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Conductivity studies of cellulose acetate-sodium nitrate polymer system

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Abstract

The effect of sodium nitrate ($NaNO_3$) salt on the conductivity of polymer system based on the bio polymer cellulose acetate (CA) has been analysed in this study. The films were prepared by solution casting technique. The sample (CA: NaNO3) with the weight ratio of (0.6:0.4) gram exhibited the highest room temperature conductivity of the order 10^{-6} Scm^{-1}. Dielectric measurements were made using ac impedance analyser in the frequency range of 10 Hz–4 MHz. It was observed that the ionic conductivity increased with the increase in salt concentration as well as temperature. The conductivity–temperature relationship was found to obey Arrhenius rule. The activation energy is calculated for the highest conducting sample.

Keywords: cellulose, acetate-sodium, nitrate, polymer system

Introduction

Research towards solid polymer electrolytes (SPEs) have grown over a large extent in recent years. This is due to the fact that SPEs have major advantages when compared to the traditional liquid electrolytes for electrochemical device applications. Properties such as its ability to be formed into desirable shape and size, high ionic conductivity and good thermal, mechanical and electrical stability make them suitable for electrochemical applications. These properties of SPE have been used widely in the fields of sensors, batteries, solar cells and fuel cells [1, 4]. SPE made up of biodegradable polymers have gained major significance due to its impact on the environment. Bio polymers such as chitosan, carrageenan, agar, starch and cellulose with its derivatives have been chosen as the host polymer and studied for its role as SPE [5, 10].

Cellulose acetate (CA) is one such material that has been studied due to its abundance in nature, non-toxic nature, low cost, biodegradability, and its effective use in industries and in research [11, 12].

The lone pair of electrons from the oxygen atom of the acetate group in CA makes it a suitable material to act as a host polymer. However cellulose acetate is crystalline in nature and processes a low ionic conductivity at ambient temperature [13]. Therefore, a suitable salt complex is chosen and incorporated to improve its ionic conductivity and decrease its crystalline nature [14]. Sodium salts have been providing a good alternate to the lithium salts and its electrical properties in polymer-salt complexes have been studied [15, 16].

In our present work we study the effect of sodium nitrate complexed with cellulose acetate with the aim of improving its ionic conductivity. The films obtained are characterized by electrochemical impedance spectroscopy at different temperatures.

Experimental

In our current study, films of cellulose acetate based polymer electrolytes were prepared using solution cast technique. Cellulose Acetate (CA) and Sodium Nitrate ($NaNO_3$) salt were mixed in a proper weight ratio as presented in table1. The solvent used here is Dimethyl formamide (DMF). The solution mixture were stirred continuously using a magnetic stirrer for 24 hours to get a clear homogenous solution. The solutions were then poured into polypropylene petri dishes and were let drying at 50 ºC until solid films were formed. Conductivity studies of polymer electrolytes were measured using HIOKI 3536 LCR meter in the frequency range from 10 Hz to 4 MHz.

Table 1: samples' code with weight ratio

Sample	CA	$NaNO_3$
A	1 g	0 g
B	0.9 g	0.1 g
C	0.8 g	0.2 g
D	0.7 g	0.3 g
E	0.6 g	0.4 g

Results and Discussion

a. Electrochemical Impedance Analysis

The Nyquist plot for the pure cellulose acetate is shown in figure 1a. Nyquist plot for the cellulose acetate doped with different salt ratio at room temperature is shown in figure 1b. The plot consists of a high frequency semicircle due to the bulk effect of the SPE, followed by a low frequency spike contributed by the stainless-steel blocking electrode. This can also be represented by the parallel combination of bulk resistance and bulk capacitance of the polymer electrolytes [17, 18]. The depressed semicircle is due to the non-Debye nature of the systems [16]. The intersection of these two regions on the real axis gives us the bulk resistance (R), using which the conductivity of the prepared film is calculated by,

$$\sigma = \frac{l}{RA}\ (Scm^{-1}) \qquad (1)$$

Where l is the thickness of the polymer electrolyte film, A is the contact area of the blocking electrode (cm^2). Using the above formula, the ionic conductivity for the various films were calculated and listed in table 2. It is seen that as the salt concentration increases, the conductivity of the film also increases. This increase in conductivity can be attributed to the increase in mobile charge carriers and the amorphous nature of the electrolyte which is brought about by the physical interactions between the polymeric chain and salt [19, 20].

Table 2: Conductivity of the prepared polymer Films.

Sample	σ (Scm^{-1})
A	1.16E-09
B	5.56E-07
C	7.12E-07
D	8.80E-07
E	2.98E-06

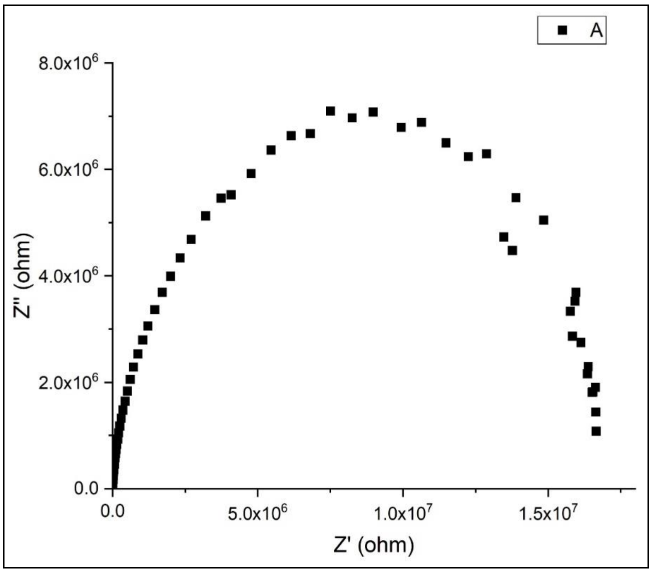

Fig 1a: Nyquist plot for pure CA polymer film

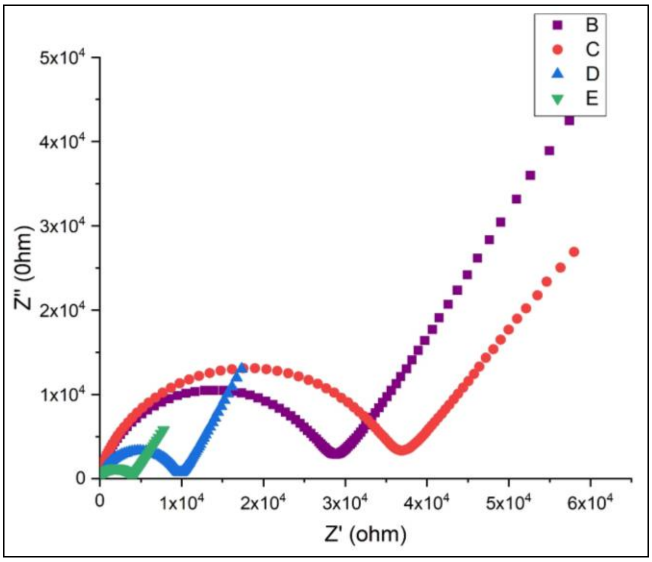

Fig 1b: Nyquist plot for different ratios of CA and $NaNO_3$.

The plot between log σ and 1/T for the various samples in the temperature range 308-343K is shown in fig 2. It is noted that the conductivity increases with temperature up to 328K, where the dc conductivity values follow the Arrhenius type thermally activated process. Above 328K conductivity decreases with increase in temperature, which may be due to the re-association of the anions into molecules due to the fast diffusion at higher temperature, thus reducing the mobility of Na^+ ions [21]. The activation energy for all the prepared polymer electrolytes was calculated by the linear fit of the Arrhenius plot using equation,

$$\sigma = \sigma_0 \exp\{-E_a/kT\}$$

Where σ_0 is the pre-exponential factor and E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

Fig. 3 represents the change in conductivity and activation energy for the various electrolytes. The activation energy decreases with increase in salt concentration indicating the increase in the amorphous nature of the films. The polymeric chains in the amorphous films are more flexible in turn enhancing the segmental motion of the host polymer. [19, 20].

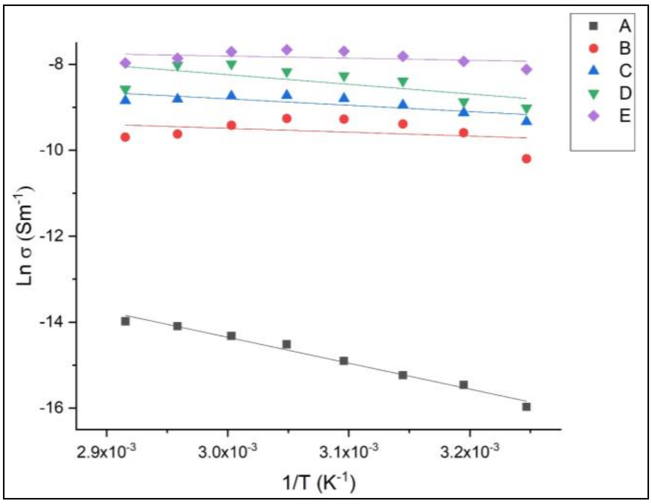

Fig 2: Temperature dependent conductivity for the different polymer electrolytes.

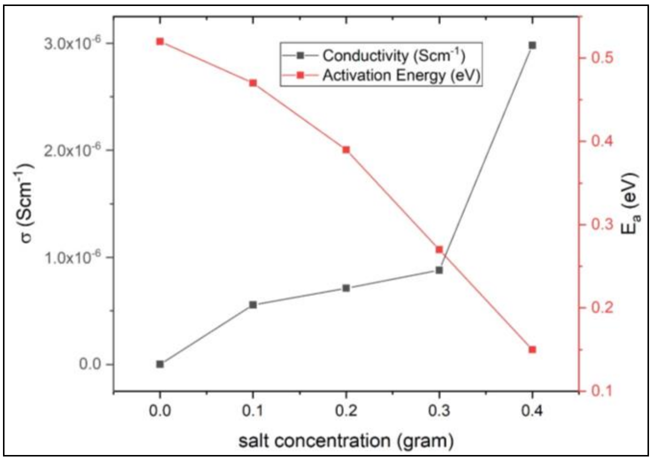

Fig 3: Variation of conductivity and activation energy with different salt concentrations.

b. Conductance Spectra

Figure 4 shows the variation of log σ with log f for all the samples at room temperature. It is evident from the plot that the curve consists of two different regions namely low frequency plateau region and high frequency dispersion region. Low frequency region is associated with dc conductivity and the extrapolation of plateau region to the Y axis gives dc conductivity value for the specific polymer electrolyte. High frequency dispersive region is attributed to the space charge polarization at blocking electrodes [22].

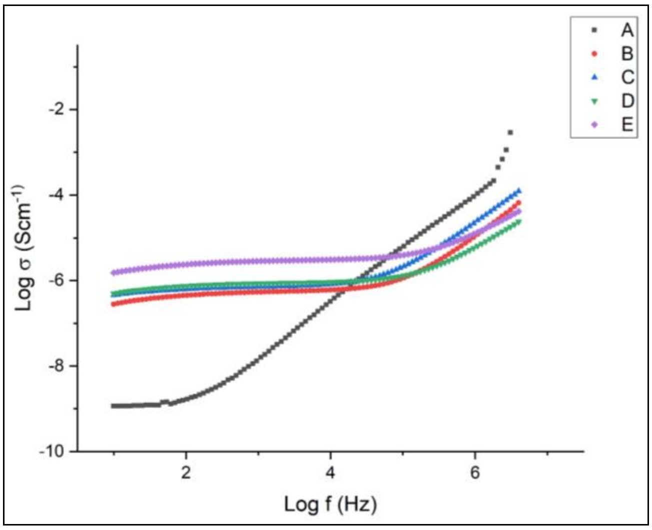

Fig 4: Conductance spectra for the different polymer electrolytes.

c. Dielectric Analysis

The dielectric behaviour of the system is defined by

$\varepsilon^* = \varepsilon' - j\, \varepsilon''$

Where ε' is the real part of dielectric constant (dielectric permittivity) and ε" is the imaginary part of dielectric constant (dielectric loss). The real and imaginary part indicates the storage and loss of energy in the applied electric field [23].

Form Figures 5 and 6, it is shown that the value of dielectric permittivity and dielectric loss decreases monotonically with increasing frequency and attains a constant minimum value at higher frequency. The values of permittivity is high at low frequency due to electrode polarization effects but as the frequency increases, the value begins to decrease, due to the fact that the dipoles are not able to follow the field variation at higher frequencies [24]. The low-frequency dispersion region is attributed to the contribution of charge accumulation at the electrode–electrolyte interface.

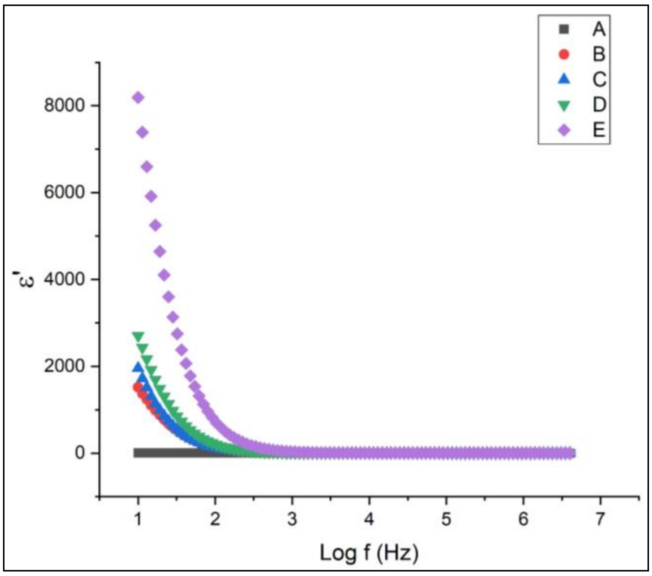

Fig 5: Variation of dielectric constant with frequency for the different polymer electrolytes.

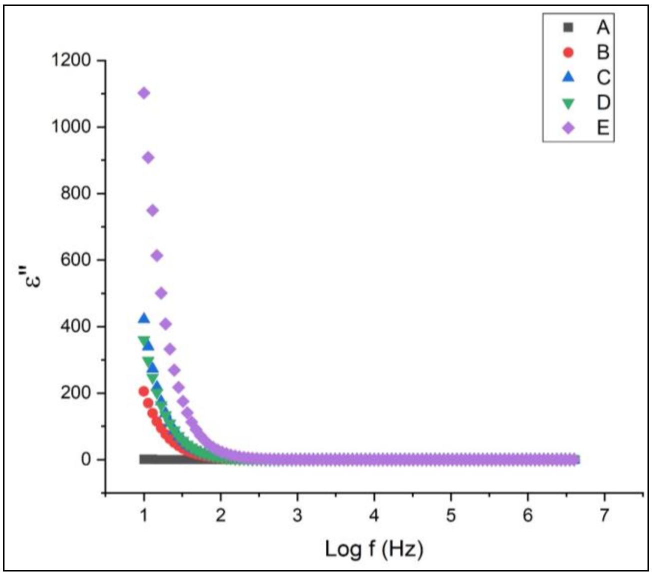

Fig 6: Variation of dielectric loss with frequency for the different polymer electrolytes.

Conclusion

Polymer films of Cellulose acetate doped with $NaNO_3$ were prepared by using solution casting technique. The maximum ionic conductivity of 2.98 x 10^{-6} S cm^{-1} was achieved for the film with weight ratio CA: SN - 0.6:0.4 g. The magnitude of ionic conductivity increases with the increase in salt concentration. The conductance spectrum shows two distinct regions: a dc plateau (low frequency region) and a high frequency dispersive region. The dependence of the ionic conductivity on temperature is of Arrhenius type up to 328K. The dielectric studies were done as a function of ferquency. The film can further be treated with plasticizer to improve its ionic conductivity.

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