

Mechanical strength and ionic conductivity of polymer electrolyte membranes prepared from cellulose acetate-lithium perchlorate

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Abstract. The need for secondary batteries is increasing every year. The secondary battery using a liquid electrolyte has some weaknesses. A solid polymer electrolyte is the alternative electrolytes developed to replace the liquid electrolyte type. This study was conducted to determine the effect of lithium perchlorate content on the polymer electrolyte membranes of cellulose acetate-LiClO₄. The cellulose acetate-LiClO₄ membranes were prepared by mixing cellulose acetate and LiClO₄ in various compositions using tetrahydrofurane (THF) as solvent. The effect of LiClO₄ ratios on the polymer electrolyte membranes was studied by analysis of the functional groups using FTIR (*Fourier Transform Infrared*) spectroscopy measurement, the ionic conductivity by EIS (*Electrochemical Impedance Spectroscopy*) method, and mechanical properties by tensile tester measurements. The ionic conductivity of the membranes increased with the increasing in the ratios of lithium perchlorate content in the membranes and reached the optimum value at $1.79 \times 10^{-4} \text{ S cm}^{-1}$ corresponded to the cellulose acetate doped with 25% (w/w) LiClO₄ membrane. The presence of 10% (w/w) LiClO₄ content within cellulose acetate membranes can increase the mechanical properties of the membranes from 19.89 to 43.29 MPa for tensile strength, and from 2.55 to 4.53% for elongation at break. However, when the cellulose acetate membranes containing ratio of LiClO₄ more than 10% (w/w), consequently the tensile strength tended to decrease and the elongation at break was increased.

1. Introduction

Lithium battery is considered as the most probable candidates for large scale electrical power storage systems due to its many advantages, such as the high specific energy density, high working voltage, low self-discharge rate, fast charging, long life usage time, and has no memory effect [1–3]. The main components of the battery consist of three parts, namely anode, cathode, and electrolyte. Electrolyte is a medium for transferring the charge and in the cell is located between the anode and cathode. Electrolytes are divided into two types, namely the solid electrolyte and liquid electrolyte. The liquid electrolyte has some weaknesses, which are prone to leakage and the difficulty in packaging as well as the storage of the liquid electrolyte [4,5]. On the other hand, the solid electrolyte is more secure, easier to use, and can be made with smaller dimensions such as thin layers [4]. The comprehensive requirements for solid polymer electrolyte used in lithium battery include high mechanical strength, excellent flame retardancy, superior thermal stability, high ionic conductivity at ambient temperature, and wide electrochemical window [6-9]. The minimum requirement of all solid



polymer electrolytes for ionic conductivity is more than 10^{-5} Scm^{-1} at 25°C and its tensile strength is more than $\geq 30 \text{ MPa}$ [4].

Polyethylene Oxide (PEO) is a synthetic polymer usually used as a solid electrolyte, especially in the lithium-ion battery [4]. The selection of PEO as electrolyte materials because PEO has good ionic conductivity as well as their compatibility with electrode used [10]. However, the PEO has low ionic conductivity at room temperature [10] and difficult to decompose in nature. To overcome these drawbacks, therefore in this research, a new host polymer electrolyte with sufficiently ionic conductivity using biodegradable polymers such as cellulose acetate has been developed to fit the requirement for lithium polymer batteries, taking into account the need for safer practical usage and a more environmentally friendly system.

Recently, the use of biodegradable polymers that have good ionic conductivity and mechanical property has been developed. Among biodegradable synthetic polymers, cellulose acetate-based solid polymer electrolyte is one of the most attractive polymers due to its availability in nature as renewable resources, non-toxic nature, low cost, environmentally friendly, and having good mechanical properties [5, 11]. Furthermore, the research regarding the cellulose acetate-based polymer electrolyte membrane for lithium battery separator was still very few reported. For example, one study reported the plasticizing effect of 1-allyl-3-methylimidazolium chloride for cellulose acetate-based polymer electrolyte membranes, and this polymer electrolyte has the ionic conductivity approximately $1.75 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature [11]. The cellulose acetate doped with LiClO_4 as a biodegradable polymer electrolyte for supercapacitors has the ionic conductivity approximately $4.9 \times 10^{-3} \text{ Scm}^{-1}$ with lithium salt content of 16% (w/w) at room temperature [5], however, the mechanical properties of the membrane has not been reported yet, even though these properties are very important in polymer electrolyte membranes. Therefore, in order to study the more comprehensive physical properties of cellulose acetate-based polymer electrolyte membranes doped with LiClO_4 , this research reported the results of mechanical properties and ionic conductivity measurements in various ratios of lithium perchlorate content in cellulose acetate-based polymer electrolyte membranes. The differences of this study compared to the other reported studies are the more detailed study concerning the mechanical properties and ionic conductivities of cellulose acetate-lithium perchlorate based polymer electrolyte membrane, therefore based on the resulting data then it could be concluded whether this polymer electrolyte membrane has the potent to be applied as electrolyte separator in lithium battery.

2. Materials and Methods

2.1. Materials

The materials used in preparation of polymer electrolyte membrane were cellulose acetate (Sigma-Aldrich; average molecular weight: 30,000; 39.8 wt% acetyl content) and LiClO₄ (Sigma-Aldrich). Tetrahydrofuran (THF) for analysis with purity (GC) $\geq 99.8\%$ were obtained commercially from E-Merck Chem.Co. All materials were used without further purification.

2.2. Preparation of Polymer Electrolyte Membranes

Polymer electrolyte membranes were prepared by mixing cellulose acetate and lithium perchlorate salt (LiClO₄) in various concentrations ranging from 1-25% (w/w) using tetrahydrofuran (THF) as solvent. An amount of cellulose acetate and lithium perchlorate was dissolved in tetrahydrofuran within a ratio of 1% (w/v) and stirred on the hotplate magnetic stirrer for approximately 3 hours to form homogenous solution. The solution was then poured into a petri dish (diameter 10 cm), and the solvent was evaporated to form thin film and dried for approximately 20 h.

2.3. Characterization of Polymer Electrolyte Membrane

2.3.1. Functional Group Analysis

The polymer electrolyte membranes were analyzed by using FTIR (Prestige 21 Shimadzu) spectroscopy method for determining its functional groups with direct firing method. The membranes were scanned within the wavenumber range of 500 to 4000 cm⁻¹.

2.3.2. Ionic Conductivity Measurements

The ionic conductivity of the polymer electrolyte membranes were measured by EIS (Electrochemical Impedance Spectroscopy) method. The membranes were cut rectangular approximately with the dimension of 2 cm \times 4 cm, and then the membrane was placed between two platinum wire electrodes within the distance of 1.5 cm and 0.4 cm long. The data of impedance was performed within the frequency range between 20 Hz and 2 MHz at 1 V using the equipment of AgilentTM LCR E4980. The impedance data were analyzed using the Zview[®] software to obtain the resistance value of membranes. The membrane resistance value was taken from the high frequency intercept on the real impedance axis of the Nyquist plot [12]. The ionic conductivity of the membrane was calculated using the following formula:

$$\sigma = \frac{1}{R} \cdot \frac{\sqrt{(d)^2 + (t)^2}}{t.s}$$

where σ , R , d , t , s , respectively, were ionic conductivity (Scm^{-1}), membrane resistance (ohm), thickness of membrane (cm), distance between two electrodes (1.5 cm), and length of electrode that contacts between membrane and electrode (0.4 cm).

2.3.3. Mechanical Strength Analysis

The mechanical strength of the polymer electrolyte membranes were measured using tensile tester (Singel Fiber Tensile Tester (Favigraph-Textechno)). Membrane was cut to rectangular with dimension of $4 \text{ cm} \times 3 \text{ mm}$ and the membrane thickness was measured using a micrometer, then the membrane was tested with the gauge length of 2 cm, load cell of 10.000 cN, and test speed of 6 mm/min. The mechanical properties of sample were performed by taking the average value of three repeated measurements.

3. Results and Discussion

3.1. Functional Group Analysis

The analysis of specific functional groups or chemical bonds that exist within a material such as coordination or complexation of Li^+ -ion with the cellulose acetate can be determined using FTIR spectroscopy measurement. The changes in the absorption peaks in terms of the wavenumber shifting, relative intensity, disappearance of the existing peak and even appearance of new peaks were evidences from the complexation of these constituents [5,11,13]. FTIR spectra of cellulose acetate and cellulose acetate doped with 25% (w/w) LiClO_4 membranes are shown in Figures 1. The widening of absorption peaks was generally observed in the region of $3400\text{--}3600 \text{ cm}^{-1}$ corresponding to the stretching of intermolecular hydrogen bonds of hydroxyl groups ($-\text{OH}$) [14]. The presence of the wide absorption peaks of pure cellulose acetate FTIR spectrum at 3485.37 cm^{-1} is due to the presence of moisture in the sample, that was not completely removed [5]. The similar wide absorption peaks shifted to 3520.09 cm^{-1} was also observed in cellulose acetate doped with lithium perchlorate (cellulose acetate- LiClO_4) membranes FTIR spectrum. The absorption peak at wavenumber of 2949.16 cm^{-1} in pure cellulose acetate FTIR spectrum corresponded to the stretching of $-\text{CH}-$ of methyl groups ($-\text{CH}_3$) [5], which has been shifted to 2945.30 cm^{-1} in FTIR spectrum of cellulose acetate- LiClO_4 membrane. The carbonyl group ($\text{C}=\text{O}$) stretching vibration at 1756.22 cm^{-1} for the pure cellulose acetate has been shifted to 1730.15 cm^{-1} for cellulose acetate- LiClO_4 membrane. The shifting of these characteristic peaks proves the occurrence of complexation between Li^+ ions and oxygen atoms in polymer backbone. The $-\text{CH}_2-$ deformation vibration occurred at 1431.18 cm^{-1} for pure cellulose acetate has been shifted to 1429.25 cm^{-1} for cellulose acetate- LiClO_4 membrane.

The occurrence of complexation between cellulose acetate and Li^+ ions was further verified by the broadening peaks at the wavenumber range of $1049\text{--}1269\text{ cm}^{-1}$ as result of the simple peaks overlapping. The characteristic peaks of 'C-O-C' anti symmetric stretching vibrations of ester group of pure cellulose acetate at 1240.23 cm^{-1} has been shifted to 1269.16 cm^{-1} in cellulose acetate- LiClO_4 membrane. The -C-OH stretching vibration of pure cellulose acetate at wavenumber of 1049.28 cm^{-1} has also been shifted to 1049.28 cm^{-1} for the cellulose acetate- LiClO_4 membrane. The presence of the absorption peaks at 904.61 cm^{-1} in pure cellulose acetate could be due to the combination of -C-O-stretching and - CH_2 - rocking vibrations that have been shifted to 912.0 cm^{-1} in cellulose acetate- LiClO_4 membrane. The symmetric vibration of -ClO^- ion (perchlorate ion) was generally observed at 940 cm^{-1} , which in this study, this peak overlaps with C-O stretching vibration of cellulose acetate, therefore the wavenumber of the same peak at 912.0 cm^{-1} shifted to the lower value in cellulose acetate- LiClO_4 membrane [5]. The shifted to the lower value of this wavenumber can be caused by the complexation effect [5,11]. The intensity of all the peaks in the FTIR spectrum of the cellulose acetate- LiClO_4 membrane is lower and broader compared to the pure cellulose acetate FTIR spectrum. These effects are generally caused by the intermolecular interactions, as well as due to the presence of the complexation between cellulose acetate and LiClO_4 [15,16].

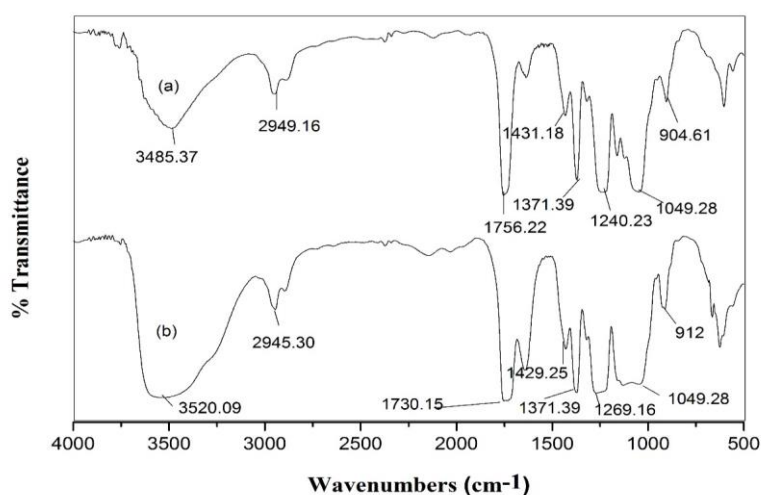


Figure 1. The FTIR spectra of: (a) cellulose acetate; (b) cellulose acetate doped with 25% (w/w) LiClO_4 (cellulose acetate- LiClO_4) membrane

3.2. Ionic Conductivity Analysis

Figure 2 shows the ionic conductivity for the polymer electrolyte membranes. The ionic conductivity of the membranes increased with the increasing in the ratios of lithium perchlorate content in the membranes and reached the optimum value at $1.79 \times 10^{-4}\text{ S cm}^{-1}$ corresponded to the cellulose acetate

doped with 25% (w/w) LiClO_4 membrane. However, the optimum ionic conductivity value in this study was still lower than the result of previous research ($4.9 \times 10^{-3} \text{ Scm}^{-1}$ for cellulose acetate doped with 16% (w/w) LiClO_4 membrane) [5]. This result is likely due to the differences in measurement conditions and the sample preparation method used. However, the optimum ionic conductivity value in this study is still appropriated with the minimum requirement of ionic conductivity for lithium battery, that should be $\geq 10^{-5} \text{ Scm}^{-1}$ [4]. The effect of amorphicity on the ionic conductivity of the polymer electrolyte membranes doped with metal salts has been extensively studied in the literatures [17–19]. The T_g (glass transition temperature) of the membranes decreased with the presence of lithium salt in the cellulose acetate [5]. The addition of lithium salt in the cellulose acetate can disrupt the intermolecular interactions within the host polymers to make new interactions between molecules, therefore, it can increase the amorphicity of membranes [5]. The decreasing in T_g accompanied by the increase in amorphicity has been reported and has led to the increase of the segmental motion in polymer electrolytes that in turn enhances the ionic conductivity [17–19].

The mechanism for ionic conductivity in polymer electrolyte membranes was developed by Druger, Nitzan, and Ratner with the dynamic percolation model [4,17]. In this case, it is envisaged ionic motion in terms of jumps between neighboring positions, a cation (M^+) such as Li^+ acts as a Lewis acid which is linked to Lewis bases (B^-), such as oxygen atoms associated within a polymer chain. The cation jumps from one site to neighboring site, which takes place by a slow change in the local environment as a linkage of single M^+-B^- evolves with time. As the polymer gradually changes its conformation due to segmental motion, an accompanying translation of the cation to the neighboring site follows. The increased polymer segmental motion in the membranes of cellulose acetate-lithium salt complex, resulting from the increase of amorphicity or disorder. The increase in the ratios of lithium salt content in the polymer electrolyte membranes led to an increase in the entropy of the system which causes the increase in the ionic conductivity [4, 17–19].

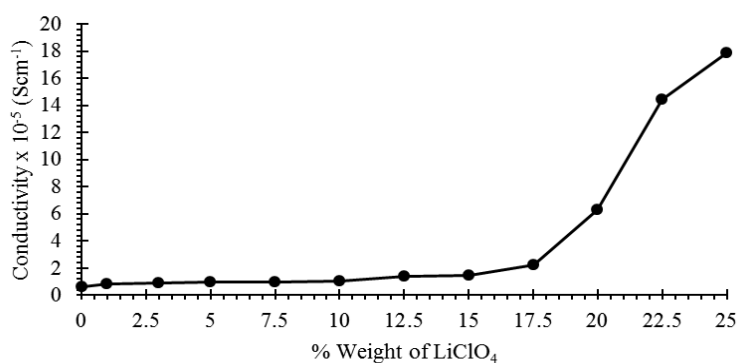


Figure 2. Ionic conductivity of the cellulose acetate membranes doped with various ratio of LiClO_4 (in % w/w)

3.3. Mechanical Strength Analysis

Figure 3 presents the mechanical properties of the cellulose acetate-lithium perchlorate polymer electrolyte membranes. The tensile strength increased with the increasing in the ratios of lithium perchlorate content in cellulose acetate membranes, and reached the optimum value at 43.29 MPa corresponded to the cellulose acetate membrane doped with 10% (w/w) LiClO_4 membrane. However, when the polymer electrolyte membranes doped with ratio of lithium perchlorate more than 10%, consequently the tensile strength of the membranes tended to decrease and the elongation at break was increased. The optimum tensile strength value in this study appropriated with the minimum requirement of a solid state polymer electrolyte membranes for lithium battery, that should be ≥ 30 MPa [4]. The tensile strength of the membran increased with the increasing in lithium perchlorate content because it can fill the cavity of the membranes that led to the more dense membranes. However, the addition of higher lithium perchlorate content tends to make the membrane more brittle due to the potent of the salt to disrupt the intermolecular interactions within the host molecule in forming new interactions, which in turn can increase the entropy of mixing between the membranes and lithium perchlorate. This increase in the entropy of mixing increases the segmental movements leading to reduction in the crystallinity [5].

The elongation at break tend increased with the increase in the ratios of lithium perchlorate content in cellulose acetate membranes, and reached the optimum value at 5.51% corresponded to the cellulose acetate doped with 20% (w/w) LiClO_4 membrane. The addition of lithium perchlorate caused the reduction in the crystallinity and the enhancement in the flexibility of the molecular system [5]. The deviation in elongation at break corresponded to sample of cellulose acetate doped with 15% (w/w) LiClO_4 membrane is due to the absence in the homogeneity of the membrane.

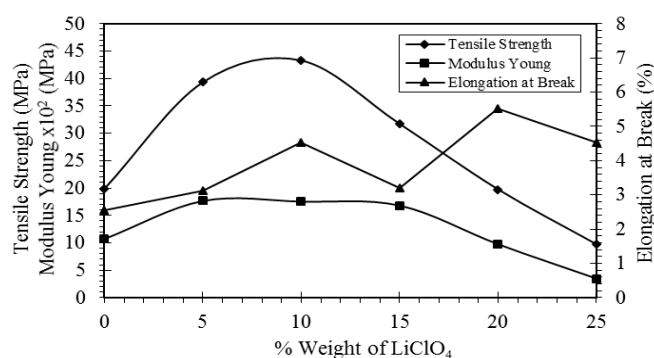


Figure 3. Mechanical properties of the cellulose acetate membranes doped with various ratio of LiClO_4

The modulus Young tends to decrease with the increase in the ratios of lithium perchlorate content in cellulose acetate membranes and reached the optimum value at 347.63 MPa corresponded

to the cellulose acetate doped with 25% (w/w) LiClO₄ membrane. This result is due to the addition of lithium salt can be caused by the increase in the amorphicity and enhancement in the flexibility of the molecular system [5].

4. Conclusion

The ionic conductivity of cellulose acetate membranes increased with the increase in lithium perchlorate content within the membranes and the maximum ionic conductivity at approximately $1.79 \times 10^{-4} \text{ Scm}^{-1}$ was observed in the membrane containing 25% (w/w) LiClO₄. The addition of lithium perchlorate in the cellulose acetate membrane can disrupt the intermolecular interactions within the host polymers to make new interactions between molecules which led to the increase in amorphicity of membranes. The presence of 10% (w/w) LiClO₄ content within cellulose acetate membranes can increase the mechanical properties of the membranes from 19.89 to 43.29 MPa for tensile strength, and from 2.55 to 4.53% for elongation at break. However, when the cellulose acetate membranes containing ratio of LiClO₄ more than 10% (w/w), consequently the tensile strength tended to decrease and the elongation at break was increased. This result is due to the increase in the amorphicity and enhancement in the flexibility of the molecular system caused by the addition of lithium perchlorate.

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