

THE CONDUCTIVITY OF ELECTROLYTE MEMBRANES BASED ON CELLULOSE ACETATE FROM CORN HUSK WASTE

Marfuatun

*Chemistry Education Department, Faculty of Mathematics and Natural Sciences,
Universitas Negeri Yogyakarta
e-mail: afu@uny.ac.id*

Abstract

This research focused on the preparation of electrolyte membranes using cellulose acetate that isolated from corn husk waste with aims to determine the optimum acetylation time of corn husk and the influence of the lithium salt composition on the membrane ionic conductivity. The electrolyte membranes were prepared by polymer solution casting method. The results showed that the optimal DS obtained in 4 hours. While the increase of lithium salts content doped in membrane, provide the increase of the membrane conductivity with the obtained optimal conductivity was 3.048×10^{-3} S/cm. (Times New Roman 10 pt, single space, right-left indent 1,5, justified)

Key words: Conductivity, Cellulose acetate, Corn husk waste

INTRODUCTION

One of the strategic issues in the field of science and technology is the new and renewable energy. The long term problem of energy regarding to the energy supply sustainability. The energy supply must consider several aspects, including environmental, economic and social humanity. Therefore, we need an innovation that is both integrative and multidimensional.

An alternative energy supply is the use of electrochemical energy source that can convert chemical energy into electrical energy. The energy source can be produced in sustainable and environmentally friendly. One common electrochemical energy sources is lithium battery technology (Winter and Brodd, 2004). The advantage of lithium ion battery development because it more efficient in converting chemical energy into electrical energy and also rechargeable.

There are three main components in lithium ion batteries: the anode, cathode, and electrolyte. Conductive electrolyte component serves as a medium of lithium ions from the anode to the cathode, and vice versa. At the beginning, this electrolyte is a solution, so it required a separator between the cathode and anode. In addition, the electrolyte solution can be harmful to the environment in case of leakage. Therefore, it needs to develop a polymer-based electrolyte membrane. The electrolyte membrane plays two role functions, as electrolyte and separator.

Polymers that used to make the electrolyte membrane must have sufficiently high mechanical strength to withstand the pressure between the cathode and anode, also having high chemical stability and ion conductivity. One commonly polymer used as electrolyte membrane material and has been produced commercially is polyethylene oxide or PEO (Osman *et al.*, 2005).

PEO has a high ionic conductivity, low toxicity, and have a fairly high chemical stability. However, the PEO has poor mechanical properties, the resulting membrane is fragile and only slightly biodegradable. In addition, the ion conductivity of PEO membrane will tend to fall at high temperatures, due to the reduction of membrane humidity (dehumidification). The development of polymer electrolyte membrane like acetate cellulose in an alternative solution to these problems.

Acetate cellulose is an acetate ester from cellulose. Selvakumar dan Bhat (2008) reported the highly conductivity acetate cellulose membrane that applied in ion lithium battery reached 4.9×10^{-3} S/cm as the minimal requirement of membrane ion conductivity is 10^{-5} S/cm in the temperature of -20°C to 60°C (Arora and Zhang, 2004). Beside that, acetate cellulose also has good mechanic properties. Acetate cellulose is a cellulose derivative. Cellulose is existed a lot in plats, it can be isolated from agriculture waste such as corn husk that contains 31.7% of cellulose (Schell *et al.*, 2003). Acetate cellulose is a biodegradable polymer, its membrane is transparent and has a sufficiently high mechanic strength. Acetate cellulose has many functions beside as electrolyte polymer membrane, also applied in textile technology, film material, absorbent tissue, specific paper, etc.

The acetate cellulose from corn husk will raise the economic value of corn husk. Usually, corn husk waste is only used for fertilizer and in some areas for food packaging. During the harvest time, the corn waste is mostly just burned. The synthesis of acetate cellulose can be done by esterification of the cellulose isolated from corn husks. The purpose of this study was to determine the optimum acetylation time of corn husk and the influence of the lithium salt composition on the membrane ionic conductivity. Membrane electrolyte for lithium ion batteries made by doping cellulose acetate with lithium salts. In this research, we isolate the cellulose from corn husk, followed by cellulose acetylation to produce acetate cellulose and continued by doping acetate cellulose with lithium salts. The resulting products were analyzed by analyzing the functional groups (FTIR), degree of substitution (DS) and the membrane ionic conductivity.

RESEARCH METHOD

Materials

Corn husk, an agricultural waste, was obtained from local market in Yogyakarta, ethanol, sodium hydroxide, sulfuric acid, sodium hypochlorite, glacial acetic acid, anhydride acetic acid, sodium chloride aquadest, lithium chloride, and dichloromethane. The materials used were analytical grade-products purchased from Merck.

Isolation of Cellulose

The isolation of cellulose form corn husk have been done following the procedure of AOAC (Raqab *et al.*, 2014). The corn husks were dried and milled into powder, then passing through messes to obtain homogeneous size. The powder corn husk was then extracted using a solvent mixture of ethanol and toluene with ratio 1:2 (v/v). The extraction aimed to remove wax, pigment, and oil, the resulting material was dried in 60°C for 3 hours. It was solvated in 2 M sodium hydrochloride solution for 3 hours to remove the lignin and finally bleached using sodium hypochloride.

Acetylation of Cellulose

Two grams cellulose was activated using 25 mL glacial acetic acid for one hour. Then, added by 15 mL anhydride acetic acid and concentrated sulfuric acid. The esterification process was conducted in time variation of 1, 2, 3, 4, and 5 hours in 40°C . The acetylation process continued by adding 25 mL glacial acetic acid. The reaction mixture was filtrated. The filtrate was dropped by aquadest until forming white powder. The powder was washed with aquades to remove acid residue and dried in 40°C .

Membrane Preparation

Membrane made by casting of the polymer solution. Cellulose acetate was dissolved in dichloromethane, then doped by lithium salts. The doped salts were 2.5%, 5%, and 10% (w/w). After the mixture become homogeneous, it molded and dried.

Determine of Degree of Substitution (DS)

DS was determined by a back-titration method. A half grams of sample was putted in Erlenmeyer, and added by 20 mL ethanol, 20 mL NaOH, and then it was heated for 15 minutes at temperature of 50-60°C. The mixture kept under stirring in room temperature, and after that it was titrated with HCl drops using phenolphthalein indicator. The mixture back titrated with NaOH. Blank samples treated with the same of acetate cellulose. DS was calculated by finding the percentage of samples with acetyl in equation 1 and 2.

$$\% \text{ acetyl} = \frac{[(A-B)M_b + (D-C)M_a] \times 43 \times 100\%}{w/g \times 1000 \text{ mg/g}} \quad (\text{eq.1})$$

With:

- A = mL NaOH required to titrate the sample
- B = mL NaOH required to titrate the sample blanko
- C = mL HCl required to titrate the sample
- D = mL HCl required to titrate the sample blanko
- Ma = Molaritas HCl
- Mb = Molaritas NaOH
- W = sample weight

$$DS = \frac{162 \times \% \text{ acetyl groups}}{4300 - (42 \times \% \text{ acetyl groups})} \quad (\text{eq. 2})$$

Characterization

The synthesized membranes were characterized using Elkahfi 100 and spectroscopy (FTIR and XRD). Elkahfi 100 used to analyze the conductivity of membranes. FTIR was used to analyze functional groups and XRD was used to determine the crystallinity of membranes.

RESULT AND DISCUSSION

Synthesis of cellulose acetate from corn husk waste included two stages: cellulose isolation from corn husks and acetylation of cellulose. Isolation from corn husk waste through two stages i.e. delignification and bleaching. The results showed that the obtained cellulose yield was 31.25% of the waste corn husk mass. It means hemicellulose and lignin content in corn husk was 69.75%. The FTIR spectra of cellulose can be seen in Figure 1.

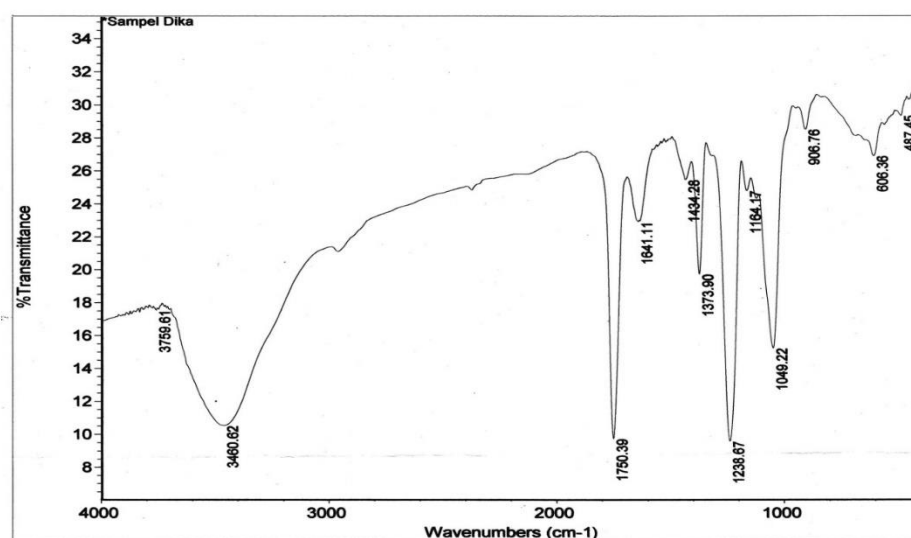


Figure 1. FTIR spectra of cellulose from corn husk

In Figure 1. The absorption at 3460.62 cm^{-1} represents the O-H stretching vibration. A broad peak indicates intramolecular and intermolecular H bridge between the OH groups (Ragab *et al.*, 2014). The peak at 1750.39 cm^{-1} represents the stretching vibration CO of the COOH group. Small peak at 1641.11 cm^{-1} relates to the presence of hydration or water absorption by cellulose. The peak at 1434.28 cm^{-1} and 1238.67 cm^{-1} relate to the presence of CH deformation. The absorption at 1373.90 cm^{-1} represents the bending vibration of-OH group. The peak at 1049.22 represents CO stretching in COC glycosidic bonds. The existence of the glycosidic bond is also supported by the presence of small peak at 906.76 cm^{-1} (β -glycosidic).

Acetylation of cellulose in this research had done following the common procedure in industry. Cellulose acetate was generally manufactured by a solution process employing sulfuric acid as the catalyst with acetic anhydride in acetic acid solvent. The acetylation was done for 4 and 5 hours, and the result of each process were cellulose acetate with percentage acetyl 45.06% and 39.130% (DS 3 and 2.38), respectively. The optimum time at 4 hours represents homogenous acetylation of cellulose. At 5 hours, DS and yield decrease due to hydrolysis of the ester groups and/or the decomposition of cellulose backbones (Li *et al.*, 2009). Based on DS value then acetylation product was cellulose triacetate and shown in figure 2.



Figure 2. Cellulose triacetate

During acetylation, the hydrophilic OH groups in cellulose is substituted by hydrophobic acetyl groups. There is four major changes can observed in the spectra of cellulose acetate (Fig.3)

as compared to the spectra of cellulose (Fig.2) are (1) A decrease in the OH stretching band at 3468.21 cm^{-1} , (2) An increase in the carbonyl (C=O) stretching vibration at 1753.74 cm^{-1} , (3) An increase in the CH bending band at 1372.43 , and (4) An increase in CO stretching vibration at 1237.10 cm^{-1} (Sun *et al.*, 2004; Ragab *et al.*, 2014). The four changes in spectra also provides further evidence of successful acetylation. No absorption was observed in the region $1840\text{--}1760\text{ cm}^{-1}$ and 1700 cm^{-1} in the spectra of cellulose acetate indicating that product are free of unreacted acetic anhydride and the acetic acid by-product (Adebajo and Frost, 2004). FTIR spectra of cellulose acetate is shown in figure 3.

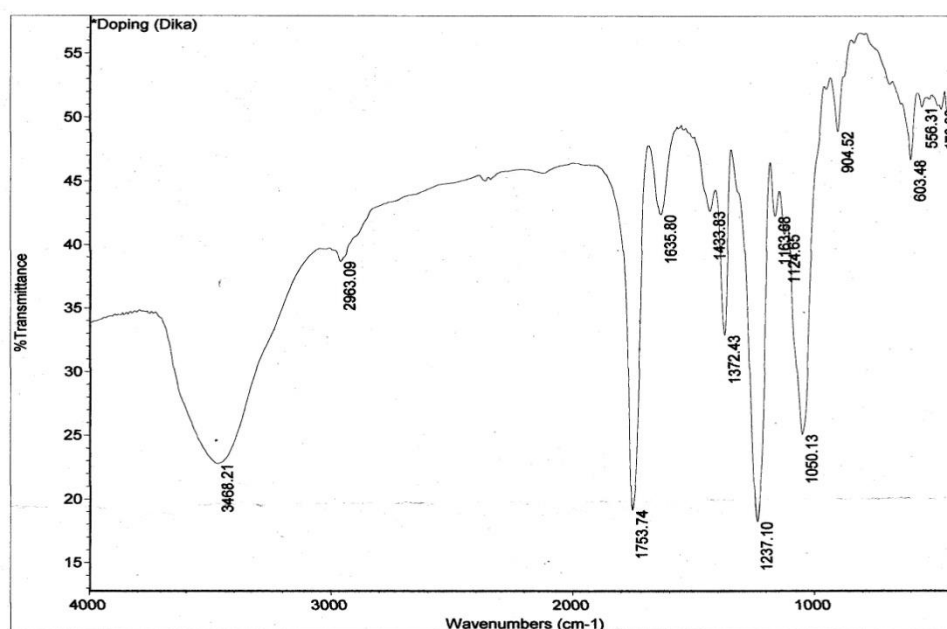


Figure 3. FTIR spectra of cellulose acetat with lithium salt

Fabrication of membrane was done by casting polymer solution with variation of lithium salts composition. Lithium salts that used was lithium chloride ($\text{LiCl}_2 \cdot 2\text{H}_2\text{O}$). The resulting membrane was brittle, thus it was difficult to analyze the mechanical properties. The membrane only analyzed the conductivity and structure (crystallinity) membrane. The result of the conductivity analysis was shown in Table 1.

Table 1. The Conductivity of Cellulose Acetate Membranes

No.	Composition Lithium Salt (%)	Conductivity (S/cm)
1.	2,5	$2,485 \times 10^{-4}$
2.	5	$5,908 \times 10^{-4}$
3.	10	$3,048 \times 10^{-3}$

Table 1 showed that the increase of lithium salts content doped in membrane, provided the increase of the membrane conductivity. This is because of the lithium ions influence that served as charge carrier. Generally, the conductivity is affected by two things, the concentration

of ions as the charge carrier and the mobility of ions (Ratna *et al.*, 2007). The optimum conductivity was 3.048×10^{-3} S/cm. The diffractograms of cellulose acetate shown in Figure 4.

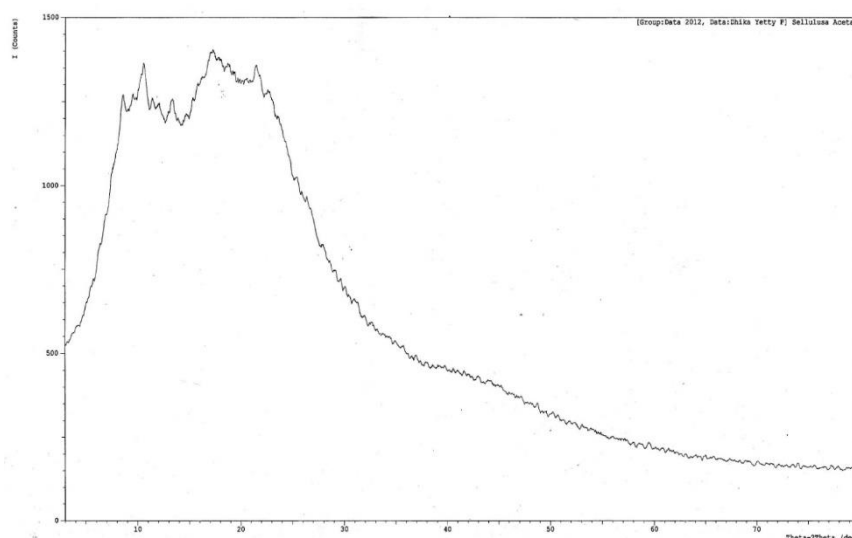


Figure 4. Diffractograms of cellulose acetate

Figure 4 displayed that cellulose acetate have low degree of crystallinity (tend to amorphous fase). The low of crystallinity due to the substitution of the hydroxyl groups in cellulose by acetyl groups that are the larger size groups, which broke the intermolecular and intramolecular hydrogen bonds of cellulose (Li, *et al*, 2009). The high degree of amorphous region make high conductivity of cellulose acetate membrane. The result describe the mechanical properties of cellulose acetate membrane was brittle.

CONCLUSION AND SUGGESTION

This study provides us a through overview of corn husk chemistry. We successfully synthesized cellulose acetate membrane from corn husk. The result showed that the acetylation was successful and the optimal DS obtained in 4 hours, i.e. cellulose triacetate (DS ~ 3). While the increase of lithium salts content doped in membrane, provided the increase of the membrane conductivity with the obtained optimal conductivity was 3.048×10^{-3} S/cm. In order to optimize the mechanical properties of membrane, it needs to use the plasticizer.

REFERENCES

- Adebajo, M.O, Frost, R.L. (2004). Acetylation of Raw Cotton for Oil Spill Cleanup Application - An FTIR and ^{13}C MAS NMR Spectroscopic Investigation. *Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy*, 60(10): p. 2315-2321
- Arora, P., Zhang, Z.J. (2004). Battery Separator. *Chemical Reviews*, 104: p.4419-4462
- Li , J., Zhang, L.P., Peng, F., Bian, J., 1, Yuan, T.Q., Cang Sun, F.X.R. (2009). Microwave-Assisted Solvent-Free Acetylation of Cellulose with Acetic Anhydride in the Presence of Iodine as a Catalyst. *Molecules*, 14: p. 3551-3566
- Osman, Z., Ansor, N.M., Chew, K.W., Kamarulzaman, N. 2005. Infrared and Conductivity Studies on Blends of PMMA/PEO Based Polymer Electrolytes. *Ionic*, 11: p. 431-435

- Ragab, T.I.M., Wasfy, A.A.F., Amer, H., El-Gendi, A., Abdel-Hady, M.S., Liebner, F. (2014). Synthesis of Cellulose Acetate Membrane from the Egyptian Rice Straws. *Journal of Applied Sciences*, 14 (24), p. 3424-3435
- Ratna, D., Divekar, S., Patchaiappan, S., Samui, A.B., Chakraborty, B.C. (2007). Poly(ethylene oxide)/Clay Nanocomposites for Solid Polymer Electrolyte Applications. *Polymer International*, 56: p. 900-904
- Schell, D.J., Farmer, J., Newman, M., McMillan, J.D. (2003). Dilute-Sulfuric Acid Pretreatment of Corn Stover in Pilot-Scale Reactor. *Applied Biochemistry and Biotechnology*, Vol. 105-108, p. 65-85
- Selvakumar, M., Bhat, D.K. (2008). LiClO₄ Doped Cellulose Acetate as Biodegradable Polymer Electrolyte for Supercapacitors. *Journal of Applied Polymer Science*, 110 (1): p. 594-602
- Sun, X.F., Sun, R.C., Sun, J.X. (2004). Acetylation of Sugarcane Bagasse Using NBS as a catalyst under mild reaction conditions for the production of soil sorption-active materials. *Bioresour. Technol.*, 95: p. 343-350
- Winter, M., Brodd, R.J. (2004). What Are Batteries, Fuel Cell, and Supercapacitors. *Chemical Reviews*, 104, p.4245-4269

