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## EFFECT OF SODIUM BISULFITE ON CORN STARCH SOLID POLYMER ELECTROLYTE

(Kesan Sodium Bisulfit terhadap Elektrolit Polimer Pepejal Kanji)

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#### Abstract

In this study, solid polymer electrolyte films were prepared using corn starch as polymer doped with various wt.% ratios of NaHSO<sub>3</sub> via solution casting technique. The SPE films have been characterized using electrical impedance spectroscopy (EIS) and X-ray diffraction (XRD). The plots of conductivity versus NaHSO<sub>3</sub> (wt.%) have shown an increasing trend along with NaHSO<sub>3</sub> content. It was found that the highest ionic conductivity at room temperature is  $2.22 \times 10^{-4}$  Scm<sup>-1</sup>. Besides, XRD analysis also indicates that the increase in amorphous content will enhance the conductivity value.

Keywords: electrical impedance spectroscopy, X-ray diffraction, solid polymer electrolyte, corn starch

#### Abstrak

Dalam kajian ini, filem elektrolit polimer pepejal telah disediakan menggunakan kanji sebagai polimer dan ditambah dengan pelbagai nisbah berat (wt.%) NaHSO3 melalui kaedah penuangan larutan. Filem-filem SPE tersebut telah diuji menggunakan spektrometer elektrokimia impedans (EIS) dan analisa pembelauan sinar-X (XRD). Plot kekonduksian melawan kandungan NaHSO3 menunjukkan peningkatan dengan meningkatnya wt.% NaHSO3. Ia telah dijumpai bahawa kekonduksian tertinggi pada suhu bilik adalah  $2.22 \times 10^{-4}~\rm S\,cm^{-1}$ . Disamping itu, analisis XRD menunjukkan peningkatan kandungan amorphous akan membantu dalam peningkatan nilai kekonduksian.

Kata kunci: spektrometer elektrokimia impedans, pembelauan sinar-X, elektrolit polimer pepejal, kanji

#### Introduction

In the past few years, solid polymer electrolytes (SPEs) have received much attention due to their wide range of applications in electrochemical devices such as batteries, solar cell, chemical sensors, and supercapacitors [1-5]. The main advantages of SPEs are

their high ionic conductivity, leakage proof, simple to prepare and have excellent mechanical strength [6-8]. However, most of the conventional synthetic polymers come from petroleum and are known as non-degradable. This is believed that synthetic-based polymer electrolytes would give an impact on the environment.

To overcome this problem, biodegradable polymer electrolytes were used to replace the traditional ones.

The uses of natural polymers such as starch [9, 10] cellulose and its derivatives [11, 12] and chitosan [13] have attracted attention in previous works due to their mechanical and electrical properties. In this study, starch is chosen as a polymer host due to its characteristics which are naturally in abundance, low cost, biodegradable [14,15] and possess high solubility. This is important to choose a suitable material to ensure it would not give a long-lasting effect on the environment. According to [16], it was mentioned that most of the natural polymers like starch relatively show a very low ionic conductivity. Then, in order to enhance the conductivity, several attempts have been taken such as blending of polymer [17], plasticization [18, 19] and the addition of ceramic fillers [20-22] into a polymer electrolyte.

The addition of salts such as sodium also helps to improve the conductivity of SPE films [23]. The selection of sodium (Na) as a dopant due to its characteristics which are low atomic mass, affordable in price, low toxicity and abundance element in nature [24]. From the previous research, it was reported that the maximum conductivity value of SPE films based on sodium ions was achieved in the range  $10^{-3}$  Scm<sup>-1</sup> [25]. The low crystallinity nature also would influence to the high conductivity of the film itself. Hence, this study focuses on the results of an investigation on the structural and ionic conductivity of corn starch doped with sodium bisulfite (NaHSO<sub>3</sub>) using EIS and XRD.

#### **Materials and Method**

#### Preparation of samples

Corn starch (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) and sodium bisulfite (NaHSO<sub>3</sub>) with a purity of 96% were used to prepare the SPE films by using a solution casting technique (Figure 1). The solvents (distilled water and glycerine) were added with various amounts (5- 40 wt. %) of NaHSO<sub>3</sub> as tabulated in Table 1 and stirred until no left residue. The weight percentage was calculated using a formula as expressed in Equation 1. Then, 1 g of corn starch was mixed with the solutions and heated at the temperature of 60-70 °C. All solutions were stirred using a magnetic stirrer until

it turned homogenous. After that, the homogenous solution was cast into a petri dish and left it dry naturally about three days until electrolyte films are formed. For a further drying process, samples were kept in a desiccator filled with silica gels.

$$wt.\% = \frac{x}{x+y} \times 100 \tag{1}$$

where, wt.% is the varying values for salt in percentage, x is the amount of dopant (g) and y is the amount of polymer.

#### Characterization techniques

Electrical impedance spectroscopy (EIS) were used to determine the electrical properties of SPE films. The impedance data were measured using HIOKI 3532-50 LCR Hi-Tester which is interfaced with a computer at room temperature in a frequency range of 50 Hz to 1 MHz. The samples were cut into 3.00 cm size of diameter and placed between two blocking electrodes. A digital micrometre screw gauge was used to measure the thickness of SPE films. The ionic conductivity was calculated by using Eq. 2 [26]. Bulk resistance,  $R_b$  can be obtained by taking average values from the plot of imaginary impedance ( $-Z_i$ ) against real impedance ( $Z_r$ ) known as the Cole-cole plot as shown in Figure 2.

$$\sigma = \frac{1}{R_{b}A} \tag{2}$$

From Equation 2, *l* is the thickness of SPE films while *A* is the surface area of blocking electrode contact.

X-ray diffraction (XRD) technique was used to identify the nature of SPE films whether they are crystalline, amorphous or both. Prepared samples were cut into a dimension of 1.00 cm  $\times$  1.00 cm and placed onto the glass slides before being measured. A MiniFlex II diffractometer with Cu K $\alpha$  radiation was used to analyse the samples in a range of  $2\Theta=10^\circ$  to  $80^\circ$  with  $5^\circ/min$  of step size. Then, the obtained data were used to analyse the phase identification, crystallinity and/or amorphosity of the SPE films by using Search-Match and Origin software.

Crystallinity (%) = 
$$\frac{A_c}{A_c + A_m} \times 100$$
 (3)

where  $A_c$  is peak areas for crystalline and  $A_m$  is corresponding to the peak areas for amorphous. Then, to study the phase of the mentioned materials with the d-spacing, it can be obtained by matching the peaks in the given datasheet from Search-Match software.

The percentage of crystallinity for SPE films can be verified by dividing the area under all peaks with the area under the whole diffractogram. Equation 3 shows the formula to calculate the crystalline value of SPE films.

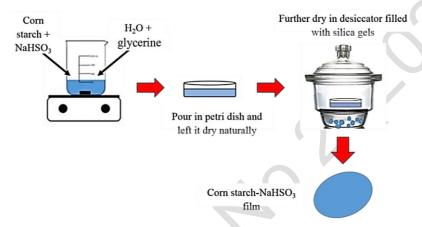


Figure 1. A schematic diagram for preparation of SPE films

Table 1. Composition of corn starch-NaHSO<sub>3</sub> SPE films

CDE complex	NaHSO <sub>3</sub>	NaHSO <sub>3</sub>	Solvent (mL)	
SPE samples	(wt. %)	<b>(g)</b>	Distilled water	Glycerine
A	0	0	20	0.6
В	5	0.053	20	0.6
C	10	0.111	20	0.6
D	15	0.176	20	0.6
E	20	0.250	20	0.6
F	25	0.333	20	0.6
G	30	0.429	20	0.6
Н	35	0.538	20	0.6
I	40	0.667	20	0.6

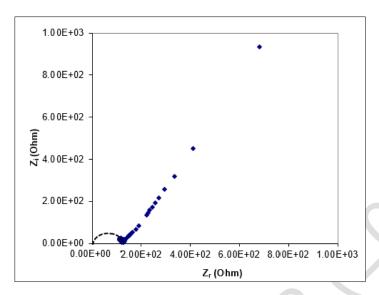


Figure 2. The Cole-cole plot for 15wt. % of NaHSO<sub>3</sub> at ambient temperature

#### **Results and Discussion**

Figure 3 shows the different images of corn starch films and corn starch doped with NaHSO<sub>3</sub> films. The images were taken by using a mobile phone camera that have 8 MP and 5× magnifications. It was observed that the SPE films had changed from transparent to translucent when the amount of salts added is increased. In addition, it is also may alter the structure and morphology of films as well.

The variation of ionic conductivity as a function of NaHSO<sub>3</sub> composition at room temperature as shown in Figure 4 while Table 2 presents the value of bulk resistance,  $R_b$  and ionic conductivity. The thickness of dried samples is measured in the range between 0.101 mm to 0.293 mm. In Figure 4, the ionic conductivity of free salt SPE is  $1.1 \times 10^{-6}$  Scm<sup>-1</sup>. The conductivity of the SPE films increased to  $7.65 \times 10^{-6}$  Scm<sup>-1</sup> when 5 wt.% of NaHSO<sub>3</sub> was added and continued the increasing trend until 15 wt.% of NaHSO3 has been added to the corn starch. Then, the addition of 20 wt.% of NaHSO<sub>3</sub> into polymer electrolyte causes the conductivity of SPE films started to drop with value  $1.06 \times 10^{-4} \text{ Scm}^{-1}$ . The decreased trend of conductivity continued in 25 wt.% to 40 wt.% of NaHSO<sub>3</sub> until the value is  $6.98 \times 10^{-6}$  Scm<sup>-1</sup>. It can be said that the increase of ionic conductivity along with the addition of NaHSO3 may be influenced

by the amorphous nature and also increase in the number of charge carriers [27]. As expected, from XRD analysis in Figure 4, it was proven that the amorphous nature of SPE films has increased with the addition of NaHSO<sub>3</sub>. This can be seen through the highest conducting SPE film (15 wt.% of NaHSO<sub>3</sub>) shows a higher amorphous nature. According to literature, the increase of amorphous state in SPE films will enhance the mobility of free ions through the system and so does the ionic conductivity [28-31]. In contrast, at higher salt concentration there will be an increase in aggregation of ions which lead to the formation of neutral ion pairs, thus limits the movement of freely ions [32]. Hence, decrease in conductivity values.

XRD patterns of corn starch with different NaHSO<sub>3</sub> composition is shown in Figure 5. The corn starch diffraction pattern can be identified with a broad peak located at  $2\Theta = 15^{\circ}$  to  $28^{\circ}$ , which known as amorphous hump [35]. This can be assigned as (002) and (112) planes with a tetragonal structure and have a lattice constant of a = 6.07 Å and c = 8.60 Å (JCPDS 80-31). Then, the presence of peaks at angle  $2\Theta = 24.6^{\circ}$ ,  $33.1^{\circ}$ ,  $39.2^{\circ}$ ,  $47.4^{\circ}$ ,  $47.7^{\circ}$ ,  $52.3^{\circ}$ ,  $61.7^{\circ}$ ,  $65^{\circ}$  and  $69.8^{\circ}$  for pure NaHSO<sub>3</sub> which correspond to the planes of (101), (103), (110), (006), (200), (115), (107), (008) and (220). It is a well agreement to the orthorhombic structure with a

lattice constant of a = 5.60 Å, b = 8.95 Å and c = 6.96 Å (JCPDS 83-1570). The appearance of a crystalline peak in the polymer-salt system indicates that sodium salts have existed. Table 3 shows the value of d-spacing for pure corn starch, NaHSO<sub>3</sub> and SPE films with various ratios of NaHSO<sub>3</sub>. D-spacing values had been obtained using Search-Match software and being compared with the data provided by the datasheet. From the results, it can be concluded that the d-spacing values of the mentioned materials are almost well-matched with the values provided in the JCPDS database.

Furthermore, to confirm the crystallinity of SPE films, the percentage of crystalline was calculated by using Equation 3 and it was tabulated in Table 4. Based on the results, the crystalline value was against the conductivity pattern. This is because the decrease in the degree of crystallinity of the SPE films will impart a better ion's diffusion in polymers, thus resulting in increases of conductivity. It also assumed that the association of ions was promoted due to the presence of glycerine as a plasticizer [33, 34]. This happened due to the properties of the plasticizer itself which is a high dielectric constant ( $\varepsilon_r = 78.5$ ) that can weaken the Coulombic force between anion and cation of salt. So, that it can help for the salts to dissociate easily, hence increased the ion's concentration [35, 36].

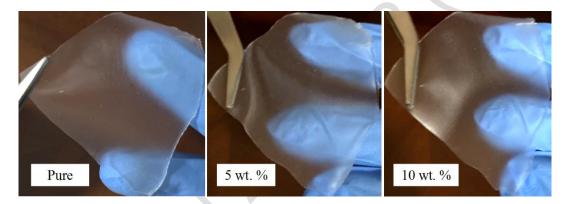


Figure 3. The selected images of corn starch-NaHSO<sub>3</sub> SPE films

Table 2.	Bulk resistance	and ionic conductivit	v of corn	starch-NaHSO <sub>3</sub> films

Samples (Content of N	JaHSO <sub>3</sub> , wt.%)	Bulk resistance, $R_b(\Omega)$	Ionic conductivity, $\sigma (\text{Scm}^{-1})$
A	0	$3.00 \times 10^3$	1.1 x 10 <sup>-6</sup>
В	5	$4.20 \times 10^2$	7.65 x 10 <sup>-6</sup>
C	10	$6.00 \times 10^{1}$	8.96 x 10 <sup>-5</sup>
D	15	$2.50 \times 10^{1}$	2.22 x 10 <sup>-4</sup>
Е	20	$4.00 \times 10^{1}$	1.06 x 10 <sup>-4</sup>
F	25	$1.47 \times 10^2$	5.43 x 10 <sup>-5</sup>
G	30	$1.60 \times 10^2$	3.69 x 10 <sup>-5</sup>
Н	35	$7.00 \times 10^2$	1.33 x 10 <sup>-5</sup>
I	40	$1.17 \times 10^3$	6.98 x 10 <sup>-6</sup>

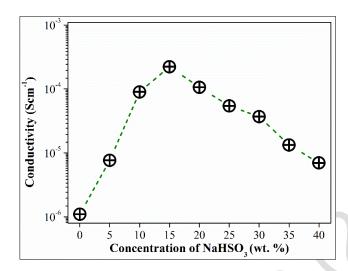


Figure 4. The trend of conductivity SPE films with various compositions of NaHSO<sub>3</sub>

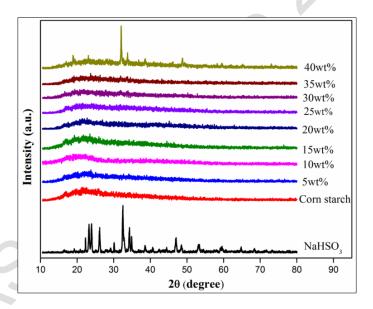


Figure 5. XRD diffraction patterns for corn starch and corn starch-NaHSO<sub>3</sub> SPE films

Table 3. The comparison between *d*-spacing values of experimental and theoretical of SPE films

Samples	Software	Experim	ental Result
Samples	d (Å)	d (Å)	2θ (°)
Pure corn starch	4.294	4.295	20.6
(JCPDS 80-31)	3.036	3.037	29.3
NaHSO <sub>3</sub>	4.752	4.748	18.6
(JCPDS 83-1570)	3.925	3.920	22.6
	3.483	3.481	25.5
	2.803	2.803	31.9
	2.061	2.061	43.8
	1.619	1.618	56.8
	1.294	1.299	72.7
5 wt.%	4.752	4.832	18.3
	2.134	2.138	42.2
10 wt.%	4.752	4.742	18.7
	2.134	3.727	23.8
15 wt.%	1.829	1.816	50.1
	1.742	1.721	53.1
20 wt.%	3.483	3.380	26.3
	2.809	2.816	31.7
	2.749	2.743	32.6
	2.376	2.389	37.6
	1.963	1.926	47.1
	1.883	1.886	48.2
	1.769	1.767	51.6
25 wt.%	2.809	2.818	31.7
	1.963	1.916	47.2
· ·	1.829	1.808	50.4
30 wt.%	4.752	4.948	17.9
	1.218	1.218	78.4
35 wt.%	3.925	3.973	22.3
	3.809	3.820	23.2
	3.483	3.463	25.7
	2.809	2.884	30.9
	2.634	2.689	33.2
40 wt.%	2.634	2.696	33.1

Composition of NaHSO <sub>3</sub> (wt. %)	Percentage of Crystallinity (%)	Percentage of Amorphosity (%)
0 (Pure corn starch)	10.51	89.49
100 (NaHSO <sub>3</sub> )	67.39	32.61
5	72.31	27.69
10	61.97	38.03
15	35.88	64.12
20	44.25	55.75
25	48.49	51.51
30	49.83	50.17
35	53.40	46.60
40	44.52	44.52

Table 4. The Percentage crystallinity and amorphosity of complexed SPE films.

#### Conclusion

In summary, solid polymer electrolytes based on corn starch with a varied amount of sodium bisulfite (NaHSO<sub>3</sub>) is successfully prepared *via* solution casting technique. EIS analysis shows that at 15 wt.% NaHSO<sub>3</sub> electrolyte obtains the highest conductivity of 2.22 x 10<sup>-4</sup> Scm<sup>-1</sup> and is supported by the amorphous phase. This also shows that the enhancement of conductivity is not only influenced by the concentration of ions but also by the high mobility and diffusion of free ions. Based on the XRD study, the addition of NaHSO<sub>3</sub> as a dopant salt also improved the amorphousness of the SPE films.

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#### References

1. Barbosa, P. C., Rodrigues, L. C., Silva, M. M., Smith, M. J., Parola, A. J., Pina, F. and Pinheiro, C. (2010). Solid-state electrochromic devices using pTMC/PEO blends as polymer electrolytes. *Electrochimica Acta*, 55(4): 1495-1502.

- 2. Dai, S., Chu, Y., Liu, D., Cao, F., Wu, X., Zhou, J., Cheng, Y. and Huang, J. (2018). Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors. *Nature Communication*, 9(1): 1-10,
- 3. Hassan, M. F. and Azimi, N. S. N. (2019). Conductivity and transport properties of starch/glycerin-MgSO<sub>4</sub> solid polymer electrolytes. *International Journal of Advanced and Applied Sciences*, 6(5): 38-43.
- Misenan, M. S. M. and Khiar, A. S. A. (2018). Conductivity, dielectric and modulus studies of Methylcellulose-NH<sub>4</sub>TF polymer electrolyte. Eurasian Journal of Biological and Chemical Sciences, 1(2): 59-62.
- Deraman, S. K., Mohamed, N. S. and Subban, R. H. Y. (2013). Conductivity and electrochemical studies on polymer electrolytes based on poly vinyl (chloride)- ammonium triflate -ionic liquid for proton battery. *International Journal Electrochemical Science*, 6(1): 1459-1468.
- 6. Chandra, A., Agrawal, R. C. and Mahipal, Y. K. (2009). Ion transport property studies on PEO–PVP blended solid polymer electrolyte membranes. *Journal of Physics D: Applied Physics*, 42(13): 135107.

- Hema, M., Selvasekarapandian, S., Arunkumar, D., Sakunthala, A. and Nithya, H. (2009). FTIR, XRD and ac impedance spectroscopic study on PVA based polymer electrolyte doped with NH<sub>4</sub>X (X=Cl, Br, I). *Journal of Non-Crystalline Solids*, 355(2): 84-90.
- 8. Hassan, M. F., Zainuddin, S. K., Kamarudin, K. H., Sheng, C. K. and Abdullah, M. A. A. (2018). Ion-conducting polymer electrolyte films based on poly (sodium 4-styrenesulfonate) complexed with ammonium nitrate: studies based on morphology, structural and electrical spectroscopy. *Malaysian Journal of Analytical Science*, 22(2): 238-248.
- 9. Ramesh, S., Liew, C.-W. and Ramesh, K. (2011). Evaluation and investigation on the effect of ionic liquid onto PMMA-PVC gel polymer blend electrolytes. *Journal of Non-Crystalline Solids*, 357(10), 2132-2138.
- Marcondes, R. F. M. S., D'Agostini, P. S., Ferreira, J., Girotto, E. M., Pawlicka, A. and Dragunski, D. C. (2010). Amylopectin-rich starch plasticized with glycerol for polymer electrolyte application. *Solid State Ionics*, 181(13-14): 586-591.
- Harun, N. I., Ali, R. M., Ali, A. M. M. and Yahya, M. Z. A. (2011). Dielectric behaviour of cellulose acetate-based polymer electrolytes. *Ionics*, 18(6): 599-606.
- 12. Lopes, L. V. S., Machado, G. O., Pawlicka, A. and Donoso, J. P. (2005). Nuclear magnetic resonance and conductivity study of hydroxyethylcellulose based polymer gel electrolytes. *Electrochimica Acta*, 50(19): 3978-3984.
- 13. Pawlicka, A., Mattos, R. I., Tambelli, C. E., Silva, I. D. A., Magon, C. J. and Donoso, J. P. (2013). Magnetic resonance study of chitosan biomembranes with proton conductivity properties. *Journal of Membrane Science*, 429: 190-196.
- 14. Xu, Y., Miladinov, V. and Hanna, M. A. (2004). Synthesis and characterization of starch acetates with high substitution. *Cereal Chemistry*, 81(6): 735-740.
- Hassan, M. F., Azimi N.S.N, Kamarudin, K. H. and Sheng, C. K. (2018). Solid polymer electrolytes based on starch- magnesium sulphate: study on morphology and electrical conductivity. ASM Science Journal, 2018: 17-28.
- Shahrudin, S. and Ahmad, A. H. (2017). Electrical analysis of corn starch-based polymer electrolyte doped with NaCl. *Solid State Phenomena*, 268: 347-351.
- Sivakumar, M., Subadevi, R., Rajendran, S., Wu, H.
  C. and Wu, N. L. (2007). Compositional effect of PVdF-PEMA blend gel polymer electrolytes for

- lithium polymer batteries. European Polymer Journal, 43(10): 4466-4473.
- 18. Seng, L. K. (2018). Preparation and characterization of solid polymer electrolyte based on carboxymethyl chitosan, ammonium nitrate and ethylene carbonate. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics* (EPSTEM), 2: 10-16.
- 19. He, R. and Kyu, T. (2016). Effect of plasticization on ionic conductivity enhancement in relation to glass transition temperature of crosslinked polymer electrolyte membranes. *Macromolecules*, 49(15): 5637-5648.
- 20. Liew, C. W. and Ramesh, S. (2015). Electrical, structural, thermal, and electrochemical properties of corn starch-based biopolymer electrolytes. *Carbohydrate Polymers*, 124: 222-228.
- 21. Teoh, K. H., Ramesh, S. and Arof, A. K. (2012). Investigation on the effect of nanosilica towards corn starch–lithium perchlorate-based polymer electrolytes. *Journal of Solid State Electrochemistry*, 16(10): 3165-3170.
- 22. Rathod, S. G., Bhajantri, R. F., Ravindrachary, V., Pujari, P. K. and Sheela, T. (2014). Ionic conductivity and dielectric studies of LiClO<sub>4</sub> doped poly (vinylalcohol)(PVA)/chitosan(CS) composites. *Journal of Advanced Dielectrics*, 4(4); 1450033.
- Mohd Asnawi, A. S. F., Mohd Azli, A. M., Hamsan, M. H., Abdul Kadir, M. F. Z. and Mohamed Yusof, Y. (2020). Electrical and infrared spectroscopic analysis of solid polymer electrolyte based on polyethylene oxide and graphene oxide blend. *Malaysian Journal of Analytical Sciences*, 24: 682-697.
- 24. Shahrudin, S. A., A. H. (2016). Corn starch based biopolymer electrolyte doped with Na<sub>3</sub>PO<sub>4</sub>. *Science Letters*, 10(2): 26-30.
- 25. Hassan, N. and Ahmad, A. H. (2016). Conductivity and FTIR Studies of NaI-Na<sub>3</sub>PO<sub>4</sub>-PLL electrolyte for solid state batteries. *Materials Science Forum*, 846: 505-509.
- 26. Khairul, W. M., Isa, M. I. N., Samsudin, A. S., Adli, H. K. and Ghazali, S. R. (2014). Conductive biodegradable film of N-N-octyloxyphenyl-N -(4 methylbenzoyl)thiourea. *Bulletin of Materials Science*, 37(2): 357-369.
- 27. Hirankumar, G. and Mehta, N. (2018). Effect of incorporation of different plasticizers on structural and ion transport properties of PVA-LiClO<sub>4</sub> based electrolytes. *Heliyon*, 4(12): 00992.

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- 28. Osman, Z., Md Isa, K. B., Ahmad, A. and Othman, L. (2010). A comparative study of lithium and sodium salts in PAN-based ions conducting polymer electrolytes. *Ionics*, 16(5): 431-435.
- 29. Fonseca, C. P., Rosa, D. S., Gaboardi, F. and Neves, S. (2006). Development of a biodegradable polymer electrolyte for rechargeable batteries. *Journal of Power Sources*, 155(2): 381-384.
- 30. Hafiza, M. N., Bashirah, A. N. A., Bakar, N. Y. and Isa, M. I. N. (2014). electrical properties of carboxyl methylcellulose/chitosan dual-blend green polymer doped with ammonium bromide. *International Journal of Polymer Analysis and Characterization*, 19(2), 151-158.
- 31. Samsudin, A. S., Lai, H. M. and Isa, M. I. N. (2014). Biopolymer materials based carboxymethyl cellulose as a proton conducting biopolymer electrolyte for application in rechargeable proton battery. *Electrochimica Acta*, 129: 1-13.
- 32. Ramya, C. S., Selvasekarapandian, S., Savitha, T., Hirankumar, G. and Angelo, P. C. (2007). Vibrational and impedance spectroscopic study on

- PVP–NH<sub>4</sub>SCN based polymer electrolytes. *Physica B: Condensed Matter*, 393(1-2): 11-17.
- 33. Kadir, M. F. Z., Majid, S. R. and Arof, A. K. (2010). Plasticized chitosan–PVA blend polymer electrolyte based proton battery. *Electrochimica Acta*, 55(4): 1475-1482.
- 34. Phetwarotai, W., Potiyaraj, P. and Aht-Ong, D. (2012). Characteristics of biodegradable polylactide/gelatinized starch films: Effects of starch, plasticizer, and compatibilizer. *Journal of Applied Polymer Science*, 126(S1): 162-172.
- 35. Arof, A. K., Shuhaimi, N. E. A., Alias, N. A., Kufian, M. Z. and Majid, S. R. (2010). Application of chitosan/iota-carrageenan polymer electrolytes in electrical double layer capacitor (EDLC). *Journal of Solid State Electrochemistry*, 14(12): 2145-2152.
- 36. Sekhar, P., Naveen Kumar, P. and Sharma, A. K. (2012). Effect of plasticizer on conductivity and cell parameters of (PMMA+NaCIO<sub>4</sub>) polymer electrolyte system. *IOSR Journal of Applied Physics*, 2(4): 1-6.