*Full Length Research Paper*

# Structural and DC Ionic conductivity studies of carboxy methylcellulose doped with ammonium nitrate as solid polymer electrolytes

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Solid polymer electrolytes have been prepared by solution casting technique. Carboxy methylcellulose (CMC)-ammonium nitrate (AN) films were studied with varied AN salt concentration from 5-50 wt.% at ambient temperature. X-ray diffraction (XRD) pattern shows the amorphous nature of polymer electrolyte samples. IR-spectra confirm the polymer-salt complexes in the range of 1633 - 829 cm$^{-1}$. Impedance analysis reveals that polymer electrolyte film containing 45wt.% AN exhibits the highest ionic conductivity of $(7.71 \pm 0.04) \times 10^{-3}$ Scm$^{-1}$, while pure CMC film gives the lowest ionic conductivity of $(1.86 \pm 0.03) \times 10^{-8}$ Scm$^{-1}$. It was evident from this study that the increase of ionic conductivity depends on the AN salt concentration. The present polymer-salt system has potential application in electrochemical devices based on the results obtained.

**Key words:** Carboxy methylcellulose, ammonium nitrate, solid polymer electrolytes, ionic conductivity.

## INTRODUCTION

Since the earliest breakthrough of polymer-salt complexes by Wright in 1975, there was a plethora of research focusing on the study and development of solvent free polymer electrolytes (PEs). Extensive research on PEs were driven by their advantages such as ease of preparation, light weight, leakage free, mechanically stable and flexibility for packaging design over gel/liquid counterparts (Ramesh et al., 2002; Quartarone et al., 1998). PEs have become promising materials for electrochemical device applications, namely, high energy density rechargeable batteries, fuel cells, supercapacitors, sensors and electrochromic displays (Bhargav et al., 2009; Ma et al., 2013). Poor ionic conductivity as a result of the low segmental mobility of the polymer chain at ambient temperature is the major drawback possessed by solid Pes (Armand, 1994;

Tarascon and Armand, 2001). To overcome the challenge, several approaches have been employed to enhance the room temperature conductivity as well as to improve the mechanical stability and interfacial activity of PEs including using chitin/chitosan, starch and cellulose derivates as organic/biodegradable polymer matrix incorporating with inorganic salts such as sodium salt and ammonium salt (Kumar et al., 2011; Hassan et al., 2010). Typically, ionic conduction in PEs are governed by the degree of crystallinity (Kumar et al., 2011), salt/acid concentration (Sit et al., 2012; Idris et al., 2009) as well as the nature of polymer and salt/acid.

Carboxy methylcellulose (CMC) is a natural anionic polysaccharide which is widely used in many industrial sectors including food, textiles, paper, adhesives, paints, pharmaceutics, cosmetics and mineral processing. CMC

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**Figure 1.** The highly translucent and flexible CMC-AN solid polymer electrolyte films.

is a cellulose derivative prepared through etherification of the hydroxyl groups with sodium monochloroacetate in the presence of aqueous alkali (Pushpamalar et al., 2006). It is a natural organic polymer that is non-toxic, renewable, available in abundance, biocompatible and biodegradable (Adinugraha et al., 2005). Due to its highly hydrophilic properties, CMC can easily dissolve in cold/hot water.

Inorganic AN salt is widely utilized in the manufacture of nitrogen-rich inorganic fertilizers, as a major component in explosive mixtures (AN-fuel oil for mining) and in gas generator propellant formulations as well as rocket propellant oxidizer (Lang and Vyazovkin, 2008). AN exhibits five polymorphic crystal phases at atmospheric pressure from cryogenic temperatures up to its melting temperature of 442 K. The IV-phase shows an orthorhombic crystal structure at room temperature (Chellappa et al., 2012).

In this paper, we report the effect of ammonium salt concentration on the structural and ionic conductivity of CMC-AN polymer electrolytes at ambient temperature in preparation of solid-state rechargeable proton battery.

## EXPERIMENTAL PROCEDURE

### Polymer electrolytes

The sodium salt of CMC was obtained from Acros Organics (purity >99.9%; average MW = 90,000 and DS = 0.7). AN was purchased from Sigma Aldrich (purity 99%) and both materials were directly used without further treatment. Solution casting method was employed to obtain film samples with varied amount of ammonium salt concentration (5 – 50 wt.%). Pure CMC film without ammonium salt was also prepared as a control. In a clean beaker, weighted amounts of CMC powder and AN crystals were dissolved in 100 ml distilled water at room temperature. Complete dissolution was achieved after several hours stirring at room temperature using magnetic stirrer. The final clear solution was then poured into separate Petri dishes and left to dry at room temperature to form

highly translucent and flexible thin films. Polymer electrolyte films were transferred to a dessicator for further drying prior to sample characterization.

### Characterization techniques

In this work, X-ray diffraction (XRD) analysis was carried out using a MiniFlex II Rigaku with CuK$_\alpha$ radiation ($\lambda$ = 1.5418 Å) at room temperature. The XRD patterns were recorded at Bragg angle ($2\theta$) in the range of 10 - 60° with a scan speed of 2°/min. This technique was employed to determine the crystallinity of polymer electrolyte films.

The occurance of complexation and the presence of functional groups of polymer electrolyte films were analyzed using IR technique. The Fourier Transform InfraRed (FTIR) spectra were recorded using Thermo Nicolet 380 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory with a germanium crystal. The sample was pressed on a germanium crystal and infrared light was passed through the sample with the frequency ranging from 700 - 4000 cm$^{-1}$ at spectra resolution of 4 cm$^{-1}$. The FTIR data was recorded in the transmittance mode.

Impedance spectroscopy measurements were performed to determine the ionic conductivity of polymer electrolyte films over a wide range of frequency. The measurements were carried out with an electrical impedance spectroscopy (EIS) HIOKI 3532–50 LCR Hi Tester interfaced to a personal computer in 50 – 1M Hz frequency range. A $\pi$ cm$^2$ round piece of electrolyte film was pressed between two steel electrodes of sample holder in a temperature controlled MEMMERT oven.

## RESULTS AND DISCUSSION

### XRD analysis

Figure 1 shows a highly translucent and flexible thin film of CMC-AN solid polymer electrolytes obtained from solution casting technique. Typical XRD patterns obtained from CMC-AN polymer electrolyte films with varied AN concentrations are shown in Figure 2i. Figure 2ii and iii represent XRD patterns of pure AN crystals and
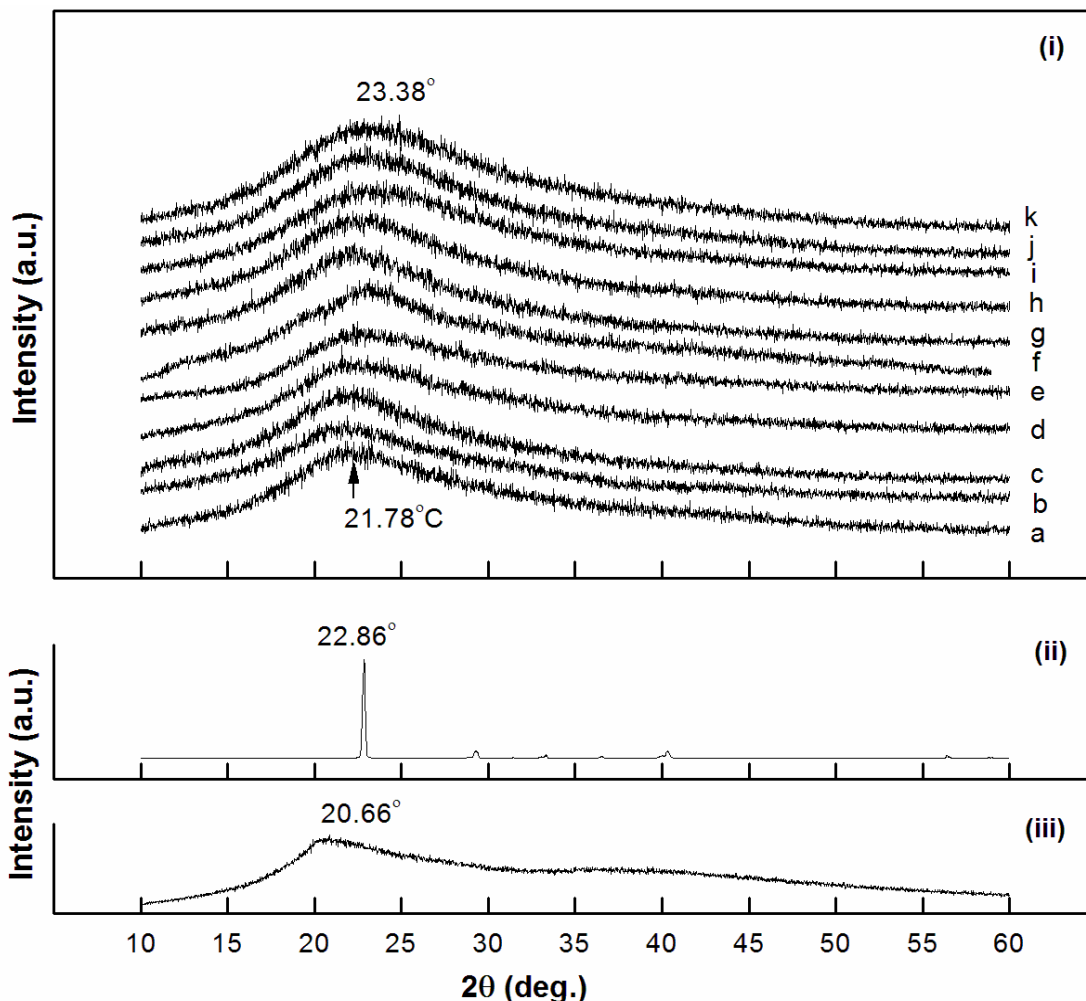
**Figure 2.** The XRD pattern of (i): Thin film samples containing CMC with varied amount of AN salt concentration, (a) Pure CMC, (b) CMC-5wt.% AN, (c) CMC-10wt.% AN,(d) CMC-15wt.% AN,(e) CMC-20wt.% AN,(f) CMC-25wt.% AN,(g) CMC-30wt.% AN,(h) CMC-35wt.% AN,(i) CMC-40wt.% AN,(j) CMC-45wt.% AN 5 and (k) CMC-50wt.% AN, (ii): Pure AN salt crystals, and (iii): Pure CMC powder.

CMC powder as references.

The XRD pattern for pure CMC powder (Figure 2iii) display a broad diffused hump centered at $2\theta = 20.66°C$ and a small shoulder between 35°C and 45°C corresponding to the amorphous nature of pure CMC. The pattern for pure AN crystals show four polycrystalline peaks with the strongest intensity peak located at $2\theta = 22.86°C$ (Figure 2ii). Upon addition of AN salt, the broad peaks tend to broaden and shift to a higher Bragg angle from $2\theta = 21.78°C$ (pure CMC film) to 23.38°C (CMC-50wt.% AN) as can be seen in Figure 2i. The increase in broadness implies the amorphous nature of polymer electrolyte films with some localized ordering of the complex system (Selvasekarapandian et al., 2010). No additional peaks have been observed in the complex system indicating a complete dissociation of AN salt in the CMC polymer matrix. XRD patterns confirmed the

amorphous nature of all polymer electrolyte films (Baril et al., 1997).

## FTIR analysis

The occurance of complexation and the presence of functional groups in polymer electrolyte films were confirmed using IR Spectrophotometer. Different vibration modes of various functional groups of CMC and AN correspond to the observed IR characteristic peaks of polymer-salt system.

## CMC and AN backbones

Pure CMC exhibits absorption band in the range of

**Table 1.** FTIR vibration modes of CMC and AN.

| Band Assignment | CMC Wavenumber (cm$^{-1}$) | AN Wavenumber (cm$^{-1}$) |
|---|---|---|
| Bending mode of ether(glycosidic) linkage, $\delta$(C-O-C) | 1040, 1110 | - |
| Bending mode of C-H band, $\delta$(CH) | 1377 | - |
| Stretching mode of O-H in plane | 1410 | - |
| Stretching mode in carboxylic group, $\upsilon$(C=O) | 1605 | - |
| Stretching mode of C-H band, $\upsilon$(CH) | 2920 | - |
| Intra-molecular hydrogen bond, $\upsilon$(OH) | 3439 | - |
| Symmetric bending band, $\delta(NO_3^-)$ | - | 828 |
| Symmetric stretching mode, $\upsilon(NO_3^-)$ | - | 1043 |
| Asymmetric stretching mode, $\upsilon(NO_3^-)$ | - | 1363 |
| Stretching mode of N-H band, $\upsilon$(NH) | - | 3031 |
| Intra-molecular hydrogen bond, $\upsilon$(OH) | - | 3251 |

1072 - 3439 cm$^{-1}$ (Lii et al., 2002; Jiang et al., 2009). The main backbones in CMC observed at 1605 cm$^{-1}$ and 1377 cm$^{-1}$ correspond to C=O band and C-H bonding, respectively. In the case of AN, vibration bands have been found in the range of 828 - 3251cm$^{-1}$ (Kadir et al., 2011; Majid and Arof, 2005). Typically, the O-H bonding can be found in the range of 3000 - 3800 cm$^{-1}$ for both backbones. The vibration modes of CMC and AN are summarized in Table 1.

## CMC-AN complexes

The occurrence of complexation between the polymer host and salt has been correlated to the spectral changes including shift of band, emergence of new bands or/and disappearance of bands. The complexation between CMC and inorganic salts/acids was reported to occur in the band range of 1600 - 1040 cm$^{-1}$ (Chai and Isa, 2013; Samsudin and Isa, 2012). Therefore, detailed observation on the frequency region of 1800 - 800 cm$^{-1}$ is required in this study. Outside of this region, insignificant or very weak peaks have been discovered.

Figure 3 depicts that adding a range of AN concentrations to CMC polymer electrolyte films resulted in the emergence of complexation bands in the range of 1633 - 829 cm$^{-1}$. The COO$^-$ stretching band of CMC shifts to the lower wavenumber from 1591 - 1583 cm$^{-1}$ and a new peak emerges at 1633 cm$^{-1}$ as the AN concentration increases to 50wt.%. The new peak is associated to the H$^+$ ion originating from AN. Strong absorption peaks at 1417 and 1321 cm$^{-1}$ assigned to O-H stretching in plane and symmetrical stretching of C-H bands of CMC respectively have shifted to 1431 and 1331 cm$^{-1}$. The shifting proved the complexation of CMC with the nitrate ions of AN. Similar behavior has been detected in the
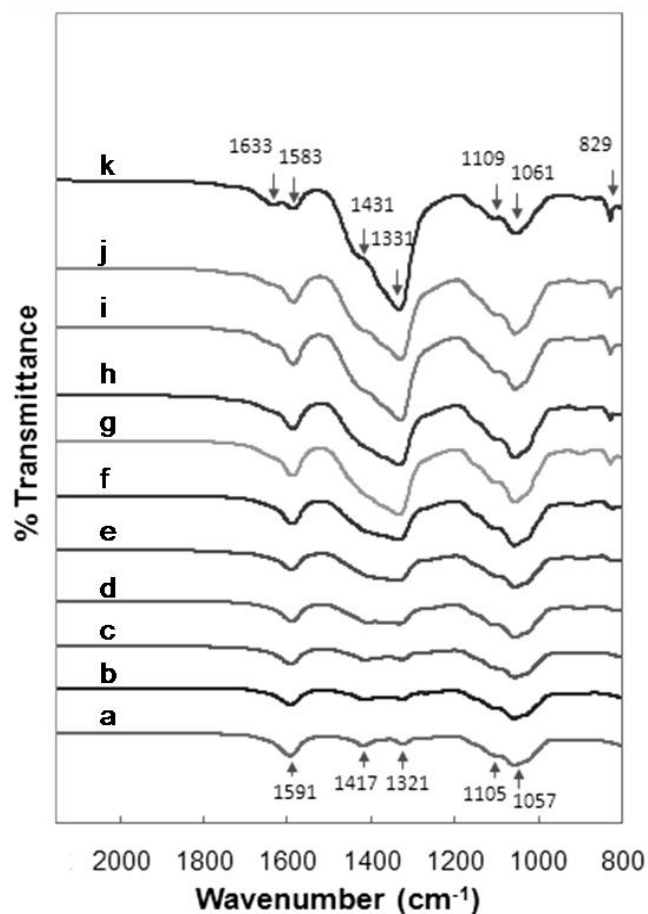


**Figure 3.** FTIR spectra of polymer electrolyte films containing CMC with varied amount of AN salt concentration, (a) Pure CMC film, (b) CMC-5wt.% AN, (c) CMC-10wt.% AN, (d) CMC-15wt.% AN, (e) CMC-20wt.% AN, (f) CMC-25wt.% AN, (g) CMC-30wt.% AN, (h) CMC-35wt.% AN, (i) CMC-40wt.% AN, (j) CMC-45wt.% AN 5 and (k) CMC-50wt.% AN.
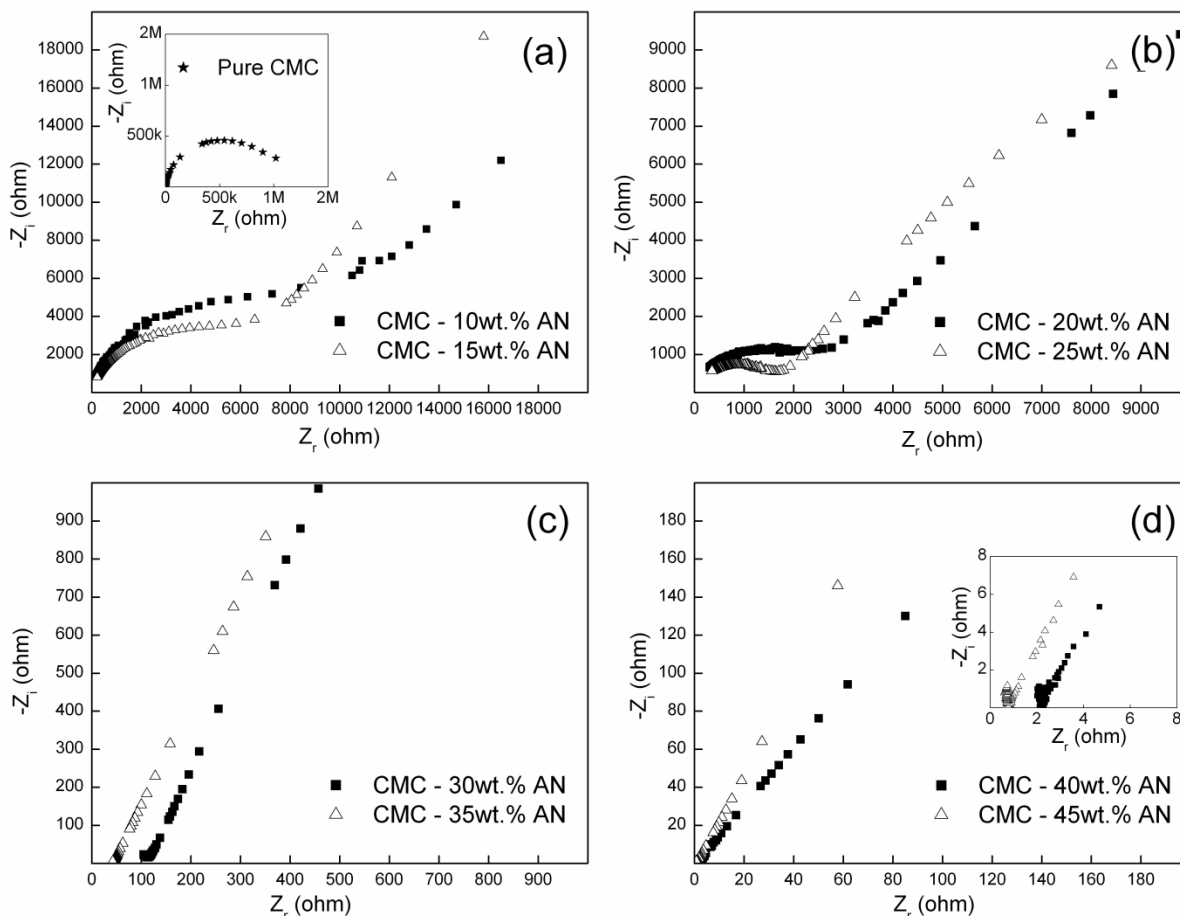
**Figure 4.** The Cole-Cole (Nyquist) plots of the real impedance, $Z_r$ versus imaginary impedance, $-Z_i$ polymer electrolytes with varied amount of AN concentration at ambient temperature; (a) CMC-10wt.% AN and CMC-15wt.% AN (Inset: Pure CMC film), (b) CMC-20wt.% AN and CMC-25wt.% AN, (c) CMC-30wt.% AN and CMC-35wt.% AN, and (d) CMC-40wt.% AN and CMC-45wt.% AN (Inset: Enlargement of (d)).

region of 1105 - 1057 cm$^{-1}$ which signifies the characteristic of polysaccharide skeleton. No obvious changes of intensity have been observed except shifting of the bands to the higher wavenumbers. A new peak at 829 cm$^{-1}$ corresponds to the nitrate ion of AN. It can be concluded from the analysis that the protonation has occurred in the present polymer-salt complexes and the interactions between CMC and AN has been established.

**Impedance analysis**

*Cole-cole plots*

Figure 4 shows the complex impedance plots of pure CMC film and CMC-AN doped with different concentration of AN at ambient temperature. The figure shows a part of a depressed semicircle for pure CMC film. The high frequency semicircle is associated to the parallel combination of the bulk resistance and bulk capacitance as a result of protons migration and immobile polymer chains, respectively (Selvasekarapandian et al., 2010; Subban et al., 2005). As the salt concentration begins to increase, the semicircle in the plots become to lessen. The depressed semicircle and inclined spikes (Figure 4a-b) implies that the ions have different relaxation times (Subban et al., 2005). Beyond 25wt.% AN, the appearance of low frequency spikes indicate that only the resistive component of the polymer electrolyte predominate (Selvasekarapandian et al., 2010) as illustrated in Figure 4c-d. The bulk resistance, $R_b$ can be calculated from the intercept of high frequency semicircle or the low frequency spike on the $Z_r$-axis.

**dc ionic conductivity**

The high ionic conductivity of solid polymer electrolytes is mainly governed by two important factors; that is, ionic
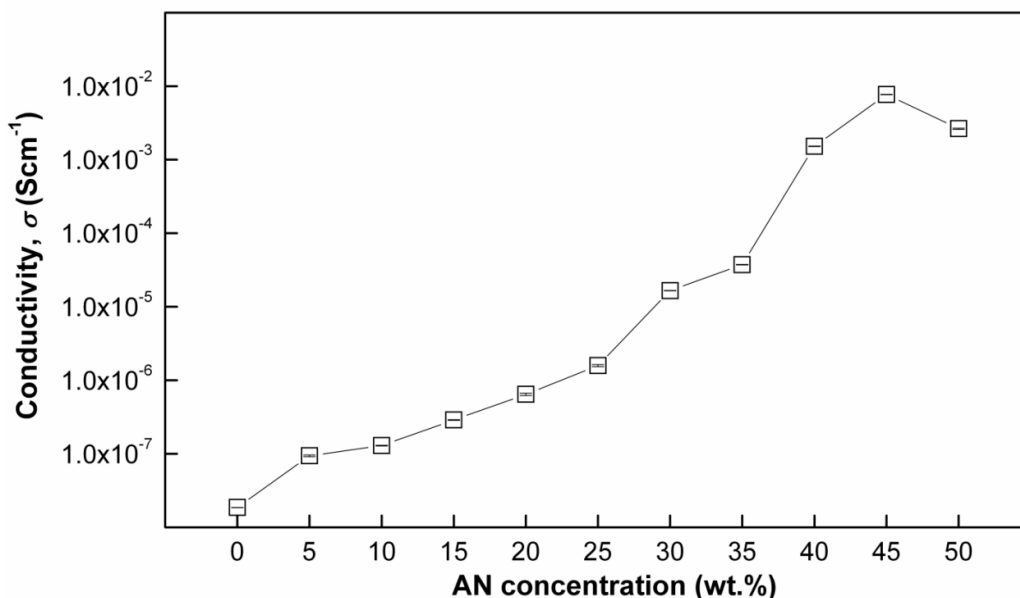
**Figure 5.** Graph of ionic conductivity, $\sigma$ versus AN salt concentration of polymer electrolyte films at ambient temperature, 303K.

conducting species concentration, $\eta$ and the charge carrier mobility, $\mu$ along with the type of charge carriers (cationic/anionic) and temperature (Hirankumar et al., 2005; Raphael et al., 2010). The evolution of the ambient temperature, 30°C (303K) ionic conductivity of polymer electrolyte films as a function of the AN concentration is shown in Figure 5. The ionic conductivity of polymer electrolyte films, $\sigma$ were calculated using Equation 1:

$$\sigma = \frac{t}{R_b A}$$

$$(1)$$

To attain the ionic conductivity, $\sigma$ ($Scm^{-1}$), the thickness of the electrolyte, $t$ (cm), the bulk resistance, $R_b$ ($\Omega$), and the area of electrolyte-electrodes contact, $A$ ($cm^2$) should be known. Concentration dependence of ionic conductivity provides information on the specific interaction between the salt and polymer matrix.

As illustrated in Figure 5, the ionic conductivity increases gradually with the addition of AN concentration up to 45wt.%. The increment of ionic conductivity with increasing AN concentration can be related to the increasing number of mobile charge carriers and/or their mobility (Samsudin and Isa, 2012). This may also be attributed to an increase of the amorphous nature of polymer electrolytes as confirmed by the XRD analysis. The optimum AN concentration of 45 wt.% gives the highest ionic conductivity of ($7.71 \pm 0.04$) $\times 10^{-3}$ $Scm^{-1}$ compared to pure CMC film of ($1.86 \pm 0.03$) $\times 10^{-8}$ $Scm^{-1}$. Beyond that, the ionic conductivity decreases. The subsequent decrease at AN concentration of 50 wt.%

could be caused by the formation of ion multiples or ion aggregates which reduces the number of mobile ions and limits its mobility in the polymer electrolytes (Woo et al., 2011; Yahya and Arof, 2003). At such high concentration, polymer electrolyte film was observed mechanically unstable. This was evidenced by the reduction in film flexibility as a consequence of rapid increase in viscosity (Ferry et al., 1998). Table 2 summarizes the ionic conductivity of single polymer-ammonium salt system at room temperature as reported in the literatures. The list indicates that the ionic conductivity obtained from the present work is higher compared to the previous works reported for similar AN salt system.

**Conclusion**

The new solid polymer electrolytes based on CMC and AN have been successfully prepared by solution cast method. XRD studies confirmed that all films were predominantly amorphous. IR spectra indicated that the complexation of polymer electrolyte films occured in the frequency range of 1633 - 829 $cm^{-1}$. The study revealed that the concentration of AN greatly influenced the ionic conductivity of the polymer electrolyte films. The pure CMC film gives the ionic conductivity in the order of $10^{-8}$ $Scm^{-1}$. Upon addition of the salt, the ionic conductivity has increased to the optimum AN concentration (45 wt.%) in the order of $10^{-3}$ $Scm^{-1}$ at ambient temperature. The present polymer electrolytes were identified as promising materials for electrochemical device applications.

**Table 2.** Ionic conductivity of solid polymer electrolytes based on single polymer and AN salt system measured at room temperature from literatures compared to the present work.

| Polymer host | AN concentration (wt.%) | Solvent | Conductivity, $\sigma$ (Scm$^{-1}$) | Reference |
|---|---|---|---|---|
| Chitosan | 45 | Distilled water | $2.53 \times 10^{-5}$ | Majid and Arof (2005) |
| Chitosan | 40 | Acetic acid | $8.38 \times 10^{-5}$ | Ng and Mohamad (2006) |
| Methylcellulose | 25 | Distilled water | $2.10 \times 10^{-6}$ | Shuhaimi et al. (2010) |
| Tapioca starch | 25 | Oxalic acid | $2.15 \times 10^{-6}$ | Azlan and Isa (2011) |
| Tapioca starch | 25 | Distilled water | $2.83 \times 10^{-5}$ | Khiar and Arof (2010) |
| CMC | 45 | Distilled water | $(7.71 \pm 0.04) \times 10^{-3}$ | Present work |

## ACKNOWLEDGEMENT

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