

## IONIC CONDUCTIVITY AND ELECTRICAL PROPERTIES OF CARBOXYMETHYL CELLULOSE - NH<sub>4</sub>Cl SOLID POLYMER ELECTROLYTES

N. H. AHMAD, M. I. N. ISA\*

School of Fundamental Science, Universiti Malaysia Terengganu,  
21030 Kuala Terengganu, Terengganu, Malaysia

\*Corresponding Author: ikmar\_isa@umt.edu.my

### Abstract

In this present work, carboxymethyl cellulose (CMC) – ammonium chloride (NH<sub>4</sub>Cl) 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. % NH<sub>4</sub>Cl exhibited the highest ionic conductivity of  $1.43 \times 10^{-3}$  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  $\epsilon'$ ,  $\epsilon''$ ,  $M'$ ,  $M''$  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 |
| $\omega$ | Angular velocity               |

**Abbreviations**

|                    |                         |
|--------------------|-------------------------|
| PVA                | Polyvinyl chloride      |
| PVC                | Polyvinyl Alcohol       |
| PEO                | Polyethylene Oxide      |
| CMC                | Carboxymethyl cellulose |
| NH <sub>4</sub> 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 NH<sub>4</sub>Cl as ammonium ions, NH<sub>4</sub><sup>+</sup> 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 NH<sub>4</sub>Cl (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 ( $\sigma$ ) was calculated from the equation,

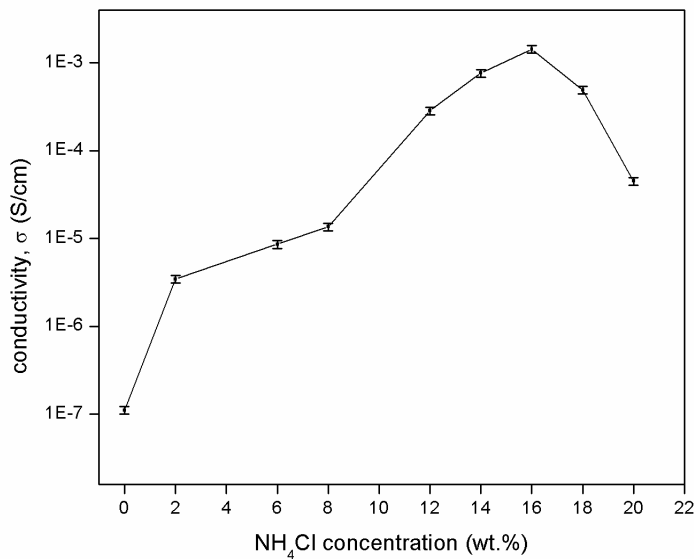
$$\sigma = \frac{t}{R_b A} \quad (1)$$

where,  $t$  is the thickness and  $A$  ( $\text{cm}^2$ ) 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 –  $\text{NH}_4\text{Cl}$  SPE films. It is shown that the decreases ionic conductivity starts when  $\text{NH}_4\text{Cl}$  concentration is beyond 16 wt. %. Therefore, the highest conductivity measured is  $1.43 \times 10^{-3}$  S/cm at 16 wt. % of  $\text{NH}_4\text{Cl}$ . The increase of ionic conductivity with the addition of  $\text{NH}_4\text{Cl}$  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. %  $\text{NH}_4\text{Cl}$  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 -  $\text{NH}_4\text{Cl}$  solid polymer electrolyte films.**

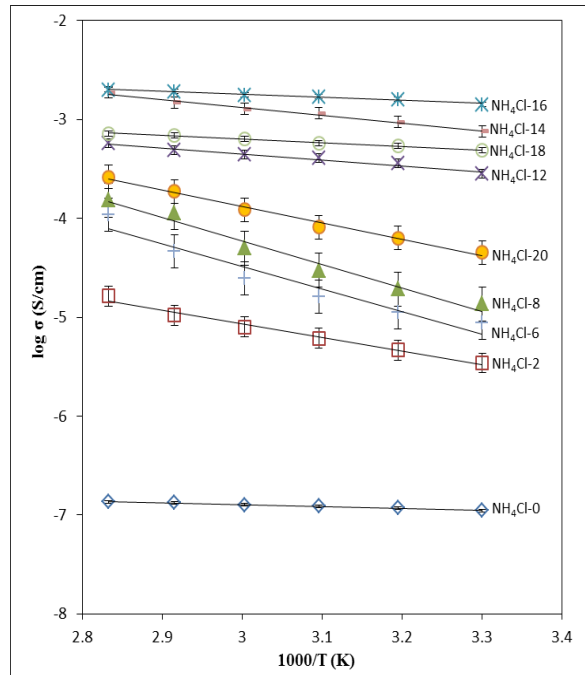
Figure 2 shows the Arrhenius plot for CMC –  $\text{NH}_4\text{Cl}$  solid polymer electrolyte films. Refer to Figure 2, log conductivity of SPE films was observed to obey Arrhenius behavior when  $R^2 \approx 1$ . Regression value,  $R^2$  is shown in Table 1.

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  $\sigma_o$  is the exponential factor,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature.



**Fig. 2. Arrhenius plot for CMC - NH<sub>4</sub>Cl 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 NH<sub>4</sub>Cl 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 – NH<sub>4</sub>Cl solid polymer electrolyte films.**

| Sample                  | Regression value, $R^2$ | Activation energy, $E_a \times 10^{-1}$ (eV) |
|-------------------------|-------------------------|--|
| NH <sub>4</sub> Cl – 0  | 0.99                    | 3.74   |
| NH <sub>4</sub> Cl – 2  | 0.98                    | 3.37   |
| NH <sub>4</sub> Cl – 6  | 0.93                    | 3.28   |
| NH <sub>4</sub> Cl – 8  | 0.98                    | 3.17   |
| NH <sub>4</sub> Cl – 12 | 0.98                    | 2.00   |
| NH <sub>4</sub> Cl – 14 | 0.99                    | 1.82   |

|                         |      |      |
|-------------------------|------|------|
| NH <sub>4</sub> Cl – 16 | 0.98 | 1.39 |
| NH <sub>4</sub> Cl – 18 | 0.99 | 1.71 |
| NH <sub>4</sub> Cl – 20 | 0.99 | 2.75 |

### 3.2. Dielectric studies

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

The  $\epsilon_r$  and  $\epsilon_i$  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  $C_o = \frac{\epsilon_o A}{t}$ ,  $\epsilon_o$  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  $\epsilon_r$  and  $\epsilon_i$  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].

### 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,  $\omega$ , 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 ( $>10^5\text{Hz}$ ) 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.

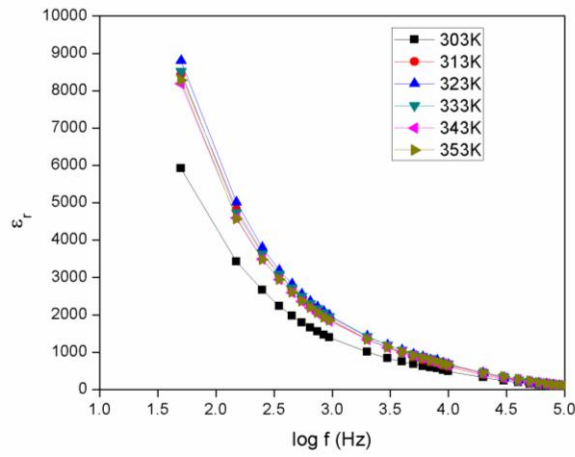


Fig. 3.  $\epsilon_r$  versus  $\omega$  for CMC – 16 wt. %  $\text{NH}_4\text{Cl}$  at selected temperatures.

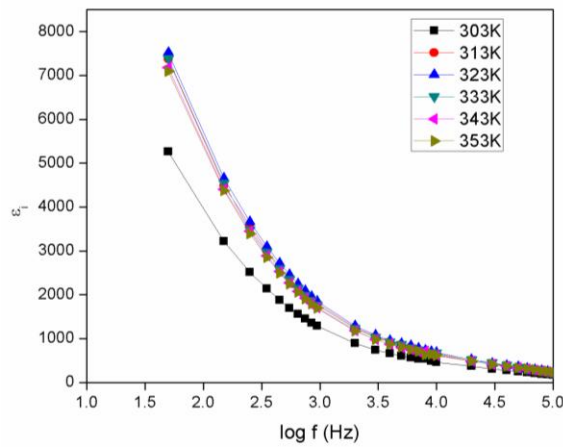


Fig. 4.  $\epsilon_i$  versus  $\omega$  for CMC – 16 wt. %  $\text{NH}_4\text{Cl}$  at selected temperatures.

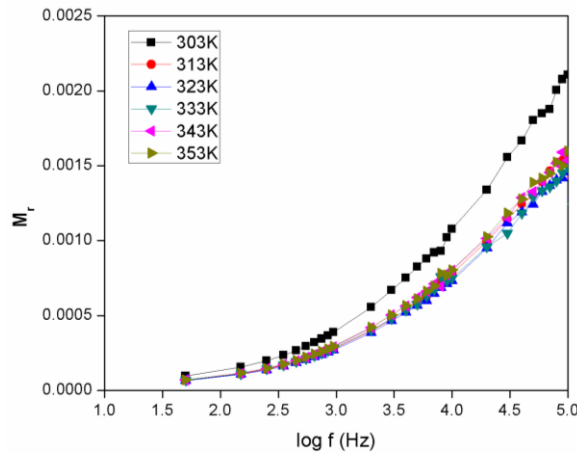


Fig. 5.  $M_r$  versus  $\omega$  for CMC – 16 wt. %  $\text{NH}_4\text{Cl}$  at selected temperatures.

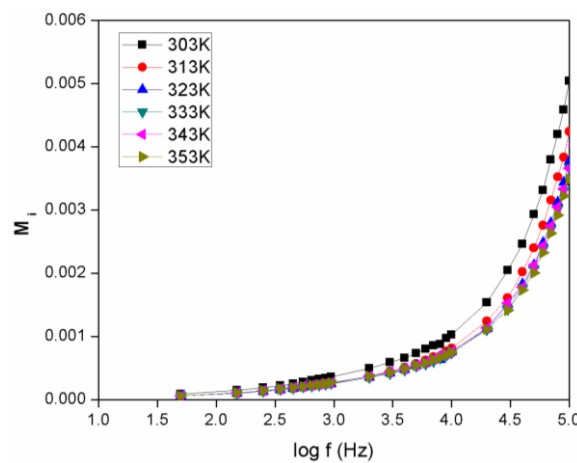


Fig. 6.  $M_i$  versus  $\omega$  for CMC – 16 wt. %  $\text{NH}_4\text{Cl}$  at selected temperatures.

#### 4. Conclusions

The CMC -  $\text{NH}_4\text{Cl}$  solid polymer electrolytes exhibited highest ionic conductivity of  $1.43 \times 10^{-3}$  (16 wt. %  $\text{NH}_4\text{Cl}$ ) 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  $\mathcal{E}_r$ ,  $\mathcal{E}_i$ ,  $M_r$ ,  $M_i$  were observed to be non-Debye type.

#### Acknowledgement

The authors would like to thank Ministry of Education Malaysia (MOE) for financial support through Fundamental Research Grant Scheme (FRGS) Vot. 59271 and Exploratory Research Grant Scheme (ERGS) Vot. 55101, and Universiti Malaysia Terengganu (UMT) for technical support and facilities.

## References

1. Gopalan, A.I.; Santhosh, P.; Manesh, K.M.; Nho, J.H.; Kim, J.H.; Hwang, C.G.; Lee, K.P. (2008) Development of electrospun PVdF-PAN membrane based polymer electrolytes for lithium batteries. *Journal of membrane science*, 325: 683-690.
2. Madhu Mohan, V.; Raja, V.; Sharma, A.K.; Narasimha Rao V.V.R. (2005). Ionic conductivity and discharge characteristics of solid-state battery based on novel polymer electrolyte (PEO + NaBiF<sub>4</sub>). *Materials Chemistry and Physics*, 94: 177-181.
3. Chandra Sekhar. P.; Naveen Kumar P.; Sasikala, U.; Rao. V.V.R.N.; Sharma. A.K. (2012). Investigations on lithium ion complexed polyvinyl chloride (PVC) solid polymer electrolyte films. *Engineering Science and Technology: An International Journal*, 2: 908-912.
4. Ramesh, S.; Arof, A.K. (2001). Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes. *Materials Science and Engineering: B*, 85: 11-15.
5. Selvasekharapandian, S.; Hirankumar, G.; Kawamura, J.; Kuwata, N.; Hattori, T. (2005). <sup>1</sup>H solid state NMR studies on the proton conducting polymer electrolytes. *Materials Letters*, 59: 2741-2745.
6. Sreenivasachari, A. (2013). Preparation , Investigation and discharge characteristics of ( PVC + PC + NaClO<sub>4</sub> ) Polymer Electrolyte Systems. *International Journal of Applied Research and Studies*, 2: 1-12.
7. Michael, M.S.; Jaacob, M.M.E.; Prabakaran, S.R.S.I Radhakrishna, S. (1997). Enhanced lithium ion transport in PEO-based solid polymer electrolytes employing a novel class of plasticizers. *Solid State Ionics*, 98: 167-174.
8. Chai, M.N.; and M.I.N. Isa. (2011). Carboxyl methylcellulose solid polymer electrolytes: Ionic conductivity and dielectric study. *Journal of current engineering research*, 1: 1-5.
9. Nik Aziz, N.A.; Idris, N.K.; and Isa, M.I.N. (2010). Solid Polymer Electrolytes Based on Methylcellulose: FT-IR and Ionic Conductivity Studies. *International Journal of Polymer Analysis and Characterization*, 15: 319-327.
10. Majid, S.R.; Arof, A.K. (2007). Electrical behavior of proton-conducting chitosan-phosphoric acid-based electrolytes. *Physica B*, 390: 209-215.
11. Teeters, D.; Neuman, R.G.; and Tate, B.D. (1996). The concentration behavior of lithium triflate at the surface of polymer electrolyte materials. *Solid State Ionics*, 85: 239-245.
12. Ahmad, N.H.; and M.I.N. Isa. (2015). Structural and Ionic Conductivity Studies of CMC Based Polymer Electrolyte Doped with NH<sub>4</sub>Cl. *Advanced Materials Research*, 1107: 247-252.
13. Isa, M.I.N. (2012). Poly(Methyl Methacrylate)-Salicylic Acid-Oleic Acid Plasticized Gel Electrolyte System: Electrical and Ionic Transport Study. *Research Journal of Physics*, 6: 50-58.



14. Latif, F.; Aziz, M.; Katun, N.; Malik, A.B.; Ali, M.; Zuazhan, M. (2006). The role and impact of rubber in poly ( methyl methacrylate )/ lithium triflate electrolyte. *Journal of Power Sources*, 159: 1401-1404.
15. Samsudin, A.S.; and Isa, M.I.N. (2012). Structural and Electrical Properties of Carboxy Methylcellulose-Dodecyltrimethyl Ammonium Bromide-Based Biopolymer Electrolytes System. *International Journal of Polymeric Materials*, 61: 30-40.
16. Rozali, M.L.H.; and Isa, M.I.N. (2014). Electrical Behaviour of Carboxy Methyl Cellulose Doped Adipic Acid Solid Biopolymer Electrolyte. *International Journal of Material Sciences*, 4: 59.
17. Gray, F.M., (1991). *Solid Polymer Electrolytes: Fundamentals and Technological Applications* (1<sup>st</sup> ed.). New York: VCH Publisher Inc.
18. Abdullah, A.; Abdullah, S.Z.; Ali, A.M.M.; Winie, T.; Yahya, M.Z.A.; Subban, R.H.Y. (2009). Electrical properties of PEO–LiCF<sub>3</sub>SO<sub>3</sub>–SiO<sub>2</sub> nanocomposite polymer electrolytes. *Materials Research Innovations*, 13: 255-258.
19. Khair A.S.A.; and Arof, A.K. (2010). Conductivity studies of starch-based polymer electrolytes. *Ionics*, 16: 123-129.
20. Khair, A.S.A.; Puteh, R.; and Arof, A.K. (2006). Conductivity studies of a chitosan-based polymer electrolyte. *Physica B: Condensed Matter*, 373: 23-27.
21. Ramesh, S.; and Chai, M.F. (2007). Conductivity , dielectric behavior and FTIR studies of high molecular weight poly ( vinylchloride )– lithium triflate polymer electrolytes. *Materials Science and Engineering B*, 139: 240-245.