

# FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ELECTRICAL CHARACTERIZATION OF METHYLCELLULOSE BASED SOLID POLYMER ELECTROLYTE DOPED WITH SODIUM IODIDE

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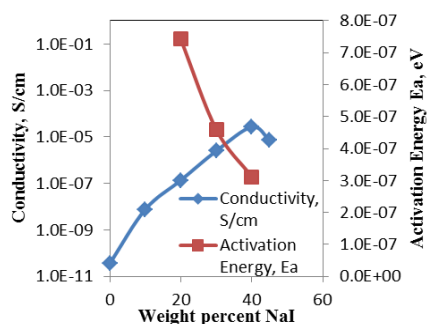
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## Graphical abstract



## Abstract

Methylcellulose-Sodium Iodide (MC-NaI) solid polymer electrolyte was prepared using solution cast technique and the conductivity and permittivity characteristics of the material were studied. FTIR studies confirmed that NaI plays a role as the conducting ions without altering the molecular structure of the polymer. Using Electrical Impedance Spectroscopy technique, it was found that the conductivity of MC-NaI polymer matrix to be the highest at 40 wt% NaI ( $2.70 \times 10^{-5}$  S/cm). Conductivity of MC-NaI also increases with temperature, but decreases as temperature exceeds 333K. Dielectric studies of the material also confirm these findings, where it was found that dielectric constant and dielectric loss to be the highest at 40 wt% NaI at low frequency.

**Keywords:** Methyl cellulose, MC, nai, electrical impedance spectroscopy and fourier transform infrared spectroscopy, conductivity, dielectric properties, dielectric constant, dielectric loss

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## 1.0 INTRODUCTION

Interest in sodium ion conducting polymer electrolyte has been increasing in recent years, despite the wide usage of Lithium based polymer. This is due to several setbacks from Li-Polymer materials, which include a highly volatile nature, high hygroscopicity, relatively more expensive, and less abundant, compared to sodium [1-5]. Although some would argue that lithium ions possess higher gravimetric density [6] due to its size, Stavrinidou [7] argues that as the ionic radius of alkali metal increases, the mobility of each ion also increases due to smaller hydronamic radius and thus drags along fewer molecules during ionic transport. As such, many

researches have been done to optimize the usage of sodium ion conducting polymer in order to substitute the need of Lithium based conducting polymer. Methylcellulose (MC), was chosen as a polymer base due to the abundance of lone pair electrons from Oxygen in the C-O-C and carbonyl constituents to assist sodium ion transport [6,7]. Methylcellulose is also a green and non-toxic material and is relatively easy to be synthesized [8,9]. Conductivity studies were carried upon at varied temperatures and FTIR was done to reaffirm that the molecular structure of methylcellulose is not significantly modified with the presence of sodium ions and that the high conductivity is due to the ionic transport mechanism.

## 2.0 EXPERIMENTAL

### 2.1 Chemicals and Materials

Solid polymer electrolyte thin films were prepared using solution cast technique, added with various composition of Sodium Iodide salt (NaI) from Sigma Aldrich ranging from 0 – 45% weight percent salt content. Methylcellulose powder, which was also acquired from Sigma Aldrich, has a paradoxical effect [8,9] where it can only dissolve in water at a temperature below its lower critical solution temperature (LCST) of 40°C, and precipitate out at temperature above it. However, MC creates a gel-like membrane if it is simply added into cold water. Hence, MC needs to be added in boiling distilled water and stirred for 45 minutes minimum at 80°C to disperse MC particles and ensure homogenous solvation before being cooled down to 5°C, creating a highly viscous gel-like solution. NaI was then added into the mixture and stirred for another 48 hours to make sure that salt and polymer complex were homogeneously mixed before they were poured into polystyrene petri dishes to evaporate the solvent under room atmosphere. This technique created thin films with thickness ranging from 60 µm to 120 µm as the amount of salt increases.

### 2.2 Sample Characterization

FTIR studies of the samples were done using Perkin Elmer FT-IR Spectrometer Spectrum 2000 at the range of 400 to 4000 cm<sup>-1</sup> at 4 cm<sup>-1</sup> number resolution to determine the structure and confirm salt complexation with the polymer base. Electrical Impedance Spectroscopy Analysis were then done on all samples at constant humidity and temperatures ranging from 25°C to 80°C using HIOKI 3531 Z LCR Hi-Tester with frequency of 100Hz to 1MHz. Samples were placed on a sample holder and sandwiched between two stainless steel electrodes with the diameter of 2.4 cm. Bulk resistance, R<sub>b</sub> for each thin films were acquired from the Nyquist/Cole-Cole plots of each samples and conductivity was calculated using equation (1) below

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where t is the thickness of sample (cm), A is the contact area (cm<sup>2</sup>) between the samples and the electrodes, and R<sub>b</sub> is the bulk resistance from the plot.

The activation energy, E<sub>a</sub> of each sample can also be calculated based using Arrhenius equation that relates temperature dependence of sample with conductivity, which is shown in equation (2). Dielectric studies were done using equation (3) and (4) where C<sub>0</sub> = ε<sub>0</sub> as permittivity in free space, A is the interface between electrode/electrolyte, t is the thickness of the sample, and ω = 2πf where f is the frequency in Hz.

$$\sigma = \sigma_0 e^{\left(\frac{-E_a}{kT}\right)} \quad (2)$$

$$\epsilon_r = \frac{Z_i}{\omega C_0 (Z_i^2 + Z_f^2)} \quad (3)$$

$$\epsilon_i = \frac{Z_f}{\omega C_0 (Z_i^2 + Z_f^2)} \quad (4)$$

## 3.0 RESULTS AND DISCUSSION

FTIR Spectra shown in Fig. 1 shows characteristic peak of C-O-C at 1041 cm<sup>-1</sup> due to the antisymmetric stretching of asymmetric oxygen bridge in the cyclohexane ring [6,10]. Although two peaks are observed on pure NaI spectra, namely a sharp peak at 1617 cm<sup>-1</sup> and a broad peak at 3487 cm<sup>-1</sup>, only 1617 cm<sup>-1</sup> is characteristic to NaI while the latter peak represents O-H bond stretching due to water impurities from the salt [11]. 1617 cm<sup>-1</sup> and 1041 cm<sup>-1</sup> peaks seen in Fig. 2 (i) and (ii) respectively, are observed to increase in transmittance number as the weight percent of salt is increased. Further analysis of the spectra concludes that complexation between Na<sup>+</sup> ion and MC polymer base occur, which is proven by the peak shifting from 1041 cm<sup>-1</sup> to 1053 cm<sup>-1</sup>. The complexation does not heavily alter the molecular structure of the polymer shown from the slight shift on the C-O-C peak and is only due to Na<sup>+</sup> ion transport. From Fig. 3, the conductivity of each samples increases as the wt% of NaI salt increases up to 40 wt% NaI where it reached the maximum value of conductivity of 2.7x10<sup>-5</sup> S/cm and decreases as the weight percent of NaI salt is increased. The increase in conductivity at 40 wt% NaI is due to the increase in ionic carrier in the sample although an excess of Na<sup>+</sup> ions reduces the mobility of ion in the polymer chain [12]. At 45% NaI however, the mechanical stability of the sample is low since the sample physically appears near gel-like state, which consequently hinders further EIS analysis.

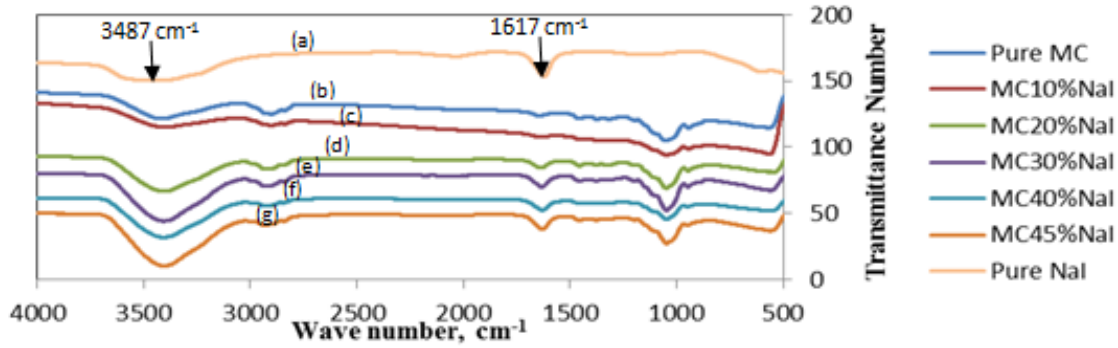


Figure 1 (a) FTIR Analysis on Pure NaI while (b-g) are FTIR of Methylcellulose with various NaI compositions, namely; (b) Pure MC, (c) 10 wt% NaI, (d) 20 wt% NaI, (e) 30 wt% NaI, (f) 40 wt% NaI, (g) 45 wt% NaI.

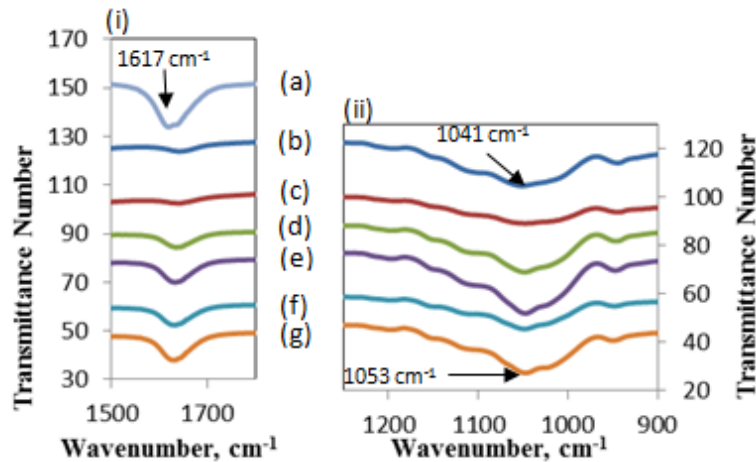


Figure 2 (i) Increment of MC-NaI peak intensity (b-g) at 1617 cm-1 compared to pure NaI (a). (ii) C-O-C peak shift from 1041 cm-1 to 1053 cm-1 (b-g) as NaI salt increases.

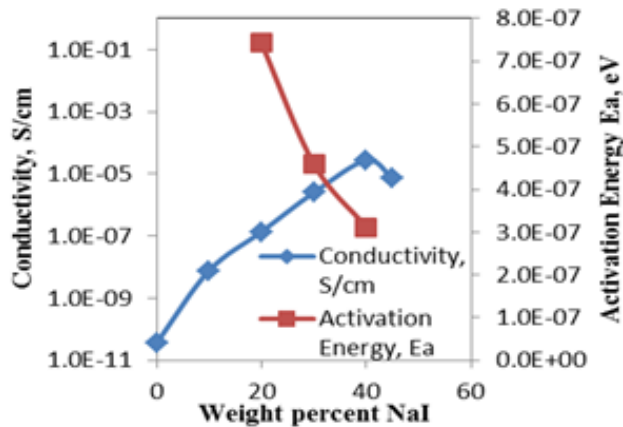


Figure 3: Conductivity of Methyl Cellulose with different composition NaI salt at 298K.

It is observed from Fig. 4 that the conductivity of pure methylcellulose does not significantly increase as a function of temperature. This is to be expected since the mechanisms available for the electric field is minute and significantly less compared to the MC-NaI salt complex. For methylcellulose doped with NaI salts,

the conductivity increases as a function of temperature until 333K, which obeys the Arrhenius law but decreases as it is heated past 333K degree. This decrease is due to high diffusion rate of iodide ions at high temperature and which then re-associate into neutral iodine molecules, and consequently reduces

the mobility of Na<sup>+</sup> ion transport [13]. This explanation is based on the observation of substantial amount of

dark brown spots presence on the sample at high temperature.

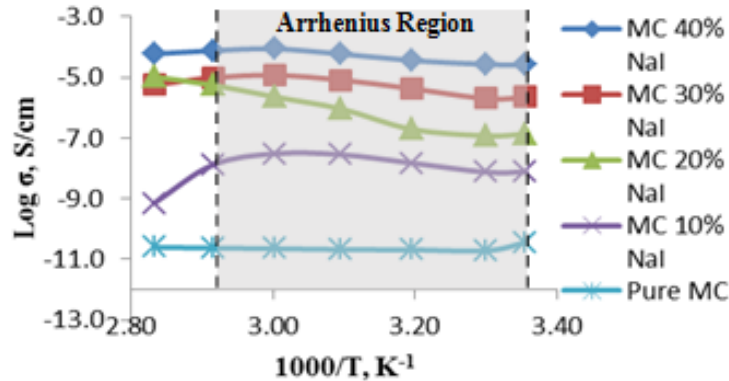


Figure 4 Logarithmic values of MC Conductivity with different composition NaI salt at 298-353K.

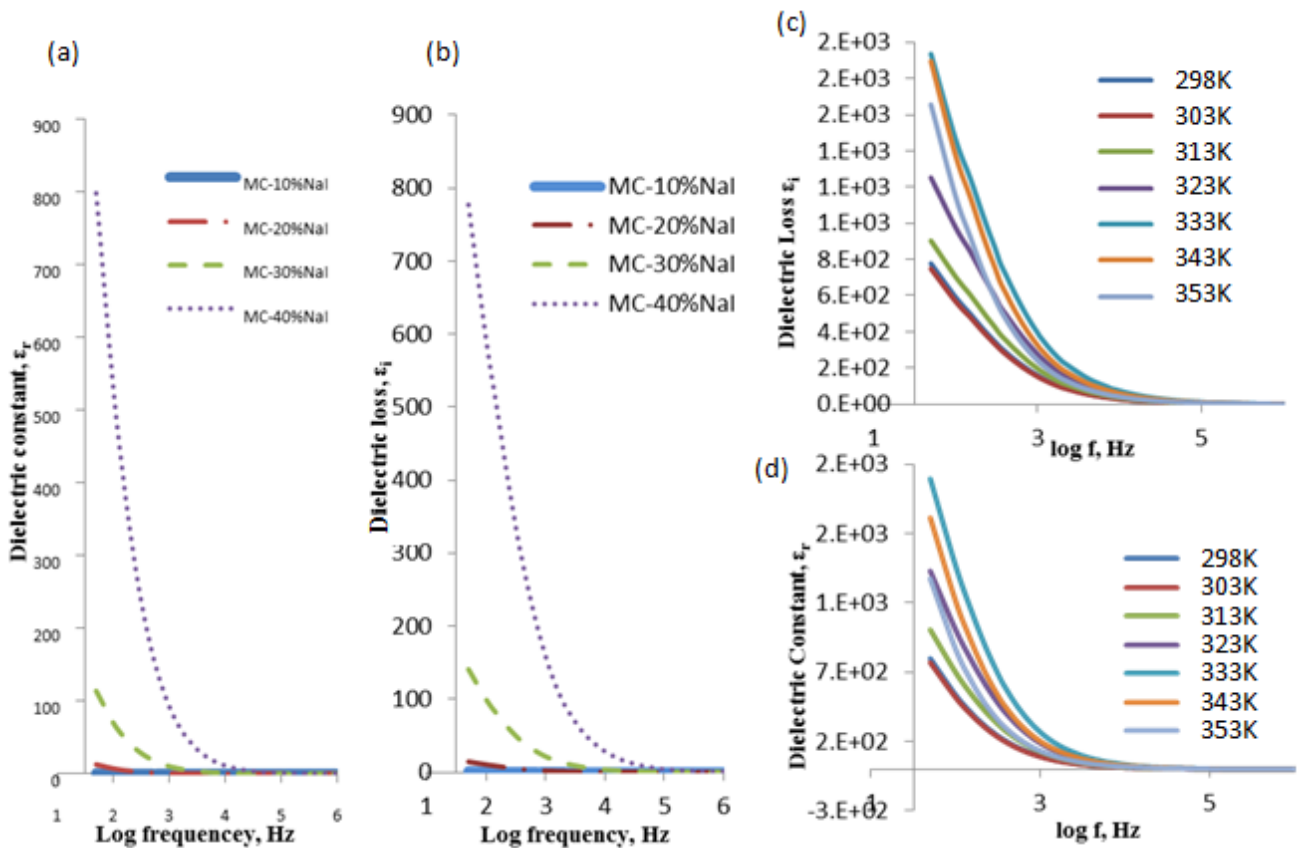


Figure 5 Dielectric constant (a) and dielectric loss (b) of MC-NaI polymer salt complex at different concentration. (c)  $\epsilon_r$  and (d)  $\epsilon_i$  of MC-NaI at different temperature.

Dielectric constant,  $\epsilon_r$ , of MC-NaI polymer salt system as a function of frequency at ambient temperature is shown in Fig. 5 (a) above. It is observed that at low frequency,  $\epsilon_r$  increases as the weight percent of NaI salt is increased up to 40 wt% NaI, which is in

agreement with the trend for composition versus conductivity in Fig. 3. Higher concentration of salt causes an increase in stored charge amount, which also means that the number of mobile cations, Na<sup>+</sup> that migrate in the polymer salt complex has

increased. At high frequency however, the dielectric constant values decreases up to a point of being nearly independent of wt%. This may be attributed to the loss of orientation source of polarizability due to inertia of mobile ions, which leads to dielectric relaxation process [14]. The dielectric loss,  $\epsilon_i$ , can also be observed in Fig. 5(b) above where the  $\epsilon_i$  values are relatively high at low frequency due to the charge accumulation at the electrode/electrolyte interfaces when electrical charge is applied. As a result, the  $\epsilon_i$  values increases as conductivity increases as a function of NaI wt%. Still,  $\epsilon_i$  decreases rapidly as frequency increases due to the decreases in polarizability of mobile ion inertia [15].

Fig. 5 (c) and (d) shows the relationship between  $\epsilon_r$ , and  $\epsilon_i$  of MC-NaI with 40 wt% composition at different temperature variation. It is seen that both values follows the trend in Fig. 4 where the sample reaches maximum  $\sigma$  at 333K and decreases when heated more than 333K. The dielectric constant and dielectric loss both follow the same trend where at low frequency,  $\epsilon_r$ , and  $\epsilon_i$  increases as T increases to 333K but takes a downfall afterwards.

#### 4.0 CONCLUSION

Conductivity of MC-NaI solid polymer electrolyte increases as a function of wt% NaI. The highest conductivity of this polymer-salt complex was  $2.7 \times 10^{-5}$  S/cm at 40 wt% NaI due to complexation of NaI into MC polymer base, which was confirmed from FTIR analyses. Dielectric studies were also done to study the effect of dielectric constant,  $\epsilon_r$ , and dielectric loss,  $\epsilon_i$ , as a function of frequency, where it was found that  $\epsilon_r$  and  $\epsilon_i$  increases as a function of NaI wt% at low frequency, but the effect of NaI wt% towards  $\epsilon_r$  and  $\epsilon_i$  becomes more negligible at high frequency.

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