# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Currently, a lot of research is being carried out all over the world to develop solid-state batteries since these types of batteries have many appealing features such as leakage free, flexibility in size and shape and have a wide temperature operation range. Flexibility in size and shape, for example can spur creativity in the design of many electrochemical devices. An important component of solid-state electrochemical devices e.g. batteries that in the opinion of the author, delays the emergence of solid-state batteries in the commercial scene is the solid electrolyte. Solid-state electrolytes have good mechanical strength, easy to process and can prevent leakages in electrochemical devices. However, solid-state electrolytes suffer from ageing effects that result in the electrolytes becoming more crystalline with lower conductivity. This chapter deals with solid-state proton conducting polymer electrolytes, their development and the problems encountered. Proton conducting solid-state electrolytes consists of a polymer host added with a salt to provide the charge carriers. A lot of polymers have been used as a host in proton conducting solid-state electrolytes such as poly(ethylene oxide) (PEO) [Srivastava, *et al.,* 1995], poly(vinyl alcohol) (PVA) [Hema *et al.,* 2008] and chitosan [Khiar *et al.,* 2006; Majid and Arof, 2005, 2007, 2008, 2009].

Examples of salts that can provide protons or $H^+$ ions are ammonium iodide ($NH_4I$) [Buraidah *et al.,* 2009, 2010; Hema *et al.,* 2009a, 2009b], ammonium chloride ($NH_4Cl$) [Hema *et al.,* 2009b], ammonium bromide ($NH_4Br$) [Hema *et al.,* 2007, 2008, 2009b] and ammonium thiocyanate ($NH_4SCN$) [Srivastava *et al.,* 1995]. Besides ammonium salt, acids can also provide the $H^+$ carriers such as acetic acid [Rinaudo *et al.,* 1999] and phosphoric acid [Majid and Arof, 2007; Kufian *et al.,* 2007]. In general, Cha and Park, (1998) have listed disadvantages of polymer electrolytes that include low room temperature ionic conductivity and low cation transference number.

According to Agrawal *et al.,* (2007), it is difficult to establish $H^+$ ion transport within the proton conducting polymer electrolytes. This is due to its short lifetime and its tendency to form bonds with other negative ions. In spite of these disadvantages , the size of the $H^+$ ion allows its intercalation in a large number of layered host materials that makes proton conductors suitable for the development of “intercalation based devices” such as secondary proton batteries.

## 2.2 Polymer Electrolytes

Ever since the discovery that poly(ethylene oxide) can form complexes with alkali metal salts (MX) [Fenton *et al.,* 1973] and the application of polymer electrolytes in solid state electrochemical devices [Armand *et al.,* 1979], R&D of polymer electrolytes and solid-state electrochemical devices have been intensively carried out worldwide.

Polymer electrolytes have reserved a crucial position in solid-state ionics due to their ability to form thin film membranes, good electrode-electrolyte interfacial contacts and reasonably good ionic conductivity [Sekhon *et al.,* 1995]. Low cost packaging and low cost fabrication of electrochemical devices such as lithium ion batteries can be expected when the liquid electrolyte has been replaced by polymer electrolyte [Mahendran and Rajendran, 2003]. For use in devices [Kumar and Sekhon, 2002a], polymer electrolytes should have high ambient ionic conductivity, poor electronic conductivity, high mechanical strength, good chemical stability and easy to process.

## 2.3 Proton Conducting Polymer Electrolytes

Proton conducting polymer electrolytes normally consist of polymer (host) and salt (proton or $H^+$ source) to provide the charge carriers. Polymers that have been used as a host material are poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(methyl methachrylate) (PMMA) and chitosan. Apart from the properties mentioned previously, Reiter *et al.,* (2008) added that proton conducting polymer electrolytes must also have good thermal and interfacial stability. Examples of proton conducting polymer electrolytes are listed in Table 2.1

**Table 2.1: Examples of proton conducting polymer electrolytes.**

| Electrolyte composition | Conductivity (S $cm^{-1}$) | Reference |
|---|---|---|
| PEO-$(NH_4)_2SO_4$ | $9.3 \times 10^{-7}$ | Maurya *et al.,* (1992a) |
| PEO-$NH_4I$ | $\sim 10^{-5}$ | Maurya *et al.,* (1992b) |
| PEO-$NH_4SCN$ | $\sim 10^{-6}$ | Srivastava *et al.,* (1995) |
| PESc-$NH_4ClO_4$ | $\sim 10^{-7}$ | Srivastava and Chandra, (2000) |
| PEO-$NH_4ClO_4$ + PC | $\sim 10^{-4}$ | Pratap *et al.,* (2006) |
| Cellulose acetate-$NH_4CF_3SO_3$-EC | $1.19 \times 10^{-4}$ | Saaid *et al.,* (2009) |

$(NH_4)_2SO_4$ – Ammonium Sulfate

$NH_4SCN$ – Ammonium thiocyanate

PC – Propylene carbonate

PESc – Poly(ethylene succinate)

| | |
|---|---|
| EC – Ethylene carbonate | $NH_4CF_3SO_3$ – Ammonium triflate |
| $NH_4I$ – Ammonium Iodide | PEO – Poly(ethylene oxide) |
| $NH_4ClO_4$ – Ammonium perchlorate | |

## 2.4 Models for Ionic Conduction

According to Selvasekarapandian *et al.,* (2005a) information on salt-polymer interaction can be understood from the dependence of ionic conductivity on the salt concentration. Factors that affect conductivity include temperature, type and concentration of salt. It is crucial to optimize the ionic conductivity, σ and the charge mobility, $\mu$ in an electrolyte since the conductivity and mobility are related by the equation:

$$\sigma = \sum \eta_m q_m \mu_m \tag{2.1}$$

Here $\eta_m$, $q_m$ *and* $\mu_m$ are the number density, charge and the mobility of charge carriers of type *m* respectively. Electrical conductivity is the most important property of a solid electrolyte, in particular its relationship with temperature [Ratner, 1987]. Conductivity-temperature relationship can follow:

- Arrhenius behavior
- Vogel Tamann Fulcher (VTF) behavior

### 2.4.1 Arrhenius Behavior

There are lots of works reporting Arrhenius relationship between conductivity and temperature for polymer electrolytes. The Arrhenius equation can be represented as:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \tag{2.2}$$

Here, $\sigma_o$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is the Boltzmann constant and $T$ is the absolute temperature. The use of the equation can be made when plots of log σ versus 1000/T show a linear relationship. Buraidah *et al.*, (2009) have reported that the conductivity-temperature relationship of chitosan-$NH_4I$ polymer electrolytes follow Arrhenius equation. This is depicted in Figure 2.1.

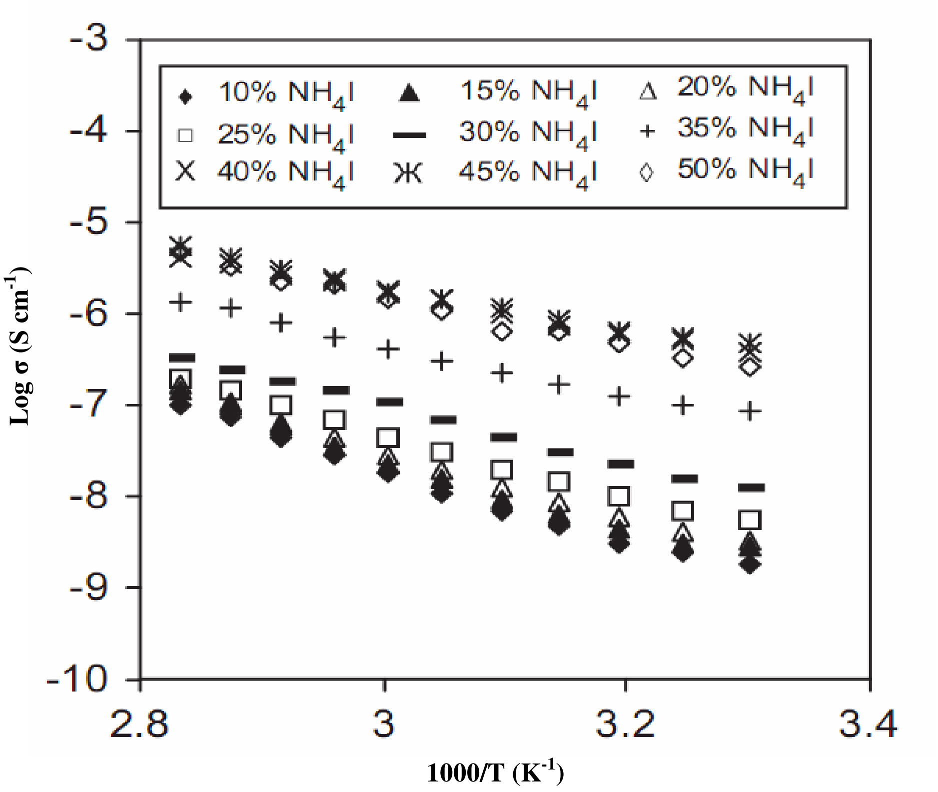

**Figure 2.1: Conductivity-temperature dependence for chitosan-$NH_4I$** [Buraidah *et al.,* 2009].

### 2.4.2 Vogel-Tamann-Fulcher (VTF) Behaviour

The VTF equation is given as:

$$\sigma = \sigma_o T^{-\frac{1}{2}} \exp\left[\left(\frac{-B}{k(T_o - T)}\right)\right] \tag{2.3}$$

Here, $\sigma_o$ is the pre exponential factor, $B$ is the pseudoactivation energy of the ion and $T_o$ is the thermodynamic glass transition or the ideal glass transition temperature. Shuhaimi *et al.,* (2009) reported that the plot of log σ versus 1000/T for the methyl cellulose-$NH_4NO_3$ system follows VTF equation, Figure 2.2.

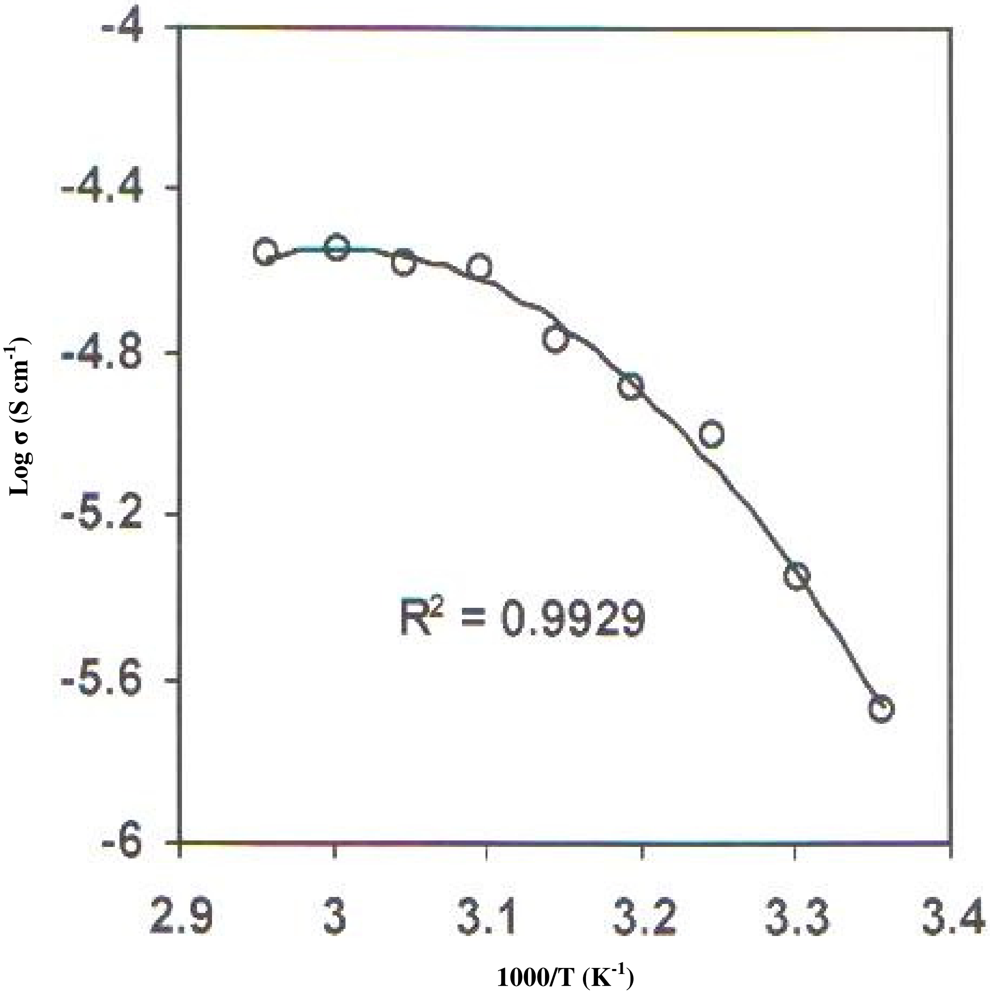

**Figure 2.2: Conductivity-temperature dependence for highest conducting film in methyl cellulose-$NH_4NO_3$ complex system** [Shuhaimi *et al.,* 2009].

According to Mohamed *et al.,* (2008), the non-linearity of the conductivity with temperature shows that ion transport obeys the VTF rule indicating that conductivity depends on the existence of free volume [Bohnke *et al.,* 1993]. The existence of the free volume is a result of segmental motions. The ions will diffuse into this free volume when electrical field is applied [Bruce and Vincent, 1993].

### 2.4.3 Activation Energy ($E_a$)

In order for an ion to begin its movement, energy is required. The energy can be obtained from its environment or through heat supplied. When the ion has gained enough energy to detach from its initial site, it becomes a "free ion". The energy possessed by the ions is called the activation energy.

As the conductivity of sample increases, it can be noticed that $E_a$ decreases indicating that the ions in highly conducting samples require lower energy for migration. The calculation of the activation energy can be made by using the Arhenius equation as in Equation (2.2) if the log $\sigma$ versus 1000/T plot is a straight line and an example of activation energy relationship with conductivity is given in Figure 2.3. From the work on chitosan-ammonium triflate by Khiar *et al.,* (2006), it can be observed that the highest conducting sample at 50 wt. % of $NH_4CF_3SO_3$ possessed the lowest activation energy.

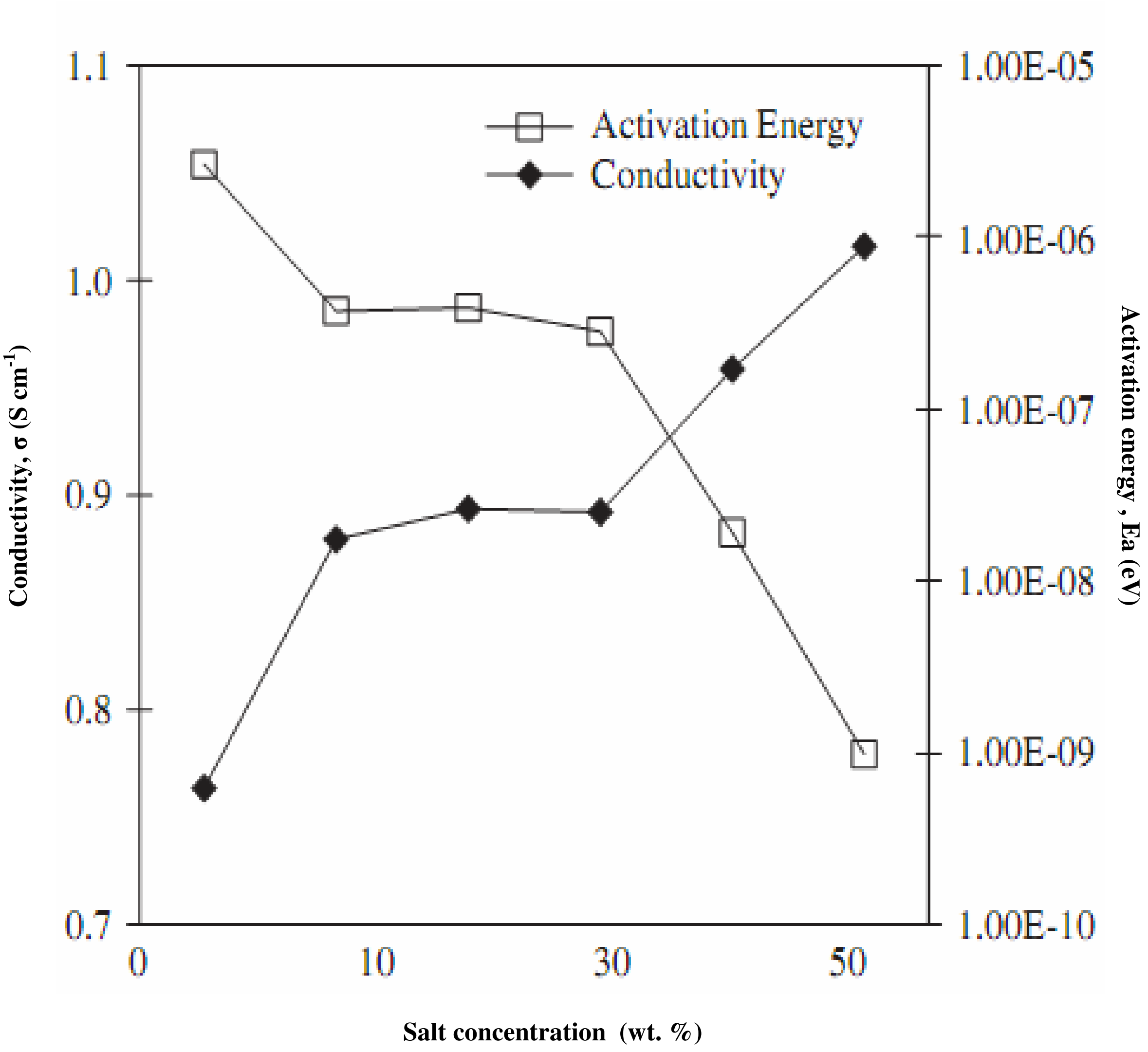

**Figure 2.3: Activation energy and room temperature conductivity variation with $NH_4CF_3SO_3$ concentration** [Khiar *et al.,* 2006].

### 2.4.4 Grotthus Mechanism in Proton Conducting Polymer Electrolyte

The mobile ionic species in polymer electrolytes are cations and anions. In polymer-ammonium salt system, the cation is the proton [Chandra *et al.,* 1989]. It was reported by Srivastava and Chandra, (2000) and Hashmi *et al.,* (1990) that $H^+$ is the conducting species in poly(ethylene succinate) complexed with ammonium perchlorate and in PEO-$NH_4ClO_4$ systems. The $NH_4^+$ cations have ideal tetrahedral structure as depicted in Figure 2.4. The hydrogen atom that is most weakly bound to the nitrogen atom in $NH_4^+$ ion can dissociate easily under the influence of an electric field.

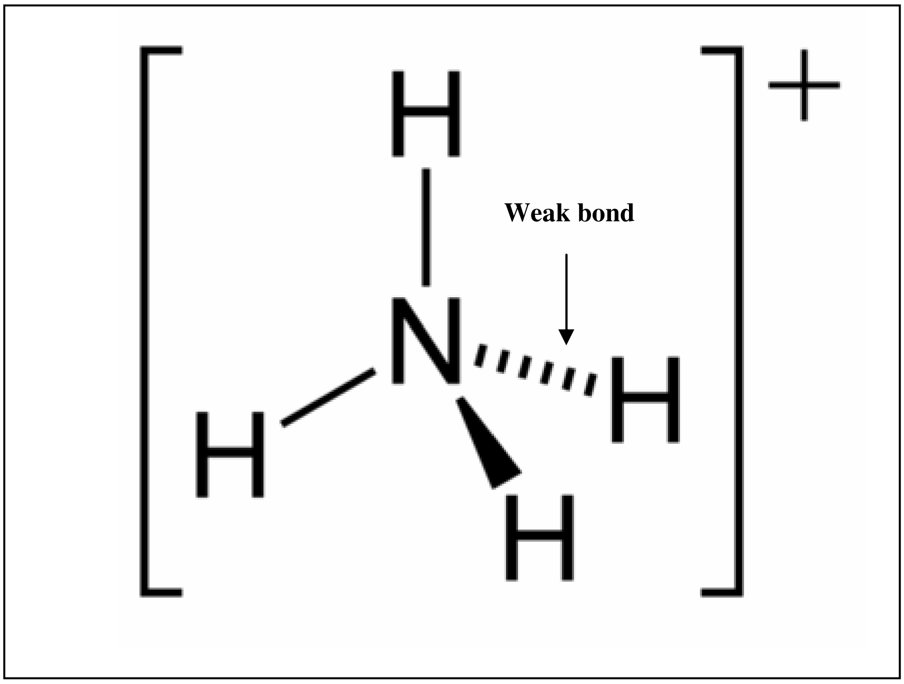

**Figure 2.4: Structure of $NH_4^+$ cation.**

The vacancy in the $NH_4^+$ structure that resulted from $H^+$ migration will be filled by another $H^+$ ion from a neighboring site [Buraidah *et al.,* 2009]. This is the Grotthus mechanism, where conduction occurs through proton exchange between the polymer-salt complexed sites. In an earlier report, Hema *et al.,* (2007, 2008) also suggested proton migration ($H^+$) mechanism in PVA-ammonium bromide polymer electrolyte. The $H^+$ ion is coordinated with the oxygen (coordinating site) of the polymer host (PVA). $H^+$ ion transport mechanism was also reported in chitosan-ammonium triflate by Khiar, (2006) and the schematic diagram of the mechanism may be depicted in Figure 2.5.

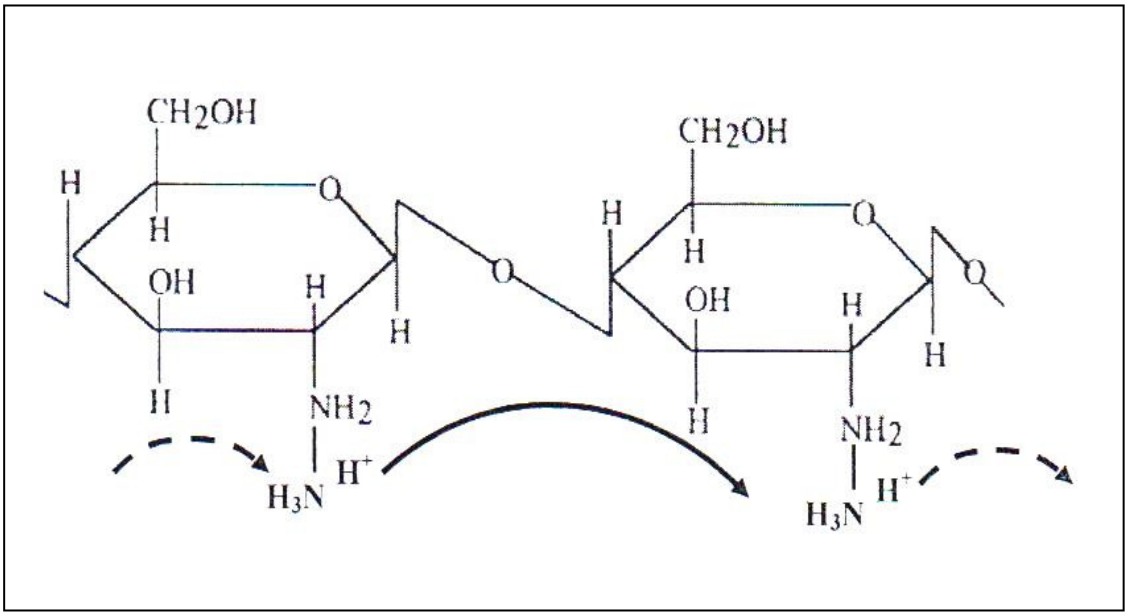

**Figure 2.5: $H^+$ ion transport mechanism in chitosan-salt system** [Khiar, 2006].

## 2.5 Chitosan

Chitosan is a natural polymer that can be obtained from the mollusc shell and its chemical structure (1→4)-2amino-2-deoxy-β-D-glucan, contains *N*-deacetylated derivatives of chitin, (1→4)-2-acetamido-2-deoxy-β-D-glucan [Majeti and Ravi, 2000; Rhazi *et al.,* 2002; Desbrieres *et al.,* 1996]. Chitosan is popular for its biocompatible and biodegradable properties [Mi *et al.,* 2002]. The chemical structures of chitin and chitosan are depicted in Figure 2.6 and 2.7 respectively.

Chitosan has been extensively used in a wide range of applications such as membrane separation in medicine and biotechnology [Aiba *et al.,* 1986], chelation of heavy metals and radioisotopes for prevention of water pollution [Muzarelli, 1977], as food packaging materials because of its antimicrobial action [Ghaouth *et al.,* 1991] and dietary fiber and a potential medicine against hypertension [Furda and Brine, 1990]. Polymer electrolyte based on chitosan has been widely studied [Osman *et al.,* 2001; Osman and Arof, 2003; Yahya and Arof, 2003, 2004; Majid and Arof, 2005; Khiar *et* *al.,* 2006] and has potential for application in electrochemical devices such as battery [Subban *et al.,* 1996; Mohamed *et al.,* 1995; Morni and Arof, 1999]. Donoso *et al.,* (2007) have shown that the nitrogen atoms in chitosan serve as complexation sites for cation coordination.

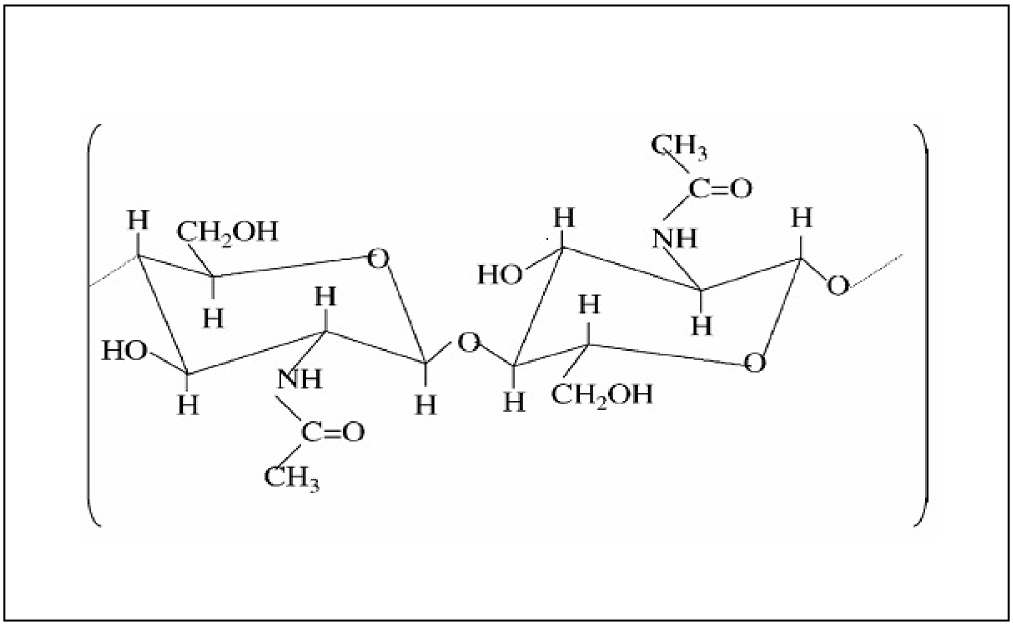

**Figure 2.6: Structure of chitin** [Wan *et al.,* 2003].

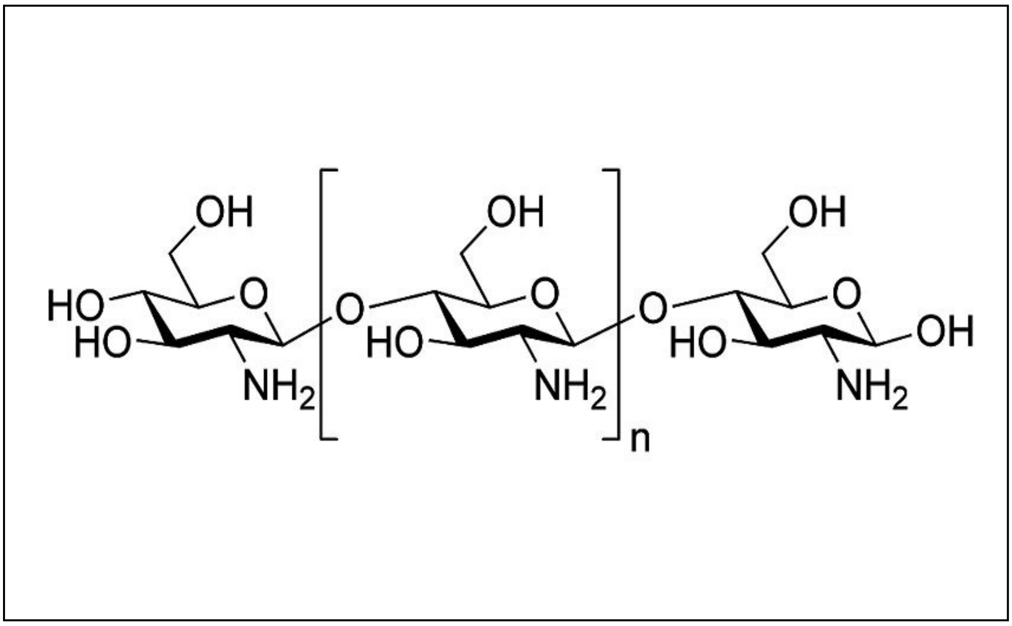

**Figure 2.7: Structure of chitosan.**

### 2.5.1 Chitosan Based Proton Conducting Polymer Electrolyte

Chitosan can serve as a polymer host for ionic conduction as it is able to solvate ionic salts [Fuentes *et al.,* 2003; Morni *et al.,* 1999; Yahya and Arof, 2003]. When chitosan membrane is swollen with water, its amino group maybe protonated. This can lead to protonic conductivity [Chávez *et al.,* 2005]. Donoso *et al.,* (2007) have shown that the nitrogen atoms in chitosan serve as complexation sites for cation coordination. Majid and Arof, (2005) have reported that with addition of 45 wt.% of $NH_4NO_3$ to the chitosan, the carbonyl and amine bands in their infrared spectrum has shifted to lower wavenumbers and due to that they have concluded that complexation has occurred. The examples of chitosan based proton conducting polymer electrolytes are shown in Table 2.2.

**Table 2.2: Examples of chitosan based proton conducting polymer electrolytes.**

| Electrolyte composition | Conductivity (S $cm^{-1}$) | Reference |
|---|---|---|
| Chitosan-$NH_4CF_3SO_3$ | $8.91 \times 10^{-7}$ | Khiar, (2006) |
| Chitosan-$NH_4NO_3$ | $2.53 \times 10^{-5}$ | Majid and Arof, (2005) |
| Chitosan-$H_3PO_4$ | $4.9 \times 10^{-4}$ | Majid and Arof, (2007) |
| Chitosan-$NH_4I$ | $3.7 \times 10^{-7}$ | Buraidah *et al.,* (2009) |
| Chitosan-$NH_4I$-EC | $7.6 \times 10^{-6}$ | Buraidah *et al.,* (2009) |
| Chitosan-$NH_4I$-BMII | $8.47 \times 10^{-4}$ | Buraidah *et al.,* (2010) |

$NH_4CF_3SO_3$ – Ammonium triflate

$H_3PO_4$ – Orthophosphoric acid

EC – Ethylene carbonate

BMII – 1-butyl-3-methylimidazolium iodide

$NH_4I$ – Ammonium iodide

$NH_4NO_3$ – Ammonium nitrate

### 2.5.2 Application of Chitosan Based Proton Conducting Polymer Electrolyte in Electrochemical Devices

Today, polymer electrolyte based on chitosan has been extensively studied and was observed to have a good conductivity value. To obtain cheap electrochemical devices, the material used also has to be considerably cheap and chitosan is one of the good candidates. Also due to its good mechanical strength, chitosan based proton conducting polymer electrolyte has good potential for application in electrochemical devices such as proton batteries, electric double layer capacitors, fuel cells and solar cells. Examples of electrochemical devices based on chitosan proton conducting polymer electrolytes is listed in Table 2.3

**Table 2.3: Examples of electrochemical devices based on chitosan based proton conducting polymer electrolytes.**

| Electrochemical devices | Electrolyte composition | Reference |
|---|---|---|
| Proton battery | Chitosan-$NH_4NO_3$-EC | Ng and Mohamad, (2006) |
| Electric double layer capacitor (EDLC) | Chitosan-$H_3PO_4$-$NH_4NO_3$ | Arof and Majid, (2008) |
| Fuel cell | Chitosan-$H_3PO_4$-$Al_2SiO_5$ | Majid and Arof, (2009) |
| Solar cell | Chitosan-$NH_4I$-BMII | Buraidah *et al.,* (2010) |

$Al_2SiO_5$ – Alumino silicate

$H_3PO_4$ – Orthophosphoric acid

EC – Ethylene carbonate

BMII - 1-butyl-3-methylimidazolium iodide

$NH_4I$ – Ammonium iodide

## 2.6 Poly(vinyl alcohol) PVA

PVA is a carbon chain backbone polymer with hydroxyl groups attached to the methylene carbons [Rajendran and Mahendran, 2001]. It is semi-crystalline. PVA is a low cost polymer with good mechanical properties. It is highly hydrophilic, non-toxic and exhibits good thermal and chemical stability. It has excellent film forming properties [Yang *et al.,* 2009]. Besides that, PVA has a hydroxyl group that produces inter and intra-molecular hydrogen bonding [Masuda, 1991; Briscoe *et al.,* 2000]. PVA is biocompatible, non toxic and exhibits minimal cell adhesion and protein absorption. PVA membrane was reported to have good application in the biomedical field [Koyano *et al.,* 2000]. Due to solubility and biodegradability, PVA films are also used as packaging materials [Alexy *et al.,* 2002]. Schematic diagram of chemical structure of PVA is depicted in Figure 2.8.

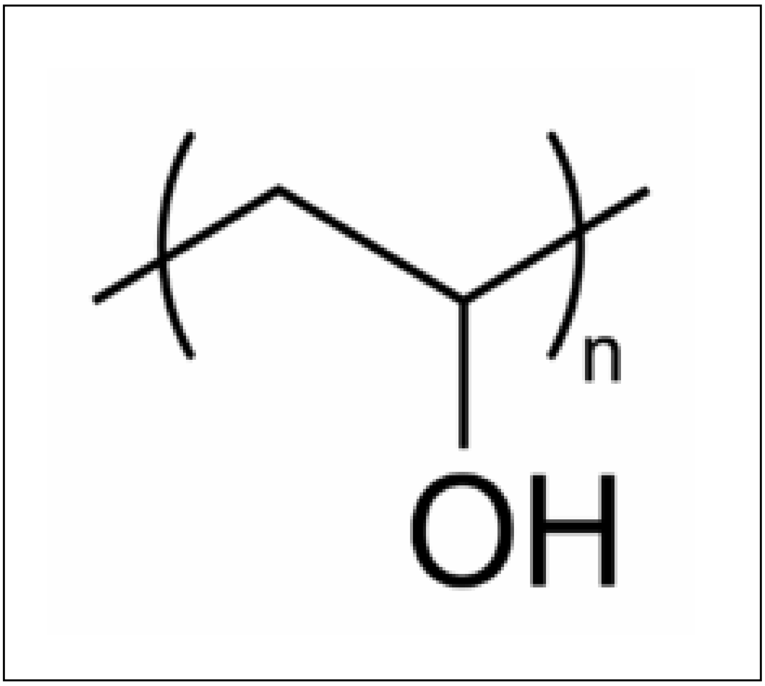

**Figure 2.8: Structure of PVA.**

### 2.6.1 PVA Based Proton Conducting Polymer Electrolyte

PVA has good film forming abilities and the mechanical strength is also good. Towards supporting the green energy, PVA has been chosen by lots of researchers all over the world to become a host for polymer electrolyte since it is water soluble and it is biodegradable, more over polymer electrolyte based on PVA has been reported to exhibit a good conductivity value. Hema *et al.,* (2008, 2009a, 2009b) have shown that in PVA based polymer, the conduction takes place when the proton source from the salt hops along the oxygen atom coordinating site of the polymer. Table 2.4 shows some examples of proton conducting polymer electrolytes based on PVA.

**Table 2.4: Examples of PVA based proton conducting polymer electrolytes.**

| SPE composition | Conductivity (S $cm^{-1}$) | Reference |
|---|---|---|
| PVA-$CF_3SO_3H$-$H_2O$ | ~ $10^{-2}$ | Lewandowski and Skorupska, (2001a) |
| PVA-$CH_3COONH_4$ | 5.62 x $10^{-6}$ | Hirankumar *et al.,* (2005) |
| PVA-$H_3PO_4$ | ~ $10^{-4}$ | Kufian *et al.,* (2007) |
| PVA-$NH_4Br$ | 5.7 x $10^{-4}$ | Hema *et al.,* (2008) |
| PVA-$NH_4I$ | 2.5 x $10^{-3}$ | Hema *et al.,* (2009a) |
| PVA-$NH_4Cl$ | 1.0 x $10^{-5}$ | Hema *et al.,* (2009b) |

$CH_3COONH_4$ – Ammonium acetate
$H_3PO_4$ – Orthophosphoric acid
$NH_4I$ – Ammonium iodide
$CF_3SO_3H$ – Trifluoromethane sulfonic acid
$NH_4Br$ – Ammonium bromide
$NH_4Cl$ – Ammonium chloride
$H_2O$ – Water

### 2.6.2 Application of Polymer Electrolyte Based on PVA in Electrochemical Cells

In order to build any electrochemical device, cost of the materials must be reasonable and cheap. PVA is a cheap polymer [Martinelli *et al.,* 2006]. Hence the cost of fabricating any electrochemical devices based on PVA can be reduced. Polymer electrolyte based on PVA has been reported to exhibit good conductivity [Hema *et al.,* 2008, 2009(a), 2009(b)]. Besides that, PVA based electrolyte is favorable in the application of electrochemical devices simply because PVA has a good mechanical strength [Yang *et al.,* 2006]. Polymer electrolyte based on PVA is potentially employed in the application of electrochemical devices such as lithium battery [Subramania *et al.,* 2006], Zn/AgO battery [Vatsalarani *et al.,* 2009] zinc-nickel battery [Wu *et al.,* 2008], nickel-MH battery [Mohamad, 2005], and capacitors, [Yang *et al.,* 2005]. Examples of electrochemical devices based on PVA proton conducting polymer electrolytes are listed in Table 2.5.

**Table 2.5: Examples of electrochemical devices based on PVA based proton conducting polymer electrolytes.**

| Electrolyte composition | Application | Reference |
|---|---|---|
| PVA-$H_2SO_4$-$H_2O$ | EDLC | Lewandowski and Galinski, (2001b) |
| PVA-$H_3PO_4$ | Fuel cell | Ramesh *et al.,* (2003) |
| PVA/SSA | Fuel cell | Yang *et al.,* (2006) |
| (PVA)-$H_4SiW_{12}O_{40}$ | Capacitor | Lian and Li, (2009) |

$H_4SiW_{12}O_{40}$ – Silicotungstic acid
$H_2SO_4$ – Sulfuric acid
$H_3PO_4$ – Orthophosphoric acid
SSA – Sulfosuccinic acid
$H_2O$ – Water

## 2.7 Polymer Blend

A blend is formed when two or more different polymers are mixed together without covalent bond formation. A blend can be formed by dissolving the polymers in a common solvent followed by evaporation of the solution. Materials with different properties from the parent polymers can be obtained. Other methods have been described by Neto *et al.,* (2005).

Polymer blends have attracted the concern of many researchers due to the possibility of developing new materials with properties that could not be obtained with the use of a single polymer [Acosta *et al.,* 1996]. The properties exhibited by polymer blends are better than those exhibited by single polymers [Sandoval *et al.,* 2005]. It has been reported that the conductivity of a polymer electrolyte can be improved if the host is a blend of two polymers [Rajendran and Mahendran 2001; Inganàs, 1987; Kim *et al.,* 1996]. Polymer blending is one of the methods suggested to guarantee structural stability [Sivakumar *et al.,* 2006]. Examples of polymer blend based electrolytes are listed in Table 2.6.

**Table 2.6: Examples of electrolytes based on polymer blend.**

| Electrolyte composition | Conductivity (S $cm^{-1}$) | Reference |
|---|---|---|
| PMMA/PVA-$LiClO_4$-DMP | $6.0 \times 10^{-5}$ | Rajendran and Mahendran, (2001) |
| PVC/PMMA-$Li_2SO_4$-DBP | $1.24 \times 10^{-8}$ | Uma *et al.,* (2003) |
| PMMA/PVdF- DMP-$LiCF_3SO_3$ | $9.1 \times 10^{-4}$ | Mahendran and Rajendran, (2003) |
| PVP/PVA-$KIO_3$ | $1.22 \times 10^{-4}$ | Subba Reddy *et al.,* (2003) |
| PVC/PVdF-$NaClO_4$-PC | $9.24 \times 10^{-4}$ | Subba Reddy *et al.,* (2007) |
| PVdF/PVC-$LiClO_4$-EC/PC | $3.68 \times 10^{-3}$ | Rajendran and Sivakumar, (2008) |
| PANI/PVF-DBSA | $2.5 \times 10^{-4}$ | Ebrahim *et al.,* (2009) |

PMMA – Poly(methyl methacrylate)
PVC – Poly(vinyl chloride)
PANI – Poly(aniline)
PVF – Poly(vinyl formal)
PVdF – Poly(vinylidene fluoride)
PC – Propylene carbonate
PVP – Poly(vinyl pyrrolidone)
DBP – Dibutyl phthalate
PVA – Poly(vinyl alcohol)

$NaClO_4$ – Sodium perchlorate
$LiClO_4$ – Lithium perchlorate
DBSA - Dodecylbenzene sulfonic acid
$LiCF_3SO_3$ – Lithium triflate
EC – Ethylene carbonate
$KIO_3$ – Potassium iodate
$Li_2SO_4$ – Lithium sulfate
DMP – Dimethyl pthalate

### 2.7.1 Polymer Electrolyte Based on Chitosan Blend

Polymer blends can be formed using chitosan as one of the component polymers [Sandoval *et al.,* 2005]. Chitosan has many functional groups [Muzarelli, 1997; Zong *et al.,* 2000]. Mucha *et al.,* (1998) reported that blends of chitosan and PEO and chitosan with PVA exhibit a good mechanical strength.

Many laboratories including ours have studied chitosan blend based films, [Mohamad *et al.,* 2007a, 2007b; Idris *et al.,* 2007; Shuhaimi *et al.,* 2008; Abdul Kadir *et al.,* 2009] and it was reported that polymer electrolyte based on chitosan blend has good potential in the application of electrochemical cells such as solar cells [Mohamad *et al.,* 2006; 2007a; 2007b] and electric double layer capacitors [Shuhaimi *et al.,* 2008]. Examples of polymer electrolytes based on chitosan blends are listed in Table 2.7.

**Table 2.7: Examples of chitosan polymer blend based electrolytes.**

| SPE composition | Conductivity (S $cm^{-1}$) | Reference |
|---|---|---|
| Chitosan/PEO-$NH_4I$ | $4.32 \times 10^{-6}$ | Mohamad *et al.,* (2007a) |
| Chitosan/PEO-LiTFSI | $1.40 \times 10^{-6}$ | Idris *et al.,* (2007) |
| Chitosan/κ-carragenan-$NH_4NO_3$ | $2.39 \times 10^{-4}$ | Shuhaimi *et al.,* (2008) |
| Chitosan/PEO-$NH_4NO_3$-ES | $3.01 \times 10^{-4}$ | Abdul Kadir *et al.,* (2009) |
| Chitosan/PVA-$LiCF_3SO_3$-(L-Leucine) | $1.27 \times 10^{-4}$ | Razak *et al.,* (2009) |

ES – Ethylene sulfite
LiTFSI – Lithium trifluoromethane sulfonimide
$LiCF_3SO_3$ – Lithium triflate
PEO – Poly(ethylene oxide)
$NH_4I$ – Ammonium iodide
$NH_4NO_3$ – Ammonium nitrate

### 2.7.1.1 Chitosan-PVA Polymer Blend

Pure chitosan based fiber and films are relatively brittle and to make the chitosan based film more elastic is a topical problem [Bel'nikevich *et al.,* 2004]. It has been proposed that improvements on performance of polymers can be obtained by modifying polymers with other polymers [Mahendran and Rajendran, 2003; Bel'nikevich *et al.,* 2004]. Blending allows preparation of systems with properties significantly different from those of the starting components, without sophisticated chemical modification procedures or synthesis of new macromolecular compounds.

Chitosan-PVA blend has been studied by researchers all over the world and results show enhancement in the mechanical characteristics of films prepared [Mukhina *et al.,* 2001]. The blend between chitosan and PVA exhibits good mechanical strength [Mucha *et al.,* 1998]. It has been reported that the strong intermolecular interactions that would lead to a formation of interpolymeric complexes do not occur in blends based on chitosan-PVA film and the experiment on the sorption of solvent vapor showed that chitosan and PVA are compatible [Bel'nikevich *et al.,* 2004]. Miya *et al.,* (1984) have reported that chitosan forms a clear homogeneous blend with polyvinyl alcohol (PVA) suitable for polymer membranes. Razak *et al.,* (2009) has reported that the chitosan-PVA blend can be a polymer host for $Li^+$ ion conduction. Jiang *et al.,* (2008) has fabricated a direct methanol fuel cells (DMFC) using PVA-chitosan blend membrane as a barrier materials.

## 2.8 Acetic Acid

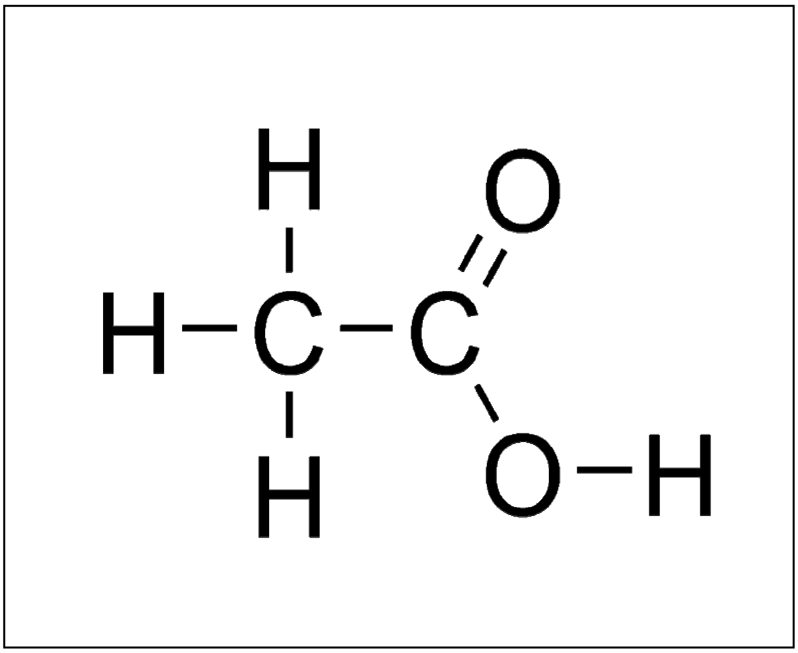

**Figure 2.9: Structure of acetic acid ($C_2H_4O_2$).**

The Latinized word for "acetic" is *acetum*, meaning "vinegar". It is a carboxylic acid with chemical formula $C_2H_4O_2$, often written as $CH_3COOH$ and the structure is depicted in Figure 2.9. Acetic acid has become a common solvent for polymers. Chitosan can be dissolved in dilute acetic acid [Khiar *et al.,* 2006; Buraidah *et al.,* 2009, 2010]. Majid and Arof, (2005) have reported that acetic acid and chitosan can form chitosan-acetic acid salt. Polymer blending method using dilute acetic acid as solvent also has been reported to exhibit a good mechanical strength [Bel'nikevich *et al.,* 2004].

## 2.9 Plasticization

The conductivity of polymer electrolytes can be enhanced with the addition of plasticizers [Mahendran *et al.,* 2005; Yang *et al.,* 1990; Song *et al.,* 1999]. The examples of plasticizers are ethylene sulfite, ethylene carbonate, propylene carbonate and polyethylene glycol. The addition of a plasticizer to a polymer-salt complex can increase amorphousness and segmental mobility of the polymer and lower $T_g$ [Hardy and Shriver, 1984; Pitawala *et al.,* 2008]. Plasticizers should have low viscosity, low melting point and high dielectric constant.

Low viscosity plasticizers help to increase mobility of carriers and plasticizers with low melting point result in an increase in the amorphous content of the polymer electrolytes. High dielectric constant plasticizers can help to dissociate the salt [Osman *et al.,* 2001]. Plasticizers with dielectric constant lower than that of the polymer may not help to dissociate the salt significantly that the conductivity remains low. Lowering $T_g$ increases local chain flexibility and ionic mobility resulting in conductivity enhancement. Kumar and Sekhon, (2002b) have summarized that plasticizers should have dielectric constant higher than the host polymer, have good miscibility with polymer-salt complexes, high donor numbers [Kim *et al.,* 2000], low freezing temperature, high boiling temperature and must be stable towards electrode materials.

The use of plasticizer in polymer electrolyte is one of the easiest and the most practical way to obtain an optimum conductivity value. Examples of various type of plasticizers in polymer electrolytes are tabulated in Table 2.8.

**Table 2.8: Examples of polymer electrolytes with various plasticizers.**

| SPE composition | Conductivity (S cm$^{-1}$) | Reference |
|---|---|---|
| PEO-LiClO$_4$-DOP | $9.755 \times 10^{-5}$ | Michael *et al.,* (1997) |
| PEO-LiClO$_4$-DMP | $1.762 \times 10^{-5}$ | Michael *et al.,* (1997) |
| PVC-PMMA-LiBF$_4$-DBP | $2.482 \times 10^{-5}$ | Rajendran and Uma, (2000) |
| PVP-PVA-KClO$_3$-DMF | $7.4 \times 10^{-7}$ | Subba Reddy *et al.,* (2002) |

**Table 2.8 continued……**

| | | |
|---|---|---|
| PDMAEMA-PEO-LiTFSI-Tetraglyme | 4.74 x $10^{-4}$ | Cha *et al.,* (2004) |
| (PVdF-HFP)-OA-DMA | 1.2 x $10^{-4}$ | Missan *et al.,* (2006) |
| PMMA-grafted natural rubber-$NH_4CF_3SO_3$-PC | 3.29 x $10^{-2}$ | Kamisan *et al.,* (2009) |

PVP- Poly(vinyl pyrrolidone)
$KClO_3$ – Potassium chlorate
DMF – Dimethyl formamide
PVdF-HFP – Polyvinylidinefluoride-co-hexafluoro propylene
DMA – Dimethylacetamide
OA – Oxalic acid
PDMAEMA – Poly(*N,N*-dimethylamino-ethyl-methacrylate)
LiTFSI – Lithium triluoromethane sulfonimide
Tetraglyme – Tetraethylene glycol dimethyl ether
$LiClO_4$ – Lithium perchlorate
PVC – Poly(vinyl chloride)
$LiBF_4$ – Lithium tetrafluoroborate
PMMA – Poly(methyl methacrylate)
DBP – Dibuthyl pthalate
DOP – Dioctyl pthalate
DMP – Dimethyl pthalate
PEO – Poly(ethylene oxide)
$NH_4CF_3SO_3$ – Ammonium triflate
PC – Propylene carbonate

### 2.9.1 Ethylene Carbonate (EC) as Plasticizer

According to Ramesh *et al.,* (2007), one of the factors that enhanced conductivity on addition of EC is the increase in flexibility of the polymer electrolyte. EC has a donor number of 16.4 [Kim *et al.,* 2000]. It has a relatively low viscosity. Hence, the addition of EC to a polymer-salt system can decrease local viscosity in the vicinity of the transporting ions leading to mobility enhancement.

The high dielectric constant of EC can weaken the force of attraction between the cation and anion of the salt and finally results in salt dissociation [Wintersgill, 1987]. Hence more undissociated salt become ions. According to Pitawala *et al.,* (2008), the addition of low molecular weight and high dielectric constant plasticizers increases the amorphous phase, flexibility of the polymer segment and the number of mobile charge carriers that contribute to conductivity.

Osman *et al.,* (2001) have proven that plasticized chitosan based polymer electrolyte exhibited a higher conductivity value when EC added and the conductivity enhancement was due to ion dissociation. The use of EC also can reduce the crystallinity of the polymer electrolyte hence enhancing conductivity [Suthanthiraraj *et al.,* 2009; Pitawala *et al.,* 2007]. Chintapalli and Frech, (1996) have proven that the addition of plasticizer such as EC increases the amorphousness of the crystalline region of PEO polymer matrix that leads to the increase in conductivity value. Table 2.9 shows some examples of plasticized polymer electrolytes with EC.

**Table 2.9: Examples of polymer electrolytes with EC as plasticizer.**

| SPE composition | Conductivity (S cm$^{-1}$) | Reference |
|---|---|---|
| Chitosan-$LiCF_3SO_3$-**EC** | $3.0 \times 10^{-4}$ | Morni and Arof, (1999) |
| PVA-PMMA-$LiBF_4$-**EC** | $1.2886 \times 10^{-3}$ | Rajendran *et al.,* (2003) |
| PMMA-PEO-**EC**-$LiPF_6$ | $\sim 10^{-6}$ | Osman *et al.,* (2005) |
| PEO-$LiCF_3SO_3$-**EC**-$Al_2O_3$ | $1.5 \times 10^{-4}$ | Pitawala *et al.,* (2007) |
| PMMA-**EC**-$LiCF_3SO_3$ | $3.40 \times 10^{-5}$ | Othman *et al.,* (2007) |
| H-chitosan-$LiCF_3SO_3$-**EC**-$Al_2O_3$ | $1.01 \times 10^{-4}$ | Muhammad *et al.,* (2009) |
| PVdF-$AgCF_3SO_3$-**EC** | $1.5 \times 10^{-4}$ | Suthanthiraraj *et al.,* (2009) |
| PVC-PEO-$LiCF_3SO_3$-DBP-**EC**-$SiO_2$ | $\sim 10^{-4}$ | Ramesh and Arof, (2009) |

H-chitosan – Hexanoyl chitosan

$LiCF_3SO_3$ – Lithium triflate

PVdF – Poly(vinylidine fluoride)

$AgCF_3SO_3$ – Silver triflate

PEO – Poly(ethylene oxide)

PMMA – Poly(methyl methacrylate)

PVA – Poly(vinyl alcohol)

$Al_2O_3$ – Alumina

PVC – Poly(vinyl chloride)

DBP – Dibuthylpthalate

$SiO_2$ – Silicon dioxide

$LiPF_6$– Lithium hexafluorophosphate

$LiBF_4$ – Lithium tetrafluoroborate

## 2.10 Solid-State Battery

Lithium and proton batteries based on solid polymer electrolytes have been widely developed [Pratap *et al.,* 2006; Ng and Mohamad, 2006, 2008; Saaid *et al.,* 2009] due to the fact that solid state batteries have great potential towards becoming a new source of energy. The use of solid polymer electrolyte (SPE) in electrochemical devices is a good attempt to overcome many problems or disadvantages, of liquid electrolyte which includes [Armand *et al.,* 1979]:

- difficulty in handling,
- leakage
- corrosion
- low power density
- limited shelf or cycle life

According to Mohamad, (2005), the use of solid polymer electrolyte is suggested to prevent the abrupt degradation of electrodes i.e. in Ni-MH cell. Examples of solid state batteries are listed in Table 2.10.

**Table 2.10: Examples of solid-state batteries.**

| Type of solid state batteries | Electrolyte composition | Reference |
|---|---|---|
| Rechargeable lithium battery | Chitosan-EC-$LiCF_3SO_3$ | Morni and Arof, (1999) |
| Alkaline battery | P(ECH-co-EO) - KOH | Vassal *et al.,* (2000) |
| Rechargeable lithium battery | PEO-PEGDME | Kang *et al.,* (2001) |
| Lithium battery | PEO-$LiN(CF_3SO_2)_2$-$LiPF_6$-$BaTiO_3$ | Li *et al.,* (2002) |
| Lithium battery | PEO-$LiCF_3SO_3$-$ZrO_2$ | Fiory *et al.,* (2004) |

PEGDME – Poly(ethylene glycol) dimethylether $ZrO_2$ – Zirconium oxide

| | |
|---|---|
| PEO – Poly(ethylene oxide) | $LiPF_6$ – Lithium hexafluorophosphate |
| $LiCF_3SO_3$ – Lithium triflate | KOH – Pottassium hydroxide |
| $LiN(CF_3SO_2)_2$ – Lithium bis(trifluoromethanesulfonyl) imide | $BaTiO_3$ – Barium titanate |
| P(ECH-co-EO) – Copolymers epichlorohydrin with ethylene oxide | |
| EC – Ethylene carbonate | |

## 2.11 Proton ($H^+$ ion) Battery

Currently, many methods have been used to construct and develop all solid state batteries since these types of batteries have many appealing features such as fabrication, no leakage, long cycle-life, flexibility in size, and safety and have a wide temperature operating range. On top of that, many applications such as cellular phones, notebook computers and also medical instruments require high power and high specific energy batteries. On the other hand, in spite of a smaller electrochemical stability window (~ 1 V) [Pratap *et al.,* 2006], proton batteries are considered cost-effective alternative compared to $Li^+$ batteries which is generally high (~ 4 V) thus giving advantage to the former on the basis of energy density consideration. Proton battery consists of an anode that can supply protons into electrolyte and the cathode [Pratap *et al.,* 2006]. A rechargeable proton battery is possible because the intercalation efficiency for small ions is generally high [Pandey *et al.,* 1998]. The ability of the proton to intercalate and deintercalate in and out of the cathode is important for the battery to be rechargeable [Pandey *et al.,* 1998]. Examples of $H^+$ ions solid state batteries are listed in Table 2.11.

**Table 2.11: Examples of $H^+$ ion solid-state batteries.**

| Type of solid state batteries | Electrolyte composition | Reference |
|---|---|---|
| Rechargeable proton battery | $H_3PW_{12}O_{40} \cdot n\ H_2O$ | Pandey *et al.,* (1998) |
| Rechargeable proton battery | PMA-$(NH_4)_{10}W_{12}O_{41} \cdot 2H_2O$ | Lakshmi and Chandra (2002) |

**Table 2.11 continued……**

| | | |
|---|---|---|
| Primary proton battery | Chitosan-$NH_4NO_3$-EC | Ng and Mohamad (2006) |
| Rechargeable proton battery | PEO-$NH_4ClO_4$-PC | Pratap *et al.,* (2006) |
| Primary Proton Battery | PEO-$NH_4HSO_4$-$SiO_2$ | Agrawal, *et al.,* (2007) |
| Primary proton battery | Cellulose acetate-$NH_4CF_3SO_3$-EC | Saaid *et al.,* (2009) |

$H_3PW_{12}O_{40}\cdot n\,H_2O$ – Phosphotungstic acid

$NH_4ClO_4$ – Ammonium perchlorate

PMA – Phosphomolybdic acid

PC – Propylene carbonate

$NH_4HSO_4$ – Ammonium hydrogen sulfate

$NH_4NO_3$ – Ammonium nitrate

$(NH_4)_{10}W_{12}O_{41}\cdot 2H_2O$ – Ammonium paratungstate

PEO – Poly(ethylene oxide)

EC – Ethylene carbonate

$NH_4CF_3SO_3$ – Ammonium triflate

$SiO_2$ – Silicon dioxide

## 2.12 Electric Double Layer Capacitor (EDLC)

Super capacitors or electric double layer capacitors (EDLCs) is crucial source of power for electric vehicles, memory back-ups and digital communications since they have high power density and long cycle life [Kim and Kim, 2008]. EDLCs are normally fabricated using a pair of carbon electrodes where the electrolyte separates the two electrodes. Usually liquid electrolytes are used in EDLCs, but such EDLCs are prone to leakage of the liquid components [Gu *et al.,* 2000]. Table 2.12 shows some examples of EDLC using proton conducting polymer electrolytes as a separator.

**Table 2.12: Examples of EDLC using proton conducting polymer electrolytes as a separator.**

| Type of devices | Electrolyte composition | Reference |
|---|---|---|
| EDLC | PAN-PC-$TBABF_4$ | Ishikawa *et al.,* (1995) |
| EDLC | Chitosan-$H_3PO_4$ | Arof and Majid (2008) |

**Table 2.12 continued……**

| | | |
|---|---|---|
| EDLC | Chitosan/κ-carragenan-$NH_4NO_3$ | Shuhaimi *et al.,* (2008) |
| EDLC | Cellulose-PVA-$H_3PO_4$ | Hashim *et al.,* (2005) |
| EDLC | Methyl cellulose-$NH_4NO_3$ | Shuhaimi *et al.,* (2009) |

PAN – Poly(acrylonitrile)
$TBABF_4$ – Tetrabutylammonium tetrafluoroborate
$NH_4NO_3$ – Ammonium nitrate
PC – Propylene carbonate
$H_3PO_4$ – Orthophosphoric acid
PVA – Poly(vinyl alcohol)

## 2.13 Summary

From this chapter, knowledge on polymer electrolytes and the application in solid-state electrochemical devices can be understood.