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Electrical and ionic transport properties of carboxymethyl cellulose doped ammonium thiocyanate proton conducting solid biopolymer electrolytes

[1]N.A.M. Noor and [1,2]M.I.N. Isa

[1,2]Advanced Materials Research Group, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
[2]Corporate Communication and Image Development Centre, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu.

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ABSTRACT

In this present paper, a proton conducting solid biopolymer electrolytes (SBE) based on carboxymethyl cellulose (CMC) as polymer host and ammonium thiocyanate (NH_4SCN) as the proton donor have been prepared via solution casting method to investigate their ionic conductivity and ionic transport behaviour. The ionic conductivity of the CMC-NH_4SCN SBE film have been carried out by Electrochemical Impedance Spectroscopy (EIS) over a wide range of frequency between 50 Hz to 1 MHz at temperatures ranges 303 - 353 K. The CMC-NH_4SCN SBE system exhibited the highest ionic conductivity is 6.48 x 10^{-5} Scm^{-1} for SBE containing 25 wt.% of NH_4SCN at room temperature. The conductivity by various temperatures obey Arrhenius rule ($R^2 \approx 1$). The activation energy was found decreases with enhancement of NH_4SCN concentration. Calculations using the Rice and Roth model provide number of mobile ions (η), mobility of ions (μ) and diffusion coefficient (D). It has been shown that the conductivity is found to be influenced by the diffusion coefficient (D) and mobility (μ). The transference number measurement (TNM) of mobile ions has been investigated using dc polarization method. The value of diffusion coefficient (D) and ionic mobility (μ) of the cation were higher than the values of anion and it has proves that the conducting species are predominantly due to protons.

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INTRODUCTION

In recent years, solid polymer electrolytes (SPE) have been progressing actively, both in academia and industry in the development of science and technology (Song *et al*., 1999). The study on polymer-salt complexes started upon its first discovery by Wright *et al*. in 1973 and nowadays, its application as a battery electrolyte has been more attention in research as a result of proposals made by Armand *et al*. (Aihara *et al*., 1997). The great advantages of using SPE systems successfully while replacing normal liquid electrolytes has growing more interest because it can lead to flexible, compact, laminated solid-state structures, no leakage, low self discharge in batteries, relax elasticity under stress conditions, available in different geometries, easy processing and continuous production (Kuila *et al*., 2007). SPE finds their potential applications in new generation electronic devices like rechargeable secondary batteries, fuel cells, sensors, solid state electrochromic windows or displays, analog devices and super capacitors (Wang and Min, 2010; Nik Aziz *et al*., 2010).

Most important requirements of any material for such applications are centered on favorable electrical and optical properties, thermal, chemical, electrochemical, mechanical and interfacial stability, ease of formation in thin film form and ability to form effective electrode-electrolyte contacts (Bhide and Hariharan, 2007). However, the low ionic conductivity of SPE limits their applications. In order to enhance the ionic conductivity of the SPE system, the polymer have been complexed with various salts (organic or inorganic salts), which provide the ions for conduction (Ramya and Selvasekarapandian, 2008). Strong inorganic acids such as phosphoric acid (H_3PO_4) (Prajapati *et al*., 2010) and sulfuric acid (H_2SO_4) (Raj and Varma, 2010) have been used as proton donor for SPE. However, polymer-inorganic acid complexes suffer from chemical degradation and mechanical integrity causing them unsuitable for practical applications. Therefore, a lot of ammonium salts have been used to act as the proton donor, for example, ammonium thiocyanate (NH_4SCN) (Woo *et al*., 2012), ammonium nitrate (NH_4NO_3) (Kadir *et al*., 2011), and ammonium chloride (NH_4Cl) (Vijaya *et al*., 2012).

Corresponding Author: M.I.N. Isa, Corporate Communication and Image Development Centre, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu.

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A number of synthetic polymers materials (petroleum resources) have been studied as polymer hosts in SPE, such as poly (ethylene oxide) (Sekhon *et al*., 1995), poly(vinyl alcohol) (PVA) (Awadhia *et al*., 2006), poly(vinyl chloride) (PVC) (Ramesh and Arof, 2000) and poly(acrylo nitrile) (Perera *et al*., 2000). However, these polymers are high in cost and the depletion of petroleum resources coupled with increasing environmental regulation a reacting synergistically to provide the impetus for new materials and products that are compatible with the environment and independent of fossil fuels (Samsudin *et al*., 2014). Over the past few years, researchers have been working in the development of natural polymers due to their availability, renewability, biocompatibility and biodegradability (Yu, Dean and Li, 2006). Polymer electrolytes obtained from natural polymers such as starch, cellulose, chitosan, pectin and so on, have attracted attention in recent years because of their superior mechanical and electrical properties (Finkenstadt & Willett, 2005). In addition, the efficient utilization of biodegradable polymers from renewable sources is becoming increasingly important due to diminishing resources of fossil fuels as well as white pollution.

In this research, CMC was chosen as the polymer host due to its great properties such as provide a good electrode electrolyte contact, a water soluble materials, low cost material and easier process ability (Othman *et al*., 2012). Moreover, CMC is a naturally occurring polysaccharide and the most abundant organic on the earth (Rozali *et al*., 2012). 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 is a cellulose derivative prepared through etherification of the hydroxyl groups with sodium monochloro acetate in the presence of aqueous alkali (Pushpamalar *et al*., 2006). NH_4SCN was used as dopant material because ammonium salts have been reported as good proton donor to the polymer matrix (Samsudin and Isa, 2012). The CMC-NH_4SCN SBE system produced was studied for its conductivity, electrical and ionic transport properties.

Methodology:

Sample preparation:

In order to prepare the CMC-NH_4SCN SBE films, 2g of CMC obtained from Acros Organic Co and M_w = 90000 g/mol was dissolved in 100 ml of distilled water. The solution was stirred until the CMC was completely dissolved. Next, various weight percentages (wt. %) of NH_4SCN obtained from Sigma Aldrich and M_w = 76.11 g/mol were added into CMC solution and stirred continuously until homogeneous mixture solutions were achieved with no phase separation. Then, the mixture solutions were poured in different glass petri dishes and left to dry at room temperature for CMC-NH_4SCN SBE films to form. The CMC-NH_4SCN SBE films were stored in a desiccators for further drying to ensure there is no water content in the films.

Electrical Impedance Spectroscopy (EIS):

HIOKI 3532-50 LCR Hi-Tester was used to measure ionic conductivity of the films in the frequency range from 50 Hz to 1 MHz at room temperature (303 K) until 353 K. The CMC-NH_4SCN SBE films were cut into small discs and sandwiched between two stainless steel electrodes under spring pressure. The diameter of the stainless steel electrode is 2 cm. The conductivity of the film was calculated using equation 1:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

Here, σ (Scm^{-1}) is the conductivity, t (cm) is the thickness of the film, A (cm^2) is the area of surface contact between electrode and electrolyte and R_b (Ω) is the bulk resistance. The bulk resistance, R_b was obtained from the Cole-Cole plot at the low frequency side at the intersection of the plot the imaginary impedance and the real impedance axis.

Transference Number Measurement (TNM):

Transference number measurements (TNM) were carried out to investigate the CMC-NH_4SCN SBE films conductivity of being ether more cationic than anionic or otherwise via DC polarization technique. The technique will determined the ionic transference number (T_{ion}) by monitoring the current as a function of time on application of a fixed dc voltage (1.5 V) across the film sandwiched between two stainless steel electrodes. The ionic transference number (T_{ion}) is given by the relation:

$$T_{ion} = \frac{I_{ion}}{I_o} \tag{2}$$

Here, I_{ion} is the saturated current and I_o is initial current. If the SBE films is purely ionic, then T_{ion} = 1.

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RESULTS AND DISCUSSIONS

Electrical and Conductivity Study:

There are various factors that influence ionic conductivity such as ionic conducting species concentration, cationic or anionic types charges carriers, the charge carriers mobility and the temperature (Samsudin *et al*., 2012). Figure 1 depicts the effect of the NH_4SCN concentration on the conductivity of the CMC-NH_4SCN SBE films. It was observed that the ionic conductivity of film increased with the addition of NH_4SCN concentration as shown in Figure 1. The maximum conductivity obtained at room temperature is 6.48 x 10^{-5} Scm^{-1} for sample containing 25 wt. % of NH_4SCN. According to (Chai and Isa, 2011), the dependence of ionic conductivity on the salt concentration provides information on the specific interaction among the salt and the polymer matrix. The increases of ionic conductivity can be explained by association of ions at higher salt concentration, which leads to the formation of ion clusters and the number of charge carriers and their mobility.

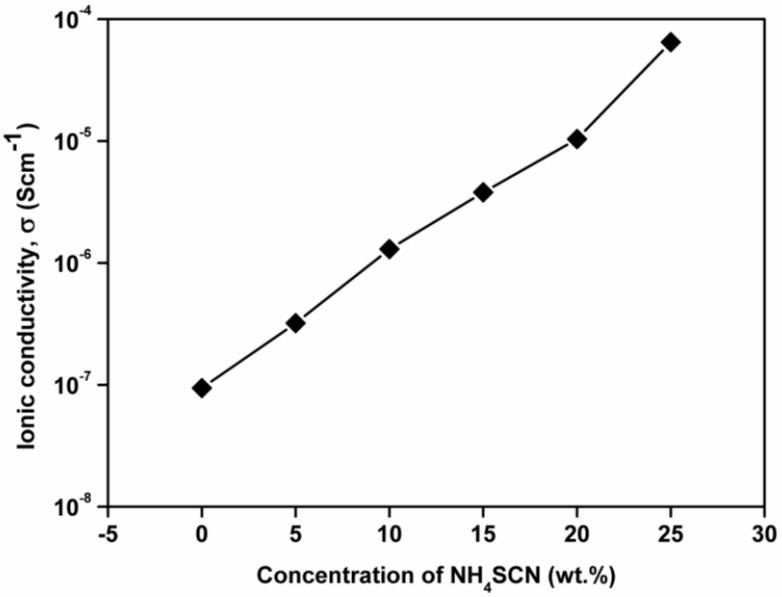

Fig. 1: The ionic conductivity of CMC-NH_4SCN SBE system at room temperature.

Figure 2 represents the temperature-dependent of ionic conductivity measurement that were carried out to investigate the mechanism of ionic conduction of CMC-NH_4SCN SBE system. The log σ versus 1000/T in temperature range 303 K to 353 K plot for the CMC-NH_4SCN SBE system is shown in Figure 2 which confirms that the ionic conductivity of the CMC-NH_4SCN SBE increases with increasing of temperature for all compositions. From Figure 2, it can be observed that the relationship between conductivity and temperature of the SBE system are characteristically Arrhenius behavior where the regression values, R^2 is almost unity ($R^2 \approx 1$) and the conductivity is thermally assisted (Chai and Isa, 2012). According to (Samsudin and Isa, 2012), R^2 are close to unity suggesting that all the points lie on a straight line. This indicated that the plots obey Arrhenius behaviour which can be presented as below:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

Where σ_o is the pre-exponential factor, E_a is activation energy, k is the Boltzmann constant and T is the absolute temperature.

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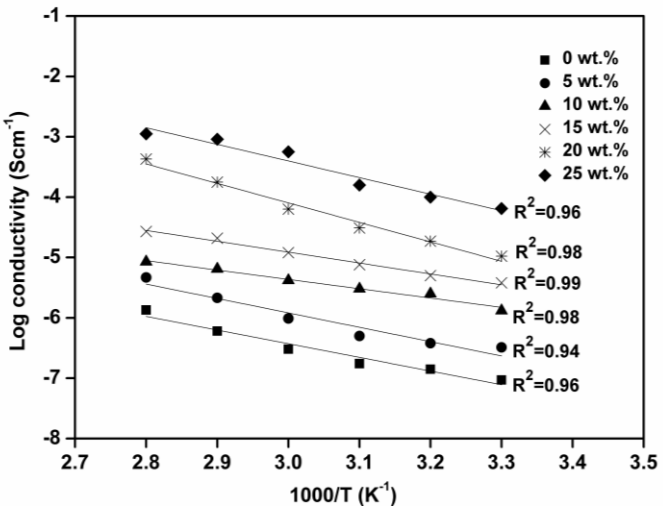

Fig. 2: The Arrhenius plot of CMC-NH_4SCN SBE system at various temperatures.

The activation energy (combination of the energy of defect formation and the energy for migration of ions) can be calculated from Equation (3) and the value of activation energy shown in Figure 3 (Sit *et al*., 2012). Principally, activation energy is the energy required for an ion to initiate movement. When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site (Ahmad and Isa, 2012). It can be observed from Figure 3, the value of E_a lower at higher conductivity and higher at low conductivity. According to (Selvasekarapandian *et al*., 2005), this phenomena is due to the fact that the density of ions in the polymer electrolyte increases with increasing the NH_4SCN concentration, hence the energy barrier to the proton transport decreases, which would lead to a decrease in the activation energy.

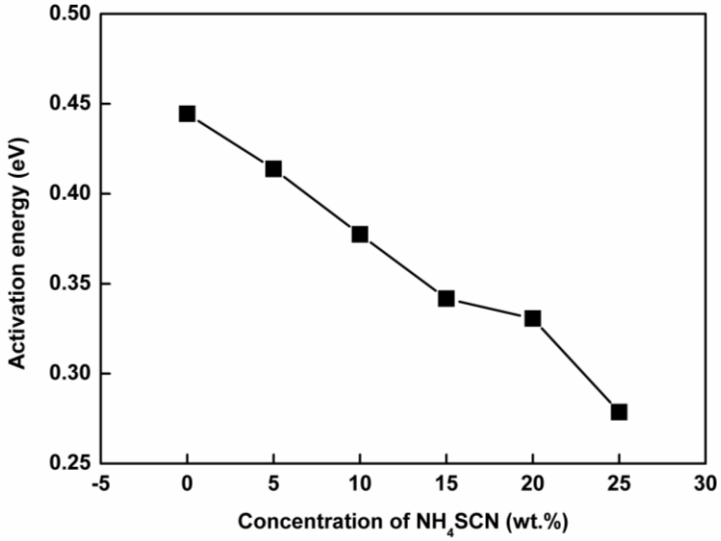

Fig. 3: The activation energy of CMC-NH_4SCN SBE at room temperature.

Ionic Transport Study:

It is a very important parameter in understanding the transport properties of SBE. The number of mobile ions was obtained from Rice and Roth using the equation:

$$\sigma = \frac{2}{3}\left[\frac{(Ze)^2}{kTm}\right]\eta\, E_a t \exp\left(\frac{-E_a}{kT}\right) \quad (4)$$

Where Z is the valency, E_a is activation energy, m is mass of the conducting ion, T is absolute temperature, k is Boltzmann constant and e is electron charge and t is the time for an ion to travel between sites. The Rice and Roth mode hypothesized that an energy gap exists in the ionic conductor and the ions of mass belonging to the conducting species can be thermally excited from localized ionic states to free-ion-like states in which an ion

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propagates throughout the solid with a velocity given by $v = (2\ E_a / l)^{1/2}$ (Chai and Isa, 2013). Finite lifetime, *s*, is needed for such an excited free-ion-like state. The mean free path or distance from one complexed site to another, *l* is given by $l = \tau\ v$. The mean free path between two coordinating sites or two atoms with the lone pair electrons across which the ions may hop was taken as 1.5 nm. According to (Samsudin *et al*., 2013), ionic conductivity of SBE films influence by the number density and mobility of ions. Via the Nernst–Einstein equation, the value of diffusion coefficient of the mobile ions, *D*, can be calculated. By knowing η and the conductivity value, the mobility of the ionic charge carrier, μ and diffusion coefficient, *D* can be calculated for every sample as follow. The ionic mobility relationships between conductivity can be expressed by the equation

$$\sigma = \eta\ q\ \mu \tag{5}$$

Where, *q* is the number of electron. Diffusion coefficient, *D* is given by Nernst–Einstein equation:

$$D = \frac{kT\sigma}{n\ e^2} \tag{6}$$

Table 1 represents the transport properties that are related to the ionic conductivity of the CMC-NH_4SCN SBE system. From the transport properties shown in Table 1, it can be inferred that the conductivity is governed by number density of ions *(η)*, mobility of ions *(μ)* and diffusion coefficient (*D)*. It can be explained as the conductivity, σ increase, the E_a require lower energy to move the ion due to increasing of *η*, *μ* and *D* in this SBE system. According to Majid and Arof, the ionic conductivity in a polymer is generally linked to the number of ions and the mobility of conducting species in the polymer complexes (Idris *et al*., 2009). However, in this study, the number density of mobile ions does not give significant contribution to the conductivity compared to diffusion coefficient and mobility. These results clearly reveal that the values of *μ* and *D* influenced the ionic conductivity of the CMC-NH_4SCN SBEs films.

Table I: Transport parameter of CMC-NH_4SCN SBEs at room temperature.

Sample (wt. %)	η (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)	D (cm^2s^{-1})
0	8.04×10^{22}	7.31×10^{-12}	1.91×10^{-13}
5	1.18×10^{23}	1.71×10^{-11}	4.46×10^{-13}
10	1.07×10^{23}	7.07×10^{-11}	1.85×10^{-12}
15	7.27×10^{22}	3.26×10^{-10}	8.53×10^{-12}
20	1.33×10^{23}	4.90×10^{-10}	1.28×10^{-11}
25	1.23×10^{23}	3.29×10^{-9}	8.60×10^{-11}

TNM study:

TNM was carried out to investigate the types of ionic mobility, *(μ)* and the diffusion coefficient, (*D)* either cationic or anionic. The diffusion coefficients of cations and anions in each of the samples were calculated from the measured values of conductivity and cation transference number, t_+ according to the following equations:

$$t_+ = \frac{t_{cation}}{I_{ion}} \tag{7}$$

$$D = D_+ + D_- = \frac{kt\sigma}{ne^2} \tag{8}$$

$$t_+ = \frac{D_+}{D_+ + D_-} \tag{9}$$

Besides, the ionic mobility, μ can be defined according to the following equations:

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{n\ q} \tag{10}$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \tag{11}$$

The sample tested for TNM study were 5 wt. %, 15wt.% and 20wt.%. The values obtained were then used to plot graphs of normalized polarization current versus time, as shown in Figure 4. It can be observed in Figure 4, the initial total current decreased with time due to the depletion of the ionic species in the SBE film and became constant in the fully depleted situation and the current-normalized ionic transference number, t_{ion}, in the

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electrolytes was determined. When the value of voltage V is applied to the cell, ionic migration will occur until steady state is achieved. At the steady state, the cell is polarized and any residual current flows because of electron migration across the electrolyte and interfaces. This is because the ionic currents through an ion-blocking electrode fall rapidly with time if the electrolyte is primarily ionic (Chai *et al*., 2013).

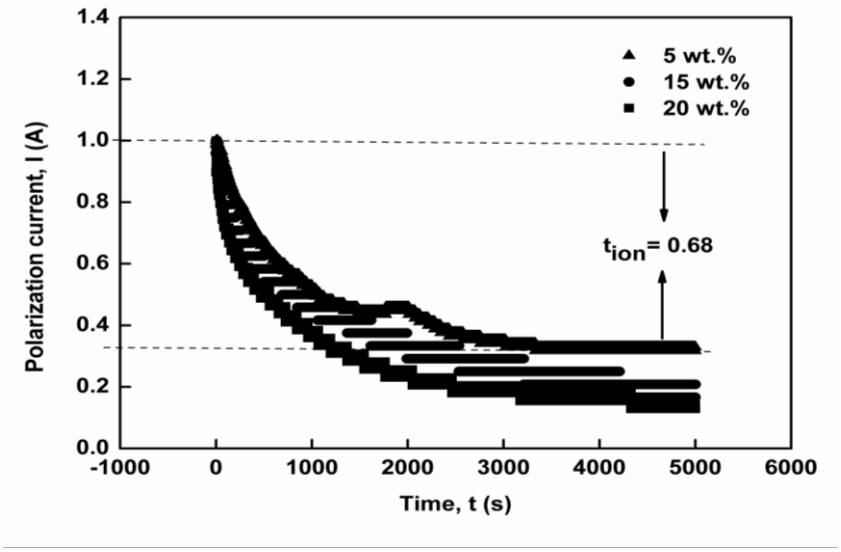

Fig. 4: Normalized polarization current versus time for sample 5 wt. %, 15 wt.% and 20 wt.%.

Table 2 depicts the value of cation and anion of ionic mobility and diffusion coefficient for sample 5 wt.%, 15 wt.% and 20 wt. % respectively. From the Table 2, it can be observed that, the value ionic mobility of cation, μ_+ is higher than ionic mobility of anion, μ_- and the value diffusion coefficient of cation, D_+ obtained is higher than the diffusion coefficient of anion, D_-. So that, it can be concluded that the CMC-NH_4SCN SBE films is more cationic than anionic conductor and it can be said that the film is proton conducting solid biopolymer electrolytes.

Table II: Ionic mobility and diffusion coefficient of cations and anions of CMC-NH_4SCN SBE system.

Sample (wt.%)	t_{ion}	D_+ ($cm^2\ s^{-1}$)	D_- ($cm^2\ s^{-1}$)	μ_+ ($cm^2V^{-1}\ s^{-1}$)	μ_- ($cm^2V^{-1}\ s^{-1}$)
5	0.68	3.03×10^{-13}	1.423×10^{-13}	1.16×10^{-11}	5.47×10^{-12}
15	0.79	6.74×10^{-12}	1.79×10^{-12}	2.58×10^{-10}	6.80×10^{-11}
20	0.87	1.11×10^{-11}	1.69×10^{-12}	4.26×10^{-10}	6.44×10^{-11}

Conclusion:

The transparent SBE films based on CMC doped with NH4SCN were successfully prepared via solution casting techniques. The highest conductivity achieved by the CMC-NH_4SCN films at room temperature is 6.48×10^{-5} Scm^{-1} with 25 wt. % of the NH_4SCN concentration. The temperature dependence of conductivity at various temperature obey Arrhenius rule. It is observed that the highest ionic conductivity has lowest activation energy (~0.28 eV). The number of mobile ions was calculated using Rice and Roth model. By using the Rice and Roth model, the increases conductivity of CMC-NH_4SCN films is affected by an increase in the concentration due to the addition in ionic mobility and diffusion coefficient of ions. The value of μ_+ and D_+ were higher than the value of μ_- and D_-. These proved that CMC-NH_4SCN SBE film was a proton conductor and the main conducting species is cationic.

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