Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society

IONIC TRANSPORT AND STRUCTURAL ANALYSIS OF BIOPOLYMER ELECTROLYTE BASED ON AGAROSE INTEGRATED WITH SODIUM NITRATE

(Kajian Pengangkutan Ion dan Struktur kepada Elektrolit Biopolimer Berdasarkan Penggabungan antara Agarose dan Natrium Nitrat)

Nur Farisha Sulthan Hussain[1], Siti Zafirah Zainal Abidin[1,2*], Nora Aishah Ahmad Shaharuddin[1], Raja Nur Qurratu Ain Raja Syiarizzad[1], Siti Rudhziah Che Balian[3]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[2]*Ionic Materials and Devices (iMADE) Research Laboratory, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[3]*Centre of Foundation Studies, Universiti Teknologi MARA, Cawangan Selangor, Kampus Dengkil, Dengkil 43800, Selangor, Malaysia*

**Corresponding author: szafirah@uitm.edu.my*

Received: 15 September 2023; Accepted: 30 December 2023; Published: 28 February 2024

Abstract

The central focus of this paper revolves around investigating biopolymer electrolyte films characterized by exceptional ionic conductivity, a prerequisite for the practical implementation of sodium-ion batteries. This study successfully prepared the agarose-based biopolymer electrolyte using the solution casting method. The effects of adding various weight percentages (0, 10, 20, 30 and 40 wt.%) of sodium nitrate salt ($NaNO_3$) to agarose-based biopolymer electrolytes were characterized. Electrochemical Impedance Spectroscopy (EIS) was adapted to analyze the conductivity and dielectric relaxation phenomena of the agarose-$NaNO_3$ complex. The conductivity of agarose-based biopolymer electrolytes increases with the increasing salt concentration. The increase in ionic conductivity is due to the increase in the number of charge carriers and the mobility of the sodium ions. The highest room temperature conductivity was 3.44×10^{-5} S·cm^{-1} for the agarose-$NaNO_3$ biopolymer electrolytes containing 30 wt.% sodium nitrate. X-ray diffractometer (XRD) spectroscopy was employed to investigate the crystallinity of the agarose-based biopolymer electrolyte. It was confirmed that the agarose-based biopolymer with 30 wt.% of sodium nitrate is the most amorphous compared to the others, as it has the largest full width at half maximum (FWHM) and the smallest crystallite size. This indicated that the amorphousness of the biopolymer electrolyte boosts the Na^+ ions' mobility, increasing the ionic conductivity of the samples.

Keywords: biopolymer electrolyte, agarose, sodium nitrate, conductivity, dielectric constant, crystallite size

Abstrak

Tumpuan utama dalam artikel ini adalah berkisar tentang penyelidikan untuk filem electrolit biopolymer yang dicirikan oleh kekonduksian ionik yang luar biasa, prasyarat untuk pelaksanaan praktikal dalam bateri natrium-ion. Dalam kajian ini, elektrolit biopolimer berasaskan agarosa telah disediakan dengan jayanya menggunakan kaedah penuangan larutan. Kesan penambahan pelbagai peratusan berat (0, 10, 20, 30 dan 40 wt.%) garam natrium nitrat ($NaNO_3$) kepada elektrolit biopolimer berasaskan agarosa dicirikan. Spektroskopi impedans elektrokimia (EIS) telah disesuaikan untuk menganalisis fenomena masa pengenduran kekonduksian dan dielektrik kompleks agarosa-$NaNO_3$. Kekonduksian elektrolit biopolimer berasaskan agarosa meningkat dengan kepekatan garam yang semakin meningkat. Peningkatan kekonduksian ionik adalah disebabkan oleh peningkatan bilangan pembawa cas dan mobiliti ion natrium. Kekonduksian suhu bilik tertinggi ialah 3.44×10^{-5} $S\cdot cm^{-1}$ untuk elektrolit biopolimer agarose-$NaNO_3$ yang mengandungi 30 wt.% natrium nitrat. Spektroskopi pembelauan sinar-X (XRD) digunakan untuk menyiasat kehabluran elektrolit biopolimer berasaskan agarosa. Telah disahkan bahawa biopolimer berasaskan agarosa dengan 30 wt.% natrium nitrat adalah yang paling amorf berbanding yang lain, kerana ia mempunyai lebar penuh terbesar pada separuh maksimum (FWHM) dan saiz hablur halus terkecil. Ini menunjukkan bahawa amorfus elektrolit biopolimer meningkatkan mobiliti ion-ion Na^+ sekali gus meningkatkan kekonduksian ionik sampel.

Kata kunci: elektrolit biopolimer, agarose, natrium nitrat, kekonduksian, pemalar dielektrik, saiz kristal

Introduction

Sodium-ion batteries offer promise as a feasible choice for large-scale energy storage owing to their advantages, such as the plentiful availability and cost-effectiveness of sodium-based components. The same organic liquid electrolytes used in lithium-ion batteries also contribute to continued safety issues, such as the risk of fire [1]. Polymer electrolytes provide an attractive alternative to liquid electrolytes, boosting sodium-ion batteries' safety. To ensure the success of this technique, all other battery components must be further developed. Electrolytes are essential to sodium batteries since they facilitate the transit of ions inside the cell. Polymers containing amorphous polymer-salt complexes are leading candidates to replace liquid electrolytes. This is because of its good temperature stability, large electrochemical window, and low electrolyte solution leakage.

Biopolymer electrolytes have gained significant attention in the field of sodium battery technology. These electrolytes are composed of natural biopolymers, such as agarose [2], chitosan [3], and alginate [4], which offer several advantages over traditional polymer or liquid electrolytes. Biopolymer electrolytes are environmentally friendly since they are derived from renewable sources. This makes them a sustainable alternative to conventional materials used in batteries. Additionally, these biopolymers possess good mechanical properties and high ionic conductivity, allowing for efficient ion transport within the battery system. A high concentration of functional groups allows for strong coordination interactions between ions and polymers. This leads to improved electrochemical performance, enhanced cycling stability, increased specific capacity retention rates, and low charge transfer resistance at electrode-electrolyte interfaces [5].

Agarose is a biopolymer from seaweed used as a host polymer to conduct ions. Biopolymer electrolytes based on agarose are an excellent potential replacement for synthetic-based polymer electrolytes in electrochemical devices [2]. Fossil fuels play a crucial role in producing synthetic polymers. However, substituting agarose for these synthetic materials can help reduce our reliance on fossil fuels, preserving them for future generations when their scarcity might pose a significant challenge. Fossil fuel formation is a time-consuming process, and our current consumption rate could eventually deplete this finite resource if we do not adopt more sustainable practices [6].

Adding sodium nitrate ($NaNO_3$) improves ionic conductivity in polymer electrolytes because it breaks down into sodium ions (Na^+) and nitrate ions (NO_3^-) when mixed with the polymer. These ions help electric charges move easily through the polymer's ion channels. This addition also boosts bulk and surface conductivities, as shown in X-ray studies revealing a stronger bond between $NaNO_3$ and the polymer, improving ion-polymer interactions and mobility [7]. Using sodium nitrate salts as dopant in polymer electrolytes has much potential to improve their performance in batteries. By interacting with polymers, these additives increase ionic conductivity, making it easier for charges to move while keeping the structure intact at normal temperatures.

This study is about cultivating a biopolymer electrolyte that combines agarose and sodium nitrate. The biopolymer electrolytes that will be utilized in this research are biopolymer electrolytes, which possess a greater conductivity when compared to solid polymer electrolytes. Thin films of biopolymer electrolytes will be produced and studied in this research. The thin films will be subjected to two methods of characterization of biopolymer electrolytes: Electrochemical Impedance Spectroscopy (EIS) to investigate ionic conduction analysis and X-ray Diffractometer (XRD) to determine the structural properties.

Materials and Methods

Preparation of biopolymer electrolyte

The biopolymer, agarose (molecular weight, Mw: 630.5 $g \cdot mol^{-1}$), was acquired from Next Gene in Puchong, Malaysia. Meanwhile, sodium nitrate ($NaNO_3$; Mw: 84.99 $g \cdot mol^{-1}$) as a dopant was attained from Chemiz (M) Sdn. Bhd. in Shah Alam, Selangor. Fisher Scientific, which is in Hampton, NH, USA, was where dimethyl sulfoxide (DMSO) (Mw: 256.41 $g.mol^{-1}$, ≥99.7%), which acts as a solvent, was obtained. The biopolymer electrolyte with a base of agarose and the integration of sodium nitrate was prepared using the method of solution casting. Firstly, 0.5 g of agarose was dissolved in 20 ml of the solvent dimethyl sulfoxide (DMSO). Next, sodium nitrate of different concentrations were added to the solution containing agarose and DMSO. The different concentrations of sodium nitrate are based on the weight percentages of 0, 10, 20, 30 and 40. The solution was stirred continuously at room temperature (300 K) using a magnetic stirrer at room temperature until a homogenous solution was obtained. The solution was cast on a petri dish and the sample was left to dry. The sample was dried in an oven to speed up the process of evaporation. The solvent that underwent evaporation was primarily composed of dimethyl sulfoxide, and upon its complete volatilization, autonomous biopolymer electrolyte films were effortlessly detached from the petri dishes, a visual representation of which is depicted in Figure 1.

Characterization of biopolymer electrolyte

The thin films of biopolymer electrolytes were characterized, and their ionic conductivity and electrical properties were analyzed based on impedance data from Electrochemical Impedance Spectroscopy. The apparatus that was used for this is the HIOKI 3532-50 LCR Hi-tester. The apparatus is consolidated with a computer of the frequency ranging between 100 Hz and 10 MHz at varying temperatures (303-373 K). The ionic conductivity, σ of an electrolyte, can be calculated using the formula in Equation 1. The distance between the electrodes in centimeters (cm) is t. At the same time, A is the contact area of the electrolyte and the electrodes in square centimeters (cm^2), whereas R_b is the bulk resistance of the sample electrolyte. Equation 1 can also be used to determine the ionic conductivity of a polymer electrolyte in the form of a thin film.

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

The thin films of the biopolymer electrolytes were characterized using X-ray diffractometer spectroscopy. Other than that, the structural behavior of the thin films was observed to identify the existence of amorphous and crystalline peaks in the thin films. The nature of the thin films, whether crystalline or amorphous, was determined. The apparatus in use for this is the PANalytical X'pert PRO diffractometer. The diffractometer has a copper K-alpha (Cu K-α) radiation of wavelength (λ) equal to 1.5418 Å. The angle of diffraction (2θ) of the diffractometer was set between 5° to 90° at room temperature.

Figure 1. The stand-alone thin film of agarose-$NaNO_3$ biopolymer electrolyte.

Results and Discussion

Conductivity analysis at room temperature

Impedance plot (Figure 2) of biopolymer electrolyte with 30 wt.% $NaNO_3$ shows a smaller depressed semicircle in the high-frequency region by comparing with 40 wt.%, and both samples containing an inclined spike in the low-frequency region. The semicircle indicates ionic conduction within the electrolyte, while the spike is linked to the impact of blocking electrodes. This impedance analysis employed blocking electrodes, creating a double-layer capacitance at the interface between the electrodes and the electrolyte.

The value of the bulk constant, R_b, for each sample at different weight percentages was determined by finding the value on the real impedance, the Z_r axis at which the semi-circular arc converges with the spike. The value of the bulk constant is observed to be reduced as the weight percentage of the samples increases from 0 to 30 wt. %. The bulk constant, R_b, then increases as the weight percentage of the sample rises to 40 wt.%.

Table 1 and Figure 3 demonstrate the ionic conductivity of the samples with different weight percentages of $NaNO_3$ at room temperature. The ionic conductivity of the agarose-based biopolymer electrolyte starts at 1.21×10^{-9} S·cm^{-1} when devoid of $NaNO_3$ (0 wt.%), which shows that polymer agarose is the best choice for host polymer as it satisfies the conductivity ranges for pure polysaccharides biodegradable materials from ~10^{-14} to 10^{-8} S.cm^{-1} [8]. Steadily escalating to 3.69×10^{-7} S·cm^{-1} at 10 wt.% of $NaNO_3$, with a continuous ascent peaking at the highest conducting of 3.44×10^{-5} S·cm^{-1} at 30 wt. %. However, beyond this concentration, the ionic conductivity experiences a decline, diminishing to 6.84×10^{-7} S·cm^{-1} at 40 wt.%.

The enhancement of ionic conductivity is attributed to the higher number of ion dissociation events obtained because of the addition of $NaNO_3$ from 0 to 30 wt.% into the agarose-based polymer electrolyte system that results in the production of free ions (Na^+ cation and NO_3^- anion) that can be incorporated in the polymer host matrix [9]. Therefore, a high salt concentration promotes the degree of ion dissociation, thus increasing the ionic conductivity of the agarose-$NaNO_3$ biopolymer electrolyte system. On the other hand, the increase in the amorphous nature of the system also affects the enhancement of ionic conductivity. It leads to the flexibility of the agarose polymer chain and promotes segmental motion in this system. However, when ions are abundant in the samples, the viscosity increases, which leads to the formation of ion cluster carriers that cause a decline in both the number of ions and their mobility, which impedes ion movement. Therefore, the ionic conductivity of the samples is reduced to 40 wt.% of $NaNO_3$ because of the change in the flow of charge carriers [2].

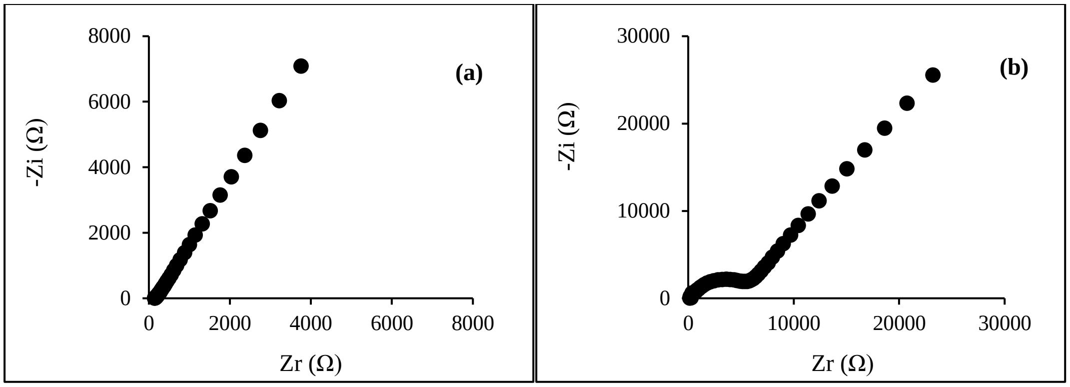

Figure 2. Impedance plot of agarose-based biopolymer electrolyte containing (a) 30 wt.% and (b) 40 wt.% $NaNO_3$ at room temperature.

Table 1. The bulk resistance and conductivity values of respected biopolymer electrolyte

$NaNO_3$ Content (wt. %) in Biopolymer Electrolyte	**Bulk resistance, R_b (Ω)**	**Conductivity, σ (S·cm^{-1})**
0	4.96×10^{7}	1.21×10^{-9}
10	8.33×10^{4}	3.69×10^{-7}
20	2.85×10^{3}	1.67×10^{-5}
30	9.57×10^{1}	3.44×10^{-5}
40	5.58×10^{3}	6.84×10^{-7}

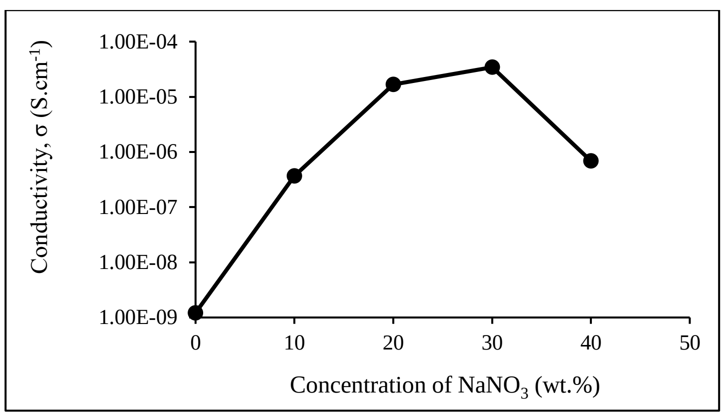

Figure 3. Conductivity plot of agarose-based biopolymer electrolyte containing $NaNO_3$ at room temperature

Temperature dependence conductivity analysis

One of the preliminary indicators for such electrolytes to have good thermal stability is that their ionic conductivity could be measured over a wide range of temperatures. In this work, the temperature dependence of the conductivity of agarose-$NaNO_3$ biopolymer electrolyte was carried out for the highest conducting sample containing 30 wt.% sodium nitrate salt within the temperature range between 303 K and 363 K (Figure 4).

The conductivity of polymer electrolyte films is linearly dependent on the temperature, and this relation can be related to the Arrhenius rule as given in the following equation (2), where σ_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature [10].

$$\sigma = \sigma_0 \exp\left(-E_a / k\,T\right) \qquad (2)$$

The increase in ionic conductivity of biopolymer electrolytes with temperature can be attributed to the segmental motion of the agarose chain, which provides a higher free volume in the electrolyte upon an increase in temperature. The segmental motion in agarose allows Na^+ ions to hop from one site to another or provides a pathway for its movement. For that reason, it is inferred that the ionic motion in the agarose-$NaNO_3$ biopolymer electrolyte system is due to ion hoping facilitated by the dynamic segmental motion of the agarose. The conductivity amplifies with the temperature. This is due to the fact that the reintegration of ions during the step of solvent desiccation in the formation of thin films is weaker when heat energy is applied to the sample [2]. As a result, when the temperature rises and additional ions become accessible for conduction, it leads to the conductivity being significantly greater [2]. Therefore, at higher temperatures, the amorphous region progressively increases, and agarose chains obtain a faster internal mode in which bond rotations produce segmental motion to favor interchain and intrachain ion hopping. Fortunately, the degree of conductivity becomes appreciable.

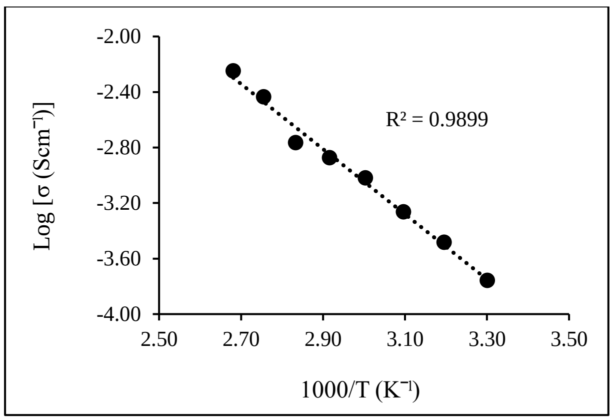

Figure 4. Arrhenius plots for the biopolymer electrolyte containing 30 wt.% of sodium nitrate

Dielectric properties analysis

Their dielectric behaviour is studied to better understand the ionic transport phenomenon in biopolymer electrolyte systems. The dielectric study in electrolyte systems helps us understand the polarization effect of the electrode–electrolyte interface and ionic conduction behaviour. In addition, the dielectric study is favourable due to the contribution of bulk material and interfacial effects at the electrode that are separable. The dielectric constant, ε_r, measures the ability of a material to polarise the amount of dipole alignment in a given volume and correlate with the capacity to store electric charge. Using the impedance data, the real component of complex permittivity is given by equation (3).

$$\varepsilon_r = \frac{Z_i}{\omega\, C_0\, ({Z_r}^2 + {Z_i}^2)} \quad (3)$$

Figure 5(a) illustrates the temperature dependence dielectric constant at different frequencies for the highest conducting sample of Agarose-$NaNO_3$ biopolymer electrolyte with 30 wt.% $NaNO_3$ at various temperatures. At low frequencies, the plots rise sharply, indicating that the Na+ ions accumulate at the electrode–electrolyte interface and lead to the formation of an electrical double layer or space charge region in the electrolyte system. Therefore, it contributes to a high dielectric constant value by measuring stored charge directly related to charge carriers. It asserts the non-Debye dependence as the high reversal of the external electric fields [3]. No peak has been seen in the plots of the dielectric constant, which reaffirms that the increase in ionic conductivity is affected by an increase in Na^+ ions density. The increase in dielectric constant supposedly reflects the increase in the density of charge carriers.

A further analysis of the dielectric behavior would be more successfully achieved by using the formulation of the dielectric modulus. A complex dielectric modulus formalism facilitates the identification and separation of the polarization effect from the bulk relaxation phenomenon in the electrolyte system. The electrical modulus is defined as the [11]:

$$M_r = \frac{\varepsilon_r}{\varepsilon_r^2 + \varepsilon_i^2} \quad (4)$$

Figure 5(b) demonstrates the real part of electric modulus against log f at different temperatures for the most favorable conductivity sample of Agarose-$NaNO_3$ biopolymer electrolyte containing 30 wt.% of $NaNO_3$. A decreased electric modulus is observed at lower frequencies, linked to the hidden electrode polarization impact. Conversely, at higher frequencies, both the real and imaginary electric modulus show an increase without a clear peak formation, and this rise in values can be attributed to the overall influence of the electrolyte samples. Furthermore, as the temperature rises, the M_r values incline, indicating an increased rate of movement for the charge carriers [2, 4].

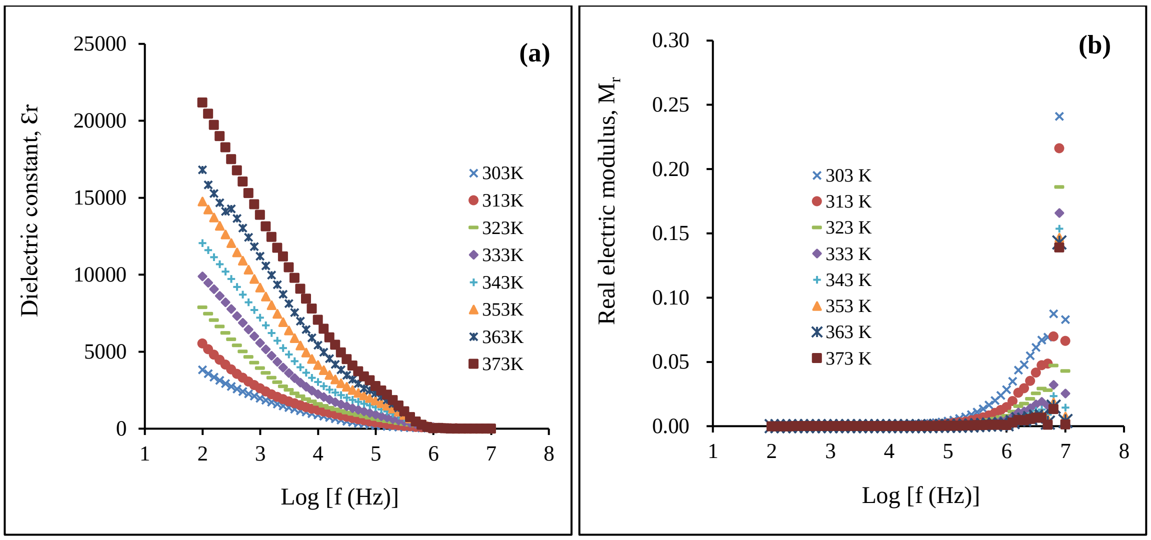

Figure 5. Variation of dielectric constant and real modulus component for optimized Agarose-30 wt.% $NaNO_3$ biopolymer electrolyte as a function of frequencies at various temperatures

The dielectric analysis is further parameterized by the loss tangent (tan $\delta = \varepsilon_i / \varepsilon_r$), and the relaxation time. Relaxation occurs when the loss tangent, tan δ, reaches its peak. The frequency at which the loss tangent, tan δ, reaches its peak is the maximum frequency (relaxation frequency), f_{max}, which is the frequency used to calculate the relaxation time, τ. The relaxation time is calculated using the formula [12]:

$$2\pi f_{max} \tau = 1 \quad (5)$$

Figure 6 shows the plot of loss tangent, tan δ, against the natural logarithm of frequency for selected samples with 20 wt.% $NaNO_3$ best represents the time relaxation trend for the Agarose-$NaNO_3$ biopolymer electrolyte (313 K, 333 K, 353 K and 373 K). It is noticed that the calculated values of relaxation time, as tabulated in Table 2, decrease as the temperature increases. This is caused by the fact that when the temperature rises, ions transition between coordinate sites more quickly, which results in a shorter relaxation time. The results of the relaxation studies in this research correspond with the findings attained by Shetty et al. [13]. Temperature influences the graphs' frequency position and peak intensities, confirming the thermally activated dielectric relaxation process. The relaxation time describes how ionic charge carriers in materials align with the applied field's direction, and at higher temperatures, longer relaxation times are achieved. In high-temperature environments, more mobile ions involved in conduction are generated and undergo relaxation at higher frequencies.

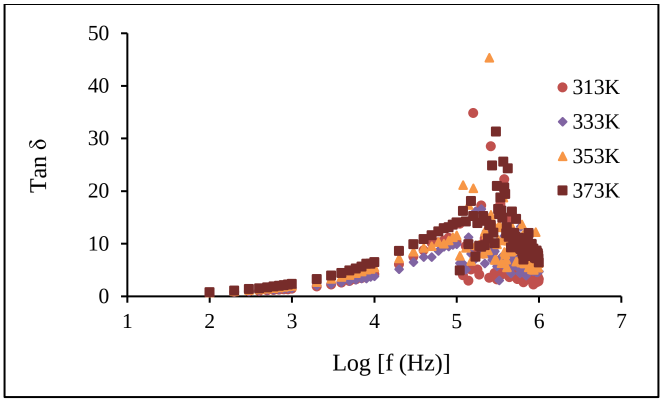

Figure 6. The plot of loss tangent as a function of the logarithm for biopolymer electrolyte with 20 wt.% of $NaNO_3$ at selected temperatures

Table 2. Relaxation time for agarose-$NaNO_3$ biopolymer electrolyte with 20 wt.% of $NaNO_3$

Temperature (K)	**Maximum Loss Tangent, $\tan\delta_{max}$**	**Maximum Frequency, f_{max} (Hz)**	**Relaxation Time, τ (s)**
313	34.82	5.20	3.06×10^{-2}
333	16.57	5.30	3.00×10^{-2}
353	45.33	5.40	2.95×10^{-2}
373	31.32	5.48	2.91×10^{-2}

Structural properties analysis

The structural or semicrystalline properties of the agarose-$NaNO_3$ biopolymer electrolyte were investigated through XRD analysis. Figure 7(a-c) displays XRD spectra of agarose-$NaNO_3$ biopolymer electrolyte with varying $NaNO_3$ concentrations (0, 30 and 40 wt.%). The presence of amorphous peaks at approximately 2θ = 20° in the absence of $NaNO_3$ (0 wt.%) confirms that agarose exhibits a semicrystalline structure [2]. As more $NaNO_3$ is added to the agarose matrix, the peak broadens, where this broadening indicates an increased amorphous character in the biopolymer electrolyte system, leading to enhanced $NaNO_3$ dissociation into free ions and greater ion migration through the polymer chains. At a 40 wt.% of $NaNO_3$ concentration, the peak narrows compared to the electrolyte with the highest conductivity (30 wt.% $NaNO_3$), suggesting a reduction in the electrolyte's amorphous nature due to the reassociation of ions within the agarose matrix.

The peak was slightly absent in agarose-30 wt.% $NaNO_3$ biopolymer electrolyte indicating the complete dissociation of salts in the electrolytes [8]. The highest conducting sample confirms its characteristic as the most amorphous sample due to the broadest amorphous hump. Elevated amorphous eases the path for the Na^+ ions migration and mobility in the biopolymer electrolyte regions, thus facilitate superior ionic conductivity. A decrease in the degree of crystallinity is also implied by improved amorphousness, which serves as a boost to the ionic conductivity. The dominance of the amorphous region is mathematically confirmed by determining the degree of crystallinity, X_c and crystalline size, L of the electrolyte and evaluated by using equations (6) and (7), respectively [14, 15]:

$$X_c = \frac{A_c}{A_T} \times 100\% \tag{6}$$

$$L = \frac{0.9\,\lambda}{\text{FWHM}\,\cos\theta} \tag{7}$$

where A_c is area under the peak of crystalline region while A_T is the total area under the peak, λ is the X-ray wavelength (fixed at 1.5406Å), FWHM is the full width at half maximum (a measure of the peak broadness) and θ is Bragg's diffraction angle.

In amorphous regions, the polymer chains are less organized, thus making it easier for salt to dissociate into free ions. The detail analysis of degree of crystallinity and crystallite size of 0 wt.%, 30 wt.% and 40 wt.% agarose-$NaNO_3$ biopolymer electrolyte are illustrated in Table 3 and Figure 8. The analysis supports the sample (agarose-30 wt.% $NaNO_3$) which exhibit the broadest XRD peak at 2θ = 20° which also demonstrate its amorphous nature by having the broadest FWHM, lowest degree of crystallinity (16%) and smallest crystallite size (0.0145 nm) among other samples.

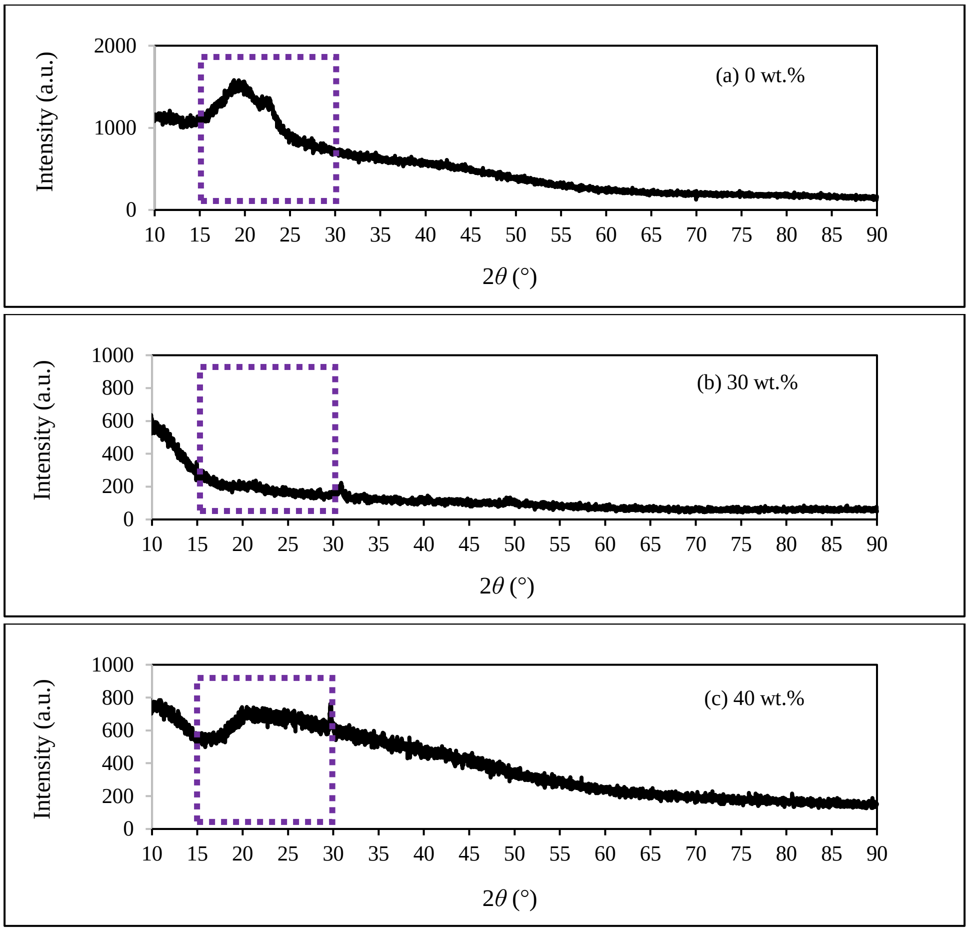

Figure 7. XRD pattern of agarose-$NaNO_3$ biopolymer electrolyte with different concentrations of sodium nitrate

Table 3. The analysis of agarose-$NaNO_3$ biopolymer electrolyte with different concentrations of sodium nitrate

$NaNO_3$ Content (wt.%)	Full Width Half Maximum (FWHM)	Degree of Crystallinity, X_c (%)	Crystallite Size, L (nm)
0	6.70	29	0.0219
30	10.44	16	0.0145
40	9.31	22	0.0161

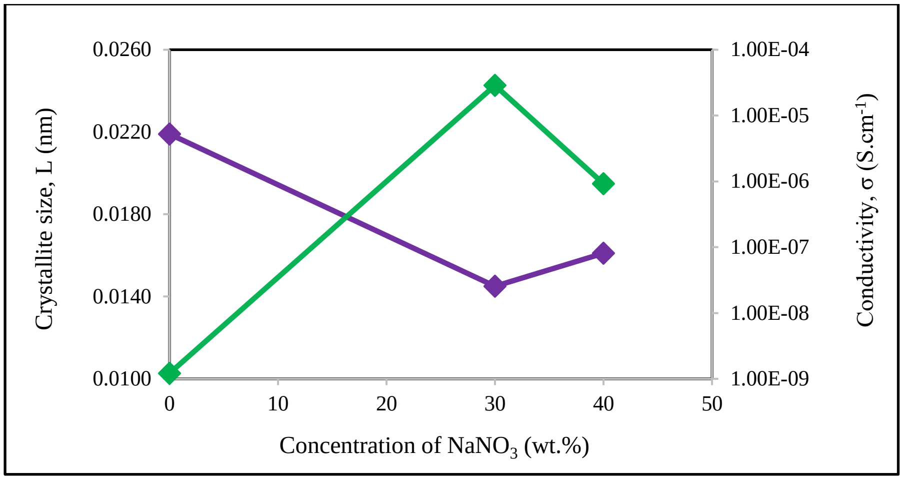

Figure 8. The size of crystallite of selected agarose-$NaNO_3$ biopolymer electrolyte with the respective room temperature conductivity values

Conclusion

In conclusion, Agarose-$NaNO_3$ biopolymer electrolyte was prepared in five different weight percentages of $NaNO_3$ by using the method of solution casting with the weight percentages of 0 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% $NaNO_3$. Electrochemical Impedance Spectroscopy (EIS) was employed to determine the biopolymer electrolyte's ionic conductivity and electrical properties. In contrast, X-ray diffractometer (XRD) spectroscopy was performed to observe the biopolymer electrolyte's structural behavior and amorphous nature. The conductivity studies at room temperature showed increased conductivity with the increasing sodium salt concentration. The increase in ionic conductivity is due to the increase in the number of charge carriers and the mobility of the sodium ions. The highest room temperature conductivity was 3.44×10^{-5} $S\cdot cm^{-1}$ for the agarose-30 wt.% $NaNO_3$ biopolymer electrolytes and beyond that, the ionic conductivity for agarose-40 wt.% $NaNO_3$ becomes reduced (6.84×10^{-7} $S\cdot cm^{-1}$) as the aggregation of ions starts to occur. The dielectric properties analysis of the selected biopolymer electrolyte sample indicates a strong dependence on frequency and temperature. The structural properties analysis based on FWHM, degree of crystallinity and crystallite size for agarose-based biopolymer electrolytes confirm that the amorphous regions tend to facilitate higher ion mobility compared to crystalline regions, therefore contributing to higher conductivity, as ions can move more freely through the amorphous parts of the polymer.

Acknowledgement

The authors appreciatively acknowledge the financial support for this work by the Fundamental Research Grant Scheme (FRGS, Sponsorship File No: FRGS/1/2019/STG07/UITM/02/2; and FRGS/1/2019/STG02/UITM/02/6), Ministry of Higher Education of Malaysia (MOHE), The authors would like to thank iMADE Research Laboratory, Institute of Science and Faculty of Applied Sciences, UiTM for all the support in providing research facilities to carry out this project.

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