

## CHAPTER 2

### LITERATURE REVIEW

#### 2.0 Introduction

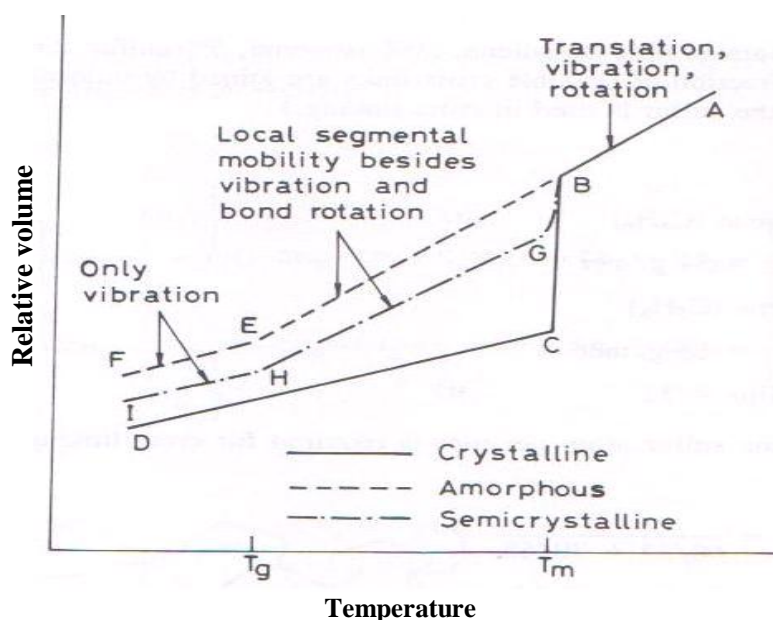
The word *poly* means “many parts”. A polymer is a long-chain molecule composed of a large number of identical repeating units [Fried, 2003]. Natural polymers include cellulose, proteins, silk. Artificial polymers include polystyrene, nylon and polyethylene.

Generally, polymers are insulators since their conductivity is very low ( $10^{-12}$  to  $10^{-18}$  S cm<sup>-1</sup>). Conductivity is due to solvent or ion contaminants [Rajendran and Sivakumar, 2008]. Polymer research has attracted much attention due to the ability of some polymers to host ionic conduction. This has led to the development of “polymer electrolytes”. The development of polymer electrolytes is one of the aims in polymer research [Acosta and Morales, 1996].

#### 2.1 Polymer electrolytes (PEs)

Polymer electrolytes (PEs) are formed by dissolving a salt in a polymer host [Forsyth *et al.*, 2000; Gadjourova *et al.*, 2001]. Dissolution of the salt in a polymer matrix provides ions that contribute to ionic conductivity under the influence of an electric field.

For a polymer to serve as a host for ionic conduction, it should contain polar groups in which one of the atoms can act as electron donors (i.e. atoms that possess lone pair electrons) in order to bond datively with cations of the incorporating salt. The polymers should also have a low glass transition temperature so that the polymer will be highly amorphous at room temperature when solvated with salt. Some polymers with high glass transition temperature can also exhibit high ionic conductivity. Glass transition temperature,  $T_g$  of a non-crystalline polymer is the temperature at which the polymer begins to change from a hard glassy form to a soft rubbery phase [Gómez-Carracedo *et al.*, 2003]. Below  $T_g$ , polymer is in glassy state (hard and rigid). Above  $T_g$ , the polymers are soft and flexible or rubber-like [Pouplin *et al.*, 1999]. In general, polymers have two phases either amorphous or semi-crystalline. Amorphous polymers only exhibit  $T_g$  and do not exhibit melting temperature,  $T_m$  because  $T_g$  is 2/3 lower than  $T_m$ , but semi-crystalline polymers exhibit both  $T_g$  and  $T_m$  as depicted in Figure 2.1 [Fried, 2003].



**Figure 2.1: Determination of glass transition and crystalline melting temperatures by changes in specific volume. A: liquid region; B: liquid with some elastic response; BE: rubbery region; EF: glassy region; GH: crystallite in a rubber matrix; HI: crystallites in a glassy matrix; CD: crystallite solid [Chanda and Roy, 1993]**

Amorphous polymers have received more attention because ionic conductivity occurs only in the amorphous phase (above  $T_g$ ), where ion transport is induced by local motion of polymer chain segments repeatedly creating new coordination sites into which the ions may then migrate [Gadjourova *et al.*, 2001]. Andreev and Bruce (2000) state that conductivity is confined largely to amorphous polymer electrolytes. Above  $T_g$  free volumes arising from the dynamics of the polymer chain are created that led to maximized segmental motion and suppress the crystalline phase of the polymer electrolytes. Examples of host polymer are listed in Table 2.1.

**Table 2.1: Lists of some polymers with their glass transition temperature, dielectric constant and their polar groups**

Polymers	Glass transition temperature, $T_g$ (°C)	Dielectric constant, $\epsilon_r$	Polar groups
Polyethylene oxide (PEO)	-64	5	O
Poly(methyl methacrylate) (PMMA)	105	2.6 at 1 MHz	O
Poly(vinyl chloride) (PVC)	85/81	3.4	Cl
Poly(vinyl alcohol) (PVA)	85	1.9-2.0	O
Poly(vinylidene fluoride) (PVdF)	-40	7.72 at 103 Hz	F
Poly(ethylene imine) (PEI)	215	-	N
Chitosan	-	-	O and N

**- Information not found**

A solvent is used to dissolve the polymer and salt. The criteria to choose a solvent are high dielectric constant,  $\epsilon_r$  to ensure dissolution and dissociation of polymer and salt. It should have low viscosity which results in higher mobility of free ions, low melting point

and high boiling point. Dielectric constant of solvents provides a rough measure of a solvent's polarity. A solvent can be, i) polar solvent and ii) non-polar solvent. Solvent with dielectric constant below 15 is non-polar solvent [Brown *et al.*, 2009]. The polarity of a solvent determines the type of compound it is able to dissolve or with what other solvent it is miscible. Normally polar solvent dissolve polar compounds. For example, water dissolves inorganic salt. Non-polar solvent dissolve non-polar compounds. Another parameter that influences dissociation of salt in PEs is the donor number of the solvent,  $D_N$ .  $D_N$  is a measure of the ability of a solvent to solvate cations and Lewis acids. Some examples of solvents are shown in Table 2.2.

**Table 2.2: Lists of some solvents with their density, viscosity, melting point and boiling point**

Solvents	Density (g/mL)	Viscosity	Melting point, (°C)	Boiling point, (°C)
Tetrahydrofuran	0.8892 at 20 °C	0.48 cP at 25 °C	-108.4	66
Dimethylformamide	0.944	0.92 cP at 20 °C	-61	153
Water	1	0.001 Pas at 20 °C	0	100
Acetic acid	1.049	1.22 mPas at 20 °C	16.5	118.1
Acetone	0.7925	0.3075 cP	-94.9	56.53
Methanol	0.7918	0.59 mPas at 20 °C	-97	64.7
Toluene	0.8669	0.59 cP at 20 °C	-93	110.6

The incorporating salt makes the polymer conductive. The salt must have low lattice energy [Scrosati, 1993; Bamford *et al.*, 2001] and large anion radius [Thompson *et al.*, 1996; Lin *et al.*, 2000]. Lattice energy is the energy required to completely separate 1 mole of a solid ionic compound into gaseous ions. Lower lattice energy helps the salt to dissolve in polymer because a lower energy is required to break the ionic bond between the

cation and anion leading to more charge carriers and conductivity enhancement. The relationship between lattice energy and anion radius is shown by equation below:

$$U \propto \frac{z^+ z^-}{r} \quad (2.1)$$

Here  $U$  is lattice energy,  $z^+ z^-$  is magnitude of charge and  $r$  is size or radius of ions.

Below are some examples of salt with their lattice energy.

**Table 2.3: Some examples of the lattice energy of ammonium and lithium salts**

Anion	Lattice energy (kJ mol <sup>-1</sup> )	
	NH <sub>4</sub> <sup>+</sup>	Li <sup>+</sup>
CH <sub>3</sub> COO <sup>-</sup>	626.3	786.8
NO <sub>3</sub> <sup>-</sup>	620.5	764.8
BF <sub>4</sub> <sup>-</sup>	606.5	756.0
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	569.6	694.2

A salt with highly delocalized electrons in the anion such as CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> or N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub><sup>-</sup> is used because it is capable of producing a high electrical conductivity [Ramesh and Ng., 2009]. Ideally, the anion should have a low tendency to coordinate to the cation [Ali *et al.*, 2007]. Kumar and Chandramani (2010) stated that the thermally generated carriers and suitable dopants will influence the conductivity of polymers.

Polymer electrolytes doped with salt are not suitable for electrochemical device application since conductivity at ambient temperature ranging from 10<sup>-6</sup> to 10<sup>-5</sup> S cm<sup>-1</sup> is still low [Selvasekarapandian *et al.*, 2005]. Special interest today is focused on polymer systems having high ionic conductivity at ambient and sub-ambient temperatures since they

find unique applications such as separators in rechargeable lithium batteries, electrical double layer capacitors, proton batteries and polymer exchange membrane fuel cells.

Examples of electrical conductivity of polymer electrolytes reported by researchers are shown in Table 2.4.

**Table 2.4: Some examples of the polymer electrolytes and their conductivity**

<b>Electrolyte Composition</b>	<b>Conductivity, <math>\sigma</math> (S cm<sup>-1</sup>)</b>	<b>References</b>
70 wt.% Poly (vinyl alcohol) + 30 wt.% Cu(NO <sub>3</sub> )	$1.6 \times 10^{-5}$ at 30 °C	Ramya <i>et al.</i> , 2005
73.7 wt.% Gelatin + 26.3 wt.% CH <sub>3</sub> COOH	$4.5 \times 10^{-5}$ at RT	Vieira <i>et al.</i> , 2007
Poly(propylene glycol) + AgCF <sub>3</sub> SO <sub>3</sub> (O:M concentration:16)	$8.1 \times 10^{-6}$ at 28 °C	Eliasson <i>et al.</i> , 2000
80 wt.% Poly (ethylene oxide) + 20 wt.% KI	$1.96 \times 10^{-5}$ at 25 °C	Reddy and Chu, 2002
60 wt.% Chitosan acetate + 40 wt.% LiTFSI	$5.09 \times 10^{-7}$ at RT	Puteh <i>et al.</i> , 2005

## 2.2 Plasticized Polymer Electrolytes (PPE)

Plasticizing a polymer electrolyte is one of the ways to increase the conductivity of polymer electrolytes. This idea was introduced first by Feuillade and Perche in the year 1975 [Periasamy *et al.*, 2000]. According to Kumar and Sekhon (2002) plasticizers should have (i) low glass transition temperature,  $T_g$  that helps to increase the amorphous content of polymer electrolytes, (ii) high dielectric constant that helps in dissociating the salt (iii) low viscosity to increase mobility of the conducting ions, (iv) low volatility, (v) high boiling temperature, (vi) low freezing temperature (vii) good miscibility with polymer salt (viii)

good compatibility with polymer matrix and (x) good chemical and electrochemical stability.

Bishop *et al.* (1996) pointed out that plasticization decreased the amount of ion pairing and  $T_g$  of the electrolytes. Ion mobility increased when  $T_g$  decreased and can lead to increase in conductivity. Every *et al.* (1996) pointed that, plasticizers increased segmental motion of the polymer backbone that produces free volume, reduce  $T_g$  of the polymer and increase the amorphous nature of the polymer. All these factors can lead to conductivity enhancement. There are also reports where the addition of plasticizers results in a decrease in conductivity [Kumar and Sekhon, 2002]. This is due to leakage of plasticizer out of the PE.

Table 2.5 lists examples of plasticizers with their properties and Table 2.6 lists the conductivity of plasticized polymer electrolytes.

**Table 2.5: Some examples of the plasticizers**

Plasticizers	Dielectric constant, $\epsilon_r$	Viscosity, $\eta$ mPas at 25 °C	Boiling point, $T_b$ (°C)	Melting point, $T_m$ (°C)
<sup>a</sup> Dimethyl carbonate	3.12	0.585	90	2.4
<sup>a</sup> Diethyl carbonate	2.82	0.748	126	-43
<sup>a</sup> Ethylene carbonate	89.78	1.93	248	36.4
<sup>a</sup> Propylene carbonate	66.14	2.53	242	-48.8
<sup>a</sup> $\gamma$ -butyrolactone	39.0	1.7	204	-43.3
<sup>b</sup> N, N-Dimethyl formamide	36.7	0.80 cP	153	-61
<sup>b</sup> N-methyl-2-pyrrolidine	32.0	2.15 cP	202	-24
<sup>c</sup> Poly (ethylene glycol ) 200	19.95 at 293 K	50 cP	-	-

- **Information not found**

References: (a) Song *et al.*, (2000), (b) Khiar (2006), (c) Kinart *et al.*, (2007)

**Table 2.6: Some examples of the plasticized polymer electrolytes and their conductivity**

Electrolyte Composition	Conductivity with plasticizer, $\sigma$ (S cm <sup>-1</sup> )	References
70 wt.% PVAc + 20 wt.% DMF + 10 wt.% LiClO <sub>4</sub>	$4.1 \times 10^{-4}$ at 30 °C	Baskaran <i>et al.</i> , 2004
15 wt.% PVdF-HFP + 70 wt. % PC +15 wt.% H <sub>3</sub> PO <sub>4</sub>	$2.1 \times 10^{-4}$ at 30 °C	Choi <i>et al.</i> , 2004
30 wt.% PVA + 10 wt.% LiClO <sub>4</sub> + 60 wt.% DMP	$1.49 \times 10^{-4}$ at 29 °C	Rajendran <i>et al.</i> , 2004
10 wt.% PMMA + 5 wt.% LiBF <sub>4</sub> + 85 wt.% DBP	$4.54 \times 10^{-3}$ at 31 °C	Rajendran and Uma, 2000
85 wt.% (PVC-LiCF <sub>3</sub> SO <sub>3</sub> ) + 15 wt.% DMF	$6.48 \times 10^{-5}$ at RT	Subban and Arof, 2004
64 wt.% (PVdF-HFP + OA) + 36 wt.% DMA	$1.2 \times 10^{-4}$ at RT	Missan <i>et al.</i> , 2006

## 2.3 Basic properties of Polymer Electrolytes

### 2.3.1 Conductivity

According to Johansson and co-workers (1996) ionic conductivity in polymer matrix is due to the transport of cations and anions. The ionic conductivity,  $\sigma$  of polymer electrolytes is given by the product of the concentration of ionic charge carriers and their mobility as shown by equation (2.2)

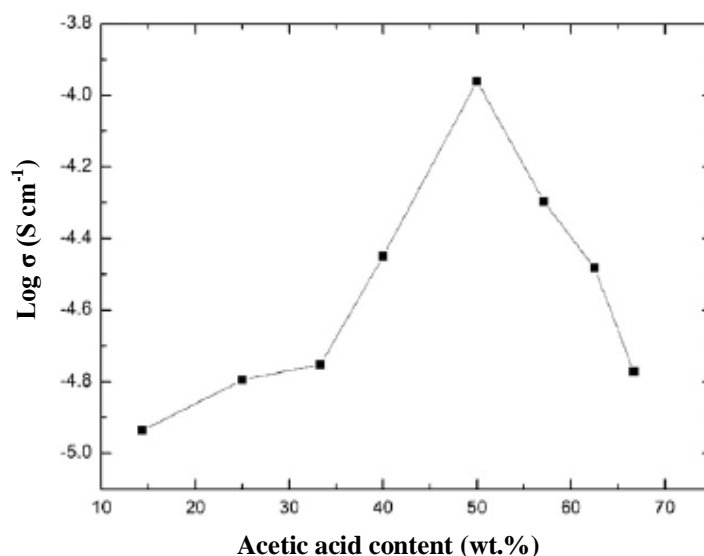
$$\sigma = \sum_i n_i \mu_i q_i \quad (2.2)$$

where  $n_i$  is the number of ionic charge carriers,  $\mu_i$  is ionic mobility and  $q_i$  is ionic charge.



From Eqn. (2.2) ionic conductivity of polymer electrolytes can be increased by increasing the number of ionic charge carriers and their ionic mobility [Liang *et al.*, 2007]. Ionic mobility is promoted by segmental motion of the polymer host and therefore, conductivity is mainly localized to the amorphous phase. Conductivity variations in polymers are attributed to ion association and dissociation [Mellander and Albinsson, 1996; Raphael *et al.*, 2010; Baskaran *et al.*, 2004].

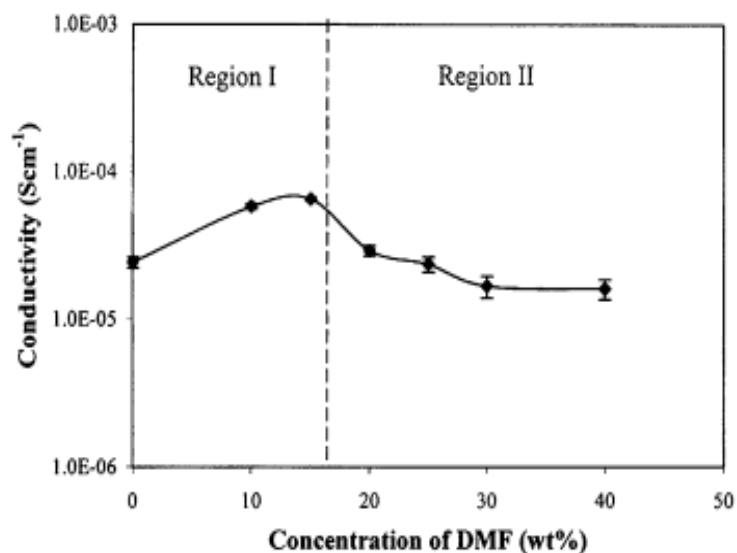
Figure 2.2 depicts the effect of the acetic acid content on the conductivity of the agar electrolyte at room temperature. The ionic conductivity increases when the acetic acid concentration is increased up to 50 wt.% and beyond it decreases [Raphael *et al.*, 2010].



**Figure 2.2: Effect of the acetic acid content on the conductivity of the electrolyte measured at room temperature (Raphael *et al.*, 2010)**

Figure 2.3 shows the example of conductivity as a function of DMF as plasticizer in PVC-LiCF<sub>3</sub>SO<sub>3</sub> complexes. Ionic conductivity increases with increasing plasticizer content up to 15 wt.% DMF (Region I). As the concentration of DMF is increased (greater than 15

wt.%), the ionic conductivity decreases gradually and approaches an almost constant value when the concentration of DMF reaches 30 wt.% (Region II) [Subban and Arof, 2004].



**Figure 2.3: Effect of the DMF concentration on the conductivity in PVC-LiCF<sub>3</sub>SO<sub>3</sub> polymer complexes (Subban and Arof, 2004)**

The variation in conductivity for Figure 2.2 and Figure 2.3 may be explained in terms of the number of free mobile ions as shown in equation 2.2. The enhancement of conductivity with increasing acetic acid concentration can be related to number of mobile charge carriers. As more dopant (salt or acid) is added, more ions will be introduced from dissociation of the dopant. Although ion association can also take place that lead to the formation of neutral ion aggregates and do not contribute to conductivity, the increase in conductivity implies that the rate of ion dissociation is greater than the rate of ion association, ion pairing and neutral aggregate formalism. Decreasing ionic conductivity at concentrations greater than 50 wt.% is attributed to the formation of neutral ion aggregates and ion-pairing [Raphael *et al.*, 2010]. For Figure 2.3, the increase in conductivity in Region I is attributed to the increase in the number of free mobile ions due to dissociation

of salt and ion pairs by DMF and the decreasing conductivity is attributed to ion pairing and formation of neutral ion aggregates.

Unfortunately, ionic interactions sometimes inhibit ion migration because of their strong cohesion which increases the glass transition temperature,  $T_g$  (Tominaga *et al.*, 2005). An increase in salt content can result in an increase in  $T_g$  of the polymer [Furlani *et al.*, 1998, Idris *et al.*, 2001]. The increase in  $T_g$  makes the polymer backbone more rigid and disallows conductivity enhancement through segmental motion [Osman *et al.*, 2001]. Guilherme *et al.* (2007) pointed that,  $T_g$  increase with addition of salt due to ion-dipole interaction between the cation and the oxygen atom of the host polymer. Forsyth *et al.* (2000) stated that  $T_g$  increase with increasing salt concentration is due to presence of ionic crosslinking suggesting a decoupling of the salt motion in the polymers. On addition of plasticizer,  $T_g$  of PE decreases because the plasticizer interacts with the cations of the salt, limiting the transient cross-linking of the cations with the polymer and hence lowering the  $T_g$  [Furlani *et al.*, 1998].

Temperature also affects conductivity. The increase in the conductivity with the temperature can be interpreted as a hopping mechanism between coordinating sites, hopping being assisted by local structural relaxations and segmental motions of the polymer salt complexes [Reddy *et al.*, 1999; Baskaran *et al.*, 2004].

Conductivity-temperature relationship can be described by several models, two of which are as follows:

**a) Vogel-Tammann-Fulcher (VTF) model**

The Vogel-Tammann-Fulcher (VTF) model can be described by the following equation:

$$\sigma = \frac{A}{T^{1/2}} \exp \left[ \frac{-E_A}{k(T - T_o)} \right] \quad (2.3)$$

Here  $\sigma$  is conductivity,  $A$  is the pre-exponential factor,  $E_A$  is the pseudo-activation energy for conduction,  $k$  is Boltzmann constant,  $T$  is absolute temperature and  $T_o$  is a quasi-equilibrium glass transition temperature at which free volumes disappear.  $T_o$  is 50 lower than the glass transition temperature [Münchow *et al.*, 2000].

According to the VTF model, ionic conduction at high temperature occurs as a result of cooperative segmental motion of polymer matrix [Shukla and Thakur, 2009]. Rajendran *et al.* (2000) pointed that ionic conduction in polymer electrolytes which obeys the VTF model describes the transport properties in a viscous matrix. Conductivity that obeys the VTF model occurs in the amorphous phase (Deepa *et al.*, 2002). As the amorphous region progressively increases, the polymer chain acquires faster internal modes in which bond rotation produces segmental motion. This in turn, favors inter-chain and intra-chain ion hopping leading to conductivity enhancement [Rajendran *et al.*, 2008].

According to Geiculescu *et al.* (2002) a VTF plot as shown in Figures 2.4 and Figure 2.5 is a curve. The curvature indicates mechanical coupling between motion of the matrix and motion of the charge carriers

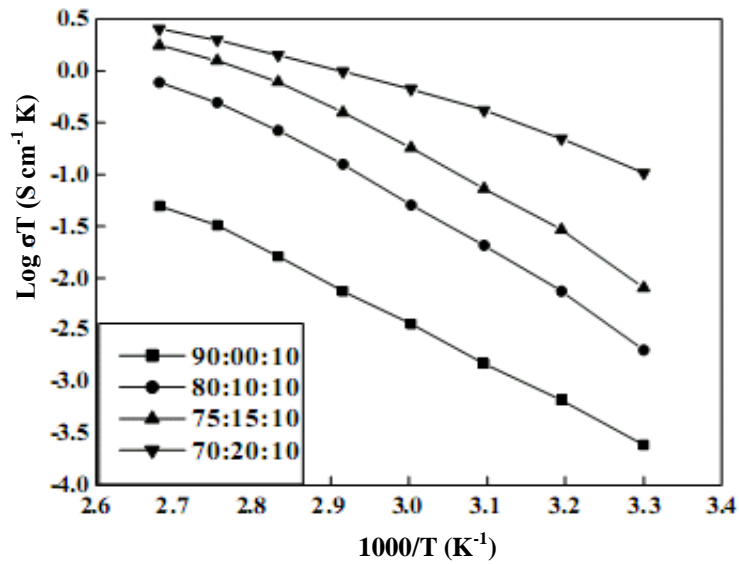


Figure 2.4: VTF plot for PVAc-DMF-LiClO<sub>4</sub> gel electrolytes of various compositions (Baskaran *et al.*, 2004).

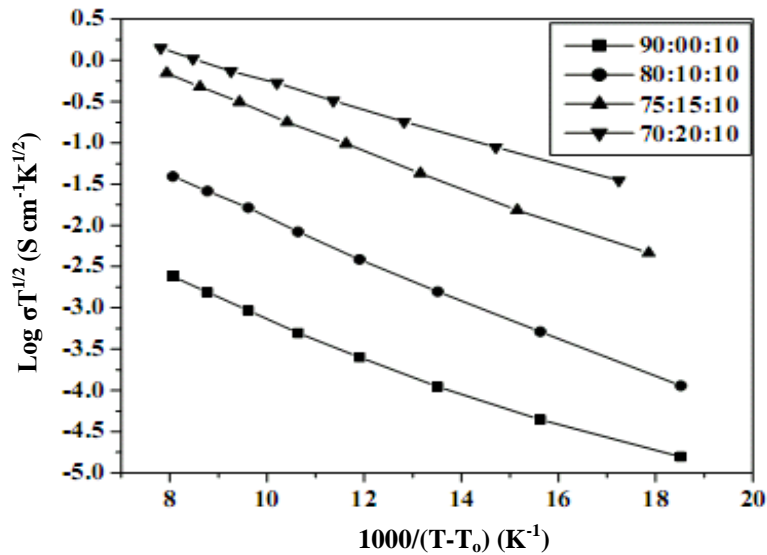


Figure 2.5: The VTF plot for PVAc-DMF-LiClO<sub>4</sub> gel electrolytes of various compositions (Baskaran *et al.*, 2004).

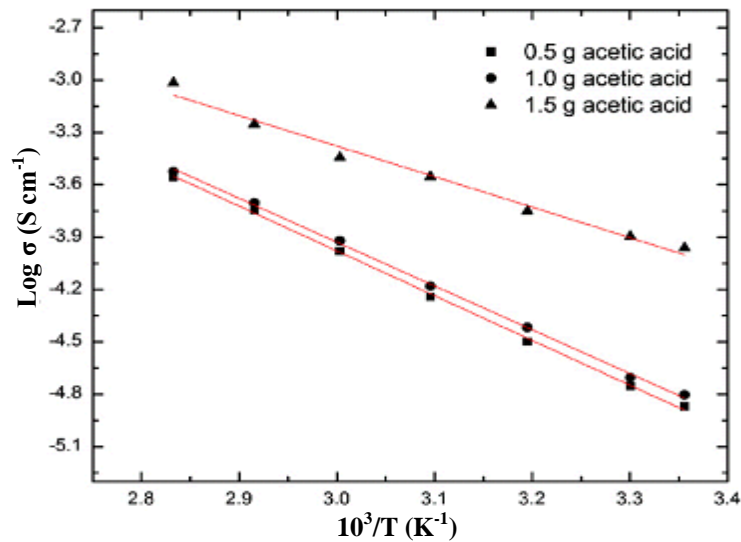
## b) Arrhenius model

The Arrhenius model describes conductivity-temperature relationship with regression value,  $R^2$  of almost 1. An example is depicted in Figure 2.6. The electrolyte is

based on agar, doped with three concentrations of acetic acid from room temperature to 80 °C. The conductivity increases from  $1.1 \times 10^{-4} \text{ S cm}^{-1}$  to  $9.6 \times 10^{-4} \text{ S cm}^{-1}$  in the temperature investigated. At higher temperatures, thermal movement of polymer chain segments and the dissociation of acid would be improved, inducing an increase in total ionic conductivity [Raphael *et al.*, 2010]. The Arrhenius model is described by the equation:

$$\sigma = \sigma_o \exp\left(\frac{-E_A}{kT}\right) \quad (2.4)$$

Here  $\sigma$  is the conductivity,  $\sigma_o$  is the pre-exponential factor,  $E_A$  is the activation energy,  $k$  is Boltzmann constant and  $T$  is absolute temperature.



**Figure 2.6: Temperature-dependence conductivity of the agar-based electrolyte as a function of the acetic acid content (Raphael *et al.*, 2010).**

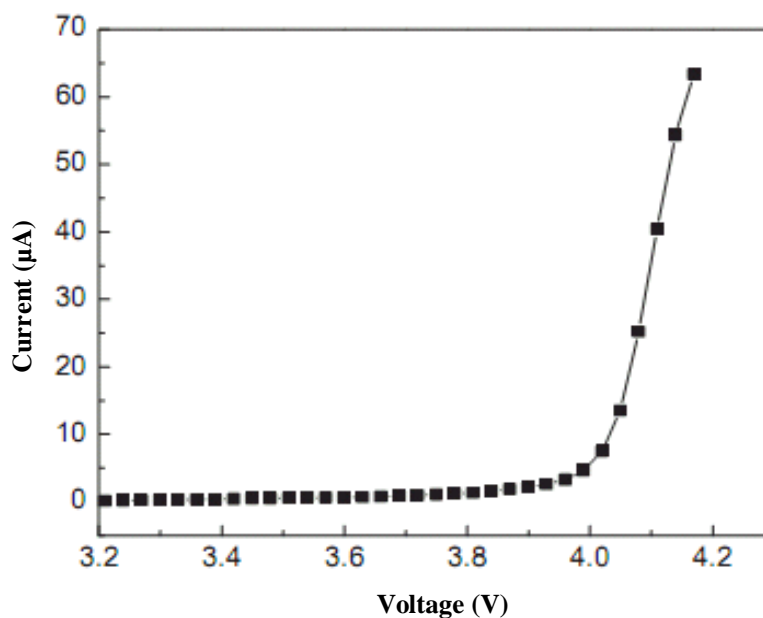
From this equation, activation energy can be calculated. For variation with dopant content, the activation energy trend is opposite to that of conductivity as shown in Table 2.7. It can be seen that the activation energy decreases with increase in conductivity. The increase in conductivity can be attributed to increase in number of charge carriers due to increase in acetic acid concentration, but also to the decrease in energy barrier for hopping.

**Table 2.7: Example of activation energy and conductivity of agar based electrolytes (Raphael *et al.*, 2010).**

Acetic acid (wt.%)	Conductivity, $\sigma$ (S cm <sup>-1</sup> )	Activation energy (kJ/mol)
25	$1.6 \times 10^{-5}$	49.11
40	$3.6 \times 10^{-5}$	48.00
50	$1.1 \times 10^{-4}$	33.51

### 2.3.2 Electrochemical stability

Electrochemical stability is an essential property for polymer electrolytes when application in batteries or capacitors are considered. Electrochemical stability gives information about voltage limitation of polymer electrolytes. Knowledge on voltage limitation prevents destruction of the electrolyte. Figure 2.7 depicts the electrochemical stability window of a polymer electrolyte based on P(VdF-co-HFP) prepared by the phase inversion process with 14% solution of 1M LiPF<sub>6</sub> in EC/DMC.

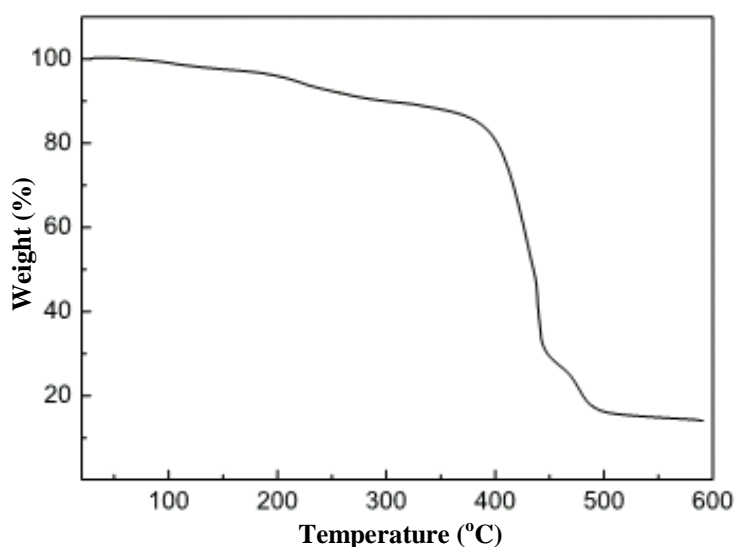


**Figure 2.7: Linear sweep voltammogram of the PVdF-co-HFP based polymer electrolyte (Zhao *et al.*, 2010)**

It can be seen that, the current onset is detected at 4 V versus Li/Li<sup>+</sup>, implying high anodic stability of the polymer electrolyte allowing the safe use of the electrolyte in lithium-ion batteries. The current onset is assumed to be the polymer electrolyte breakdown voltage [Baril *et al.*, 1997].

### 2.3.3 Thermal stability

Thermal stability of the polymer electrolyte is another important parameter to ensure acceptable performances in practical applications such as lithium batteries. Poor thermal stability is not safe for lithium batteries because lithium salt is easily decomposed and hydrolyzed and this can destroy the electrodes [Wu *et al.*, 2010]. Figure 2.8 depicts the thermal stability of polymer electrolytes. The sample starts to lose weight at around 426 °C, and this is complete at around 500 °C. This decomposition temperature is considered high and suitable for use in lithium- ion batteries.



**Figure 2.8: TGA curve of PHEMO/PVdF-HFP electrolyte containing 10 wt.% LiBOB (Wu *et al.*, 2010)**



## 2.4 Types of electrolytes

### i) Liquid electrolytes (LEs)

Generally, liquid electrolytes, LEs consist of a salt and solvent. As an example, LE for lithium batteries can be prepared by dissolving a lithium salt in a solvent mixture composed of alkylcarbonate solvent [Taggougui *et al.*, 2008]. Commonly used lithium salt is  $\text{LiPF}_6$  and the solvent is based on alkyl carbonate such as propylene carbonate (PC), ethylmethyl carbonate (EMC), ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC). LEs are used in commercial lithium-ion batteries due to high room temperature conductivity. However, LEs have drawbacks especially in safety and self-discharge.  $\text{LiPF}_6$ , has poor thermal stability because of spontaneous thermal degradation [Blomgren, 2003]. The solvents used are flammable and may cause fire under abuse conditions of battery operation. Sugimoto *et al.* (2009) stated that Li-ion batteries with LEs exhibit irreversible charge discharge performance. LEs also have limited range of operation temperature and at times corrosive causing leakage and hence decreasing the safety and the lifetime of battery. LEs are also very sensitive to water providing handling and packaging problem.

### ii) Polymer Gel electrolytes (PGEs)

These electrolytes belong to the solvent-salt-polymer hybrid system in which the salt solution is immobilized by the addition of a suitable polymer matrix [Singh *et al.*, 2005]. Favorable properties of PGEs include high ionic conductivity approaching to that of LE and wide operating temperature window which is important for use in electrochemical

device applications such as supercapacitors, fuel cells, batteries and electrochromic windows [Awadhia *et al.*, 2006].

A variety of polymeric gel electrolytes have been developed over the years. Ng and Mohamed (2008) studied the effect of temperature on the conductivity of plasticized chitosan-NH<sub>4</sub>NO<sub>3</sub> electrolytes and tried to make the proton batteries using the membrane. Kadir *et al.* (2010) investigated the transport studies of plasticized PVA-chitosan-NH<sub>4</sub>NO<sub>3</sub> and applied these to proton batteries.

Unfortunately, plasticizers have drawbacks. Plasticizer results in electrolyte leakage and deteriorates mechanical property of the polymer electrolytes. This can cause poor connection between the electrode and electrolyte [Zhao *et al.*, 2004] leading to poor battery cyclability.

### **iii) Solid polymer electrolytes (SPEs)**

SPEs may be defined as membranes that possess transport properties comparable to that of liquid ionic solutions. SPEs have satisfactory mechanical properties. Properties of SPEs can be easily controlled by varying their composition [Baskaran *et al.*, 2004; Reddy and Chu, 2002; Stevens *et al.*, 1997; Qu *et al.*, 2000; Khalid *et al.*, 2002].

SPEs offer attractive advantages over liquid electrolytes, such as wider operation temperatures, no flowing and corrosion after damage, ease of application to electrochemical devices, major compactness, increased device flexibility, thinner configuration and low

cost [Lufrano and Staiti, 2004]. SPEs can act as membranes and separators [Rajendran *et al.*, 2003; Tang *et al.*, 2007]. Power density of EDLC can be further increased by the use of solid electrolytes [Ganesh *et al.*, 2008; Liu *et al.*, 1996].

Although it is easy to use SPEs in devices their application is restricted due to the low conductivity at room temperature, poor electrode-electrolyte contact due to dimensional changes during operation particularly during charge-discharge cycling in batteries, low mechanical strength and limited electrostatic potential window for aqueous based SPEs.

## 2.5 Proton conducting polymer electrolytes (PCPEs)

Proton conducting polymer electrolytes, PCPEs have recently become an area of widespread interest due to their possible applications in a variety of electrochemical devices such as fuel cells, chemical sensors and electrochromic display devices [Choi *et al.*, 2004]. Interest in solid proton conducting polymer electrolytes started with the development of perfluorinated sulfonic membranes in the 1960s [Bozkurt and Meyer, 2001]. PCPEs are complexes of strong inorganic acid ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ) or ammonium salts ( $\text{NH}_4\text{SCN}$ ,  $\text{NH}_4\text{CF}_3\text{SO}_3$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{NH}_4\text{ClO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{I}$ ) with commercially available electron-donor polymers (PEO, PVA, PAA and PEI).

However, proton-conducting polymers complexed with inorganic acids suffer from chemical degradation and mechanical stability making them unsuitable for practical applications (Hema *et al.*, 2008). PCPEs can be obtained by doping polymers bearing ether,

alcohol, imine, amide or imide groups with strong acids such as  $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{SO}_4$  [Lassègues *et al.*, 2001].

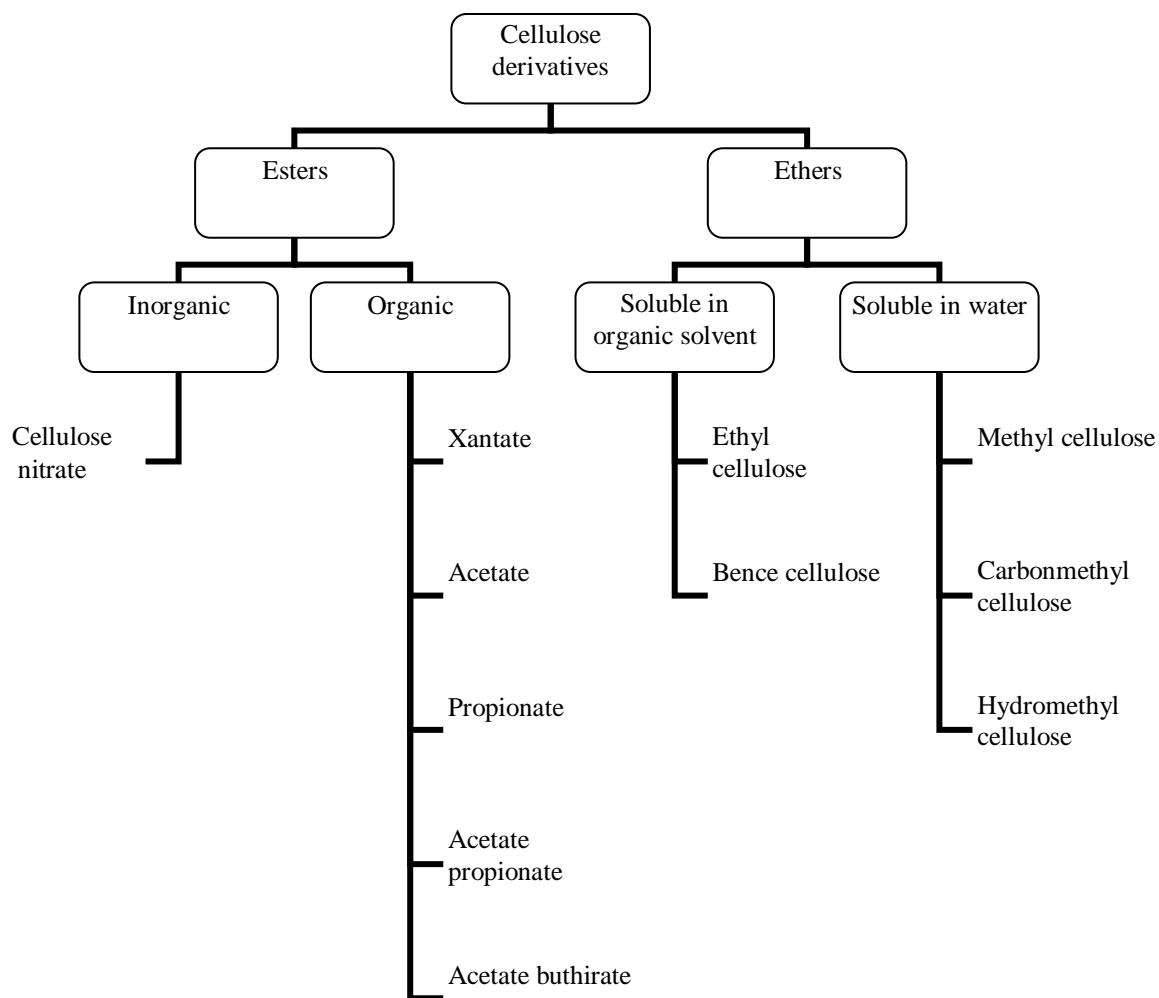
Table 2.8 lists some examples of proton conducting polymer electrolytes and their conductivity.

**Table 2.8: Some examples of proton conducting polymer electrolytes and their conductivity**

Salts	Polymer	Conductivity ( $\text{S cm}^{-1}$ )	Ref(s).
$\text{NH}_4\text{CH}_3\text{COO}$ (25 mol%)	PVP	$1.5 \times 10^{-6}$	Ramya <i>et al.</i> (2008)
$\text{NH}_4\text{F}$ (F/O:0.12)	PEO	$1.1 \times 10^{-6}$	Kumar & Sekhon (2002)
$\text{NH}_4\text{ClO}_4$	$(\text{PEG})_{x=46}$	$2.7 \times 10^{-6}$ (RT)	Binesh & Bhat (1996)
$(\text{NH}_4)_2\text{SO}_4$ ( $\text{NH}_4^+/\text{EO}=0.05$ )	PEO	$2.7 \times 10^{-6}$	Ali <i>et al.</i> (1998)
$\text{NH}_4\text{NO}_3$ (20 mol %)	PVA	$7.5 \times 10^{-3}$ (303 K)	Hema <i>et al.</i> (2009)
$\text{NH}_4\text{I}$ (45 wt.%)	Chitosan (55 wt.%)	$3.7 \times 10^{-7}$	Buraidah <i>et al.</i> (2009)
$\text{NH}_4\text{NO}_3$ (40 wt.%)	24 wt.%Chitosan- 36 wt.%PVA	$2.07 \times 10^{-5}$	Kadir <i>et al.</i> (2010)
$\text{NH}_4\text{ClO}_4$ (30 wt.%)	PESc (70wt.%)	$2.2 \times 10^{-7}$	Srivastava and Chandra (1992)
$\text{NH}_4\text{CF}_3\text{SO}_3$ (50 wt.%)	Chitosan (50 wt.%)	$1.0 \times 10^{-6}$ (298 K)	Khier <i>et al.</i> (2006)
$\text{NH}_4\text{SCN}$ (20 mol %)	PVP	$1.7 \times 10^{-4}$ (RT)	Ramya <i>et al.</i> (2007)
$\text{NH}_4\text{CH}_3\text{COO}$ ( $\text{NH}_4^+/\text{OH}^-=0.25$ )	PVA	$5.62 \times 10^{-6}$ (301 K)	Hirankumar <i>et al.</i> (2005)
$\text{NH}_4\text{CH}_3\text{COO}$ (20 wt.%)	PVA (80 wt.%)	$1.1 \times 10^{-6}$ (303 K)	Hirankumar <i>et al.</i> (2004)

## 2.6 Cellulose

Cellulose is a natural carbohydrate (polysaccharide) and highly hydrophilic polymer [Sarkar, 1995]. Pure cellulose has glass transition temperature,  $T_g$  at 220 °C by DSC analysis [Gómez-Carracedo *et al.*, 2003]. Up to 10 000  $\beta$ -1, 4-linked glucose units cellulose is a linear polymer.



**Figure 2.9: Taxonomy of cellulose and its derivatives**

This strongly favors hydrogen-bonding formation between glucose units in the chain and between adjacent chains [Luccia and Kunkel, 2002]. Due to the hydroxyl groups

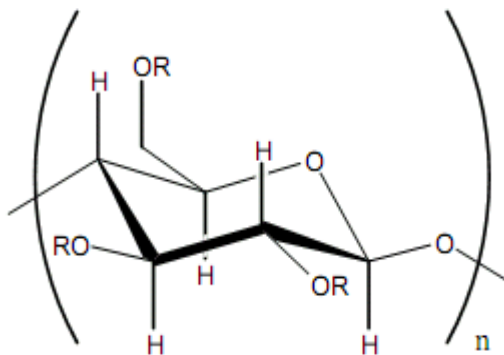
of the anhydroglucose units which form strong hydrogen bonds, cellulose is not soluble or swellable in water [Park *et al.*, 2001] hence limiting the utilization of cellulose. Pavlov (2001) pointed that cellulose is insoluble in single-component solvents and only dissolves in multicomponent solvents containing chelate complexes. To overcome this problem, some modifications have been made giving rise to two groups of cellulose derivatives; ether and ester cellulose as shown in Figure 2.9.

Cellulose esters are synthesized from inorganic acids as well as organic acids or their anhydrides. More than 100 types of cellulose esters are available with cellulose nitrate and cellulose acetate being the most important ones.

Cellulose ethers are important cellulose derivatives. They can be dissolved in water or in organic solvents. Cellulose ethers contain various substituents, varying degree of substitution and polymerization which make them suitable for a wide range of applications in food industry, oil, paper, cosmetics, pharmaceuticals, adhesive, agriculture, ceramics, textiles and construction industries [Brandt, 2001]. The most important of cellulose ether is methyl cellulose.

## 2.7 Methyl cellulose (MC)

MC is one type of modified cellulose that can be prepared from the reaction of alkali-cellulose with dimethyl sulfate (DMS) or methyl chloride [Filho *et al.*, 2007; BeMiller, 1986]. MC consists of  $\beta$  (1 $\rightarrow$ 4) glucosidic units with methyl substituents in linear chains [García, 2009].



**Figure 2.10: Methyl cellulose structure (Desbrières *et al.*, 2000) where R is H or CH<sub>3</sub>.**

Figure 2.10 shows the structure of MC. The hydrogen atoms in hydroxyl groups, OH, of cellulose are replaced by hydrophobic groups OCH<sub>3</sub> such as methyl or hydroxypropyl moieties to decrease the crystallinity of cellulose and increase the water solubility [Sarkar and Walker, 1995]. Decreasing the hydrogen bonds increases the amorphous nature of the polymer increase and reduces  $T_g$  or  $\alpha$ -transition compared to pure cellulose. Gómez-Carracedo *et al.* (2003) stated that  $T_g$  of MC is around 160 to 191 °C.

In development of polymer research, environment friendly materials have been tested to help reduce the environment impact of many hazardous products. The use of biodegradable polymers can help reduce such environmental problems. Being biodegradable, MC was studied in the development of edible films or biodegradable plastics [García, 2009]. In the food industry, MC was found to be effective in packaging squids [Sanz *et al.*, 2004], dough and fried potato [García, 2004]. In the petrochemical industry, MC was used as an agent to modify water viscosity for recovering heavy oils [Borchardt, 1991] and in civil construction, MC acts as an admixture for concrete [Fu and Chung, 1996].

The wide application of MC in industry and research is due to some properties such as biodegradability, cheap [Rimduisit *et al.*, 2008], non-toxic [Song and Zheng, 2009], good mechanical strength and excellent film forming ability [Garcia, 2009]. Due to the presence of both hydrophobic group, OCH<sub>3</sub> and hydrophilic group, OH, MC can be used as a surfactant. MC has an excellent water retention properties and can be used in water-based paints, wallpaper adhesives, cement and gypsums formulations.

MC is a nonionic water-soluble polysaccharide and has many hydroxyl groups in the molecule [Gotoh *et al.*, 2001]. The presence of polar groups at oxygen atoms (lone pair electron) in MC led to it acts as host in polymer electrolyte or to be electron donor. The existence of lone pair electrons enables the chelation of a proton donor [Yahya and Arof, 2004; Mohamed *et al.*, 1995].

The properties of MC are influenced by their molecular properties i.e. their degrees of substitution (DS), molecular weights, molecular weight distribution, degrees of polymerization (DP) and distribution of methoxyl groups along the glucose unit and polymer chain. DS is the average number of modified hydroxyl groups per glucose residue or level of methoxy substitution on the cellulose chain [Filho *et al.*, 2007].

### **2.7.1 General properties of MC**

#### **a) Solubility and viscosity of MC**

MC is soluble in different solvents depending on the DS as shown in Table 2.9.



**Table 2.9: Solubility of MC according to DS**

<b>DS</b>	<b>0.1-1.0</b>	<b>1.4-2.0</b>	<b>2.4-2.8</b>
Water	Swelling	Soluble	Insoluble
4% NaOH solution	Soluble	Swelling	Insoluble
Acetone	Insoluble	Insoluble	Insoluble
Methanol	Insoluble	Insoluble	Insoluble
THF	Insoluble	Insoluble	Soluble
Chloroform	Insoluble	Insoluble	Soluble
DMSO	Partially sluble	Soluble	Partially sluble
DMAc	Partially sluble	Soluble	Partially sluble

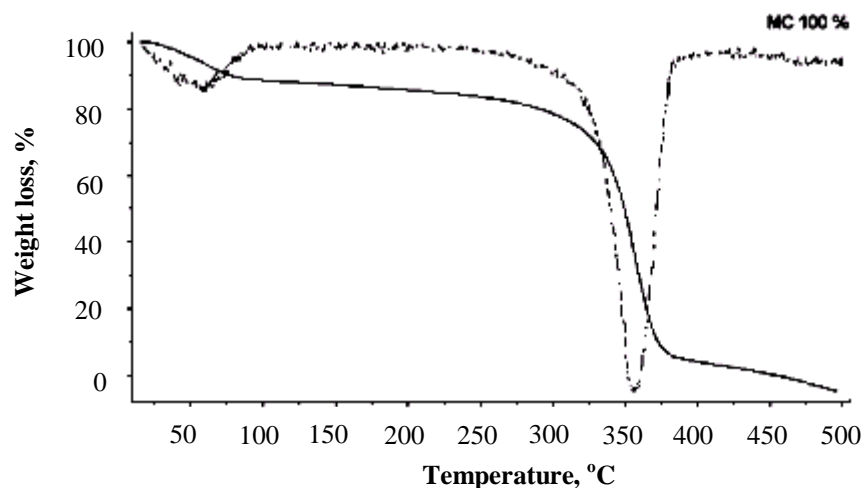
They are soluble in some binary organic and organic-water solvent systems because they have hydrophobic groups in their molecules. There are two types of commercially produced MC: (1) water-soluble MC with degree of substitution (DS) ranging from 1.4 to 2.0 (usually 1.8), (2) alkali-soluble MC with degree of substitution (DS) ranging from 0.25 to 1.0 [Brandt, 2001].

MC enhances the stability of suspension throughout the solution due to the formation of hydrogen bonds. MC is made in different viscosities ranging from 4 to 100,000 mPas in 2% aqueous solution at 20 °C with 20 rpm. Gelation temperatures of water-soluble MC drop as the degree of substitution increases [Brandt, 2001]. Gelation temperatures of a given degree of substitution decrease little as the viscosity of the solution increases [Brandt, 2001]. Addition of salt lowers gelation temperature [Kundu and Mundu, 2001]. This depends on the types and quantity of salt added. Some salts even prevent the dissolution of MC at ambient temperature [Brandt, 2001]. Both heat and electrolytes destroy hydrated structures by breaking hydrogen bonds between water and the polymer [Brandt, 2001].

When polar water-miscible organic solvents such as alcohols or glycols are added, MC solutions stabilize [Kundu *et al.*, 2003]. MC and these polar additives therefore form strong hydrogen bonds that increase gelation temperatures and lead to more stable soluble complexes in the solution [Kundu *et al.*, 2003]. MC is incompatible with some additives, such as tannin, because they form insoluble complexes even at low additive concentration [Brandt, 2001].

### b) Thermal stability of MC

Thermal stability exhibits the range of temperature that is suitable to use the polymer in any application before it decomposes. Figure 2.11 depicted the result of thermogravimetric analysis of MC polymer.



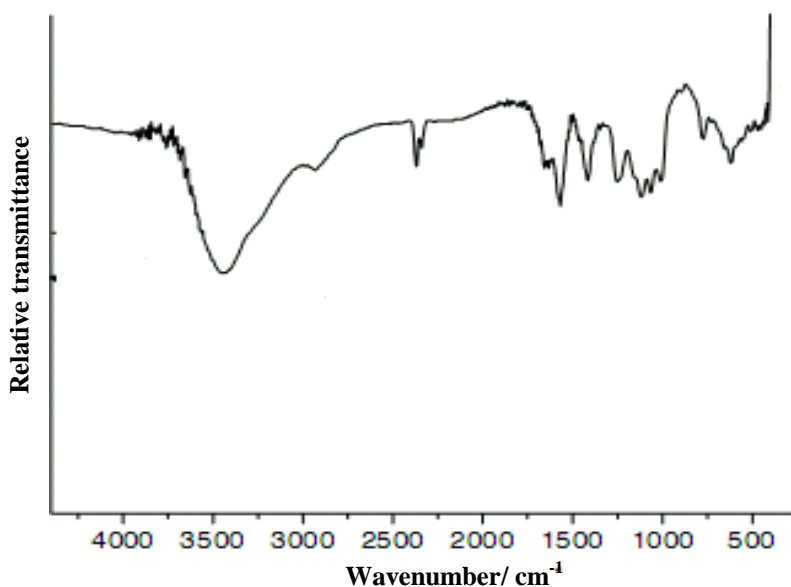
**Figure 2.11: Thermogravimetric analysis of MC (Yin *et al.*, 2006)**

Pure MC shows the first thermal weight loss at 57.8 °C which is related to the evaporation of unbound water. The second thermal event at 300 °C with the maximal rate at

355 - 356 °C is related to the degradation of MC. These result shows that MC has thermal stability up to 356 °C.

### b) Spectroscopic properties of MC

Spectroscopic studies reveal the functional groups in a polymer. FTIR spectroscopy has been used to analyze the types of functional group. Figure 2.12 shows the FTIR spectrum of pure MC.



**Figure 2.12: FTIR spectra of MC (Viera *et al.*, 2007)**

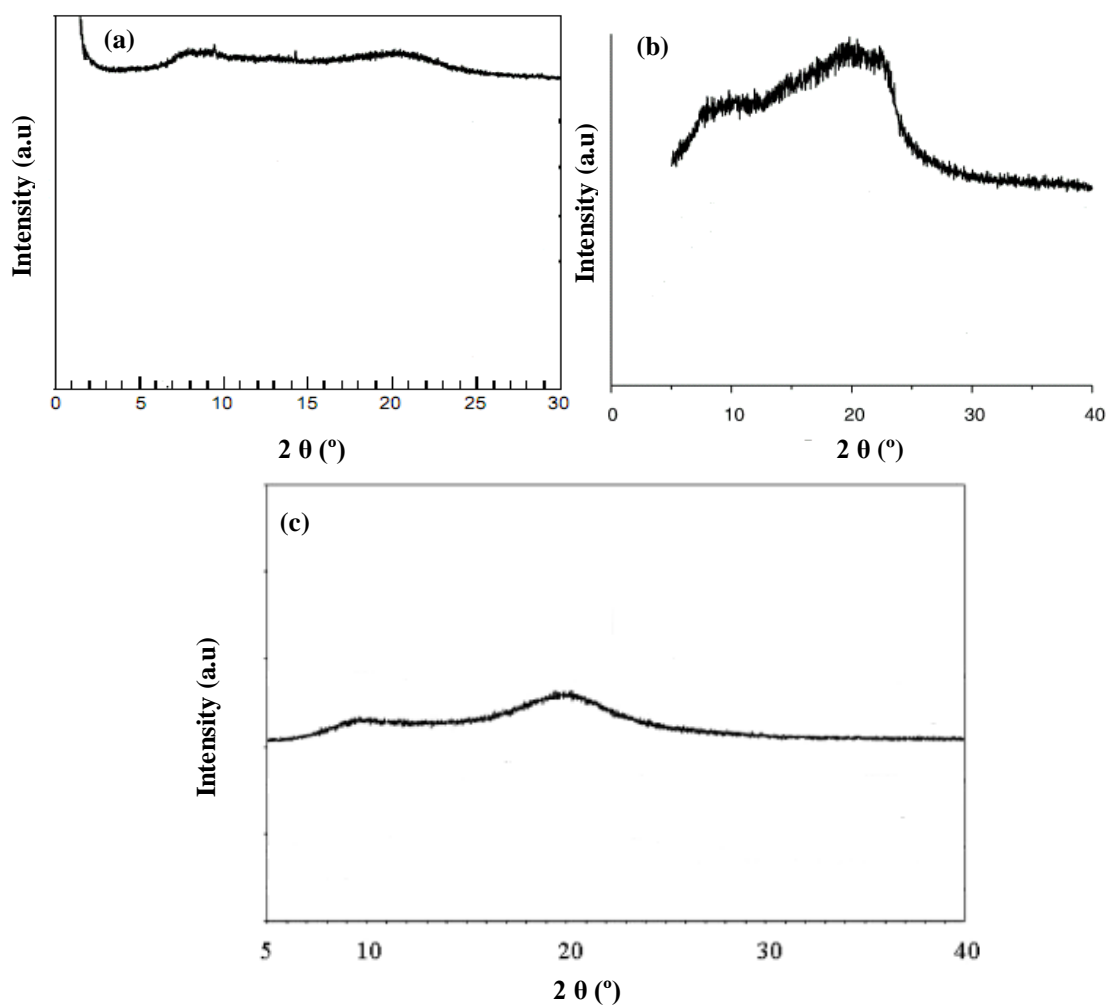
Table 2.10 shows the vibrational bands for MC.

**Table 2.10: Assignment of main absorption bands in MC polymer based on Figure 2.12**

Wavenumber (cm <sup>-1</sup> )	References	Vibrational modes
3457	Rokhade <i>et al.</i> , (2007)	O-H stretching
3455	Liu <i>et al.</i> , (2004)	
3454	Yin <i>et al.</i> , (2006)	
3448	Lin <i>et al.</i> , (2007)	
3437	Rimduisit <i>et al.</i> , (2008)	
2931, 2839	Lin <i>et al.</i> , (2007)	C-H stretching
2930, 2834	Rokhade <i>et al.</i> , (2007)	
2907	Yin <i>et al.</i> , (2006)	
2900	Filho <i>et al.</i> , (2007)	
2850-2975	Chattopadhyay and Mandal (1996)	
2837	Rimduisit <i>et al.</i> , (2008)	
2826	Babu <i>et al.</i> , (2007)	
1649	Lin <i>et al.</i> , (2007)	
1645	Yin <i>et al.</i> , (2006)	
1580-1700	Velazquez <i>et al.</i> , (2003)	
1460, 1380, 1320, 950	Filho <i>et al.</i> , (2007)	The infrared spectra of MC
1377	Yin <i>et al.</i> , (2006)	C-H bending mode of MC
1374	Lin <i>et al.</i> , (2007)	
1188	Yin <i>et al.</i> , (2006)	Anti-symmetric stretching of the C-O-C
1124	Lin <i>et al.</i> , (2007)	
1163	Rimduisit <i>et al.</i> , (2008)	C-O stretching from asymmetric oxygen bridge
1117, 1070	Liu <i>et al.</i> , (2004)	Stretching of ether bonds in MC
1055	Yin <i>et al.</i> , (2006)	Skeletal vibration involving the C-O stretch
900-1500	Lin <i>et al.</i> , (2007)	Finger print region of MC
896	Rimduisit <i>et al.</i> , (2008)	Ring stretching

**d) Structural properties of MC**

Structural studies can show amorphous or semi-crystalline nature of MC. Some researchers reported that MC is an amorphous polymer [Ozeki *et al.*, 2005] and some researchers reported MC being semi-crystalline [Gotoh *et al.*, 2004]. Figure 2.13 are examples of x-ray diffractograms that exhibit the nature of MC.



**Figure 2.13: X-ray diffraction of pure MC reported by: (a) Rimdusit *et al.* (2008), (b) Yin *et al.* (2006) and (c) Ozeki *et al.* (2005)**

Rimduisit *et al.* (2008) reported that MC has some order of intermolecular structure due to the appearance of some broad diffraction peak which can be observed between  $2\theta = 9$  and  $21^\circ$ . Yin *et al.* (2006) pointed that MC is mostly amorphous. Ozeki *et al.* (2005) suggest that MC is amorphous because x-ray diffractogram show hollow radiograph patterns. However, Gotoh *et al.* (2004) reported that MC is a semi-crystalline polymer due to some diffraction peaks were observed at  $2\theta = 8.1^\circ$ ,  $13.2^\circ$  and  $21.4^\circ$ .

To the author's knowledge, there are very few reports on MC as PE, but the appearance of MC in the conductivity studies of polyaniline dispersed with PVA has been reported by Sarkar *et al.* (2005).

## 2.8 Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ )

$\text{NH}_4\text{NO}_3$  is the doping salt used to provide protons in the MC based polymer electrolytes prepared. The proton originates from ammonium ions [Srivastava and Chandra, 2000]. Majid and Arof (2005) pointed that, proton conduction occurs in polymer electrolyte through the Grotthuss mechanism.

## 2.9 Poly (ethylene) glycol (PEG)

The general formula of poly (ethylene glycol) (PEG) is  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $n$  is the number of ethylene oxide groups. PEG of different molar masses can be obtained by varying  $n$ . PEG has been used in large quantities in pharmaceutical, cosmetics, and food industries [Ayranci and Tunc, 1997]. PEG with high molecular weight has been used as

polymer host while PEG with low molecular weight has been used as plasticizer. The examples of low molecular weight of PEG are shown in Table 2.11.

**Table 2.11: Examples of low molecular weight of PEG (Ref:\*Ayranci and Sahin, 2008)**

Molecular weight of PEG (g/mol)	*Number of repeating unit, $n$	Viscosity, $\eta$ at 25 °C (cP)	*Density, $\rho$ at 288.15 K (g cm <sup>-3</sup> )	Glass transition temperature (°C)
200	3.1	50	1.128886	-74
300	5.4	70	1.129764	-
400	7.7	90	1.131286	-62

- Information not found

Different molecular weight gives different properties and this can be observed to affect the conductivity. Park *et al.* (2005) studied the effect of relative permittivity and viscosity of PEG on conductivity at room temperature and obtained the low molecular weight PEG has higher relative permittivity and lower viscosity hence resulting in a higher conductivity. Subban and co-workers (2005) also reported similar observations when plasticizing PVC-LiCF<sub>3</sub>SO<sub>3</sub> complexes with PEG of different molecular weights. According to Kinart *et al.* (2007), the viscosity of PEG (200) is 50 cP at 25 °C and its dielectric constant at 293 K is 19.95 but decreased to 18.41 at 303 K. Awwad *et al.* (2002) reported the dielectric constant of PEG (200) as 18.43. Pradhan *et al.* (2007) reported that composite polymer electrolyte based on poly (ethylene oxide)-NaClO<sub>4</sub> dispersed with ceramic filler (SnO<sub>2</sub>) had a substantial enhancement in the electrical conductivity by two orders of magnitude at room temperature if it was plasticized with polyethylene glycol (PEG200). Lee *et al.* (2006) prepared SPEs based on polyethylene non-woven matrix with good mechanical strength and its conductivity could even reach  $3.1 \times 10^{-4}$  Scm<sup>-1</sup> at room temperature by adding PEG as plasticizer.

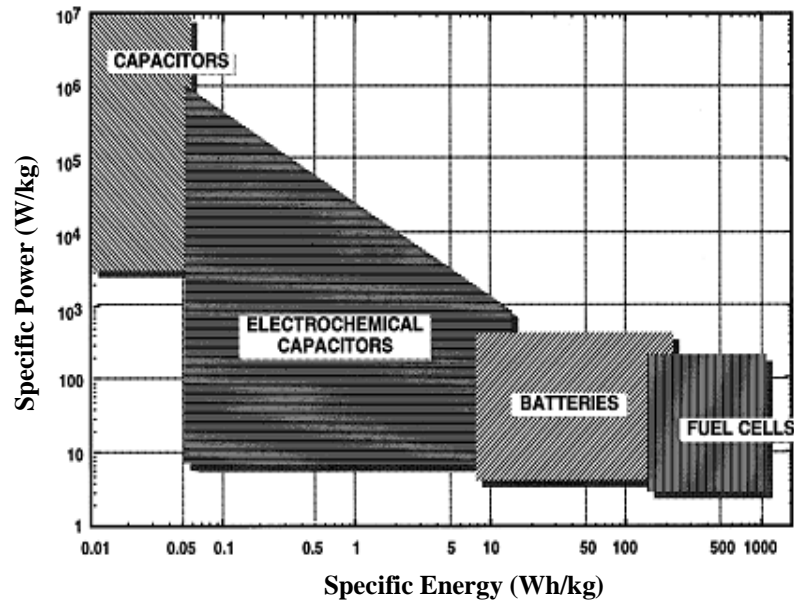
Ayranci and Tunç (1997) stated that PEG is added to edible films in order to reduce brittleness and to increase flexibility, toughness and tear resistance. However, it is also known that as the PEG content increases, the water vapor permeability of films is expected to increase. In other words, PEG provides increasing flexibility and decreasing brittleness to the films at the expense of increasing their water vapor permeability. Park *et al.* (2005) pointed that if PEG is used in a lithium anode battery, the hydroxyl groups present in the PEG chains can react with lithium metal anode and decrease performance of the battery.

## 2.10 Electrochemical Supercapacitors (ES)

Electrochemical supercapacitors (ES) are also known as supercapacitors or sometimes ultracapacitors. They are considered secondary power sources since they are normally used with primary power sources such as batteries or fuel cells [Lufrano and Staiti, 2004]. ES are getting more attention due to their possible application as power back up for electronic equipments, medical devices and electrical vehicles [Hashmi *et al.*, 2005; Matsuda *et al.*, 1999; Ganesh *et al.*, 2008]. The first development program on supercapacitors was initiated in 1989 (Gualous *et al.*, 2003).

Figure 2.14 depicts a Ragone plot, presenting the power densities at the vertical axis versus their energy densities at the horizontal axis for various energy storage devices. ES acts as intermediate power source between rechargeable batteries and conventional capacitors (CC). It fills the gap existing between batteries, fuel cells and CC [Lufrano & Staiti, 2004; Li *et al.*, 2008; Hashmi *et al.*, 2005].





**Figure 2.14: Ragone plot of energy storage devices and conversion device (Kötz and Carlen, 2000)**

Table 2.12 shows the differences between ES, CC and batteries.

**Table 2.12: The differences between ES, CC and batteries (Kötz & Carlen, 2000; Li *et al.*, 2008; Kumar & Bhat, 2009; Ganesh *et al.*, 2008; Obreja, 2008)**

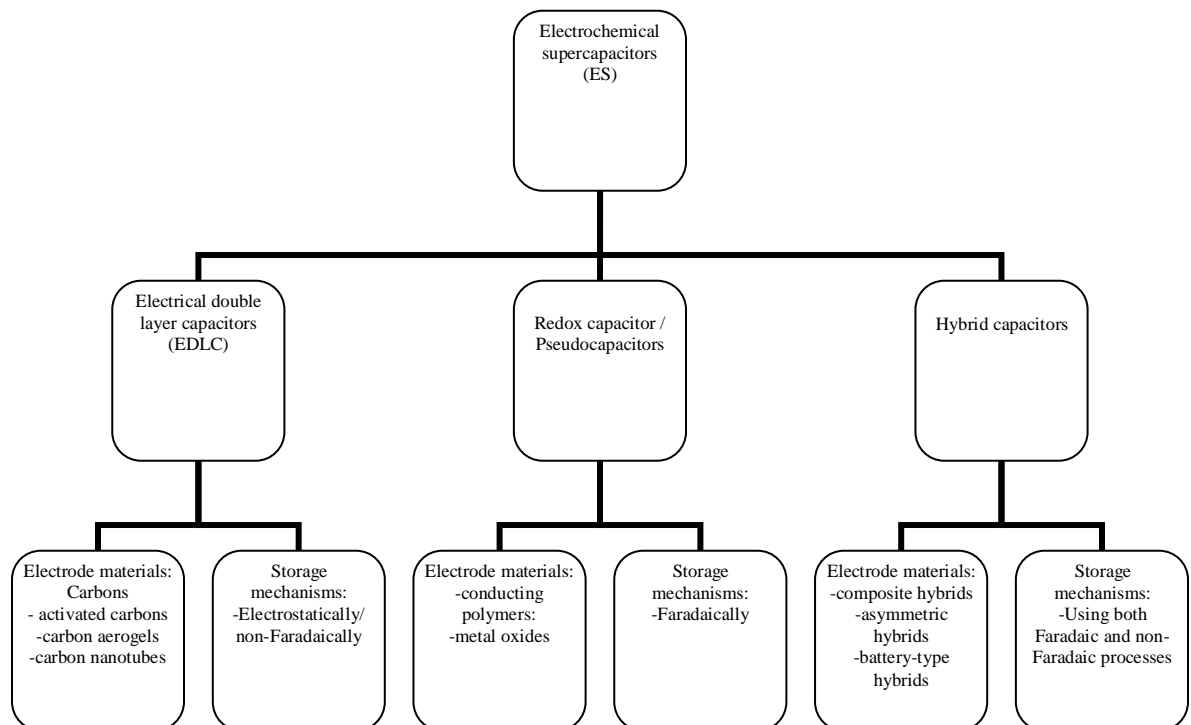
Electrochemical supercapacitor (ES)	Conventional capacitor (CC)	Batteries
Huge potential to bridge the gap between battery and capacitor	Major role in pulsed power technology.	Main choice of energy storage device.
Low power density compare to CC but higher than batteries	High power density (> 10 <sup>6</sup> watts per dm <sup>3</sup> )	Low power density (only 1000 W/kg)
Low energy density compare to batteries but higher from CC	Very low energy density	High energy density (10-500 Wh/kg)
Longer life cycle (> 10 <sup>5</sup> cycles)	-	Short life cycle (≤ 10 <sup>3</sup> cycles)
Rapid charging-discharging	Suffer high self-discharge rates Have discharge time in microseconds	-

## ...TABLE 2.12 CONTINUED...

Charge/discharge efficiency is high and the energy lost to heat during each cycle is relatively small		The energy lost to heat is a much larger amount making heat removal more crucial
Store energy physically, no major change in the structure of the material with charge state		Store energy chemically, undergoes physical change between the charged state and the discharge state

**-Information not found**

There are two main classes of ES: electrical double layer capacitors (EDLC) and redox supercapacitors (Hashmi *et al.*, 2007, Yang *et al.*, 2005). Halper and Ellenbogen (2006) pointed that, there are three classes of ES: EDLC, redox supercapacitors and hybrid capacitors. These classes of ES were based on the types of electrode materials employed and the charge storage mechanism at the electrode/electrolyte interfaces [Hashmi *et al.*, 2007, Kötzt & Carlen, 2000]. Figure 2.15 shows the taxonomy of ES.



**Figure 2.15: Taxonomy of ES (Halper & Ellenbogen, 2006)**

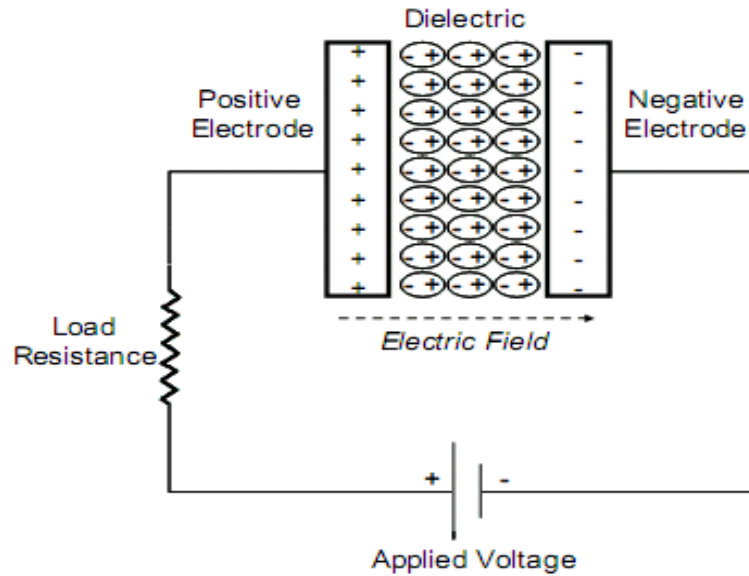
Charge storage of EDLC is electrostatic in nature [Hashmi *et al.*, 2005]. Electric charge is stored in the electric double-layer at the electrode/electrolyte interface when DC voltage is applied [Matsuda *et al.*, 1999]. EDLC is safe because the storage mechanism is non-Faradaic i.e, there are no transfer of charge between electrode and electrolyte [Halper and Ellenbogen, 2006] but based on the accumulation of charges in electrical double layers [Ganesh *et al.*, 2008; Mitra *et al.*, 2001]. For redox supercapacitors, the storage mechanism is faradaic [Hashmi *et al.*, 2007]. Faradaic process involves the transfer of charge between electrode and electrolyte such as oxidation-reduction reactions, electrosorption and intercalation process [Halper and Ellenbogen, 2006] and use two types of electrodes materials; metal oxides such as NiO<sub>x</sub>, CoO<sub>x</sub>, RuO<sub>2</sub> etc and conducting polymers. Hybrid capacitor combined both EDLC and redox capacitor technologies. It was developed to manipulate the advantages and moderate the disadvantages of EDLC and redox capacitor to improve performance characteristics [Halper and Ellenbogen, 2006].

In this work, we focused on the fabrication of electrical double layer capacitor using the highest conducting polymer electrolytes.

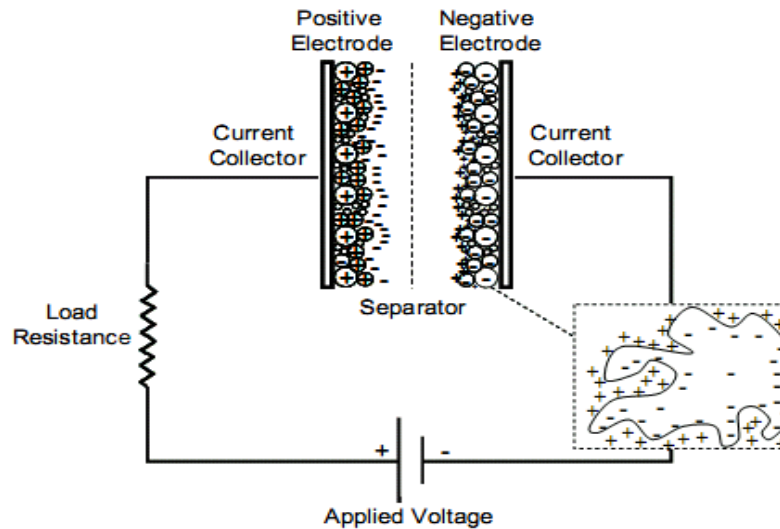
### **2.10.1 Electrical double layer capacitor (EDLC)**

The EDLC was first developed by Boos in 1971 (Tabuchi *et al.*, 1993). The same kind of electric double layer capacitor was also produced by Nippon Electric Company (NEC), Japan (Tabuchi *et al.*, 1993). NEC and Panasonic in Japan have been producing EDLC components since the 1980's. EDLCs store electrical charge in a similar manner to the conventional capacitors, Figure 2.16, but the charges do not accumulate on

two conductors. Instead the charges accumulate at the interface between the surface of a conductor and an electrolytic solution as shown in Figure 2.17. The accumulated charges hence form an electric double-layer, the separation of each layer being of the order of a few Angstroms.



**Figure 2.16: Schematic of conventional capacitor (Halper & Ellenbogen, 2006)**



**Figure 2.17: Schematic of EDLC (Halper & Ellenbogen, 2006)**

### 2.10.2 Materials for EDLC

EDLC employed two electrodes, separator and electrolyte. Electrolytes can be solid, gel or liquid as described earlier. In solid polymer electrolytes, separator is not required. The electrode consists of a current collector to which the active material is adhered. The current collector plays a role to conduct electrons while the active material plays a role to absorb charges from the electrolyte.

Capacitance of EDLC is influenced by many factors such as electrolyte conductivity and large surface area of the materials which form the electrodes. However, report has shown that the pore size of the carbon material can also influence the EDLC capacitance [Wang *et al.*, 2008]. According to Arulepp *et al.* (2004), the surface area of the activated carbon will not contribute to high capacitance if the nanopores of the active material are too small compared to the electrolyte ions. This is because large electrolyte ions cannot enter the nanopores. On the other hand, Khomenko *et al.* (2008) stated that, carbon materials with high surface area have limited long-term stability because the higher the specific surface area, the higher is the active surface area and hence the higher the risk of electrolyte decomposition.

The materials to prepare the electrode consist of active material, binder and solvent. The active material include active carbon, carbon black, carbon cloth, carbon fiber, carbon nanotubes, glassy carbons, and carbon aerogels [Zhu *et al.*, 2004; Niu *et al.*, 2006; Boskovic *et al.*, 2005]. The criteria to choose carbonaceous materials depend on specific surface area and pore size.

Electrodes of commercial supercapacitors are based on porous or activated carbon material due to its availability and low cost [Obreja, 2008]. Active carbons have attracted considerable attention because of their desirable surface area, environmental safety, low cost, physical nature and pore size distribution [Pandolfo and Hollenkamp, 2006; Chandasekaran *et al.*, 2008].

Li *et al.* (2008) prepared various types of activated carbon (AC) based on different types of starch and studied the physical properties of AC and hence investigated the electrochemical performance capacitor based the starch-derived AC using 30 wt.% KOH aqueous solution. These AC have different specific surface areas (which is 1339, 1410, 1451 and 1510 m<sup>2</sup> g<sup>-1</sup>). From density functional theory (DFT) method, the pores of starch AC are mainly micropores (< 2nm) and mesopores (2-50 nm width). Micropores play an adsorption role for the formation of the electrical double layer whereas mesopores are responsible for the adsorption and quick transportation of ions to the bulk of the electrode material. Higher capacitance can be obtained from capacitors based on high specific surface area of AC.

AC alone cannot act as a fully suitable material for the polarizable electrodes because of its low electrical conductance [Show and Imaizumi, 2007]. Electrical resistance of AC electrode is high because the electrode contains binder. Binders such as PTFE and PVdF may block entrance to the pores in the porous carbon hence resulting in diminishment of double-layer capacitance [Hsieh and Teng, 2002].

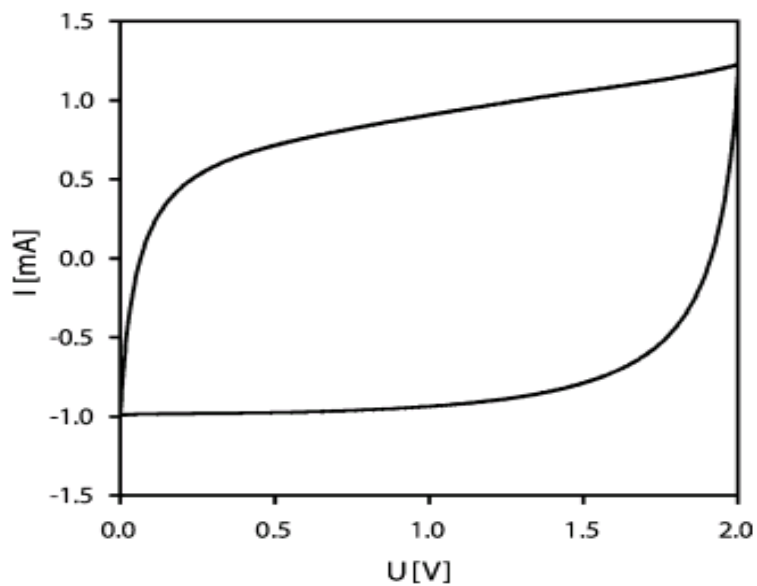
Carbon nanotubes (CNTs) and carbon black are normally added to the electrodes in order to decrease resistance. CNTs have a high electrical conductivity and chemical stability. Tube shaped with a diameter of a few nm is expected to be suitable for forming the double layer between the surface and the electrolyte by facilitating electrical conduction in the polarizable electrode and decrease the series resistance of the EDLC [Show and Imaizumi, 2006].

Carbon black (CB) added in the electrode mixture can enhance electron conduction and to decrease the ohmic resistance of the electrode [Lust *et al.*, 2004]. Sheem *et al.* (2006) pointed that CB enhances the electrical conductivity by forming conducting bridges between particles of the active materials. Activated carbon fiber (ACF) cloth has a high specific surface area and suitable pore size distribution for forming an electric double layer. ACF-cloth is a self-supported material and shows high electrical conductivity does not need binder in their application [Tanahashi, 2005]. It is also necessary to add the electrolyte in solution form in the electrode mixture. This is to ensure that polarization occurs in the bulk of the electrode system.

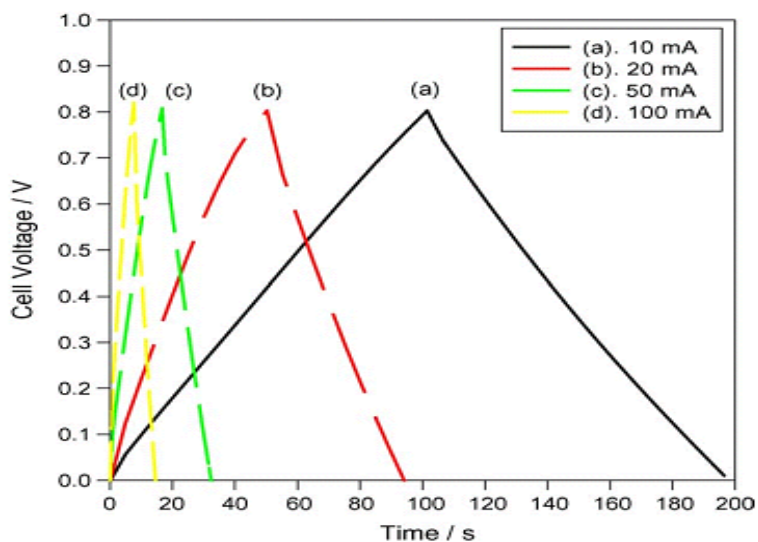
### 2.10.3 Characterization of EDLC performance

Figure 2.18 shows the cyclic voltammogram of a capacitor studied by Lewandowski and co-workers (2003). Lewandowski *et al.* (2003) studied the performance of chemical capacitor using polymer electrolyte based on poly (acrylonitrile)-sulphone- $(C_2H_5)_4NBF_4$  and electrode based on activated carbon powder. A rectangular shape was obtained from

cyclic voltammogram characteristics as shown in Figure 2.18. No faradaic process occur in the capacitor and suggesting that the pure electrostatic behavior of capacitor.



**Figure 2.18:** Cyclic voltammogram of a capacitor using poly (acrylonitrile)-sulphone- $(\text{C}_2\text{H}_5)_4\text{NBF}_4$  electrolyte (Lewandowski *et al.*, 2003)



**Figure 2.19:** Charge-discharge curves for EDLC with PVA polymer electrolyte at different charge-discharge rates and at 25 °C (Yang *et al.*, 2005).



Yang *et al.* (2005) investigated the viability of alkaline polyvinyl alcohol as a membrane in EDLC by cyclic voltammetry and charge-discharge characteristics. The EDLC shows typical charge-discharge characteristics at the working voltage as depicted in Figure 2.19. The EDLC is stable up to 1000 cycles indicating that EDLC using PVA SPE has good cycle-life characteristics and is a promising material for EDLC.

Table 2.13 gives the examples of EDLC using polymer electrolytes as reported in the literature.

**Table 2.13: Examples of EDLC using polymer electrolytes**

Electrolyte	Active material	Specific capacitance (F g <sup>-1</sup> )	References
PVA-PSA	Activated carbon (400 m <sup>2</sup> g <sup>-1</sup> )	40	Kumar and Bhat (2009)
PVA-KOH	80% BP2000 (1500 m <sup>2</sup> g <sup>-1</sup> ), 10 % graphite, 10 % PTFE	100	Yang <i>et al.</i> (2005)
PAN-(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBF <sub>4</sub>	Activated carbon powder/ acetylene black/graphite	34	Lewandowski <i>et al.</i> (2003)
PAN-Ammonium salts-PC	Activated carbon fiber cloth (> 1000m <sup>2</sup> g <sup>-1</sup> )	16	Ishikawa <i>et al.</i> (1995)
Nylon6-10, 2H <sub>3</sub> PO <sub>4</sub> blend	Activated carbon fabrics (2000 m <sup>2</sup> g <sup>-1</sup> )	70	Lassègues <i>et al.</i> (1995)

## 2.11 Summary

This chapter begins with an introduction the polymers, polymer electrolytes, plasticized polymer electrolytes and their basic properties. Some examples were listed in

several tables. Basic knowledge of materials used in this work i.e. MC,  $\text{NH}_4\text{NO}_3$  and PEG and their properties are described. Some basic information about electrical double layer capacitors (EDLC) and the materials used to prepare the electrodes were also reviewed.