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Electrical analysis of amorphous corn starch-based polymer electrolyte membranes doped with LiI

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Abstract

In this work, polymer electrolytes have been prepared by doping starch with lithium iodide (LiI). The incorporation of 30 wt% LiI optimizes the room temperature conductivity of the electrolyte at \((1.83 \pm 0.47) \times 10^{-4} \text{ S cm}^{-1}\). Further conductivity enhancement to \((9.56 \pm 1.19) \times 10^{-4} \text{ S cm}^{-1}\) is obtained with the addition of 30 wt% glycerol. X-ray diffraction analysis indicates that the conductivity enhancement is due to the increase in amorphous content. The activation energy, \(E_a\), of 70 wt% starch–30 wt% LiI electrolyte is 0.26 eV, while 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte exhibits an \(E_a\) of 0.16 eV. Dielectric studies show that all the electrolytes obey non-Debye behavior. The power law exponent \(s\) is obtained from the variation of dielectric loss, \(\varepsilon_i\), with frequency at different temperatures. The conduction mechanism of 70 wt% starch–30 wt% LiI electrolyte can be explained by the correlated barrier hopping model, while the conduction mechanism for 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte can be represented by the quantum mechanical tunneling model.

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1. Introduction

Since Wright [1] and Armand et al [2] reported the ionic conductivity of polymer–alkali metal salt electrolytes, huge attention has been paid to polymer electrolytes as the alternative to liquid electrolytes in solid-state devices. Solid polymer electrolytes (SPEs) offer advantages such as satisfactory mechanical properties, ease of fabrication as thin films of desirable size and good contact with electrode materials [3]. A number of polymers have been studied as polymer hosts in SPEs, such as poly(ethylene oxide) (PEO) [4], poly(vinyl alcohol) (PVA) [5], poly(vinyl chloride) [6] and poly(acrylonitrile) [7]. Over the past few years, researchers have been working in the development of natural polymers due to their renewable, sustainable and biodegradable properties [8–11]. Many natural polymers have been extensively studied as polymer hosts in electrolytes, such as chitosan [12, 13], cellulose with its derivative [14, 15] and starch [16]. Starch is a low-cost, renewable agro-resource made up of amylose and amylopectin polysaccharides [17]. It is a major material in industries such as coatings and sizing in paper, textiles and carpets [18, 19]. However, starch is hydrophilic and can form film with poor mechanical properties [20]. Using acetic acid as the solvent can improve the mechanical properties of starch as well as increase the hydrophobicity [21, 22]. It is reported that when starch reacts with an acid, the water solubility of the starch granules is enhanced [23]. Starch-based electrolytes doped with ammonium nitrate (NH\(_4\)NO\(_3\)) achieved a conductivity of \(2.83 \times 10^{-5} \text{ S cm}^{-1}\) at room temperature [24]. The conductivity of starch–ammonium iodide (NH\(_4\)I) electrolyte at room temperature is reported to be \(2.4 \times 10^{-4} \text{ S cm}^{-1}\) [25]. Both starch–lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and starch–lithium hexafluorophosphate (LiPF\(_6\)) exhibited a conductivity of \(\sim 10^{-7} \text{ S cm}^{-1}\) at ambient temperature [16, 26].
Since the conductivity of SPEs is lower than that of liquid electrolytes, various techniques have been employed to enhance the conductivity of SPEs, such as polymer blending [27], addition of ceramic fillers [28], copolymerization [29] and plasticization [30]. The addition of plasticizers such as ethylene carbonate, propylene carbonate, poly(ethylene glycol) and dimethyl carbonate can increase the amorphous content of the polymer, dissociate ion aggregates and lower the glass transition temperature $T_g$ of the electrolytes [31]. In this work, starch polymer electrolytes doped with lithium iodide (LiI) and plasticized with glycerol were prepared and characterized. LiI is an exciting salt for its high-temperature operation and battery application [32].

2. Experiment

LiI (Aldrich) was heated in a vacuum oven at 130°C for 2 h to eliminate traces of water [33]. For sample preparation, 2 g of corn starch (Brown and Polson) was dissolved in 50 ml of 1% acetic acid (SYSTERM) and heated at 80°C for 20 min. After the solutions cooled to room temperature, different concentrations of LiI were added to the solutions to prepare the starch–LiI (salted) system. Different amounts of glycerol (SYSTERM) were then added to the highest conducting salted electrolyte solutions for the preparation of the starch–LiI–glycerol (plasticized) system. All solutions were stirred until they become homogeneous. All homogeneous solutions were cast into different plastic Petri dishes and left to dry at room temperature to form electrolyte membranes. The samples were kept in a desiccator filled with silica gel desiccants for further drying.

In order to study the complexation between the electrolyte components, Fourier transform infrared (FTIR) spectroscopy was recorded using a Spotlight 400 Perkin–Elmer spectrometer in the wavenumber range of 450–4000 cm$^{-1}$.

Impedance measurements were conducted using a HIOKI 3532-50 LCR Hi-tester from room temperature to 353 K in the frequency range of 50 Hz–5 MHz. The electrolytes were sandwiched between two stainless steel electrodes of a conductivity holder. The impedance measurements were conducted in a vacuum oven. The values of bulk resistance $R_0$ of the electrolytes were determined from the Nyquist plots obtained. Conductivity $\sigma$ was calculated using

$$\sigma = \frac{l}{R_0 A},$$

where $l$ is the thickness of the electrolyte and $A$ is the electrode–electrolyte contact area. The impedance measurement on each electrolyte sample was done at least five times and the average value was considered for the calculation of the conductivity value.

X-ray diffraction (XRD) measurements were carried out using a Siemens D5000 x-ray diffractometer where x-rays of 1.5406 Å wavelength were generated by a CuKα source. The 2θ angle varied from 5° to 80°. The angle $\theta$ between the incident beam and the normal to the film will change as the sample rotates. When the Bragg condition is fulfilled as denoted by equation (2), x-ray beams will be reflected to the detector [34]:

$$2d \sin \theta = n \lambda.$$

Figure 1. FTIR spectra for (i) pure starch powder and (ii) pure starch film in the region of 3000–3600 cm$^{-1}$.

Here $d$ is the interplanar spacing, $\theta$ is the Bragg angle, $n$ is the order of reflection and $\lambda$ is the x-ray wavelength.

3. Results and discussion

The hydroxyl band in the spectrum of pure starch powder appears at 3290 cm$^{-1}$ as shown in figure 1(i). The hydroxyl band in the spectrum of pure starch film shown in figure 1(ii) has shifted to 3280 cm$^{-1}$. Kadir et al [35] reported that the hydroxyl band in the spectrum of pure PVA powder has shifted from 3354 to 3343 cm$^{-1}$ in the spectrum of pure PVA film. The authors claim that the result indicates the occurrence of interaction between polymer and the acetic acid solvent, which is relevant to our result. The strong and wide absorption in the hydroxyl band region of pure starch film indicates that there are several $-\text{OH}$ groups in starch [36].

Figure 2(a) shows the FTIR spectra of selected samples in the salted system in the hydroxyl band region. The hydroxyl band in the spectrum of pure starch film in figure 2(a)(i) shifts from 3280 to 3297 cm$^{-1}$ in the presence of 5 wt% LiI in figure 2(a)(ii). On addition of 30 wt% LiI, the hydroxyl band has shifted to 3341 cm$^{-1}$ in figure 2(a)(vi) and further shifted to 3351 cm$^{-1}$ with the addition of 40 wt% LiI in figure 2(a)(viii). Ramesh et al [16] reported that the hydroxyl band of native corn starch experiences an upward shift from 3402 to 3415 cm$^{-1}$ in the presence of LiPF$_6$. Ahad et al [37] also observed that the increasing sodium salicylate content to the PVA-based polymer electrolyte has shifted the hydroxyl band of pure PVA to higher wavenumbers. The FTIR spectra of selected samples in salted systems in the region of 2850–2970 cm$^{-1}$ are shown in figure 2(b). A peak that is assigned to the C–H stretching mode of starch appears at 2926 cm$^{-1}$ in the spectrum of pure starch film in figure 2(b)(i). The increasing LiI content has shifted the peak to higher wavenumber. From figure 2(b)(vi), on addition of 30 wt% LiI, the peak has shifted to 2933 cm$^{-1}$ and further
shifted to 2934 cm\(^{-1}\) with the addition of 35 wt% LiI in figure 2(b)(vii). Ramesh et al [16] reported that the C–H stretching mode of starch is shifted from 2923 to 2931 cm\(^{-1}\) with the addition of LiPF\(_6\), which is comparable with this work. From figure 2(c)(i), a peak appears at 1078 cm\(^{-1}\) in the spectrum of pure starch film. A report by Ning et al [38] shows that a peak at 1080 cm\(^{-1}\) in the spectrum of starch film can be attributed to C–O bond stretching of the C–O–C group in starch. Their result is almost similar to this work. In figure 2(c)(ii), with the addition of 15 wt% LiI the peak shifted to 1077 cm\(^{-1}\). Further shifting can be observed with increasing salt content. On addition of 40 wt% LiI, the peak is located at 1074 cm\(^{-1}\). According to Ramesh et al [16], Li\(^{+}\) cations interact with oxygen atoms in the C–O–C group. All these results concluded that starch has interacted with Li salt in this work.

Figure 3(a) shows the FTIR spectra for the plasticized system in the region of 3000–3600 cm\(^{-1}\). As shown earlier, the hydroxyl band in the spectrum of 70 wt% starch–30 wt% LiI–0 wt% glycerol film appears at 3341 cm\(^{-1}\) in figure 3(a)(i). Due to its multi-hydroxyl moiety structure, glycerol possesses the strong ability to interact with the polysaccharide matrix through hydrogen bonding interactions [39]. This fact is evidenced by the shifting of the hydroxyl band to lower wavenumbers as the glycerol content increases toward 35 wt%, where the hydroxyl band appears at 3319 cm\(^{-1}\) as shown in figure 3(a)(viii). This result implied that the addition of glycerol promotes the hydrogen bonding interactions between the electrolyte components. Liu et al [40] reported that the hydroxyl band of starch–chitosan film containing 5 wt% glycerol appears at 3339.57 cm\(^{-1}\). On addition of 10 wt% glycerol, the authors reported that the hydroxyl band has shifted to a lower wavenumber of 3336.82 cm\(^{-1}\) [40]. According to the authors, as the glycerol concentration increases, more –OH groups are available for polymer–glycerol interactions, which in turn shift the hydroxyl band to lower wavenumbers [40]. Figure 3(b) shows the FTIR spectra for the selected samples in the plasticized system in the region of 955–1055 cm\(^{-1}\). The peak observed at 1015 cm\(^{-1}\) in the spectrum of 70 wt% starch–30 wt% LiI film in figure 3(b)(i) could be associated with C–O–H bond vibration or solvation [41, 42]. According to Vicentini et al [42], the band at around 1015 cm\(^{-1}\) in the starch spectrum is characteristic of amorphous material. As the glycerol content increases to 35 wt%, the peak shifts to a higher wavenumber of 1022 cm\(^{-1}\) as shown in figure 3(b)(vi). Bergo et al [41] also observed that the peak at 1011.8 cm\(^{-1}\) in the spectrum of unplasticized starch film has shifted to higher wavenumbers with the increase in glycerol content.

The room temperature conductivity for the salted system is depicted in figure 4(a). Pure starch film has a low conductivity value of (1.59 ± 0.48) × 10\(^{-9}\) S cm\(^{-1}\). The addition of 30 wt% LiI increases the conductivity of the electrolyte up to (1.83 ± 0.47) × 10\(^{-4}\) S cm\(^{-1}\). Yang et al [43] showed that PEO–LiI and poly(vinylidene fluoride)–LiI electrolytes can yield conductivity values of ∼10\(^{-4}\) S cm\(^{-1}\).
for LiI concentrations lower than 35 wt%, which is quite comparable with this work. The addition of more than 30 wt% LiI decreases the conductivity value. The existence of ions as the charge carriers in the electrolyte has made the electrolyte more conductive. As more salt is added, more ions are provided that increase the number density of charge carriers, thus increasing the conductivity of the electrolyte. However, too many ions provided increases the possibility of ion association to become a neutral ion pair, which does not contribute toward ion conduction resulting in a decrement of conductivity value as shown in figure 4(a). Different amounts of glycerol (5–35 wt%) were added to the highest conducting electrolyte in the salted system in order to enhance the conductivity. From figure 4(b), the conductivity increases up to (9.56 ± 1.19) × 10⁻⁴ S cm⁻¹ with addition of 30 wt% glycerol. Pawlicka et al. [44] reported a conductivity value of ~10⁻⁵ S cm⁻¹ for the starch–LiClO₄–glycerol system at room temperature. A comparative study by Rahman et al. [45] showed that the conductivity decreases when the size of the anion increases due to the reduced mobility of the ions. The size of the I⁻ ion (radius = 0.211 nm) is smaller than the size of the ClO₄⁻ ion (radius = 0.225 nm), which results in a higher conductivity value for this work compared with the work by Pawlicka et al. [44]. Plasticization using glycerol seems to create more pathways for lithium ion conduction leading to conductivity enhancement [44]. However, the addition of more than 30 wt% glycerol decreases the conductivity value. This phenomenon may be caused by the displacement of the host polymer by plasticizer molecules within the salt complexes [46]. The formation of linkages between the plasticizer causes the salt to recrystallize, resulting in a conductivity decrement [47].

The XRD patterns for selected electrolyte samples in salted and plasticized systems are shown in figures 5(a) and (b), respectively. From figure 5(a), the full width at half maximum (FWHM) of the XRD hump become broader as the salt content in the electrolyte increases up to 30 wt%, figure 5(a)(iv). As ion concentrations in the electrolyte increase, both the fraction of amorphous phase and charge carriers increase simultaneously [48]. It was reported that ions are favorably mobile in the amorphous phase since their motion is assisted by polymer segmental motion [49–51]. These results explain the increasing conductivity value with increasing salt content up to 30 wt%. From figure 4(a), the conductivity decreases with addition of more than 30 wt% LiI. From the XRD diffractogram of 65 wt% starch–35 wt% LiI electrolyte in figure 5(a)(v), the FWHM of the XRD hump becomes narrower than that of 70 wt% starch–30 wt% LiI electrolyte, implying that the amorphous phase in the electrolyte decreases. The conductivity enhancement due to plasticization can also be explained by the XRD patterns as shown in figure 5(b). The addition of glycerol as a plasticizer promotes ion dissociation [52]. This is because the plasticizer has a high dielectric constant that can weaken the Coulombic force between the anion and cation of the salt so that the salt can be easily dissociated, thus increasing the ion concentration and the amorphous phase within the electrolyte [31]. The FWHM of the XRD hump in the x-ray diffractogram of the 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte is the broadest, indicating the highest amorphous content in the electrolyte. Dragunski and Pawlicka [53] reported that the crystalline peaks in the x-ray diffractogram of pure amylopectin-rich starch are absent in the diffractogram of starch–LiClO₄–glycerol complexes, confirming the amorphous structure of the electrolytes. Their observation is almost similar to that of this work. From figure 5(b)(iv), the FWHM of the XRD hump of 45.5 wt% starch–19.5 wt% LiI–35 wt% glycerol electrolyte is narrower than that of 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte, which implies that the amorphous content in the electrolyte decreases leading to a conductivity decrement.

The variation of conductivity with temperature for 70 wt% starch–30 wt% LiI and 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolytes is shown in figure 6. The conductivity of both electrolytes is observed to be increased with an increase in temperature. From the conductivity–temperature relationship, both electrolytes obeyed the Arrhenius rule. It can be assumed that the nature of the cation, in this case Li⁺, transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites [54]. The Arrhenian conductivity–temperature relationship has been observed for systems of starch–LiClO₄–glycerol [53], starch–LiPF₆ [55] and PEO–LiI [56]. The activation energies, $E_a$, of 70 wt%
Figure 4. Effect of (a) LiI concentration and (b) glycerol concentration on conductivity at room temperature.

Figure 5. (a) X-ray diffractograms for (i) pure starch film, (ii) 95 wt% starch–5 wt% LiI, (iii) 85 wt% starch–15 wt% LiI, (iv) 70 wt% starch–30 wt% LiI and (v) 60 wt% starch–40 wt% LiI electrolytes. (b) X-ray diffractograms for (i) 70 wt% starch–30 wt% LiI–0 wt% glycerol, (ii) 52.5 wt% starch–22.5 wt% LiI–25 wt% glycerol, (iii) 49 wt% starch–21 wt% LiI–30 wt% glycerol and (iv) 45.5 wt% starch–19.5 wt% LiI–35 wt% glycerol electrolytes.

Figure 6. Effect of temperature on conductivity for (a) 70 wt% starch–30 wt% LiI electrolyte and (b) 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte.

The conductivity, \( \sigma \), of the electrolytes is given by

\[
\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right),
\]

where \( \sigma_0 \) is the pre-exponential factor, \( k \) is the Boltzmann constant and \( T \) is the temperature. \( E_a \) is the energy required for an ion to migrate from one site to another. From the Anderson–Stuart model \[57, \] \( E_a \) is the sum of the binding energy of the ion to its site and the kinetic energy for migration. If the energy of the ion is only sufficient to overcome the binding energy, the ion will be dislocated from its site but will still remain at the same location. If it has more energy than the binding energy, the ion will be free to move \[58]. The 70 wt% starch–30 wt% LiI electrolyte has an \( E_a \) value of 0.26 eV, while the 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte has an \( E_a \) value of 0.16 eV. This result indicates that the higher conducting electrolyte requires only a small amount of energy to start a migration process. The low \( E_a \) value of the 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte is due to its amorphous nature, as observed from figure 5(b), that facilitates fast ion movement in the polymer network.

The complex dielectric \( \varepsilon^* \) of a system is expressed as

\[
\varepsilon^* = \varepsilon_r - i \varepsilon_i,
\]

where \( \varepsilon_r \) is the dielectric constant and \( \varepsilon_i \) is the dielectric loss. From the impedance measurements, \( \varepsilon_r \) and \( \varepsilon_i \) were calculated.
using the following equations:

\[ \varepsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \]  \hspace{1cm} (5)

\[ \varepsilon_i = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \]  \hspace{1cm} (6)

Here, \( C_0 = \varepsilon_0 A/l \) and \( \omega = 2\pi f \). \( \varepsilon_0 \) is the permittivity of free space, \( f \) is the frequency, \( Z_i \) is the imaginary part of impedance and \( Z_r \) is the real part of impedance. A study on the dielectric behavior of the polymer electrolyte helps us understand the polarization effect at the electrode–electrolyte interface [59]. \( \varepsilon_r \) is a measure of the material’s stored charge, while \( \varepsilon_i \) represents the amount of energy loss to move ions.

From figure 7(a), the \( \varepsilon_r \) value of 70 wt% starch–30 wt% LiI electrolyte is the highest in the salted system, reminding one that the electrolyte contains more charges. At 30 wt% salt concentrations, the conductivity is maximum as depicted in figure 4(a). Aziz et al [60] reported that the dielectric constant result is in agreement with the increment of the conductivity for their phthaloyl chitosan–ammonium thiocyanate (NH\(_4\)SCN) electrolyte system. When glycerol is added to the electrolyte as shown in figure 7(b), the ion dissociation rate is higher compared to the ion association rate that led toward conductivity enhancement. As reported by Ramesh et al [54], the plasticized electrolyte with a higher conductivity value shows a much higher \( \varepsilon_r \) value. The trend of \( \varepsilon_i \), figure 8, is also similar to \( \varepsilon_r \). As the polarity of ac stimulus reverses, both ion translational diffusion and dipole orientation undergo a process of deceleration, stop and acceleration in the reverse direction. This polarization generates heat through internal friction, which is produced when the ions overcome the opposition that they encounter, and thus causes energy loss. The amount of energy dissipation and phase shift relative to the incident electric field are reflected directly in \( \varepsilon_i \) [59]. At the low-frequency region, the high value of \( \varepsilon_r \) and \( \varepsilon_i \) is attributable to dielectric polarization. Under the influence of an electric field, ions tend to diffuse and migrate along the field appropriately. Since ions are not transparent to the stainless steel electrodes, they accumulate at the electrode–electrolyte interface, becoming localized, and form a heterocharge layer [59, 61]. Assuming that the thickness of the electrolyte is greater than that of the heterocharge layer, the charge density increases rapidly leading to electrode polarization [62]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of \( \varepsilon_r \) and \( \varepsilon_i \) [63]. The decrease in \( \varepsilon_r \) and \( \varepsilon_i \) with increasing frequency implies that the systems are non-Debye type.

The ac conductivity, \( \sigma_{ac} \), can be obtained using

\[ \sigma_{ac} = \varepsilon_0 \varepsilon_r \tan \delta. \]  \hspace{1cm} (7)

Here, \( \tan \delta \) is the loss tangent. Substituting \( \varepsilon_r \tan \delta = \varepsilon_i \),

\[ \sigma_{ac} = \varepsilon_0 \varepsilon_i \omega. \]  \hspace{1cm} (8)
The total conductivity, $\sigma(\omega)$, is the sum of $\sigma_{ac}$ and dc conductivity, $\sigma_{dc}$:

$$\sigma(\omega) = \sigma_{ac} + \sigma_{dc}. \quad (9)$$

Generally, the phenomenon of $\sigma_{dc}$ can be analyzed using Jonscher’s universal power law [64, 65]:

$$\sigma(\omega) = A\omega^s + \sigma_{dc}, \quad (10)$$

where $A$ is a temperature-dependent parameter, $s$ is the power law exponent and $\sigma_{dc} = A\omega^0$. The value of $s$ can be evaluated from the following relation:

$$\ln \varepsilon_i = \ln \frac{A}{\varepsilon_0} + (s - 1) \ln \omega. \quad (11)$$

The frequency dependence of $\varepsilon_i$ at various temperatures at the high-frequency region for 70 wt% starch–30 wt% LiI and 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolytes is shown in figures 9(a) and (b), respectively. The slopes of $\ln \varepsilon_i$ versus $\ln \omega$ are used to obtain the value of exponent $s$ at each temperature. In this work, the acceptable frequency range is $12.1 < \ln \omega < 12.5$. This is because no or minimal polarization of the electrode occurs at the high-frequency region [58]. As mentioned earlier, at the higher-frequency region most of the ions are static as the periodic reversal of the electric field occurs so fast, hence decreasing the electrode polarization. There are several reports which suggest that the acceptable frequency range is outside the electrode polarization region [58, 66, 67].

The temperature dependence of exponent $s$ can be related to the conduction mechanism of a system based on several theoretical models. According to the correlated barrier hopping (CBH) model, the $s$ value increases toward unity as $T \to 0$ K [68]. The quantum mechanical tunneling (QMT) model predicts that the exponent $s$ is temperature independent [69]. In the overlapping large-polaron tunneling model, $s$ decreases with increasing temperature, exhibits a minimum at a certain temperature and begins to increase with a further increment of temperature [68, 70]. The small-polaron hopping model states that $s$ increases with increasing temperature [58]. The plots of $s$ versus $T$ for 70 wt% starch–30 wt% LiI and 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolytes are shown in figure 10.

For 70 wt% starch–30 wt% LiI electrolyte, the decrease in $s$ with increasing temperature implies that the conduction mechanism of the electrolyte follows the CBH model. The plot can be fitted by the equation $s = -0.0023T + 0.9297$, where as $T \to 0$ K, the exponent $s$ approaches $\sim 1$. Buraidah et al [58] reported that the conduction mechanism for chitosan–NH$_2$I occurs by way of a CBH model in which the plot of exponent $s$ against $T$ can be fitted to the equation $s = -0.0023T + 1.0281$. Their result is comparable with that of this work. In this model, the ions reside in a potential well. The ions are assumed to be surrounded by several potentials such as the Coulombic repulsive potential between the ions and the potential well. The ions can hop from one site to another after acquiring enough energy. The ions may hop back to the initial site or there is the formation of a new absolute potential with an increase in the back-hop barrier height and the ions continue to move in the forward direction [58]. The hops are thermally activated. The $s$ value is constant with increasing temperature for 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte. Hence the conduction mechanism of 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte follows the QMT model. According to Psaras [71], ionic hopping from one site to a neighboring site occurs not just by jumping over a potential barrier but can also be accompanied by QMT. In this work, the plot of $s$ versus temperature can be fitted by the equation.

![Figure 9](image9.png)

Figure 9. $\ln \varepsilon_i$ versus $\ln \omega$ from 298 to 353 K for (a) 70 wt% starch–30 wt% LiI electrolyte and (b) 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte.

![Figure 10](image10.png)

Figure 10. Plots of exponent $s$ versus temperature for (a) 70 wt% starch–30 wt% LiI electrolyte and (b) 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte.
\( s = 0.000057 + 0.0756 \). The small gradient value implies that \( s \) is almost independent of temperature, implying that ionic conduction is also accompanied by QMT. A report by Buraidah and Arof [72] shows that the conduction mechanism for chitosan–PVA–NH\(_4\)I follows the QMT model and the plot of \( s \) versus temperature can be fitted by the equation \( s = 0.000047 + 0.1256 \). Their result is almost similar to that of this work.

4. Conclusion

Starch–LiI and starch–LiI–glycerol electrolyte systems were prepared by the solution cast technique. FTIR analysis proved the interaction of starch–LiI and starch–LiI–glycerol. The conductivity analysis shows that 70 wt% starch–30 wt% LiI electrolyte obtains a maximum conductivity of (1.83 ± 0.47) \( \times 10^{-4} \) S cm\(^{-1} \) for the salted system, while a maximum conductivity of (9.56 ± 1.19) \( \times 10^{-4} \) S cm\(^{-1} \) is achieved for 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte in the plasticized system. XRD results prove that the increasing conductivity is due to the increase of amorphous content in the electrolyte. The \( E_f \) values for 70 wt% starch–30 wt% LiI electrolyte and 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte are 0.26 and 0.16 eV, respectively, implying that lower energy is required for ionic conduction for the higher-conducting electrolyte. Dielectric analysis for both the salted and plasticized systems shows that the \( \varepsilon_\infty \) and \( \varepsilon_1 \) values decrease with increasing frequency, indicating that all electrolytes in this work are non-Debye type. The conduction mechanism for 70 wt% starch–30 wt% LiI electrolyte can be explained by the CBH model, while 49 wt% starch–21 wt% LiI–30 wt% glycerol electrolyte follows the QMT model.

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