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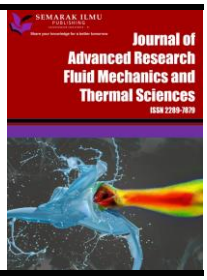

# Ionic Conductivity Studies on Proton Conducting Solid Biopolymer Electrolyte based on 2-Hydroxyethyl Cellulose (2HEC) Doped with Ammonium Chloride ($NH_4CL$)

Amzar Arif Mejenom[1], Muthiah Muthuvinayagam[2], Mohd Ikmar Nizam Mohamad Isa[1,3,*]

[1] Energy Materials Consortium, Advanced Materials Team, Ionic & Kinetic Materials Research Laboratory (IKMaR), Faculty of Science & Technology, Universiti Sains Islam Malaysia, 71800 Nilai, Negeri Sembilan Darul Khusus, Malaysia
[2] Department of Physics, Saveetha School of Engineering, Saveetha University (SIMATS), Chennai, India
[3] Advanced Nano Materials, Advanced Materials team, Ionic State Analysis (ISA) Laboratory, Faculty of Science & Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu Darul Iman, Malaysia

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**ABSTRACT**

Solution casting techniques have been used to create a solid biopolymer electrolyte (SBEs) based on 2-hydroxyethyl cellulose (2HEC) doped with varying amounts of ammonium chloride ($NH_4Cl$) to investigate the potential of $NH_4Cl$ in enhancing the ionic conductivity of SBE. Electrical impedance spectroscopy (EIS) was used to measure the impedance of the electrolytes between 50 Hz and 1 MHz in frequency. At room temperature, ionic conductivity was at its highest for 16% weight percent of $NH_4Cl$ which was $1.74 \times 10^{-3}$ $Scm^{-1}$. The temperature dependence data of 2HEC-$NH_4Cl$ SBEs abides Arrhenius behaviour. Complex electrical modulus and complex permittivity were used to assess the dielectric data for the sample at various temperatures.

## 1. Introduction

Construction, pharmaceuticals, packaging and food processing are just a few of the industries that have benefited from the use of polymer materials, particularly natural polymers [1-8]. Environmentally friendly electronic components are more in demand as technology develops, helping to reduce e-waste. In order to solve the issue and improve the efficiency of the new power sources for electrochemical devices, new electrolytes should be produced [9-12]. This has caused numerous studies to concentrate on solid biopolymer electrolytes (SBEs) [13-15].

Numerous studies have shown that SBEs have good potential in electrochemical devices (as a solid electrolyte component) such as solar cells, batteries, fuel cells, and supercapacitors [16-19]. They also have outstanding mechanical stability, are simple to make, and have zero leakage features, which are necessary characteristics in any system of electrolyes [20]. A variety of natural polymers, such as chitosan, cellulose derivatives, agar, and starch, were investigated for use in various

* *Corresponding author.*
*E-mail address: ikmar_isa@usim.edu.my*

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applications [21-26]. Despite being more prevalent, secure, and affordable than synthetic polymers, natural polymers often have low ionic conductivities at ambient temperature, which limits their potential for use in electrochemical devices [4,11,27,28]. Natural polymers frequently have issues with their relatively low ionic conductivity, which is unsuitable for electrochemical applications where the lowest value ranges from $10^{-11}$ to $10^{-7}$ S $cm^{-1}$.

Researchers also looked for ways to improve them because of their properties and their low conductivity at room temperature. This issue can be resolved by doping the polymer host system with the appropriate proton donor material. Proton donors contribute to a rise in the quantity of free, mobile ions that cause ionic conduction, improving the host polymer's overall ionic conductivity. In addition to adding proton donors, other ways to improve the host polymer include polymer blending, adding organic/inorganic compounds, and adding ionic liquids [29]. However, using a doped proton donor is the simplest and least expensive way [4]. Additionally, according to Ramlli *et al.,* [4] and Hafiza and Isa [30], the addition of ammonium nitrate and ammonium thiocyanate considerably enhanced the ionic conductivity of pure 2HEC when using the proton donor doping approach. Ammonium salts are commonly used as proton donor materials as the loosely bound proton ($H^+$) in ammonium has a tendency to move to the polymer host system in studies of solid biopolymer electrolytes. However, not all ammonium salts yield excellent results since certain of their characteristics can alter how they interact with the polymer host. High ion dissociation into the polymer host is provided by low-lattice-energy ammonium salts and substantial anionic groupings, which can aid in improving ionic conductivity [31].

In this study, the polymer of interest is 2-hydroxyethyl cellulose (2HEC). One of the best qualities of this cellulose derivative is its great water solubility, which makes it a suitable thickening and stabilizing agent. As an adhesion promoter, organic thickener, and among many other uses in the pharmaceutical industry, food industry, and manufacturing sector [2,32]. According to Ramlli *et al.,* [33], 2-HEC has also been used in the manufacture of electrodes for use in batteries, where it served as the binder material. Due to these benefits, 2HEC has emerged as a top contender for SBE development for electrochemical applications. Additionally, there aren't many publications on its potential to function as an SBE, so now is the ideal time for our work to add to the corpus of information.

Since ammonium chloride ($NH_4Cl$) has a low lattice energy of just 705 kJ mol-1, which may aid in the dissociation of mobile ions, it was chosen as a proton donor. Regarding the research of ionic conductance, temperature reliance and activation energy, dielectric permittivity, modulus research of the novel SBEs, this work concentrated on the impact of various $NH_4Cl$ concentrations on 2HEC. Electrochemical Impedance Spectroscopy (EIS) at room temperature was used for all tests after the samples were manufactured using a straightforward solution casting procedure.

## 2. Methodology

### *2.1 SBE Preparation*

Using the solution casting approach, 2.0 g of 2-Hydroxyethyl Cellulose, or 2HEC (Sigma-Aldrich Inc., 99.0% purity), was dissolved in distilled water to create a thin sheet-like of solid biopolymer electrolyte. After that, different concentrations of ammonium chloride, or $NH_4Cl$, from Sigma Aldrich were added to the 2HEC solution and stirred together until the mixture was homogeneous (Table 1). After complete dissolution, the mixture was put in a petri dish and heated for a short period of time in an oven set at a constant temperature of 50°C. After that, the films were put in a desiccator filled with silica gel to finish drying.

**Table 1**
Designation and weight percentage $NH_4Cl$ salt for SBE samples

| Sample | 2HEC (g) | $NH_4Cl$ (wt%) | $NH_4Cl$ Weight (g) |
|---|---|---|---|
| 2HECAC0 | 2 | 0 | 0.0000 |
| 2HECAC4 | 2 | 4 | 0.0833 |
| 2HECAC8 | 2 | 8 | 0.1739 |
| 2HECAC12 | 2 | 12 | 0.2727 |
| 2HECAC16 | 2 | 16 | 0.3809 |
| 2HECAC20 | 2 | 20 | 0.5000 |
| 2HECAC24 | 2 | 24 | 0.6315 |

### *2.2 Sample Characterization*

The ionic conductivity and electrical characteristics of the SBE films were assessed using electrochemical impedance spectroscopy (EIS) model HIOKI 3532-50 LCR Hi-Tester EIS with computer interface. The SBE film was divided into an appropriate size of 2cm x 2cm before being placed between two stainless steel electrodes that were attached to the EIS. The EIS measurement was made between 303 K and 373 K, with a 50 Hz to 1 M Hz frequency range. Eq. (1) was used to calculate the ionic conductivity of the SBE film.

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

where A is the region of surface contact of the SBE sample and electrodes and t is the thickness (mm) of the SBE film. When analysing the impedance properties of materials like solid polymer electrolytes, electrochemical impedance spectroscopy (EIS) frequently used the Cole-Cole plot, also referred to as the Nyquist plot. This graphic can be used to calculate the electrolyte's bulk resistance ($R_b$).

For instance, the semicircle seen in the Nyquist plot might be utilised to determine the bulk resistance, according to a study by Huggins [34]. The bulk resistance of the electrolyte is represented by the point at which the semicircle at the high-frequency end intercepts the real axis (*Z*). The data was plotted in the Cole-Cole plot form, where the imaginary part of impedance, $-Z_i$, was plotted on the y-axis and the real part of impedance, $Z_r$, was plotted on the x-axis of the chart to estimate the bulk resistance, or *Rb* value. The Arrhenius rule (Eq. (2)) can be used to calculate the activation energy, *Ea*,

$$\sigma = \sigma_0 \, exp \, (\frac{-E_a}{kT}) \tag{2}$$

Here, $\sigma_0$ is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature. The dielectric permittivity ($\varepsilon$) can be determined by using Eq. (3) and Eq. (4):

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \tag{3}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \tag{4}$$

where $C_0 = \frac{\varepsilon_o A}{t}$, $\varepsilon_o$= 8.85 x $10^{-12}$ $Fm^{-1}$. ω is the angular frequency = 2π*f*, where *f* is the frequency (Hz). By using the value obtained from dielectric permittivity ($\varepsilon$), we can calculate the value for electrical modulus (*M)* by using the Eq. (5) and Eq. (6).

$$M_r = \frac{\varepsilon_r}{\varepsilon_r^2+\varepsilon_i^2} \quad (5)$$

$$M_i = \frac{\varepsilon_i}{\varepsilon_r^2+\varepsilon_i^2} \quad (6)$$

## 3. Results

### *3.1 Ionic Conductivity Studies*

Eq. (1) was used to determine the SBEs' ionic conductivity at room temperature, which was then shown in Table 2. By referring to the table, the ionic conductivity rose according to the amount of $NH_4Cl$ present until it reached its ideal concentration at 16 wt%. Pure 2HEC (2HECAC0) sample has an ionic conductivity of 7.45 x $10^{-6}$ S $cm^{-1}$ at ambient temperature. Ionic conductivity begins to noticeably climb after the addition of 4 wt% $NH_4Cl$ and so forth, then reaches its peak at 16 wt%. 2HECAC16 was found to have the maximum ionic conductivity, 1.74 x $10^{-3}$ S $cm^{-1}$. As the addition of salt continues, the ionic conductivity tends to decrease to 6.5 x $10^{-4}$ S cm-1 for the sample with 20 wt% $NH_4Cl$ and finally to 2.95 x $10^{-4}$ S $cm^{-1}$ at 24 wt%. The SBEs were shown to inherit weak mechanical stability and can be disregarded at increasing salt contents (>24 wt% $NH_4Cl$).

**Table 2**
Designation, thickness, bulk resistance, and ionic conductivity of SBE

| Sample | Thickness (mm) | Bulk Resistance, $R_b$ | Ionic Conductivity, $\sigma$ (S $cm^{-1}$) |
|---|---|---|---|
| 2HECAC0 | 0.0174 | 7.43 x $10^2$ | 7.45 x $10^{-6}$ |
| 2HECAC4 | 0.0122 | 1.42 x $10^2$ | 2.73 x $10^{-5}$ |
| 2HECAC8 | 0.0106 | 1.13 x $10^1$ | 2.99 x $10^{-4}$ |
| 2HECAC12 | 0.0122 | 5.67 | 6.85 x $10^{-4}$ |
| 2HECAC16 | 0.0200 | 3.66 | 1.74 x $10^{-3}$ |
| 2HECAC20 | 0.0170 | 8.33 | 6.50 x $10^{-4}$ |
| 2HECAC24 | 0.0150 | 1.62 x $10^1$ | 2.95 x $10^{-4}$ |

The increased amount of free mobile ions that dissociated from $NH_4Cl$ which entered the 2HEC polymer host may be the cause of the improved ionic conductivity. The prevalence of ionic conduction in the polymer system increased with the number of ionic dopants, enhancing the SBE's total ionic conductivity [35]. More free mobile ions ($NH_4^+$) are capable of being separated in the polymer host system thanks to the addition of $NH_4Cl$ salt. The dissociated cations may potentially interact with the oxygen atom's single pair of electrons in the 2-HEC, claim by Hafiza and Isa [30]. Numerous studies lend evidence to this theory. For example, Mazuki *et al.,* [36], observed a significant rise in conductivity in polymer electrolytes upon the addition of $NH_4Cl$, which attributed to dissociation and free $NH_4^+$ ions. Similar to this article, Shukur *et al.,* [37] reported that free $NH_4^+$ ions promoted ionic transport in polymer electrolytes doped with ammonium salt. Furthermore, studies by Hamsan *et al.,* [38] noted that the contribution of dissociated $NH_4^+$ ions to the conductivity in systems based on ammonium salts. Kadir *et al.,*'s [39] discovery of increased conductivity in PEO-based electrolytes with NH4Cl addition further validated this process. In the meantime, as the concentration of $NH_4Cl$ increases, the accumulation of free mobile ions might lead to the creation of ion clusters, which can explain why ionic conductivity is decreasing. The interior space of the polymer matrix has shrunk as the number of free mobile ions has increased; as a result, the ions begin to move closer to one another and eventually form ion clusters because of the weak gravitational attraction they have on one another [40]. The aforementioned phenomenon has strong support in the literature, as evidenced by the research conducted by Lu *et al.,* [41]. Their findings showed that ion clustering results in a decrease in ionic mobility because it reduces the free volume within the

polymer matrix. According to Zhu *et al.,* [42], the creation of ion clusters can hinder the growth of ionic conductivity in polymer electrolytes by obstructing ion transport and resulting in a reduction in conductivity. The availability of free mobile ions will decrease, which will limit ionic conduction and result in a drop in the ionic conductivity of SBEs. The work done by Ahmad and Isa [43] for the polymer electrolyte Carboxymethyl Cellulose doped with $NH_4Cl$ also experiences the effect of ion clustering, leading to a decrease in ionic conductivity.

### *3.2 Temperature-Dependent Conductivity Analysis*

Figure 1 shows how the 2HEC-$NH_4Cl$ SBE system's ionic conductivity varies with temperature across the range of 303 to 353 K for 0 wt% - 20 wt%. As for the 24 wt% sample, it was not included due to the sample becoming crystalline and brittle at high temperatures. Figure 1 shows that for all electrolytes, the conductivity of the system rises linearly with an increase in temperature. Increased ionic mobility in the SBE can explain this phenomenon. By exerting force against the hydrostatic pressure while moving the polymer portion, exerted from the close-by atoms as a result of the vibrational energy, tiny voids are produced as the temperature rises [44]. By creating free space, the ensuing conductivity makes it possible for ions, solvated molecules, or polymer segments to flow. The free available volume surrounding the polymer chain affects the overall mobility of the ion and polymer. Due to the rise in temperature, it also enhances segmental ion mobility, and also lead to the increase in free volume. As a result, it leads to an increase in conductivity [45]. According to the Arrhenius behaviour of the dc conductivity values (Regression value, $R^2$), the conductivity mechanism is a thermally activated process [44].

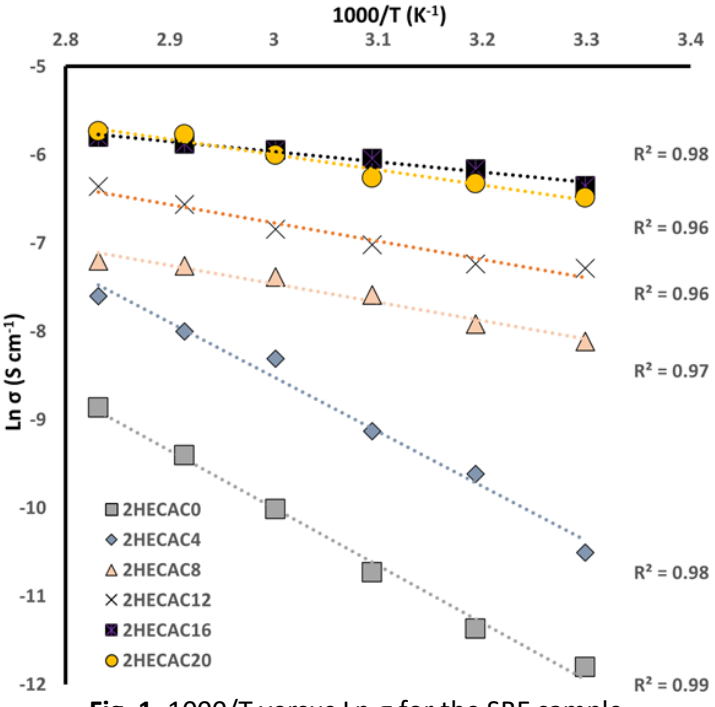


**Fig. 1.** 1000/T versus Ln σ for the SBE sample

The Arrhenius plot's linear fit is used to determine the activation energy of the sample. In Figure 2, the activation energy is shown. As the $NH_4Cl$ concentration rises, it can be observed that the activation energy decreases. The electrolyte with the highest conductivity has the lowest activation energy, which suggests that charge carriers in higher conducting electrolytes need less energy to start the migration process. Studies by Borodin *et al.,* [46], Molinari *et al.,* [47], Bakar *et al.,* [48], Patel *et*

*al.,* [49], and Li *et al.,* [50] provide evidence that although moderate concentrations of salt generally lower activation energy and improve ion conductivity in polymer electrolytes, high concentrations can cause ion aggregation and disrupt the structural order of the polymer matrix. This behaviour leads to a decrease in conductivity even with the expected rise in salt content because it promotes ion-pairing actions and hinders ion mobility, which raises activation energy. These results highlight the possibility that the rise in activation energy resulting from ion clustering and structural alterations brought on by high salt concentrations is related to the conductivity decrease observed with increased $NH_4Cl$ concentration.

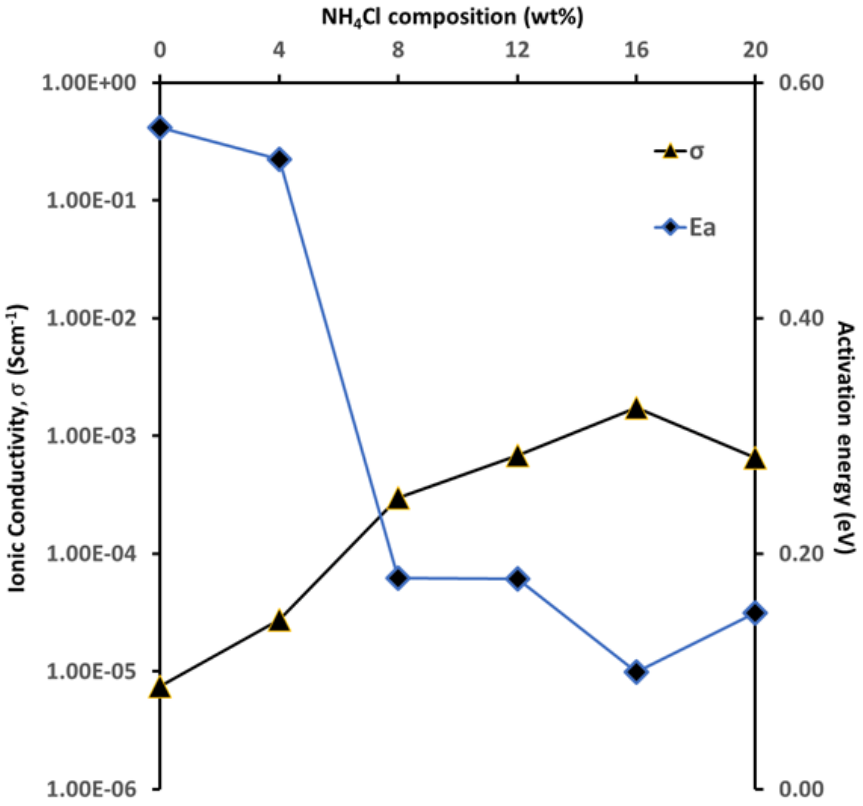


**Fig. 2.** $NH_4Cl$ composition versus ionic conductivity and activation energy

*3.3 Dieletric Studies*

For SBEs with a range of 0 wt% to 20 wt% at 303 K, the frequency-dependent dielectric constant ($\varepsilon_r$) and dielectric loss ($\varepsilon_i$) graphs are shown in Figure 3 and Figure 4. The ability of a material to hold charge is measured by its dielectric constant, whereas the energy lost as a result of the flow and motion of ions in a rapidly varying electric field is measured by its dielectric loss [51]. According to Figure 3 and Figure 4, high values of the $\varepsilon_r$ and $\varepsilon_i$ plots are visible at low frequencies before they progressively decline as frequency rises. These graphs revealed no discernible relaxation peak, indicating that the ionic conductivity was mostly caused by the rise in the amount of vacant mobile ions in the polymer matrix [4,52]. The presence of electrode polarisation and the space charge effect at lower frequencies may be explained by the high value of both $\varepsilon_r$ and $\varepsilon_i$, which diminishes as the frequency goes up. This confirms that the SBEs are not Debye-dependent [22,53,54]. The high value of $\varepsilon_i$ also suggests that there was a significant reduction during the dipole orientation [4]. The improvement of the charge stored in the SBEs may also be responsible for the increment in $\varepsilon_r$ at low frequency as the $NH_4Cl$ concentration rises. This further suggests that an increase in the number of free mobile ions in SBEs causes an increase in ionic conductivity [55]. The value of $\varepsilon_r$ and $\varepsilon_i$ steadily

decreases with frequency, and this may be attributed to the electrical field's quick reversal, which prevents ion diffusion and reduces the charge that builds up at the electrode, lowering the value of $\varepsilon_r$ [21,56]. The rises at higher temperatures are a result of the polymer electrolyte system's increased quantity of free mobile ions [16,57,58]. The significant amount of loss experienced during the alignment of the dipole may potentially be contributing to the increase in $\varepsilon_i$ with temperature. This might result in more vacant mobile ions and their random contacts, which ultimately results in a higher relaxation time [4].

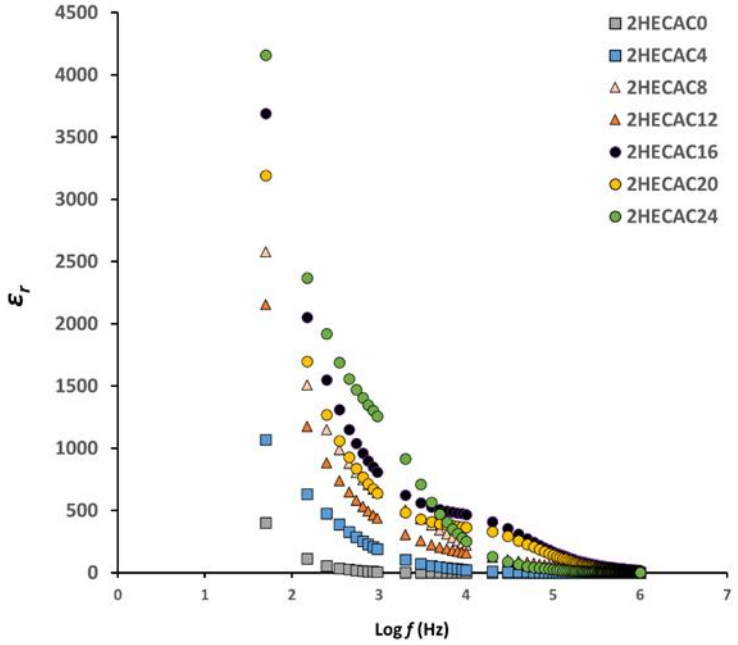


**Fig. 3.** Frequency-dependant of εr at 303 K for all SBEs

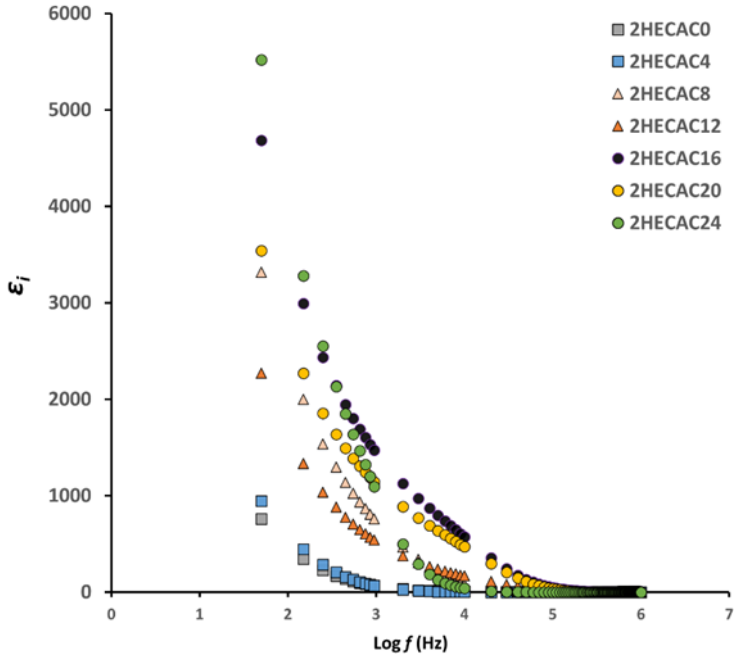


**Fig. 4.** Frequency-dependant of εi at 303 K for all SBEs

A further examination of the dielectric modulus helps to clarify the impact of electrode polarisation. Figure 5 and Figure 6 depict the fluctuation of the real component ($M_r$) and imaginary part ($M_i$) of the dielectric modulus for all SBE samples. The figure shows that the value of $M_r$ and $M_i$ is virtually nil at lower frequencies and increases as the frequency rises without a discernible relaxation peak. A large decrease in electric double layer capacitance (EDLC) at the electrode/electrolyte interface is shown by the long tail observed around the area of low frequencies, further supporting the non-Debye behaviour of the SBEs. The influence of electrode polarisation can also be disregarded due to $M_r$ low value [4,58,59]. The ionic conduction was caused by the short-ranged mobility ion carriers of the SBEs, as indicated by the rising value of $M_r$ at higher frequencies [4]. Additionally, it has been discovered that the $M_r$ decreases as concentration rises.

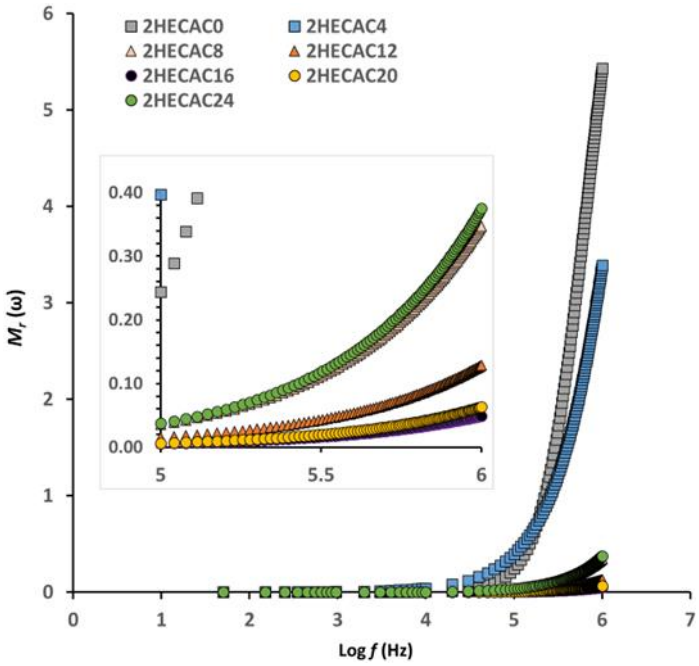


**Fig. 5.** Frequency-dependant of Mr at 303 K for all SBEs

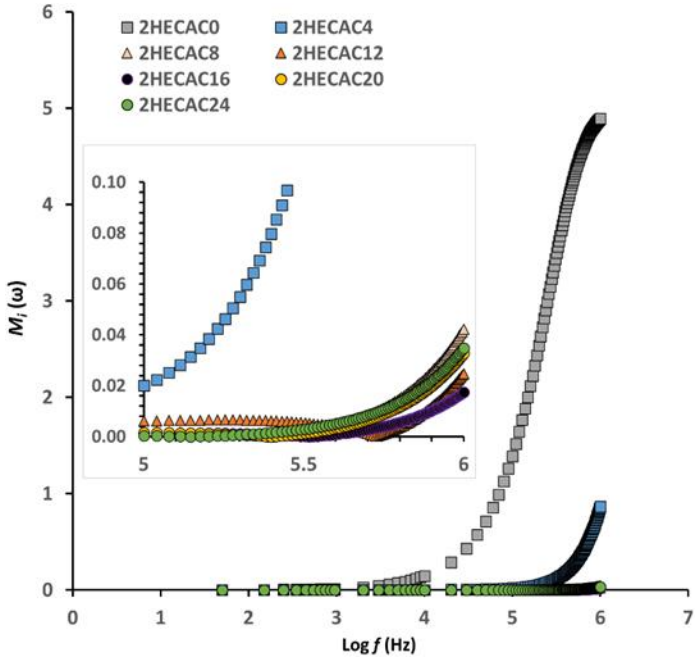


**Fig. 6.** Frequency-dependant of Mi at 303 K for all SBEs

## 4. Conclusions

An innovative solid biopolymer electrolyte system based on 2HEC doped with several $NH_4Cl$ contents (wt.%) has been properly developed by utilizing the solution casting technique. According to the EIS study, the sample containing 16 weight percent $NH_4Cl$ has an optimal value of room temperature ionic conductivity of 1.74 x $10^{-3}$ S $cm^{-1}$. In ionic conductor solid biopolymer electrolyte systems, the ionic conductivity also seems to be temperature-aided, which is a feature of Arrhenius behaviour. In addition, the ionic conductivity was influenced by the activation energy ($E_a$), where a lower value of $E_a$ yields higher ionic conductivity. The SBEs exhibit non-Debye behaviour, which supports the idea that the movement of free mobile ions causes ionic conduction in the polymer system, according to dielectric permittivity studies. Analysis of dielectric constant (εr) and dielectric loss (εi) display a high value at low frequency and rises with increasing $NH_4Cl$ content as well as temperature, indicating high dissociations of mobile ions into the polymer system. The ionic conductive property of the SBEs was further validated by modulus analysis. These findings lead to the conclusion that the 2HEC-$NH_4Cl$ SBEs have a great deal of promise for use in electrochemical devices.

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## References

[1] Villegas-Pañeda, Ximena, Silvia Pérez-Casas, Efrén Hernández-Baltazar, and Angel E. Chávez-Castellanos. "Study of interactions between octyl-β-D-glucopyranoside and the hydroxyethyl-cellulose biopolymer in aqueous solution." *The Journal of Chemical Thermodynamics* 79 (2014): 69-75. https://doi.org/10.1016/j.jct.2014.06.026

[2] Zulkifli, Farah Hanani, Fathima Shahitha Jahir Hussain, Mohammad Syaiful Bahari Abdull Rasad, and Mashitah Mohd Yusoff. "Nanostructured materials from hydroxyethyl cellulose for skin tissue engineering." *Carbohydrate Polymers* 114 (2014): 238-245. https://doi.org/10.1016/j.carbpol.2014.08.019

[3] Mianehrow, Hanieh, Mohamad Hasan Mohamadzadeh Moghadam, Farhad Sharif, and Saeedeh Mazinani. "Graphene-oxide stabilization in electrolyte solutions using hydroxyethyl cellulose for drug delivery application." *International Journal of Pharmaceutics* 484, no. 1-2 (2015): 276-282. https://doi.org/10.1016/j.ijpharm.2015.02.069

[4] Ramlli, Muhamad Amirullah, Mohd Ikmar Nizam Mohamad Isa, and Khadijah Hilmun Kamarudin. "2-Hydroxyethyl cellulose-ammonium thiocyanate solid biopolymer electrolytes: ionic conductivity and dielectric studies." *Journal of Sustainability Science and Management* 17, no. 7 (2022): 121-132. https://doi.org/10.46754/jssm.2022.07.009

[5] Siva, Pavithra, Mohammad Ali Tareq, and Kamyar Shameli. "Biodegradable Polymers for Packaging: A Bibliometric Overview of the Publication in Web of Science in Year 2012-2021." *Journal of Research in Nanoscience and Nanotechnology* 5, no. 1 (2022): 29-42. https://doi.org/10.37934/jrnn.5.1.2942

[6] Shameli, Kamyar, Syamim Arsyad Saiful, and Mostafa Yusefi. "Cross-linked Chitosan-Based Hydrogels Nanocomposites for Treatment of Disease." *Journal of Research in Nanoscience and Nanotechnology* 5, no. 1 (2022): 65-97. https://doi.org/10.37934/jrnn.5.1.6597

[7] Zulkifli, Mohamad Dzulhilmi, Mostafa Yusefi, Kamyar Shameli, and Sin Yeang Teow. "Curcumin Extract Loaded with Chitosan Nanocomposite for Cancer Treatment." *Journal of Research in Nanoscience and Nanotechnology* 6, no. 1 (2022): 1-13. https://doi.org/10.37934/jrnn.6.1.113

[8] Shafie, Nur Fathin Amirah, Nazira Syahira Zulkifli, Roshafima Rasit Ali, Zatil Izzah Tarmizi, and Syazwani Mohd Faizo. "Green Synthesis of Titanium Dioxide Nanoparticles Using Extraction of Psidium Guajava for Smart Packaging Application." *Journal of Research in Nanoscience and Nanotechnology* 11, no. 1 (2024): 16-23. https://doi.org/10.37934/jrnn.11.1.115

[9] Yang, Chun-Chen, Gwo-Mei Wu, and Sheng-Jen Lin. "Alkaline blend polymer electrolytes based on polyvinyl alcohol (PVA)/tetraethyl ammonium chloride (TEAC)." *Journal of Applied Electrochemistry* 36 (2006): 655-661. https://doi.org/10.1007/s10800-006-9117-z

[10] Vijaya, N., Subramanian Selvasekarapandian, G. Hirankumar, S. Karthikeyan, H. Nithya, C. S. Ramya, and M. Prabu. "Structural, vibrational, thermal, and conductivity studies on proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone)." *Ionics* 18 (2012): 91-99. https://doi.org/10.1007/s11581-011-0589-4

[11] Kamarudin, K. H., and M. I. N. Isa. "Structural and DC Ionic conductivity studies of carboxy methylcellulose doped with ammonium nitrate as solid polymer electrolytes." *International Journal of Physical Sciences* 8, no. 31 (2013): 1581-1587.

[12] Sohaimy, M. I. H., and Mohd Ikmar Nizam Isa. "Conductivity and dielectric analysis of cellulose based solid polymer electrolytes doped with ammonium carbonate ($NH_4CO_3$)." *Applied Mechanics and Materials* 719 (2015): 67-72. https://doi.org/10.4028/www.scientific.net/AMM.719-720.67

[13] Hafiza, M. N., and M. I. N. Isa. "Correlation between structural, ion transport and ionic conductivity of plasticized 2-hydroxyethyl cellulose based solid biopolymer electrolyte." *Journal of Membrane Science* 597 (2020): 117176. https://doi.org/10.1016/j.memsci.2019.117176

[14] Nofal, Muaffaq M., Shujahadeen B. Aziz, Hewa O. Ghareeb, Jihad M. Hadi, Elham MA Dannoun, and Sameerah I. Al-Saeedi. "Impedance and dielectric properties of PVC: $NH_4I$ solid polymer electrolytes (SPEs): steps toward the fabrication of SPEs with high resistivity." *Materials* 15, no. 6 (2022): 2143. https://doi.org/10.3390/ma15062143

[15] Rauf, Hwda Ghafur, Jihad M. Hadi, Shujahadeen B. Aziz, Rebar T. Abdulwahid, and Muhammed S. Mustafa. "A novel approach to design high resistive polymer electrolytes based on PVC: electrochemical impedance and dielectric properties." *International Journal of Electrochemical Science* 17, no. 5 (2022): 22051. https://doi.org/10.20964/2022.05.04

[16] Samsudin, A. S., and M. I. N. Isa. "Conductivity and transport properties study of plasticized carboxymethyl cellulose (CMC) based solid biopolymer electrolytes (SBE)." *Advanced Materials Research* 856 (2014): 118-122. https://doi.org/10.4028/www.scientific.net/AMR.856.118

[17] Isa, M. I. N., and A. S. Samsudin. "Potential study of biopolymer-based carboxymethylcellulose electrolytes system for solid-state battery application." *International Journal of Polymeric Materials and Polymeric Biomaterials* 65, no. 11 (2016): 561-567. https://doi.org/10.1080/00914037.2016.1149844

[18] Kannadhasan, S., Muthu Senthil Pandian, and P. Ramasamy. "Influence of 4, 4'-bipyridine doped polyvinylidine fluoride/potassium iodide/iodine solid polymer electrolytes for dye-sensitized solar cell applications." *Materials Letters* 238 (2019): 167-170. https://doi.org/10.1016/j.matlet.2018.11.173

[19] Isa, M. I. N., M. I. H. Sohaimy, and N. H. Ahmad. "Carboxymethyl cellulose plasticized polymer application as bio-material in solid-state hydrogen ionic cell." *International Journal of Hydrogen Energy* 46, no. 11 (2021): 8030-8039. https://doi.org/10.1016/j.ijhydene.2020.11.274

[20] Rasali, N. M. J., Y. Nagao, and A. S. Samsudin. "Enhancement on amorphous phase in solid biopolymer electrolyte based alginate doped $NH_4NO_3$." *Ionics* 25 (2019): 641-654. https://doi.org/10.1007/s11581-018-2667-3

[21] Aziz, Shujahadeen B., Zul Hazrin Zainal Abidin, and Abdul Kariem Arof. "Effect of silver nanoparticles on the DC conductivity in chitosan-silver triflate polymer electrolyte." *Physica B: Condensed Matter* 405, no. 21 (2010): 4429-4433. https://doi.org/10.1016/j.physb.2010.08.008

[22] Kumar, Manindra, Tuhina Tiwari, and Neelam Srivastava. "Electrical transport behaviour of bio-polymer electrolyte system: Potato starch+ ammonium iodide." *Carbohydrate Polymers* 88, no. 1 (2012): 54-60. https://doi.org/10.1016/j.carbpol.2011.11.059

[23] Hafiza, M. N., A. N. A. Bashirah, N. Y. Bakar, and M. I. N. Isa. "Electrical properties of carboxyl methylcellulose/chitosan dual-blend green polymer doped with ammonium bromide." *International Journal of Polymer Analysis and Characterization* 19, no. 2 (2014): 151-158. https://doi.org/10.1080/1023666X.2014.873562

[24] Hafiza, M. N., and M. I. N. Isa. "Conduction mechanism via correlated barrier hopping in EC-plasticized 2-hydroxyehyl cellulose-ammonium nitrate solid polymer electrolyte." In *IOP Conference Series: Materials Science and Engineering*, vol. 440, p. 012039. IOP Publishing, 2018. https://doi.org/10.1088/1757-899X/440/1/012039

[25] Hamrayev, Hemra, and Kamyar Shameli. "Synthesis and Characterization of Ionically Cross-Linked Chitosan Nanoparticles." *Journal of Research in Nanoscience and Nanotechnology* 7, no. 1 (2022): 7-13. https://doi.org/10.37934/jrnn.7.1.713

[26] Hamrayev, Hemra, Kamyar Shameli, Mostafa Yusefi, and Serdar Korpayev. "Green Route for the Fabrication of ZnO Nanoparticles and Potential Functionalization with Chitosan Using Cross-linkers: A Review." *Journal of Research in Nanoscience and Nanotechnology* 3, no. 1 (2021): 1-25. https://doi.org/10.37934/jrnn.3.1.125

[27] Schauser, Nicole S., Ram Seshadri, and Rachel A. Segalman. "Multivalent ion conduction in solid polymer systems." *Molecular Systems Design & Engineering* 4, no. 2 (2019): 263-279. https://doi.org/10.1039/C8ME00096D

[28] Liu, Wenyi, Chengjun Yi, Shuailei Liu, Qiuyue Gui, Jinping Liu, Linpo Li, Deliang Ba, Yuanyuan Li, and Dongliang Peng. "Designing polymer-in-salt electrolyte and fully infiltrated 3D electrode for integrated solid-state lithium batteries." *Angewandte Chemie (International Edition)* 60, no. 23 (2021): 12931-12940. https://doi.org/10.1002/anie.202101537

[29] Noor, N. A. M., and M. I. N. Isa. "Investigation on transport and thermal studies of solid polymer electrolyte based on carboxymethyl cellulose doped ammonium thiocyanate for potential application in electrochemical devices." *International Journal of Hydrogen Energy* 44, no. 16 (2019): 8298-8306. https://doi.org/10.1016/j.ijhydene.2019.02.062

[30] Hafiza, M. N., and M. I. N. Isa. "Solid polymer electrolyte production from 2-hydroxyethyl cellulose: Effect of ammonium nitrate composition on its structural properties." *Carbohydrate Polymers* 165 (2017): 123-131. https://doi.org/10.1016/j.carbpol.2017.02.033

[31] Brza, M. A., Shujahadeen B. Aziz, H. Anuar, Fathilah Ali, M. H. Hamsan, M. F. Z. Kadir, and Rebar T. Abdulwahid. "Metal framework as a novel approach for the fabrication of electric double layer capacitor device with high energy density using plasticized Poly (vinyl alcohol): Ammonium thiocyanate based polymer electrolyte." *Arabian Journal of Chemistry* 13, no. 10 (2020): 7247-7263. https://doi.org/10.1016/j.arabjc.2020.08.006

[32] El Fawal, Gomaa F., Marwa M. Abu-Serie, Mohamed A. Hassan, and Mohamed S. Elnouby. "Hydroxyethyl cellulose hydrogel for wound dressing: Fabrication, characterization and in vitro evaluation." *International Journal of Biological Macromolecules* 111 (2018): 649-659. https://doi.org/10.1016/j.ijbiomac.2018.01.040

[33] Ramlli, M. A., N. A. A. Bashirah, and M. I. N. Isa. "Ionic conductivity and structural analysis of 2-hyroxyethyl cellulose doped with glycolic acid solid biopolymer electrolytes for solid proton battery." In *IOP Conference Series: Materials Science and Engineering*, vol. 440, no. 1, p. 012038. IOP Publishing, 2018. https://doi.org/10.1088/1757-899X/440/1/012038

[34] Huggins, Robert. *Advanced batteries: materials science aspects*. Springer Science & Business Media, 2008.

[35] Sohaimy, M. I. H., and M. I. N. Isa. "Ionic conductivity and conduction mechanism studies on cellulose based solid polymer electrolytes doped with ammonium carbonate." *Polymer Bulletin* 74 (2017): 1371-1386. https://doi.org/10.1007/s00289-016-1781-5

[36] Mazuki, N. F., N. M. J. Rasali, M. A. Saadiah, and A. S. Samsudin. "Irregularities trend in electrical conductivity of CMC/PVA-NH4Cl based solid biopolymer electrolytes." In *AIP Conference Proceedings*, vol. 2030, no. 1. AIP Publishing, 2018. https://doi.org/10.1063/1.5066862

[37] Shukur, M. F., N. A. Majid, R. Ithnin, and M. F. Z. Kadir. "Effect of plasticization on the conductivity and dielectric properties of starch–chitosan blend biopolymer electrolytes infused with NH4Br." *Physica Scripta* 2013, no. T157 (2013): 014051. https://doi.org/10.1088/0031-8949/2013/T157/014051

[38] Hamsan, M. H., Shujahadeen B. Aziz, M. F. Shukur, and M. F. Z. Kadir. "Protonic cell performance employing electrolytes based on plasticized methylcellulose-potato starch-$NH_4NO_3$." *Ionics* 25 (2019): 559-572. https://doi.org/10.1007/s11581-018-2827-5

[39] Kadir, M. F. Z., Z. Aspanut, Siti Rohana Majid, and Abdul Kariem Arof. "FTIR studies of plasticized poly (vinyl alcohol)–chitosan blend doped with $NH_4NO_3$ polymer electrolyte membrane." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 78, no. 3 (2011): 1068-1074. https://doi.org/10.1016/j.saa.2010.12.051

[40] Ramya, C. S., S. Selvasekarapandian, T. Savitha, G. Hirankumar, and P. C. Angelo. "Vibrational and impedance spectroscopic study on PVP-$NH_4$SCN based polymer electrolytes." *Physica B: Condensed Matter* 393, no. 1-2 (2007): 11-17. https://doi.org/10.1016/j.physb.2006.11.021

[41] Lu, Yong, Lin Li, Qiu Zhang, Zhiqiang Niu, and Jun Chen. "Electrolyte and interface engineering for solid-state sodium batteries." *Joule* 2, no. 9 (2018): 1747-1770. https://doi.org/10.1016/j.joule.2018.07.028

[42] Zhu, Sheng, Qian Wang, and Jiangfeng Ni. "Aqueous transition-metal ion batteries: Materials and electrochemistry." *EnergyChem* 5, no. 3 (2023): 100097. https://doi.org/10.1016/j.enchem.2022.100097

[43] Ahmad, Nur Hidayah, and M. I. N. Isa. "Structural and ionic conductivity studies of CMC based polymerelectrolyte doped with NH4Cl." *Advanced Materials Research* 1107 (2015): 247-252. https://doi.org/10.4028/www.scientific.net/AMR.1107.247

[44] Isa, M. I. N., and N. A. M. Noor. "Conductivity and electrical studies of plasticized carboxymethyl cellulose based proton conducting solid biopolymer electrolytes." In *Micro+ Nano Materials, Devices, and Systems*, vol. 9668, pp. 592-599. SPIE, 2015. https://doi.org/10.1117/12.2202527

[45] Isa, M. I. N., and Noor Azniza Mohd Noor. "Ionic conduction mechanism of solid biodegradable polymer electrolytes based carboxymethyl cellulose doped ammonium thiocyanate." *Applied Mechanics and Materials* 719 (2015): 114-118. https://doi.org/10.4028/www.scientific.net/AMM.719-720.114

[46] Borodin, Oleg, Julian Self, Kristin A. Persson, Chunsheng Wang, and Kang Xu. "Uncharted waters: super-concentrated electrolytes." *Joule* 4, no. 1 (2020): 69-100. https://doi.org/10.1016/j.joule.2019.12.007

[47] Molinari, Nicola, Jonathan P. Mailoa, and Boris Kozinsky. "Effect of salt concentration on ion clustering and transport in polymer solid electrolytes: a molecular dynamics study of PEO–LiTFSI." *Chemistry of Materials* 30, no. 18 (2018): 6298-6306. https://doi.org/10.1021/acs.chemmater.8b01955

[48] Bakar, Recep, Saeid Darvishi, Umut Aydemir, Ugur Yahsi, Cumali Tav, Yusuf Ziya Menceloglu, and Erkan Senses. "Decoding polymer architecture effect on ion clustering, chain dynamics, and ionic conductivity in polymer electrolytes." *ACS Applied Energy Materials* 6, no. 7 (2023): 4053-4064. https://doi.org/10.1021/acsaem.3c00310

[49] Patel, Monalisa, Kodihalli G. Chandrappa, and Aninda J. Bhattacharyya. "Increasing ionic conductivity of polymer–sodium salt complex by addition of a non-ionic plastic crystal." *Solid State Ionics* 181, no. 17-18 (2010): 844-848. https://doi.org/10.1016/j.ssi.2010.04.013

[50] Li, Zhuo, Jialong Fu, Xiaoyan Zhou, Siwei Gui, Lu Wei, Hui Yang, Hong Li, and Xin Guo. "Ionic conduction in polymer-based solid electrolytes." *Advanced Science* 10, no. 10 (2023): 2201718. https://doi.org/10.1002/advs.202201718

[51] Woo, H. J., Siti Rohana Majid, and Abdul Kariem Arof. "Dielectric properties and morphology of polymer electrolyte based on poly (ε-caprolactone) and ammonium thiocyanate." *Materials Chemistry and Physics* 134, no. 2-3 (2012): 755-761. https://doi.org/10.1016/j.matchemphys.2012.03.064

[52] Nithya, H., S. Selvasekarapandian, D. Arun Kumar, A. Sakunthala, M. Hema, P. Christopherselvin, Junichi Kawamura, R. Baskaran, and C. Sanjeeviraja. "Thermal and dielectric studies of polymer electrolyte based on P(ECH-EO)." *Materials Chemistry and Physics* 126, no. 1-2 (2011): 404-408. https://doi.org/10.1016/j.matchemphys.2010.10.047

[53] Hemalatha, K. S., G. Sriprakash, M. V. N. Ambika Prasad, R. Damle, and K. Rukmani. "Temperature dependent dielectric and conductivity studies of polyvinyl alcohol-ZnO nanocomposite films by impedance spectroscopy." *Journal of Applied Physics* 118, no. 15 (2015). https://doi.org/10.1063/1.4933286

[54] Isa, M. I. N., and N. H. Ahmad. "Carboxymethyl cellulose-ammonium chloride on electrical of plasticized propylene carbonate solid bio-polymer electrolytes (SBPs) using experimental and computational studies." *Phosphorus, Sulfur, and Silicon and the Related Elements* 193, no. 2 (2018): 115-119. https://doi.org/10.1080/10426507.2017.1417308

[55] Yusof, Y. M., H. A. Illias, and M. F. Z. Kadir. "Incorporation of NH4Br in PVA-chitosan blend-based polymer electrolyte and its effect on the conductivity and other electrical properties." *Ionics* 20 (2014): 1235-1245. https://doi.org/10.1007/s11581-014-1096-1

[56] Vieira, Diogo F., César O. Avellaneda, and Agnieszka Pawlicka. "Conductivity study of a gelatin-based polymer electrolyte." *Electrochimica Acta* 53, no. 4 (2007): 1404-1408. https://doi.org/10.1016/j.electacta.2007.04.034

[57] Khiar, A. S. Ahmad, and Abdul Kariem Arof. "Conductivity studies of starch-based polymer electrolytes." *Ionics* 16 (2010): 123-129. https://doi.org/10.1007/s11581-009-0356-y

[58] Selvalakshmi, S., T. Mathavan, S. Selvasekarapandian, and M. Premalatha. "Effect of ethylene carbonate plasticizer on agar-agar: $NH_4Br$-based solid polymer electrolytes." *Ionics* 24 (2018): 2209-2217. https://doi.org/10.1007/s11581-017-2417-y

[59] Kavitha, S., N. Vijaya, R. Pandeeswari, and M. Premalatha. "Vibrational, electrical and optical studies on pectin-based polymer electrolyte." *International Research Journal of Engineering and Technology* 3, no. 7 (2016): 1385-1390.