IONIC CONDUCTIVITY OF CHITOSAN/LiOH POLYMER MEMBRANE DISPERSED SILICA FLY ASH AS SOLID ELECTROLYTE MATERIAL FOR SECONDARY BATTERY

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Abstract. One of the components of the secondary battery is the electrolyte, which acts as a bridge for ion movement within the battery. The electrolyte currently being developed is a membrane-type solid electrolyte. Membrane-type electrolytes can be modified by adding salts and inorganic fillers. The material of the solid electrolyte is chitosan modified by adding LiOH salt, and silica is added as an inorganic filler by solution casting. The silicon dioxide used is obtained from fly ash, a waste product of coal combustion with a silicon dioxide content of 65.97%. The silica contained in fly ash can be used as an inorganic filler in polymeric membranes. Variations in the addition of fly ash silica used are 0% and 12% with Electrochemical Impedance Spectroscopy (EIS) characterization. The results of the EIS characterization are aimed at determining the ionic conductivity value of the membrane. EIS characterization of chitosan, chitosan/LiOH, and chitosan/LiOH/12% silica fly ash membranes resulted in values of 1.275 x 10^{-8}, 3.824 x 10^{-6}, and 1.304 x 10^{-4} S/cm, respectively. The increase in ionic conductivity with the addition of silica indicates that the presence of silica fly ash can affect the ionic conductivity values of the solid electrolyte polymer membrane.

Keywords: secondary battery, electrolyte, chitosan, LiOH, silica fly ash

A. Introduction

The ever-evolving era of globalization has led to an increasing need for energy sources. Energy sources can be obtained through energy storage technologies, one of which is batteries [1]. Batteries are battery storage technologies that can convert chemical energy into electrical energy. There are two types of batteries: secondary batteries and primary batteries. The most efficient type of battery is secondary batteries, as they can be used repeatedly by recharging them when empty [2]. The most widely used secondary battery is the lithium battery. A lithium battery is a battery that uses lithium ions (Li+) as the positive and negative electrode materials. The advantages of lithium batteries compared to other types of batteries are their high potential difference, high specific capacity, high energy density, and long service life (500-1,000 cycles)

[3]. A lithium battery consists of several components, such as a positive electrode (cathode), a negative electrode (anode), a separator, and an electrolyte [4].

The electrolyte in the battery acts as a medium to move ions within the battery. The electrolyte used in secondary batteries may be a solid electrolyte. The advantages of solid electrolytes compared to other types of electrolytes are that they are solid, safer, more practical, and can be produced in smaller and thinner sizes, and therefore do not leak easily [5]. Solid electrolytes can be used as alternative electrolytes in secondary batteries, especially in the form of polymer membranes. Solid electrolyte polymer membranes are materials that combine inorganic materials such as lithium salts in a polymer matrix. The requirements for solid electrolyte polymer membranes are high mechanical strength, thermal stability, high ionic conductivity above 10^{-5} Scm^{-1}, chemical stability (not easy to explode), and the ability to produce samples in thin sizes [6].

Previously research, solid electrolyte polymer membranes could be fabricated using one type of polymer, namely Chitosan. Chitosan is a natural polymer consisting of amine and hydroxyl functional groups. Chitosan has the advantages of being biodegradable, non-toxic, and hydrophilic [7]. However, chitosan has the disadvantage of being an insulator. To improve the quality of the membrane as a solid electrolyte material, the properties of the insulator need to be modified. Modifications that can be made to improve the quality of the film include the addition of oxide fillers such as lithium salts and silicon dioxide (SiO_2). Silicon dioxide is a material whose main component is silicon dioxide (SiO_2). Silica compounds are found in several materials, one of which is fly ash [8][9].

Fly ash is a waste product of coal combustion and its handling is still very limited. Fly ash silica waste should be used because restricting the handling of fly ash waste could be dangerous to the environment. Fly ash contains soil mineral elements such as 65.97% silicon dioxide (SiO_2), 26.64% aluminum oxide (Al_2O_3), and 5.69% iron oxide (Fe_2O_3) [10]. The rather high silica content in fly ash can be used as a filler for solid electrolyte polymer membranes. The synthesis of CTAB-modified chitosan/silica fly ash membranes was carried out using a phase inversion method with stirring times varied from 2 h, 4 h, and 8 h. Silica amounts varied from 0, 0.5, 1, 2, and 7 h. 5% w/w. chitosan. CTAB-modified chitosan/silica fly ash membrane provided the best-performing membrane with a conductivity of 1.4634 x 10^{-4} S/cm when 5% silica fly ash was added [11]).

In this work, the synthesis of chitosan/LiOH solid electrolyte polymer membranes with dispersed silica fly ash. The silica variations used were 0% and 12% (w/w) of the chitosan mass. It is expected that the presence of dispersed silica fly ash in the chitosan/LiOH solid electrolyte polymer membranes will increase the ionic conductivity values. The synthesis method for the solid electrolyte polymer membranes is the solution casting method (simple casting method). The characterization used is electrochemical impedance spectroscopy (EIS) to determine the ionic conductivity values of the membranes can be used as a solid polymer electrolyte battery.

B. Methods

1. Materials

The materials in this research are chitosan, fly ash, lithium hidroksida (LiOH), Acetat Acid (CH_3COOH), NaOH, HCl, distilled water, pH meter, mortar, petri dish, beaker, OHAUS balance, Hot Plate Stirrer, mesh sieve, and drying oven.

2. Instruments

The silica variations used were 0% and 12% (w/w) of the chitosan mass samples were studied by an LCR Meter type Hioki 3532-50 LCR HITESTER. The data results obtained include impedance and conductance values against frequency.

3. Procedure

The synthesis research of chitosan/LiOH polymer membranes with 0% and 12% (w/w) silica variations. The synthesis process of polymer membranes was carried out using the solution casting method. Solution casting is performed by dissolving the polymers and other raw materials in a suitable solvent and then combining or mixing them. The synthesis of polymer membranes was carried out by first weighing 12% (w/w) silica fly ash from chitosan chunks, dissolving it in 100 mL of 1% CH_3COOH, and stirring with a magnetic stirrer at a speed of 750 rpm for 1 h. Further, 2 grams of chitosan was added to the solution and stirred for 2 h. After the mixture became homogeneous, 10% (w/w) LiOH salt was added and stirred for 3 hours, until the solution was homogeneous. The homogeneous solution was then poured into a Petri dish and placed in an oven/dryer until dry, then the characterization used electrochemical impedance spectroscopy (EIS) characterization. The purpose of EIS characterization is to determine the ionic conductivity, and impedance of the membrane.

C. Results And Discussion

The synthesis of chitosan/LiOH polymer membranes with dispersed silica fly ash was successfully carried out using a solution casting method. Figure 1 shows a sample of the solid electrolyte polymer membrane. The obtained polymer membrane exhibits a color close to yellow due to the influence of chitosan as a polymer host. The surface of the membrane is smooth and transparent, without spots or agglomerations (lumps). This suggests that the membrane is completely dissolved and a uniform polymer is formed. The resulting polymer film thickness is 0.100 - 0.350 mm.

(a) (b) (c)

Figure 1. Polymer membrane (a) chitosan, (b) chitosan/LiOH, (c) chitosan/LiOH dispersed with 12% silica fly ash

The results of characterization using electrochemical impedance spectroscopy (EIS) allow the determination of the ionic conductivity value of the membrane. Ionic conductivity is the electrical conductivity caused by the easy movement of charge carrier particles. Ionic conductivity is calculated using Equation 1 [12]:

$$\sigma = G\ x \frac{l}{A} \tag{1}$$

where σ is the ionic conductivity (S/cm), *l* is the sample thickness (cm), *A* is the outer surface of the material (cm), and *G* is the conductance (S). The conductivity obtained is the AC conductivity, whose value increases as the frequency used increases. Figure 2 shows the AC conductivity of chitosan, chitosan/LiOH, and chitosan/LiOH/silica polymer membranes.

From Figure 2, it can be seen that as the frequency increases, the AC ionic conductivity value increases. The ionic conductivity of the membrane can be determined by fitting using the Jonscher power law method. The Jonscher power law equation is the general equation for conductivity using Equation 2 [13], and Figure 3.:

$$\sigma_\omega = \sigma_{dc} + A\omega^s \tag{2}$$

where σ_ω is the AC conductivity, σ_{dc} is the DC conductivity, s is an exponential function of the AC conductivity whose value is in the range $0 \le s \le 1$, and A is a constant pre-exponential function of the AC conductivity.

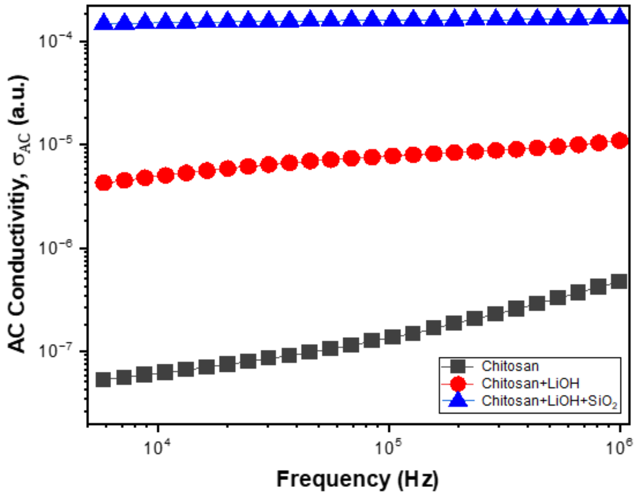

Figure 2. AC conductivity of chitosan, chitosan/LiOH, and chitosan/LiOH dispersed with 12% silica fly ash

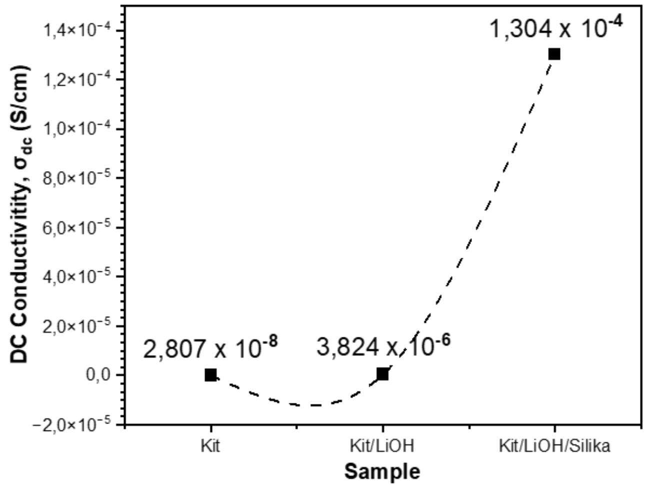

Figure 3. DC conductivity of chitosan, chitosan/LiOH, and chitosan/LiOH dispersed with 12% silica fly ash

Figure 3 shows the resulting ionic conductivity shows that the chitosan polymer membrane has the lowest value of 2.807 x 10^{-8} S/cm. The ionic conductivity value increases with the addition of LiOH resulting in a conductivity value of 3.824 x 10^{-6} S/cm. The addition of 12% silica fly ash has a significant effect on the conductivity value of chitosan/LiOH polymer membrane resulting in an ionic conductivity of 1.304 x 10^{-4} S/cm. The increase in ionic conductivity occurs due to the transition from the polymer phase to the amorphous phase, increase in the number of ions, and increase in the mobility of charge carrier ions [14].

The highest ionic conductivity was achieved in chitosan/LiOH polymer membranes with 12% silicon dioxide addition. This value can meet the requirement that the ionic conductivity of the polymer electrolyte membrane is about 10^{-5} S/cm. The addition of silica fly ash as an inorganic filler can enhance the ionic conductivity value of the polymer electrolyte membrane [15]. This is because the addition of silica fly ash can promote the migration of Li^+ ions in the polymer matrix, thereby increasing the ionic conductivity of the membrane. The addition of silica fly ash in this study was able to produce a significantly higher conductivity value compared to the previous study with the addition of silica fume, which resulted in a conductivity of 2.004 x 10^{-7} S/cm [16]. Additionally, another study added silica fly ash to chitosan/CTAB membranes and obtained a conductivity value of 1.4634 x 10^{-4} S/cm [17]. The conductivity values are higher than in previous studies, but the range of values is not too far from the results of previous studies.

D. Conclusion

The results of the study can be concluded that Chitosan/LiOH solid electrolyte polymer membranes with dispersed silica fly ash polymer membrane were successfully using the solution casting method to produce a clear, evenly colored polymer membrane with good dimensional stability or size. The variation of silica fly ash loading used was 0% (w/w) and 12% (w/w) of chitosan mass. The surface morphology of the polymer membranes showed a smooth and transparent surface with a tendency to yellow color, indicating no aggregation and homogeneous membranes. Electrochemical impedance spectroscopy (EIS) results showed that chitosan/LiOH polymer membranes with 12% silica fly ash loading had the highest ionic conductivity value compared to chitosan and chitosan/LiOH polymer membranes. The conclusion is that fly ash silica can be used as an alternative synthesis of solid electrolyte membranes for secondary batteries.

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F. References

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