

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

We should remind ourselves the objectives of this present work before making the conclusions for this thesis. In order to employ solid polymer electrolytes with high conductivity as a membrane in capacitors, two methyl cellulose (MC) based polymer electrolyte systems have been prepared. The first is MC-NH₄NO₃ system where NH₄NO₃ is the proton source. The maximum conductivity at room temperature i.e. $2.10 \times 10^{-6} \text{ S cm}^{-1}$ for sample containing 25 wt.% NH₄NO₃. To enhance the room temperature conductivity for this polymer electrolyte, poly (ethylene glycol) (PEG) with low molecular weight (200 g mol⁻¹) was added to the 75MC25AN electrolyte in various concentrations. The conductivity was further increased by two orders of magnitude ($1.14 \times 10^{-4} \text{ S cm}^{-1}$) for 75MC25AN added with 15 wt.% PEG.

The increase in room temperature ionic conductivity for the MC-NH₄NO₃ complexes with salt concentration is attributed to the increase in charge carriers and the increase of amorphousness of the samples. The decrease in conductivity for samples containing more than 25 wt.% salt is due to increase in crystallinity and recrystallisation of salt out of the polymer, and this is also indicated from FTIR spectroscopy. From calculations using Rice and Roth model the lowest conducting sample has the lowest number density of charge carriers i.e. $8.21 \times 10^{12} \text{ cm}^{-3}$ and the highest conducting sample

has the highest number density of charge carriers i.e. $1.26 \times 10^{17} \text{ cm}^{-3}$. Dielectric behavior at room temperature also supports conductivity increase due to increase in charge carriers. Plasticization with PEG enhances the conductivity at room temperature and is attributed to the increase of mobility and diffusivity of charge carriers as verified by Rice and Roth model. PEG in this work helps in dissociating the NH_4NO_3 salt by increasing the relative permittivity of the plasticized samples as shown in ϵ_r versus frequency plot. The conductivity drop after addition of 15 wt.% salt can also be verified from XRD results when the lowest crystalline fraction has the highest conductivity. Plasticization also helps to decrease local viscosity which is manifested by the increase in mobility with temperature.

The temperature dependence conductivity for the unplasticized MC based polymer electrolyte obeys Vogel-Tamman-Fulcher relationship and on the other hand, the plasticized MC based polymer electrolyte follows the Arrhenius rule. Temperature caused the conductivity increase in this work by heating which make the ions to vibrate faster and achieve sufficient energy to dissociate. For unplasticized samples, conductivity-temperature relationship show the conductivity drop after 60 °C due to decrease of the number density of hydroxonium ions when water molecules in the sample is removed upon heating. With addition of PEG, the conductivity increases with temperature up to 100 °C because PEG is hygroscopic enough to enable it to retain moderate moisture in the samples.

The second objective was achieved when the supercapacitor worked. The capacitor was fabricated using the highest conducting sample, 63.75MC21.25AN15PEG. This sample has a wide stability window. The capacitance of the capacitor is dependent on the internal resistance, contact between electrode and electrolyte interface and current density.

The capacitors in this work do not exhibit Faradic processes as shown by cyclic voltammogram. No electrochemical reaction occurs in this capacitor because all the charges accumulated and build up a double layer between electrode and electrolyte. From charge-discharge characteristics, capacitance decreases with increasing current density. High EDLC internal resistance restricts the electrical energy to be stored in the EDLC. The internal resistance of EDLC decreases with decreasing current density. The decrease in the specific maximum energy for high current density is due to the large internal resistance. The internal resistance also results in specific power loss because the charge and discharge current flows according to the series resistance. Hence at lower current density EDLCs deliver higher specific power. Hence the advantage of a larger surface area EDLC. The specific power delivered from EDLC obtained is still lower, between 0.09 to 0.14 mW. This is due to the high EDLC internal resistance. The coulombic efficiency calculated using the equation in Chapter Three is quite high (in the range 73 to 95 %).

Further work studies should be extended to improve conductivity and mechanical and thermal strength of MC based polymer electrolytes. Since MC is very sensitive to moisture, there is a need upgrade MC based polymer electrolytes by decreasing water solubility and improve moisture barrier properties. Cross-linking is one method to enhance the performance of water soluble polymer electrolytes like MC. Water uptake, ion exchange capacity and the mechanical strength need to be carried out to quantify the improvements required.

Further studies in preparation of electrode should be done to produce low resistance electrodes with high mechanical strength and good surface morphology. To decrease the resistance of electrode, carbon nanotubes, carbon aerogels or activated carbon fiber cloth

should be used to replace activated carbon as electrode materials. Self discharge must be minimized to obtain the excellent voltage retention. All these can be minimized if internal resistance can be minimized.