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## Conductivity and dielectric analysis of cellulose based solid polymer electrolytes doped with ammonium carbonate ( $\text{NH}_4\text{CO}_3$ )

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**Keywords:** Solid polymer electrolytes, carboxy methylcellulose, conductivity, ammonium carbonate

**Abstract.** The present work investigated the effect of carboxy methylcellulose (CMC) solid polymer electrolytes doped with ammonium carbonate (AC) prepared from solution cast technique. The CMC-AC solid polymer electrolytes system has been analyzed using EIS to understand its conductivity and dielectric behavior at temperature range of 303 K to 363 K. The highest conductivity achieved at room temperature (303K) is  $7.71 \times 10^{-6} \text{ S cm}^{-1}$  doped with 7wt.% of AC and all samples follows Arrhenius behaviour. The dielectric constant ( $\epsilon_r$ ) value was found to be dependent of ionic dopant.

### Introduction

Good dimensional and thermal stability, no leakage, flexibility, ease to fabricate and good electrode-electrolyte contact is the important criteria in selecting solid polymer electrolytes (SPE) which make it a promising prospect for electrochemical device applications such as fuel cell, supercapacitors and rechargeable batteries [1,2,3,4]. However, its major downside is it has low conductivity at room temperature which what has propel extensive research in SPE [5]. Incorporating ionic dopant into the SPE to provide ions for conduction was the best way to overcome the problems.

Currently, cellulose based polymer has attracted much attention in SPE development [6,7,8]. Carboxy methylcellulose (CMC) is a derivative of cellulose. It is an abundant natural product which has a white- to cream-colored, tasteless, odorless and free-flowing powder. Due to its biodegradable properties and good film forming abilities, CMC is chosen as the polymer host. [9,10,11,12]. Present work aim to develop new type of SPE with CMC as host and doped with ammonium carbonate (AC) since Ammonium salts has been reported as a good proton donor in SPE polymer matrix. On top of that, AC contains high weight percentage of hydrogen since it has 2 ammonium group ( $\text{NH}_4$ ) [13,14].

### Methodology

#### Sample preparation

2gof CMC was stirred in distilled water until homogenous solution was obtained. Then, different amount of AC (1-11wt.%) was added into the CMC solution and stirred continuously until AC is completely dissolved. Then, the CMC-AC solution was casted into Petri dishes for drying process at room temperature (303 K). Once dried, the CMC-AC film was placed in a desiccator to further eliminate water content in the film for one week. The CMC-AC film was cut into suitable sizes for analysis.

### Electrical Impedance Spectroscopy (EIS)

EIS (HIOKI 3532-50 LCR Hi-Tester) interfaced to a computer with frequency of 50 Hz to 1MHz was used to investigate the conductivity of CMC-AC polymer electrolyte film. The film was placed between the stainless steel blocking electrodes of the sample holder which connected to the LCR tester. The plots of negative imaginary impedance ( $Z_i$ ) versus real impedance ( $Z_r$ ) were obtained from the measurement.

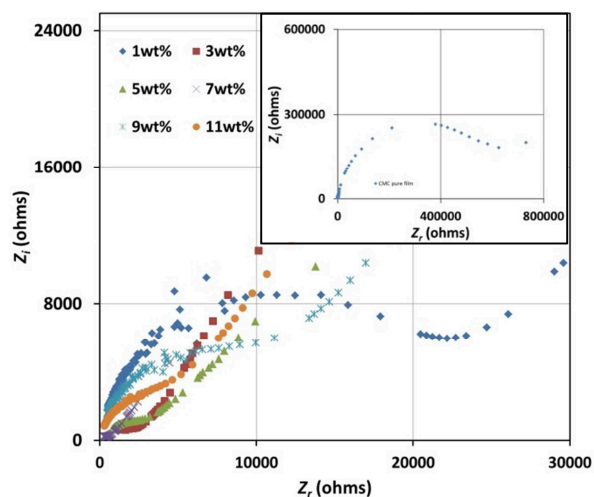


Fig. 1: The Cole-Cole plot for CMC polymer electrolytes at different AC concentration obtained at room temperature. (Inset is the plot for pure CMC film.)

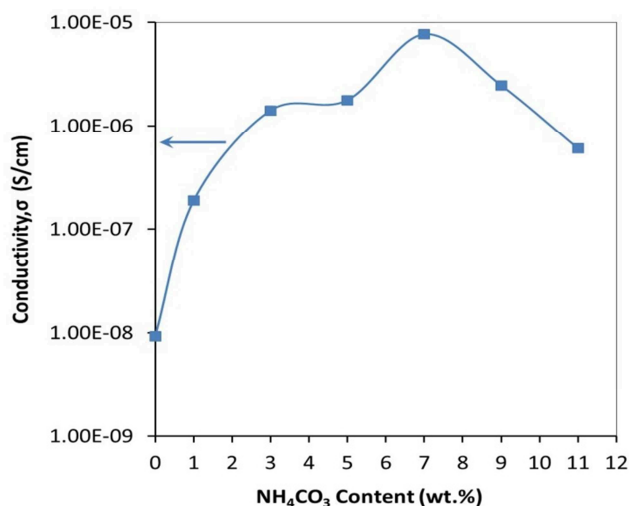


Fig. 2: Conductivity plot of CMC polymer electrolytes doped with different amount of AC at room temperature.

## Results and Discussion

### Impedance analysis

Fig. 1 (a) shows the Cole-Cole plot for different concentration of AC at room temperature. There are two regions observed from the plot. The low frequency inclined line and high frequency semi-circle. Inclined line is due to electrode double layer at the electrode-electrolyte interface. Since the blocking electrodes have been used in the impedance analysis, the electrolyte/electrode interface could be regarded as a capacitance. Vertical spike is expected in the plot if capacitance is ideal. However, the spike is inclined at an angle ( $\theta$ ) less than  $90^\circ$  which may be attributed to the non-homogeneity or roughness of the electrolyte/electrode [15]. The bulk resistance ( $R_b$ ) was obtained from the intercept on the real axis ( $Z_r$ ) and tabulated in Table 1. The semi-circle becomes less and disappears with increasing addition of AC until 7wt.% which suggests only resistive element remains.

### Conductivity analysis

The conductivity is calculated from the equation below:-

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

where  $t$  is the film thickness,  $R_b$  the bulk resistance and  $A$  is the contact area of electrode and electrolyte. The conductivity of CMC-AC polymer electrolytes measured at room temperature is tabulated in Table 1. The conductivity value appears to increase from  $9.33 \times 10^{-9} \text{ S cm}^{-1}$  to  $7.71 \times 10^{-6} \text{ S cm}^{-1}$  with each increment of ionic dopant content (1-7wt.%). The increment is due to decreasing value of  $R_b$  which implies that lower  $R_b$  allow for greater conductivity. Increase of AC content appears to attribute to enhancement of ion density and mobility by increasing the dissociation of ions and create more free ions. Other factor affecting the conductivity value is

because of the amorphous nature of the system. The amorphous nature will results in greater ion diffusion and thus creates a greater conductivity. Furthermore, it also causes a reduction in the energy barrier to the segmental motion of the polymer [16,17]. Beyond 7wt.% addition of AC into the polymer system seems to decrease the conductivity value. This behaviour may be due overcrowding of ions which increased the  $R_b$  and thus lower conductivity.

The  $\log \sigma$  vs  $1000/T$  plot (Fig. 2) show all samples conductivity increase with increasing temperature without sudden drop or jump in values which confirms amorphous structure. The regression values are close to unity ( $R^2 = 1$ ) for all samples suggesting the system follows Arrhenius behavior and can be expressed as

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{2}$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  the activation energy,  $k$  is the Boltzman constant and  $T$  is the absolute temperature. The increment can be explained by the free volume model where free volume increase when temperature increase due to lattice vibration. Which, in turn promotes ions mobility in inter and intra-chain hopping and hence increase the conductivity [13,18].

Dielectric analysis

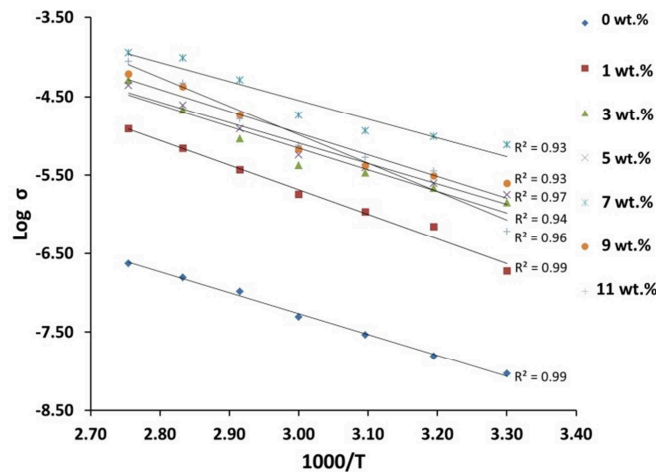


Fig. 2: Temperature dependence of conductivity CMC-AC polymer electrolytes at temperature 303 K – 363 K.

The dielectric property indicates the amount of charge that can be stored by a material and it can be used as an indicator to prove that the increase in conductivity is due to an increase in the charge carriers or free mobile ions [20]. The amount of stored charge will increased with increase dielectric. The dielectric constant ( $\epsilon_r$ ) of a system is defined by:-

$$\epsilon_r = \frac{Z_i}{\omega \epsilon_0 (Z_r^2 + Z_i^2)} \tag{3}$$

where  $C_0 = \epsilon_0 A/t$  and  $\omega = 2\pi f$ .  $\epsilon_0$  is the permittivity of free space. The dielectric constant value of the CMC-AC system against ionic dopant content at selected frequency obtained at room temperature is shown on Fig. 3. The  $\epsilon_r$  value appears to increase with every increment of AC until 7wt.% and drops afterwards. This suggests that the density of mobile ions has increased which increased the stored charged. Decrement of  $\epsilon_r$  is probably due to ions reassociation that decrease mobile ions density [21].The  $\epsilon_r$  value keeps decreasing with increasing frequency for each AC addition. The fast reversals of electric field at higher frequency give a lower  $\epsilon_r$  value due to the inability of charge carriers to orient itself to the electric field and less time for charge to build up [22]. From Fig.5,  $\epsilon_r$  rise sharply at low frequencies and higher temperature. At high frequencies  $\epsilon_r$  dropped and become saturated. At low frequencies region, the mobile ions have ample time amass

and build up charges, hence giving large value of  $\epsilon_r$ .  $\epsilon_r$  increases at higher temperature is due to higher charge carrier density [23]. Since no relaxation peak observed in Fig. 5, it shows that increased in conductivity value is due to increase in number of mobile ions.

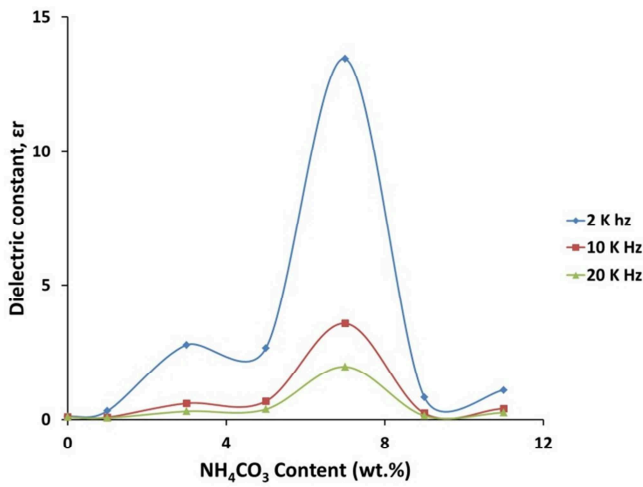


Fig. 4: Dielectric constant value of CMC-AC system against AC content at selected frequency.

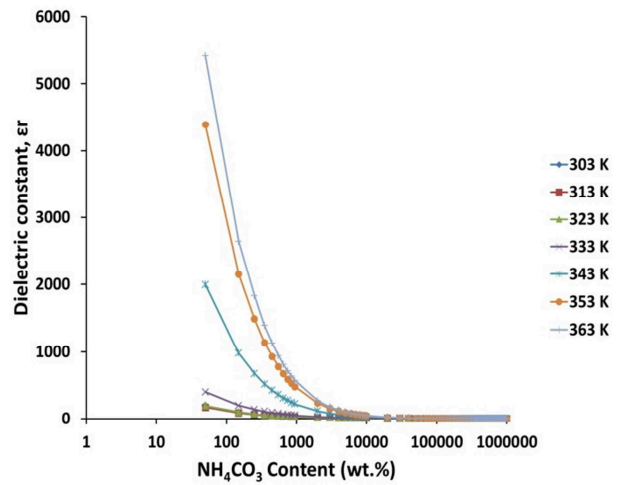


Fig. 5: Dielectric constant value of CMC polymer electrolytes doped with 7wt.% of AC at different temperature.

Further analysis of dielectric behavior can be obtained by using dielectric modulus, which will suppress the effect of electrode polarization. The modulus can be calculated using the following relations:-

$$M_r = \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_i^2} \quad (4)$$

$$M_i = \frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \quad (5)$$

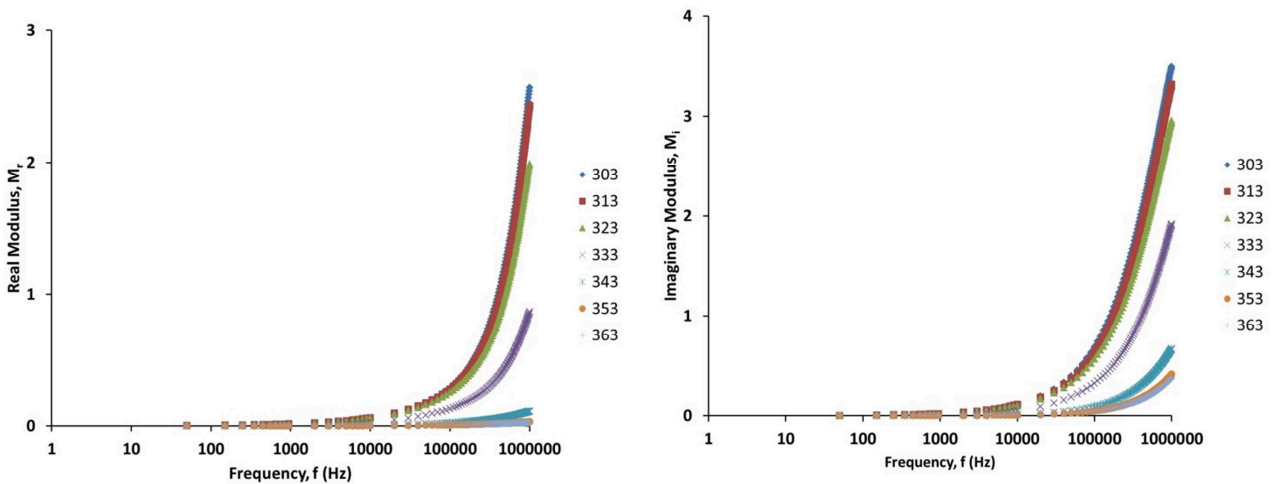


Figure 6: Dielectric modulus of CMC polymer electrolytes doped with 7wt.% of AC at different temperature. (left is real modulus and right is imaginary modulus)

The almost zero value of  $M_r$  at low frequencies indicates the removal of electrode polarization and low frequency tail is due to large capacitance of the electrodes [24]. Both modulus plot show a higher value at lower temperature which might be due to the material bulk effect. With the raise of temperature, the peak decreases implying plurality of relaxation mechanism [25]. An increase in temperature cause mobile charge carriers to move faster and decreased relaxation time.

## Conclusion

The cellulose based (CMC) solid polymer electrolytes doped with AC has been prepared successfully. The bulk resistance ( $R_b$ ) decreased with increment of AC and the conductivity value increase from  $9.33 \times 10^{-9} \text{ S cm}^{-1}$  to  $7.71 \times 10^{-6} \text{ S cm}^{-1}$  when doped with 7wt.% of AC. The system also follows Arrhenius behavior when the temperature increased. The  $\epsilon_r$  increased with ionic dopant as a result of increased number of mobile ions but decreased with increasing frequency due to fast reversal of electric field.

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