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CONDUCTIVITY AND DIELECTRIC BEHAVIOR OF CELLULOSE ACETATE-AMMONIUM BROMIDE SOLID POLYMER SYSTEM

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ABSTRACT- Solution casting cellulose acetate and ammonium bromide resulted in a rigid polymer film. At 106 Scm1, the polymer solution had the maximum ionic conductivity. Researchers used electrochemical impedance spectroscopy to explore polymer fluids. Insulation and conductivity tests were also performed between 10 Hz and 4 MHz, and between 303 K and 343 K, respectively

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

1. INTRODUCTION

Because of their minimal environmental effect and ease of biodegradation, biopolymer-based polymer electrolytes are becoming increasingly popular. Several biopolymer devices have showed the capacity to store polymer electrolytes. This description also applies to cellulose acetate (CA), which is nontoxic, widely available, biodegradable, and affordable. Many studies have been conducted on gel polymer electrolyte strengthening agents, electrodes, and separators manufactured from solid polymer electrolytes for use in lithium-ion batteries. Although CA's single pair of electrons promotes ion mobility, its crystallization and high glass transition temperature make it unsuitable for use in electrochemical devices. The addition of synthetic salts can hasten ion transport.

Ammonium salts are effective at adding protons to polymer substances. These compounds use substances such as hydrogen sulfate (NH_4HSO_4), nitrate (NH_4NO_3), ammonium triflate ($NH_4SO_3CF_3$), per chlorate (NH_4ClO_4), and thiocyanate (NH_4SCN). There have been no reports of CA treated with ammonium bromide. Carbon black (CA) was used as the host polymer and ammonium bromide (AB) as the proton source to create a proton-carrying polymer membrane. Electrochemical impedance spectroscopy is used by researchers to characterize the films.

2. EXPERIMENTAL

Polymer electrolyte films could be made via solution-cast CA. Using a magnetic mixer, half a milliliter of dimethyl formamide was blended with two grams of CA and various concentrations of NH_4Br (AB) (Table 1) and allowed to stand for 24 hours. The chemicals were placed in Petri plates and allowed to dry until a very thin coating was produced. We investigated the impedance and dielectric properties of the polymer solutions

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3. RESULTS AND DISCUSSION

Impedance Analysis

Electrical impedance spectroscopy was performed on the samples using an HIOKI 3536 LCR in the frequency range of 10 Hz to 4 MHz. Figure 1 depicts a part of a Cole-Cole curve. Ionic conductivity increases up to 0.2 g of salt content and subsequently declines with greater concentrations. Because of its amorphous shape and greater charge carrier mobility, the polymer electrolyte is more conductive. Ionic clusters arise when salt crystallizes, slowing ionic flux. When ionic groups become less mobile, the polymer matrix becomes more stiff.

The Cole-Cole plot has a slanted line and a half-circle due to capacitance, parallel resistance, and space charge polarization. The bulk resistance (Rb) of the electrolyte was measured at the junction of the straight line and the Z′ plane.

The conductivity calculation formula

$$\sigma = \frac{l}{RA}\ \mathrm{Scm}^{-1}$$

Rb denotes the bulk resistance of the electrolyte sheet. Its active area is represented by A, while its width is represented by l. Table 2 shows the bulk resistance and conductivity. At room temperature, the ionic conductivity of the film containing 2 grams of CA and 0.2 grams of AB was 8.1 E-06.

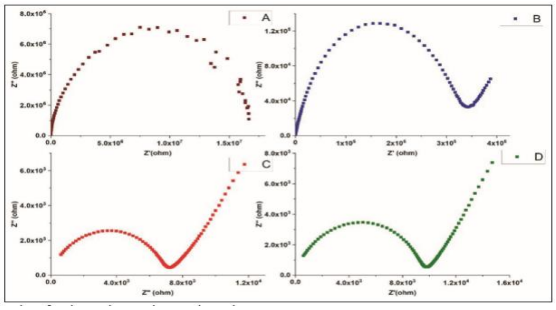

Figure 1: Cole-Cole plots for the various polymer electrolytes

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 (Ea) 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

Temperature Dependent Conductivity

From 303 K to 343 K, Figure 2 depicts the temperature dependency of ionic conductivity for various AB-doped polymer solution mixes and pure CA. This is due to local voids in the polymeric substance, which cause it to expand as temperature rises. This frees up more area for polymer segments. The viscosity reduces as the temperature rises, while the free volume and segmental mobility increase, resulting in an increase in ionic conductivity.

The graph depicts the relationship between conductivity () and temperature (T) as described by Arrhenius' hypothesis.

where σ_o is pre exponential factor, Ea is activation energy, k is Boltzmann constant, and T is absolute temperature

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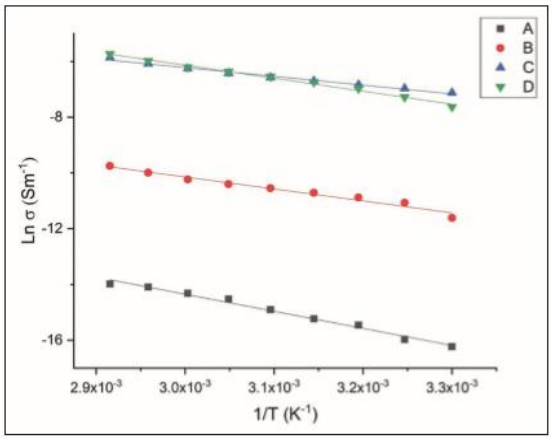

Figure 2: Temperature dependent conductivity for the prepared polymer electrolytes

With increasing temperature, the ion-conducting properties of pure CA and other polymer electrolytes improved. Table 2 shows the activation energy (Ea) calculated using Equation 2. As the salt content increases, the activation energy drops and the conductivity increases. Because the polymer electrolyte is completely amorphous, NH4+ ions can diffuse across it quickly. Because salt keeps ions together, it lowers conductivity while increasing activation energy in sample D. The sample C has the lowest activation energy and is the most permeable.

Conductance Spectra

Figure 3 depicts the frequency-dependent conductivity of the samples. A frequency-dependent high-frequency dispersive area and a frequency-invariant low-frequency peak characterize the spectra. It is linked to the frequency-independent plateau area by the polymer electrolyte's DC conductivity. This image depicts the sample's mass conductivity. An increase in frequency causes an increase in ac conductivity in the high-frequency zone. Space charge polarization creates a high-frequency dispersive area at the blocked electrodes. Figure 4 depicts the spectra of the sample's maximum conducting conductivity at various temperatures. The line demonstrates that as the temperature rises, so does the dc conductivity.

Dielectric Analysis

The maximum charge that a material can hold is indicated by the dielectric constant. Dielectric response is commonly defined as

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon' - j\left(\frac{\sigma'}{\omega\varepsilon_0}\right)$$

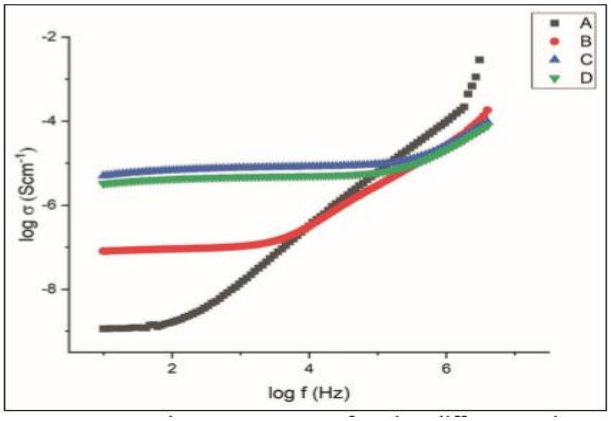

Figure 3: Conductance spectra for the different polymer electrolytes

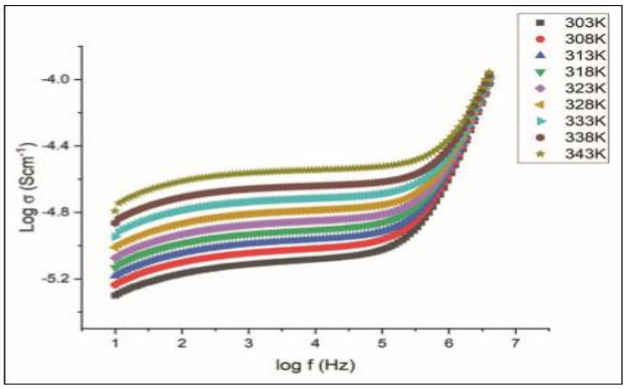

Figure 4: Variation of conductance spectra for the highest conducting electrolyte with temperature

The imaginary and real parts of *, conductivity, angular frequency, and free space permittivity are represented by the values ', ', ', and o, respectively.

Figures 5 and 6 show the frequency

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dependence of imaginary and real dielectric permittivity. The values of and' drop with increasing frequency and increase with decreasing frequency, as seen in the photos. The greater' and 'values at low frequencies are due to polarization at the electrode-liquid contact.

Because dipoles cannot align with the applied electric field, the values of' and " remain constant. They are at their lowest in the high frequency spectrum. A space charge zone forms when an electrode comes into contact with an electrolyte. This causes' to change as the frequency increases, and is known as (n1) variation or non-Debye behavior.

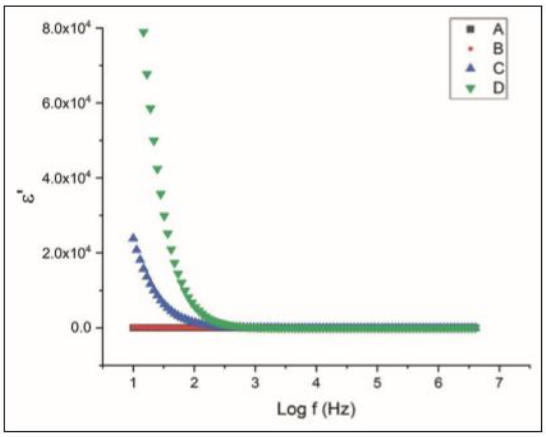

Figure 5: Variation of dielectric loss with frequency for the different polymer electrolytes

1. CONCLUSION

Solution casting was used to create the CA-AB polymer electrolyte. When the proportion of CA to AB was 2:0.2 g, the sample's ideal ionic conductivity was 8.1 106 Scm1. Ionic conductivity increases as temperature rises. The activation energy of the most conductivity-rich sample was 0.27 eV, according to the Arrhenius plot. Because of the electrode polarization effect, the'and'quantities increase in the low frequency range. The use of plasticizers or nanocomposites can improve ionic transmission for electrochemical applications.

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