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Corn Starch-Sodium Acetat Composite Material from Industrial Waste Fly Ash for Solid Electrolyte Polymer Ionic Conductivity in Supercapacitor Application

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Abstract. Solid polymer electrolyte (SPE) is a safer alternative to use than liquid electrolytes. This research focuses on the highest conductivity with fly ash filler in solid polymer electrolyte (SPE) based on corn starch, using the solution casting method. The crystallinity and interaction between fly ash and Na^+ ions of solid polymer electrolyte were seen by X-ray Diffraction (XRD), then Fourier Transform Infra-Red (FTIR), showing a shift in functional groups due to the interaction of SiO_2 in fly ash and Na^+ ions, and surface morphology forms was observed by Scanning Electron Microscopy (SEM). Ionic conductivity was analyzed by Electrochemical impedance Spectrometry (EIS). solid polymer electrolyte with fly ash showed the highest ionic conductivity 2,51 x 10^{-4} S/cm, at room temperature with addition fly ash 10%. the highest conductivity result was corresponding with amorphous peak with same concetration on XRD. SPE based on corn starch with Fly ash filler has potential to be used as a solid polymer electrolyte in supercapacitors.

Introduction

The supercapacitor design is almost the same as the ordinary capacitor design which consists of a pair of electrodes filled with electrolyte and separated by a dielectric material as an insulator. In general, electrolytes are in the form of liquids, but the use of liquid electrolytes has drawbacks including being less practical, leaking easily and easily corroding [1]. Therefore, to overcome this problem Solid Polymer Electrolyte (SPE) as an alternative electrolyte in supercapacitors. SPE can overcome some of the problems inherent in liquid electrolytes, namely, it is safer than liquid electrolytes, electrode systems that have non-flammable electrolytes, better storage capacity and in terms of safety, will not leak as in liquid electrolytes [2].

Starch easily ionizes in water and forms a thin film easily. When compared to corn starch, arrowroot starch, potato starch, they have good morphology and form a flexible film that produces high ionic conductivity [3].Therefore, solid polymer electrolytes are prepared by dissolving inorganic salts such as potassium acetate and sodium acetate in a polymer matrix. In the research of F.F. Awang (2020) added $NaIO_3$ to SPE corn starch, and got an increase from 1.1×10^{-6} Scm^{-1} to 1.08×10^{-4} with 3% $NaIO_3$. Therefore, in this study, sodium acetate (CH_3COONa) was used as a salt solution in the polymer because it is an abundant natural earth element and is widely used [8,9]. Supercapacitors are one of the energy storage devices that can use solid electrolytes, but the lower ionic conductivity of liquid polymer electrolytes and poor accessibility to ions in the device limit their wide application in the electronics industry [13]. Therefore, to increase the ionic conductivity in several previous studies, fillers such as SiO_2, Al_2O_3, and fly ash were added [2,14] it was found that the highest conductivity was obtained by the addition of fly ash.In the study of Ni'mah Y,L, et al, the maximum ion conductivity was 2.13 x 10^{-4} S/cm^{-1} at 60ºC with PEO-Na polymer and 5% fly ash, then research by Wardhani A,S,S, obtained a maximum ionic conductivity of 1,730 x 10^{-4} S/cm^{-1} at 60ºC with PEO - $LiClO_4$ and fly ash 5%. This is because the excess in Fly Ash is rich in a mixture of oxides containing silicon (SiO_2), iron (Fe_2O_3), and aluminum (Al_2O_3) [2]. Fly Ash is a waste from coal combustion in conventional power plants so it is cheap and easy to obtain. So in this study it is hoped that the use of fly ash as a filler on solid polymer corn starch and sodium acetate can increase the SPE ion conductivity in the supercapacitor and is friendly to the environment.

Materials and Methods

A.Experiment

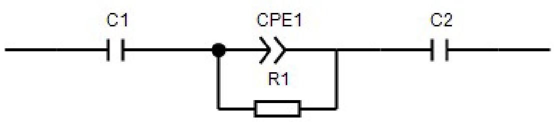
The manufacture of SPE in this study was carried out by the solution casting method [2,4], Fly ash was added as a filler referring to the journal in the manufacture of electrolyte polymers which made the ionic conductivity of the spe more better [1,2]. The homogeneous solution is heated to evaporate the solution and make a solid electrolyte polymer. Heating using the oven for 8-12 hours at a temperature of 50ºC.Synthesis of solid electrolyte polymer using Corn Starch as polymer, Sodium Acetate (CH_3C00Na) 15% as salt, Glyserol 85%, Aquades and using fly ash with variations of 0%, 10%, and 20% as filler.

B. Materials Characterization And Electrochemical Test

The synthesized SPE samples were then characterized using an X-ray diffractometer (XRD). X-ray diffraction measurements were carried out at an angle of 5º - 90º and used a CuKα wavelength of 1.54056 , Ni filter, 40 kV and 100 mA. All samples were analyzed in the range of 2θ = 10º - 70º. FTIR Thermo Scientific Nicolet iS10 to Identification of functional groups, ionic interactions with polymers,salt and flyash. SEM (Scanning Electron Microscope) type Type FEI Inspect S50, analysis was carried out to determine the surface morphology of the solid polymer electrolyte (SPE). Image images are captured at various magnifications of 2500x, 5000x, 10,000x and 15,000x.

C. Electrochemical Test

Electrochemical Impedance Spectroscopy (EIS) test to Measurement of resistance and capacitance using type CS Series 5 Electrochemical Workstation. Conductivity value is observed with a frequency range of (1 MHz – 1 Hz).



Rb **(Ω)**

Fig. 4.1 Equivalent circuit from of EIS test on SPE [16].

The measurement results is in the form of a Nyquist plot between the imaginary impedance (Z") and the real impedance (Z') which shows the capacitance and resistance value of the material and resulting semicircle graph [16]. The equivalent circuit obtained from this SPE is as shown in Figure 4.1.

$$\sigma = \frac{l}{R\text{b } x \; A} \tag{1.1}$$

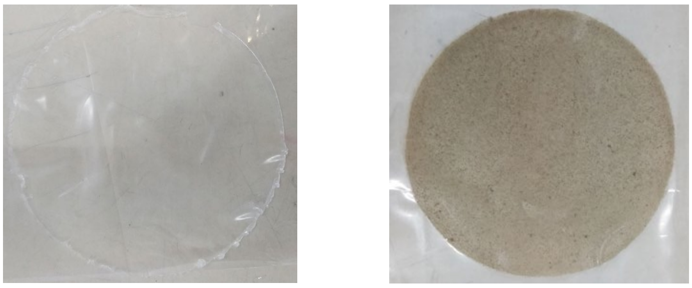
From result test can determine the ionic conductivity of the SPE sample according to equation 1.1.Where the ionic conductivity (σ) is calculated in units of S/cm, I is the thickness of the SPE sheet in centimeters, Rb is the resistance in Ohms, and A is the cross-sectional area.

Result and Discussion

Solid polymer electrolytes (SPE) generally use natural polymers such as corn starch as a home or host, and salts as ionic dopants such as the use of sodium acetate (CH_3COONa). The performance of the solid polymer electrolyte (SPE) is based on higher value of ionic conductivity. in this case the Na^+ ion in sodium acetate (CH_3COONa) and SiO_2 and other element in fly ash is very important for higher ionic conductivity. The greater the number of Na^+ ions in the polymer, under the same ion mobility conditions, the conductivity also tends to increase.

A. Solid Polymer Electrolyte (SPE) Synthesis Results

The results of the synthesis will be in the form of SPE film sheets like the results of previous solid polymer synthesis experiments[2,4,6].



without fly ash with fly ash

Fig. 4.2 Solid electrolyte polymer (SPE)

The results of the SPE film sheet in Figure 4.2 with different variations of fly ash. It can be seen that the variation without using fly ash has a transparent white color and a smoother surface. fly ash variation which has a contrast apperance with brown color and a rougher surface than non varian fly ash, the higher the flyash concentration added it have darker color and the rougher surface [2].

B. XRD Analysis

XRD characterization aims to identify the pattern of crystalline and amorphous microstructures that occur in the synthesis of solid electrolyte polymers. The diffraction pattern of the addition of corn starch, CH_3COONa and fly ash samples.

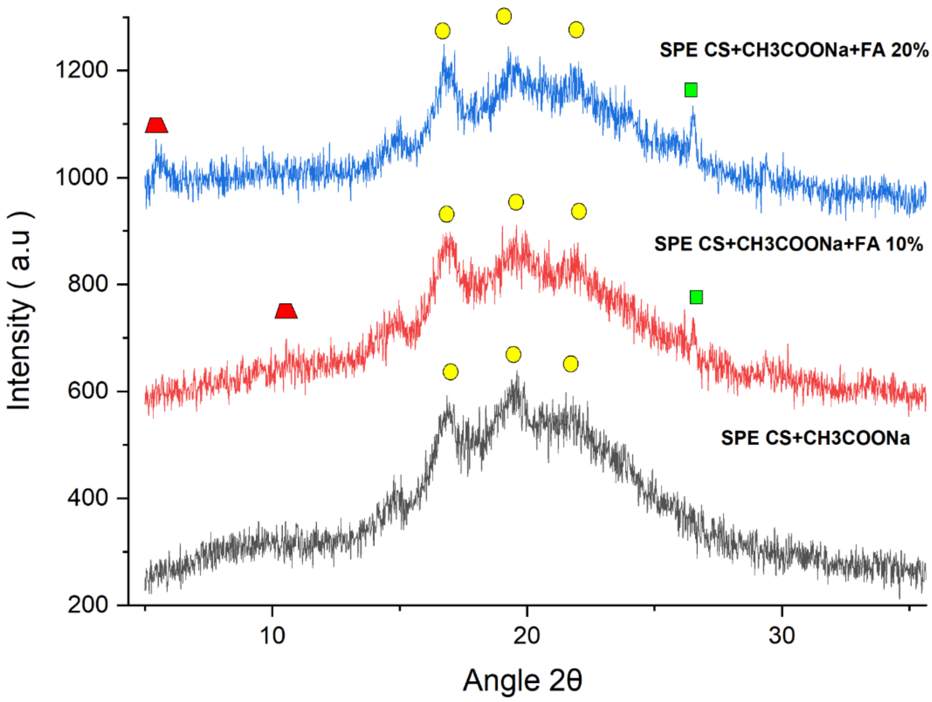


Fig. 4.3 Comparison of XRD pattern of SPE

The results of the XRD pattern show that the increase of amount fly ash increases, the diffraction peaks gradually decrease and there is new identical peak at 2θ = 26,55328° with increase of amount fly ash from SiO_2 content in fly ash (green color symbol). The results figure 4.3, its seen how to corn starch as host polymer at peak 2θ = 5,63°, 10,54° (red color symbol) and sodium acetat (CH_3COONa) produces an amorphous SPE [11] at peak (yellow color symbol) 2θ = 14,76°- 14,99°, 2θ = 16,90°- 14,86°, 2θ = 19,24°- 14,60° and 2θ = 21,54°- 22,06°. The addition of filler fly ash 10% and 20% show XRD pattern and with there no fly ash addition (0%) have more sharp amorphous peak.

The result indicates that fly ash can be reduces crystallinity of entirety XRD pattern but show a new peaks but still more amorphous than without addition of fly ash and XRD peaks are increasingly sloping down accordance with amorphous structure [2,3,4,11]. The decrease in crystallinity of the spe to amorphous makes the solid polymer properties change to be more electrolyte and higher ionic conductivity. The amorphous polymer electrolyte matrix facilitates the mobility of Na^+ ions in the matrix, with an increase in the mobility of Na^+ ions in the matrix, charge transfer increases so that the Solid Polymer Electrolyte becomes more conductive [2,12].

C.FTIR Analysis

Change in the frequency of the strain or bending vibration of a particular bond of the SPE sample can be characterized by FTIR and local interactions of the polymer with the salt and fly ash. The peak intensity, peak shift associated with the presence of salt and the emergence of new bonds due to the presence of fly ash in the polymer.

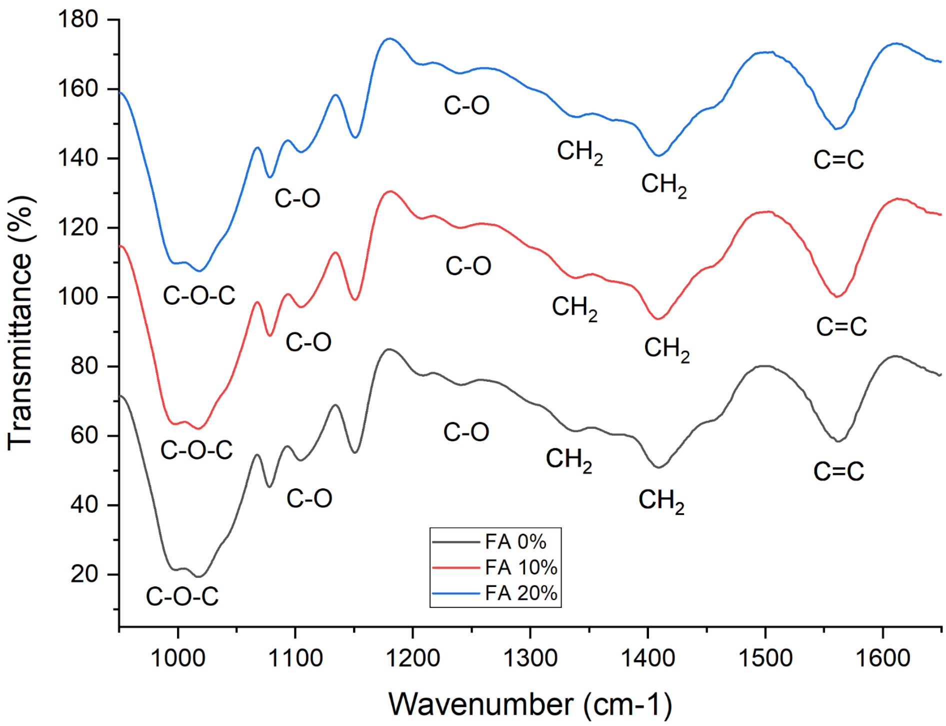
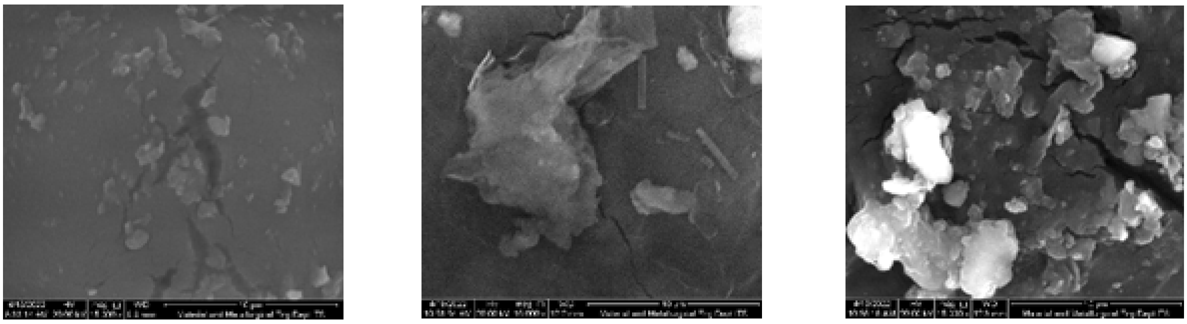


Fig. 4.4 FTIR Spectrum Result of SPE

The FTIR spectrum without fly ash and with various concentrations of fly ash filler obtained by FTIR spectrophotometer in the range of 900-1700 cm^{-1} can be observed in Fig. 4.4. Infrared spectra of corn starch polymer and CH_3COONa without fly ash filler identified characteristic peaks at CH_2 ,C-O, C=C, C-O-C group. After adding Fly Ash with various variations, the peaks in the wave number are identified. Fly ash peaks can usually be observed in the wavelength range of 1250 cm^{-1} and the activation of fly ash creates vibrations that make the peaks sharper [2].

D. Morphological Analysis

SEM (Scanning Electron Microscope) analysis was carried out to determine the surface morphology of the solid polymer electrolyte (SPE)



(a) 0% fly ash (b) 10% fly ash (c) 20% fly ash

Fig. 4.5 Surface Morfology of SPE with 15,000x magnification

In sample solid polymer electrolyte with the addition of fly ash 0%, 10% and 20% show membrane looks rough, textured and hollow be arranged randomly (irregularly), while the bond between the polymer chains are well arranged. It can be seen that the three components of the raw material react to form, which and pull the polymer chains to form pores in the spe film, figure 4.5. In addition, larger pore size will also contribute to higher ion penetration through the system for ion conduction. Therefore, it is clear that the number of voids or pores formed causes the porosity of the SPE film to increase. This makes that the higher conductivity value is influenced by the porosity of the SPE film [8,9].

E. Electrochemical Analysis

The most important thing about solid polymer electrolyte (SPE) is the conductivity value. To determine the conductivity value, it is necessary to know the value of the bulk resistance (Rb). To analyze the Electrochemical Impedance Spectroscopy (EIS) test, and use the CS Studio 5 software. The conductivity value is observed with a frequency range of (1 MHz – 1 Hz). From the results of a quarter circle nyquist plot at low frequencies on the real Z axis, it shows that there is a change in the conductivity of the added fly ash concentration figure 4.6

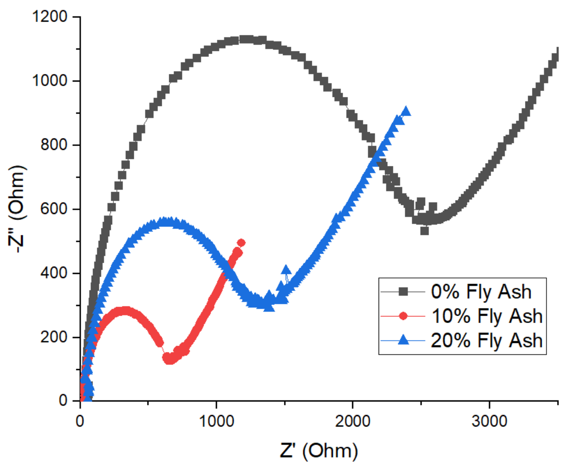


Fig. 4.6. Nyquist Plot SPE at Room Temperature

In addition to confirming the value of bulk resistance (Rb) obtained from the results of electrochemical semicircle fit fittings, the equivalent circuit, Figure 4.1 explains how the SPE is assembled. A battery based on the equivalent circuit in Figure 4.6, it can be seen that the bulk resistance (Rb) is the SPE resistance value between the capacitance units.The conductivity value is influenced by the bulk resistance and the thickness of the sample. the lower the bulk resistance, the greater the conductivity and the thicker the sample, the higher the ion conductivity.

The results Table 4.1 of the Ionic Conductivity based on Equivalent circuit from EIS test determine the ionic conductivity of the SPE sample according to equation 1.1. Table 4.1 shows, FA+10% have the highest Ionic conductivity of 2.51 $\times 10^{-4}$ S/cm and lowest bulk resistance (Rb) to. The conductivity reuslt are related to the amorphicity properties of the starch host, also reported by previous experiment.

Table 1. Ionic Conductivity Value ($S.cm^{-1}$) for Each Sample

Sample	*l* (cm)	*Rb* (Ω)	*σ* (S/cm)
CS - CH_3COONa	0,22 x10^{-1}	256.7632	8,56 x 10^{-5}
CS - CH_3COONa + FA 10%	0,32 x10^{-1}	127.4762	2,51 x 10^{-4}
CS - CH_3COONa + FA 20%	0,22 x10^{-1}	147.4804	1,49 x 10^{-4}

Conclusion

Based on the results of research analysis on SPE samples, it can be concluded as follows: The addition of fly ash filler can affect the characteristics of the SPE show from EIS analysis of 10% addition of fly ash have more higher ionic conductivity with σ = 2,51 x 10^{-4} it consist From the XRD results, it is known that the addition of Fly Ash to SPE can reduce the level of crystallinity and turn it into a more amorphous one, and identical peak at 2θ = 26,55° with increase of amount fly ash. Then from the results of the ftir there is a minor shift of the functional group due to the presence of CH_3COONa salt, The results of the SEM also shows that the surface structure is more larger area with cracks existence with addition of fly ash indicate more ion store in SPE and higher ionic conductivity.

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