Synthesis and characterization of chitosan – LiClO₄ solid electrolyte membrane and its application in batteries

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Abstract. The Synthesis of chitosan - LiClO₄ solid electrolyte membrane has been carried out. The membrane is prepared by using a casting method. Chitosan 0.6 gram, LiClO₄ (Sigma-Aldrich ≥ 95%) with variations of 10% and 40% (w / w) and 10% PVA (w / w) put into the measuring cup. Furthermore, the mixture was dissolved in a 2% acetic acid solution of 30 mL (v / v) and stirred evenly at room temperature. The solution is then put into an acrylic casting plate measuring 30x5 cm and allowed to stand dry. The electrolyte membrane was then analyzed for functional groups using FTIR and conductivity using the HICRI 3532-50 Hi-Tester LCR. The FTIR results stated that the addition of lithium caused a shift in the wave number 2871 to 2920 cm⁻¹ which showed the presence of the OCH₃ group, while the highest conductivity value was 3.98 x 10⁻⁷ - 3.16 x 10⁻⁶ at a frequency of 42 Hz - 5MHz. These results provide information that the synthesized membrane can be applied as an electrolyte membrane on the batteries.

1. Introduction
The utility of electrical energy in the past decade has tended to increase along with the rapid development of portable electronic technology [1]. Therefore, various attempts have been made by researchers in the development of electrical energy storage media that have high performance and also a long usage period including batteries [2]. One of the most important components of a battery is an electrolyte. Developers of types of materials that can be used as electrolytes continue to be carried out. The material that can be used as an electrolyte must meet the requirements of which must have a high conductivity value so that the current delivery process can run well [3].

Currently the electrolyte material that is often used and also a source of power in batteries is lithium. Lithium ion batteries have several advantages such as high energy density and long life cycles [2]. The electrolyte used in lithium batteries is in the form of liquid electrolyte so that it has several disadvantages including being vulnerable to leaking and easily producing gas in the process of overcharging [4]. Therefore, the use of solid electrolytes is increasing with consideration of safety factors and high-safety awareness. In addition to these two factors, polymer electrolytes which are
more widely developed because they have several advantages, for example, are easily fabricate, easily formed and have good mechanical properties [5].

These solid polymer electrolytes can be obtained either synthetically or naturally. However, synthetic polymers tend to cause new problems including expensive, difficult to degrade naturally and also not environmentally friendly [6]. Therefore the use of natural polymeric materials which are able to be a solution to these problems continues to be developed. One of the natural polymer materials that is currently being developed is chitosan. Chitosan is a polymeric material produced through the process of deacetylation of chitin, which is found in many shells of crustacean animals which are very abundant in nature.

One of the abundant sources of chitosan in Indonesia is from crab shells (Portunus pelagis). Small crab shells (Portunus pelagis) are still untapped waste, especially on the island of Bangka. This shell waste actually has a high value due to its chitin and chitosan content. The results of previous studies showed that chitosan content in crab shells reached 13.27% while chitin reached 23.98%. Therefore, the high content of chitosan in the crab shell (Portunus pelagis) has the potential to be further developed into polymers which have high ecological values such as lithium battery electrolyte membranes.

Chitosan tends to be an insulator, so to increase the ionic conductivity it is necessary to add salts or add oxide fillers. [7] has conducted a study on the addition of lithium salts (LiPF6 and Li-Triplat) to the properties of chitosan-based solid electrolytes and obtained conductivity values of around 10-6 S/cm. [8] examined the conductivity value of chitosan-based solid electrolyte membranes by varying the concentration of LiOH salts of 0.1301 S/cm in the chitosan-LiOH variation (85:15)% w/w. Lithium energy with low lattice energy has more potential as an electrolyte. This is because it has a greater degree of dissociation, thus helping to transport Li+ ions [9]. Some studies report that lithium salts that are good as electrolyte membranes are salts that have large anions such as BF4- (tetrafluoroborate ions), CF3SO3- (triflate ions), DFOB- (difluoro (oxalato) borate), and ClO4- (perchlorate). Based on these problems, this study examines the synthesis and characterization of chitosan-LiClO4 solid electrolyte membranes and their application to batteries.

2. Research Methods
2.1 Manufacturing of Chitosan-Lithium Electrolyte Polymer Membranes
Polymers are made using the casting method. Chitosan 0.6 gram, LiClO4 (Sigma-Aldrich ≥ 95%) with variations of 10% and 40% (w/w) and 10% PVA (w/w) put into the measuring cup. Furthermore, the mixture was dissolved in a 2% acetic acid solution of 30 mL (v/v) and stirred evenly at room temperature. The solution was then placed in a 30x5 cm acrylic casting plate and allowed to dry (Figure 1).

![Figure 1. Electrolyte membrane preparation.](image-url)
The electrolyte membrane was then analyzed for functional groups using FTIR and conductivity using the HICRI 3532-50 Hi-Tester LCR. Variations and sample codes are shown in table 1.

| Sample | Composition | % LiClO₄ (w/w) | % PVA (w/w) |
|--------|-------------|----------------|-------------|
| A      | 0.6         | 30             | 10%         | 0           |
| B      | 0.6         | 30             | 40%         | 0           |
| C      | 0.6         | 30             | 40%         | 10%         |

2.2 Ionic Conductivity Study

The ionic conductivity test of the three electrolyte membrane sample was measured using the Electrochemical Impedance Spectroscopy (EIS) method using the HIOKI 3532-50 Hi-Tester LCR in the 42 Hz - 5 MHz frequency range with 1 Volt AC amplitude. By using parameters generated from EIS methods such as $Z'$ (real) and $Z''$ (imaginary), the magnitude of the ionic conductivity can be calculated using equation [1], which is:

$$\sigma = G \left( \frac{d}{A} \right)$$  \hspace{1cm} (1)

where $d$ is the thickness of the polymer electrolyte film, $A$ is the electrode area and $G$ is the conductance.

3. Result and Discussion

3.1 IR Analysis of electrolyte membrane

FT IR analysis functions to determine the functional groups on the electrolyte membrane. Based on the results of the FT IR spectrum (figure 2) shows that the addition of lithium makes the shift in wave number 2871 to 2920 cm⁻¹ which indicates the presence of OCH₃ groups. Some intensity changes occur. Changes in the intensity of these bands are closely related to changes in the order of macromolecules. These bands in the complex spectrum can be produced from increasingly ordered structures due to the addition of LiClO₄ salt.

![Figure 2. IR analysis of: a. Chitosan; b. Sample A; c. Sample C](image-url)
3.2 Ionic Conductivity Study

One method of characterizing the electrical properties of a material is the impedance spectroscopy method. The parameters measured in impedance spectroscopy are parameters that depend on frequency functions such as $z'$ (real) and $z''$ (imaginary) which are then processed in the form of cole-cole plot. The graph pattern for the three electrolyte polymer membrane samples is shown as in Figure 3. The graph pattern in Figure 3 consists of a semicircular curve in the high frequency region related to the nature of the parallel combination between bulk capacitance and bulk resistance of the material and the straight-line slope curve in the frequency region low associated with the inhomogeneous nature of the interface between the electrode and the electrolyte [10].

![Figure 3. Nyquist Plot of the Electrolyte Membrane Samples](image)

In sample A as shown in Figure 3 the half circle pattern tends to be imperfect so that the straight line slope pattern has not yet formed which means that the bulk resistance of the sample is very large. Bulk resistance is obtained from the point of interception between the semicircular curve with the $z$ real axis of complex impedance plotting. This is different from samples B and C, where bulk resistance has been observed. This bulk barrier will affect the conductivity value. Conductivity which is a measure of the ability to conduct electricity in this case the movement of ions or can also be called ionic conductivity. The ionic conductivity of the electrolyte membrane sample is measured at a frequency of 42 Hz - 5MHz, as shown in Figure 4.

![Figure 4. Conductivity of electrolyte membrane samples as a function of frequency](image)
The pattern shown for all electrolyte membrane samples tends to have a plateau pattern which means that the conductivity values tend not to be frequency dependent in the low to moderate frequency region. The highest conductivity value is given by sample B in order $10^{-6}$ and the lowest sample A is in order $10^{-7}$. This result is consistent with data from the cole-plot plot shown in Figure 3.

Table 2. The conductivity values of the electrolyte membrane samples were measured at a frequency of 42 Hz - 5 MHz

| Sample code | Thickness (cm) | Surface area (cm$^2$) | Conductivity (S/cm)       |
|-------------|----------------|------------------------|---------------------------|
| A           | 0.0066         | 0.7694                 | $2.52 \times 10^{-8} - 2.43 \times 10^{-7}$ |
| B           | 0.0048         | 0.7694                 | $3.98 \times 10^{-7} - 3.16 \times 10^{-6}$ |
| C           | 0.0053         | 0.7694                 | $5.2 \times 10^{-7} - 2.58 \times 10^{-6}$ |

4. Conclusion

The electrolyte polymer membrane synthesized from chitosan with the addition of lithium salt made a shift in wave number 2871 to 2920 cm$^{-1}$, which indicates the presence of OCH$_3$ groups. While the value of ionic conductivity measured at a frequency of 42 Hz - 5 MHz has the highest value of $3.16 \times 10^{-6}$ S/cm which has met the standard as an electrolyte membrane for battery application.

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