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IONIC CONDUCTIVITY AND ELECTRICAL PROPERTIES OF CARBOXYMETHYL CELLULOSE - NH₄Cl SOLID POLYMER ELECTROLYTES

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Abstract

In this present work, carboxymethyl cellulose (CMC) – ammonium chloride (NH₄Cl) solid polymer electrolyte (SPE) films were prepared by solution casting method. The ionic conductivity and electrical properties of SPE films were investigated using Electrical Impedance Spectroscopy. SPE film containing 16 wt. % NH₄Cl exhibited the highest ionic conductivity of 1.43×10^{-3} S/cm at ambient temperature, 303K. The temperature dependence SPE films showed an Arrhenius-type relation where the regression values obtained from the log conductivity versus reciprocal temperature is close to unity ($R^2 \approx 1$). The electrical properties have been measured as a function of frequency of ϵ' , ϵ'' , M' , M'' shown a non-Debye type behavior.

Keywords: Solid polymer electrolyte, carboxymethyl cellulose, ammonium chloride, ionic conductivity, electrical properties

1. Introduction

Solid polymer electrolytes (SPEs) have received widespread attention due to their technological applications in rechargeable batteries, super capacitors, fuel cells, gas sensors and electrochromic power sources [1]. SPEs have several been reported to exhibit several advantages including favorable electrical, optical and mechanical properties, ease of fabrication in the thin film form and ability to form effective electrode–electrolyte contacts [2].

Nomenclatures

C_o	Capacitance without dielectric
ω	Angular velocity

Abbreviations

PVA	Polyvinyl chloride
PVC	Polyvinyl Alcohol
PEO	Polyethylene Oxide
CMC	Carboxymethyl cellulose
NH ₄ Cl	Ammonium chloride

PVA, PVC and PEO are some examples of biodegradable polymers used to prepare SPE films [2-7]. One of the promising materials which are biodegradable is carboxymethyl cellulose (CMC).

CMC deserves a special attention due to its superior mechanical, good electrical properties and easy processability. CMC contains a hydrophobic polysaccharide backbone and it shows CMC one of hydrophilic carboxyl groups. Hence, it is showing water-soluble features [8].

This research focuses to employ CMC as a polymer host due to numerous advantages as previously reported [8]. CMC was doped with NH₄Cl as ammonium ions, NH₄⁺ were believed to be responsible for the ionic conduction in SPE [9]. SPE films were characterized using electrical impedance spectroscopy (EIS) to investigate the ionic conductivity and electrical behavior in a temperature range of 303 K – 353 K.

2. Materials and method

2.0 g of CMC (Acros Organic Co.) was dissolved in 100 ml distilled water at room temperature. A varied amount of NH₄Cl (Sigma Aldrich) in weight percentage (0 – 20 wt. %) was added into the CMC solution. The mixed solution was stirred until complete dissolution was achieved and cast into petri dishes before left to dry at room temperature for film to form.

Electrical impedance spectroscopy (EIS) was utilized to determine the ionic conductivity of SPE films in the frequency range of 50 Hz to 1MHz. The range of the frequency has been used because of the bulk resistance, R_b exists at that range. Electrical measurements were performed on a HIOKI 3532-50 LCR Hi-Tester by using temperatures between 303K and 353K. SPE film was placed between the blocking stainless steel electrodes of a sample cell holder connected EIS. The bulk resistance (R_b) of SPE film was obtained from the plot of imaginary part ($-Z_i$) versus real part (Z_r) of impedance. The ionic conductivity (σ) was calculated from the equation,

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

where, t is the thickness and A (cm^2) is the electrode-electrolyte contact area of SPE films.

3. Results and discussion

3.1. Salt dependence of ionic conductivity

Figure 1 illustrates the ionic conductivity plot of CMC – NH_4Cl SPE films. It is shown that the decreases ionic conductivity starts when NH_4Cl concentration is beyond 16 wt. %. Therefore, the highest conductivity measured is 1.43×10^{-3} S/cm at 16 wt. % of NH_4Cl . The increase of ionic conductivity with the addition of NH_4Cl concentration can be attributed to ion dissociation between host polymer and ionic dopant. As the ionic dopant content increases, more protons are supplied due to the dissociation of the ionic dopant into the polymer matrix [10]. Above 16 wt. % NH_4Cl the conductivity decreases and can be attributed to the reassociation of the ions into neutral aggregates [11, 12]

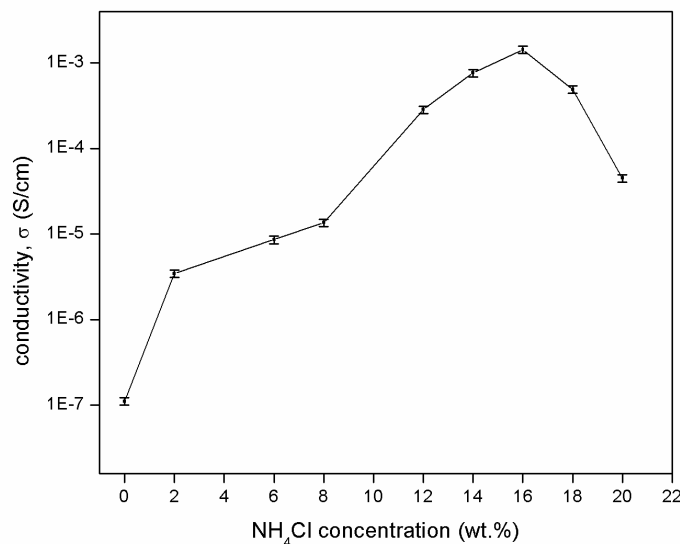


Fig. 1. Ionic conductivity plot of CMC - NH_4Cl solid polymer electrolyte films

Figure 2 shows the Arrhenius plot for CMC – NH_4Cl solid polymer electrolyte films. Refer to Figure 2, log conductivity of SPE films was observed to obey Arrhenius behavior when $R^2 \approx 1$. Regression value, R^2 is shown in Table 1.

Arrhenius plot describes the thermally activated process for SPEs. The relationship between conductivity and temperatures of SPE illustrated by slopes

of $\log \sigma$ versus $1000/T$. According to [6], the ionic conductivity increases with increasing of temperatures due to mobility of carrier of ion concentration.

From the slope of Arrhenius plot, the activation energy, E_a , can be calculated [13],

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where σ_o is the exponential factor, k is the Boltzmann constant and T is the absolute temperature.

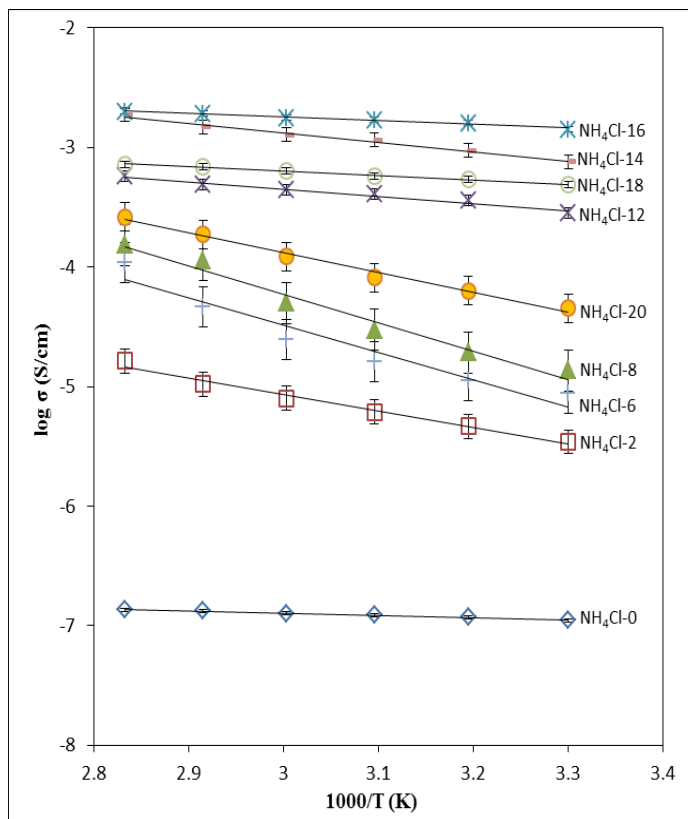


Fig. 2. Arrhenius plot for CMC - NH₄Cl solid polymer electrolyte films

Refer to Table 1 tabulates the regression value and activation energy. From calculation of activation energy, the results were found to increase and then decrease at 12 wt. % in NH₄Cl concentration. Comparing with the values of ionic conductivity, it is inversely proportional with activation energy. According to [7,

12], the value of ionic conductivity values do not show any sudden jump indicating the fact that the polymer electrolyte exhibit a completely amorphous structure. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration [14]. Therefore, it suggests that the value of E_a is due to the energy that is required to provide a conductive condition for the migration of ions [3].

Table 1. The regression values and activation energy of CMC – NH₄Cl Solid Polymer Electrolyte films

Sample	Regression value, R ²	Activation energy, $E_a \times 10^{-1}$ (eV)
NH ₄ Cl – 0	0.99	3.74
NH ₄ Cl – 2	0.98	3.37
NH ₄ Cl – 6	0.93	3.28
NH ₄ Cl – 8	0.98	3.17
NH ₄ Cl – 12	0.98	2.00
NH ₄ Cl – 14	0.99	1.82
NH ₄ Cl – 16	0.98	1.39
NH ₄ Cl – 18	0.99	1.71
NH ₄ Cl – 20	0.99	2.75

3.2 Dielectric studies

The dielectric study was performed on the highest ionic conductivity SPE film (16 wt. % NH₄Cl). Figure 3 shows the plot of frequency dependence of dielectric constant, ϵ_r , while figure 4 shows the plot of frequency dependence of dielectric loss, ϵ_i , at selected temperature. Dielectric constant, ϵ_r , is known as stored charge in a material while dielectric loss, ϵ_i , is a measure of energy losses to move ions when the polarity of electric field turns rapidly.

The ϵ_r and ϵ_i can be defined as [8, 15-17],

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

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

where $C_o = \frac{\epsilon_o A}{t}$, ϵ_o is the permittivity of free space. $\omega = 2\pi f$ and f is frequency.

From Figure 3, it can be observed that there were no appreciable relaxation peaks observed in the frequency range employed in this study. No relaxation peaks are observed could be used as the indicator to show that the increasing conductivity is mainly attributed to the increasing free mobile ions [18]. Both ϵ_r and ϵ_i rise sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming non-Debye dependence [19]. Otherwise, at high frequencies, the occurrence of periodic reversal of the electric field so fast that there is no excess ion diffusion in the direction of the field. Polarization due to charge accumulation decreases, leading to the observed decrease in dielectric constant and dielectric loss [4, 20].

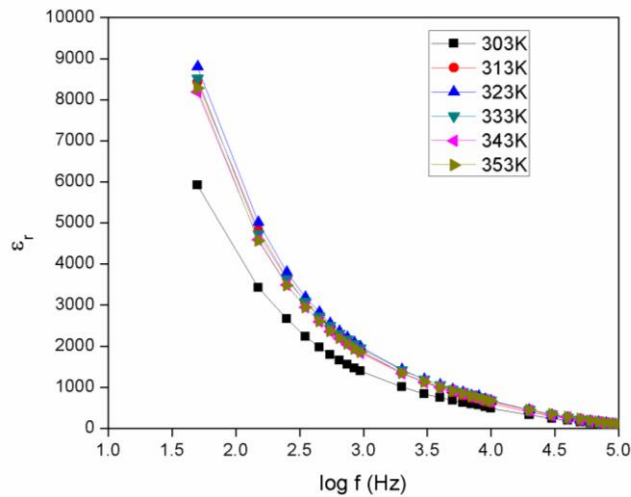


Fig. 3. ϵ_r versus ω for CMC – 16 wt. % NH_4Cl at selected temperatures.

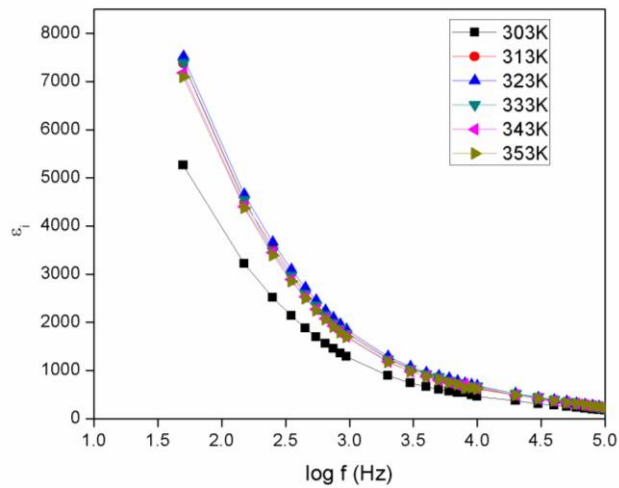


Fig. 4. ϵ_i versus ω for CMC – 16 wt. % NH_4Cl at selected temperatures.

3.3 Modulus studies

Modulus studies highlight the bulk dielectric behavior and suppress the effects of electrode polarization. The real electric modulus, M_r , in Figure 5 and imaginary modulus, M_i , in Figure 6 can be analyzed using equations,

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

$$M_i = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)} \quad (6)$$

The real part of electrical modulus, M_r , versus frequency, ω , at selected temperatures is shown in Figure 5. The long tail in the plot appeared at lower frequencies indicating that the SPE film is capacitive in nature conductors [13]. The slightly peaking curve at higher frequencies ($>10^5$ Hz) might have been caused by the bulk effect [21].

The imaginary part of electrical modulus, M_i , increases with the increasing frequency, however decreases with the temperature. This indicates to the relaxation time for the proton at high temperature is shorter than at lower temperature.

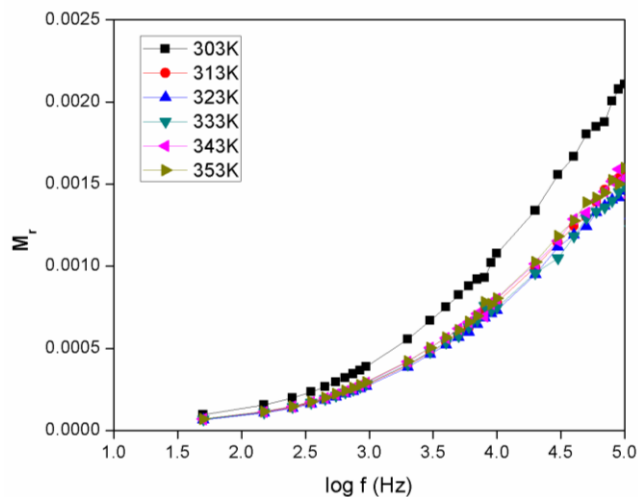


Fig. 5. M_r versus ω for CMC – 16 wt. % NH_4Cl at selected temperatures.

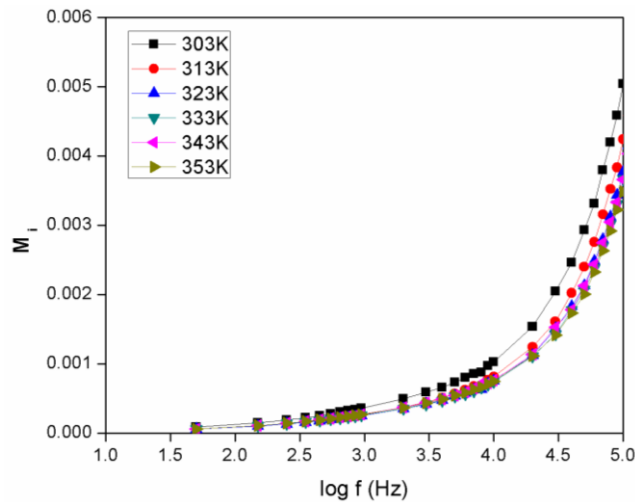


Fig. 6. M_i versus ω for CMC – 16 wt. % NH_4Cl at selected temperatures.

4. Conclusions

The CMC - NH_4Cl solid polymer electrolytes exhibited highest ionic conductivity of 1.43×10^{-3} (16 wt. % NH_4Cl) at ambient temperature. The conductivity arises with temperature following the Arrhenius behavior. The electrical behavior of the SPE films showed a strong dependence on frequencies and temperatures. The frequency dependence of ϵ_r , ϵ_i , M_r , M_i were observed to be non-Debye type.

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