CURRENT SCIENCE AND TECHNOLOGY
E-ISSN: 2785-8804
VOLUME 3, ISSUE 2, 2023, 13 – 18
DOI: https://doi.org/10.15282/cst.v3i2.10370

RESEARCH ARTICLE

Study on the Relations of Ionic Conductivity and Transport Properties of Alginate-PVA Based Bio-Polymer Blend Electrolytes System

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ABSTRACT - The growing interest in green energy storage materials has led to a renewed focus on creating biopolymer materials as electrolytes for electrochemical devices. In addition to being environmentally benign, it may result in lower costs and many financial prospects. This study sheds light on the protonation process of bio-polymer blend electrolytes based on alginate-poly (vinyl alcohol) (Alg-PVA) synthesized using the solution cast method and doped with varying concentrations of ammonium sulphate $(NH_4)_2SO_4$. The impedance spectroscopy obtained the Cole-Cole plot, and the bulk resistance value decreased when $(NH_4)_2SO_4$ was added. The calculated ionic conductivity showed the optimum value at 1.26×10^{-4} S cm^{-1} for a sample containing 15 wt.% of $(NH_4)_2SO_4$. The dielectric responses were used to assess the transport parameters of ion conduction, and it was shown that the principal causes of the increase in ionic conductivity are increased ion mobility and diffusion coefficient caused by the addition of $(NH_4)_2SO_4$.

ARTICLE HISTORY

Received	:	22nd Feb. 2023
Revised	:	06th May 2023
Accepted	:	07th Oct. 2023
Published	:	29th Dec. 2023

KEYWORDS
Biopolymer blend
Dielectric response
Conduction mechanism
Ionic transports

1. INTRODUCTION

The switch from conventional liquid electrolytes to solid polymer electrolytes (SPEs) is a significant development in electrochemical energy systems, especially in electrochemical devices. This change addresses issues with liquid electrolytes, such as restricted design flexibility and safety concerns. By providing improved safety features and reducing the flammability and leakage hazards associated with liquid electrolytes, particularly in high-energy-density applications, SPEs bring about a paradigm change. One of the main features of SPEs is that they have a lower ionic conductivity than liquids, which means that continuous research is needed to enhance conductivity using novel polymer matrices and inorganic additions. Notable properties of these SPEs include the convenience of production, flexibility, transparency, freedom from solvents, and lightweight and large electrochemical windows [1]. The optimal host polymer matrix for producing high ion conducting SPEs films typically possesses favorable characteristics such as flexibility, amorphous properties, low viscosity, and a glass transition point. When alkali metal salts are combined with crystalline polymer hosts, ionic conductivity is minimal [2].

Blends of polymers have been thoroughly researched to enhance ionic conductivity. The current system utilises the polymer blending technique for its cost-effectiveness and ability to yield promising ionic conductivity values. Research indicates that blending two polymers instead of one result in the production of more intricate sites. This enhances ion mobility and enhances the flexibility of polymer chains. Blending two polymers has been found to enhance both amorphous and flexible properties, leading to improved conduction characteristics [3]. Alginate is a complex bio-based polymer that is naturally derived from brown seaweeds. Alginate was chosen as the host polymer because of the carboxylate anion group in its polymer backbone chain, which aids in electrical conduction. Poly (vinyl alcohol) (PVA) is a synthetic polymer that is soluble in water and possesses non-toxic, biocompatible, and biodegradable properties. Combining with alginate is an appealing choice due to these features. Introducing an ionic dopant can improve the electrochemical properties of bio-polymer blend electrolytes (BBEs) systems by providing many ions to interact with the polymer backbone [4]. Ammonium sulphate ($(NH_4)_2SO_4$) was selected as the ionic dopant in this work due to its ability to act as a proton donor (H^+) and enhance the ionic conductivity of the BBEs system.

This work primarily investigates the impact of varying contents of ammonium sulfate $(NH_4)_2SO_4$ on the transport properties of a BBEs system composed of alginate and PVA. The purpose is to investigate the ion conduction mechanism and determine the ideal composition that will boost the ionic conductivity and be inline with the transport properties of the present BBEs system.

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2. METHODS AND MATERIAL

2.1 Preparation of Bio-Polymer Blend Electrolytes System

The BBEs system used alginate (Sigma Aldrich, MW: 70,000 g mol^{-1}), 87-90 percent partially hydrolyzed PVA (Sigma Aldrich, MW: 30,000-70,000 g mol^{-1}) and ammonium sulphate (Merck, MW: 132.14 g mol^{-1}). This study used distilled water as a solvent to dissolve the polymers and salt. All BBE films were made using the low-cost solution casting method. Alginate is the primary biopolymer, and PVA is the secondary biopolymer in the ratio of 70:30 wt.% [5]. Preparation of BBEs entails blending of alginate and PVA in distilled water at room temperature while continuously stirring for several hours. A viscous solution was formed because of this process. Then, different amounts of $(NH_4)_2SO_4$ (5–25 wt.%) were added to the Alg-PVA biopolymer blend solution. Continual stirring was employed to ensure the polymers and salt underwent a successful and intricate bonding process, resulting in a homogeneous mixture. The solution was then carefully transferred into several glass Petri dishes, then desiccated for 8 hours at 60 ℃ in a drying oven. The resulting dried BBEs films were placed in a desiccator (filled with silica gel) until further characterization.

2.2 Bio-Polymer Blend Electrolytes Characterization

The HIOKI 3532-50 LCR Hi Tester was used to measure the impedance of the BBE films at room temperature (303 K) over a frequency range of 50 Hz to 1 MHz. Each prepared film was sandwiched between stainless-steel electrodes using spring pressure. Equation (1) was used to calculate each film's ionic conductivity value.

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

In this context, t represents the thickness of the BBEs film, A signifies the contact area measured in cm^2, while R_b denotes the bulk resistance of the BBEs system extracted from the Cole-Cole plot.

3. RESULTS AND DISCUSSION

Impedance analysis was employed to determine the BBEs system's ionic conductivity. Figure 1 shows the resulting Cole-Cole plots corresponding to the theoretical and experimental data fitting for the selected BBEs system samples. Equations (2) and (3) were used to fit the Cole-Cole plot consisting of a depressed semicircle and a tilted spike.

$$Z_r = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2R k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-1} \omega^{2p_1}} + \frac{\cos\left(\frac{\pi p_2}{2}\right)}{k_2^{-1} \omega^{p_2}} \tag{2}$$

$$Z_i = \frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2R k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-1} \omega^{2p_1}} + \frac{\sin\left(\frac{\pi p_2}{2}\right)}{k_2^{-1} \omega^{p_2}} \tag{3}$$

where k_1^{-1} is the geometrical capacitance of the BBEs system, and k_2^{-1} is the capacitance at the electrode-electrolyte interface. Parameters R, p_1, and p_2 represent the bulk resistance, ratio of the angle between the depressed semicircle and the Z_i axis to the right angle subtended by the real and imaginary impedance, and the skew parameter that controls the degree of inclination of the tilted spike from the Z_r axis, respectively.

Figure 1 shows that a parallel combination of a resistor and a capacitor can reflect the bulk properties of the electrolyte, which is responsible for the occurrence of a semicircle in the high-frequency area. A bulk capacitor represents a stationary polymer chain, whereas a bulk resistor represents ion mobility from H+ carriers across the polymer matrix. An electrical double layer between an electrode and a polymer electrolyte is visible when a low-frequency spike is present. The diameter of the depressed semicircle determines the charge transfer resistance, and the diffusion process in the BBEs system is reflected in the system's linear section. The Cole-Cole plots of sample 5 wt.% show an inclined spike and semicircle that suggest the presence of a parallel arrangement of CPE and R_b element, with another CPE element in series. This indicates the equivalent circuit of semiconducting properties, as the inclined spike indicates. On the other hand, only an inclined spike is visible in the Cole-Cole plot of the BBEs sample containing 15 wt.% of $(NH_4)_2SO_4$, suggesting the existence of an equivalent circuit of R_b and CPE components in series. As ions flow in an electric field and aggregate on the electrodes to create the electrical double layer, electrode polarization occurs on the electrode-electrolyte interface, causing the inclined spike [6-8]. This phenomenon may bring an understanding of ions' conductivity. However, a semicircle reappears with the sample containing 25 wt.% of $(NH_4)_2SO_4$. This observation may result from salt aggregation and the crystalline characteristics of the BBEs. Reduced ionic conductivity is produced by a reduction in the number of free ions, which limits ionic mobility. The electrical equivalent circuit based on the Cole-Cole patterns was depicted in Figure 2.

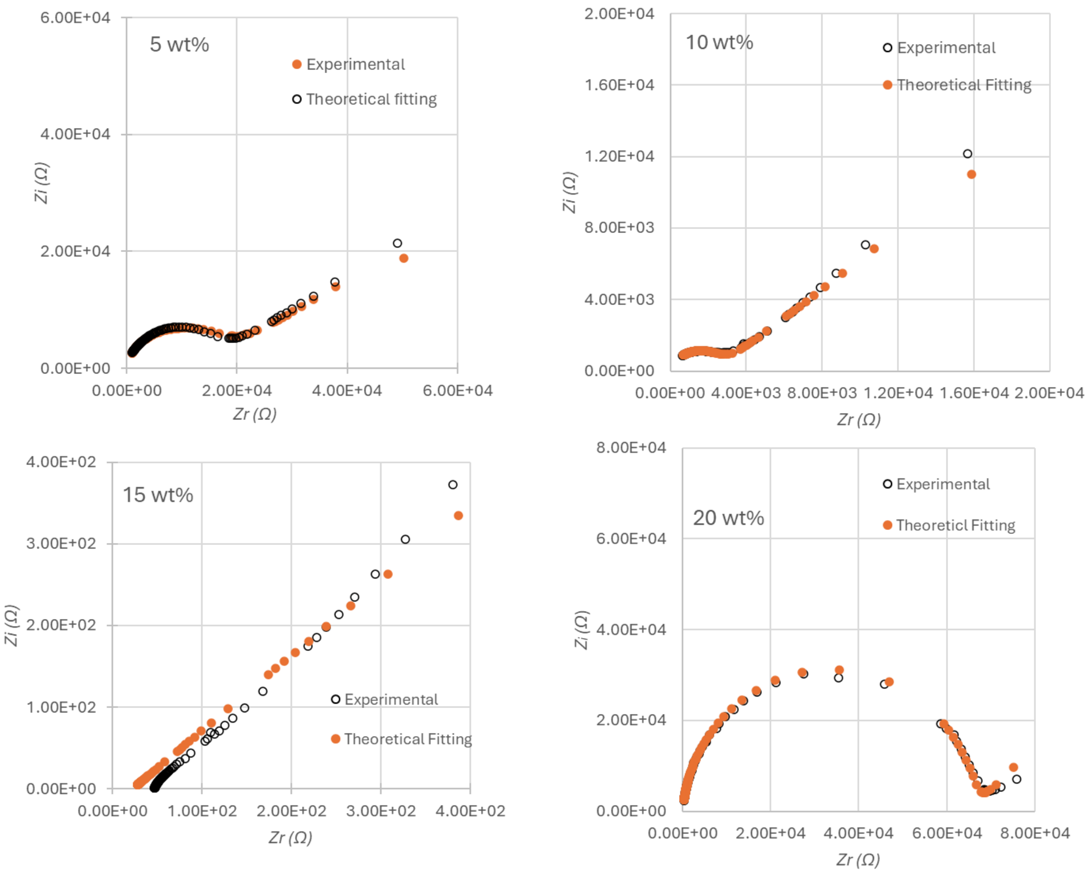
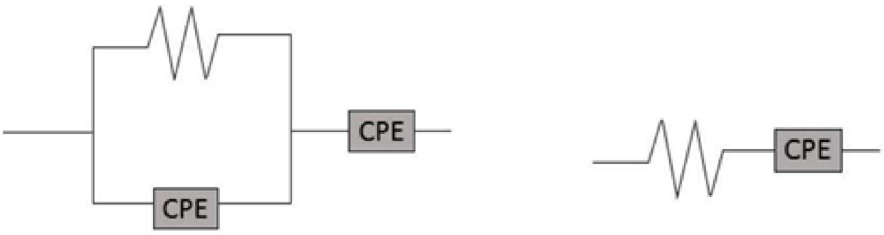


Figure 1. Cole-Cole plot and equivalent circuit for the selected samples of Alg-PVA-$(NH_4)_2SO_4$



(a) (b)

Figure 2. The equivalent circuit of alginate-PVA-$(NH_4)_2SO_4$ for (a) semicircle with inclined spike and (b) inclined spike Cole-Cole plot's profile

The parameters p_1, p_2, C_1, and C_2, which were stated in Table 1, can be identified using the Cole-Cole plot fitting formulae previously reported by other studies [9, 10]. Here, p_2 is the skew parameter that determines how far the inclined spike extends, and p_1 is the angle between the diameters of the semicircle. The results of the computations demonstrate how closely the data produced by the fitting procedure matches the measured R_b values that were received from the experiment. Moreover, sample 15 wt. % exhibits the highest ionic conductivity because of its significantly lower R_b value. The current system's spike inclination was less than 90°, as shown by the p_2 value, which falls between 0 and 1. According to these results, the samples have both capacitive and resistive properties [11].

Table 1. Fitting parameters for the BBEs system's equivalent circuit

Sample (wt. %)	R_b (Ω) Experimental	R_b (Ω) Theoretical	p_1 (rad)	C_1 (F)	p_2 (rad)	C_2 (F)
5	14046	14121	0.83896	8.41×10^{-12}	0.34489	3.31×10^{-6}
10	2708	2663	0.79437	3.31×10^{-9}	0.43465	4.71×10^{-6}
15	53.4	48.2	-	-	0.49700	5.19×10^{-5}
20	69700	68850	0.95901	1.23×10^{-10}	0.50972	4.01×10^{-6}
25	70277	70145	0.81400	3.54×10^{-10}	0.66300	2.11×10^{-6}

The bulk resistance (R_b) can be found using the Cole-Cole plot, which displays the relationship between the semi-circle and the real axis. Plots of ionic conductivity for a blend of Alg-PVA biopolymer with various contents of $(NH_4)_2SO_4$ at room temperature are shown in Figure 3. Since ammonium salt can produce H^+ ions by dissociating $(NH_4)_2SO_4$ and improving ionic conductivity, adding it to the BBEs system is essential. Figure 3 shows that the ionic conductivity increased from ~10^{-7} S cm^{-1} (sample 5 wt.%) to 1.26×10^{-4} S cm^{-1} (sample 15 wt.%). The dissociation of H^+ is the primary reason for the observed rise in ionic conductivity in the BBEs system with increasing ammonium salt concentration. This H+ ion dissociation is anticipated to boost ionic mobility and mobile ions [12]. Additionally, as the blended biopolymer creates more empty spaces for ion conduction between H^+ and oxygen in the Alg-PVA polymer backbone chain through the ion-dipole interaction, the blended Alg-PVA can be responsible for the enhanced ionic conductivity value. With 15 wt.% of $(NH_4)_2SO_4$, the BBEs system demonstrated the highest ionic conductivity level, measuring 1.26×10^{-4} S cm^{-1}. Increases in H^+ ion concentrations, ion mobility, and polymeric backbone flexibility allowed for the highest reasonable degree of ionic conductivity. Due to their increased ability to move around, mobile ions have the potential to cause more disorder in the biopolymer structure [13]. As a result, ionsigrate more naturally [14]. Nevertheless, adding more than 15 wt.% of $(NH_4)_2SO_4$ decreased ionic conductivity. H^+ ions are abundant because of the elevated concentrations of $(NH_4)_2SO_4$, and they have a higher tendency to agglomerate and form neutral ion pairs.

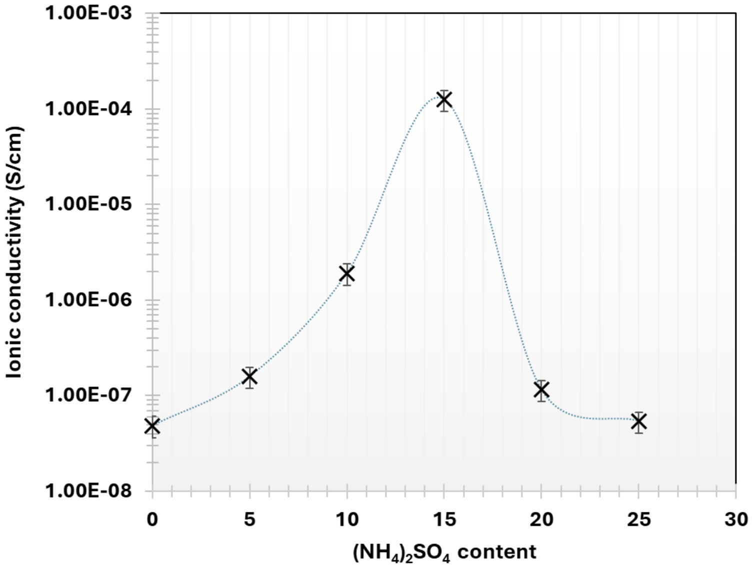


Figure 3. Plot of ionic conductivity for Alg-PVA-$(NH_4)_2SO_4$ BBEs system at room temperature.

The BBEs system's ionic conductivity was enhanced by the addition of $(NH_4)_2SO_4$, which led to an assessment of the transport characteristics. Faster ion dynamics are made possible in large part by the transport parameters. The number of charge carriers (η), ion mobility (μ), and diffusion coefficient are the three main transport parameters (D). Equation following can be used to predict the transport parameters of the BBEs system based on the dielectric constant response:

$$D = \frac{(k_2 s_r s_0\, A)^2}{\tau_2} \tag{4}$$

where D is diffusion coefficients, k_2 is capacitance of the constant phase element (CPE) caused by the electrical double layer formed at the electrolyte-electrode interface during the impendence measurement, ε_o is the vacuum permittivity, A is the electrode-electrolyte contact area and τ_2 is a time constant corresponding to the maximum dissipative loss curve, which is equal to $1/\omega_2$.

$$\mu = \frac{e(k_2 s_r s_0\, A)^2}{k_b T \tau_2} \tag{5}$$

where μ is the mobility of the charge carriers, k_b is the Boltzmann constant T is the absolute temperature in Kelvin and e is the electron charge (1.602×10^{-19}). The number density of charge carriers (η) can be obtained using below:

$$\eta = \frac{\sigma k_b T \tau_2}{(e k_b \varepsilon_r . \varepsilon_o A)^2} \tag{6}$$

$$k_2 = \frac{\lambda_D}{\varepsilon_r . \varepsilon_o A} \tag{7}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_r . \varepsilon_o k_b T}{Z^2 e^2 n}} \tag{8}$$

Based on the parameters in Table 1, the transport properties of the BBEs system were calculated and presented in Figure 4. The improvement in transportation parameters is due to the following factors: (1) increased polymer chain segmental motion, (2) lower polymer chain viscosity, and (3) high ionic conductivity. It is worth noting that the transport parameters are linked to the fraction of free ions and impedance measurements. The addition of $(NH_4)_2SO_4$ has a considerable effect on ionic dynamics. Increasing ionic conductivity improves the entire transport parameter. The increased η was produced by enhanced free ion dissociation in the BBEs. In contrast, as ionic conductivity diminishes, so do transport parameters. The drop in η when more than 15 wt. % was added is due to the increased production of contact ions. Large fraction of $(NH_4)_2SO_4$ result in excess free ions in BBEs. This lowers the distance between SO_4^- and H^+ ions, creating contact ions via ion interaction [15]. As a result, the number of charge carriers reduced as the free volume in the electrolyte system rose, lowering the ionic conductivity of the BBEs system.

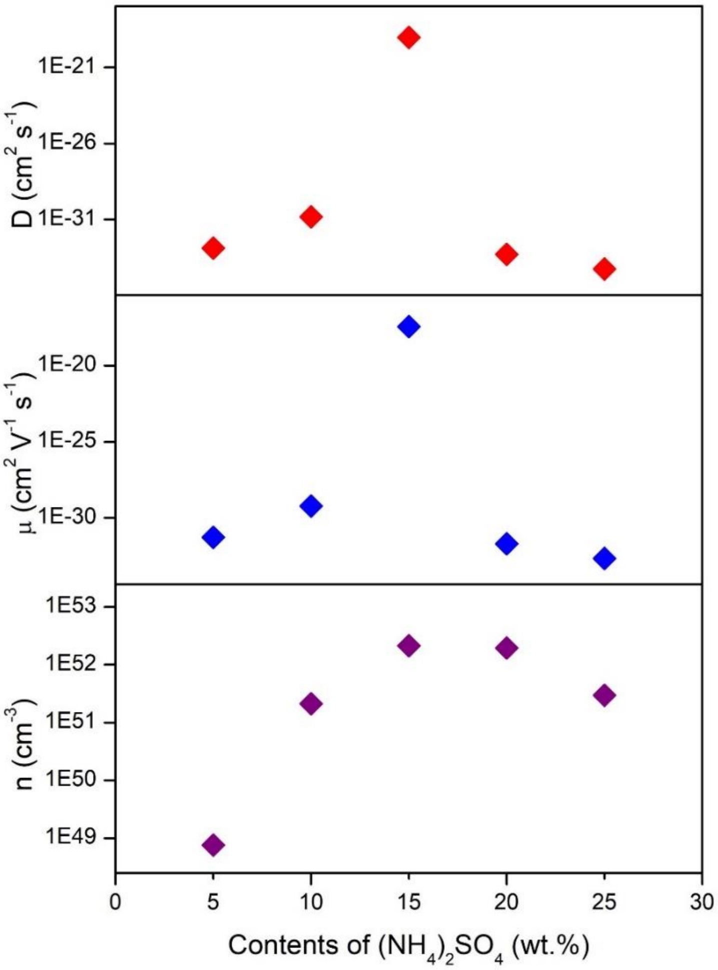


Figure 4. Transport properties for various $(NH_4)_2SO_4$ composition at ambient temperature

4. CONCLUSION

The immittance response on Alg-PVA complexed with $(NH_4)_2SO_4$ solid biopolymer blend electrolytes (BBEs) system was successfully carried out in the current work, which was produced using the solution casting approach. An ion transport strategy has been proposed to highlight how $(NH_4)_2SO_4$ affects the way the ionic dopant and biopolymer blend interact. There was a clear correlation between the rise of $(NH_4)_2SO_4$ compositions and the degree of ionic conductivity. At 303 K, the Alg-PVA doped with 15 wt.% of $(NH_4)_2SO_4$, demonstrated the highest ionic conductivity of 1.26×10^{-4} S cm^{-1}. The transport properties show that adding $(NH_4)_2SO_4$ caused the conductivity of ions value to rise due to significant ion dissociation. The outcomes showed the good ionic conductivity properties of the current system, which is based on Alg-PVA doped with $(NH_4)_2SO_4$ as BBEs and suggested that it may be utilized in an electrochemical deviceThe outcomes demonstrated the good ionic conductivity properties of the current system, which is based on Alg-PVA doped with $(NH_4)_2SO_4$ as BBEs and its suggested that it may be utilized in an electrochemical device.

ACKNOWLEDGEMENTS

The authors would like to thank you to Ministry of Higher Education (MOHE) Malaysia for the grant under FRGS (FRGS/1/2023/STG05/UMP/02/2) and Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA) under Distinguish

Grant (RDU 233001). We also wish to thank Faculty of Industrial Sciences and Technology, UMPSA, and Ionic Materials team members for the assistance given in this work.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHORS CONTRIBUTION

S.N.A. Azahar: Writing - original draft; Formal analysis; Data curation; Formal analysis; Investigation

N.M. Ghazali: Writing - review & editing; Investigation; data curation.

M. Diantoro: Resources; Review & Editing

A.S. Samsudin: Conceptualization; Funding; Visualisation; Supervision

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