

Study on Dielectric Properties of Gel Polymer Electrolyte Based on PVA-K₂CO₃ Composites

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The advance of gel polymer electrolyte (GPEs) based on conducting salt-polymer has been a subject of concern recently due to their significant applications. This work presents a study of dielectric properties of GPE based on polyvinyl alcohol (PVA) and potassium carbonate (K₂CO₃) (PVA-K₂CO₃) electrolyte for electrochemical applications. The electrolyte material was synthesized by mixing a conducting salt (K₂CO₃) with PVA in different proportions (from 10 - 50 wt. %) in order to study the effect of the salt on the dielectric properties of the electrolyte. The synthesized GPE was characterized using X-ray powder diffraction (XRD) to study electrolyte's crystal phase. Both complex permittivity and complex modulus formalism (dielectric behaviour) of the electrolyte were analysed through electrochemical impedance spectroscopy (EIS). The characterization result shows that the peak intensity of the PVA is significantly reduced with the increase of K₂CO₃ wt.%. which could be attributed to the decrease of PVA crystallinity which can enlarge the amorphous region of the polymer due to the strong plasticizing effect of the salt. High values of complex permittivity (dielectric constant and dielectric loss) were observed at low frequencies, which increased with increasing temperature, indicating an increase in conductivity. From the real part of electric modulus, the material is featured to be highly capacitive. Based on the asymmetrical peak shape of the imaginary part of electric modulus, the non-Debye type relaxation is predicted. Straight-line graphs were observed from the frequency dependency of loss tangent ($\tan \delta$), showing no single relaxation process is present.

Keywords: electrical modulus, dielectric, polymer electrolyte, Impedance spectroscopy

1. INTRODUCTION

The properties of gel polymer electrolyte (GPE) was found to mainly depend on the structure of the polymer matrix that makes up the gel in addition to the interaction of the network and the salt. The

polymers are known to be dissolved in a large amount of the confined solvent, so GPEs commonly possess high mobility [1]. GPE generally made by the addition of polymer into the solution of salt (K_2CO_3) and solvent (H_2O). The ionic conductivity of GPE generally depends on the lattice energy of the salts and the dielectric constant of the host polymer [2]. The conducting salt in GPE usually offers free mobile ions that play a vital role in the conduction mechanism while the solvent supports in dissolving the salt and acts as a conducting medium where the polymer provides mechanical stability by increasing the viscosity of the electrolyte [3]. The apply conducting salt must possess a significant amount of ions (both anions and cations) and low dissociation energy so as to allow easy dissociations. Previous study reveals that electrical transport properties in GPE occur via an amorphous structure relatively than in the crystalline phase. Hence, its better to choose a polymer host that is predominantly amorphous or semi-crystalline for example polyvinyl alcohol (PVA) having an amorphous content at room temperature [4]. Moreover, PVA is a flexible and translucent material with lesser reactivity to metal-based anode, thus providing the possibility for the enhancement of electrode/electrolyte interfacial strength. These merits provide considerable motivation to transform PVA that is mainly insulating into an ionically conducting system [5].

The ionic conductivity of an electrolyte material can be understood by studying its dielectric constant. Dielectric studies of solid electrolyte offer an important understanding of the polarization influence at the electrode-electrolyte behaviour and help additional understanding of the conductivity trend [6]. The complex dielectric constant ε^* of a system is expressed as in equation (1):

$$\varepsilon^* = \varepsilon_r + \varepsilon_i \quad (1)$$

where ε_r is the dielectric constant that denotes the stored charge in a system and ε_i is the dielectric loss that denotes the loss energy to transfer ions when the polarity of electric field reverses rapidly in a system [7].

The concentration of charge carriers in GPE depend mainly on the ε_r of the host polymer and the dissociation energy of the salt. This means, the higher ε_r of the polymer and the lower dissociation energy of the salt, the higher concentration of the charge carrier or ionic species. Hence, the ionic conductivity, σ , can be written as [3]:

$$\sigma = \sum_i \eta_i q_i \mu_i \quad (2)$$

where η_i is the concentration of charge carrier, q_i is the charged electron and μ_i is the ion mobility, i denotes to the nature of the ions. It is obvious from Eq. (2) that σ can be improved by increasing the concentration of charge carrier (η_i) or the ions mobility in the system. It was reported that the concentration of charge carrier, η , depends mostly on dissociation energy (U) and ε_r of the polymer as specified by equation (3) [8]:

$$\eta = \eta_o \exp(-U/\varepsilon_r k_B T) \quad (3)$$

where k_B denotes the Boltzmann constant and T denote absolute temperature. Though, owing to the existence of the link between ε_r and η_i , an increase in ε_r might be deduced as a fractional increase in η_i . This is because ε_r is connected to the ratio of the material capacitance (C) to the capacitance of the empty cell (C_o) ($\varepsilon_r = C/C_o$) whereas the capacitance is linked to the stored charge amount ($C = Q/V$), where Q is the total charge and V is the voltage applied [8]. As specified in Eq. (2), σ relied on the sum

of charge carrier concentration (η) and the ionic mobility in the system [3]. Nevertheless, from Eq. (3), the concentration of charge carrier (η) can be increase by increasing ϵ_r . Therefore, the conductivity increases with the increase in ϵ_r based on eq. (2 and 3). The above equations designate the fact that the dielectric study is an instructive approach to explore the conductivity mechanism of GPEs[9].

The study of dielectric behaviour of GPE based on PVA-salt complex electrolytes is found to be a remarkable research area recently for ionic transport properties. The dielectric behaviour of the GPEs in this study was examined according to complex permittivity (ϵ^*), complex dielectric modulus (M^*) and dissipation factor or loss tangent ($\tan \delta$) formalisms. This study aims to investigate the vital role of dielectric behaviour on cation transport mechanism in PVA-K₂CO₃ composite materials.

2. MATERIAL AND METHODS

2.1. Materials

The PVA and potassium carbonate used in this study were purchased from Sigma-Aldrich (002008792-H), WI, USA. All the chemicals are of analytical grade and used as received. For all the experiments preparation, deionized water was used.

2.2. Preparation of PVA-K₂CO₃

The GPE of K₂CO₃ doped PVA (PVA-K₂CO₃) were synthesized by incorporating certain amount of K₂CO₃ and PVA into 20 mL of distilled water in a separate glass containers until complete dissolution as described in our previous work [10]. The PVA was used as host matrix while K₂CO₃ was used as a charge carrier provider. The two solutions were mixed and heated continuously with a constant stirring at 80 °C until homogeneous, clear and viscous solution was formed. The optimization study was conducted by changing the amount of salts while keeping the polymer constant as shown in Table 1.

Table 1. Composition and description of the synthesized gel polymer electrolytes

Designation	PVA composition (wt. %)	K ₂ CO ₃ composition (wt. %)
PK0	100	0
PK10	90	10
PK20	80	20
PK30	70	30
PK40	60	40
PK50	50	50

2.3. Characterization

X-ray diffraction (XRD) is a potential non-destructive technique for characterizing crystalline material for phase identification [11]. The crystalline phases and structure of the synthesized electrolyte were analyzed by XRD and it was conducted using Bruker D8 Advance Power diffractometer with Cu

$K\alpha$ radiation ($\lambda=1.54\text{\AA}$) for a 2θ scattering angle in the range of 0° to 100° at scanning rate $5^\circ/\text{min}$. The result was collected with a step time of 0.3 s and step of 0.03° .

2.4. Electrochemical Impedance Spectroscopy (EIS)

The Impedance Spectroscopy of the prepared electrolyte was studied using AUTOLAB/AUT51018 (potential/galvanostat) electrochemical impedance spectroscopy (EIS). A stainless steel cell blocking electrodes completely sandwiched with GPE was used for the analysis [12]. Measurements were conducted over a frequency range of 0.1 Hz to 10^5 Hz and a temperature range of 303.15 – 383.15K.

3. RESULT AND DISCUSSION

3.1. Crystal phase

The effect of K_2CO_3 on the structural arrangement of PVA was analyzed by means of XRD and the result is presented in Figure 1. Pure PVA (PK0) shows semi-crystalline nature, which could be attributed to the free hydroxyl groups in its sidechain. The result shows that pure PVA exhibit a semi-crystalline structure with a strong peak detected at 2θ angle of 11.45° , 20.0° , 22° and 39.8° which corresponds to 001, 101, 200 and 002, respectively, crystallographic plane of PVA [11, 13-14]. However, after successful incorporation of the K_2CO_3 and the formation of PVA- K_2CO_3 composites, it is visibly observed that the peak intensity of the PK0 has significantly reduced with the increase of K_2CO_3 wt.%. This reduction in peak intensity could be ascribed to the decrease in PVA crystallinity, which results from the separation of polymer chains and the restructuring of its structure. The previous study has reported that the lowering of the peak intensity in the XRD pattern shows an increase in the amorphous region of the polymer electrolyte [15]. Moreover, the disappearance of some peaks (11.45° , 22° and 39.8°) with the incorporation of K_2CO_3 designates good miscibility between PVA and the salt and a confirmation of the formation of a successful composite of PVA- K_2CO_3 [11].

Also, for the PVA- K_2CO_3 composites, the hydroxyl groups (-OH) of the PVA molecules reacted with the cations (K^+) from the K_2CO_3 species which results in a decrease in crystallinity. Therefore, it can be established that the addition of K_2CO_3 into PVA polymer matrix can enlarge the amorphous region due to the strong plasticizing effect of the salt [15]. It was reported that an increase in the amorphous region of the GPE was favourable to the local PVA chain segment motion, as this will promotes the ions migration and accordingly improving the ionic conductivities of electrolyte. Similarly, the increase in the amorphous characteristics of the PVA and the disappearance of small peaks (11.45° , 22° and 41.8°) after successful incorporation of the conducting salt was reported to accelerate the ionic transport in the polymer framework that further enhanced the conductivity of the GPE [9].

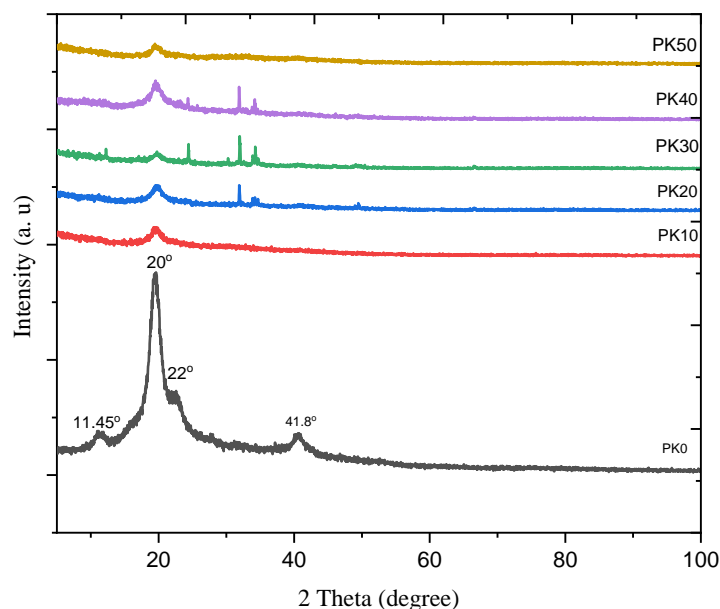


Figure 1. The XRD patterns of PVA- K_2CO_3 composites.

3.2. Dielectric studies

The ionic conductivity of an electrolyte material can be studied by ϵ_r and ϵ_i . The ϵ_r studies are necessary to understand and appreciate the conduct and performance of GPEs and other polymers electrolyte and this is because it can provide vital understandings into the polarization effect at the electrode-electrolyte interface, and assist in further understanding of the conductivity trend [6]. The ϵ_r denotes stored charges of the materials while ϵ_i represents the amount of energy loss to move ions and align dipoles when the electric field polarity reverses rapidly [16]. From the impedance measurement real and imaginary components, ϵ_r and ϵ_i were calculated following equations (4) and (5):

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

$$\epsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \quad (5)$$

where Z_i is the imaginary part of impedance, Z_r is the real part of impedance, and $\omega = 2\pi f$, where f is the frequency, $C_o = \epsilon_o A/t$ which is the vacuum capacitance of the measuring cell, where A and t denote area and separation length of the electrode. The quantity ϵ_o is the dielectric permittivity of free space that is equal to 8.854×10^{-12} F.m⁻¹ [3]. The ϵ_r implies the capacitive nature of the electrolyte material. It was reported that an increase in ionic conductivity with increase in salt wt.% could be ascribed to the higher number of dissociation and free mobile ions while the decrease in conductivity could be attributed to the ions association that leads to a generation of more non-conductive neutral ion-pairs [16]. The increase or decrease in conductivity is also in accordance with the increase or decrease in ϵ_r and ϵ_i . Figure 2 (a and b) shows the variations of ϵ_r and ϵ_i against the frequency for the synthesized GPE composites (PVA- K_2CO_3) with different weight percentages of K_2CO_3 at ambient temperature. It can be noticed that there is a change in both ϵ_r and ϵ_i with a different weight percentage of K_2CO_3 with a change in frequencies.

Both values are high and show dispersive behaviour at low frequencies owing to the polarization influence near electrodes or the accumulation of the charge carriers [17]. The increase in ϵ_r is more noticeable to the low frequencies owing to the polarization effect. Generally, it can be noticed that the ϵ_r begin to decrease at higher frequencies for all the samples. This decreased might be attributed to the lack of extra ion diffusion, and the dipole molecules in the system lack sufficient time and energy to orient themselves in the direction of the applied electric field [11]. Similarly, the reduction in dielectric permittivity with increasing frequency could be linked to the failure of dipoles in K_2CO_3 salt system to rotate quickly, leading to a lag between the frequency of oscillating dipole and that of applied filed [3].

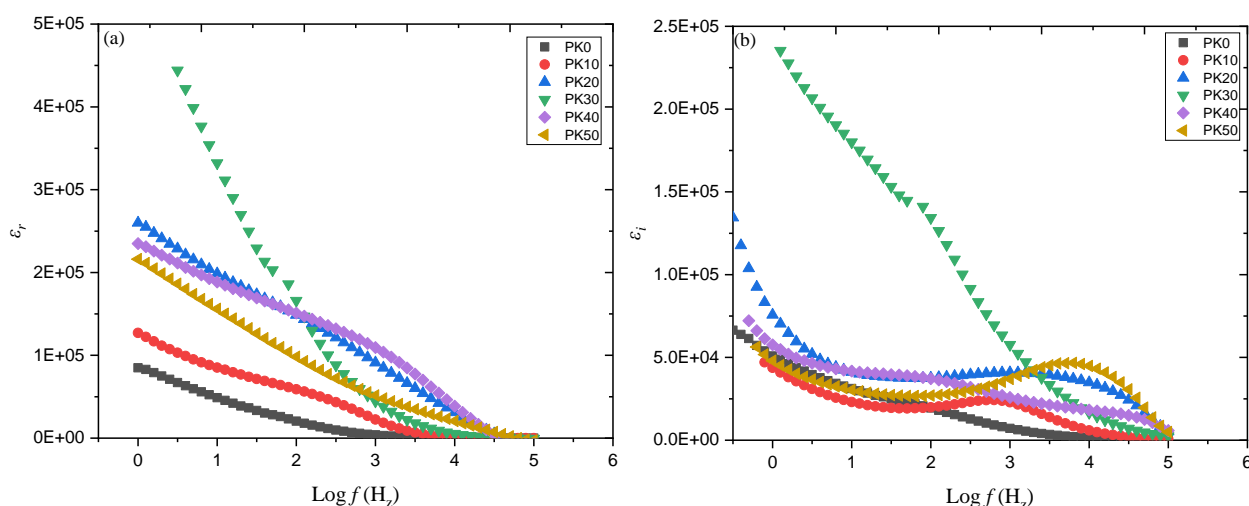


Figure 2. The plots of (a) ϵ_r and (b) ϵ_i against frequency for PVA and PVA- K_2CO_3 samples at ambient temperatures

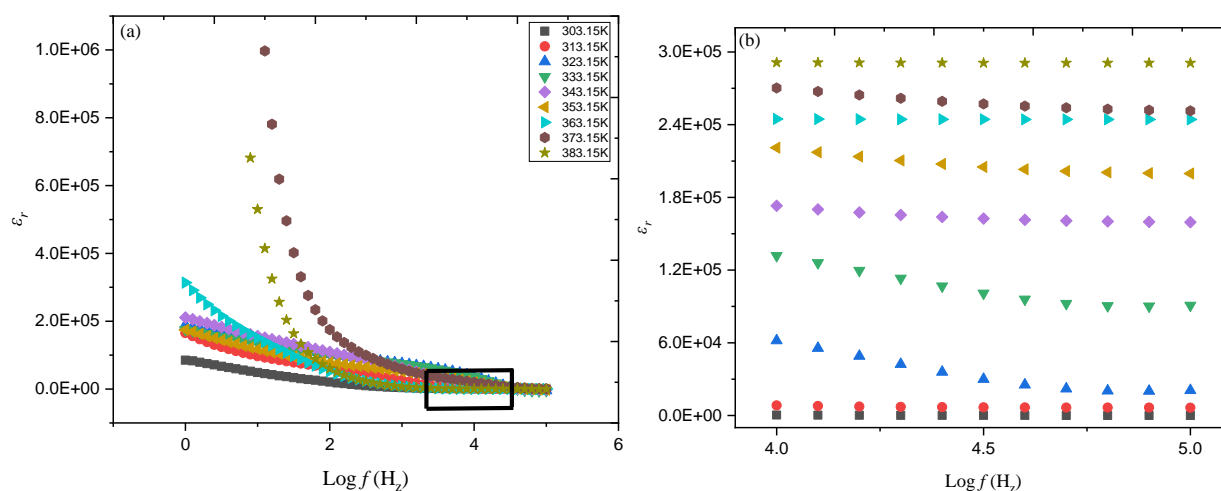
From Figure 2, it is noticed that the electrolyte containing 30 wt% K_2CO_3 (PK30) shows higher conductivity at a lower frequency, consequently, the sample with the highest ϵ_r and ϵ_i . This is because the charge starts to accumulate at the electrode surface causing the electrode polarization to occur owing to the tendency of dipoles in macromolecules to place themselves in the direction of the applied field [18]. Higher frequency causes a rapid rate of periodic reversal of the electric field that reduces the ϵ_r [16]. Similarly, it can be observed that there are no relaxation peaks in almost all the results suggesting that, increasing ϵ_r and ionic conductivity is primarily ascribed to the increasing free mobile ions in the electrolytes [16]. The study found that, as the volume of salts increased to 30 wt.%, the ϵ_r and ϵ_i values increased which could be due to the increment of charge carriers. Furthermore, the incorporation of conducting salts into the polymer matrix increases the amorphous in the polymeric fabric and consequently increased in ϵ_r and ϵ_i were observed. Moreover, as more K_2CO_3 is incorporated, more undissociated salt become ions, thus, the charge stored in the electrolyte increases that lead to increase in ϵ_r values [19]. However, when the salt amount exceeds 30 wt.%, the ϵ_r and ϵ_i values were observed to decrease. With a higher concentration of salt, re-association and recombination of ions are favourable which reduce the number density of charge carriers. A decrease in both ϵ_r and ϵ_i were observed at a higher frequency and level off at a certain level which could be ascribed to the polarization effect due to the ion accumulation

at the interface of electrode and electrolyte and hence confirming non-Debye dependence. The result in this study was found to be in agreement with the previous work earlier reported [19, 16] while working on chitosan-PEO and PMMA-PAN/KI, respectively, for EDLC application and other similar studies on GPEs.

3.3. Temperature dependence of ϵ_r and ϵ_i at selected temperatures

The use of dielectric studies to examine the conductivity behaviour of a polymer electrolyte has reached key importance, especially in GPE. Dielectric studies can be considered as a suitable way to study ion transport together with polymer segmental relaxation process [11, 20]. The complex permittivity, ϵ^* , in polymer electrolyte depends on the structural identity of the polymer electrolytes, temperature, and frequency of the applied field [21]. In this study, the effect of temperature on dielectric behaviour of the synthesized GPE from PVA- K_2CO_3 was analysed using electrolyte with the highest ϵ_r obtained in Figure 2 and the result is shown in Figure 3 (a and b). It could be noticed from the result that, both ϵ_r and ϵ_i increase sharply by the increase in temperature until 373.15 K where the highest dielectric was obtained. Such an increase could be attributed to the increase of both mobility and carrier concentration within the sample in which the movement of dipoles is simplified with the increase in temperature and thus increase in permittivity [22]. Kumar and Bhat [23] reported an increase in both ϵ_r and ϵ_i with the increase in temperatures which could be due to the increase in carrier density of the electrolyte.

Similarly, re-dissociation of ion aggregates arises at higher temperatures and hence an increase in the number of free ions. Moreover, it was reported that the increase in the ϵ_r could be characterized by the small increase in charge carrier concentration [22]. The dependence of η upon U and ϵ_r can be illustrated according to equation (3). The increase in η by the increase in temperature was reported to the effects of an increase in ionic conductivity as shown in equation (2) [3, 24]. Therefore, an increase in ϵ_r will lead to an increase in η that subsequently lead to a rise in ionic conductivity of the electrolyte.



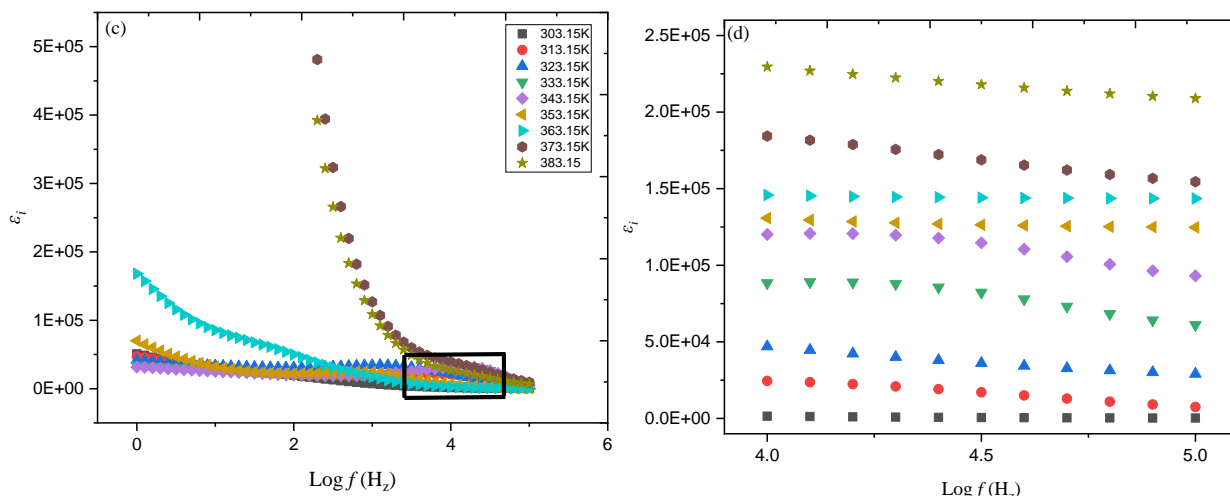


Figure 3. Temperature dependence of (a) dielectric constant (ϵ_r), (b) enlarged dielectric constant, (c) dielectric loss and (d) enlarged dielectric loss (ϵ_i) for PVA- K_2CO_3 (PK30) electrolytes at different temperatures

Furthermore, it can be observed that, ϵ_r show higher values than ϵ_i , which could be associated with the contributions of relaxation phenomenon, that is, dipole losses, conduction losses and vibrational losses [25]. The plateau of both ϵ_r and ϵ_i with respect to temperature could be ascribed to the strong and fast reversal of the electric field at higher frequencies [22]. Moreover, the higher value of ϵ_r values than that of ϵ_i at a temperature of 373.15 K, shows that greater number of ions accumulate at the electrode-electrolyte surface rather than flow through the polymer [26-27].

However, a decrease in both ϵ_r and ϵ_i was observed with further increase in temperature beyond 373.15K. The decrease in both values at higher temperature could be associated with the removal of the remaining water molecules in the polymers that have a significant effect on polymers physical properties [25, 28]. It has been reported that most proper binding sites for water molecules in polymers are the functional groups (-OH) present in the polymer [11]. Also, Ng and Mohamad [29] reported that it is particularly hard to remove the absorbed water in polymer materials without the temperature of the samples being raised to above 361 K. This process of water desorption at higher temperatures leads to the shrinking of the adhesiveness between an electrode and the electrolyte. Therefore, a further increase in temperature may damage the electrolyte and convert it into a hard material because of water desorption. Hence, the interfacial resistance at the electrolyte and electrodes increases and thus increases the resistance of the electrolyte at the higher temperatures, consequently both ϵ_r and ϵ_i drops. Previous studies observed and reported similar behaviour of decrease in both ϵ_r and ϵ_i at higher temperatures [20, 22].

Consequently, previous studies have reported that a characteristic peak of dielectric behaviour with respect to frequency and temperature has three domains: (i) low-frequency dependent domain, (ii) medium frequency, and (iii) high-frequency dependent/independent domain [30]. For instance, the frequency-dependent dielectric performance was observed for all temperatures. The charts of samples at 303.15K, 313.15K, 363.15, and 383.15K involved two different domains. At lower frequencies, there is an increase in ϵ_r with the frequency, which is associated to the electrode polarization phenomena whereas, at higher frequencies, there is a flat region associated with the frequency non-dependent domain

as shown in the enlarged image in Figure 3 (b and d) [31]. However, the charts of samples at 323.15K, 333.15K, 343.15, 353.15K and 373.15K had the third, high frequency dependent domain where ϵ_r continue to decrease. A very similar pattern was observed in ϵ_i with the exception of 383.15K where a decrease in ϵ_i was observed at the higher frequency.

3.4. Electric modulus analysis at ambient temperature

Charge transport and accumulation are issues of concern mainly for GPEs dielectrics studies like PVA that ultimately result in partial discharges. Likewise, charge buildup nearby electrode that is regularly called electrode polarization induces a huge permittivity [32]. Such electrode polarization complicates the relaxation process and makes it difficult to study its behaviour. Here, the use of M^* , which is defined as the opposite of the ϵ^* , offers significant information. M^* has been widely used to study conductivity relaxation behaviour of polymer electrolyte since it has the capacity to destroy the effects of electrode polarization to provide a perfect picture of electrical property [11]. From the ϵ^* , real (M') and imaginary (M'') modulus are calculated using the equations (6 and 7) [21, 24, 30]:

$$M^l = \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_i^2} \tag{6}$$

$$M^{ll} = \frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \tag{7}$$

Figure 4 (a and b) show the M' and M'' of the electric modulus against $\log f$ with respect to the salt content in which the graphs display a substantial decline in strength with increase in salt concentration.

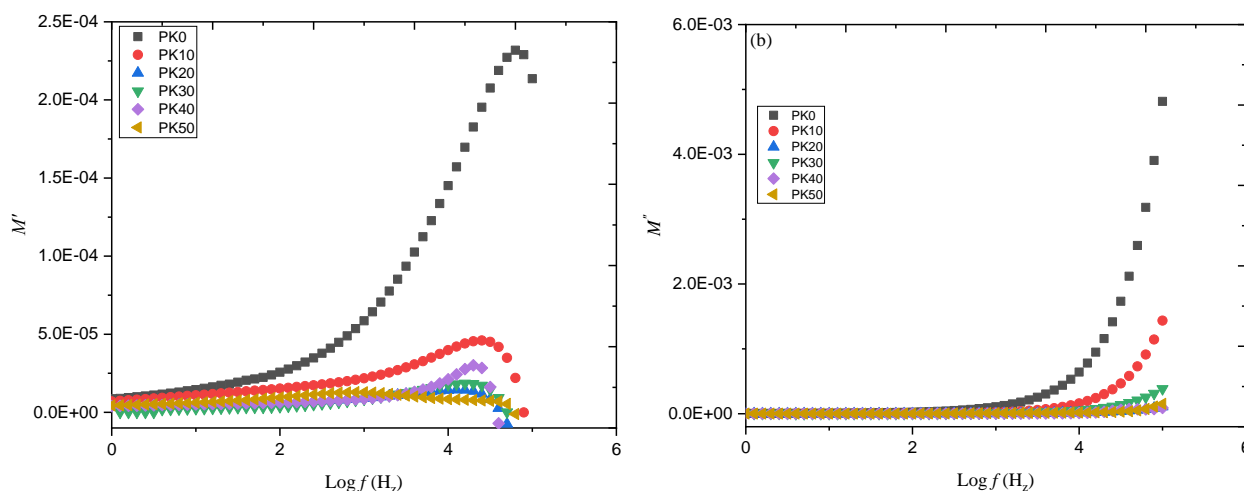


Figure 4. The plots of (a) M' and (b) M'' against frequency for PVA and PVA- K_2CO_3 samples at ambient temperatures

It can be noticed that both M' and M'' increase towards high frequencies, which is in accordance with the previous studies earlier reported [30]. The existence of the peak curve in the M' at higher frequencies suggests that the synthesized GPEs are good ionic conductors. This could be ascribed to the bulk effect of the K^+ ions and the transformation of the polymer from semi-crystalline to an amorphous form as observed in XRD results in Figure 1. Similarly, the observed small values for M' and M'' in the low-frequency region have been found to simplify and expedite the migration of ions conduction in polymer electrolyte [20].

The presence of the peak observed in the M' shown in Figure 4 could be attributed to the fact that M' in the M^* is comparable to ϵ_r in ϵ^* that is M' signifies the ability of the electrolyte to store energy [33]. However, it could be noticed that, both M' and M'' decline with lengthy extension at lower frequencies confirming that the electrode polarization phenomena make a small influence. It was reported that the occurrence of the extended train at lower frequencies is possible as a result of the good capacitance related to the electrode materials [23].

3.5. Temperature dependence of M' and M'' at selected temperatures

The previous study has reported that the use of electric modulus to study the space relaxation charge phenomena of an electrolyte material was initially introduced by Macedo [26]. The study of M^* is determined as the reciprocal of the ϵ^* and is important in electrolyte because it is used to evaluate conductivity relaxation processes of the materials.

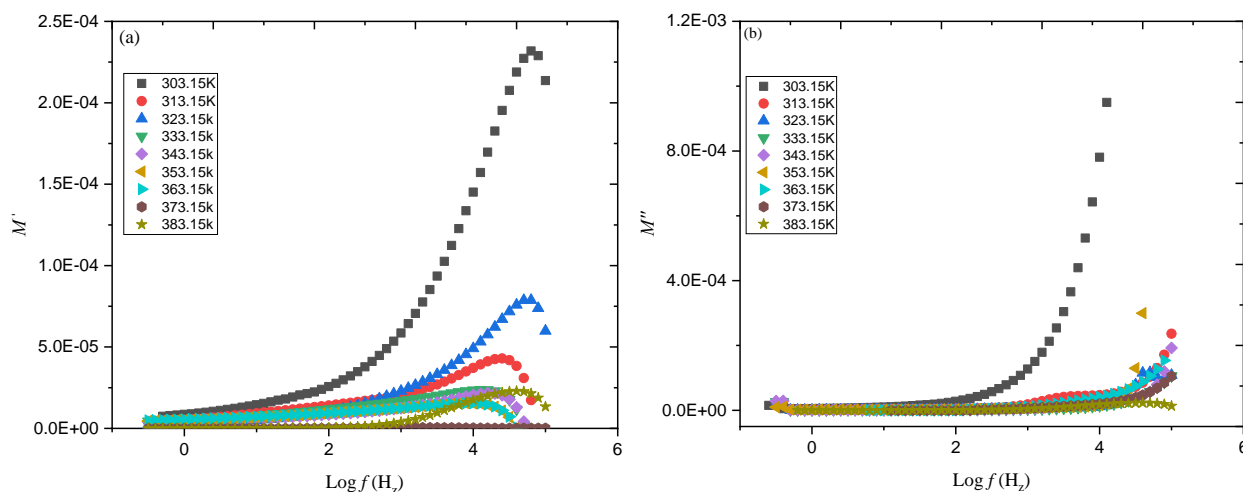


Figure 5. Temperature dependence of real (M') and imaginary part (M'') of M^* for PVA- K_2CO_3 (PK30) electrolytes at selected temperatures

To study the influence of temperature on the electric modulus behaviour of the synthesized electrolyte, different temperatures were investigated to interpret the conductivity relaxation behaviour and ionic transport mechanisms (hopping) in GPEs. The spectra of both M' and M'' using a sample with the highest ϵ_r observed in Figure 3 (PK30) is presented in Figure 5 (a and b). The result presents the M' and M'' , respectively, with respects to the frequency at different temperatures. Here, M' displays the

common trend that is similar to the previous studies in polymer electrolyte materials [23, 30, 34]. It can be observed, for each temperature, M' reached a constant value at certain frequencies. At lower frequencies, M' was observed to approach zero, which confirmed the presence of a considerable electrode or ionic polarization in the investigated temperature range. The small value of M' at lower frequencies shows the removal of electrode polarization, which could be ascribed to the amount of capacitance related to the effect of electrode polarization because of a buildup of charge carriers at the interface of electrode-electrolyte [28].

The value of M' increased with the increased in frequency and reached a maximum value at higher frequencies for all the temperatures range measured, which is due to the relaxation processes over a range of frequencies and polymer segmental motion [28, 35-36]. Moreover, the decrease in M' with further increase in temperature comes from the movement of the polymer segments and the carrier charges. It was reported that the alignment of the carrier charges and molecular dipoles turn out to be easier at high temperatures, hence a decrease in M' was observed [37].

3.6. Loss tangent ($\tan \delta$) at ambient temperature

The study of dielectric properties of polymer electrolyte is very crucial in gathering information about the distribution of relaxation time that is associated with jumping probability per unit time of carrier charges. Previous study reported that the dielectric features of the electrolyte can also be analyzed by $\tan \delta$ with changing temperature and frequencies [24]. This allows resolving the spatial relaxation process such as dipole reorientation owing to the long-range electric conductivity. The $\tan \delta$ similarly called dissipation factor can be defined as the ratio of loss energy (ε_i) to the stored energy (ε_r) in a periodical field. The $\tan \delta$ value was calculated using equation (8). [30]

$$\tan \delta = \frac{\varepsilon_i}{\varepsilon_r} \quad (8)$$

Figure 6 shows the variants of $\tan \delta$ with respect to the logarithm of the frequency for PVA- K_2CO_3 at different salt concentrations. The result shows that the peaks of $\tan \delta$ increased with increasing K_2CO_3 in the high-frequency region to a maximum value, which represents the relaxation peak. The increase in the $\tan \delta$ peak can be attributed to the existence of the free K^+ ions from the K_2CO_3 that contributed to the relaxation process [38]. Moreover, the increase of $\tan \delta$ with the increase in the concentration of K_2CO_3 could be ascribed to the increase in the charge carriers' concentration, which reduced the resistivity of the electrolytes [33, 37]. However, a decrease in the value of $\tan \delta$ was observed with the increase in conducting salt beyond 30 wt.% and this can be ascribed to the buildup and agglomeration of carrier charges in PVA- K_2CO_3 composites [22]. Similarly, it was reported that large quantity of ions in GPE makes the ions pairs to aggregates which result in blocking conducting pathway and obstruct the ions from transportation which can lead to a decrease in the concentration of mobile ions that subsequently leads to a decrease in stored energy or $\tan \delta$ [39]. The decrease in $\tan \delta$ at higher wt.% salt concentration could be ascribed to the reduction in free ions due to formation of ion-ion pairing [19].

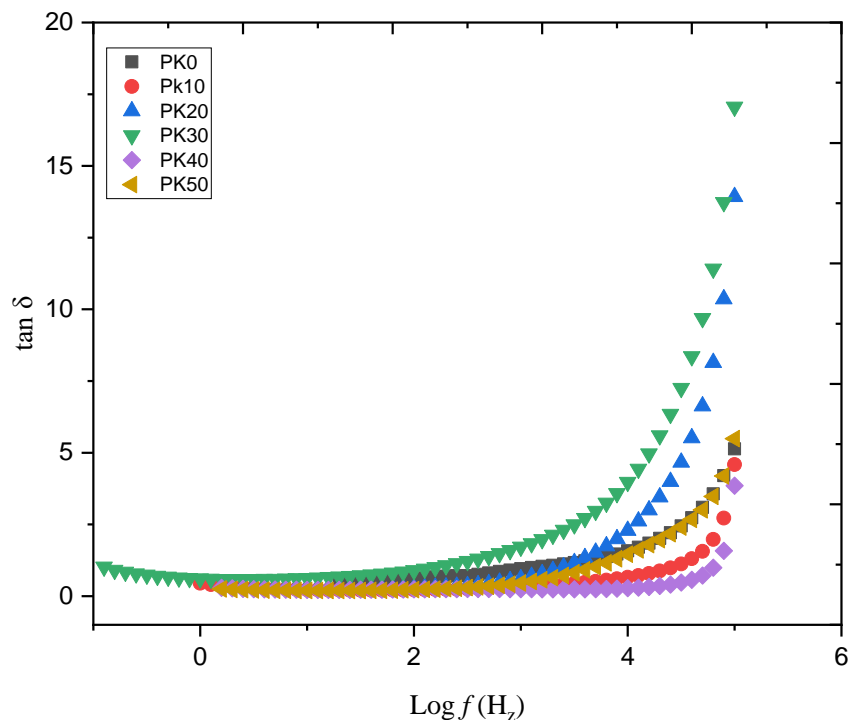


Figure 6. Variation of $\tan \delta$ with frequency for PVA-K₂CO₃ at a different salt concentration at ambient temperature

3.7. Loss tangent ($\tan \delta$) at selected temperatures

Figure 7 shows the graph of $\tan \delta$ versus frequency for electrolyte with 30 wt.% K₂CO₃ (PK30) at various temperatures. Trends observed show that the $\tan \delta$ peaks intensity increases with an increase in conductivity at a higher temperature, which indicates that the charge carriers are thermally activated via hopping mechanism [36]. The previous study has reported that, with the increase in temperature, the charge carrier from the ions have been thermally activated and the $\tan \delta$ peak will move to a higher frequency region. The shift of the maximum value of $\tan \delta$ towards higher frequencies with the increase in temperatures shows a decrease in the value of relaxation time as well as indicating a dielectric relaxation [40]. Dave and Kanchan [24] similarly observed an increase in $\tan \delta$ value with the increase in temperature in which they associated it to the resistive losses in the electrolyte material. Shifting of the peak frequencies in the forward direction with temperature indicates that as the temperature increases the relaxation time decreases [41]. However, it can be observed from the plots that, $\tan \delta$ value decreases at higher temperatures and this could be linked to the ion jumping and loss of conduction of ions that is accompanied with polarization losses [30].

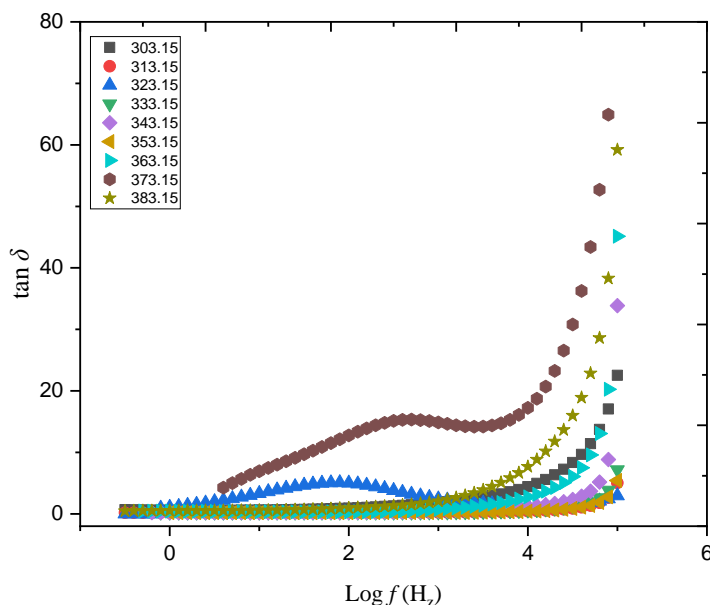


Figure 7. Variation of $\tan \delta$ with frequency for PVA- K_2CO_3 (PK30) at different temperatures

4. CONCLUSION

The electrochemical properties of a newly synthesized GPE based on PVA- K_2CO_3 have been studied to understand the carrier transport behaviour of the electrolyte. The XRD results confirmed that the semi-crystalline nature of PVA is affected significantly by the successful incorporation of K_2CO_3 due to the strong plasticizing effect of the conducting salt. The dielectric studies indicate the high capacitive nature and nonexistence of any relaxation process in the synthesized electrolyte. The increase in temperature displayed an increase in both dielectric constant and dielectric loss at a given frequency due to the fractional increase in the number of charge carrier concentration. Similarly, the dielectric behaviour of the synthesized electrolytes displayed a strong dependence on the frequency and the amounts of K_2CO_3 . It can be observed that $\tan \delta$ increases with the frequency increase until it reached a maximum value and afterwards decreases which is ascribed to the increase in a number of carrier charges for conduction that lead to a decrease in the resistivity of the electrolytes. Based on the asymmetrical peak shape of ϵ_r , ϵ_i , M_r , M_i and $\tan \delta$, the non-Debye type relaxation is predicted. Therefore, it can be concluded that dielectric studies is a great way to study the dielectric relaxation and charge transport mechanism of electrolyte materials.

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