CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The alternative sources of energy are constantly evolving to decrease long-term confidence on oil, nuclear and other fossil fuels. Environmentally friendly fuel cells are strong candidates for this reason. Electrolytes are the heart of electrochemical devices. SPEs effectively separates the anode and cathode and mediates the electrochemical reaction occurring at the electrodes through conduction of a specific ion [Chávez et al., 2010]. Polymer electrolyte membranes can be produced by mixing polar polymers with inorganic salts. Electrical conduction through such a membrane occur by ion transport when induced by an electric field [Ravanchi et al., 2009]. Polar polymer materials containing electron donating atoms in combination with suitable low dissociation energy metal salts give electrolytes for advanced, high energy electrochemical devices, e.g. batteries / fuel cells, electrochemical display devices/smart windows and photoelectrochemical cells. These polymer electrolytes offer many important properties such as fast cation transport combined with plasticity, satisfactory mechanical properties, ease of fabrication as thin films, high electrochemical stability and ability to form good electrode/electrolyte contact [Kumar et al., 2001, Perera et al., 2000].

2.2 Polymer Electrolyte Classifications

On the basis of the materials used to prepare polymer electrolyte films and their properties, the polymer electrolyte materials have been divided into the following broad categories.

2.2.1 Polymer-salt complex or dry solid polymer electrolyte (SPE)

The concept of dissolving the salts of an alkaline metal in a polar macromolecular polymer and thus creating an ion conducting solid electrolyte is known as solid polymer electrolyte (SPE) [Edman et al., 2000]. Interactions of metal ions with polar polymers are mainly due to electrostatic forces and the formation of coordinating bonds. The variables that may affect the polymer-metal ion interactions are nature of atoms in the backbone chain, nature of functional groups attached to the backbone, molecular weight, degree of branching, distance between functional groups, nature and charge of metal and counter ions [Rivas et al., 2003]. The cations are weakly coordinated to sites along the polymer chain and they can transfer from one coordinated site to another if an electric field is applied. Much research effort has since then been directed toward understanding the complex chemistry and ionic transport properties of these technologically important materials [Edman et al., 2000].

2.2.2 Plasticized Polymer Electrolyte (PPEs)

Plasticized polymer electrolytes are prepared by adding low molecular weight compounds such as ethylene carbonate, propylene carbonate, and poly ethylene glycol (PEG), etc. to the polymer host [Stephan et al., 2009]. According to gel theory, active center forces joint polymer molecules to each other in solution. These bonds are in a dynamic equilibrium in solution form. Water molecules and plasticizers are in competition for the same sites and reduce the number of active centers and the number of polymer-polymer contacts, thus they decrease the rigidity of the three dimensional structure formed on drying and change mechanical and thermo mechanical properties of the prepared films [Honary and Golkar, 2003]. Thus addition of low molecular weight plasticizers results in the decrease of glass transition temperature of the complex, the reduction of crystallinity and the increase of salt dissociation capability and charge carrier transport. However, a decrease in mechanical strength of the resulting polymer electrolytes is predictable [Samir et al., 2004]. From the above discussion, it is understood that the increase of ambient conductivity by incorporation of plasticizer results in the loss of mechanical strength. Furthermore, plasticized electrolytes also exhibit drawbacks, such as reactivity of polar solvents with lithium electrode, poor mechanical properties at high degree of plasticization, and solvent volatility [Saikia et al., 2011, Stephan et al., 2009].

2.2.3 Gel Polymer Electrolytes (GPEs)

Much attention has been paid to gel polymer electrolyte (GPE), because it combines the advantages of liquid electrolytes (high ionic conductivity) and solid-state electrolytes (high safety). GPE uses polymer as a matrix to entrap liquid components, thus it is much safer than conventional liquid electrolyte when used in lithium ion batteries [Liao et al., 2010]. Gel electrolytes can be prepared by incorporating a large amount of organic solvent or plasticizer into the polymer host [Agrawal and Pandey, 2008]. The incorporated molecules can form a network through which ion conduction occurs, with the host polymer providing mostly structural support. Gel electrolytes offer high ambient conductivities but suffer the same disadvantages as the plasticized electrolytes- namely release of volatiles and increased reactivity towards the metal electrode [Jacob et al., 2003].

2.2.4 Composite polymer electrolytes (CPEs)

One of the major reasons for poor ionic conductivity and concentration polarization has been attributed to the possibility of an ion-association (ion-pairing) effect. This is due to weak dielectric permittivity of host polymers [Mohapatra et al., 2009]. A number of approaches have been proposed to solve the state-of-the-art problems of ion-conducting polymers. Nanocomposite formation is the latest suggestion to overcome the disadvantages and improve the properties of SPEs, the method applied mostly is to disperse inorganic inert fillers in the SPE [Mulmi et al., 2009]. Electrical properties such as dielectric permittivity can be suitably adjusted, simply by controlling the type and the amount of ceramic inclusions. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to be processed requiring high temperatures [Kontos et al., 2007]. On the other hand, polymers possess relatively low dielectric permittivity, they can withstand high fields, are flexible and easy to process. By combining the advantages of both, one can fabricate new hybrid materials with high dielectric permittivity [Thomas et al., 2010]. When these inorganic fillers are of nano dimensions, the composite polymer electrolyte formed is called nanocomposite polymer electrolyte (NCPE). Till now, the nanoparticles most used are TiO_2, Al_2O_3, SiO_2, MgO etc. Adding these nanoparticles to SPE is found to be one of the most effective routes of achieving balanced characteristics of ionic conductivity and mechanical stability. These and many more recent studies have demonstrated that the size and shape of the nanoparticle filler have a very important role in improving the quality of the NCPE. But till now there is no fully satisfactory explanation available regarding the role played by these nanoparticles [Mulmi et al., 2009]. Composite materials of an amorphous polymeric matrix and fine ceramic particles are considered as heterogeneous disordered systems. Their electrical performance is directly related to the permittivity and conductivity of their constituents, the volume fraction of the filler and the size and shape of its particles [Kontos et al., 2007].

2.3 Ion Transport Models in Polymer Electrolytes

An essential feature which distinguishes polymer electrolytes from ionic conductors formed by dissolving salts in low molar mass solvents arises from the mechanism of cation motion. A fundamental assumption in theories of cationic transport in high molar mass polymer electrolytes is that, since net displacement of the “centre of gravity” of polymer chains is not significant, long range cation transport must involve dissociative steps in which cations are transferred between neighboring coordinating sites located either on the host molecule or on an adjacent host molecule; i.e. polymer segmental motion arising from bond rotations provides only for short range motion of coordinated cations within limited regions of space. It might therefore be predicted that cations which form non-labile bonds with a polymer host would not contribute to the dc conductivity of a polymer electrolyte [Vincent, 1995]. The DC conductivity study versus 1000/T can be used to investigate the effect of segmental mobility on cation transport in polymer electrolytes. This is due to the fact that the DC conductivity versus reciprocal of temperature can be interpreted in terms of one of the following models:

2.3.1 Arrhenius Model for Ion Transport

In this model the relationship between DC conductivity and temperature can be represented by the equation:

$$\sigma_{dc}(T) = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right) \qquad (2.1)$$

where σ_o is the pre-exponential factor, E_a the activation energy, and K_B the Boltzmann constant. According to Carvalho et al., (2000), the Arrhenius like relationship indicates the fact that the motion of mobile ions does not result from the polymer host motion. This means that when the temperature dependence conductivity obeys Arrhenius relationship, the nature of cation transport is similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and, hence, increases the ionic conductivity to a higher value [Othman et al., 2007]. Recently Hema et al., (2009b) observed the Arrhenius relationship between DC conductivity and 1000/T for proton conducting solid polymer electrolyte system based on PVA:NH_4NO_3 as depicted in Fig. 2.1. Similar Arrhenius behavior has been reported by Baskaran et al. (2007), for PVA:$LiClO_4$ and by Kadir et al. (2010) for chitosan-PVA:NH_4NO_3 polymer electrolytes.

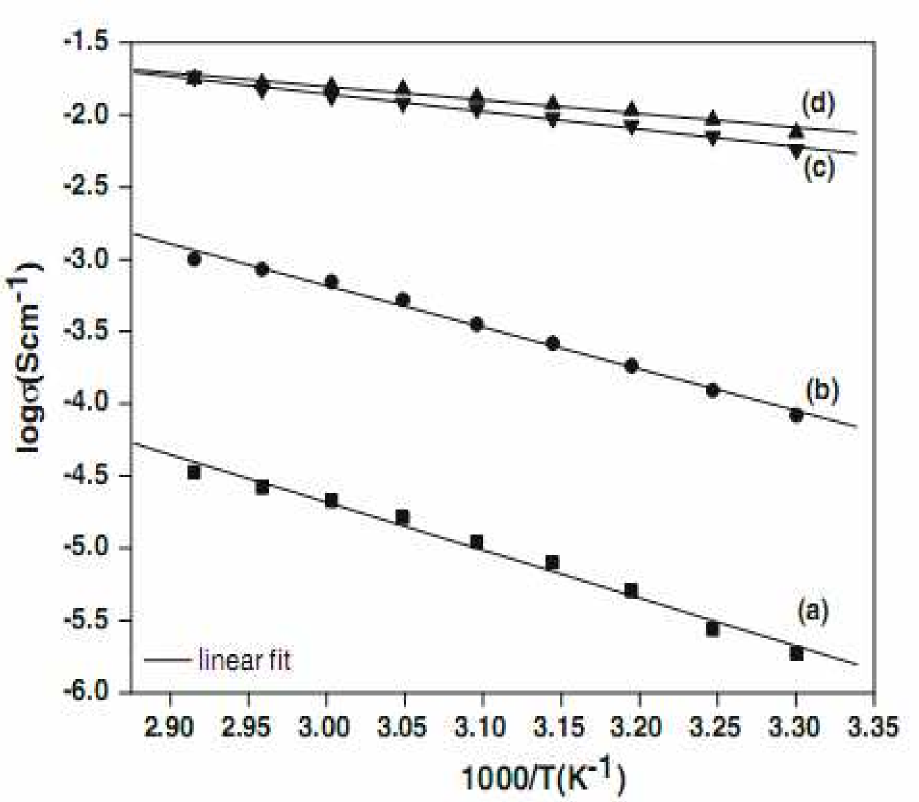


Figure 2.1 Temperature dependence of ionic conductivity of PVA doped with (a) 0 mole%, (b) 5 maol%, (c) 30 mol%, and (d) 20 mol% of NH_4NO_3 [Hema et al., 2009]

2.3.2 Vogel–Tammann–Fulcher (VTF) Model for Ion Transport

A Vogel-Tammann-Fulcher (VTF) analysis of the conductivity data confirms the (expected) strong inter-relation between conductivity and the relaxation behavior of the polymer chain segments [Mertens et al., 1999]. The non-linear Arrhenius behavior between DC conductivity versus 1000/T can be described in terms of VTF equation [Bobade et al., 2009] as follows:

$$\sigma(T) = AT^{-1/2}\exp\left[-\frac{B}{K_B(T-T_0)}\right] \qquad (2.2)$$

Here *A* is the pre-exponential factor, which is related to the number of charge carriers, *B* is the pseudo-activation energy of ion transport, K_B is the Boltzmann constant, and T_o is defined as the temperature at which the configurational entropy becomes zero, i.e., the disappearance of free volume is complete. Karan et al. (2008), reported the VTF behavior for polymer electrolytes based on PEO:$LiCF_3SO_3$. This is depicted in Fig. 2.2.

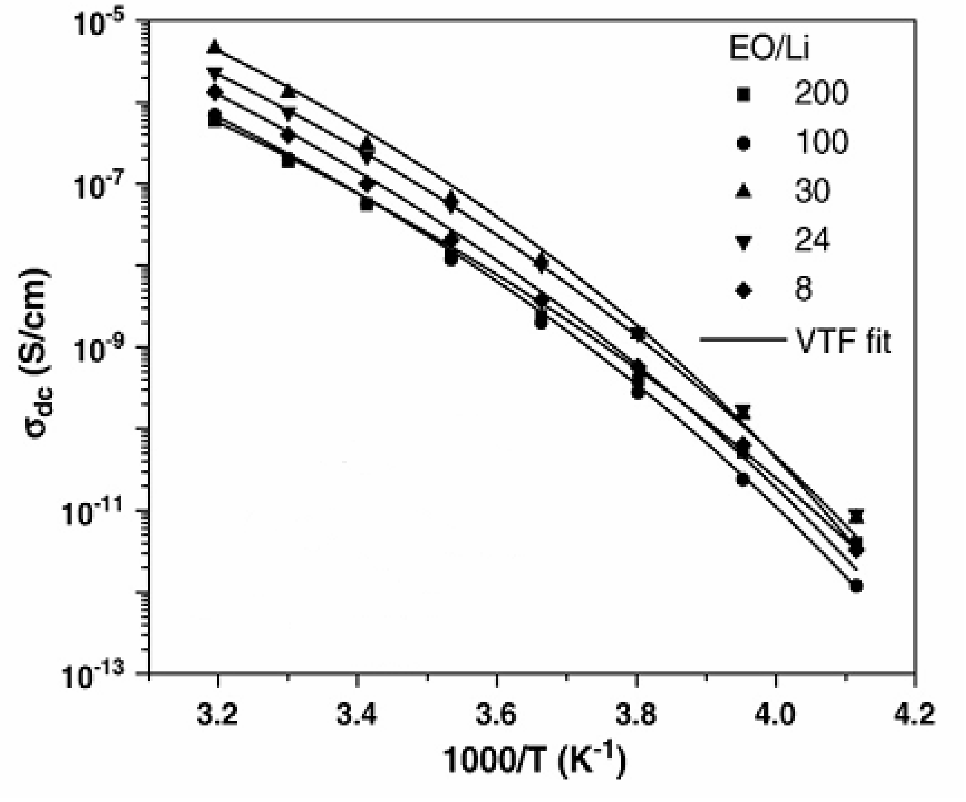


Figure 2.2 Temperature dependence plots of the conductivity of polymer electrolytes with various EO/Li ratios [Karan et al., 2008].

According to Kim et al., (1999) and Uma et al., (2005a), the curvature feature of DC conductivity versus reciprocal of absolute temperature indicates that the ionic conduction obeys the VTF relation, in which the ion transport is correlated with polymer segmental motion. This correlation between ion transport and segmental mobility can be understood by recognizing the free volume model [Uma et al., 2005b]. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules or polymer segments can move into the free volume. Therefore, as the temperature increases, the free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport.

From the discussion on Arrhenius and VTF models it is understood that the increase of ion conductivity is related to the increase in hopping rate and segmental mobility respectively. In addition to Arhenius and VTF models for ion transport and conductivity behavior, dielectric constant and ion dissociation energy also have great influence on conductivity behavior of polymer electrolyte.

2.4 Role of Dielectric Constant on Ion Conduction

Ionic conductivity of electrolyte can be described by the relation,

$$\sigma = \sum_i n_i q_i \mu_i \tag{2.3}$$

Here n_i is the concentration of charge carriers, q is the electron charge, and μ_i is the mobility of ions and i is the type of ions. It is clear from the above relation that the conductivity (σ) depends on the amount of charge carrier concentration (n), and the mobility of the ionic species in the system. The charge carrier concentration , n depends upon both the dissociation energy U involved and dielectric constant ε' as [Awadhia and Agrawal, 2007, Ramya et al., 2008],

$$n = n_o \exp\left(-U / \varepsilon' K_B T\right) \qquad (2.4)$$

where K_B is the Boltzmann constant and T, the absolute temperature. Due to the direct relationship between ε' and charge, the increase of ε' can be ascribed to the increase in the amount of charge in the sample i.e., the increase in the dielectric constant represents a fractional increase in charges within the electrolyte. This is due to the fact that dielectric constant is related to the ratio of capacitance (C) of the material to the capacitance of the empty cell (C_o) ($\varepsilon' = C/C_o$), and the capacitance is related to the amount of stored charge ($C = Q/V$) where Q is the total charge and V is applied voltage. Now it is clear from Equation (2.3), that the conductivity (σ) depends on the amount of charge carrier concentration (n), and the mobility of the ionic species in the system. From Equation (2.4), n will increase with increase in dielectric constant. Consequently conductivity increases according to Equation (2.3). The above equations indicate the fact that dielectric analysis is an informative technique to study conductivity behavior of polymer electrolytes. Thus, from the models for ion transport and the correlation between DC conductivity and dielectric constant ε', it is understood that the ion transport and conduction mechanism is a complicated subject in condensed matter physics. The incomplete understanding of the conduction mechanism in polymer electrolytes is considered to be one of the main hurdles in achieving the required ambient conductivity [Natesan et al., 2006a, Natesan et al., 2006b]. Furthermore from the above discussion, it is understood that not only the ion concentration and segmental mobility governs the conductivity behavior of polymer electrolyte but dielectric constant and ion dissociation energy also have the crucial role on conductivity behavior. Ramesh et al., (2002), used dielectric constant to study the conductivity behavior of non-plasticized and plasticized PVC-PMMA-$LiCF_3SO_3$ polymer electrolyte, in which they attributed the increase of dielectric constant of plasticized system to the increase of charge carrier density as shown in Fig 2.3.

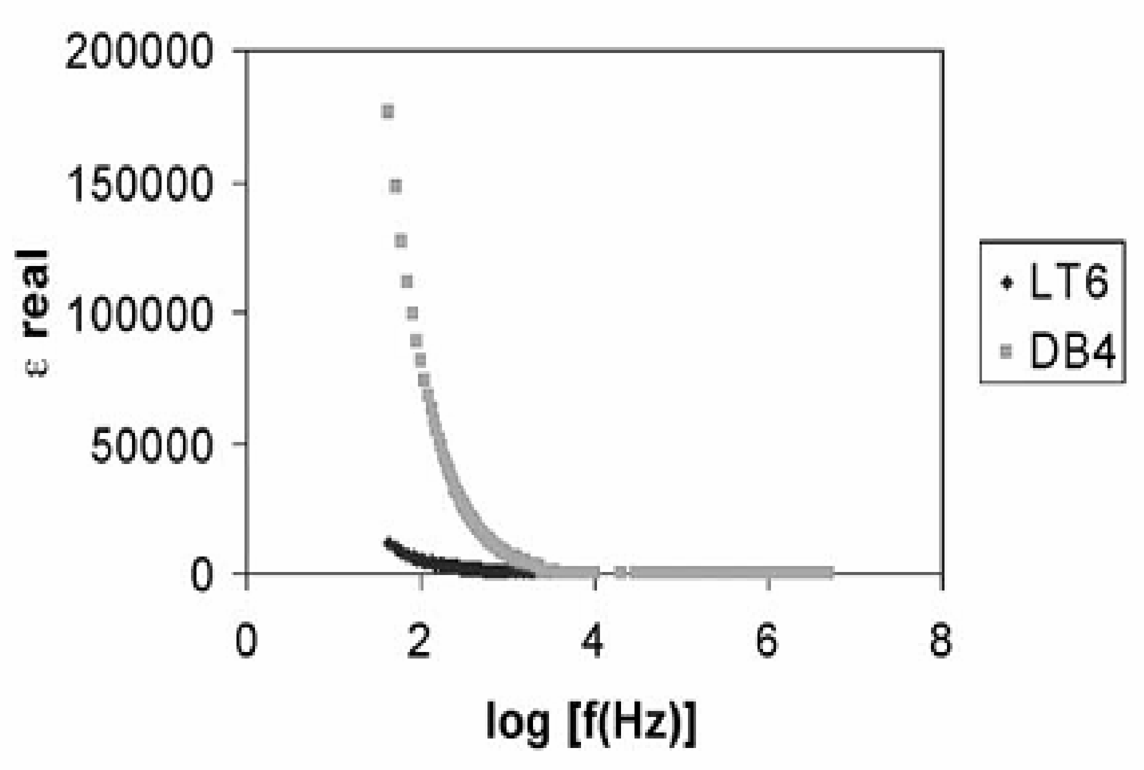


Figure 2.3 Variation of ε′ as a function of frequency for PVC/PMMA-based electrolytes. LT6 represent PVC:PMMA:$LiCF_3SO_3$ (18:42:40) system and DB4 represent PVC:PMMA:$LiCF_3SO_3$:DBP (11:25:24:40) system. [Ramesh et al., 2002].

Sheha (2009), have studied the effect of ethylene carbonate (EC) on the dielectric properties of PVA:LiBr:H_2SO_4 polymer electrolyte. He ascribed the increase of the dielectric constant to the increase of storage charge in the material due to the ion dissociation by the EC plasticizer as depicted in Fig. 2.4. This is consistent with Equation (2.4).

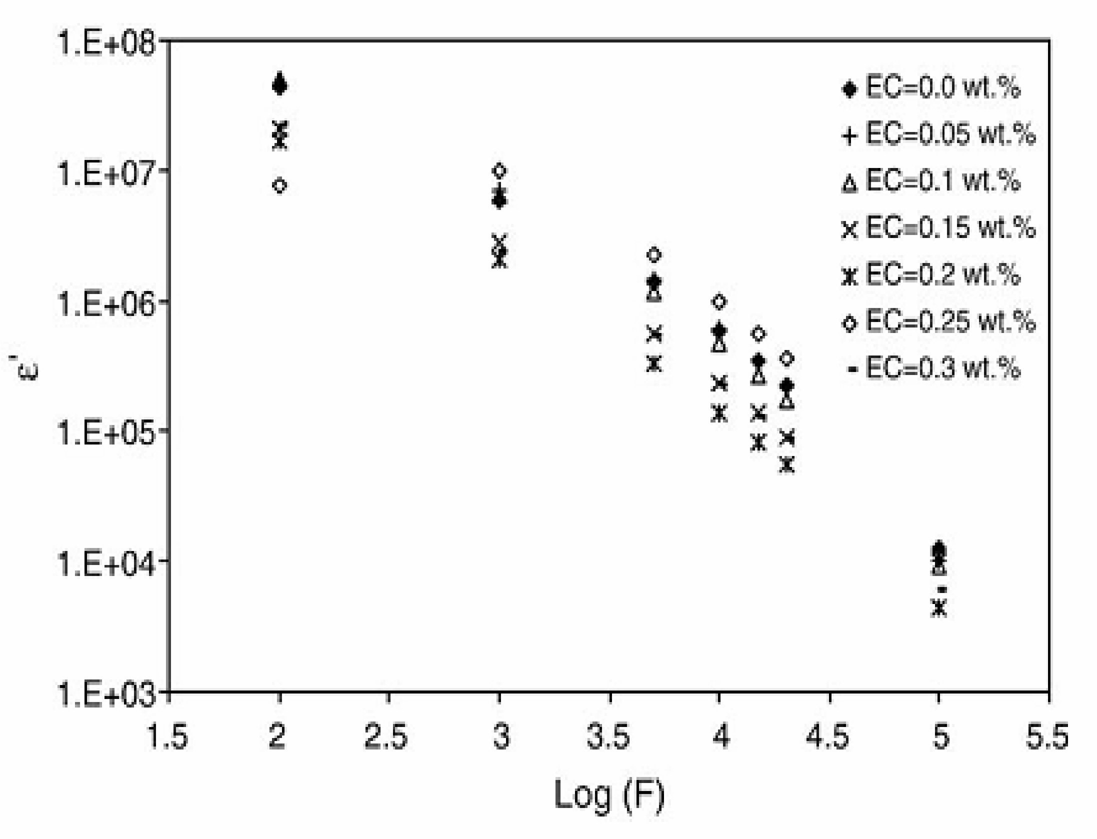


Figure 2.4 Variation of dielectric constant as a function of frequency for different EC concentrations at room temperature [Sheha, 2009].

Dielectric properties of polymer electrolytes and nanocomposite polymer electrolytes have been studied by other researchers [Baskaran et al., 2004, Selvasekarapandian et al., 2005, Ramesh et al., 2007, Hema et al., 2008, Hema et al., 2009c, and Nithya et al., 2011].

The basic experimental technique for characterizing the dynamics of ion transport is electrical relaxation or impedance spectroscopy, in which an ac device is used to measure the capacitive and resistive component of the inserted sample as a function of frequency between two conducting electrodes [Hodge et al., 2005].

2.5 Electrochemical Impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is the currently used technique to study the electrical properties of materials and their interface with electronically conducting electrodes over a wide range of frequency and temperature. EIS can be used to separate the bulk and electrode contribution of charge species in the sample.

2.5.1 Origin of EIS Theory

Electrical charge displacements in the bulk material yield two types of distinct physical phenomena: (i) if the charge motion is strictly confined in a localized volume of the matter then a polarization phenomenon occurs or (ii) if the electrical charges can collectively diffuse over long distances then diffusion is possible and a dc conductivity, σ_{dc} , is established. Further, because of the blocking nature of the metallic electrode used to measure the conductivity of ionically conducting solids, polarization at the solid/electrode interface is also observed. To limit this interfacial polarization as much as possible, it is necessary to perform conductivity measurement by means of complex impedance spectroscopy, i.e., using an ac electric field [Henn et al., 2007]. Dielectric spectroscopy is based on the tendency of ions and dipoles to orient in an electric field (Figure 2.5) [Nahm, 2006]. When an ac electric field is applied to a parallel plate capacitor separated by a dielectric material like polymeric materials, the electric charges of atoms, molecules and ions suffer local displacement relative to their original equilibrium positions and the material is polarized. Generally the polarization can be classified in four categories namely: electronic, atomic, dipolar and migrating charge polarization [Nicolau etal., 2007]. Ions often originate as impurities in the raw materials. Dipoles result when atoms with unequal electro negativities are attached to each other in a chemical bond [Nahm, 2006]. The dielectric relaxation processes are normally related to one or more polarization processes of the studied material. The contributions of atomic and electronic charges, which occur at still higher frequencies, are considered to be instantaneous in dielectric studies of polymers. Therefore, the two major components of the dielectric response of polymers in an applied electric field are the dipolar polarization and the polarization due migrating charges. Dipolar and migrating charge polarizations can be detected in frequencies smaller than 10^9 Hz [Nicolau etal., 2007].

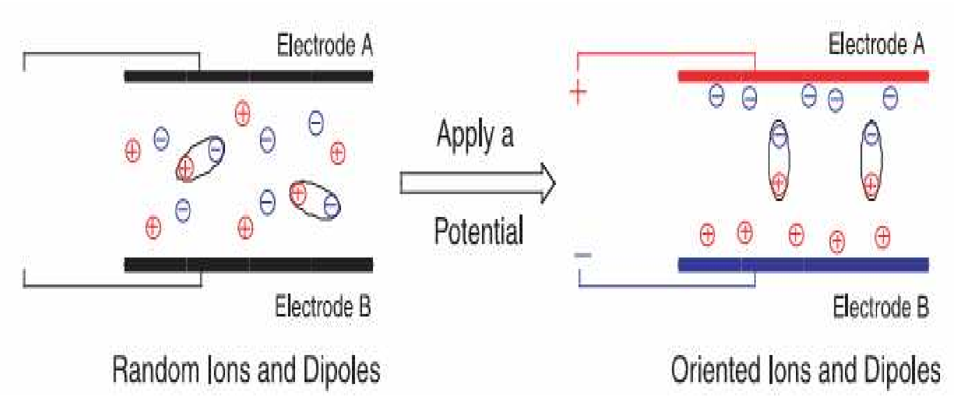


Figure 2.5 Effect of electric field on ions and dipoles [Nahm, 2006].

If the electric field is reversed, the dipoles will reorient with the field and the ions migrate (diffuse) to the other electrode. As the field reversal rate (frequency) increases, it becomes increasingly difficult for the ions and dipoles to keep up, so a phase delay develops and the separation of the ions or orientation of the dipoles becomes less distinct (lower signal strength). As the groups on either side of the dipole become larger, as in a growing polymer, it becomes more difficult for them to reorient with the field, independent of the frequency of reversal, and signal strength (capacitance) decreases. Finally, as the system becomes more viscous, ion diffusion (conductivity) becomes slower, and signal strength decreases with increasing frequency [Nahm, 2006]. The investigation of conduction and different dielectric polarizations can lead to information on the dynamic behavior in terms of relaxation processes.

2.5. 2 Complex Impedance Spectroscopy

Characterization of heterogeneous systems requires in situ and non-invasive measurement. Dielectric spectroscopy that measures permittivity and conductivity as a function of frequency in a non-invasive way is well suited for this purpose and can provide insights into the structures and electrical properties of heterogeneous systems at molecular and macroscopic levels. Materials are polarized in ac fields by various polarization mechanisms and their permittivity, as a measure of the polarization, shows frequency dependence, namely dielectric relaxation or dielectric dispersion [Asami, 2002 46]. The complex impedance spectroscopy technique offers several advantages such as the determination of relaxation frequency and separation of grain, grain boundary and grain-electrode effects. The complex impedance spectroscopic studies involve measurement of real and imaginary parts of impedance for a wide range of frequency. In recent years, this technique has become a well-accepted fundamental tool for characterizing ionic conductors in terms of ionic conductivity, electrode polarization and activation energy for ion migration [Mahato et al., 2010].

Impedance measurements were carried out by applying an alternating voltage, in a wide range of frequencies, to an electrochemical cell and by measuring the resulting electric current [Fortunato et al.,2006]. The voltage applied (V) is a sine wave input, varying with time (t), defined as

$$V(t) = V_o \sin(\omega t) \tag{2.5}$$

where V_0 is the maximum voltage intensity and ω is the angular frequency. The resulting electric current (I) is also a sine wave but with a phase difference:

$$I(t) = I_o \sin(\omega t + \varphi) \tag{2.6}$$

where I_o is the maximum current intensity and φ is the phase angle between the applied voltage and the current intensity. The electrical impedance, $Z(\omega)$, defined as the ratio between the applied voltage and the resulting electric current, $Z(\omega) = V(t)/I(t)$, is expressed as

$$Z^*(\omega) = Z_{real} + j\,Z_{img} \tag{2.7}$$

where Z_{real} is the real part of the electrical impedance and Z_{img} is the imaginary one and they can determined at a given frequency by [Maoxu et al., 2001],

$$Z_{real} = |Z|\cos\theta \quad (2.8)$$

$$Z_{img} = |Z|\sin\theta \quad (2.9)$$

The analysis of the impedance experimental data obtained *Z(ω)* can be carried out by the complex plane Z* method, plotting the imaginary impedance part ($-Z_{img}$) versus the real part (Z_{real}) in a diagram called a Nyquist plot.

2.5.3 Impedance Plots and Equivalent Circuits

In fact one of the most important features of complex impedance spectroscopy is the direct correlation between the response of the system and the equivalent circuit which represents the behavior of the electrical property of the system [Benavente et al., 2000]. Phenomenologically, a resistance (R) is taken to represent the dissipative component of the dielectric response, while a capacitance (C) describes the storage component of the dielectric material [Benavente et al., 2000, Benavente et al., 2005].

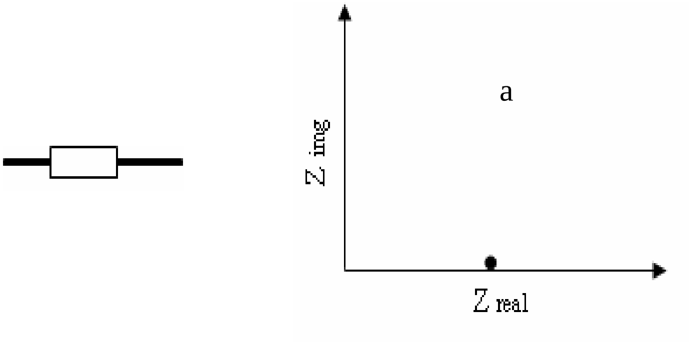
One of the outputs of EIS is a graph of the imaginary part of the impedance versus the real part. Information about the equivalent circuit can be extracted from this graph. Some examples of EIS graphs and equivalent circuits can be seen in Figure 2.6. The impedance of a resistor Z_R is simply its resistance R, which is in phase with an applied AC voltage signal. On the other hand, the impedance of a capacitance Z_C is out-of-phase with the applied AC signal, and is called the reactance X ($X = Z_i$), [Huggins, 2002], were

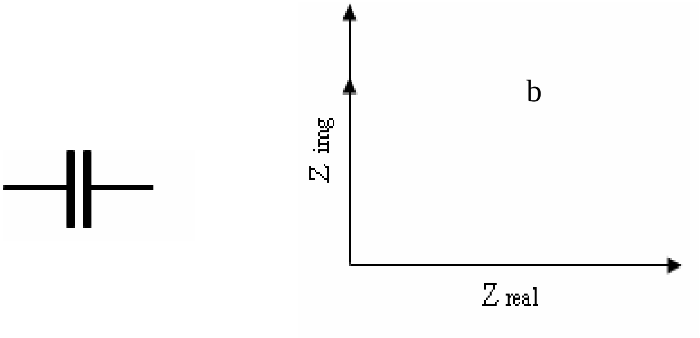
$$X = -j/(\omega C) \qquad (2.10)$$

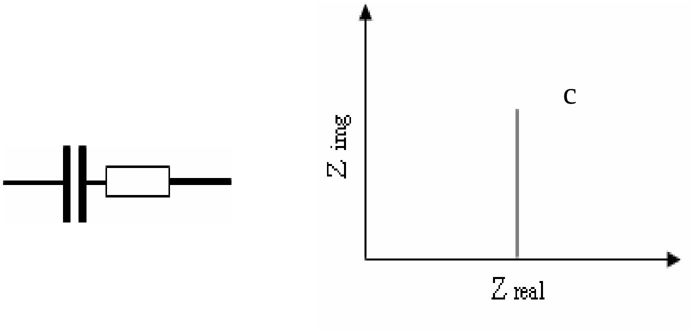
The representation of these simple elements on the complex impedance plane, some times called an "Argand diagram", is illustrated in Figs. 2.6(a) and 2.6(b), in which the negative value of the imaginary part of the impedance, the reactance, is plotted versus the real part, the resistance over a range of frequency. If there is a resistance in series with a capacitance the impedance of this combination Z_{RC} is given by

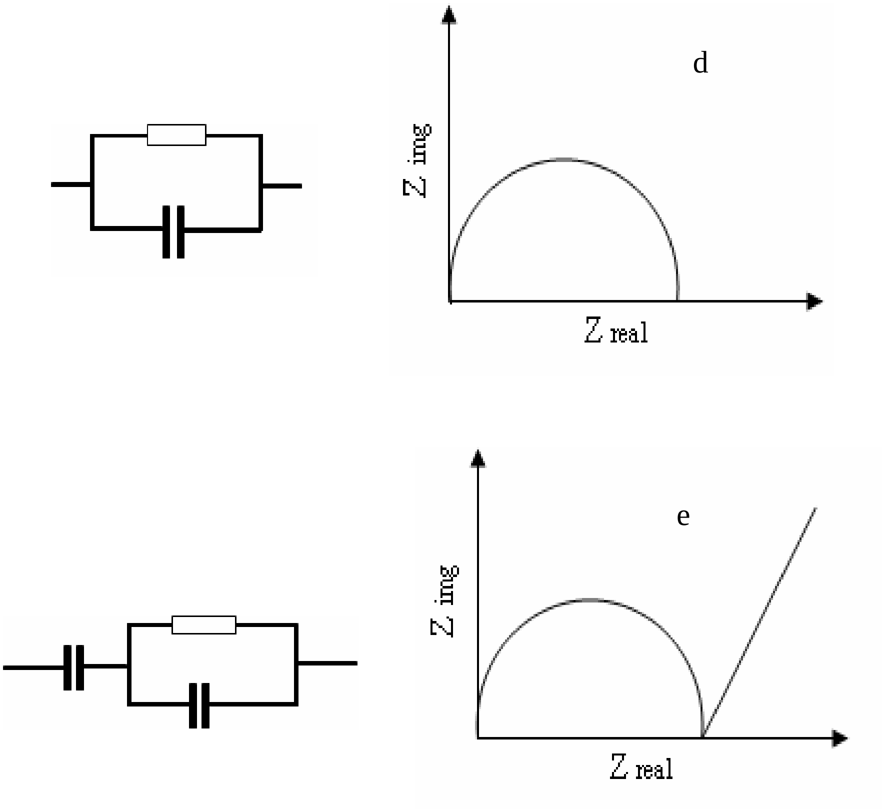
$$Z_{RC} = R + X = R - j/(\omega C) \qquad (2.11)$$

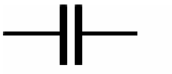
and thus varies with the measurement frequency. The complex impedance plot will appear as shown in Fig. 2.6(c). On the other hand, the impedance of a parallel configuration of a resistance and a capacitance, $Z_{R\text{-}C}$ has the shape of a semicircle on the complex impedance plane, as shown in Fig. 2.6(d). One can readily understand this behavior qualitatively. At very low frequencies the impedance of the capacitor is very large. Thus essentially all the current flows through the resistor and its properties dominate the behavior. At very high frequencies the impedance of the capacitor becomes very small, so that it effectively shorts out the resistor and the total impedance tends toward zero [Huggins, 2002].










This symbol represents a capacitor

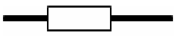

This symbol represents a resistor

Figure 2.6 Cole-Cole plots and their equivalent cicuits for (a) pure resistor, (b) pure capacitor, (c) capacitor and resistor in series, (d) capacitor and resistor in parallel combination and (e) a leaky system [Huggins, 2002].

A common experimental observation is that the low frequency tail in complex impedance plots is not truly vertical, but is a straight line inclined at a finite angle from the vertical, at lower frequencies and/or higher temperatures, as illustrated schematically in Fig. 2.6(e). An example of experimental data showing this behavior is presented in Fig. 2.7. In most cases the ac response could not be explained using simple ideal circuits. The semicircles in the complex plane (Z″-Z′) are often broadened and distorted into asymmetric arcs [Eid and Mahmoud, 1997]. The center of these semicircles lies under the real Z′ axis as depicted in fig 2.7.

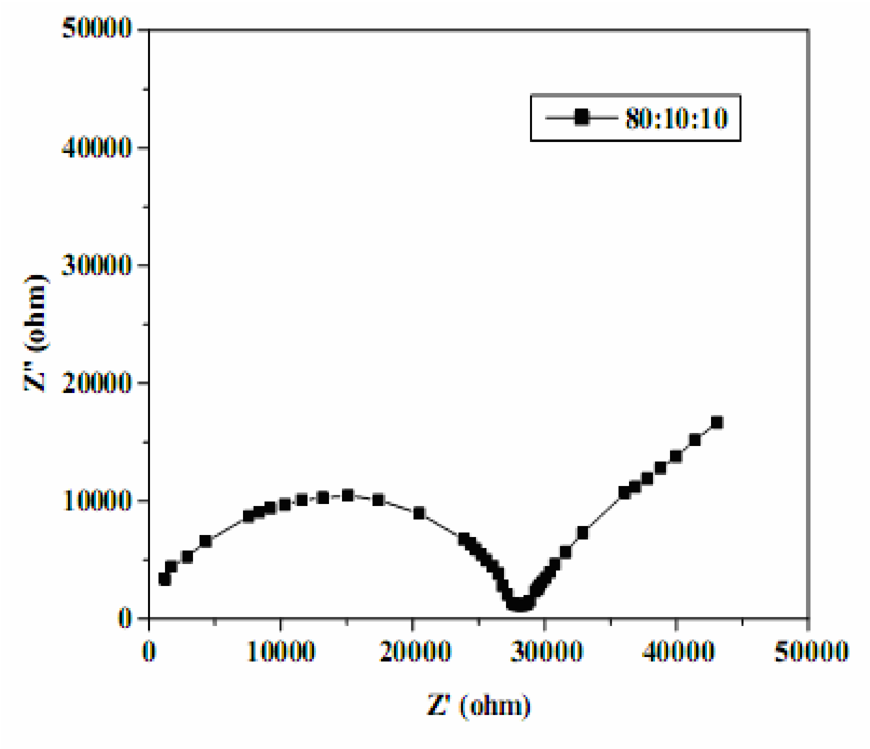


Figure 2.7 Impedance plot of PVAc–DMF–LiClO$_4$ complex at 303 K [Baskaran et al,2004].

The impedance response of PVAc–DMF–LiClO$_4$ (80:10:10) shows a semicircular portion at high frequency and a spike region at low frequency. The high frequency semicircle indicates the bulk response of the sample. The low frequency spike region can be ascribed to the double layer capacitance formed between the solid polymer electrolyte and electrodes. At low frequencies, the impedance plots should exhibit a straight line parallel with the imaginary axis; however the double layer at the blocking electrodes causes the curvature [Jacob, et al., 1997, Baskaran et al,2004].

2.5.4 Impedance-Related Functions

Impedance spectroscopy (IS) is a powerful method for characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic–ionic, and even insulators (dielectrics). There are several other measured or derived quantities related to impedance which often play important roles in IS. Impedance spectroscopy is particularly characterized by the measurement and analysis of some or all of the four impedance-related functions Z^*, Y^*, M^*, and ε^* and the plotting of these functions in the complex plane [Barsoukov and Macdonald, 2005]. Dielectric measurements (ε^*) such as dielectric constant (ε') and dielectric loss (ε'') reveal significant information about the chemical and physical state of polymers. These properties are drastically affected by the presence of another polymer or a dopant in the polymer [Rao et al., 2000]. The detailed investigation of the dielectric parameters, electrode and interfacial polarization effects of polymers is of great importance [Dutta et al., 2002]. On the other hand, the study of conductivity relaxation behavior in conducting polymer materials has become an interesting area of active research because of their potential applications in solid state devices. A method of predicting the relaxation behavior is the electric modulus (M^*) theory. The electric modulus spectrum, provides an opportunity to investigate conductivity and its associated relaxation in polymers [Migahed et al., 2004]. The two quantities are usually defined as the complex dielectric constant or dielectric permittivity $\varepsilon^* = (j\omega C_o Z^*)^{-1} = \varepsilon' - j\varepsilon''$ and the modulus function $M^* = j\omega C_o Z^* = M' + jM''$. In these expressions $C_o = \varepsilon_o A/d$ is the capacitance of the empty measuring cell of electrode area A and electrode separation length d. The quantity ε_o is the dielectric permittivity of free space, 8.854× 10^{-12} Fm^{-1}. The interrelations between the four immittance functions are summarized in Table 1.1 [Barsoukov and Macdonald, 2005].

Table 2.1 Relations between the four basic impedance functions [Barsoukov and Macdonald, 2005]

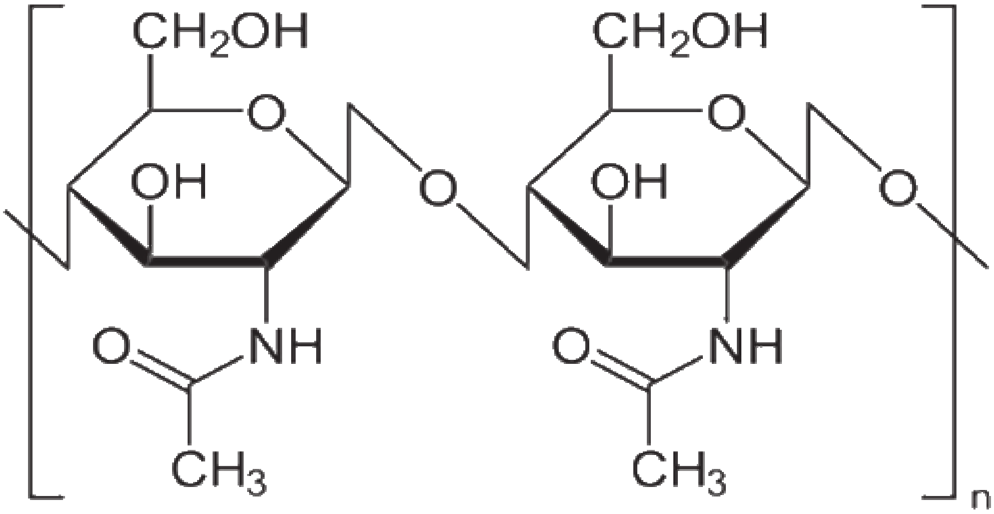
Functions	M^*	Z^*	Y^*	ε^*
M^*	M^*	μZ^*	μY^{*-1}	ε^{*-1}
Z^*	$\mu^{-1} M^*$	Z^*	Y^{*-1}	$\mu^{-1} \varepsilon^{*-1}$
Y^*	μM^{*-1}	Z^{*-1}	Y^*	$\mu \varepsilon^*$
ε^*	M^{*-1}	$\mu^{-1} Z^{*-1}$	$\mu^{-1} Y^*$	ε^*

$\mu = j\,\omega\,C_o$, were C_o is the capacitance of the empty cell

2.6 Chitosan and Chitosan Based Polymer Electrolytes

2.6.1 Chitosan Structure and Properties

Chitin, poly (β-(1→4)-N-acetyl-D-glucosamine), is a natural polysaccharide of major importance, first identified in 1884. This biopolymer is synthesized by an enormous number of living organisms; and considering the amount of chitin produced annually in the world, it is the most abundant polymer after cellulose [Rinaudo, 2006]. On the other hand chitosan is a cationic polysaccharide, which contains β-1-4-linked 2-amino-2 deoxy-D-glucopyranose repeat units and is readily obtained by alkaline N-acetylation of chitin [Lima et al., 2006]. Chitosan has great potential as a biomaterial because of [Agrawal et al., 2010] good biocompatibility, biodegradability, low toxicity, low cost [Cheng et al., 2003], antimicrobial activity [Nagahama et al., 2009] hydrophilicity which certainly be of benefit to the fuel cell operation, chemical and thermal stability at higher temperatures [Wan et al., 2006]. Thus, chitosan has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields [Pillai et al., 2009]. The unique properties which separate chitosan from other biopolymers is the presence of amino groups [El-Sawy et al., 2010] as depicted in Fig. 2.8(b).



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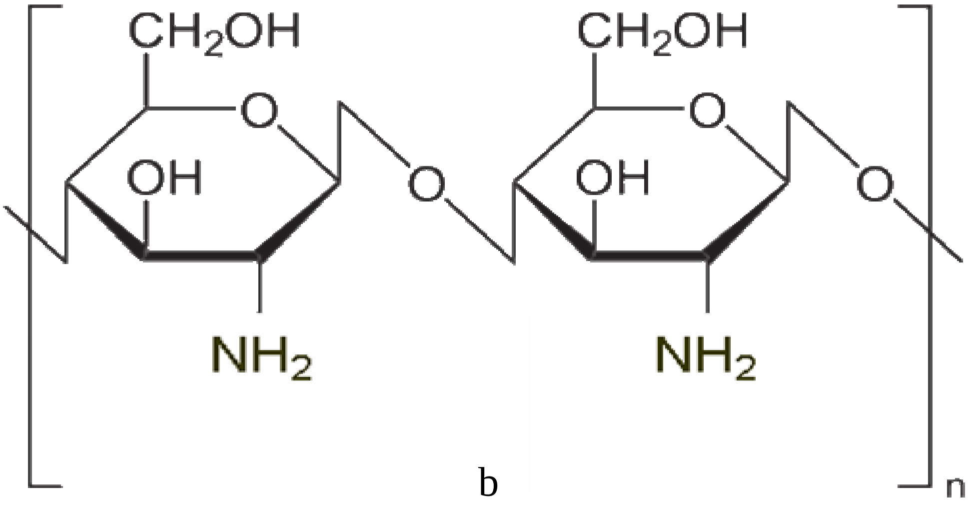

Figure 2.8 Structure of (a) chitin and (b) chitosan [López-Chávez et al., 2005].

Thus, the poly cationic nature of chitosan due to the abundance of free amino (NH_2) groups (Fig.2.8b) on the backbone of chitosan makes it possible to produce ion conducting polymer electrolyte [Wan et al., 2003]. This is related to the fact that the amine groups in chitosan structure can act as electron donors and interact with inorganic salts [Osman and Arof, 2003], and therefore chitosan meets an important requirement for acting as a polymer host for the solvation of salts [Costa et al., 2010].

2.6.2 Chtiosan Based Electrolyte

Chitosan is actually a heteropolymer containing both glucosamine units and acetylglucosamine units. The presence of amine groups explains its unique properties among biopolymers such as its cationic behavior in acidic solutions, and its affinity for metal ions. Metal ion sorption can occur through chelation mechanisms for metal cations in near neutral solutions or through electrostatic attraction and ion exchange for metal anions in acidic solutions [Guibal, 2005]. Some of the ion-conducting solid polymer electrolytes based on chitosan that have been reported are shown in Table 2.1.

Table 2.2: Examples of chitosan based solid polymer electrolytes.

Chitosan Electrolyte composition	Reference
Citosan-NaI	Subban and Arof (1996)
Chitosan-$NaClO_4$	Subban et al., (1996)
Chitosan-$AgNO_3$	Morni et al., (1997)
Chitosan-NH_4NO_3	Majid and Arof (2005)
Chitosan-$NH_4CF_3SO_3$	Khiar et al., (2006)
Chitosan-KOH	Wan et al., (2006)
Chitosan-PVPA	Göktepe et al., (2008)
Chitosan-$LiClO_4$	Costa et al., (2010)

To enhance the electrical conductivity and flexibility some researchers have added plasticizers into the chitosan host polymer. The biocompatibility of the plasticizer is an important consideration for the safe use of polymer electrolytes [Yahya et al., 2006].

Examples of plasticized ion-conducting polymer electrolytes based on chitosan that have been reported are shown in Table 2.2.

Table 2.3 Examples of plasticized chitosan based polymer electrolyte.

Composition of plasticized chitosan based electrolyte	Reference
Chitosan-$LiCF_3SO_3$-EC	Morni and Arof (1999)
Chitosan-$LiCF_3SO_3$-EC	Osman et al., (2001)
Chitosan-LiOAc-EC	Yahya and Arof (2002)
Chitosan-LiOAc-OA	Yahya and Arof (2003)
Chitosan-NH_4NO_3-EC	Ng and Mohammed (2006)
Chitosan–NH_4I-EC	Buraidah et al., (2009)
Chitosan–PVA-NH_4NO_3-EC	Kadir et al., (2010)

2.7 Summary

Polymer electrolytes and their classifications were presented in this chapter. Models of ion conduction in polymer electrolytes with some examples were exhibited. The role of dielectric constant on conductivity enhancement and some basic equations are also presented. The basic principle of electrical impedance (EIS) theory and the relation between complex impedance plots and equivalent circuits are described. Finally the structure and properties of chitosan which is used as a host polymer in this work is described.