Conductivity and transport properties of starch/glycerin-MgSO₄ solid polymer electrolytes

Mohd Faiz Hassan *, Nur Syazwan Nor Azimi

Advanced Nano Materials (ANoMa) Research Group, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

A B S T R A C T

The thin films of solid polymer electrolytes were based on corn starch doped with magnesium sulphate (MgSO₄) with different ratios of polymer and salt added. They were prepared using a single-solvent technique. The glycerin was added to the mixture of the solution to offer more elasticity to the polymer film and by increasing the flexibility of the thin-film membrane. The conductivity and electric studies were carried out on these thin films to understand the ion transport properties of the polymer electrolytes. The highest conductivity obtained was 8.52×10^{-5} S cm^{-1}, which for the 35 wt. % MgSO₄ salt-doped polymer electrolyte system at room temperature. From the evaluation on the transport properties, the conductivity of the system was generally influenced by n, μ and D of charge carriers. MgSO₄ helped to increase the ionic conductivity and further increase the salt content, while the diffusion coefficient and mobility of charge carriers were increased.

1. Introduction

Solid polymer electrolyte thin films are solid ionic conductors that are made by the dissolving salts in appropriate polymers. This outcome results in solid polymer electrolytes having good flexibility, mechanical stability, light weight, durability, low cost, and corrosion-free properties (Vincent, 1987; Xu, 2014; Kulshrestha et al., 2014; Hassan and Ting, 2018). Solid polymer electrolytes are seen as a vital component; having a wide range of applications in electrochemical devices such as high energy density batteries, super capacitors, fuel cells, sensors, organic transistor and dye-sensitized solar cells (Dai et al., 2018; Verma and Sahu, 2017). Extensive exploration to cultivate a new solid polymer electrolyte with good electrical conductivity and environmental stability has been on the rise, specifically with regard to their ionic, dielectric and transport properties (Prajapati and Gupta, 2009; Zamri et al., 2014; Chai and Isa, 2016; Bandara and Mellander, 2011; Koduru et al., 2017; Gohel and Kanchan, 2018). Electrochemical impedance spectroscopy (EIS) technique is among the most commonly used technique for the evaluation and study of the ionic conductivity, dielectric, and transport properties of solid polymer electrolytes. EIS is a great technique for distinguishing a comprehensive variation of electrochemical systems and for defining the contribution of electrodes or electrolytic processes in these systems (Ribeiro et al., 2015; Hassan and Noruddin, 2018). Many past research works have used EIS to investigate the mentioned parameters.

They found that the irradiated samples had altered significantly on their conductivity and dielectric properties significantly. In the investigation of PVDF-HFP:PMMA-LiClO₄ electrolyte system, Gohel and Kanchan (2018) revealed that at room temperature, the conductivity of 7.5 wt.% LiClO₄ can reach as high as 2.83×10^{-4} S cm^{-1} and the ionic conductivity, dielectric and transport properties had changed with the change in temperatures and salt content. The effect of fume silica on PVA:NaI electrolyte system had been studied by Kulshrestha et al. (2014). From the EIS analysis, they found that the maximum conductivity was approximately 3.8×10^{-3} S cm^{-1} at room temperature, which was obtained for PVA:NaI (60:40) film containing 0.5% fumed silica nanoparticles and from the dielectric relaxation studies related to temperature. It can be seen that the relaxation time shifted towards higher values for the samples of nanocomposite polymer electrolyte films.

Nowadays, the EIS analysis technique has been improved where Bandara and Mellander (2011) proposed a new approach by employing impedance spectroscopic data that not only can determine the ionic conductivity and dielectric properties, but can also be used to calculate the mobile charge carrier concentration and mobility in different ways. Interestingly, Arof et al. (2014) discovered an alternative method based on impedance spectroscopy to determine transport properties of polymer electrolyte. In the study, they revealed that their novel method was more accurate and could be proven using another technique based on Fourier Transform Infrared (Ftir) analysis. As cited above, there is no doubt that EIS is one of the non-destructive and powerful techniques to investigate ionic conductivity, dielectric, and transport properties which should be applicable for a wide range of electrolytes including ionic solid polymer electrolytes (Hassan and Arof, 2005).

In the present study, the effect of $MgSO_4$ salt concentration were studied based on conductivity and transport properties of a new type of solid polymer electrolyte film in which the corn starch is complexed with magnesium sulfate (Starch-$MgSO_4$ system). The picking of the $MgSO_4$ salt is principally because of its ready accessibility, lesser harmfulness, and high potential in electrochemical applications (Byrne et al., 2017; van Essen et al., 2009; Wang et al., 2017; Masse et al., 2015; Lota et al., 2013; Hongois et al., 2011; Zhu et al., 2018; Mahon et al., 2017).

2. Experimental method

The solid polymer thin films were prepared using a single solvent by the solution casting technique (Fig. 1). The mixture was stirred constantly using magnetic stirrers at a temperature of 60°C, to obtain the desired homogenous solution. Subsequently, the solution was transferred into different plastic Petri dishes and was left for the evaporation process to form solid state film. After 24 h, a mechanically strong, transparent, and free-standing film was obtained. The details of the compositions of corn starch doped with $MgSO_4$ (Sigma-Aldrich, 99.99% purity) and their resulting mechanical properties are as per listed in Table 1.

Table 1: Composition and mechanical strength of starch-$MgSO_4$ films

$MgSO_4$ content (wt. %)	Solvent (ml)	Corn starch (g)	$MgSO_4$ (g)	Film Strength
5	30	1	0.053	Very good
10	30	1	0.111	Very good
15	30	1	0.177	Very good
20	30	1	0.250	Very good
25	30	1	0.333	Very good
30	30	1	0.429	Very good
35	30	1	0.548	Very good
40	30	1	0.667	Good
45	30	1	0.834	Good

The ionic conductivity was measured using HIOKI 3532-02 LCR Hi-Tester which was interfaced to the computer. This tester was used to determine the conductivity of the polymer thin film membrane over a frequency range of 50 Hz to 1MHz.

The prepared samples were cut into 2 cm diameter size and placed between two stainless steel blocking electrodes of the sample holder. The bulk resistance, R_b, was obtained from the real impedance value of the Cole–Cole plot. The ionic conductivity was calculated from the measured bulk resistance, area, and thickness of the polymer film using the following formula:

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

where l is the thickness of the polymer electrolyte (cm) measured by the micrometre screw gauge, A is the area of the blocking electrode contact (cm^2), and R_b is the bulk resistance (Ω). A digital micrometre-screw gauge was used to measure the thickness of the polymer films.

The dielectric constant, ε_r for a Starch-$MgSO_4$ system is defined by:

$$\varepsilon_r = \frac{Z_i}{(Z_r^2 + Z_i^2)}\left(\frac{d}{\omega \varepsilon_o A}\right) \tag{2}$$

where Z_r and Z_i are the real and imaginary part of complex permittivity, d is half the thickness of the polymer electrolyte, ω is equal to $2\pi f$ or the angular frequency corresponding to the minimum in the imaginary impedance, f being the frequency in Hz, ε_o is the permittivity of free space (8.85 x 10^{-14} F cm^{-1}), A is the electrolyte-electrode contact area.

Transport properties (D, μ and n) of the Starch-$MgSO_4$ system are determined by Eqs. 3, 4, and 5:

$$D = \frac{(k_2 \varepsilon_r \varepsilon_o A)^2}{\tau_2} \tag{3}$$

where, D is diffusion coefficient, k_2 is capacitance, ε_o is the vacuum permittivity, A is the electrode/electrolyte contact area and τ_2 is a time constant corresponding to the maximum dissipative loss curve which is equal to $1/\omega_2$.

$$\mu = \frac{e(k_2 \varepsilon_r \varepsilon_o A)^2}{k_b T \tau_2} \tag{4}$$

here, μ is mobility of the charge carriers, k_b is the Boltzmann constant (1.38 x 10^{-23} J K^{-1}), T is the absolute temperature in Kelvin and e is the electron charge (1.602 x 10^{-19} C).

The number density of charge carriers (n) can be obtaining using the Eq. 5:

$$n = \frac{\sigma k_2 T \tau_2}{(e k_2 \varepsilon_r \varepsilon_o A)^2} \tag{5}$$

k_2 in Eqs. 3, 4, and 5 were calculated from

$$k_2 = \frac{\lambda_D}{\varepsilon_r \varepsilon_o A} \tag{6}$$

where, λ_D is the Debye length and its calculation is obtained from Lin et al. (2012). Fig. 2 describes the

exact location of the Debye length in the solid electrolyte film during EIS measurement. The Stern

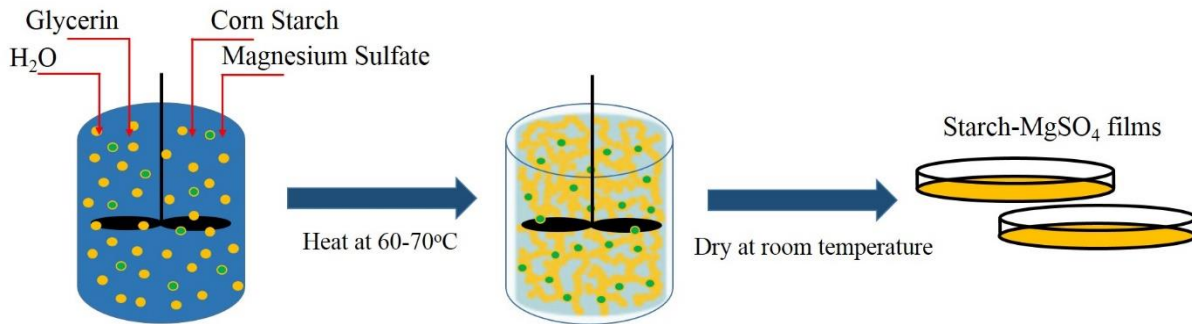layer has a very small thickness (< 1nm), so it is not taken into consideration in this study.

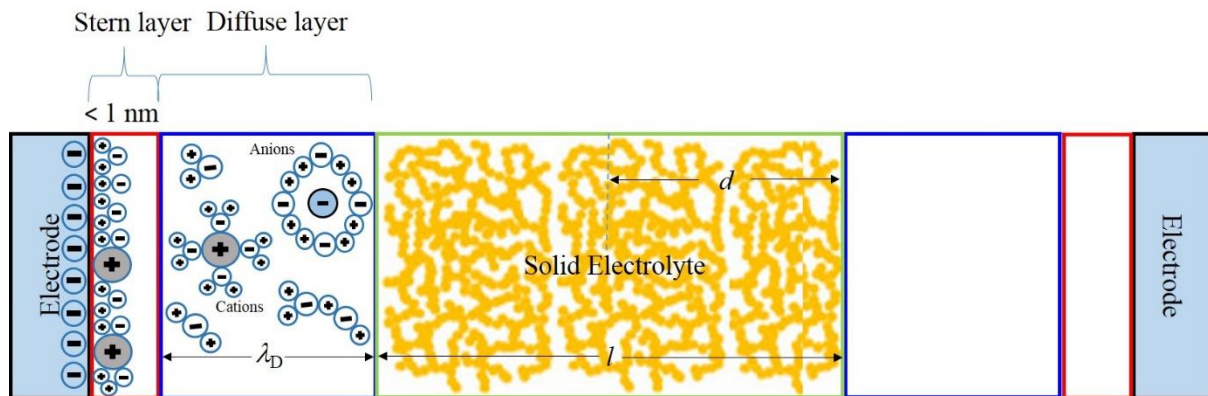**Fig. 1:** A schematic diagram to prepare starch-MgSO$_4$ complex films

Fig. 2: A schematic diagram for arrangement of starch-MgSO$_4$ films during electrochemical impedance measurement

3. Results and discussion

The electrical properties of the starch-MgSO$_4$ films were studied using the impedance spectroscopy analysis. Eq. 1 was used to calculate the conductivity of each sample and its corresponding electrical conductivity variation was used as a function of the MgSO$_4$ concentration at room temperature as depicted in Fig. 3. It can be seen from the Fig. 3 that the addition of MgSO$_4$ had significantly increased the ionic conductivity. By adding 5-15 wt. % MgSO$_4$ to the starch film, the ionic conductivity gradually increased to 2.59×10^{-6} S cm^{-1}. The conductivity kept increasing (4.70×10^{-6}) for 20 wt. % MgSO$_4$. Additional MgSO$_4$ with 25 wt. % to 35 wt. % evidently increased the ionic conductivity to a high level of (8.52×10^{-5} S cm^{-1}). The conductivity values started to decrease after further addition of 40 to 45 wt. % MgSO$_4$.

By using the technique as explained by Arof and coworkers, the dielectric constant, ε_r, for each sample was obtained by a plot of the real part of the complex permittivity, ε_r versus frequency, f and were substituted in Eq. 2. In this case, the real part of the complex permittivity, ε_r, for all samples showed a constant value in between log f = 5.5 and 6.0. Therefore, the values of the dielectric constant, ε_r, for all samples were taken at 630 kHz and were calculated at a location between 1 and 130, respectively. Another important parameter that had to be determined in the first stage was λ_D and thus it was calculated using the equation mentioned by Lin

et al. (2012). These values (ε_r, λ_D) were used to calculate the parameters of the diffusion coefficient, mobility of ions, the number density of charge carriers and capacitance of samples using Eqs. 3, 4, 5, and 6.
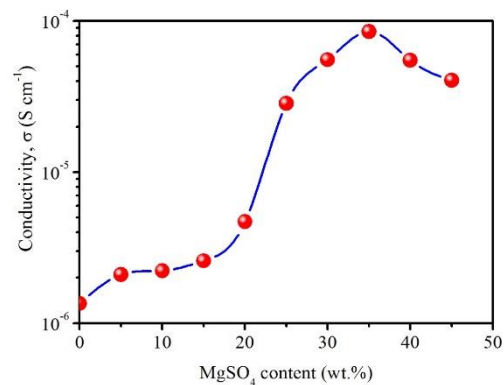

Fig. 3: The conductivity variation as a function of salt content at room temperature

Table 2 shows the values of λ_D, D, μ, n and k_2 of the starch-MgSO$_4$ electrolytes as a function of MgSO$_4$ concentration. It was observed that the λ_D had a value in between 1.66×10^{-8} and 6.38×10^{-7} cm. The λ_D for the highest conductivity among the samples was 6.38×10^{-7} cm. The calculated values of k_2 were in between 6.19×10^3 and 6.49×10^4 F^{-1} with the highest conductivity found in sample 1.76×10^4 F^{-1}. The value of diffusion coefficient for the highest conductivity sample was 1.03×10^{-8} cm^2 s^{-1} with the value located in between 1.02×10^{-11} and 5.18×10^{-7}

cm^2 s^{-1}. It is can be seen that the starch-MgSO$_4$ films system had mobility values in between 4.08 x 10^{-10} cm^2 V^{-1} s and 2.02 x 10^{-5} cm^2 V^{-1} s with the highest conductivity found in sample 4.03 x 10^{-7} cm^2 V^{-1} s. The calculated value of the number density of charge carriers for this system was in between 1.24 × 10^{20} cm^{-3} and 3.99 x 10^{23} cm^{-3} with the highest conductivity sample recording the value of 1.31 x 10^{22} cm^{-3}.

Table 2: The values of λ_D, τ_2, D, μ and n of hybrid starch-MgSO$_4$ films

MgSO$_4$ content (wt.%)	λ_D (cm)	k_2 (F^{-1})	τ_2 (s^{-1})	D (cm^2 s^{-1})	μ (cm^2 V^{-1} s)	n (cm^{-3})
5	1.67 × 10^{-8}	6.32 × 10^3	2.65 × 10^{-5}	1.05 × 10^{-11}	4.08 × 10^{-10}	3.18 × 10^{23}
10	7.45 × 10^{-8}	6.19 × 10^3	1.22 × 10^{-6}	4.54 × 10^{-9}	1.77 × 10^{-7}	7.74 × 10^{20}
15	1.81 × 10^{-8}	6.49 × 10^4	3.18 × 10^{-5}	1.03 × 10^{-11}	4.00 × 10^{-10}	3.99 × 10^{23}
20	6.99 × 10^{-8}	3.35 × 10^4	2.65 × 10^{-5}	1.85 × 10^{-9}	7.19 × 10^{-8}	4.03 × 10^{21}
25	7.76 × 10^{-8}	5.35 × 10^4	5.30 × 10^{-6}	1.14 × 10^{-9}	4.42 × 10^{-8}	3.97 × 10^{22}
30	4.53 × 10^{-7}	1.52 × 10^4	3.18 × 10^{-6}	6.45 × 10^{-8}	2.51 × 10^{-6}	1.36 × 10^{21}
35	6.38 × 10^{-7}	1.76 × 10^4	3.94 × 10^{-5}	1.034 × 10^{-8}	4.03 × 10^{-7}	1.30 × 10^{22}
40	3.28 × 10^{-7}	5.08 × 10^4	8.84 × 10^{-7}	1.22 × 10^{-7}	4.74 × 10^{-6}	7.15 × 10^{20}
45	4.91 × 10^{-7}	5.31 × 10^4	4.65 × 10^{-7}	5.18 × 10^{-7}	2.02 × 10^{-5}	1.24 × 10^{20}

The graphs of D, μ, and n were plotted versus the salt content; using the Origin software and can be seen in Fig. 4. From this software, the non-linear curve fitting technique based on Boltzmann and Dose-response functions were used to obtain the fitting curves. It can be observed that the n of the system is opposite trend to the conductivity, whereas the D and μ had followed the trend of conductivity value, respectively. It seems that the increasing trend of conductivity is due to an increase in the D and μ of charge carriers as the MgSO$_4$ concentration increased in the samples.

As discussed by Hassan and coworkers, the increasing trend of ionic conductivity had been contributed by two main factors, the amorphous structure of complex samples and the sufficient ionic conductors in the close system (Hassan et al., 2018). For the amorphous structure, it could acts as a supportive medium for fast ionic movement. A few researchers claimed that the ionic conductivity is higher in amorphous complex structures as compared to crystalline polymer salt complex; this is due to the interfacial resistance is low in between the solid electrolyte and the electrode surface (Bruce and Vincent, 1993; Maurya et al., 1992; Reddy et al., 2007; Srivastava et al., 1995). Another aspect is associated to the D and μ of ionic conductors in the electrolyte system. The increase in conductivity with the salt content is due to the increase in diffusion coefficient and mobility of charge carrier as shown in Fig. 4. As for the decreasing trend in conductivity, this could be because of the reduction on the number of charge carriers and increase the empty space in the electrolyte system (Rajendran et al., 2000). The wrecked film and the increase in crystallinity of film might be the extra factors of the conductivity drop in this electrolyte system.

As for comparison purposes, the conductivity and transport property values of our prepared starch-MgSO$_4$ films in this study and those other systems reported in the literature are updated in Table 3.

The results studied here showed that the current Starch-MgSO$_4$ films had high conductivity (8.52 x 10^{-5} S cm^{-1}) and comparable transport properties (D = 1.04 x 10^{-8} cm^2 s^{-1}, u = 4.03 x 10^{-7} cm^2 V^{-1} s, n = 1.31 x 10^{22} cm^{-3}) to those studies in similar starch based compounds. These results are important as a reference for current and future work, and most significant since such information is seldom documented in other reports.
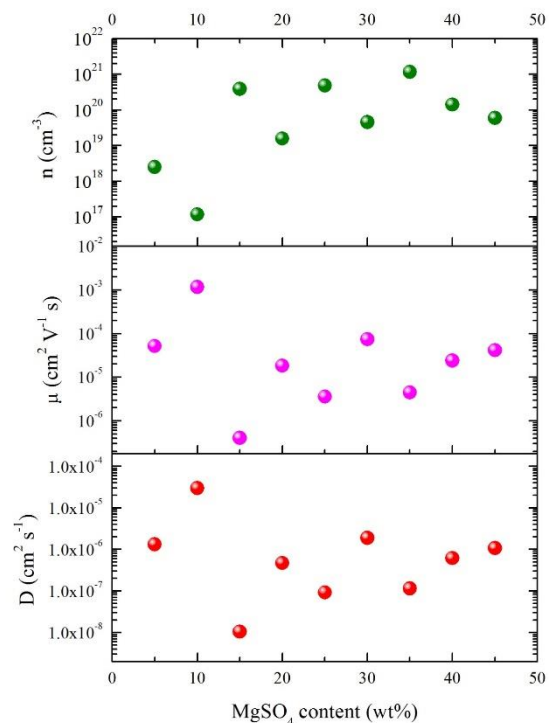

Fig. 4: Plots of diffusion coefficient, D, charge carrier mobility, μ and charge carrier number density, n, against the MgSO$_4$ concentration

4. Conclusion

As seen in this study, polymer electrolytes based on corn starch and magnesium sulphate were prepared via a solution casting method. The transport properties of the corn starch and magnesium sulphate were determined. Magnesium sulphate contents with Mg^{2+} mobile ions directly affected transport parameters and ionic conductivity. The addition of MgSO$_4$ resulted in an increase of disffussion coefficient and mobility of mobile ions which are main reasons to increase and enhancement in ionic conductivity. The highest conductivity was achieved at 8.52 x 10^{-5} S cm^{-1}.

Table 3: Comparison of the conductivity and transport values of hybrid starch-MgSO$_4$ film prepared in this work with other systems which reported in literature

System	Conductivity(S cm^{-1})	Transport Properties			Reference
		D (cm^2 s^{-1})	μ (cm^{2}V^{-1}s)	n (cm^{-3})	
Corn starch-MgSO$_4$	8.52×10^{-5}	1.04×10^{-8}	4.03×10^{-7}	1.31×10^{22}	This work
Rice Starch-LiI	4.68×10^{-5}	5.53×10^{-9}	2.15×10^{-7}	1.36×10^{21}	(Khanmirzaei and Ramesh, 2013)
CMC-NH$_4$Br-PEG	2.48×10^{-3}	$\sim 1.40 \times 10^{-8}$	$\sim 1.80 \times 10^{-7}$	$\sim 2.80 \times 10^{22}$	(Zainuddin et al., 2018)
CMC-NH$_4$F	$\sim 1.52 \times 10^{-6}$	9.66×10^{-19}	1.12×10^{-13}	1.52×10^{23}	(Ramlli and Isa, 2016)
Starch–chitosan–NH$_4$I	3.04×10^{-4}	–	3.45×10^{-4}	5.50×10^{18}	(Yusof et al., 2014)
Potato Starch/Chitosan-LiCF$_3$SO$_3$	7.11×10^{-7}	1.12×10^{-6}	4.38×10^{-5}	1.01×10^{17}	(Navaratnam et al., 2015)
Cellulose Acetate-NH$_4$NO$_3$	1.02×10^{-3}	3.28×10^{-8}	9.84×10^{-7}	6.47×10^{21}	(Monisha et al., 2017)
Chitosan-NH$_4$NO$_3$-Al$_2$SiO$_5$	2.10×10^{-5}	–	$\sim 1.51 \times 10^{-4}$	$\sim 3.52 \times 10^{17}$	(Majid et al., 2005)
Corn Starch-NaI-GO	2.61×10^{-3}	–	–	–	(Shahrudin and Ahmad, 2016)
Sago starch					
-LiClO$_4$	9.91×10^{-4}				
-NaCl	2.55×10^{-3}				
-NaClO$_4$	1.38×10^{-3}	–	–	–	(Pang et al., 2014)
-Na$_2$SO$_4$	5.23×10^{-4}				
-LiCl	3.37×10^{-3}				
-KCl	3.80×10^{-3}				

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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