

# ELECTRICAL AND FTIR STUDY OF CHITOSAN COMPLEXED WITH ADIPIC ACID PROTON CONDUCTING POLYMER ELECTROLYTES

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## Introduction

One of the factors that contribute to the battery performance is the electrolyte. Electrolytes can be classified into three main groups which are liquid polymer electrolyte, gel polymer electrolyte and solid polymer electrolyte. There are several advantages had been discovered on solid polymer electrolytes (SPEs). Good contact between electrode and electrolyte, simple preparation in different forms, good mechanical and adhesive properties are the advantages of the SPE which played vital role as ionic conductor [1].

The main objective of this work is to study proton conducting SPE consists of chitosan and adipic acid. In addition, this work studied the characterizations of the chitosan-adipic acid (C-AA) solid electrolyte in the effort to find alternative natural polymer based electrolytes in battery. Furthermore the understanding of proton conducting solid polymer electrolytes doped with adipic acid (AA) as a proton source and the interactions between salt and polymer were developed.

## Experimental Method

### Sample Preparation

1 g of chitosan (EASTERN GLOBAL,  $M_r = 60\ 000$ , deacetylation  $\sim 85\%$ ) was mixed into 100 ml of 1% acetic acid (AJAX) and the mixture was stirred continuously until chitosan dissolved. Then, AA was added and stirred until a homogenous solution obtained. The mixture was casted into Petri dishes and let dry at room temperature before further drying in the desiccators. The composition of AA was varied (10–45 wt.%) and samples obtained will be designated by an abbreviation; for example, the sample containing AA of 10 wt% will be called S1.

### Apparatus and Procedures

The infrared spectra were recorded at room temperature (r.t) using the Alvarat 380 FTIR Thermo Nicolet in the region between  $550 - 4000\text{cm}^{-1}$  and resolution of  $4\text{ cm}^{-1}$ .

Electrical Impedance Spectroscopy (EIS) was performed with HIOKI 3531 Z Hi-Tester interfaced to a computer. The frequency ranging from 42 Hz to 1 MHz in the temperature range between r.t and 353 K. The bulk impedance ( $R_b$ ) value obtained from the Cole-Cole was used to calculate the ionic conductivity ( $\sigma$ ) of the sample following the work done by [24]. Various dielectric data

such as complex dielectric constant  $\epsilon^*$  and complex electrical modulus,  $M^*$  were evaluated from the recorded complex impedance data, for each temperature.

## Results and Discussion

All samples prepared were colorless and transparent films with good mechanical properties. Fig.1 depicts the spectra of pure AA, chitosan acetate (CA) and sample S0 to S8 between  $700\text{ cm}^{-1} - 2000\text{ cm}^{-1}$ . The band at  $1560\text{ cm}^{-1}$  is assign to asymmetrical  $\text{COO}^-$  stretching of the acetic acid which indicates that chitosan and acetic acid formed CA. Upon addition of AA, the peak shifted to  $1550\text{cm}^{-1}$  and the intensity of the peak increase gradually with the addition of AA until 35 wt.% indicating that the deprotonation of the AA increases. Further addition of AA caused the decrease of the peak intensity. This is accommodating to the values of the conductivity obtained for the samples. The peak at  $1689\text{ cm}^{-1}$  belongs to  $\text{C}=\text{O}$  stretching of AA. The intensity of the peak increases with the addition of AA. Peak at  $1650\text{ cm}^{-1}$  is due to the carbonyl stretching of amide in chitosan, shifted to lower wavenumber which indicates the complexation occurred between chitosan and salt, thus indicative of the protonation of  $\text{COOH}$  [4].

The  $\sigma_{\text{r.t}}$  of chitosan-adipic acid system is depicted in Fig.2. The highest  $\sigma_{\text{r.t}}$  is  $1.40 \times 10^{-9}\text{ Scm}^{-1}$  for S6. The conductivity increases gradually with AA concentration due to the increasing of the number of mobile charge carriers [2]. As the amount of salt added increases, the host matrix became more crowded with the dopant ions, thus, overcrowding reduces the number of charge carriers due to limitation of ionic mobility. Hence, the conductivity decreases after 35 wt.% [24].

Fig.3 depicts the plot of  $\sigma$  versus  $1/T$  for samples S1–S8 from r.t to 353 K. The linear variations of the plot suggest an Arrhenian behavior [24] which implies that the conductivity is influence by the temperature.

The variation of dielectric loss and constant are shown in Figure 5(a) and (b). There are no appreciable relaxation peaks observed in the frequency range employed. Both dielectric constant and loss rise sharply at low frequencies indicating that electrode polarization and space charge effects occurred confirming non-Debye dependence.

The variations of real ( $M_R$ ) and imaginary ( $M_I$ ) parts of electrical modulus are depicted in Figure 6(a) and (b) respectively. Both  $M_R$  and  $M_I$  show an increase at higher frequency end and in the low frequency regime, the

values tend to zero.  $M_i$  peaks position is observed to shift towards higher frequencies. The presence of such relaxation peaks indicates that the samples are ionic conductors. That has been shown to be  $H^+$  in the FTIR study. The appearance of long tail at low frequencies is due to the large capacitance associated with the electrodes, hence, implies that the relaxation time for the protons at high temperature is shorter than that at lower temperature which explains why the conductivity of the film is higher at higher temperature.

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Fig.1. FTIR for Adipic Acid (AA), Chitosan (CS) and S0 to S8.

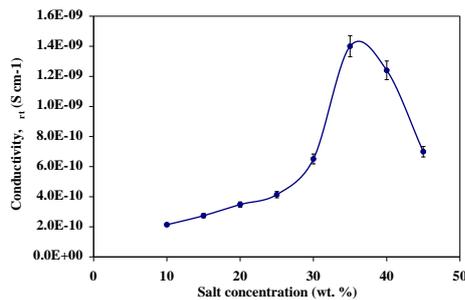


Fig.2 Variation of room temperature conductivity as function of salt concentration.

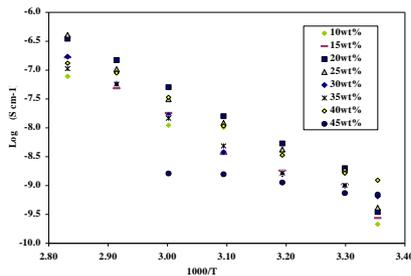
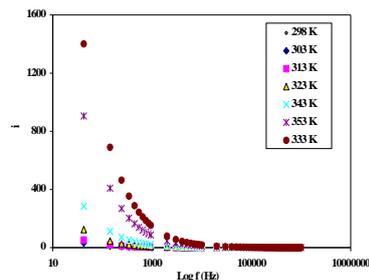


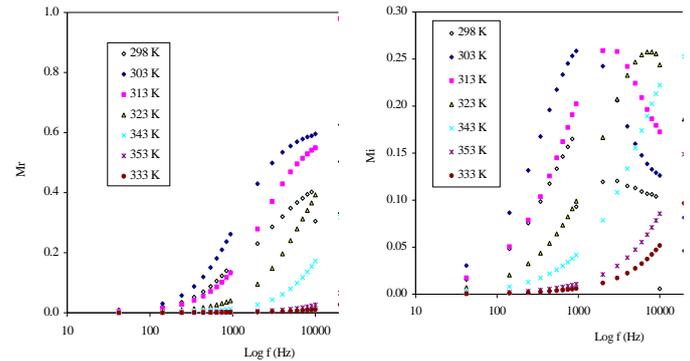
Fig.3 The conductivity versus temperature plot for different concentration of Adipic Acid

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(b)

Fig.5 (a) Dielectric constant and (b) dielectric loss as a function of frequency at various temperatures for sample S6.



(a)

(b)

Fig.6 Frequency dependence of (a) real part and (b) imaginary part of electrical modulus at various temperatures for sample S6

### Conclusion

The FTIR and electrical properties of C-AA film electrolytes were investigated. The wt.% of AA and temperature was found to influence the proton conduction, thus, influence the conductivity. The shifts in the higher to lower wavenumbers and the changes in the peak intensity in the FTIR study indicates that complexation occurs between the polymer host and the salt, thus the deprotonation of  $H^+$  occurs in the electrolytes.

### References

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