

Conductivity Improvement of Chitosan Membranes through Modification with Lithium for Lithium Polymer Battery Application

S. N. ASNIN¹, WAHAB², DIAN PERMANA³, L. O. AHMAD^{1*}, S. H. SABARWATI¹, L. O. A. N. RAMADHAN¹

¹Department of Chemistry, Universitas Halu Oleo, Kendari

²Department of Mining Engineering, Universitas Halu Oleo, Kendari

³ Department of Agriculture, University of Sembilanbelas November, Kolaka
INDONESIA

la.ode.ahmad@gmail.com http://www.uho.ac.id

Abstract: - Batteries are being developed to solve the global energy crisis. Using portable electronic devices has been increasing and leading to a strong need of their power-sources. However, secondary batteries using a liquid electrolyte have weaknesses, such as prone to leakage and difficulty of packing. Solid polymer electrolyte is a solution to the existing problems. The aims of this research were to determine the effect of deacetylation degree towards the ion conductivity properties of chitosan membranes, the effect of concentration of chitosan-lithium membranes and capability of ionic conductivity as electrolyte polymer for lithium polymer battery application. The membranes were prepared by the solvent evaporation method. Synthesis of chitosan-lithium has been successfully carried out, which indicated by the characteristic peaks at 1573.8 cm^{-1} correspond to ionic interaction between lithium salt with NH_2 groups from chitosan. Modification of chitosan by the addition of lithium salt increases the membrane ionic conductivity. Chitosan membrane conductivity was $1.70 \times 10^{-2}\text{ S.cm}^{-1}$ while the conductivity of chitosan after adding lithium salt increased to $8.53 \times 10^{-2}\text{ S.cm}^{-1}$. This solid polymer electrolyte membrane was suggested to have a potential used for polymer electrolyte in lithium battery applications.

Key-Words: - chitosan, deacetylation, membrane, lithium, conductivity, polymer battery

1 Introduction

Electricity is one form of energy and can very easily converted into other form of energy such as heat or mechanical energy. Electrical energy can be produced from a chemical reaction. An electrochemical energy system can produce electrical energy from a chemical reaction. Some examples of electrochemical system are fuel cells, capacitors and batteries [1].

The battery is an electrochemical cell circuit composed of cathode, anode, electrolyte, and a conductor capable of generating electrical energy with a certain potential. The batteries are common in portable tools that today is lithium batteries. Initially, the electrolyte lithium batteries used in the form of a solution, but it gives rise to various disadvantages such as less practical, easy to leak, and easily corroded. Because of these weaknesses, the electrolyte in liquid form is becoming obsolete and switch on the solid polymer electrolyte as an ionic conductor polymer battery that called lithium/lithium polymer of LiPo.

Battery of lithium polymer is using dry polymer electrolyte that is shaped like a thin film layer. The film layer is structured in layers between the anode and cathode resulting ion exchange [2]. The type of polymer that has been used as the matrix that was nafion [3], PMM (polymethyl methacrylate) [4], and PVDF (Polyvinyl Diflourida) [5].

Chitosan is a natural polymer chitin derivative that can be used as a proton conducting membrane [6]. But under normal circumstances, chitosan has low electrical conductivity because chitosan can not be immobilized under the influence of an electric field to generate a proton conductor [7]. The ability of chitosan to deliver ion depends on the magnitude of the degree of deacetylation. The increasing of deacetlation degree leads to better solubility of chitosan in aqueous organic acids, therefore chitosan can be protonated polyelectrolyte through group NH_2 [8].

In order to produce chitosan with high deacetylation degree without decreasing of the molecular weight can be prepared by repeated deacetylation [9]. Based on the previous research,

chitosan with variation of deacetylation degree (DD) was modified by LiNO_3 to investigate the ionic conductivity properties of the membrane.

2 Materials and Methods

2.1 Materials

Chitosan with a deacetylation degree of 73%, 92.9%, and 96% were obtained from the previous research team by Wahab. Acetic acid, oxalate acid and LiNO_3 were purchased from Merck. Sodium hydroxide was purchased locally. De-ionized water was used in all experiments.

2.2 Preparation of chitosan and chitosan-lithium dope solution

The chitosan with variation of DD and molecular weight (MW) from deacetylation of 1x3 h (DD = 73 %; MW = 5.24×10^5 KDa), 2x3 h (DD = 92.9 %; MW = 2.8×10^5 KDa) and 3x3 h (DD = 96 %; MW = 2.5×10^5 KDa), were prepared to make chitosan dope solution with variation of 1%, 1.5% and 2%. The chitosan dope solution of 1% was prepared from 1 g of chitosan was dissolved in 100 ml of 2% acetic acid. The same procedure was used for the preparation of the chitosan dope solution of 1.5% and 2%.

2.3 Fabrication of chitosan (CS) and chitosan-lithium (CS-Li) membranes

The chitosan and chitosan-lithium dope solution were filtered by Buchner funnel and cast onto clean glass plate. The dope solutions were dried at room temperature for 72 h. The chitosan membranes were neutralized by adding 1 N sodium hydroxide in the Petri dishes several times. Subsequently, the neutralized chitosan membranes were washed several times with deionized water. The chitosan-lithium membranes neither washed by sodium hydroxide nor de-ionized water.

2.4 Instrumentation

Fourier transform infrared spectroscopy (4,000-500 cm^{-1} , resolution 4 cm^{-1}), Scanning electron microscope, *Impedance Analyzer* (Agilent™ E4980A).

2.5 Water uptake measurements

The water uptake of membrane was determined by measuring the weight difference of membrane before and after immersion in water. Membrane samples dried at room temperature for 24 h were weighted, and the immersed in water at room temperature for 24 h. After removing residual water on the surface membrane, the wet membrane was weighted. The water calculated based on Eq. 1.

$$\text{Water uptake\%} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 \quad (1)$$

where M_{wet} and M_{dry} are the weights of the membrane in the wet and dry states, respectively.

2.6 Proton conductivity

The membranes were cut to size of 12 cm^2 . Proton conductivity of fully hydrate membranes was measured as a function of temperature. Measurements were carried out in two points-probe conductivity cells using two platinum wire electrodes as working electrode. The electric resistance data were obtained using impedance analyzer (Agilent™ E4980A) and were recorded between 20 Hz – 2 MHz at working voltage amplitude of 1 V. The impedance spectra were fitted on Z-View 2 software by Scribner Associates Inc. for curve fitting procedure. The proton conductivity values were obtained according to Eq. 2.

$$\sigma = \frac{S}{R \times A \times L} \quad (2)$$

where S is gap of electrodes, A is wide of electrodes, L is thickness of membrane and R is membrane resistance derived from the low intersection of the high frequency semicircle on a complex impedance plane with Re (z) axis.

3 Results and Discussion

3.1 FTIR analysis

Fig. 1 shows FTIR spectra of CS and CS-Li membranes. The characteristic band at 3446.6 cm^{-1} , 2904.6 cm^{-1} , 1413.21 cm^{-1} and 1595.4 cm^{-1} are attributed to stretching of O-H and N-H amine, stretching C-H, stretching C-N aliphatic amine and N-H amide, respectively. The absorption of amide groups mean that chitosan is not all deacetylated. It is supported with chitosan deacetylation degree of 92.9%.

The new peak appears at 1573.8 cm^{-1} for CS-Li membrane. It is attributed to ionic interaction between lithium salt with NH_2 groups from chitosan. In addition, the peak of N-H groups at 3446.56 cm^{-1} broadened to 3423.4 cm^{-1} . Stretching vibration of C-H also shift to 2937.4 cm^{-1} . Base on FTIR data, the synthesis of chitosan and chitosan-lithium was success.

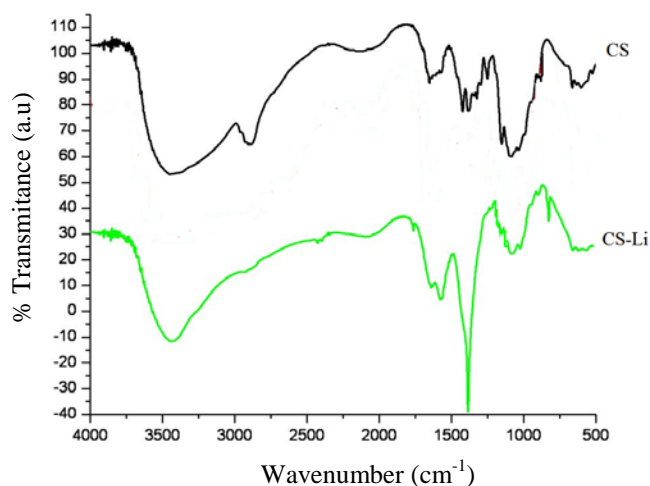


Fig. 1 FTIR spectra of chitosan (CS) and chitosan-lithium (CS-Li) membranes

3.2 Water uptake

Chitosan membrane is a membrane that can be chemically modified into other forms for their hydroxyl and amine groups. These groups are a hydrophilic so that membranes can absorb water, then the water uptake of a membrane effect on the ability of ions across the membrane. Water molecules are absorbed by the polymer causes the polymer chains so as to facilitate the mobility of ions stretchable. Therefore, water uptake is also very influential in the membrane conductivity.

Table 1 Water uptake of CS and CS-Li in variation deacetylation time

Deacetylation time (h)	Concentration of chitosan (%)	% Water uptake	
		CS	CS-Li
1x3	1	33.33	-
	1.5	58.33	-
	2	64.29	-
2x3	1	94.74	400
	1.5	85.29	700
	2	67.86	870
3x3	1	54.54	-
	1.5	50.00	-
	2	71.42	-

The results show that water uptake of CS membrane increase with increasing concentrations of chitosan as shown in Table 1. The membrane with deacetylation time 2x3 hours has highest water uptake than 1x3 and 3x3 hours.

The water uptake of CS-Li membranes still greater than chitosan membrane. This is due to the crystalline nature of chitosan membrane that makes the water difficult to pass through the membrane. However, the presence of salt LiNO_3 bulky causes crystallinity of CS-Li membranes decrease and more hydrophilic than hydroxy groups on chitosan. Therefore, reducing the crystallinity of the membrane causes the hydrophilicity membrane to grow and produce greater water uptake. Water uptake of CS-Li membranes is larger than the value of water uptake of PMM (polymethyl methacrylate) that reported by Luo et al. [3] which is 286% - 292% as a polymer electrolyte commonly used in lithium polymer battery.

3.3 Electrical conductivity

Determination of the electrical conductivity is the main characteristics of the proton conductive membranes. Under normal circumstances, chitosan has low electrical conductivity. Although the structure monomer of chitosan has three atoms of hydrogen, but hydrogen atoms are strongly bound to the framework so that chitosan can not be mobilized under the influence of an electric field to generate a proton conductor. However, if the chitosan dissolved in the acetic acid H^+ or H_3O^+ and CH_3COO^- ions in the chitosan will be dispersed in the chitosan solvent and the ions can be mobilized under the influence of an electric field. If the H^+ or H_3O^+ ions easier to move than CH_3COO^- then a layer of chitosan will be a proton conductor [7].

Based on data from the conductivity measurement of membrane in Table 2, the largest membrane conductivity that is chitosan membrane with deacetylation time of 2x3 hour (DD = 92.9%). The increasing of amine groups, then DD of chitosan increases and conductivity increases. But in this study the results of deacetylation of chitosan membrane 3x3 hour (DD = 96%) have a lower conductivity than other chitosan membrane, it causes by decreasing of molecular weight of chitosan (2.5×10^5 KDa). Therefore, the physical appearance is wrinkled to membrane deacetylation of 3x3 hour.

Table 2 Conductivity of the CS and CS-Li membranes

Deacetylation time (h)	Concentration of chitosan (%)	σ (S.cm ⁻¹)	
		CS	CS-Li
1x3	1	7.4×10^{-4}	-
	1.5	1.1×10^{-3}	-
	2	1.2×10^{-3}	-
2x3	1	1.7×10^{-2}	2.2×10^{-2}
	1.5	1.6×10^{-2}	3.8×10^{-2}
	2	1.7×10^{-3}	8.5×10^{-2}
3x3	1	4.5×10^{-7}	-
	1.5	7.1×10^{-4}	-
	2	3.3×10^{-3}	-

The conductivity value which generated from chitosan membrane was still lower than chitosan-lithium membrane. This is because in the chitosan membrane ion H_3O^+ transported from one side of the membrane to the other side of the membrane. In contrast to chitosan membrane that its amine groups protonated into NH_3^+ and chitosan-Li membrane causes more electrolyte contained within the matrix of chitosan-Li membrane that can conduct electricity very well. This data is supported by data from water uptake which shows an increase in water uptake of chitosan membrane on the degree of deacetylation of 92.9% resulting from the presence of $LiNO_3$ salt and water uptake value declined in the degree of deacetylation 96%. In this study only chitosan membrane of 2x3 hour deacetylation modified with salt $LiNO_3$ so in other words chitosan membrane's water uptake is lower than chitosan-lithium membrane. Theoretically, decreasing the water uptake lead to decrease the proton conductivity, because the fewer water molecules in the membrane can be proton transfer media [10].

According to Wiczorek et al. [4] PMM electrolyte membrane that is commonly used in lithium polymer battery with a conductivity of 10^{-3} - 10^{-2} S.cm⁻¹. Therefore, the chitosan-lithium of 2% with deacetylation 2x3 hours degree of deacetylation of 92.9% have been quite suitable to be used as the polymer material in lithium polymer battery.

3.4 Application of CS-Li membrane in lithium polymer battery

Testing of chitosan-lithium membranes in the application as a matrix batteries lithium polymer was conducted by making a simple lithium polymer battery used battery electrode TCL Hyperpower. Simple battery made in the form of a sheet of

chitosan membranes are squeezed in between two pieces of electrodes as shown in Fig. 2.

Fig. 2 A simple lithium polymer battery using chitosan membrane as electrolyte matrix

Test of battery capacity of circuit was also conducted to determine the current and voltage generated when the battery is used and after recharging process as shown in Fig. 3.

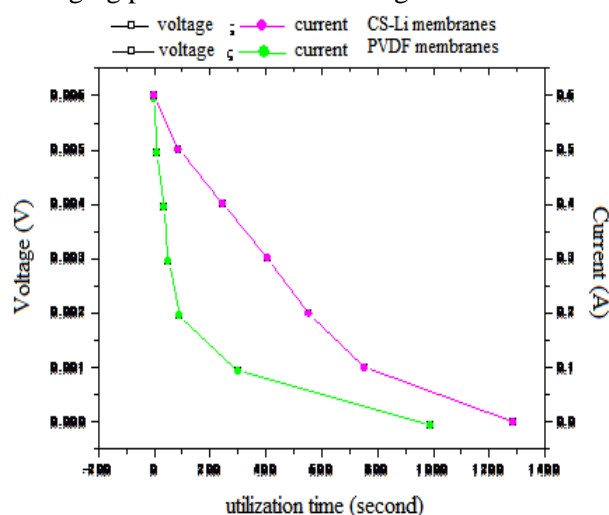


Fig. 3 Graph of voltage and current of CS-Li membranes in utilization battery

Based on Fig. 3, the voltage and electric current of simple battery was obtained using chitosan membrane that are 0.6 A and 0,006 volts, respectively for 1 layer membrane in the first second of the utilization of membranes in a simple battery. These values continue to decline during utilization and until the voltage or electric current to zero is obtained in 1287 seconds. This indicates that the capacity utilization after the battery has run time during the 1287 second. Utilization time of CS-Li membranes are still longer than PVDF membranes which were only able to produce electric current and voltage up to 989 seconds on a simple battery. Recharging is needed when the capacity of battery is zero. Based on Table 3, the capability rechargeable batteries obtained increase for every 30 second in voltage is ± 0.70 volts. The results obtained are in accordance with PVDF polymer membrane that is

used by commercial lithium batteries as a solid polymer electrolyte.

Table 3. Data of voltage recharging of lithium polymer battery for CS-Li and PVDF

Time (second)	Charging the battery voltage (Volt)	
	CS-Li	PVDF [5]
0	0.04	1.3×10^{-6}
30	0.70	15×10^{-6}
60	1.30	2.1×10^{-6}

4 Conclusion

Deacetylation process does not give the orderliness for water uptake, ion exchange capacity as well as proton conductivity. The results show that increasing of chitosan concentration lead to increase ion conductivity of chitosan-lithium membranes. The best membran for lithium polymer battery is chitosan from deacetylation 2x3 h.

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