



The Synthesis of Chitosan Polymer Membrane/PVA as an Eco-Friendly Battery for Alternative Energy Resource

Nuni Widiarti✉, Woro Sumarni, Lysa Setyaningum

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Jurusan Kimia, Universitas Negeri Semarang, Gedung D6 Lantai 2, Kampus Sekaran, Gunungpati, Tlp.(024) 8508112 Semarang 50229

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Abstract

The eco-friendly materials which have not commonly developed as energy storage alternative sources are solid electrolytes. Chitosan is one of the natural polymer potentially used as the material of solid electrolytes. The purpose of this study is to determine the conductivity value of chitosan polymer's electrolytes-PVA-glutaraldehyde-NH₄Br by varying amount of chitosan and ammonium bromide salt (NH₄Br). The polymer electrolyte membrane was made using phase inversion method. Electrolyte polymer is made by mixing chitosan, PVA, glutaraldehyde, and NH₄Br to become homogenous liquid and then printed it in petri dish. Polymer electrolyte with chitosan variation of 2; 2.4; 2.8 and 3.2 g has highest ionic conductivity of 1.4983×10^{-2} S/cm with the addition of 2.8 g that can be used as the optimum composition. The variations of salt (NH₄Br) were 0; 0.2; 0.4; 0.6; 0.8 and 1 g has the highest ionic conductivity in the point of 2.4385×10^{-2} S/cm with the addition of 0.6 g. The characterization result of FTIR shows OH group at the wavenumber of 3362.02 cm^{-1} , C-O group at 1740.43 cm^{-1} , and C=N group at 1542.41 cm^{-1} . Synthesized polymer can be used as a battery that has 0.43 V voltage.

INTRODUCTION

Recently, natural polymer material are widely studied as polymer electrolyte because of their eco-friendly nature. Chitosan is one of the most investigated natural polymer material. Electrolytes consist of liquid and solid electrolytes. Disadvantages of using liquid electrolytes are vulnerable to the leakage, flammable if exposed to spark of fire and also poisonous. Meanwhile, solid electrolytes are safer, free from leaks, and can be produced in smaller dimension, like a thin layer (Gray & Armand, 1999). Polymer electrolyte can replace liquid electrolyte. The conductivity of polymer electrolyte can be increased by using two different types of polymers and also modifying the suitable polymer type (Rajendran et al., 2001). The

materials which are commonly used as membrane stabilizers are glutaraldehyde and genipin. Both of them are the cross-link agents in chitosan (Jin et al., 2004). Osman *et al.* (2001) stated that the conductivity of chitosan comes from the salt ion movement, this movement can subsequently be fixed with the addition of plasticizer. Several plasticizers which have been used in cross linking of chitosan were oleic acid (Yahya & Arof, 2003), phosphoric acid, PEO (Polyethylene Oxide) (Donoso et al., 2007) and PVA (Polyvinyl Alcohol) (Kumar et al., 2010).

The research conducted by Kadir *et al.* (2010) focused on solid electrolyte from the mixture of chitosan-PVA yields ion conductivity of 10^{-11} S cm^{-1} at room temperature. The addition of NH₄NO₃ and ethylene carbonate polymer as

plasticizer can increase the ion conductivity value significantly as much as $6.0 \times 10^{-3} \text{ S cm}^{-1}$. Similarly, the research conducted by Riyanto et al. (2011) on polymer electrolyte from chitosan-PVA-glutaraldehyde. The addition of NH_4NO_3 to the polymer can increase ionic conductivity from $4.8 \times 10^{-10} \text{ S cm}^{-1}$ to $2.2 \times 10^{-5} \text{ S cm}^{-1}$. Another research was done by Hema et al. (2009) to solid polymer electrolyte from PVA. The addition of ammonium halide salt (NH_4X) obtained conductivity value of PVA- NH_4Cl of 1.0×10^{-5} , PVA- NH_4Br of 5.7×10^{-4} , and PVA- NH_4I of 2.5×10^{-3} .

Based on several studies that have been done, chitosan modification can increase the value of electrical conductivity, thus it can be used as polymer electrolytes for battery production. Therefore, this research is aimed to find the conductivity value of polymer electrolytes from the variation of chitosan added with PVA-glutaraldehyde- NH_4Br , combined with the addition of ammonium bromide salt (NH_4Br). It is expected that the addition of ammonium bromide salt (NH_4Br) obtained high electrical conductivity value so that it can be used as an energy source in battery.

RESEARCH METHODOLOGY

The equipment used in this research were multimeter, LCR Meter (EDLaboratory EDC-1630) and FTIR (PerkinElmer Spectrum Version 10.4.00) and analytical balance AND GR-200. The materials used were chitosan, PVA technical analysis, acetic acid (Merck) 100%, glutaraldehyde and ammonium bromide with pro analysis grade manufactured by Merck. The production of chitosan polymer electrolytes/PVA, author refers to the research conducted by Riyanto *et al.* (2011) using PVA with the addition of ammonium nitrate. Polyvinyl alcohol of 1.20 g and chitosan was firstly dissolved in 100 ml 1% acetic acid for 2 hours with the variation of chitosan addition (2; 2.4; 2.8 and 3.2 g). The dissolved material was then homogenized using magnetic stirrer at 80 °C for 5 minutes until it is well mixed. The solution was then chilled until reached 25 °C. Gradually, 1 mL of 6% glutaraldehyde was added and stirred well, then rest it for 15 minutes until it was homogenous. Ammonium bromide salt (NH_4Br) was added slowly as much as 0.4 g. After the solution was homogenized, it is then printed in petri dish and dried in the oven for 15 hours at 60°C. It was then dried at room temperature. Produced polymer

electrolyte was then tested its conductivity value by using LCR meter. The variation of chitosan addition with highest conductivity was then used as the optimum composition for the variation of ammonium bromide salt (NH_4Br). The optimum composition of polyvinyl alcohol and chitosan is processed into polymer electrolytes using previous steps with the addition of different variations of ammonium bromide salt (NH_4Br), i.e. 0; 0.2; 0.4; 0.6; 0.8 and 1 g.

The polymer electrolyte film structure analysis was performed using FTIR spectroscopy. Polymer electrolyte films to be characterized is a polymer with highest conductivity value. The measurements were done at wavelength of 4000 – 650 cm^{-1} . Polymer electrolyte with highest conductivity value is then used as a battery by utilizing used battery. Graphite from used battery is taken off and cleansed. The chitosan polymer electrolyte /PVA was wounded on the graphite which was layered by zinc until it was fully covered. The voltage of new battery was then measured using multimeter.

RESULTS AND DISCUSSION

The polymer electrolyte membrane was prepared by using phase inversion method. Phase inversion is a process where polymer was converted from liquid to a controlled solid form.

The formation of membrane with this technique was done through several stages. First, the production of homogenous print solution, solvent evaporation, and the submersion in non-solvent solution. The preparation of 1% chitosan membrane was initially started with adding chitosan powder as the material of chitosan membrane to 1% of acetic acid since the best solubility of chitosan was in 1% acetic acid solution. In order to obtain soft and homogenous membrane, chitosan should be perfectly dissolved in the solvent. Subsequently, it was stirred for 2 hours at room temperature using magnetic stirrer until thick yellow solution was formed. If the mixing was carried out at high temperature then the solvent in this case is acetic acid (CH_3COOH) will be decreased due to evaporation. The reduction in solvent volume will result in the increase of dope solution's viscosity. It causes the unevenness of dope solution when it was poured in the mold. The higher the concentration of chitosan used, the viscosity of solution also increases. Wang et al.

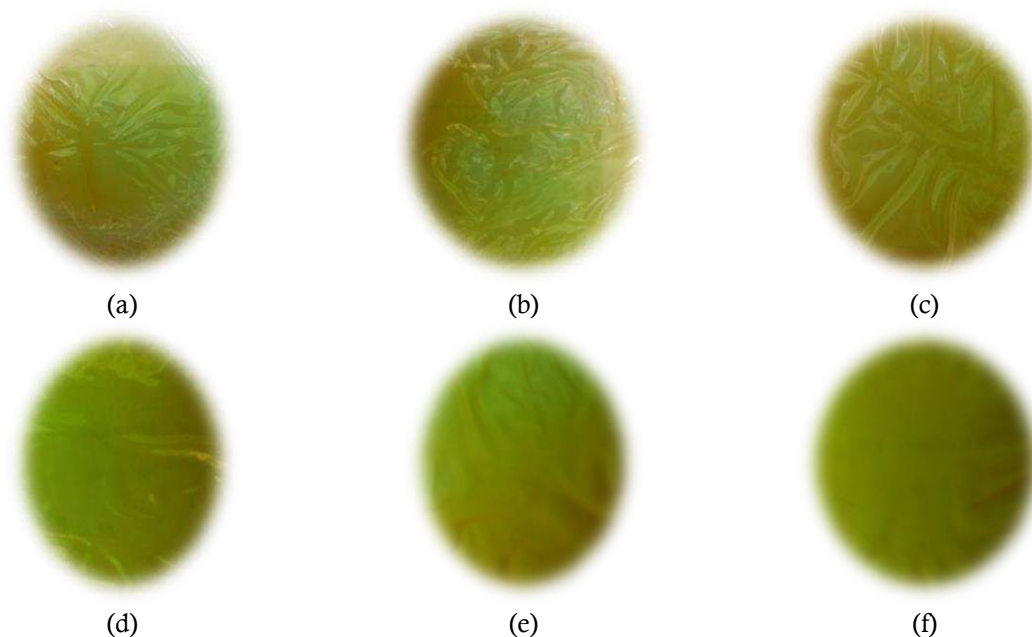


Figure 1. Polymer electrolyte with variation of NH_4Br (a) without NH_4Br , (b) 0.2 g, (c) 0.4 g, (d) 0.6 g, (e) 0.8 g, and (f) 1 g

(1991) reported that in certain solution, the high level of positive charge will result repel force which makes previously formed polymer chitosan as a roll opened up becoming a straight chain resulting in the increasing viscosity of solution. Kumar et al. (2010) reported that the increasing concentration of chitosan causes cross links and the increasing number of hydrogen bonds. Park et al. (2002) added that during the production of films, the number of hydrogen bonds will increase and this increase is correlated to the increasing number of amino and hydroxyl group caused by the addition of chitosan concentration resulting in high viscosity.

The addition of PVA was performed after homogenous chitosan solution was obtained. Polyvinyl alcohol was formed as dried solid and white powder. The addition of PVA in certain amount will improve the structure of the membrane, increase the strength of chitosan membrane, and be able to stabilize the produced membrane forms (Hassan & Peppas 2000). PVA which is a derived compound of Poly Vinyl Acetate will melt at a temperature above 72°C because the melting point of Poly Vinyl Acetate was 72°C . PVA is homogeneously soluble with chitosan solution since there was a hydrogen bound between PVA and chitosan. After chitosan and PVA are mixed, glutaraldehyde was added. In this case, Glutaraldehyde acted as the cross linkage to form an intra-bond formation and between tissues (Wang

et al., 2004). When glutaraldehyde was used for crosslinking, small fraction of hydroxyl group and amine group were bonded, but most of the hydroxyl and amine groups still exist for proton exchange (Smitha et al. 2006).

Pre-printed solution should be left for 24 hours to remove the air bubbles. Existed trapped air bubble during membrane molding may tear up the membrane. The immersing process of solution before printing process has important role to produce a good membrane. Then, the mold that has been filled with membrane solution was roasted at temperature 60°C . Removing membrane should be done carefully since the layer was very thin and easy to be ripped or leaked. To remove it carefully the dried membrane need to be soaked with 1% NaOH solution. NaOH solution was serves as the non-solvent solution which can diffused to the bottom of membrane which coincides with the mold surface so that the membrane will be pushed and peeled (Kusumawati & Tania, 2012). The peeled membrane from petri dish was then washed consecutively with aquadest to remove the NaOH.

The shape of polymer electrolyte was looks like a thin and transparent plastic sheet with a yellowish color. The shape of polymer electrolyte at various ammonium bromide salt (NH_4Br) can be seen in Figure 1.

Figure 1 shows the surface on polymer electrolyte with NH_4Br variation. The addition of NH_4Br producing transparent yellowish-green

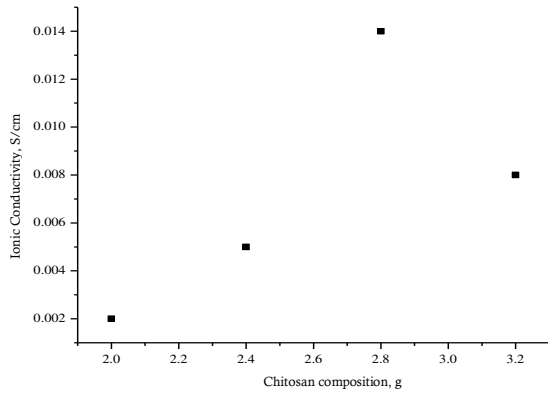


Figure 2. Effect of chitosan addition on Ionic conductivity value.

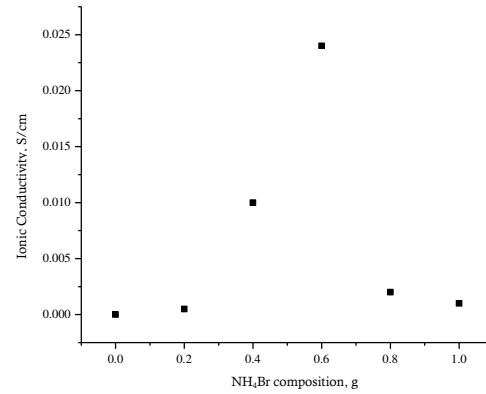


Figure 3. Effect of NH₄Br addition on the Ionic conductivity value.

Table 1. The thickness of polymer electrolyte using variation of chitosan addition

Chitosan (g)	Thickness (millimeter)
2	0,02
2,4	0,03
2,8	0,05
3,2	0,05

Tabel 2. The thickness of polymer electrolyte with the variation of NH₄Br addition

NH ₄ Br (g)	Thickness (millimeter)
0	0,04
0,2	0,05
0,4	0,05
0,6	0,05
0,8	0,05
1	0,05

membrane with relatively equal thickness. The membrane looks wrinkled in Figure A B C since it was very thin. Nevertheless, the increasing thickness of membrane from 0.04 to 0.05 on the surface of the membrane making it seems soft.

Chitosan polymer electrolyte-PVC has a thickness level between 0.02 – 0.06 millimeters. The thickness value of packaging material film produced was different, but the increase of chitosan concentration can increase the thickness of packaging material film. Table 1 shows the thickness of polymer electrolyte films which is increases with the addition of chitosan amount used in the membrane production. However, the addition of NH₄Br salt did not give significant influence to the film thickness. It is shown in Table 2 that the increasing thickness of films only occurs on sample without the addition of NH₄Br, with NH₄Br amount of 0,2 g. The increasing number of NH₄Br does not produce thicker films.

Figure 2 shows that the addition of 2 g chitosan until 2.8 g experienced the increasing value of conductivity. Meanwhile, the addition of 3.2 g experienced the decreasing conductivity, and, the electrolytes produced form were not rigid and thick. The optimum conductivity was obtained with the addition of 2.8 g chitosan was 1.4983×10^{-2} S/cm.

The optimum conductivity value of mixed chitosan electrolyte, PVA, glutaraldehyde with the variation of NH₄Br can be seen Figure 3. Polymer electrolyte without the addition of ammonium bromide salt (NH₄Br) has the lowest conductivity value, while the optimum conductivity value of polymer electrolyte was obtained in the addition of 0.6 g NH₄Br which was 2.4385×10^{-2} S/cm. The increasing ionic conductivity was expected from the high number of ion number and the mobility of the existing ions. The addition of NH₄Br with optimum percentage will produce polymer electrolyte with the highest ionic conductivity. The best percentage of NH₄Br depends on the polymer used. However, the addition of 0.8 g or more NH₄Br was producing polymer electrolyte more with decreasing ionic conductivity. This is due to the polymer electrolyte already reaches the saturation composition limit. The high ion concentration in polymer can inhibit the movement of these ions and cause stiffness in the polymer chain resulting in decreasing of ionic conductivity value of polymer electrolytes (Singh & Bhat, 2003). It becomes possible when the addition of more than 0.8 g concentration of ammonium bromide salt (NH₄Br), there might be an increase in the solid density, so, the movements of ion will be decreasing, and it can cause the decrease of ion conductivity.

In polymer electrolytes of chitosan/PVA there were –OH group; –CH₂–; –C–O–; –CH₃ and –NH₂ (Nugroho et al., 2014). Figure 4 shows the

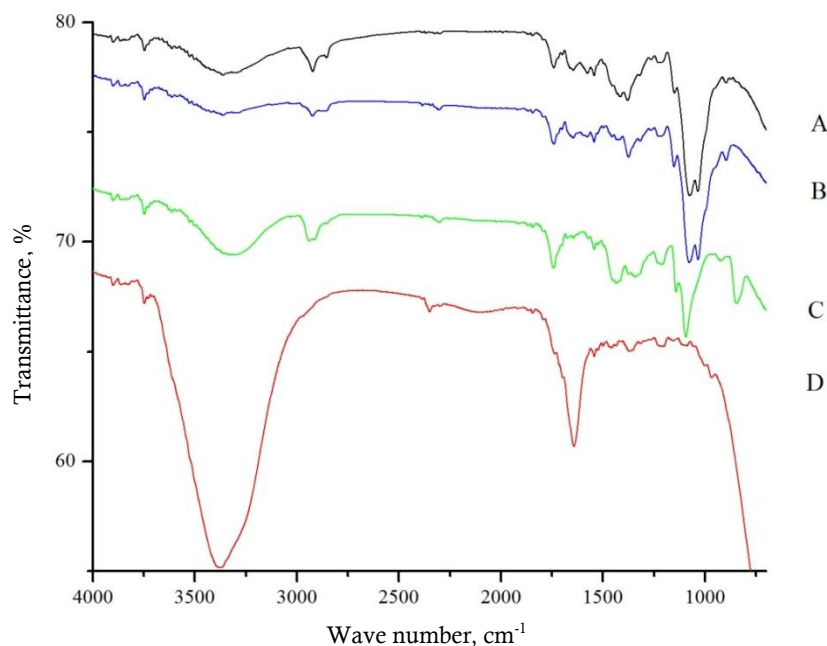


Figure 4. Infrared Spectrum from (A) polymer electrolyte, (B) chitosan, (C) PVA, and (D) glutaraldehyde

spectra of polyvinyl alcohol group which is formed on the wave numbers of 3309.77 cm^{-1} and 1741.55 cm^{-1} including hydroxyl (OH) and ketones group. The spectra of polymer electrolyte was formed at wave numbers of 3362.02 cm^{-1} and 1740.43 cm^{-1} . The pure chitosan spectra was found at the wave numbers of $3362.23 - 3611.51\text{ cm}^{-1}$ resulted from the range vibration of -OH group. The widespread absorption and shifted -OH group wave number in this chitosan is due to the overlap with NH group from amines. The wavenumber of 1644.86 cm^{-1} shows the existence of NH_2 group in the polymer electrolytes. In the wave number of 1415.01 cm^{-1} , it was formed weak C=C aromatic group. There were C-N and C-O group in the band absorption numbers of 1034.74 cm^{-1} and 1075 cm^{-1} . The research conducted by Riyanto (2011) showed that the polymer electrolyte made from chitosan-PVA-glutaraldehyde- NH_4Br had OH spectra group at wave number 3431 cm^{-1} , NH_2 group at wave number 1653 cm^{-1} , C=C group at wave number 1424 cm^{-1} , C-N group at wave number 1320 cm^{-1} , and the C-O group at wave numbers 1157 cm^{-1} and 1068 cm^{-1} .

According to Nisa (2005), chitosan-PVA-polyethylene glycol membrane had spectra of C=N group at wave number 1651.4 cm^{-1} . The peak that appears at wavelength of 1542.41 cm^{-1} identifies the existence of an imine (C=N) group which is a covalent bonds made from the nucleophilic substitution reaction (nitrogen from amine group

on chitosan chain) to the aldehyde group in glutaraldehyde.

Polymer electrolyte with highest conductivity value which was found in the addition of 0.6 g of NH_4Br , wounded between carbon and zinc from used battery as shown in Figure 5. The battery was tested using multimeter and obtained voltage value of 0.43 V which is relatively small compared to the voltage value set by BSN (2004) for carbon-zinc batteries which is 1.5 V. Based on this result, the produced batteries has not met the standard and also has low voltage. This is because the battery pack assembly was done manually, this might result imperfection polymer electrolyte winding on the electrode. In addition, the polymer electrolyte form used in this research was quite rigid. According to Linden & Reddy (2002), battery design can affect the outcome of the voltage and current of the battery. However, the advantages of polymer electrolyte battery was it used chitosan and PVA as the main material which can be degraded by nature, making it eco-friendly and flexible.

CONCLUSION

In the variation of chitosan with 2.8 g addition had highest conductivity value of $1.4983 \times 10^{-2}\text{ S/cm}$, while for the addition of 0.6 g ammonium bromide salt had highest value of $2.4385 \times 10^{-2}\text{ S/cm}$. The polymer electrolyte from the combination of chitosan, PVA, NH_4Br and

glutaraldehyde with highest conductivity value can be used as a battery with the voltage of 0.43 V.

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