FUNCTIONAL GROUP AND IONIC CONDUCTIVITY OF CARBOXYMETHYL CELLULOSE (CMC)/LITHIUM TRIFLATE ($LiCF_3SO_3$) POLYMER MEMBRANE DISPERSED WITH RICE HUSK ASH SILICA AS SOLID ELECTROLYTE IN SECONDARY BATTERY

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Abstract. One of the components of the battery is an electrolyte that acts as an ion transfer medium. The solid electrolyte is currently being developed as a membrane because of its higher level of safety. The solution casting method modifies the solid electrolyte by adding rice husk ash silica to the CMC/$LiCF_3SO_3$ membrane. The rice husk ash silica concentration was 0% and 12% w/w. The characterization carried out in this study was Fourier-Transform Infrared (FTIR) and Electrochemical Impedance Spectroscopy (EIS). The results of FTIR showed the presence of functional groups of CMC formed on each polymer membrane, namely O-H, and COO^- stretching at wave numbers 3380-3396 cm^{-1} and 1593-1595 cm^{-1}. Adding rice husk ash silica to the polymer membrane causes the formation of Si-O-Si functional groups at wave numbers 641 cm^{-1} and 1028 cm^{-1}. The EIS result of CMC, CMC/$LiCF_3SO_3$, and CMC/$LiCF_3SO_3$/Silica produced ionic conductivity of 1.262×10^{-7}, 6.792×10^{-7}, and 2.684 × 10-6 S/cm, respectively. This study concluded that rice husk ash silica is evenly dispersed in the CMC/$LiCF_3SO_3$ solid electrolyte polymer membrane to be used as a solid electrolyte for the secondary battery.

Keywords: polymer membrane, rice husk ash silica, CMC, $LiCF_3SO_3$

A. Introduction

A battery is a device that can convert chemical energy into electrical energy through electrochemical reactions of reduction and oxidation. Battery components consist of a cathode (positive terminal), anode (negative terminal), and electrolyte [1]. Battery electrolytes act as an ion transfer medium, so electrolytes are important in producing environmentally friendly, inexpensive, durable batteries with high energy density [2]. Electrolytes are divided into liquid electrolytes and solid electrolytes. Solid electrolytes in batteries are safer than liquid electrolytes. One of the solid electrolytes is a solid electrolyte polymer membrane [3] [4].

Carboxymethyl cellulose (CMC) is a good biopolymer candidate for solid polymer electrolyte (SPE) due to the presence of hydrophilic carboxyl groups (CH_2COONa), which allow the biopolymer to dissolve in water solvents [5]. In addition, CMC naturally has a high amorphous phase, enabling easier transport of conduction ions such as lithium (Li^+). CMC comes from a cellulose derivative, a straight, long-chain, and anionic polysaccharide. The properties of CMC are known as biodegradable, colorless, odorless, and non-toxic [6]. The addition of oxide filler in silica (SiO_2) is a filler in the formation of crystalline structures, morphology, molecular relationships, and ionic conductivity of electrolytes. Rice husk is one of the largest producers of silica after perfect combustion at high temperatures [7].

The silica content in rice husk ash is 90-98% dry weight, which can be utilized for various chemical processes. Compared to mineral silica, rice husk has great potential as a source of silica (SiO_2) [8]. Lithium triflate salt ($LiCF_3SO_3$) was chosen because it can produce an ionic conductivity value of 8.37 × 10-4 S/cm [9]. Another modification to the $CMC/LiClO_4$ membrane is adding Citric Acid (CA) doping with variations of 0, 5, and 10% w/v using the solution casting method. Synthesis of the $CMC/LiClO_4/CA$ membrane results in a conductivity value of 1.24 x 10^{-7} S/cm [10]. The addition of silica (SiO2) is a filler in the formation of crystalline structures, morphology, molecular relationships, and ionic conductivity of electrolytes. Rice husk is one of the largest producers of silica after perfect combustion at high temperatures [11].

In this work, the synthesis of $CMC/LiCF_3SO_3$ polymer membranes dispersed with rice husk ash silica with 0% and 12% concentrations using the solution casting method. The characterization carried out was the Fourier-Transform Infrared Spectrometer (FTIR) to determine the functional groups and vibrations of the membrane. The FTIR and EIS results provide the $CMC/LiCF_3SO_3$ membrane, adding rice husk ash silica, which can be used as a solid polymer electrolyte.

B. Methods

1. Materials

The materials in this research are rice husk ash, carboxymethyl cellulose, lithium triflate, NaOH, HCl, distilled water, pH meter, mortar, petri dish, beaker, OHAUS balance, Hot Plate Stirrer, mesh sieve, and drying oven.

2. Instruments

FTIR spectra of the samples were recorded on Shimadzu 8201 PC with 1 cm^{-1} resolution with the wavenumber 400 to 4000 cm^{-1}. The sample was blended as a KBr pellet and scanned into a blank KBr pellet before measurement. The ionic conductivity of the samples was studied by an LCR Meter type Hioki 3532-50 LCR HITESTER.

3. Procedure

The synthesis research of the samples was carried out through 3 stages, namely the stage of synthesis of rice husk ash silica (RHA), polymer membrane synthesis, and polymer membrane characterization using FTIR and EIS with solution casting.

4. Preparation Synthesis of silica from rice husk ash (RHA)

Rice husk ash was extracted by mixing rice husk ash with 1M NaOH solution with a ratio of 1:6, then stirred with a magnetic stirrer for 90 minutes. After that, the solution was washed with distilled water and filtered, and HCL was added until the pH was 7 (neutral). Furthermore, precipitation was carried out for 18 hours, the formed silica gel was filtered. The resulting silica gel was then dried and ground using a mortar to obtain silica powder. The resulting silica can be used as a filler in $CMC/LiCF_3SO_3$ polymer membranes.

5. Preparation Synthesis of CMC, CMC/$LiCF_3SO_3$ and CMC/$LiCF_3SO_3$/Silica Membranes

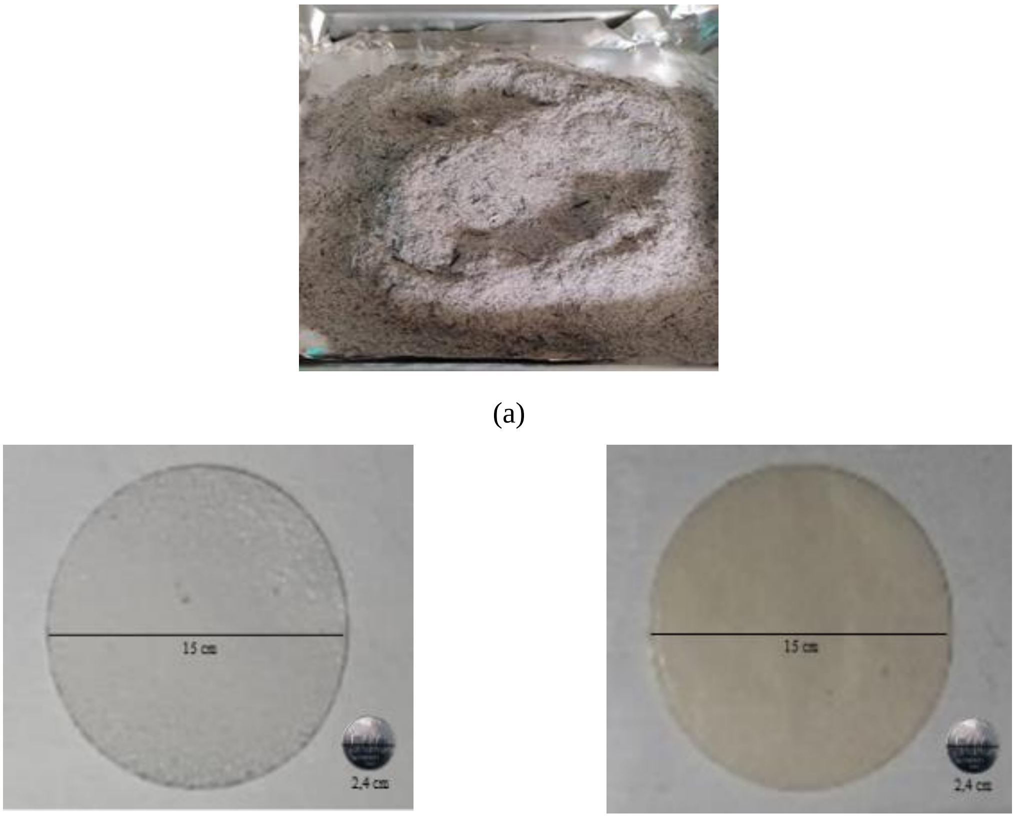
Synthesis was done by inserting rice husk ash silica into distilled water in a beaker. Then, the solution was stirred using a magnetic stirrer until the solution was homogeneous. Furthermore, CMC and $LiCF_3SO_3$ powders were added gradually and stirred until the solution was homogeneous. The homogeneous solution was poured into a petri dish and put into an oven/dryer until it became a thin membrane. The ready solid electrolyte membrane was then characterized by a Fourier-Transform Infrared Spectrometer (FTIR) and Electrochemical Impedance Spectroscopy (EIS).

6. Characterization of CMC, CMC/$LiCF_3SO_3$ and CMC/$LiCF_3SO_3$/Silica membranes

FTIR and EIS were used to characterize the membranes. The characterization of the membranes was carried out using the FTIR (Fourier Transform Infra-Red) spectrometry to determine the Si-O functional groups present in the CMC, CMC/$LiCF_3SO_3$ and CMC/$LiCF_3SO_3$/Silica membranes. Electrochemical Impedance Spectroscopy (EIS) was performed to determine the ionic conductivity of the membranes.

C. Results And Discussion

The synthesis of silica from RHA powder, CMC, CMC/$LiCF_3SO_3$, and CMC/$LiCF_3SO_3$/Silica membranes was successfully carried out in this study, as seen in Figure 1.



(a)

(c) (b)

Figure 1. (a) Silica from Rice Husk Ash, (b) CMC/$LiCF_3SO_3$ membrane, (c)) CMC/$LiCF_3SO_3$/Silic membrane

The resulting polymer membrane tends to be clear in color with a 0.125 - 0.236 mm thickness. The surface of the polymer membrane looks transparent and smooth, and there is no clumping (agglomeration). This indicates that the polymer membrane is homogeneously dissolved. Furthermore, the solid electrolyte polymer membrane is cut with a cutting die machine to form a small circle with a diameter of 1.5 cm. FTIR and EIS characterization is carried out.

1. Fourier-Transform Infrared Spectrometer (FTIR)

Fourier Transform Infrared (FTIR) is one of the analysis methods used to determine the absorption area of a compound. In FTIR analysis, the sample is exposed to infrared radiation. This makes FTIR useful for determining the vibrations of the molecules contained in the sample. This FTIR analysis is recorded on FTIR spectrometry with an infrared wave number range between 400-4000 cm^{-1}. The results of the CMC/$LiCF_3SO_3$ polymer membrane dispersed with rice husk ash silica spectra are shown in Figure 2.

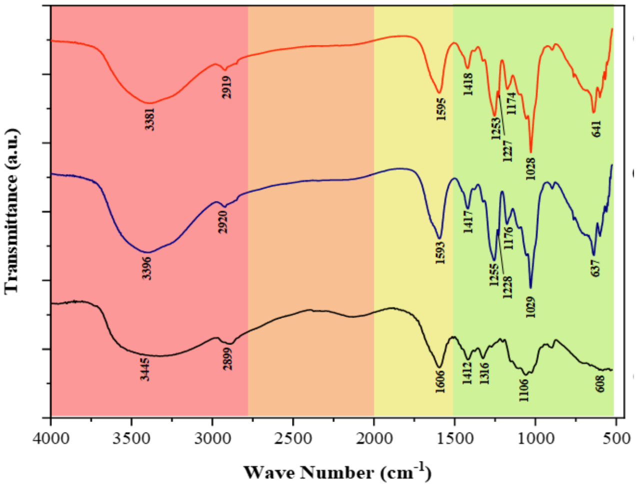


Figure 2. FTIR spectra of membrane the CMC (a), CMC/$LiCF_3SO_3$ (b), and CMC/$LiCF_3SO_3$/SiO_2 (c)

The results of the FTIR spectrometry of the CMC membrane are characterized by the presence of O-H stretching functional groups at wave number 3445 cm^{-1}. Absorption at wave number 2899 cm^{-1} indicates the C-H stretching functional group. Wave numbers 1606 cm^{-1} and 1412 cm^{-1} indicate the presence of asymmetric C=O stretching and CH2 bending functional groups, characteristic of CMC. The asymmetric stretching vibration of the C-O-C functional group occurs at wave number 1316 cm^{-1}. The C-O and C-H functional groups are shown at wave numbers 1106 cm^{-1} and 608 cm^{-1} [12] [13]. The FTIR spectra of the CMC/$LiCF_3SO_3$ and CMC/$LiCF_3SO_3$/silica polymer membranes in Figure 2 show the presence of O-H stretching functional groups at wave number 3396 cm^{-1} with a fairly wide peak for the CMC/$LiCF_3SO_3$ membrane. The peak position of O-H stretching shifted to 3381 cm^{-1} after adding 12% rice husk ash silica [14]. The shift in wave numbers occurs due to the interaction between the hydroxyl groups (O-H) of carboxymethyl cellulose with silica. Stretching vibration is the movement of atoms or molecules that occurs regularly. C-H stretching vibration occurs at wave numbers 2920 cm^{-1} and 2919 cm^{-1} for CMC/$LiCF_3SO_3$ and CMC/$LiCF_3SO_3$/silica polymer membranes. The carbonyl group (COO^-) is a characteristic of CMC formed at wave numbers 1593 cm^{-1} and 1595 cm^{-1} [15]. The shift in the wave number value can occur due to the interaction between the atoms in each membrane. The change in wave numbers occurs due to the interaction between the hydroxyl groups.

2. Electrochemical Impedance Spectroscopy (EIS)

EIS characterization was performed to determine the ionic conductivity value of the solid electrolyte polymer membrane. Conductivity values can be divided into two, namely AC and DC conductivity. AC conductivity can be calculated using the LCR-meter measurement conductance parameters with a frequency value of around 42 Hz - 1 MHz, as well as the membrane thickness and the contact surface area of the membrane with the electrode. The EIS result of the CMC, CMC/$LiCF_3SO_3$, and CMC/$LiCF_3SO_3$/Silica membranes can be seen in Figures 3 and 4.

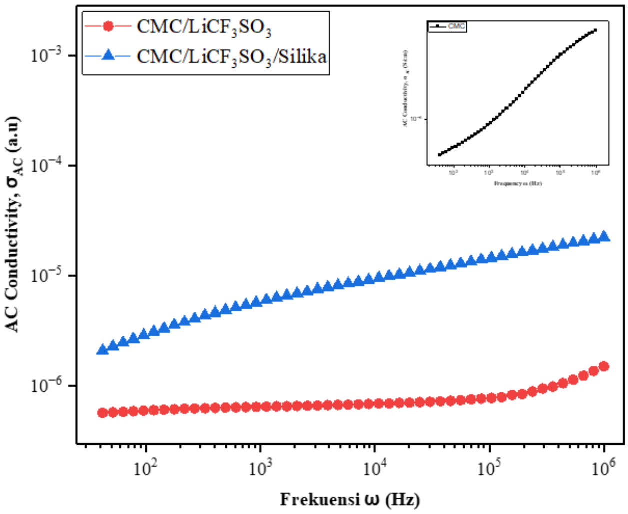


Figure 3. AC conductivity of the CMC, CMC/$LiCF_3SO_3$, and CMC/$LiCF_3SO_3$/SiO_2 membranes

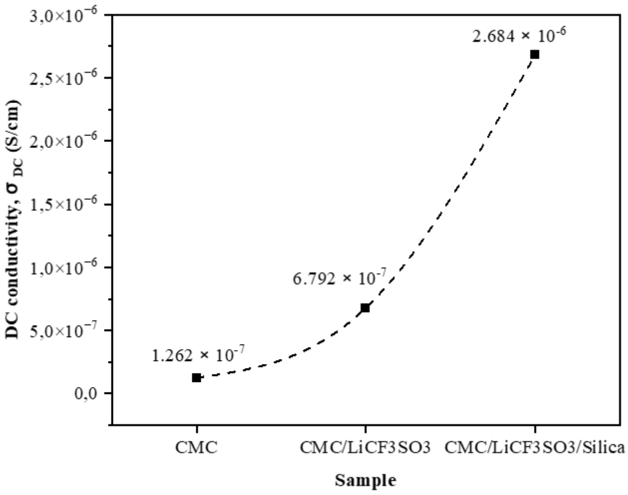


Figure 4. Ionic Conductivity of the CMC, CMC/$LiCF_3SO_3$, and CMC/$LiCF_3SO_3$/SiO_2 membranes

Figure 3 shows the conductivity curve resulting from measurements, which shows an increase in ionic conductivity values and frequency increase [1]. The AC conductivity curve results are then fitted using the Jonsher Power Law equation to determine the DC conductivity value [16]. Figure 4 depicts the CMC membrane produces an ionic conductivity value of 1.262×10^{-7} S/cm. Adding lithium triflate salt to the CMC/$LiCF_3SO_3$ membrane increases the membrane conductivity value to 6.792×10^{-7} S/cm. This conductivity value proves an interaction between Li^+ ions from lithium triflate salt and COO- (carboxylate) from CMC [17].

Meanwhile, the conductivity value of the CMC/$LiCF_3SO_3$ membrane with the addition of rice husk ash silica is 2.684×10^{-6} S/cm. The results of this EIS characterization show an increase in the ionic conductivity of the CMC/$LiCF_3SO_3$/Silica membrane. The increase in the ionic conductivity is due to the addition of silica, which acts as the mobility of Li^+ ions through the Si-O-Li bonds in the polymer matrix [18]. The easier for Li^+ ions to move in the polymer matrix, the higher the ionic conductivity [19] [20].

D. Conclusion

The study results show that the polymer membrane was successfully made using the solution casting method to produce a clear, evenly colored polymer membrane with good dimensional stability or size. The Fourier Transform Infrared (FTIR) characterization showed a shift in the absorption wave number due to the interaction between rice husk ash silica and the polymer matrix. They formed a new functional group, siloxane (Si-O-Si), at wave numbers 641 cm^{-1} and 1028 cm^{-1}. The Electrochemical Impedance Spectroscopy (EIS) characterization shows that the addition of rice husk ash silica can increase the ionic conductivity of the CMC/$LiCF_3SO_3$ polymer membrane by 2.684×10^{-6} S/cm. The increase in conductivity occurs because rice husk ash silica acts as the mobility of Li+ ions in the polymer matrix. The conclusion is that rice husk ash silica can be used as an alternative synthesis of solid electrolyte membranes for secondary batteries.

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