this time can be termed as *'Relaxation Time (τ_σ)'*, given as [107,113-115]:

$$\tau_\sigma \, . \, \omega_{\max} = 1 \qquad \ldots\ldots\ldots\ldots\ldots (2.26)$$

where,

$$\tau_\sigma \, . \, 2\pi f_{\max} = 1 \; (\because \omega_{\max} = 2\pi f_{\max}) \qquad \ldots\ldots\ldots\ldots\ldots (2.27)$$

$$\Rightarrow \tau_\sigma = \frac{1}{2\pi f_{\max}} \qquad \ldots\ldots\ldots\ldots\ldots (2.28)$$

where, '$f_{\max}$' is the characteristic relaxation frequency related to the relaxation time (τ_σ) obtained from the peak value of 'M''' i.e. '$M''_{\max}$' as shown in Fig. 2.8.

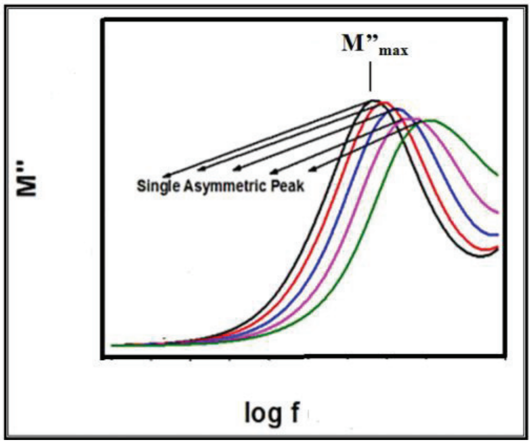


Fig. 2.8 Schematic representation of variation in M" with logarithmic frequency

The ion can absorb certain electric field energy during this relaxation time if the frequency of applied electric field is low. The hopping motion of ions still continues to occur with the increasing frequency of applied electric field. But as these ions possess electronic cloud around themselves, they face difficulty to cope up with the quickly reversing cycles of the electric field at high frequencies thus, developing a lag or a delayed response. In this case, the ion is unable to gain energy from such a high frequency electric field and hence, fails to get polarized at the respective electrode. Hence, as the frequency increases, polarization effect gradually slows down thus, making the processes of adjustments in local environment of ion substantially inactive and inoperative [115]. In this way, the modulus formalism plays a major role in investigating the relaxation dynamics of a material under test.

As per previous discussion, when an electric field of low frequency is applied to an electrolyte placed between the two conducting parallel plates, polarization phenomenon dominates at low frequency side. But when the field is removed, polarization disappears. Hence, it becomes highly difficult in this case to differentiate (i) dc conductivity from total conductivity and (ii) polarization effects from relaxation processes, which further lead to the experimental errors. However, this task is made possible by the modulus formalism which eliminates spurious (Maxwell-Wagner) effects of electrode-electrolyte polarization existing in the frequency dependent conductivity and/or dielectric data and aids in providing an insight regarding relaxation phenomenon taking place in solids such as polymer electrolytes.

References

[1] M.B. Armand, J.M. Chabagno, M.J. Duclot, in: P. Vashishta, J.N. Mundy, G.K. Shenoy (eds.), *Fast Ion Transport in Solids,* Elsevier North Holland, 1979, pp. 131.

[2] P.G. Bruce, C.A. Vincent, *J. Chem. Soc. Faraday Trans.* 89 (17) (1993) 3187.

[3] M.P. Stevens, *Polymer Chemistry: An Introduction,* third ed., Oxford University Press, Inc., New York, 1999.

[4] S. Furusawa, in: T. Sakuma, H. Takahashi (eds.), *Physics of Solid State Ionics,* India, 2006, pp. 301.

[5] P. Bahadur, N.V. Shastry, *Principles of Polymer Science,* second ed., Narosa Publishing House Pvt. Ltd., India, 2005.

[6] P. Judeinstein, D. Reichert, E.R. deAzevedo, T.J. Bonagamba, *Acta Chim. Slov.* 52 (2005) 349.

[7] M.C. Lonergan, A. Nitzan, M.A. Ratner, D.F. Shriver, *J. Chem. Phys.* 103 (1995) 3253.

[8] E.T. Crawford, Arrhenius, *Uppsala Studies in History of Science,* Canton, MA: Science History Publications, 1996, pp. 23.

[9] A.K. Nath, A. Kumar, *Electrochimica Acta* 129 (2014) 177.

[10] M. Pant, D.K. Kanchan, N. Gondaliya, *Mater. Chem. Phys.* 115 (2009) 98.

[11] P. Colomban, *Proton Conductors: Solids, Membranes and Gels-Materials and Devices,* Cambridge University Press, 1992.

[12] H. Yugami, M. Ishigame, *Jpn. J. Appl. Phys.* 32 (1993) 853.

[13] P. Sharma, *Ph.D. Thesis*, Department of Physics, The M.S. University of Baroda, Vadodara, 2013.

[14] C. Julien, G.A.N. *Solid State Batteries: Materials Design and Optimization,* Kluwer Academic Publisher, London, 1994.

[15] T. Uma, T. Mahalingam, U. Stimming, *Mater. Chem. Phys.* 85 (2004) 131.

[16] L.H. Sperling, *Introduction to Physical Polymer Science,* second ed., John Wiley & Sons, Inc., Singapore, 1993.

[17] T. Uma, T. Mahalingam, U. Stimming, *Mater. Chem. Phys.* 85 (2004) 131.

[18] H. Vogel, *Phys. Z.* 22 (1922) 645.

[19] V.G. Tamman, H.Z. Hesse, *Anorg. Allg. Chem.* 19 (1926) 245.

[20] G.H. Fulcher, *J. Am. Ceram. Soc.,* 8 (1925) 339.

[21] D. Baril, C. Michot, M. Armand, *Solid State Ionics* 94 (1997) 35.

[22] S.J. Pas, M.D. Ingram, K. Funke, A.J. Hill, *Electrochim. Acta.* 50 (2005) 3955.

[23] M.L. Williams, R.F. Landel, J.D. Ferry, *J. Am. Chem. Soc.* 77 (1955) 3701.

[24] S.I. Tabata, T. Hirakimoto, H. Tokuda, Md. A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B.* 108 (2004) 19518.

[25] J.M.G. Cowie, in: J.R. MacCallum, C.A. Vincent (eds.), *Polymer Electrolyte Reviews,* Vol. 1, Elsevier Applied Science Publisher, London, 1987, pp. 185.

[26] P.E.J. Rouse, *J. Chem. Phys.* 21 (1953) 1272.

[27] A. van Zon, S.W. de Leeuw, *Electrochimica Acta* 46 (2001) 1539.

[28] W. Weiczorek, Z. Florjancyk, J.R. Stevens, *Electrochim. Acta* 40 (1995) 2251.

[29] J. Przyluski, M. Siekierski, W. Wieczorek, *Electrochim. Acta* 40 (1995) 2101.

[30] J. Przyluski, W. Wieczorek, *Solid State Ionics* 53-56 (1992) 1071.

[31] C.W. Nan, *J. Appl. Phys.* 76 (1994) 1155.

[32] C.W. Nan, D.M. Smith, *Mater. Sci. Eng. B* 10 (1991) 99.

[33] R. Landauer, *J. Appl. Phys.* 23 (1952) 779.

[34] A.K. Harrison, R. Zwanzig, *Phys. Rev.* A 32 (1985) 1072.

[35] M.H. Cohen, D. Turnbull, *J. Chem. Phys.* 31 (1959) 1164.

[36] D. Turnbull, M.H. Cohen, *J. Chem. Phys.* 52 (1970) 3038.

[37] M.H. Cohen, G.S. Grest, *Annal. New York Acad. Sci.* 371 (1981) 199.

[38] D. Turnbull, M.H. Cohen, *J. Chem. Phys.* 34 (1) (1961) 120.

[39] A.J. Kovacs, *Annal. New York Acad. Sci.* 371 (1981) 38.

[40] J.M. Hutchinson, A.J. Kovacs, *J. Polym. Sci.* 14 (1976) 1575.

[41] G. Choudalakis, A.D. Gotsis, *Current Opinion in Colloid & Interface Science* 17 (2012) 132.

[42] J.H. Gibbs, E.A. DiMarzio, *J. Chem. Phys.* 28 (1958) 373.

[43] G. Adam, J.H. Gibbs, *J. Chem. Phys.* 43 (1965) 139.

[44] K. Funke, *Radiation Effects and Defects in Solids,* Gordan & Breach, SA, Vols. 119-121, 1991, pp. 463.

[45] K. Funke, *Prog. Solid State Chem.* 22 (1993) 111.

[46] K. Funke, *Solid State Ionics* 94 (1997) 27.

[47] K. Funke, *J. Non-Crystal. Solids,* 172-174 (1994) 1215.

[48] B. Natesan, N.K. Karan, R.S. Katiyar, *Physical Review E* 74 (2006) 042801.

[49] K. Funke, R. Hoppe, *Solid State Ionics* 40-41 (1990) 200.

[50] P. Ganguly, A.K. Jha, *Bull. Mat. Sci.* 34 (4) (2011) 907.

[51] L.L. Hensch, J.K. West, *Principles of Electronic Ceramics,* John Wiley & Sons, Singapore, 1990.

[52] A.K. Jonscher, *Phys. Thin. Films* 11 (1980) 23.

[53] A.K. Jonscher, *J. Mater. Sci.* 16 (1981) 2037.

[54] M.D. Ingram, *Phys. Chem. Glasses* 28 (1987) 215.

[55] A.K. Jonscher, *Nature* 267 (1977) 673.

[56] A.K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London, UK, 1983.

[57] J.O. Lopez, R.G. Aguilar, *Rev. Mex. Fis.* 49 (2003) 529.

[58] A.N. Papathanassiou, I. Sakellis, J. Grammatikakis, *Appl. Phys. Lett.* 91 (2007) 122911.

[59] K. Funke, R.D. Banhatti, C. Cramer, *Phys. Chem. Chem. Phys.* 7 (2005) 157.

[60] S.J. Pas, R.D. Banhatti, K. Funke, *Solid State Ionics* 177 (2006) 3135.

[61] S. Ke, H. Huang, S. Yu, L. Zhou, *J. Appl. Phys.* 107 (2010) 084112.

[62] J.P. Tiwari, K. Shahi, *Philosophical Magazine* 87 (29) (2007) 4475.

[63] B. Deb, S. Bhattacharya, A. Ghosh, *EPL* 96 (2011) 37005.

[64] D.P. Almond, A.R. West, R.J. Grant, *Solid State Comm.* 44 (1982) 1277.

[65] D.P. Almond, G.K. Duncan, A.R. West, *Solid State Ionics* 8 (1983) 159.

[66] D.P. Almond, A.R. West, *Solid State Ionics* 9-10 (1983) 277.

[67] D.P. Almond, A.R. West, *Solid State Ionics* 11 (1983) 57.

[68] D.P. Almond, A.R. West, *Solid State Ionics* 23 (1987) 27.

[69] H. Jain, J.N. Mundy, *J. Non. Cryst. Solids* 91 (1987) 315.

[70] A.R. West, *Elements of Solid State Chemistry,* Wiley, New York, 1987.

[71] M. Siekierski, K. Nadara, P. Rzeszotarski, *J. New Mat. Electrochem. Systems* 9 (2006) 375.

[72] S. Sen, R.N.P. Choudhary, *Mater. Lett.* 58 (2004) 661.

[73] S.R. Broadbent, J.M. Hammersley, *Proc. Cambridge Philos. Soc.* 53 (1957) 629.

[74] A. Bunde, S. Havlin, *Fractals and Disorderd Systems,* Springer, 1994.

[75] J.M. Ziman, *Models of Disorder-Theoretical Physics of Homogeneously Disordered Systems,* Cambridge Univ. Press, Cambridge, 1979.

[76] S. Kirkpatrick, *Rev. Mod. Phys.* 45 (1973) 574.

[77] D. Stauffer, *Introduction to Percolation Theory*, Taylor & Francis, London, 1985.

[78] C.A. Edmondson, J.J. Fontanella, *Solid State Ionics* 152-153 (2002) 355.

[79] M.A. Ratner, D.F. Shriver, *Chemical Reviews* 88 (1988) 109.

[80] M.A. Ratner, In: J.R. MacCullum, C.A. Vincent (eds.), *Polymer Electrolyte Reviews-I*, Elsevier Applied Science, London, 1987, pp. 173.

[81] R. Zallen, *The Physics of Amorphous Solids,* Wiley, New York, 1983.

[82] S.D. Druger, A. Nitzan, M.A. Ratner, *J. Chem. Phys.* 79 (6) (1983) 3133.

[83] S.D. Druger, M.A. Ratner, A. Nitzan, *Solid State Ionics* 9-10 (1983) 1115.

[84] A. Nitzan, M.A. Ratner, *J. Phys. Chem.* 98 (1994) 1765.

[85] M.A. Ratner, A. Nitzan, *Solid State Ionics* 28-30 (1988) 3.

[86] S.D. Druger, M.A. Ratner, A. Nitzan, *Solid State Ionics* 18-19 (1) (1986) 106.

[87] R. Granek, N.A., D.S.D., R.M.A., *Solid State Ionics* 28-30 (1988) 120.

[88] S.D. Druger, M.A. Ratner, A. Nitzan, *Phys. Rev. B.* 31 (1985) 3939.

[89] C.A. Vincent, *Prog. Solid State Chem.* 17 (1987) 145-261.

[90] J.R. Macdonald, *Impedance Spectroscopy,* John Wiley & Sons, New York, USA, 1987.

[91] E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy Theory, Experiment, and Applications,* second ed., John Wiley & Sons, Inc., New Jersey, USA, 2005.

[92] J.R. Macdonald, *Impedance Spectroscopy Emphasizing Solid Materials and Systems,* Wiley, New York, 1987.

[93] J.M.G. Cowie, in: J.R. MacCallum, C.A. Vincent (eds.), *Polymer Electrolyte Reviews,* Vol. 1, Elsevier Applied Science Publisher, London, 1987, pp. 259.

[94] J.R. Macdonald, L.D. Potter, *Solid State Ionics* 23 (1987) 61.

[95] A.N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, E. Dalas, *Appl.Phys. Lett.* 87 (2005) 154107.

[96] C. Odin, M. Nechtschein, *Phys. Rev. Lett.* 67 (1991)1114.

[97] S. Capaccioli, M. Lucchesi, P.A. Rolla, G. Ruggeri, *J. Phys.: Condens. Matter* 10 (1998) 5595.

[98] D. Kumar, S.A. Hashmi, *Solid State Ionics* 181 (8-10) (2010) 416.

[99] N. Srivastava, M. Kumar, *Solid State Ionics* 262 (2014) 806.

[100] S. Ramesh, A.H. Yahaya, A.K. Arof, *Solid State Ionics* 152-153 (2002) 291.

[101] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, *Mater. Chem. Phys.* 98 (2006) 55.

[102] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, *Solid State Ionics* 177 (2006) 2679.

[103] S.A. Acharya, K. Singh, *Adv. Mater. Lett.* (2013) 1.

[104] F.M. Reicha, M. El-Hi-Ti, A.Z. El-Sonabati, A.M. Diab, *J. Phys. D* 24 (1991) 369.

[105] J. Swiergiel, J. Jadzyn, *J. Phys. Chem. B* 116 (2012) 3789.

[106] M.S. Jayswal, *Ph.D. Thesis*, Department of Physics, The M.S. University of Baroda, 2014.

[107] K. Pandey, M.M. Dwivedi, M. Singh, S.L. Agrawal, *J. Polym. Res.* 17 (2010) 127.

[108] P.B. Macedo, C.T. Moynihan, R. Bose, *Phys. Chem. Glasses* 13 (1972) 171.

[109] C.T. Moynihan, L.P. Boesch, N.L. Laberge, *Phys. Chem. Glasses* 14 (1973) 122.

[110] R. Bergman, *J. Appl. Phys.* 88 (2000) 1356.

[111] R. Vaish, K.B.R. Verma, *J. Appl. Phys.* 106 (2009) 064106.

[112] A.S. Ayesh, *Polymer Journal* 41 (8) (2009) 616.

[113] D.K. Ray, A.K. Himanshu, T.P. Sinha, *Indian Journal of Pure & Applied Physics* 45 (2007) 692.

[114] S. Szu, Fu-S. Chang, *Solid State Ionics* 176 (2005) 2695.

[115] D.H. Kothari, *Ph.D. Thesis*, Department of Physics, The M.S. University of Baroda, Vadodara, 2014.