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Ionic Conduction Mechanism of Solid Biodegradable Polymer Electrolytes Based Carboxymethyl Cellulose Doped Ammonium Thiocyanate

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Abstract. A conducting solid biodegradable polymer electrolytes based carboxymethyl cellulose (CMC) doped ammonium thiocyanate (NH$_4$SCN) system with concentration in the range 0 – 25 wt.% of NH$_4$SCN have been prepared via solution casting method. The impedance study of CMC-NH$_4$SCN system was measured via Electrical Impedance Spectroscopy (EIS) in the temperature range 303 K – 353 K. The highest ionic conductivity at room temperature (303 K) is 6.48 x 10^{-5} Scm^{-1} for sample containing 25 wt.% NH$_4$SCN. The temperature dependence of CMC-NH$_4$SCN system was found to obey the Arrhenius behaviour where the ionic conductivity increases with increase of temperature. Dielectric data were analyzed using complex permittivity, ε_i for sample with the highest ionic conductivity at various temperatures and found was non Debye behavior. The conduction mechanism of the charge carrier of CMC-NH$_4$SCN system can be presented by quantum mechanical tunneling (QMT) model.

Introduction

The pioneering work in the field of solid polymer electrolytes (SPE) was carried out by Wright and co-workers in 1975, who reported ionic conductivity of the order of 10^{-5} Scm^{-1} at 330 K in highly crystalline PEO-NaSCN complexes [1]. Since then, studies on SPE have been progressing actively due to their possible application as solid electrolytes in a variety of electrochemical devices such as energy conversion units (batteries/fuel cells), electrochromic display devices, photochemical solar cells, supercapacitors and sensors [2]. Among the advantages of SPE as compared to conventional liquid electrolytes include prevention of internal short-circuiting due to formation of dendrites, leakage of electrolyte and volume expansion due to electrochemical reactions on the electrolyte/electrode interface and reactive explosion. The development of SPE has led to improved overall safety, portability and durability of various electrochemical devices [3].

Several polymers have been studied as polymer hosts in SPE, such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) and poly(acrylo nitrile) (PAN). Over the past few years, researchers have been working in the development of natural polymers due to their renewable, sustainable and biodegradable properties. Many natural polymers have been extensively studied as polymer hosts in electrolytes, such as chitosan, starch and cellulose with its derivative [4]. This present study focused on developing CMC as polymer host doped with NH$_4$SCN as ionic dopant of solid biodegradable polymer electrolytes (SBPE). Polymer host from cellulose or cellulose derivative which is carboxyl methylcellulose (CMC) was choosen because of its superior properties such as provide a good electrode electrolyte contact, a water soluble materials, abundant in nature, low cost material and biodegradable [5]. The effect of temperature on conductivity, dielectric and AC conductivity were investigated to study the conduction mechanism of the CMC-NH$_4$SCN system.

Methodology

Sample preparation. The CMC-NH$_4$SCN films were prepared via solution casting method. 2 g of CMC (Acros Organic Co.) was dissolved in 100 ml distilled water. The CMC solution was stirrer continuosly with magnetic stirrer for several hours at room temperature until the CMC have completely dissolved. Then, the various concentration of NH$_4$SCN (0 - 25 wt.%) was added to CMC solution and stirred until homogenous solution were obtained. The mixture were poured into petri dish and left to dry at room temperature for films to form. The films were kept in dessicators for further drying to ensure there is no water content in films.

Characterization. Impedance analysis of the CMC-NH$_4$SCN films was characterized via HIOKI-LCR Hi-tester 3525-50 interfaced to a computer in frequency of 50 Hz - 1 MHz. The measurement were carried out at the temperature range of 303 K to 353 K. The CMC-NH$_4$SCN films was sandwiched between two stainless steel electrodes with diameter 2 cm under spring pressure. The ionic conductivity of CMC-NH$_4$SCN films can be calculated using equation.

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

Here A (cm^2) is the electrode-electrolyte contact area of the film, t (cm) is thickness of film and R$_b$ is bulk resistance. R$_b$ was obtained from the complex impedance plot (Cole-Cole plot) at the intersection of the imaginary and the real impedance axis.

The dielectric loss (the imaginary part of complex permittivity), ε_i is defined as,

$$\varepsilon_i(\omega) = Z_r / \omega C_o (Z_i^2 + Z_r^2) \tag{2}$$

where C$_o$= ε_o A/t, ε_o is permittivity of free space, $\omega = 2\pi f$ (f is frequency), Z$_r$ is the real part of the complex permittivity and Z$_i$ is the imaginary part of the complex permittivity.

Results and Discussion

Ionic conductivity analysis. Conductivity is related to the number of charge carriers (η) and their mobility (μ) according to the following equation:

$$\sigma = \Sigma \eta . q . \mu \tag{3}$$

where q is the charge on each charge carrier. The ionic conductivity of CMC-NH$_4$SCN system at room temperature is depicted in Fig. 1. It can be observed from Fig. 1, by increasing the ionic dopant contentration, the conductivity was found to increase. This is may be due to the increase in the number of mobile charge carriers [6]. The highest ionic conductivity obtained is 6.48×10^{-5} Scm^{-1} for sample containing 25 wt% NH$_4$SCN.
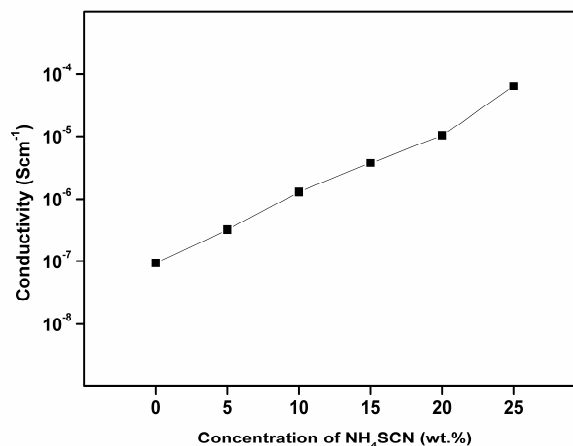

Fig. 1. Ionic conductivity of CMC-NH$_4$SCN system at room temperature.

The temperature dependence of ionic conductivity measurements have also been carried out to examine the conductivity mechanism of the CMC-NH$_4$SCN system. The plot of log conductivity vs 1000/T was constructed for various concentration of CMC-NH$_4$SCN system in temperature ranges from 303 - 353K depicted in Fig. 2. It can be observed in Fig. 2, conductivity increases when temperature was increase. The increase in conductivity with temperature can be attributed to the increase in number density of ions and or increase in mobility of ions [7]. The conductivity-temperature relationship for CMC-NH$_4$SCN system obeys Arrhenius behaviour where regression value is almost unity ($R^2 \sim 1$) suggesting that all points lie on a straight line indicating that the conductivity mechanism is thermally assisted [8].
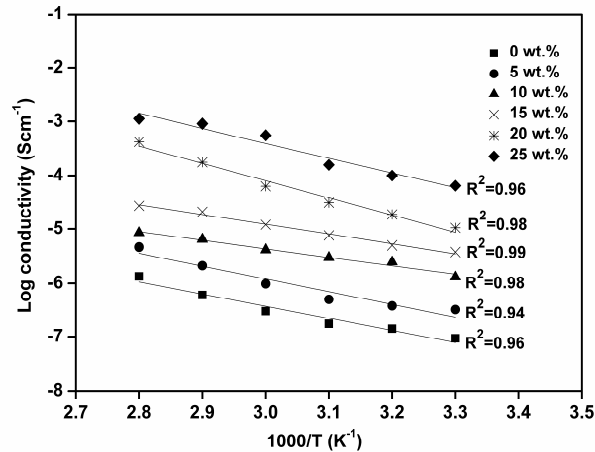
Fig. 2. Temperature dependence for ionic conductivity of CMC-NH$_4$SCN system.

Conduction mechanism analysis. The study of dielectric in polymer electrolytes is a powerful approach for obtaining information about the characteristics of ionic and molecular interactions. From dielectric study, some of the physical and chemical properties of the polymer can evaluate and help in understanding the conductive behavior of polymer electrolytes [9]. Fig. 3 presents frequency dependence of dielectric loss for highest ionic conductivity of CMC-NH$_4$SCN system at various temperature. From Fig. 3, it can be observed that the dielectric loss rise sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming non-Debye dependence. On the other hand, at high frequencies, periodic reversal of the electric field occurs 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 loss [10].
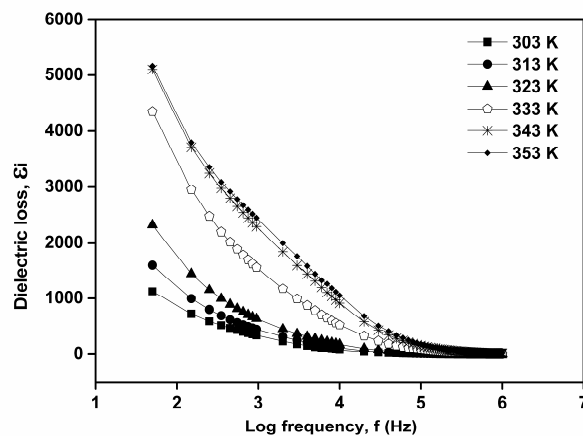
Fig. 3. Dielectric loss versus log frequency for the highest ionic conductivity of CMC-NH$_4$SCN system at various temperature.

The phenomenon of ac conductivity can be analyzed using Jonscher's universal power law (UPL) [4].

$$\sigma(\omega) = A\omega^s + \sigma_{dc} \tag{4}$$

Here, tan δ is the loss tangent. Substituting $\mathcal{E}_r$ tan $\delta = \mathcal{E}_i$,

$$\sigma_{ac} = \mathcal{E}_o \mathcal{E}_i \omega \tag{5}$$

where A is a parameter dependent on temperature, s is the power law exponent with value in the range between 0 and 1. The value of s can be evaluated from the following relation:

$$\ln \mathcal{E}_i = \ln A/\mathcal{E}_o + (s-1) \ln \omega \tag{6}$$

From the Fig. 4, exponent s can be calculated from the slope at high frequency region. The acceptable range was at high frequency where there is no minimal space charge polarization. In this frequency, the electronic hops between pairs of sites can be explained when the relaxation process occur with local character. It was contributed by the superposition of the potential which yield a single ion potential that is actually felt by ion [11]. In this work, the acceptable frequency range is from 11< $\ln \omega$ < 16.
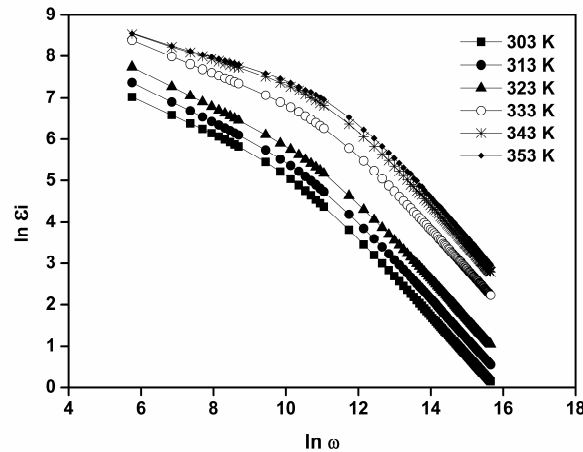

Fig. 4. Ln $\mathcal{E}_i$ versus ln ω for the highest ionic conductivity of CMC-NH$_4$SCN system at various temperature.

Up to now, a few of theoretical models have been proposed based on the analysis of ac conductivity such as quantum mechanical tunneling (QMT), overlapping large polaron tunneling (OLPT), small polaron hopping (SPH) and correlated barrier hopping (CBH) [12]. Fig. 5 illustrates the variation of frequency exponent s versus temperature. Thus, it can be inferred that QMT model is most suitable in explaining the conduction mechanism of CMC-NH$_4$SCN system due to the variation of the index s with temperature. In this QMT model, it can be assumed that the polarons (in this case is made up of the protons and their stress fields) are able to tunnel through the potential barrier that exists between two possible complexation sites [13].
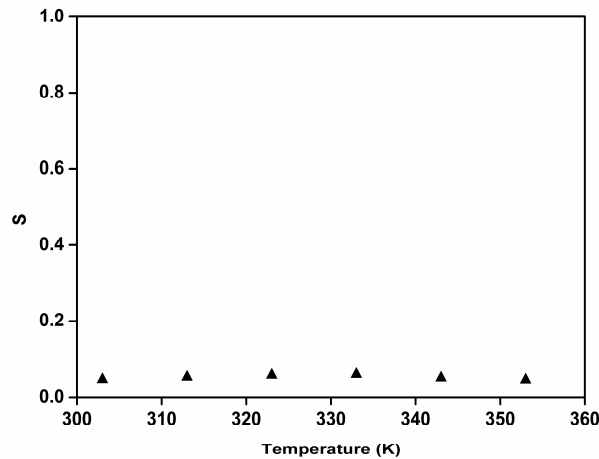
Fig. 5. Variation of exponent s versus temperature for the highest conductivity of CMC-NH$_4$SCN system.

Conclusion

Solid biodegradable polymer electrolytes based on CMC and NH$_4$SCN were successfully prepared via solution casting method and found to be transparent film. The CMC-NH$_4$SCN system obtained the highest conductivity of 6.48 x 10^{-5} Scm^{-1} at room temperature for sample with NH$_4$SCN concentration of 25 wt.%. The temperature dependence of ionic conductivity of the CMC-NH$_4$SCN system exhibits Arrhenius behavior. The conduction mechanism of the CMC-NH$_4$SCN system can be best presented by QMT model.

Acknowledgement

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