

Conductivity and Dielectric behavior of Cellulose Acetate-ammonium Bromide Solid Polymer System

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ABSTRACT

A solid polymer film based on cellulose acetate and ammonium bromide was prepared using solution casting method. The highest ionic conductivity in the polymer electrolyte was observed to be in the order of 10^{-6} Scm^{-1} . The prepared polymer electrolytes were characterized using electrochemical impedance spectroscopy. Dielectric and temperature dependent conductivity studies were also performed in the frequency range of 10 Hz-4 MHz and in the temperature range of 303 K-343 K.

Key words: Biopolymers, Solid polymer electrolyte, Impedance analysis, Dielectric spectra

1. INTRODUCTION

Biopolymer-based polymer electrolytes have become the subject of interest in recent years, due to its biodegradability and its eco-friendly impact on the society. Many such biopolymeric systems have been studied and reported as suitable host for polymer electrolytes [1-5]. Cellulose acetate (CA) is one such biopolymer that is known for its abundance in nature, low cost, biodegradability, and biocompatibility. It has been widely studied in the field of solid polymer electrolytes and has been successfully employed in Li-ion batteries for the production of electrodes, separators, or as reinforcing agents in gel polymer electrolytes.

CA has lone pair of electrons that facilitate ionic conduction; however, its crystalline nature and high glass transition temperature have become a setback to its application in electrochemical devices. This can be overcome by the addition of inorganic salts making it a suitable material for ionic transport [6-8].

Ammonium salts have been reported to be good proton donors to the polymer matrix. The commonly used ammonium salts in these complexes include ammonium triflate ($\text{NH}_4\text{SO}_3\text{CF}_3$), ammonium thiocyanate, (NH_4SCN), ammonium hydrogen sulfate (NH_4HSO_4), ammonium perchlorate (NH_4ClO_4), and ammonium nitrate (NH_4NO_3) [6,7,9]. No reports are available on CA doped with ammonium bromide (NH_4Br).

In this present work, a proton conducting polymer membrane was prepared based on CA as host polymer and ammonium bromide (AB) as the proton source. The films obtained are characterized by electrochemical impedance spectroscopy.

2. EXPERIMENTAL

Films of CA based polymer electrolytes were prepared using solution cast technique. Two gram of CA doped with different concentration of NH_4Br (AB) (Table 1) was dissolved in 50 ml of dimethyl formamide using magnetic stirrer for 24 h. Each sample was then cast into petri dishes and left to dry until a thin film was formed. Impedance analysis and dielectric studies were carried out in the prepared polymer electrolytes.

3. RESULTS AND DISCUSSION

3.1. Impedance Analysis

The samples were characterized through electrical impedance spectroscopy using HIOKI 3536 LCR in the frequency range 10 Hz-4 MHz. The Cole-Cole plots obtained for the different samples are shown in Figure 1. It has been observed that the ionic conductivity increases with the increase in the concentration of the salt up to 0.2 g followed by a decrease in ionic conductivity at higher concentration. The increase in conductivity can be attributed to the increase in mobile charge carriers and amorphous nature of the polymer electrolyte. Ionic mobility decreases due to the aggregation of the salt to form ionic clusters. The ionic clusters are less mobile and stiffens the polymer matrix [10,11].

The Cole-Cole plot shows a semicircle and an inclined line which is due to the parallel combination of resistance with capacitance and space charge polarization. The bulk resistance of the electrolyte (R_b) has been retrieved from the intercept of the straight line on the Z' axis.

The conductivity is calculated using the formula,

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

where l and A are the thickness and the active area of the electrolyte film, and R_b is the bulk resistance of the electrolyte film [12,13]. The conductivity and bulk resistance values are listed in Table 2. The maximum ionic conductivity achieved was 8.1 E-06 at ambient temperature for the film containing 2 g CA and 0.2 g AB.

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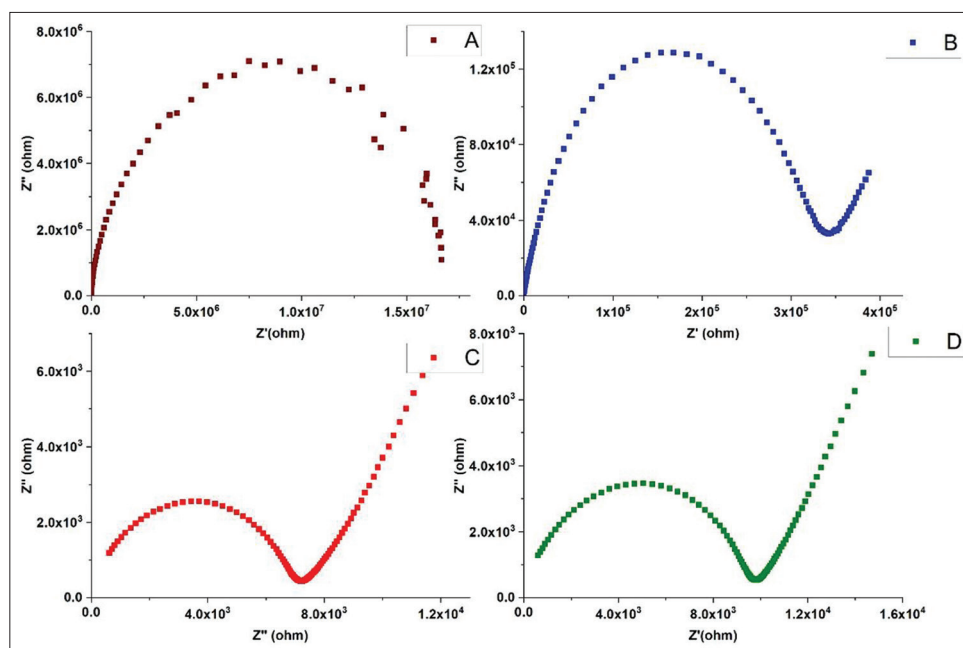


Figure 1: Cole-Cole plots for the various polymer electrolytes.

Table 1: Different samples and their corresponding compositions.

Sample	CA	AB
A	2 g	0 g
B	2 g	0.1 g
C	2 g	0.2 g
D	2 g	0.3 g

Table 2: Bulk resistance, conductivity, and activation energies (E_a) of the prepared polymer samples.

Sample	R_b (ohm)	σ (Scm ⁻¹)	E_a (eV)
A	1.665 E+07	1.16 E-09	0.53
B	3.43 E+05	9.03 E-08	0.37
C	7.23 E+03	8.10 E-06	0.27
D	9.81 E+03	4.85 E-06	0.4

3.2. Temperature Dependent Conductivity

Figure 2 shows the variation of ionic conductivity as a function of temperature for pure CA and for different compositions of AB doped polymer electrolytes in the temperature range 303 K–343 K.

The polymeric material expands due to the production of local voids as the temperature increases, which, in turn, increases the free volume into which the polymer segments can move. Hence, as temperature increases, the ionic conductivity also increases due to the increased free volume and segmental motion with decreased viscosity [10,14].

The conductivity (σ) versus temperature (T) follows Arrhenius behavior according to the equation,

$$\sigma = \sigma_0 \exp\{-E_a / kT\} \quad (2)$$

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

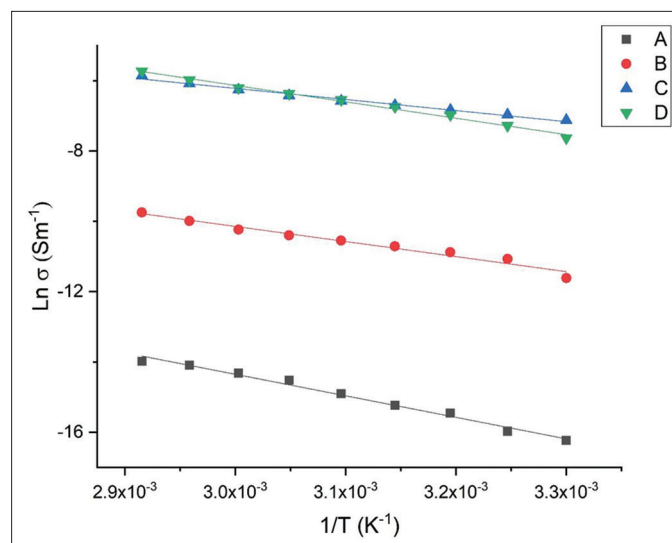


Figure 2: Temperature dependent conductivity for the prepared polymer electrolytes.

The ionic conductivity was found to increase with increasing temperature for pure CA as well as for the other compositions of polymer electrolytes. Activation energy (E_a) calculated using equation 2 is given in Table 2. It is seen that as the conductivity increases with the addition of salt, the activation energy decreases. This can be attributed to the complete amorphous nature of the polymer electrolyte that facilitates the fast NH_4^+ ion motions in the polymer network. For sample D, the conductivity decreases with the addition of salt, and thus, the activation energy is increased due to the aggregation of ions. It is concluded that the sample C with the highest conductivity has the lowest activation energy [14,15].

3.3. Conductance Spectra

The variation of conductivity as a function of frequency for all the samples is shown in Figure 3. The spectra consist of two regions: Low frequency plateau (frequency independent) and high frequency

dispersive region (frequency dependent). The frequency-independent plateau region is connected with the DC conductivity of the polymer electrolytes. This conductivity value has been assigned to the bulk conductivity of the sample. In high frequency region, conductivity increases with increasing frequency which is associated with ac conductivity. High-frequency dispersive region is attributed to the space charge polarization at blocking electrodes [16]. Figure 4 shows the conductance spectra for highest conducting sample at different temperatures. It is evident from the plot that the value of dc conductivity increases with increasing temperature.

3.4. Dielectric Analysis

Dielectric property indicates the amount of charge stored by a material. The dielectric response is generally described by

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon' - j \left(\frac{\sigma'}{\omega\epsilon_0} \right)$$

where ϵ' is real part and ϵ'' is imaginary part of ϵ^* , σ' is the real part of conductivity, ω is angular frequency and ϵ_0 is permittivity of free space.

Figures 5 and 6 show the variation of real and imaginary part of dielectric permittivity with frequency, respectively. It is evident from the figures that the value of ϵ' and ϵ'' is high at low frequency and decreases at higher frequency. The higher values of ϵ' and ϵ'' at low frequency are due to polarization at electrode-electrolyte interface [17].

However, in the high frequency range, dipoles cannot orient themselves in the applied electric field direction, and hence, the values of ϵ' and ϵ'' are constant and reach its minimum values. The observed variation in ϵ' with frequency can be attributed to the formation of space charge region at the electrode and electrolyte interface, which is known as $\omega^{(n-1)}$ variation or the non-Debye behavior [18].

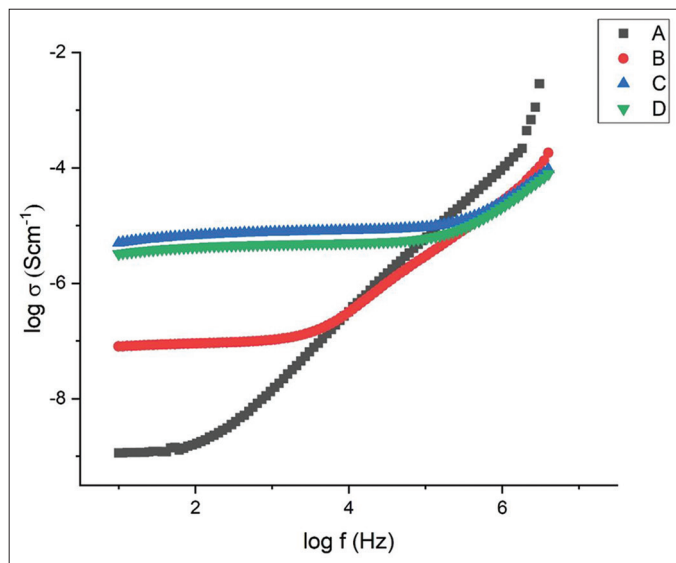


Figure 3: Conductance spectra for the different polymer electrolytes.

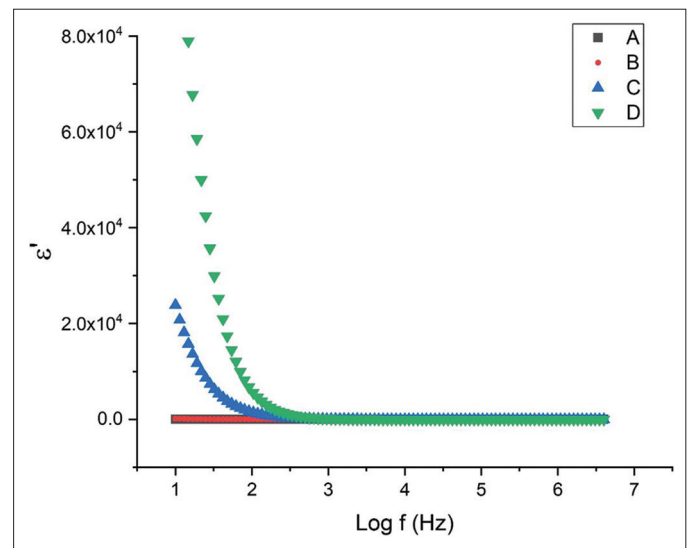


Figure 5: Variation of dielectric constant with frequencies for the different polymer electrolytes.

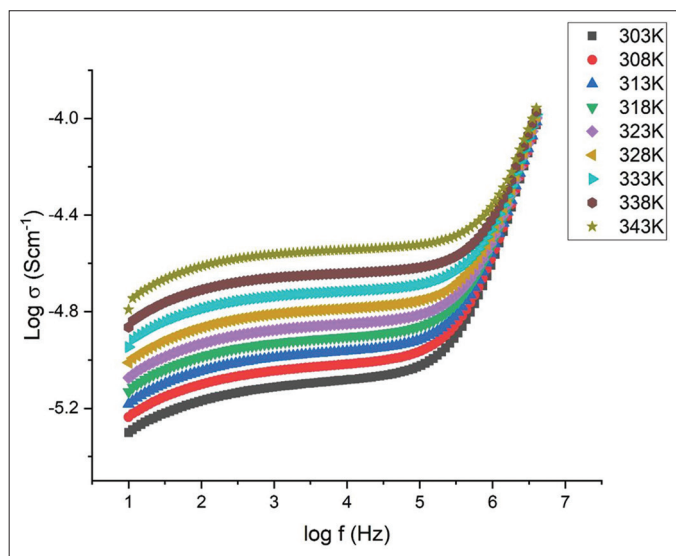


Figure 4: Variation of conductance spectra for the highest conducting electrolyte with temperature.

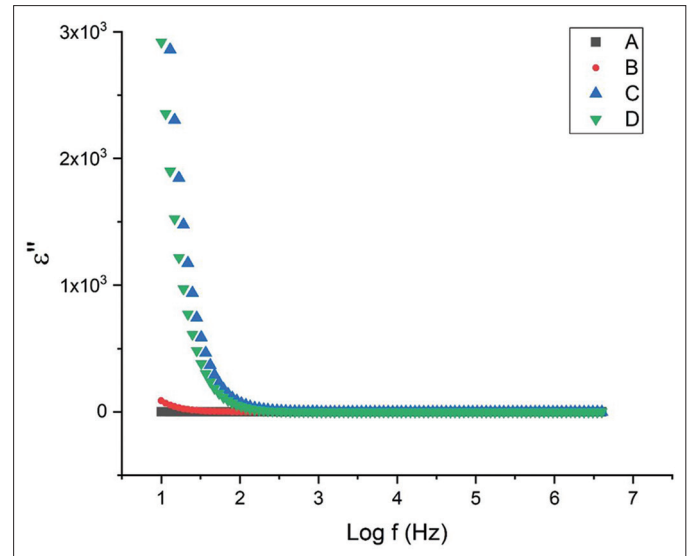


Figure 6: Variation of dielectric loss with frequency for the different polymer electrolytes.

4. CONCLUSION

The polymer electrolyte based on CA–AB has been prepared by solution casting technique. The maximum ionic conductivity of the sample $8.1 \times 10^{-6} \text{ Scm}^{-1}$ was achieved for the ratio CA:AB - 2:0.2 g. The ionic conductivity increases with increase in temperature. The activation energy of all the samples was calculated using Arrhenius plot and it has been found to be 0.27 eV for the highest conducting sample. Larger values of ϵ' and ϵ'' observed in the low frequency range are due to electrode polarization effect. The ionic conductivity can further be improved by adding nanocomposites or plasticizer and can be used in electrochemical applications.

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*Bibliographical Sketch



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