Enhanced Conductivity of Corn Starch Polymer Film Doped with Sodium Phosphate

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Abstract. Solid polymer electrolyte (SPE) is one of the new invention components which can replace the traditional liquid electrolyte in a conventional battery system that sometimes experience some drawbacks, specifically is a leakage problem. Solid polymer electrolyte was successfully prepared using corn starch as the host and sodium phosphate (Na3PO4) as an ionic dopant which both of them mixed in a combined solvent of distilled water and glycerin via a solution casting technique. FTIR was confirming that the complex films were successfully prepared based on the coexistence of the material peaks (starch and Na3PO4). The highest ionic conductivity of 4.62 x 10⁻⁴ Scm⁻¹ was obtained at room temperature (303K) for the sample containing 40 wt. % of Na3PO4. Based on the results, this SPE is proposed to have great potential in current and future energy storage applications.

1. Introduction
A system consisting of salt dissolved in a polymer matrix that acts as a macromolecular solvent with significant ionic conductivity is referred to solid polymer electrolyte (SPE). Wright has firstly reported the solid polymer electrolyte complex with ionic salts in 1978 [1]. However, this solid polymer electrolyte (SPE) results in low performance at room temperature, which shows the limit to its advantage compared to the current hybrid electrolytes or conventional liquid [2]. Therefore, many research studies have been carried out to enhance the conductivity at room temperature without the fall of mechanical and potential polymer stability through the addition of plasticizer [3], blending various polymers [4,5], the inclusion of fillers [6,7], and doping with ionic salts [8]. It helps to improve the flexibility, processability, and hence utility. The addition of plasticizer such as glycerol have been reported can improve polymeric molecule movement and ionic conductance as it has an ability to reduce the crystallinity [9].

A preferred polymer electrolyte is flexible, dry, not tacky, and lends itself to economical manufacture in very thin film shape. Polymer electrolyte is unique because the molecule of polymer serves as a salt solvent, which is partially dissolved in the polymer matrix, leads to electrolyte behaviour. The starch that is used as the polymer host is a renewable agro-resources, low in cost, and one of the essential food...
materials with broad applications [10]. It is preferred to use renewable sources because it supports the cycle of sustainable growth [11,12]. Corn starch is selected as the primary raw material in the experiment based on the comparison complex of corn starch [13] and rice starch using the same ionic compound as a dopant [14]. In some research studies, starch was used as a host polymer to generate a high ion membrane, and has been proven that its pure ionic conductivity may be improved if doped with suitable ionic salt [15,16].

Compared to liquid electrolytes, SPE has the potentiality to create metallic lithium as a negative electrode in secondary cells and the capability to produce flexible thin-film batteries [17]. The significant advantages of SPE are their mechanical properties, the desirable size thin-film fabrication, and their capability to form good electrode-electrolyte contacts [18]. The main issue in solid polymer electrolyte systems is its low ionic conductivity, which is practically insufficient for use in energy storage devices. Hence, these drawbacks can be overcome by preparing it in a solid form of polymer-salt matrix, using the compounds which is more environmentally friendly, easy to manage, and can avoid the leakage problem. In this present work, solid polymer electrolytes based on starch as the polymer host and sodium phosphate as the ionic dopant has been prepared using a solution casting technique, which both of them mixed in a combined solvent of distilled water and glycerin. Fourier transforms infrared spectroscopy (FTIR) and electrochemical impedance spectroscopy (EIS) were used to analyze the composition and complex formation of the film and to examine the ionic properties of the film respectively. Figure 1 illustrated the synthesis process of solid polymer electrolytes based on corn starch-Na$_3$PO$_4$.

![Synthesis of solid polymer electrolytes based on starch-Na$_3$PO$_4$.](image)

2. Experimental

2.1. Material
Corn starch with a purity of 99% was purchased from GCH Retail Sdn. Bhd., Malaysia. Glycerin and sodium phosphate, both with the purity of 96% was purchased from Sigma Aldrich, USA. The materials used were taken directly without any further purification or treatment.

2.2. Solution Preparation
Briefly, 1 g of corn starch with 20 ml of distilled water and 0.6 ml of glycerine was added to a small beaker and heated at 60 to 70°C. Sodium phosphate was added according to wt. %, as listed in Table 1. A magnetic bar was placed into the beaker, and the solution was stirred at 500 rpm using a magnetic stirrer for an hour. Next, the solution was poured into a plastic Petri dish and was left for 24 hours to
form a thin film via the evaporation process. This process is called a solution casting technique. Then, a desiccator with silica gel was used to further dried and reduce the water content of the thin film for three days. Figure 2 shows a diagram of the overall preparation process.

![Diagram of the overall preparation process](image)

**Figure 2.** The overall process for the preparation of starch-\(\text{Na}_3\text{PO}_4\) complex films.

| Designation | Solvent | Polymer | Sodium Phosphate |
|-------------|---------|---------|------------------|
|             | Distilled water (ml) | Glycerine (ml) | (g) | (wt.%) | (g) |
| Pure | 20 | 0.6 | 1 | 0 | 0.000 |
| A | 20 | 0.6 | 1 | 5 | 0.053 |
| B | 20 | 0.6 | 1 | 10 | 0.111 |
| C | 20 | 0.6 | 1 | 15 | 0.176 |
| D | 20 | 0.6 | 1 | 20 | 0.250 |
| E | 20 | 0.6 | 1 | 25 | 0.333 |
| F | 20 | 0.6 | 1 | 30 | 0.429 |
| G | 20 | 0.6 | 1 | 35 | 0.538 |
| H | 20 | 0.6 | 1 | 40 | 0.667 |
| I | 20 | 0.6 | 1 | 45 | 0.818 |

The amount of sodium phosphate used in gram (g) was calculated by using equation (1) below [19], where \(x\) is the weight of salt in gram, \(y\) is the weight of starch in gram, and \(wt\) is the total weight of salt and cornstarch in weight percent.

\[
x = \frac{wt \cdot y}{100 - wt}\]

(1)

2.3. Characterization

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)
Thermo Nicolet Avatar 380 FT-IR spectrometer was used to analyze the composition and complex formation in the sample. The spectral data were collected in the spectral range from 4000 to 500 cm\(^{-1}\)
with a spectral resolution of 4 cm\(^{-1}\). The sample was cut into a small size and was put on the germanium crystal; infrared light will pass through the sample.

### 2.3.2. Electrochemical Impedance Spectroscopy (EIS)

Impedance spectroscopy measurement was used to determine the bulk resistivity and electrolyte conductivity. The sample impedance was measured with a HIOKI 353101 LCR Hi-Tester that has been interfaced with a computer. The sample was cut to a suitable size that enough to cover the conductive holder of the electrodes. The bulk resistivity, \(R_b\), was obtained from the Cole-Cole plots from the EIS.

By using the bulk resistivity, the ionic conductivity, \(\sigma\) (Scm\(^{-1}\)), was calculated by using formula (2) [20] where \(R_b\) is the bulk resistance, \(t\) is the thickness of the thin film, and \(A\) is the surface area of contact.

\[
\sigma_{dc} = \frac{t}{R_b A}
\]  

### 3. Results and Discussion

#### 3.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectrum for starch and starch-Na\(_3\)PO\(_4\) films are shown in Figure 3. Based on the results, there were some major bands displayed at 3290 cm\(^{-1}\), 1656 cm\(^{-1}\), 1402 cm\(^{-1}\), and 1026 cm\(^{-1}\) can be observed for almost spectra, which were attributed to the starch. These patterns are similar to the FTIR pattern that has been achieved by Hassan et al., in 2018 [21]. The observation bands at 3290 cm\(^{-1}\) corresponded to the O-H stretching due to water absorption. The FTIR spectrum of the complex films also showed a C-O stretching at the plane 1026 cm\(^{-1}\) and O-H vibration bending at 1402 cm\(^{-1}\). The band at 1656 cm\(^{-1}\) was attributed to water existence in the starch molecules [22]. From the observation, there were a few modified peaks that can be detected, first at 2364 cm\(^{-1}\) with 5 wt.% of Na\(_3\)PO\(_4\); the peak started to emerge until 35 wt.% of Na\(_3\)PO\(_4\). The other peak is at 2943 cm\(^{-1}\), which is attributed to the starch peak as the Na\(_3\)PO\(_4\) is added, the peak started to disappear. Based on the spectrum of starch and starch-Na\(_3\)PO\(_4\), it can be confirmed that no chemical reactions occurred between starch and Na\(_3\)PO\(_4\) as the typical bands of starch and Na\(_3\)PO\(_4\) did not shows any new bands. The coexistence of peaks of the starch and Na\(_3\)PO\(_4\), confirming that the complex films were successfully prepared, and it can be concluded that the significant change in the chemical structure was affected by the addition of Na\(_3\)PO\(_4\) into the corn starch polymer.

![Figure 3. FTIR spectra for pure starch and starch-Na\(_3\)PO\(_4\) complex films.](image-url)
3.2. Electrochemical Impedance Spectroscopy (EIS) Analysis

The value of bulk resistances, $R_b$, and the ionic conductivity, $\sigma$, of the films are tabulated in Table 2. Figure 4 shows the trend of ionic conductivity of the film versus salt content at room temperature. The measured thicknesses of the samples were between $1.58 \times 10^{-2}$ to $2.56 \times 10^{-2}$ cm. They were used together with the bulk resistances to calculate the ionic conductivity of the films using the Equation (2).

The bulk resistance of the pure starch film was $8.40 \times 10^2 \Omega$ with an ionic conductivity of $0.06 \times 10^{-4}$ S cm$^{-1}$. The increasing trend of ionic conductivity can be seen in 30 to 40 wt.% of Na$_3$PO$_4$ with the highest value of $4.62 \times 10^{-4}$ S cm$^{-1}$ was obtained in 40 wt.% of Na$_3$PO$_4$ complex film. With the addition of 45 wt.% of Na$_3$PO$_4$, the bulk resistance rise to $0.19 \times 10^2 \Omega$ and decreased the ionic conductivity to $3.33 \times 10^{-4}$ S cm$^{-1}$. The increase in the number of free mobile ions resulted in the conductivity increment. For the decline in ionic conductivity trend, it due to ion association, which decreases the number of free ions available for conduction [23]. There are major factors that influence the raising ionic conductivity trend; first is the amorphous structure of the films that serve as a supporting medium for rapid ionic motion [19]. The second factor relates to the inorganic salt, which acts as the ionic dopant to the closed system until a saturated state is reached.

It also proved that the addition of glycerol with an increasing amount of Na$_3$PO$_4$ added in polymer matrix-salt diminishes the recrystallization of the salt. Besides, plasticizer generates alternate forms for the conduction of ion, which helps the salt to be accommodated by the polymer host, thus increased the polymer electrolytes ionic conductivity. The addition of salt enhanced the mobile ions density, which is the main reason for the increasing and enhancement of ionic conductivity, as reported by Khanmirzaei and Ramesh in 2013 [24]. Frequency and temperature also were found to affect the conductivity. The accumulation of charge carriers at the electrode-electrolyte interface resulted in lower conductivity at low frequency [25].

**Table 2.** The bulk resistance and conductivity of pure starch and starch-Na$_3$PO$_4$ complex films.

| Sample (wt.%) | $R_b (\Omega) \times 10^2$ | $\sigma$ S cm$^{-1} \times 10^{-4}$ |
|--------------|--------------------------|-----------------------------------|
| Pure         | 8.40                     | 0.06                              |
| 5            | 2.59                     | 0.21                              |
| 10           | 1.18                     | 0.56                              |
| 15           | 2.43                     | 0.28                              |
| 20           | 0.90                     | 0.75                              |
| 25           | 1.21                     | 0.51                              |
| 30           | 0.86                     | 0.84                              |
| 35           | 0.38                     | 2.17                              |
| 40           | 0.12                     | 4.62                              |
| 45           | 0.19                     | 3.33                              |
4. Conclusion
In this work, solid polymer electrolytes based on starch as the polymer host and the sodium phosphate (Na$_3$PO$_4$) as the ionic dopant has been successfully prepared using a solution casting technique. The effects of Na$_3$PO$_4$ on the starch structure were investigated using Fourier transform infrared spectroscopy (FTIR) and electrochemical impedance spectroscopy (EIS). The FTIR was confirming that the complex films were successfully prepared based on the coexistence of peaks of the starch and Na$_3$PO$_4$. The highest ionic conductivity of $4.62 \times 10^{-4}$ S cm$^{-1}$ was obtained at room temperature (303K) for the sample containing 40 wt % of Na$_3$PO$_4$, which is corresponding to the high number of free mobile ions in the complex films. This SPE is believed to have great potential in current and future energy storage applications.

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