

UNDERSTANDING THE EFFECTS OF GLYCEROL ON THE ELECTRICAL AND STRUCTURAL PROPERTIES OF PLASTICIZED AGAROSE/NaNO₃ BIOPOLYMER ELECTROLYTES

(Memahami Kesan Gliserol Terhadap Sifat Elektrik dan Struktural Elektrolit Biopolimer Agarose/NaNO₃ yang Diperplastikan)

Raja Nur Qurratu Ain Raja Syiarizzad¹, Siti Rudhziah Che Balian^{2,*}, Nur Farisha Sulthan Hussain¹, Nora Aishah Ahmad Shaharuddin¹, Siti Zafirah Zainal Abidin^{1,3,*}

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

³Centre of Foundation Studies, Universiti Teknologi MARA, Cawangan Selangor, Kampus Dengkil, 43800 Dengkil, Selangor, Malaysia

²Ionic Materials and Devices (iMADE) Research Laboratory, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

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

Received: 14 March 2024; Accepted: 21 August 2024; Published: 29 December 2024

Abstract

The goal of developing sustainable and environmentally friendly energy storage solutions can be explored by combining biopolymers with plasticizers. This is a crucial development in ensuring the desired electrical and structural properties in biopolymer electrolytes. In this current study, the plasticizer agarose/NaNO₃ biopolymer electrolyte thin film has been carried out with the addition of glycerol as a plasticizer using a solution casting technique. The effect of the addition of glycerol on the electrical and structural properties of the plasticized biopolymer electrolyte thin film was performed using electrochemical impedance spectroscopy (EIS) and X-ray diffraction (XRD). The plasticized biopolymer electrolyte thin film with 20wt.% of glycerol had the highest amorphous region, resulting in the highest ionic conductivity of 4.32×10^{-4} S cm⁻¹. These results were confirmed by XRD and EIS analysis. The plasticizer agarose/NaNO₃-glycerol biopolymer electrolyte could be used in sodium-ion batteries.

Keywords: biopolymer, sodium-ion, electrical, structural, green technology, plasticizer index

Abstrak

Tujuan membangunkan penyelesaian penyimpanan tenaga yang mampan dan mesra alam boleh dikaji dengan menggabungkan biopolimer dengan plastik. Ini merupakan pembangunan penting dalam memastikan sifat elektrik dan struktur yang diperlukan dalam elektrolit biopolimer. Dalam kajian ini, filem nipis elektrolit plastik biopolimer berdasarkan agarose/NaNO₃ telah dijalankan dengan penambahan gliserol sebagai bahan plastik menggunakan teknik tebararan larutan. Kesan penambahan gliserol terhadap sifat elektrik dan struktur filem nipis elektrolit biopolimer plastik telah dijalankan menggunakan spektroskopi impedans elektrokimia (EIS) dan pembelahan sinar-X (XRD). Filem nipis elektrolit biopolimer plastik dengan 20% berat gliserol mempunyai

kawasan amorf tertinggi, menghasilkan kekonduktifan ionik tertinggi sebanyak 4.32×10^{-4} S cm⁻¹. Keputusan ini disahkan oleh analisis XRD dan EIS. Elektrolit biopolimer plastik agarose/NaNO₃-gliseral boleh digunakan dalam bateri ion sodium.

Kata kunci: biopolimer, ion natrium, elektrik, struktur, teknologi hijau, indeks plastikiser

Introduction

Gasoline or petrol has become the primary source of vehicles for centuries. However, this source is a type of non-renewable energy and badly impacts the environment and humans across from Sustainable Development Goals (SDGs). To overcome these problems, people started to look for electric vehicles (EVs), which use lithium-ion batteries to generate electricity and replace conventional petroleum-based materials in vehicles. However, lithium-ion batteries (LIBs) have several disadvantages compared to sodium-ion batteries (SIBs), which gain more attention as technological advancements could achieve similar performance. SIBs have similar operations mechanical like LIBs; and they have the potential to offer greater advantages in terms of electrical efficiency, conductivity, safety, and cost of production [1]. With all the benefits of using SIBs, it is convincing to make a revolution in the materials of electrolytes. SIBs are non-flammable due to the ultrathin protective layer that forms on the anode, making SIBs have longer-lasting batteries [2]. Long-lasting batteries will produce less waste and positively impact the environment. SIBs can provide longer run time even with the same size as lithium-ion batteries (LIBs) due to the ultrathin layer of protective layer that forms on the anode [3].

Sodium Nitrate (NaNO₃) based plasticized polymer electrolytes are strong electrolytes and more reactive because they almost dissociate into Na⁺ and NO⁻³, which will produce high ionic conductivity to perform high efficiency in batteries. For plasticized polymer electrolytes, agarose is the most suitable host polymer, which can form a stable gel and thick film that is mechanically strong [4,5]. However, the main problem with agarose-based electrolytes is that they tend to have relatively low ionic conductivity (10^{-8} S·cm⁻¹) due to their low segmental motion, chemical structure, high crystallinity, and low amorphous region [6]. The low segmental motion is due to high crystallinity in agarose-based electrolytes that will affect ion diffusion and

mobility in agarose as a polymer host, which leads to low ionic conductivity [7].

Recent studies have indicated that plasticizing biopolymer electrolyte systems is a common approach to address the problem of low ionic conductivity issues [8-11]. Since the early 1800s, plasticizers have been extensively employed to enhance polymers. Plasticizers are relatively inert and have a low molecular weight. They influence viscosity, dielectric constant, dissociation rate, and the interaction with ions and functional groups within the polymer. Furthermore, they expand intermolecular spaces and reduce polymer polarity. Consequently, plasticizers enhance a material's mechanical and chemical durability, texture, and flexibility [10-13]. Various plasticizers, including glycerol [12,14], PEG [13, 15, 16], Succinonitrile [17, 18], and EC [19,20] were commonly employed to enhance the properties of the polymer. Apart of these plasticizers, glycerol signifies out due to its high dielectric constant. It has the ability to decrease internal hydrogen bonds and increase the distance between positively and negatively charged particles. This promotes the flow of ions and the separation of salts. Glycerol also improves the interfacial characteristics between the electrode and electrolyte, which is crucial for applications in energy storage devices [21, 22]. Therefore, adding an additive glycerol plasticizer to the agarose-based electrolytes can improve and boost the ionic conductivity of agarose-based electrolytes by promoting segmental motion. It will allow ions to flow and move freely to transport electrons in the biopolymer electrolytes because it increases the amorphous region.

In this study, a biopolymer electrolyte with high ionic conductivity and mobility was created by mixing agarose/NaNO₃ with glycerol as a plasticizer using a solution casting technique. EIS and XRD analysis are performed to investigate the effect of glycerol on the electrical and structural properties of agarose/NaNO₃ biopolymer electrolyte with concentrations ranging from 0% to 40% wt.% of glycerol.

Materials and Methods

Material

Agarose, NaNO_3 , glycerol, and dimethyl sulfoxide (DMSO) were purchased from Aldrich and used without further purification.

Method

Plasticizer agarose-based gel biopolymer electrolyte was prepared by using a solution casting technique by mixing agarose/ NaNO_3 with glycerol. 0.6250 g of agarose and NaNO_3 was dissolved in 20 mL of dimethyl sulfoxide (DMSO) solvent to form a solution. Subsequently, glycerol was introduced into the agarose/ NaNO_3 solution at various concentrations ranging from 0 wt.% to 40 wt.%. The glycerol concentrations examined were limited to a range of 0 wt.% to 40 wt.% due to the instability of the sample beyond 40 wt.%. The solution was continuously stirred for several hours at room temperature (300K) using a magnetic stirrer until a homogenous solution formed. After that, the samples were left until dry in an oven and formed a thin layer of GPE. To ensure full elimination of moisture from the samples, further drying was carried out by placing them in a desiccator containing silica gel. The plasticized thin films of different concentrations of glycerol are shown in Figure 1.

The thin film of plasticized agarose/ NaNO_3 -glycerol was subjected to EIS and XRD analysis to investigate the structural and electrical properties. The electric conductivity and electrical properties of GPEs will be determined by using this EIS spectroscopy. This technique uses HIOKI 3532-50 LCR Hi tester with different frequency ranges between 100 Hz to 1 MHz from room temperature 303K to 363K. XRD analysis was used to determine the structure of plasticized agarose/ NaNO_3 -glycerol films which were either crystalline or amorphous for various concentrations of glycerol. XRD pattern and behavior were observed with the existence of wave peaks of electromagnetic radiation. The observation was done in XRD at room

temperature, 300K with operating voltage and current of 40 kV and 40 mA respectively. The sample was scanned using a monochromatic beam with X-radiation wavelength $\lambda = 1.5406 \text{ \AA}$ with angle ranges of $5^\circ \leq 2\theta \leq 80^\circ$.

Results and Discussion

Ionic conductivity at room temperature

Figure 2 shows the impedance plot for plasticized agarose/ NaNO_3 -glycerol biopolymer electrolyte with different concentrations of glycerol, those 0 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.% and 40 wt.% at room temperature. From the plot, the horizontal axis or x-axis indicates real impedance, Z_r and vertical axis or y-axis indicate imaginary impedance. The plot of Z_r against Z_i can be used to estimate bulk resistance, R_b of the electrolytes, which express the total resistance of plasticized polymer electrolytes across the electric circuit under AC over a range of frequencies. The R_b of the electrolytes can be determined manually using a graphical method for the impedance plot with a nearly perfect semicircle by locating the crossing point or from the spike intercept of the semicircle and the x-axis at the low-frequency zone at an angle less than 90 degrees. Based on the results shown in Figure 2, as the weight percentage increases from 0 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.%, and 40 wt.% the value of R_b becomes decreased but when the weight percentage at 35 wt.% and 40 wt.% the R_b value becomes increased. The value of the R_b , for each sample at different weight percentages was obtained by locating the value on the Z_r axis where the semicircular converges with the spike. Figure 4.1 shows that the value of the R_b , decreases as the weight percentage of the samples increases from 0 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.%, and 40 wt.% The value of R_b , then rises and undergoes constant as the sample weight percentage rises from 35 wt.% to 40 wt.%.

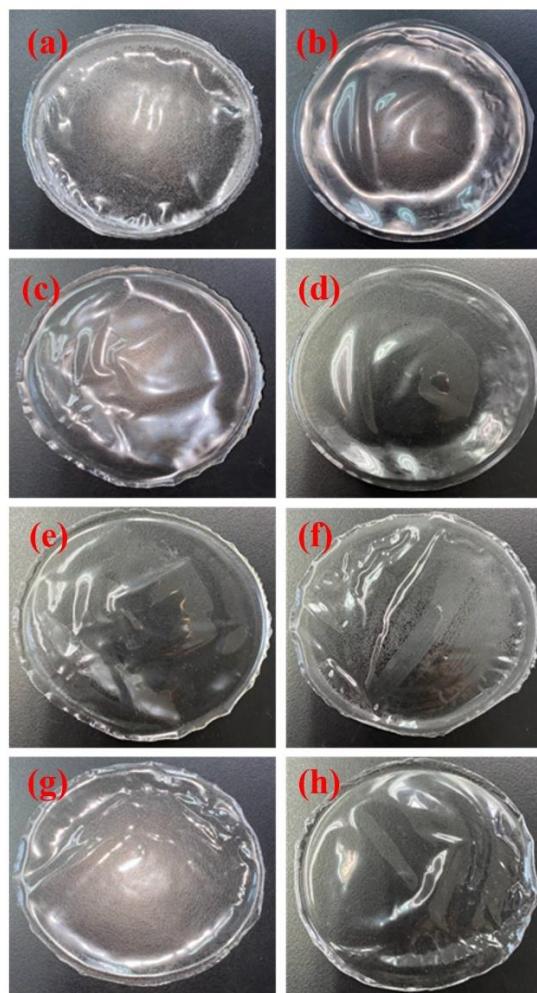


Figure 1. The thin film of plasticized agarose/NaNO₃-glycerol biopolymer electrolyte with (a) 0 wt.%, (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.%, (e) 25 wt.%, (f) 30 wt.%, (g) 35 wt.%, (h) 40 wt.% of glycerol

Figure 3 and Table 1 show the bulk R_b and ionic conductivity (σ) of plasticized agarose/NaNO₃-glycerol in different weight percentages of glycerol at room temperature. The ionic conductivity of the plasticized agarose/NaNO₃-glycerol biopolymer electrolyte was determined by using the following equation:

$$\sigma = \frac{t}{R_b \cdot A} \quad (1)$$

where σ is the ionic conductivity in Scm⁻¹, t is for the distance of the electrode-electrolyte interface, R_b is the bulk resistance which obtained from impedance plots and A is the surface area of the electrode-electrolyte. The ionic conductivity of the plasticized

agarose/NaNO₃-glycerol electrolyte film at 0 wt.% glycerol is 6.79×10^{-5} Scm⁻¹. The ionic conductivity increases to 8.52×10^{-5} Scm⁻¹ with the addition of 10 wt.% and continues increasing until it reaches 4.32×10^{-4} Scm⁻¹ at 20 wt.% of glycerol and inaugurates to become the highest ionic conductivity of an agarose/NaNO₃-glycerol before the ionic conductivity slightly decreases. It shows that the highest ionic conductivity of agarose sodium-nitrate with 20 wt.% of glycerol has the smallest R_b value obtained at room temperature. The conductivity of plasticized biopolymer electrolytes based on agarose sodium-nitrate (20 wt.%) is marginally greater than that of other biopolymer electrolytes, such as CS/PVA/NaI-glycerol [23] and

CH/PVA/NaOAc-glycerol [12], respectively. However, the ionic conductivity of agarose/NaNO₃-glycerol begins to decrease to 2.42×10^{-4} Scm⁻¹ when the weight percentage is 25 wt.% and continues falling until the

weight percentage reaches 40 wt.% and the value of R_b becomes bigger as the ionic conductivity started to decrease.

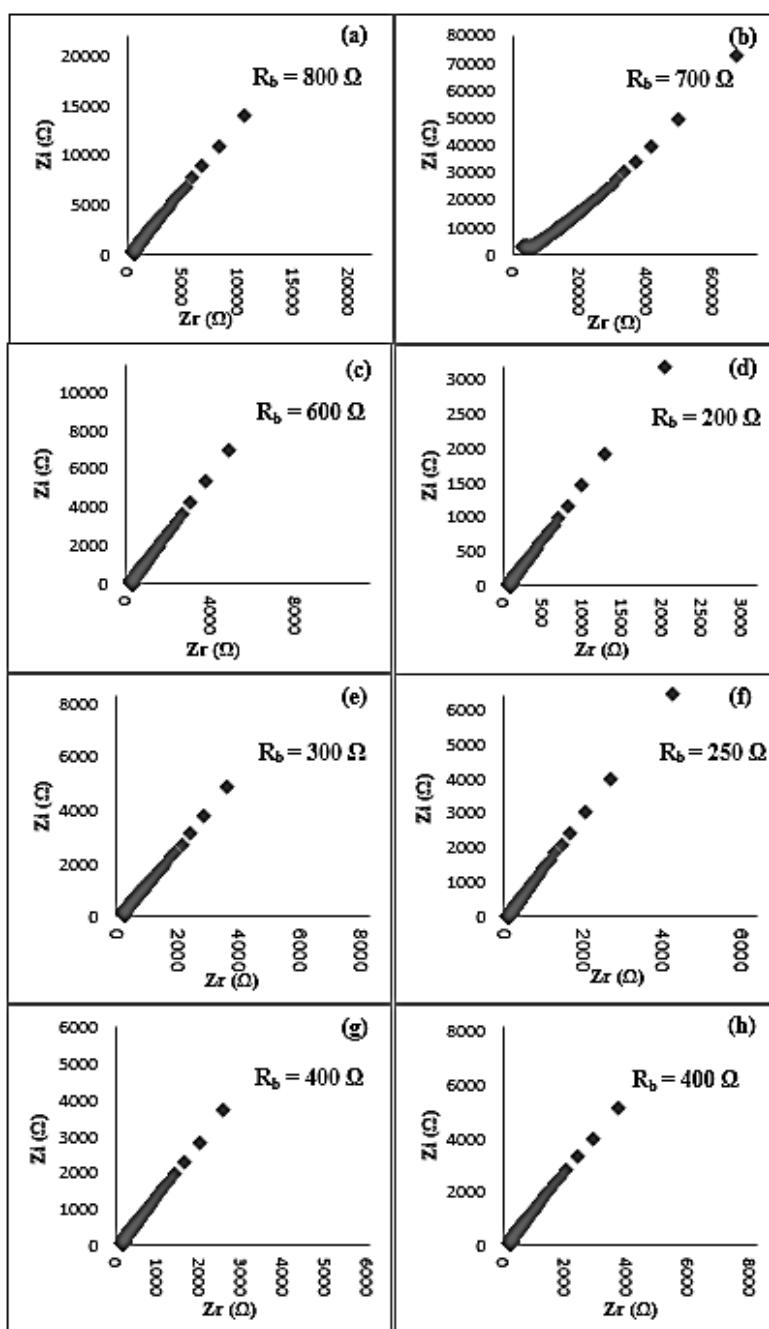


Figure 2. Impedance plot for (a) pure agarose-sodium nitrate with 0 wt.%, (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.%, (e) 25 wt.%. (f) 30 wt.%, (g) 35 wt.%, (h) 40 wt.% of glycerol

The increased conductivity of agarose/NaNO₃-glycerol with increased glycerol weight percentage is due to the glycerol molecules in the agarose/NaNO₃-glycerol sample escalated. These molecules break down more into sodium and nitrate ions, thus increasing the charge carrier concentration which makes it more available for ion transportation. Moreover, the segmental mobility is increased due to the glycerol that has a high polar molecule that will effectively promote the segmental mobility of the chains in the plasticized agarose/NaNO₃-glycerol polymer electrolytes which will allow more ion movement through the polymer matrix that will enhance the ion transportation. The increased ionic conductivity of plasticized polymer electrolytes from 0 wt.% to 20 wt.% is also affected by the increasing weight percentage and concentration of the glycerol which will reduce and disturb the polymer structure of crystallinity in the samples. It will cause the sample to become more amorphous and less ordered. Thus, it will promote ion diffusion due to the matrix structure of the samples [24].

The increase of glycerol concentration will also promote greater percolation of charge due to the increment of the amorphous region in polymer electrolytes, the presence

of molecule disorder, and the removal of the long-range order that will allow ions to move more freely through the sample. This improved ion mobility and promoted charge percolation by allowing ions to move through and effectively transfer charge. Nonetheless, excessive concentration of glycerol in plasticized agarose/NaNO₃-glycerol at 25 wt.%, 30 wt.%, 35 wt.% and 40 wt.% increased the concentration that can impede the ion mobility which can make it more challenging for ions to penetrate in diffuse from one molecule to another and reduce the charge transfer. Besides, the excessive amount of glycerol will cause substantial swelling of polymer electrolytes due to high water affinity in glycerol which will result in interfacial contact between the electrolyte and electrodes that will lower charge transfer [25-27]. The electrode-electrolyte interface issues will occur leading to an increase in the interfacial resistance and hindering the formation of a stable and well-defined interphase between the electrolyte and the electrodes. Thus, it has impacted the ions flow and mobility of charge carriers which result in the value of R_b and ionic conductivity of the samples becoming smaller and reduced.

Table 1. Bulk resistance and ionic conductivity at room temperature for the plasticized agarose/NaNO₃-(wt.%) glycerol biopolymer electrolyte thin film prepared

Concentration of Glycerol (wt.%)	Thickness, t (cm)	Bulk resistance, R _b (Ω)	Ionic conductivity, σ (S·cm ⁻¹)
0	0.015	7.67×10^2	6.79×10^{-5}
10	0.018	7.33×10^2	8.52×10^{-5}
15	0.018	6.00×10^2	1.04×10^{-4}
20	0.025	2.00×10^2	4.32×10^{-4}
25	0.021	3.00×10^2	2.42×10^{-4}
30	0.017	2.67×10^2	2.22×10^{-4}
35	0.025	4.30×10^2	2.02×10^{-4}
40	0.022	4.35×10^2	1.78×10^{-4}

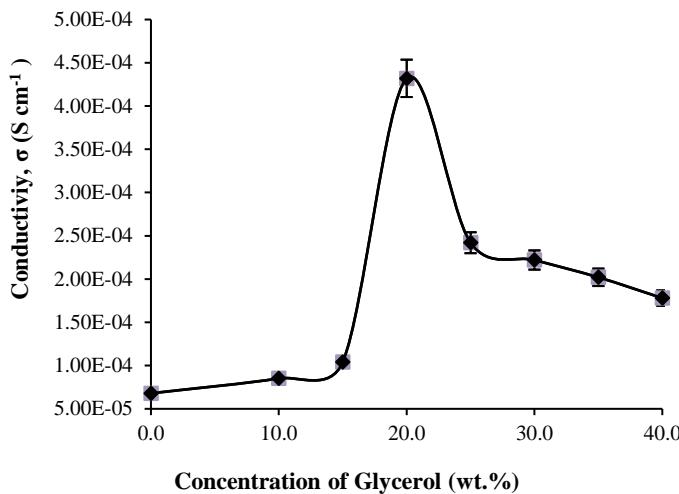


Figure 3. Plot of room temperature conductivity of plasticized agarose/NaNO₃-glycerol biopolymer electrolytes at different concentrations of wt.% of glycerol

Temperature dependence conductivity

Figure 4 shows the natural logarithm of ionic conductivity ($\log \sigma$) as a function of reciprocal temperature ($1000/T$) for 10 wt.% and 20 wt.% of glycerol. The natural logarithm of ionic conductivity ($\log \sigma$) as a function of reciprocal temperature ($1000/T$) can be described by the Arrhenius equation below, which relates the ionic conductivity and temperature.

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}} \quad (2)$$

where $\log \sigma$ is the natural logarithm of the ionic conductivity, σ_0 represents the pre-exponential factor or the conductivity at infinite temperature, E_a is the activation energy for ions transportation (eV), k is the Boltzmann constant of $1.380649 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ and T is the absolute temperature. In the studies of the Arrhenius relationship, it is important to note that the value of electrical conductivity is directly proportional to temperature when the ionic conductivity value increases

with the increase in temperature. The increase in conductivity with temperature can be explained as a hopping process between coordinating sites, local structural relaxations, and polymer electrolyte segmental movements. Ionic transportation is influenced by the activation energy or energy barrier that needs to be overcome by ions to diffuse through the electrolyte.

Table 2 indicates the value of E_a that has been calculated by using the following equation. Based on the studies by Vignarooban et al. [28] plasticized polymer electrolyte indicates Arrhenius's behavior of ionic conductivity with inverse temperature. The rise in conductivity with temperature is thought to be caused by the polymer matrix expanding, resulting in an increase in free volume. The greater free volume will enhance the polymer segment and ionic species mobility, resulting in better conductivity. The thin film of 20 wt.% of glycerol has the lowest E_a .

Table 2. The value of EA for plasticized agarose/NaNO₃-glycerol biopolymer electrolytes thin

Weigh Percentage (wt.%)	Conductivity, σ ($\text{S}\cdot\text{cm}^{-1}$)	Activation energy, E_a (eV·K ⁻¹)
10	8.52×10^{-5}	0.6842
20	4.32×10^{-4}	0.3394

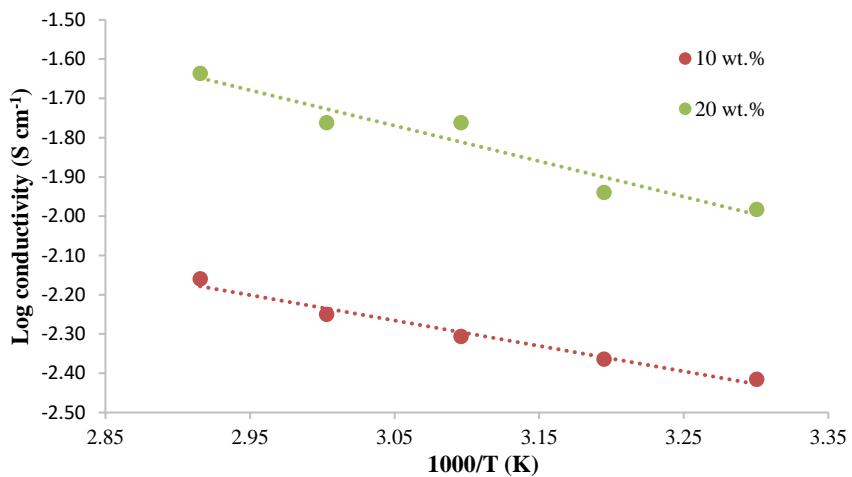


Figure 4. The natural logarithm of ionic conductivity ($\log \sigma$) as a function of reciprocal temperature ($1000/T$) for 10 wt.% and 20 wt.% of glycerol in agarose/NaNO₃-glycerol

Dielectric studies

Figure 5 (a) and (b) shows the dielectric constant and dielectric loss of plasticized agarose/NaNO₃-glycerol with 20 wt.% of glycerol at different temperatures have been calculated using:

$$\varepsilon_r = \frac{z_i}{\omega c_0(z_r^2 + z_i^2)} \quad (3)$$

$$\varepsilon_i = \frac{z_r}{\omega c_0(z_r^2 + z_i^2)} \quad (4)$$

It can be observed that at low frequencies, the value of ε_r and ε_i is high and vice versa. The ε_r and ε_i have the highest conductivity at temperature 363K. While at temperature 303K, they have the lowest conductivity for ε_r and ε_i . This situation happens due to the accumulation of the charge carriers at the electrode-electrolyte interface. The accumulation happens when a current flows through a contact between two metals of different conductivities, and the charge accumulates in the

surroundings of the contact. While at high frequency, it can be observed that the value of ε_r and ε_i decrease when the frequency is high due to the high periodic reversal of the applied electric field. It also indicates low polarization effects, which cause ion mobility to arise [29]. The polarization of molecules in plasticized polymer electrolytes with 20 wt.% of glycerol will cause the separation of positive charges and negative charges that result in high energy required for ions movement from one molecule to another. Thus, it will reduce the value of ε_r and ε_i , leading to low ionic conductivity. Conversely, plasticized agarose/NaNO₃-glycerol polymer electrolytes indicate high dielectric exhibits lower ionic conductivity due to the increasing ion-polymer interaction and ion mobility restriction, decreasing the ion transfer within the materials. The higher permittivity, the more electric field resistance will result in high energy stored compared to the energy used for ionic conductivity [30].

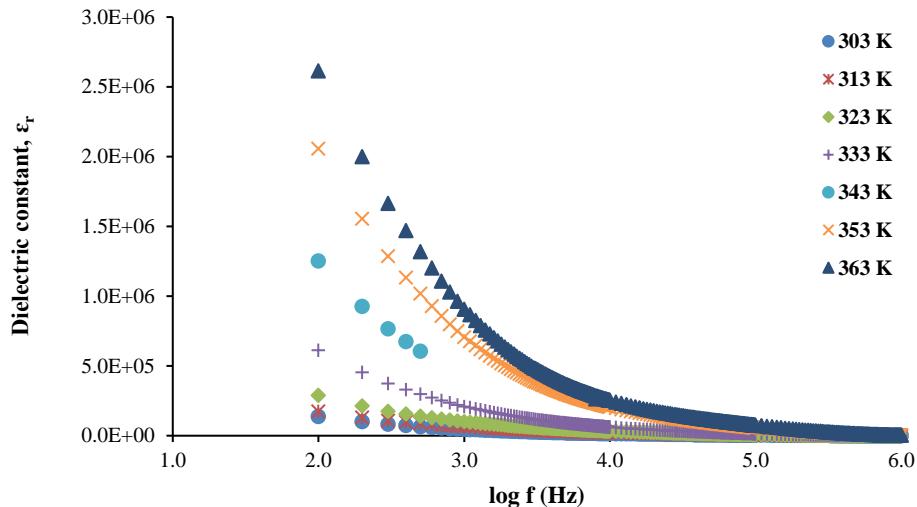


Figure 5 (a). The dielectric constant, ϵ_r of plasticized agarose/NaNO₃-glycerol with 20 wt.% of glycerol at different temperatures.

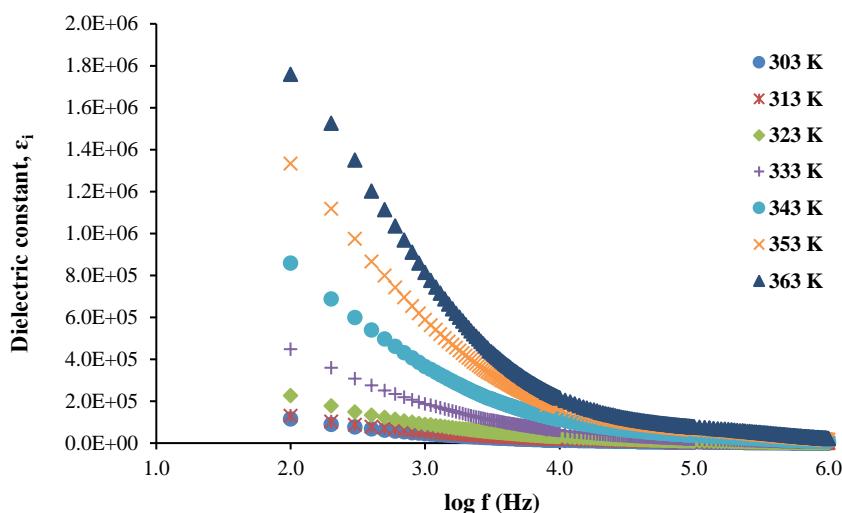


Figure 5 (b). Dielectric loss of plasticized agarose/NaNO₃-glycerol polymer electrolytes thin film with 20 wt.% of glycerol at different temperatures

Modulus studies

The dielectric behavior of plasticized agarose/NaNO₃-glycerol caused by ion relaxation has been studied using the electrical modulus which provides information on ion transportation, distinguishes electrode-polarization effects and ionic conductivity relaxation phenomenon. The charge accumulation at an electrode, which is known as electrode polarization will produce a larger permittivity. Therefore, by having the permittivity data it is possible to determine the complex electrical

modulus to study its behaviors. In this research, the electrical modulus real (M_r) and imaginary (M_i) were studied as a function of log frequency for the sample with 20 wt.% of glycerol at different temperatures. The electrical modulus can be calculated by using the following equation:

$$M_r = \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_i^2} \quad (5)$$

$$M_i = \frac{\epsilon_i}{\epsilon_i^2 + \epsilon_r^2} \quad (6)$$

Figure 6 shows the x-axis or horizontal axis that indicates the natural logarithm of frequency while the y-axis or vertical axis represents the modulus real and imaginary. It can be shown that both M_r and M_i increase approaching high frequency which is compatible with previous studies conducted by [31]. At low frequency, the value of M_r and M_i are close to zero, but it keeps increasing when the frequency increases. Furthermore,

at low temperatures, it exhibits the highest peaks of M_r and M_i . This could be described by ion mobility and polymer segments decreasing due to thermal energy that provides energy transfer to allow ions movement which is related to the law of thermodynamics. The limited ion mobility will restrict the ion movements and the potential of the polymer segments to cooperate with an applied electric field. Thus, the plasticized polymer electrolyte will indicate a higher value of electrical modulus at low temperatures that will result in low ionic conductivity and a higher value of ϵ_r .

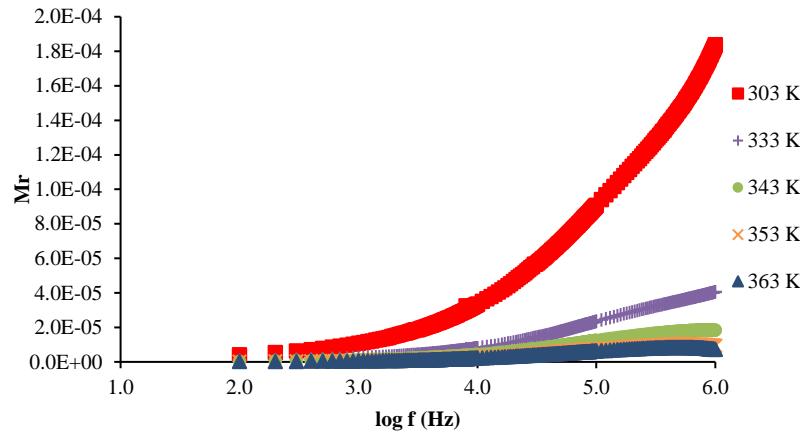


Figure 6 (a). The real Modulus, M_r of plasticized Agarose/NaNO₃-glycerol biopolymer electrolyte thin film with 20 wt.% of glycerol at various temperatures

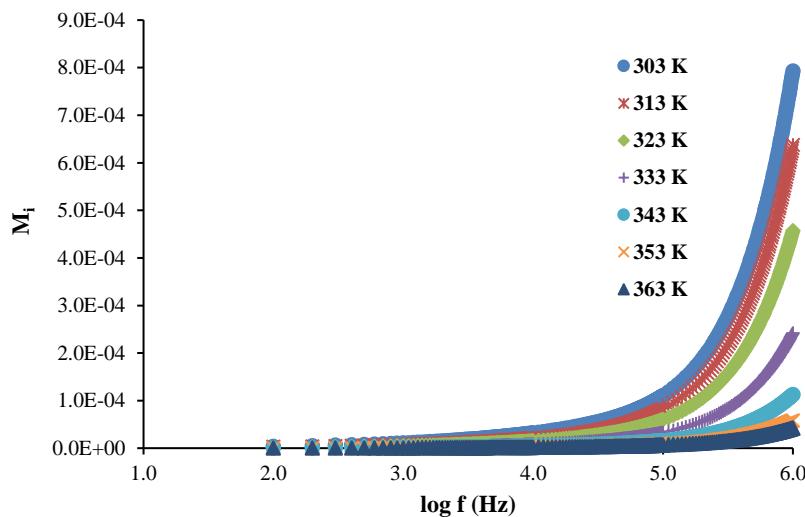


Figure 6 (b). The Imaginary Modulus, M_i of plasticized Agarose/NaNO₃-glycerol biopolymer electrolyte thin film with 20 wt.% of glycerol at various temperatures

Structural studies

XRD measurements were performed to study the crystallinity and to support the formation complexes in plasticized Agarose/NaNO₃-glycerol biopolymer electrolyte. Figure 7 shows XRD pattern for (a) 0 wt.%, (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.%, (e) 25 wt.%, (f) 30 wt.%, (g) 35 wt.% (h) 40 wt.% of glycerol in Agarose/NaNO₃. The result shows that several values of 2θ can be observed from high diffraction intensity and sharp crystalline peaks that indicate a semi-crystalline structure. When the concentration of glycerol increases, the peaks become broader as the weight percentage increases from 0 wt.% to 25 wt.%. At weight percentage 20 wt.%, the peaks become broader and low intensity is shown compared to 0 wt.%, and 25 wt.%. Peak broadening occurs because of greater disorder or smaller crystallite size in the electrolyte film. In addition, there are no further peaks in the plasticized system, indicating that the salt has completely dissociated in the polymer electrolytes and the interaction occurrence between glycerol and agarose/NaNO₃ salts. This will reduce the intermolecular interaction within glycerol polymer chains, thereby increasing the segmental motion of the plasticized polymer electrolytes decreasing crystalline phases and increasing in amorphous regions. As a result, the increase of amorphous region increases ion mobility and ion diffusion [32-34]. Hence, the plasticized polymer electrolytes sample of 20 wt.% glycerol has the highest ionic conductivity with the lowest crystallinity pattern and the lower intensity peaks. A similar observation has been reported by Abdulah et al [33]. According to their study, the addition of glycerol to the PVA:MC:NaI resulted in a decrease in peak strength and an improvement in the broadness of the peaks. This suggests that the degree of crystallinity is reduced. The results confirm the idea that the polymer electrolytes possess an irregular structure, which enhances its conductivity through the augmentation of ionic diffusivity. Adam et al. [13] found that the addition of glycerol to the MC/PC/K₃PO₄ system reduced the crystalline behavior of the polymer electrolyte. This was due to the interactions between the MC/PC host, K₃PO₄, and glycerol, which increased the movement of the

polymer electrolyte segments. Similar to Ali and Kareem [32], they reported that the polymeric chain is more flexible in the amorphous phase, resulting in an enhancement of segmental motion in the polymer and thus increased ionic conductivity. Furthermore, they reported that the orderly structure and crystalline phase of PVA/CuSO₄ fully was transformed to amorphous after adding glycerol. The transformation could be due to salt and plasticizer dissolution disrupting the polymer's semicrystalline structure and decreasing the intermolecular interaction among the polymer chains.

Conclusion

The effect of glycerol on the electrical and structural properties of plasticized Agarose/NaNO₃-glycerol biopolymer electrolyte was investigated. The enhancement of the ionic conductivity with the increase of glycerol concentration was due to the improvement of ion mobility and ion diffusion which contributes to ion dissociation and polarization at the electrode-electrolyte interface. Hence it increases the ionic conductivity of the plasticized Agarose/NaNO₃-glycerol biopolymer electrolytes. Furthermore, the film with the broadest peak and low intensity had the lowest crystallinity structure and was more amorphous. Plasticized Agarose/NaNO₃-glycerol polymer electrolytes thin film with 20 wt.% of glycerol had the highest ionic conductivity of 4.32×10^{-4} Scm⁻¹ and the lowest crystallinity structure indicating that this plasticized electrolyte has the potential to be used as electrolytes in sodium ion battery.

Acknowledgement

The authors appreciatively acknowledge the financial support for this work by the Fundamental Research Grant Scheme (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.

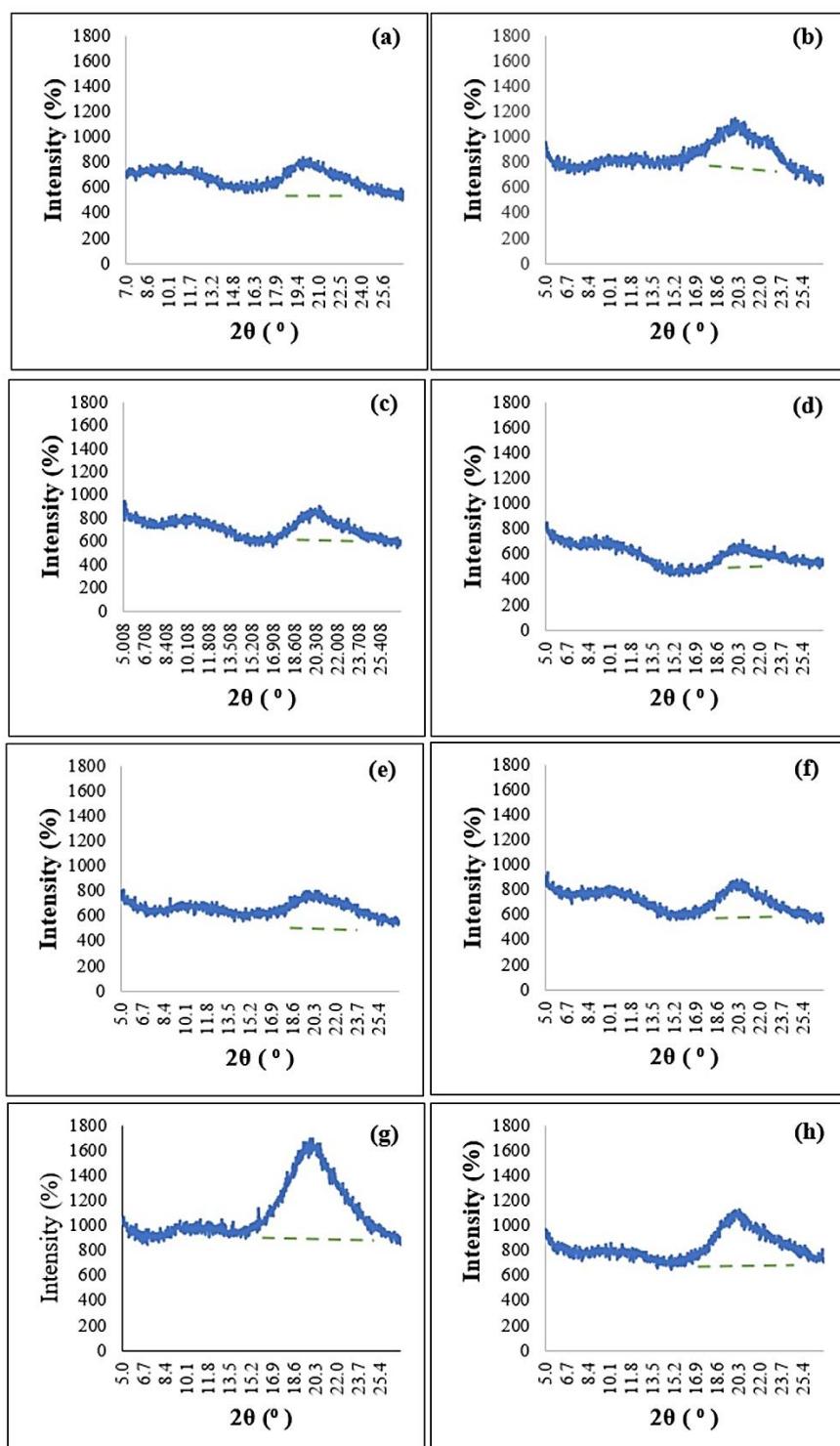


Figure 7. XRD pattern of (a) 0 wt.%, (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.%, (e) 25 wt.%, (f) 30 wt.%, (g) 35 wt.% (h) 40 wt.% of glycerol in plasticized Agarose/NaNO₃ polymer electrolyte thin film

References

- El Kharbachi, A., Zavorotynska, O., Latroche, M., Cuevas, F., Yartys, V., and Fichtner, M. (2020). Exploits, advances and challenges benefiting beyond Li-ion battery technologies. *Journal of Alloys and Compounds*, 817: 153261.
- Ni, Q., Yang, Y., Du, H., Deng, H., Lin, J., Lin, L., Yuan, M., Sun, Z., and Sun, G. (2022). Anode-free rechargeable sodium-metal batteries. *Batteries*, 8(12): 272.
- Jin, Y., Le, P. M., Gao, P., Xu, Y., Xiao, B., Engelhard, M. H., Cao, X., Vo, T. D., Hu, J., and Zhong, L. (2022). Low-solvation electrolytes for high-voltage sodium-ion batteries. *Nature Energy*, 7(8): 718-725.
- Ali, N. I., Abidin, S. Z. Z., and Majid, S. R. (2024). The high-performance polymer electrolytes based on Agarose–Mg (ClO₄)₂ for application in electrochemical energy storage devices. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 118(1): 65-85.
- Hussain, N. F. S., Abidin, S. Z. Z., Shaharuddin, N. A. A., Syarizzad, R. Q. A., and Rudhzhiah, S. (2024). Ionic transport and structural analysis of biopolymer electrolyte based on agarose integrated with sodium nitrate. *Malaysian Journal of Analytical Sciences*, 28(1): 236-246.
- Selvalakshmi, S., Vijaya, N., Selvasekarapandian, S., and Premalatha, M. (2017). Biopolymer agar-agar doped with NH₄SCN as solid polymer electrolyte for electrochemical cell application. *Journal of Applied Polymer Science*, 134(15): 44702.
- Elmanzalawy, M., Sanchez-Ahijón, E., Kisacik, O., Carretero-González, J., and Castillo-Martínez, E. (2022). High conductivity in a fluorine-free K-ion polymer electrolyte. *ACS Applied Energy Materials*, 5(7): 9009-9019.
- Hadi, J. M., Aziz, S. B., Abdulwahid, R. T., Brza, M. A., Tahir, H. B., Hamad, S. M., Shamsuri, N., Woo, H., Alias, Y., and Hamsan, M. (2024). Characterizing sodium-conducting biopolymer blend electrolytes with glycerol plasticizer for EDLC application. *Ionics*, 30(4): 2409-2423.
- Helen, P. A., Selvin, P. C., and Sakthivel, P. (2024). Quasi-solid-state plasticized chitosan biopolymer electrolyte with enhanced Mg²⁺ ion mobility for next-generation Mg ion battery. *Journal of Solid State Electrochemistry*, 28: 3147-3161.
- Shamsuri, N., Majid, S., Hamsan, M., Halim, S., Manan, N., Sulaiman, M., Jahidin, A., Halim, N., Aziz, S., and Kadir, M. (2024). Enhancing ionic conductivity and flexibility in solid polymer electrolytes with rainforest honey as a green plasticizer. *Journal of Applied Polymer Science*, 141(18): e55303.
- Maithilee, K., Sathya, P., Selvasekarapandian, S., Chitra, R., and Meyvel, S. (2023). Investigation on tamarind seed polysaccharide biopolymer electrolyte doped with sodium nitrite and EC plasticizer for primary sodium battery. *Bulletin of Materials Science*, 46(3): 114.
- Adam, A. A., Soleimani, H., Dennis, J. O., Aldaghri, O. A., Alsadig, A., Ibnaouf, K. H., Abubakar Abdulkadir, B., Wadi, I. A., Cyriac, V., and Shukur, M. F. B. A. (2023). Insight into the effect of glycerol on dielectric relaxation and transport properties of potassium-ion-conducting solid biopolymer electrolytes for application in solid-state electrochemical double-layer capacitor. *Molecules*, 28(8): 3461.
- Lai, W.-C., Liu, L.-J., and Tseng, S.-J. (2024). Green polymer electrolytes prepared by a cost-effective approach. *Langmuir*, 40(31): 16492-16501.
- Aziz, S. B., Hamsan, M. H., Abdulwahid, R. T., Halim, N. A., Hassan, J., Abdulrahman, A. F., Al-Saeedi, S. I., Hadi, J. M., Kadir, M. F., and Hamad, S. M. (2024). Green polymer electrolyte and activated charcoal-based supercapacitor for energy harvesting application: Electrochemical characteristics. *Green Processing and Synthesis*, 13(1): 20230109.
- Mohammed, M., and El-Sayed, F. (2023). PEG's impact as a plasticizer on the PVA polymer's structural, thermal, mechanical, optical, and dielectric characteristics. *Optical and Quantum Electronics*, 55(13): 1141.
- Abdullah, O. G., Ahmed, H. T., Tahir, D. A., Jamal, G. M., and Mohamad, A. H. (2021). Influence of PEG plasticizer content on the proton-conducting

PEO: MC-NH4I blend polymer electrolytes based films. *Results in Physics*, 23: 104073.

17. Wang, L., He, Y., and Xin, H. L. (2023). Transition from Vogel-Fulcher-Tammann to Arrhenius ion-conducting behavior in poly (ethyl acrylate)-based solid polymer electrolytes via succinonitrile plasticizer addition. *Journal of The Electrochemical Society*, 170(9): 090525.

18. Lu, T., Zhou, Y., Zeng, X., Hao, S., and Wei, Q. (2024). Study of the ion transport properties of succinonitrile plasticized poly (vinylidene fluoride)-based solid polymer electrolytes. *Materials Letters*, 360: 135912.

19. Yalla, M. R., Jeedi, V. R., Shashi Devi, S., Narender Reddy, S., and Sadananda Chary, A. (2023). Impact of EC-plasticizer on electrical and dielectrical properties of PEO/PVdF/NaNO₃ solid polymer electrolyte systems. *Bulletin of Materials Science*, 46(3): 167.

20. Singh, P., Sachdeva, A., Bhargava, C., Alheety, M. A., and Sharma, J. (2023). Electrical and Structural Properties of PEMA-Based Plasticized Polymer Electrolyte. *Macromolecular Symposia*, 407(1): 2200107.

21. Abdulwahid, R. T., Aziz, S. B., and Kadir, M. F. (2023). Replacing synthetic polymer electrolytes in energy storage with flexible biodegradable alternatives: sustainable green biopolymer blend electrolyte for supercapacitor device. *Materials Today Sustainability*, 23: 100472.

22. Ibrahim, S., Yasin, S. M. M., Nee, N. M., Ahmad, R., and Johan, M. R. (2012). Conductivity and dielectric behaviour of PEO-based solid nanocomposite polymer electrolytes. *Solid state communications*, 152(5): 426-434.

23. Brza, M. A., and Aziz, S. B. (2024). The study of ion transport parameters using two models in plasticized sodium ion conducting polymer blend electrolytes. *Polymer Bulletin*, 81(4): 3021-3042.

24. Ahad, N., Saion, E., and Gharibshahi, E. (2012). Structural, thermal, and electrical properties of PVA-sodium salicylate solid composite polymer electrolyte. *Journal of Nanomaterials*, 2012(1): 857569.

25. Chen, M., Zhou, W., Wang, A., Huang, A., Chen, J., Xu, J., and Wong, C.-P. (2020). Anti-freezing flexible aqueous Zn-MnO₂ batteries working at-35 C enabled by a borax-crosslinked polyvinyl alcohol/glycerol gel electrolyte. *Journal of Materials Chemistry A*, 8(14): 6828-6841.

26. Wong, C. Y., Wong, W. Y., Loh, K. S., Daud, W. R. W., Lim, K. L., Khalid, M., and Walvekar, R. (2020). Development of poly (vinyl alcohol)-based polymers as proton exchange membranes and challenges in fuel cell application: a review. *Polymer Reviews*, 60(1): 171-202.

27. Musa, M. T., Shaari, N., Kamarudin, S. K., and Wong, W. Y. (2022). Recent biopolymers used for membrane fuel cells: Characterization analysis perspectives. *International Journal of Energy Research*, 46(12): 16178-16207.

28. Vignarooban, K., Badami, P., Dissanayake, M., Ravirajan, P., and Kannan, A. M. (2017). Polyacrylonitrile-based gel-polymer electrolytes for sodium-ion batteries. *Ionics*, 23: 2817-2822.

29. Psarras, G. (2018). Fundamentals of dielectric theories. In *dielectric polymer materials for high-density energy storage* (pp. 11-57). Elsevier.

30. Zha, J.-W., Zheng, M.-S., Fan, B.-H., and Dang, Z.-M. (2021). Polymer-based dielectrics with high permittivity for electric energy storage: A review. *Nano Energy*, 89: 106438.

31. Kumar, D., Gohel, K., Kanchan, D., and Mishra, K. (2020). Dielectrics and battery studies on flexible nanocomposite gel polymer electrolyte membranes for sodium batteries. *Journal of Materials Science: Materials in Electronics*, 31:13249-13260.

32. Ali, N., and Kareem, A. (2022). Ionic conductivity enhancement for PVA/20wt.% CuSO₄ gel polymer electrolyte by using glycerin. *Chalcogenide Letters*, 19(3): 217-225.

33. Abdullah, A. M., Aziz, S. B., Brza, M., Saeed, S. R., Al-Asbahi, B. A., Sadiq, N. M., Ahmed, A. A. A., and Murad, A. R. (2022). Glycerol as an efficient plasticizer to increase the DC conductivity and improve the ion transport parameters in biopolymer-based electrolytes: XRD, FTIR and EIS studies. *Arabian Journal of Chemistry*, 15(6): 103791.

34. Bhargav, P. B., Mohan, V. M., Sharma, A., and Rao, V. N. (2007). Structural, electrical and optical characterization of pure and doped poly (vinyl

alcohol)(PVA) polymer electrolyte films.
International Journal of Polymeric Materials,
56(6): 579-591.