Mechanistic Insight of Ionic Conduction on Agarose and Poly(1-vinylpyrrolidone-co-vinyl-acetate) [P(VP-co-VAc)] based Polymer Gel Electrolytes by Incorporating Lithium Bis(oxalato) Borate [LiBOB]

M. S. Sak Ari[1,2], S. Z. Z. Abidin[1,2,*], M. F. M. Taib[1,2], M. Z. A. Yahya[3], N. I. Ali[1,2] and N. S. Mohd Rafi[1,2]

[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] Faculty of Defence Science and Technology, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia.
*E-mail: szafirah@uitm.edu.my

This study focuses on the preparation and characterization of polymer gel electrolyte (PGE) based on two different host polymers in a separated system: agarose [PGE_agar] and P(VP-co-VAc) [PGE_vpvac]. In this work, lithium LiBOB salt was incorporated as the source of charge carriers. PGE was prepared by mixing various host polymer ratios with a dimethylsulfoxide (DMSO) solvent. The ionic conductivity of polymer gel electrolyte was calculated using the bulk resistance value gained from the complex impedance plot in the frequency range 100 Hz-1 MHz and temperature (T) range 298-373 K. The plot of log σ versus 1000/T obeys Arrhenius' rule where it indicates that the ionic conductivity of PGE was thermally assisted. In comparison, PGE_agar and PGE_vpvac had demonstrated the same transport mechanism in a similar experimental configuration. The conduction mechanism in PGEs in both systems can be explained using the small polaron hopping (SPH) model.

1. INTRODUCTION

Many polymer electrolytes for the lithium-based battery were widely studied, which refers to polymer electrolyte based on polyethylene oxide (PEO) as the first battery in history. These polymer electrolytes based on the polymer that contains a polar group interact with lithium ions from lithium salt. Subsequently, various host polymers have been applied, such as polyacrylonitrile,

polymethylmetacrylate, and chitosan. However, they still do not meet the requirements for practical lithium-ion batteries due to the polymers' intrinsic crystal structure resulting in poor ionic conductivity [1]. A favourable electrolyte is urgently required for durable batteries to develop a sustainable future [2].

Various advantages have been found in lithium bis(oxalato) borate (LiBOB) salt, including improved safety, superior thermal stability and prevention of unstable solid electrolyte interphase (SEI). Moreover, LiBOB can efficiently stabilize the graphite anode surface even in pure propylene carbonate-based electrolytes. Batteries containing purified (recrystallized) LiBOB can enhance cycling behaviour and thermal stability [3]. LiBOB is preferred due to its high dissociation energy, making it readily soluble in most solvents, and its high diffusion rate of ions since the small cation (Li^+) size [4]. These features are particularly important in increasing the ionic conductivity of polymer electrolytes.

Polymer electrolytes became vital in fabricating many electrochemical devices [5]. An intensive study has been taken to research and focus on polymer-based electrolytes as an upcoming and promising electrolyte shortly [6]. Two polymers were being used, agarose and Poly(1-vinylpyrrolidone-co-vinyl-acetate) [P(VP-co-VAc)]. Agarose is a group of marine algae polymers produced from red seaweed polysaccharides. Agarose is an effective polymer matrix and can benefit the ionic transport properties because it can form a good crosslink polymer matrix. Agarose or agar is insoluble in cold water, but it swells greatly. Agarose was reported to have a good ionic conductivity of 10^{-4}-10^{-2} S.cm^{-1} [5]. Based on previous studies, intensive research has been done on the P(VP-co-VAc) copolymer applied as the backbone of the polymer electrolytes for electrical performance. The result of studies shows the usage of the copolymer in the polymer electrolytes giving a promising result. Polymer electrolyte samples that were put together with copolymer were found to have high ionic conductivity, high stability and high electrochemical properties [7]. The unique characteristic of this P(VP-co-VAc) polymer is the amorphous PVAc region support in refining the flow of the charged ions, which could lead to improved electrical performances [8–10].

Solid polymer electrolytes (SPEs) have been widely applied due to their wide application and ease of preparation as a polymer film. The main advantages of SPE are their mechanical properties, ease of fabrication of thin films, a wide range of composition and ability to form electrode-electrolyte contacts [11]. However, SPEs showed poor ionic conductivity and mechanical strength in the high-temperature region [12]. A very high ionic conductivity found in liquid electrolyte become a powerful advantage however face, disadvantages such as leakage and corrosion during packaging were discovered [13]. Liquid electrolyte is limited for long-term application due to volatility [14]. Polymer gel electrolytes (PGEs) are the method to solve the problems between solid polymer electrolytes and liquid polymer electrolytes while also preserving the high ionic conductivity and good mechanical strength and possess no problem for packaging. In his research, Kufian and his team said PGEs are non-aqueous liquid electrolytes immobilized in a polymer matrix and have characteristics similar to liquid electrolytes [15]. Furthermore, PGEs also could provide a good electrode-electrolyte contact compared to SPEs [16]. Most research has been done on various polymer gel electrolytes (PGEs) based on lithium salts.

In the present studies, agarose-LiBOB and P(VP-co-VAc)-LiBOB polymer electrolytes were prepared and subjected to ionic conduction mechanisms and other relevant analyses. Both agarose and P(VP-co-VAc) as the gelling polymer and LiBOB salt in dimethylsulfoxide (DMSO) were prepared and characterized in the polymer gel electrolyte systems.

2. EXPERIMENTAL METHOD

High purity white powder form of LiBOB salt with a molecular weight of 193.79 g.mol^{-1} was acquired from Sigma-Aldrich. The solvent, dimethyl sulfoxide (DMSO), containing 78.13 g.mol^{-1} was procured from R&M Chemicals. Agarose in the form of fine white powder with the molecular weight of 438.4 g.mol^{-1} was acquired from Next Gene Scientific Sdn. Bhd. Poly(1-vinylpyrrolidone-co-vinyl acetate) polymer in the appearance of cotton shaped-like was obtained from Sigma-Aldrich with a molecular weight of 197.23 g.mol^{-1}.

Liquid electrolyte solution (0.8 M of LiBOB-DMSO) was prepared by dissolving 3.10 g of LiBOB in 20 mL of DMSO. Agarose and P(VP-co-VAc) at different concentrations (1-8 wt.%) were added to the prepared liquid electrolyte solution. They were stirred for 72 hours at room temperature (298 K) until uniform polymer gel electrolytes were formed and no visible agglomerates occurred. PGE based on agarose and P(VP-CO-VAc) were labelled as PGE$_{agar}$ and PGE$_{vpvac}$ respectively.

Ionic conduction studies were conducted based on Electrochemical impedance spectroscopy (EIS) characterization using HIOKI 3532-50 LCR Hi-tester at a 298-373 K temperature range. Impedance spectra, real part (Z_r) and imaginary part (Z_i) were recorded from 100 Hz-1 MHz frequency range. The value of ionic conductivity (σ) was calculated with the equation:

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

where t for distance between electrodes and A referring to electrolyte–electrode contact area, and bulk resistance (R_b) was determined based on the intersection of complex impedance.

3. RESULT AND DISCUSSION

The ionic conductivity of polymer gel electrolyte at room temperature as a function of PGE$_{agar}$ and PGE$_{vpvac}$ composition in dimethylsulfoxide (DMSO) solvent is illustrated in Figure 1. It is shown that the ionic conductivity slowly decreases with increasing polymer content from 0 wt.% until 8 wt.%. At 0 wt.% of PGE$_{agar}$ composition, the ionic conductivity is 9.54 x 10^{-3} S.cm^{-1} and reaches a minimum ionic conductivity value of 3.17 x 10^{-3} S cm^{-1} at 8 wt.% of PGE$_{agar}$ composition. For PGE$_{vpvac}$ composition, the ionic conductivity at 0 wt.% is 9.54 x 10^{-3} S.cm^{-1} and reaches minimum ionic conductivity value of 4.06 x 10^{-3} S.cm^{-1} at 8 wt.% of P(VP-co-VAc) composition.

Therefore, 1 wt.% of PGE$_{agar}$ and PGE$_{vpvac}$ concentration has been chosen as the most appropriate ionic conductivity because of the value of ionic conductivity of both PGEs, 6.91 x 10^{-3} S.cm^{-1} and 7.83 x 10^{-3} S.cm^{-1} are nearly good as the value of ionic conductivity at 0.8 M LiBOB of liquid electrolyte which is 9.54 x 10^{-3} S.cm^{-1}. Comparing both systems from Figure 1, the ionic conductivity of PGE$_{vpvac}$ concentration is a bit higher than the ionic conductivity of PGE$_{agar}$ concentration. Also, the ionic conductivity drops gradually at a concentration greater than 1 wt.% more on PGEagar than on the PGE$_{vpvac}$ concentration. On increasing the agarose and P(VP-co-VAc) host polymer, the ionic conductivity drops gradually due to the decreasing charge carrier number with both addition of host polymer to the LiBOB salt. Increasing the host polymer concentration can lead to the bulk resistance increases and thus decreases in ionic conductivity.

The current study found that the ionic conductivity of PGE$_{vpvac}$ is higher than PGE$_{agar}$, indicating that the increase in viscosity makes Li$^+$ movement a more tortuous path in PGE$_{agar}$ compared to PGE$_{vpvac}$ concentration [15]. Another important finding is the reduction of ionic conductivity for both PGE$_{agar}$ and PGE$_{vpvac}$ caused by a competing phenomenon due to ionic association taking over the PGE systems. Hence the amount of Li$^+$ ions concentration that contributes to the conduction process decreased in PGE$_{agar}$ more than in PGE$_{vpvac}$ [17]. Finally, the ionic conductivity decreases as LiBOB concentration increases caused by the strong van der Waals interactions between cation and anion of LiBOB salt and agarose in contrast to P(VP-co-VAc) polymer [18, 19].
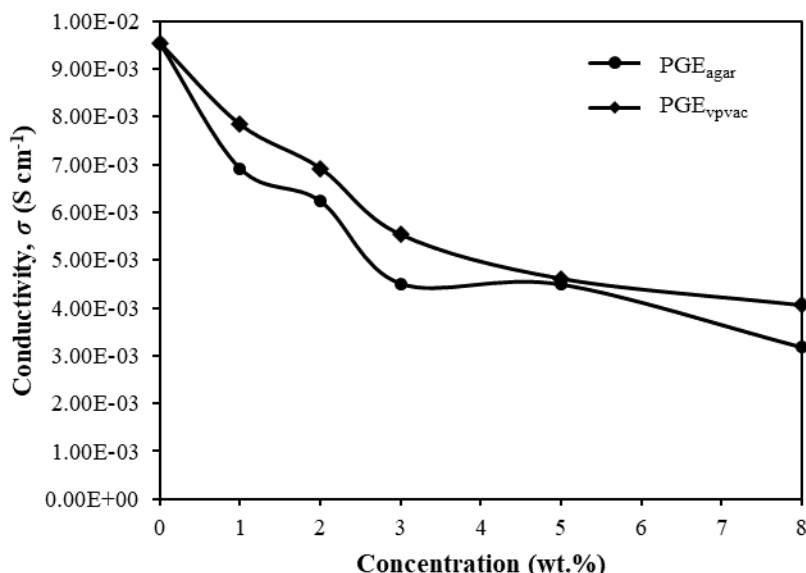

Figure 1. Ionic conductivity of PGE with various concentrations of PGE$_{agar}$ and PGE$_{vpvac}$ at 298 K.

Dielectric behaviours analyses are required to understand ionic conduction in PGEs. The dielectric constant describes the reduction of Coulomb attraction between ion pairs in polymer electrolyte systems. The increasing value of the dielectric constant enhances ionic conductivity [20]. Based on impedance data, the real component of complex permittivity can be obtained as:

$$\varepsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 - Z_i^2)} \tag{2}$$

where C_o is equal to $\varepsilon_o A/t$ and ε_o is the permittivity of free space. Then, Z_r is the real part of impedance and Z_i is the imaginary part of the impedance.

At various temperatures in Figure 2, ε_r increases sharply towards low frequency because of the electrode polarization. The low-frequency dispersion region is attributed to the accumulated free charges at the electrode-electrolyte interface [21], [22].

The dielectric constant (ε_r) and dielectric loss (ε_i) shows that the increase in ionic conductivity is due to the growth of the number of free mobile ions and can be known as a fractional increase in charge. Figure 2 shows that ε_r and ε_i increase as the frequency decreases for a different concentration of PGE$_{agar}$ and PGE$_{vpvac}$. The increased number of Li$^+$ ions is due to the ion dissociation and the decrease because of ion association [23].

$$n = n_0 \, exp \, \frac{-U}{\varepsilon_r kT} \tag{3}$$

The increase of dielectric constant express shows the growth of Li$^+$ ion concentration, therefore, polarization and conduction increase. An enhancement in ionic conductivity will increase the charge carrier concentration can be explained through this expression of ionic conductivity [24].

$$\sigma = \sum nq\mu \tag{4}$$

Based on Equation (4), the concentration of charge carriers (n) and the mobility (μ) of ions play an important role in increasing the value of ionic conductivity. Hence, if the dielectric constant increases meaning that the charge carrier concentration increases according to Equation (3), and as a result, the ionic conductivity will increase too.

Dielectric loss becomes large in low-frequency regions due to the free charges at the electrolyte-electrode interface. At higher temperatures, dielectric constant and dielectric loss values have undergone an increment related to the increase in dissociation of ion aggregates [25].

The real complex impedance (Z_r) and imaginary complex impedance (Z_i) were used to calculate the real and imaginary parts of the impedance data as follows [26]:

$$\varepsilon_i = \frac{Z_r}{\omega C_0 (Z_r{}^2 + Z_i{}^2)} \tag{5}$$

where C_0 is the vacuum capacitance and given by $\varepsilon_o A/t$, where ε_o is the permittivity of free space equal to 8.85 x 10^{-12} F/m. The angular frequency ω is equal to $\omega = 2\pi f$ where f is the frequency of the applied field.

The frequency dependence of AC ionic conductivity at selected temperatures has been analyzed for the highest conducting sample to comprehend the ion dynamics in polymer electrolytes. The ionic conductivity of two phenomena is discovered in polymer electrolytes. The first is ionic conduction in the PGE$_{agar}$ and PGE$_{vpvac}$ is due to the transport of Li$^+$ ion between permitted sites in both agarose and P(VP-co-VAc) host polymer and the second is due to the rises in ionic conductivity caused by the polymer segmental motion.
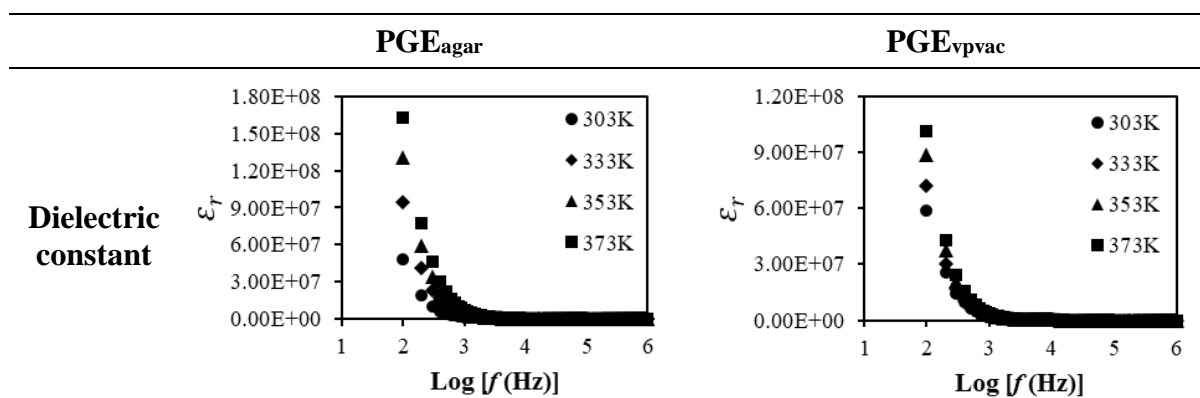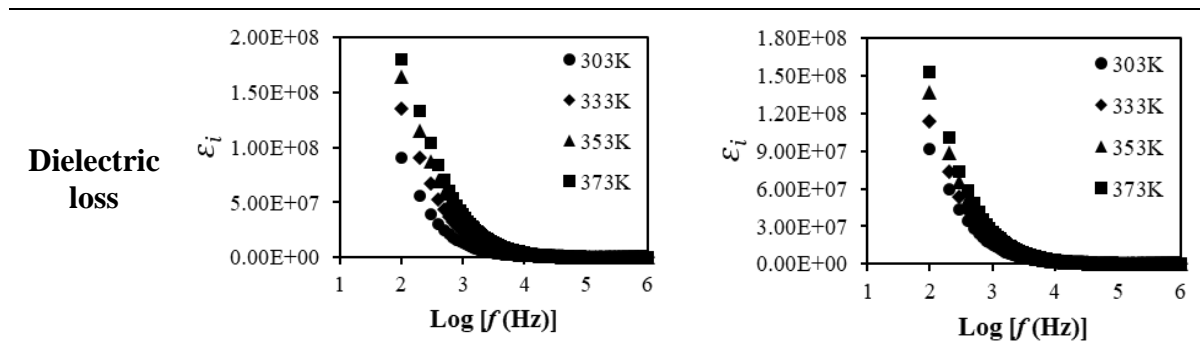
Figure 2. Frequency-dependent dielectric constant and dielectric loss of PGE$_{agar}$ and PGE$_{vpvac}$ at 303 K, 333 K, 353 K and 373 K.

The ionic conductivity plot of the two frequency-dependent systems at various temperatures is presented in Figure 3. The spectra of $\sigma(\omega)$ versus *log f* show two different areas, low-frequency and plateau parts. The low-frequency range ionic conductivity is based on the polarization effects at the electrode-electrolyte interfaces. There is more accumulation charge present at the electrode-electrolyte interface as the frequency decreases, which results in a reduction in ionic conductivity. At the plateau area, ionic conductivity is almost independent of frequency. The frequency-dependent ionic conductivity follows Jonscher's power law [24], [27]:

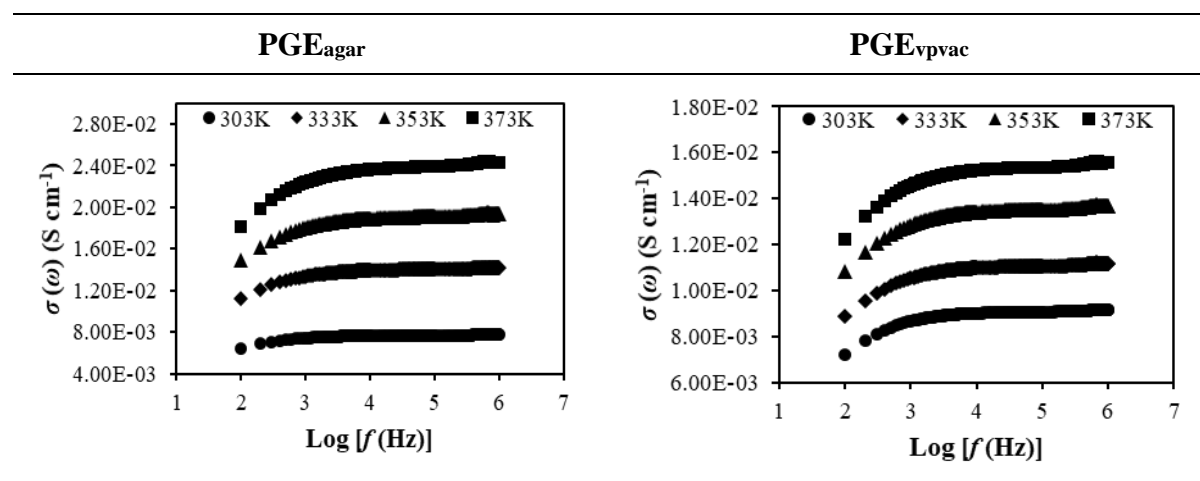$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \tag{6}$$

Figure 3. Frequency-dependent AC ionic conductivity for PGE$_{agar}$ and PGE$_{vpvac}$ at 303 K, 333 K, 353 K and 373 K.

From the equation (6), it can be simplified for a frequency-dependent region as $\sigma_{AC}(\omega)$ is equivalent to $A\omega^s$. The value of *s* can be determined from the gradient of the plot in Figure 3 [28]. The power law exponent *s* can be gained from the graph $\ln \epsilon_i$ vs $\ln \omega$ as the equation below [17]:

$$\ln \epsilon_i = \ln(A/\epsilon_0) + (s - 1) \ln \omega \tag{7}$$

where *A* refers to the second term coefficient from AC ionic conductivity and s has a value from 0 to 1. Plots of $ln\,\varepsilon_i$ versus $ln\,\omega$ for both PGE systems are shown in Figure 4.
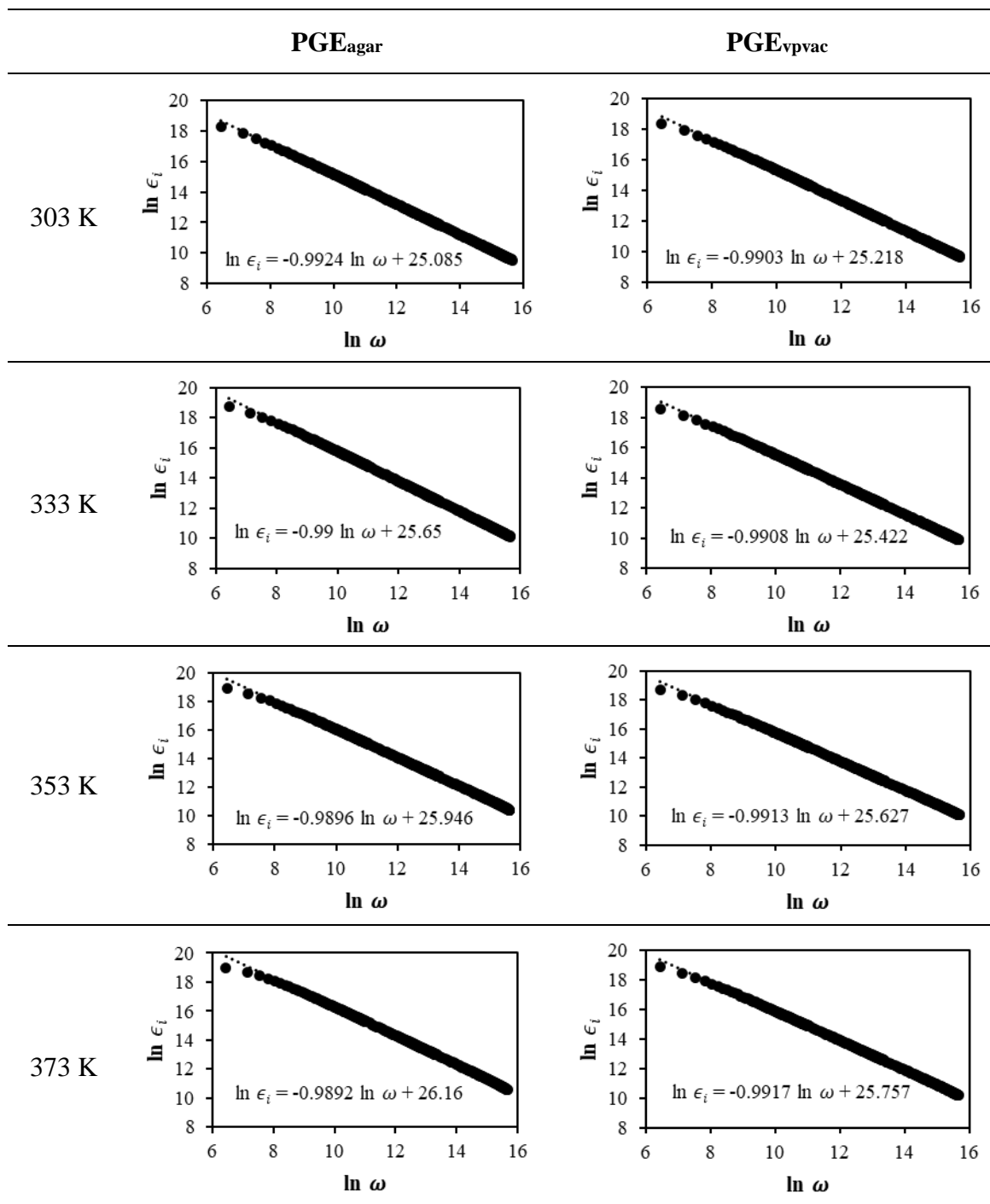

Figure 4. $ln\,\varepsilon_i$ versus $ln\,\omega$ for optimized PGE$_{agar}$ and PGE$_{vpvac}$ at 303 K, 333 K, 353 K and 373 K.

In Figure 5 (a) and (b), the analysis of exponent *s* with temperature can be described through equation s=8×10^{-5}T–0.0184, which belongs to PGE$_{agar}$ system and *s*=2×10^{-5}T+0.0008, which belong to

PGE_{vpvac} system. The exponent *s* increase slightly with temperature, from 303 K to 373 K. The small polaron hopping (SPH) is a suitable model to explain the predominant conduction mechanism of AC ionic conductivity in this both PGE_{agar} and PGE_{vpvac} systems since the value of *s* increases with increasing temperature [27].

The transport mechanism of polarons in polaronic conductors can be assumed to have similar to the conduction of ions in these both PGE systems. The Li^+ ions move from one site to a neighbouring site through the additional path given by agarose as an additive polymer.
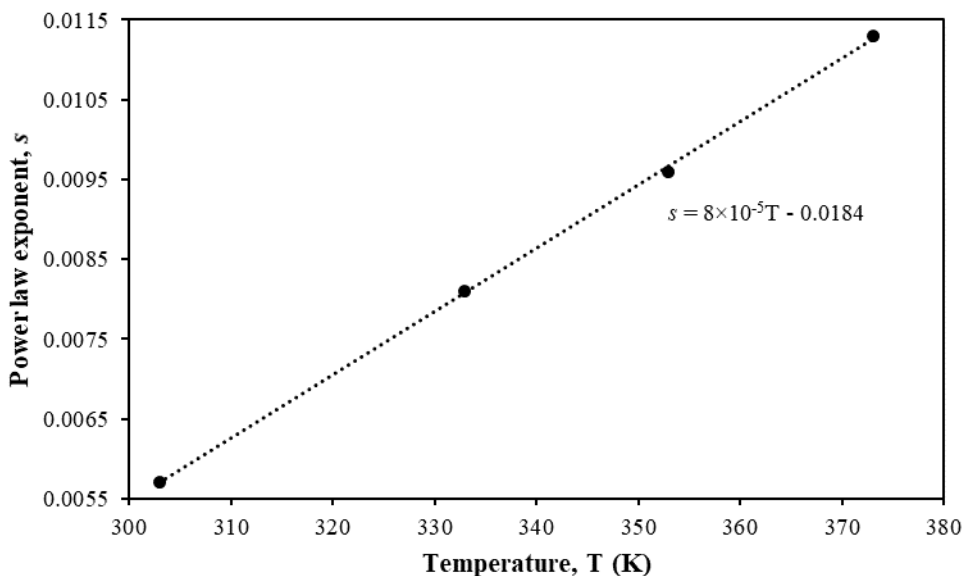

Figure 5 plot a:
$$s = 8\times10^{-5}T - 0.0184$$

Figure 5. (a) Variation of exponent s with temperature for the highest conducting for PGE_{agar}.

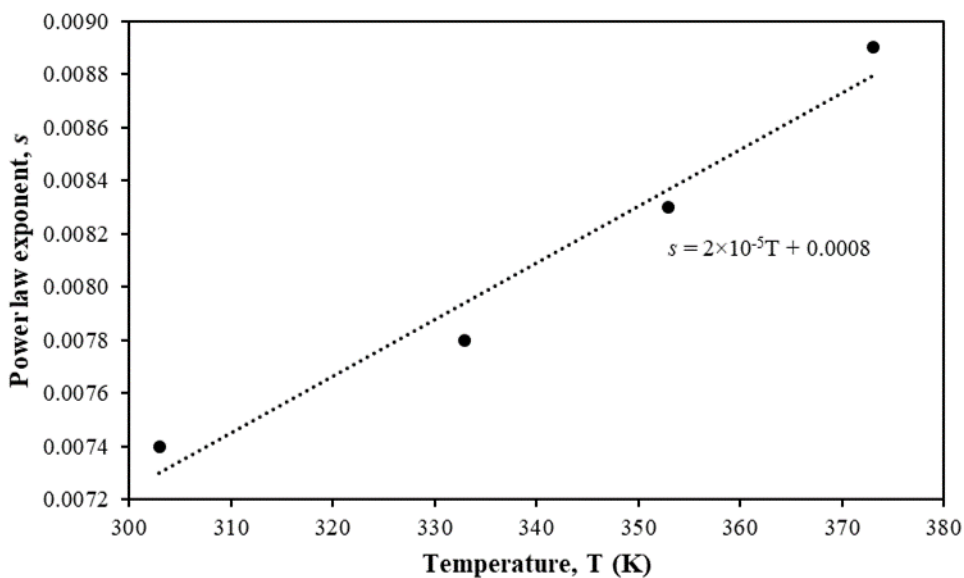

Figure 5 plot b:
$$s = 2\times10^{-5}T + 0.0008$$

Figure 5. (b) Variation of exponent s with temperature for the highest conducting for PGE_{vpvac}.

4. CONCLUSION

Ionic conductivity of both PGE$_{agar}$ and PGE$_{vpvac}$ decreases with the addition of selected host polymer from low to high concentration. Due to the number of Li$^+$ contributions, the ionic conductivity of PGE$_{vpvac}$ is slightly higher than PGE$_{agar}$. Besides that, PGE$_{agar}$ have a greater viscosity and strong van der Waals interaction compared to PGE$_{vpvac}$. Polymer gel electrolytes with PGE$_{agar}$ and PGE$_{vpvac}$ complexations verified the same conduction mechanism using the small polaron hopping (SPH) model.

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