

PREPARATION AND CHARACTERIZATION OF NAFION COMPOSITE MEMBRANES CONTAINING MICRO AND NANOCRYSTALLINE CELLULOSE FOR DIRECT METHANOL FUEL CELL APPLICATIONS

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Abstract

This work demonstrated the use of a microcrystalline cellulose (MCC) and a nanocrystalline cellulose (NCC) reinforced with Nafion (NF) composite membrane for direct methanol fuel cells (DMFC). The study compared membranes properties of MCC/NF composite membrane and NCC/NF composite membrane with recasted NF membrane by ex-situ test. The result of SEM/EDS with elemental mapping showed that NCC dispersion within the membrane was better than that of MCC. The water uptake result showed that NCC/NF composite membrane was higher than that of MCC/NF membrane. The solubility property of NCC/NF composite membrane was better than that of MCC/NF membrane (both composite membranes were less than 5% solubility). It was found that ion exchange capacity of recasted NF membrane was higher than both composite membranes but chemical degradation of both composite membranes was lower than that of recasted NF membrane. For MeOH permeability, it was found that adding cellulose on NF reduced MeOH crossover for both composite membranes and MCC/NF composite membrane had the lowest MeOH permeability among all.

Keywords: Microcrystalline cellulose, Nanocrystalline cellulose, Nafion, Direct methanol fuel cell

Introduction

Nowadays, many researchers have studied new energy technology to replace energy from fossil fuel due to an increasing of greenhouse gas. Fuel cells are one an new energy technology. It is electrochemical cell that converts the chemical energy to electricity (Saikia *et al.*, 2018). Fuel cells

have high potential and environmentally friendly energy (Benipal *et al.*, 2017). Direct alcohol fuel cell (DAFC) is one type of fuel cell which produce electricity by use alcohol such as methanol, ethanol, and glycerol. Direct methanol fuel cell (DMFC) is one type of DAFC which use methanol as fuel

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source. It has good electrochemical activity and low cost (Ong *et al.*, 2017). Nafion (NF) is used as proton exchange membrane (PEM) because it has high proton conductivity due to NF composes of perfluoro sulfonated polymers which is hydro-philic sulfonic acid that allow only protons to crossover (Yao *et al.*, 2019). DMFC has high methanol crossover from anode to cathode which causes DMFC performance decrease (Taechaboonsermsak *et al.*, 2020). There are many researchers studied reducing of MeOH crossover in DMFC such as Wang, B. use sulfonated poly (arylene ether ketone) as filler for composite membrane which the MeOH crossover was 1.1 times lower than that of recast Nafion (Wang *et al.*, 2017). Parthiban, V. studied Nafion composite membrane by using nanoporous carbon (NPC) as the filler of DMFC. The results of MeOH permeability at 30°C, Nafion -NPC was 1.6 times lower than that of Pristine Nafion (Parthiban *et al.*, 2017). Zhang, C. studied PEEK/sPEEK as filler in Nafion and found that it decreased MeOH crossover 4 times of that of Nafion 117 at 25°C (Zhang *et al.*, 2020).

In this research, cellulose was used as filler in Nafion composite membrane to decrease methanol crossover due to the structure of cellulose is hydrophilic polymer. It can help transportation of water in membrane (Hou *et al.*, 2014). The cellulose was used as reinforcement in composite membrane. Cellulose is a biopolymer composes of C, O, and H and it has good barrier properties to gas such as H₂, O₂, N₂, and CO₂. Proton conductivity was at 120-140°C (Hosseinpour *et al.*, 2019). Cellulose can be found in wood, cotton, rice, straws and pineapple leaves etc. Pineapple leaves is a remainder from an agriculture which is produced in large quantities every year. Pineapple leaves contains 36.3±3.8% cellulose which is in the crystalline structure. Another component in pineapple leaves is hemicellulose as much as 22.9±2.0% which is an amorphous polymer. The rest is mostly lignin which is about 27.53±1.94% (Santos *et al.*, 2013).

Nanocrystalline cellulose (NCC) have been isolated from cellulose in pineapple leaves by acid hydrolysis to decreases particle size of microcrystalline cellulose. NCC composes of crystallites with diameter range from 2 to 20 nm and length varies between 100 nm to microns (Bhat *et al.*, 2017). Acid hydrolysis uses strong acid such as H₂SO₄ and HCl to break the glycoside bond in cellulose. It is has high modulus, low density, negligible thermal expansion ionic and good conductivity (Wu *et al.*, 2014).

The goal of this work was to improve the cellulose composite membrane performance for

DMFC, it is necessary to reduce crossover of methanol. In this work, MCC and NCC were added into NF membrane to decrease methanol crossover. The composite membranes were test by WU, solubility, IEC, chemical degradation, and methanol permeability.

Materials and Methods

Material

Cellulose powder 97.00% were supplied from HIMEDIA, sulfuric acid (H₂SO₄) 98.0 wt% from QRëCTM, Deionized water (15.2 MΩ), hydrogen peroxide (H₂O₂) 35 wt% from Chem-supply, Nafion® 20 wt% soution from Ion Power, methanol (MeOH) 99.99% purity from ACI Labscan, dimethylformamide (DMF) 99.8% purity from QRëCTM, Iron(III) sulfate hydrate from Flurochem, sodium hydroxide (NaOH) from Flurochem, sodium chloride (NaCl) 99.9% from Ajax Finechem and Phenolphthalein.

Synthesis of MCC to NCC

First, 1 g MCC was hydrolyzed with 64% (w/w) 10 mL sulfuric acid at 45°C for 60 min. Then cool water was added for stop reaction. After that, it was centrifuged at room temperature at 8,000 rpm for 10 min. Then, cellulose gel was adjusted to neutralize by dipping the dialysis membrane in water. Finally, cellulose gel was homogenized and kept in refrigerator.

Casting of Recasted NF Membrane

First, 7.445 g Nafion solution was dried for 5-7 days. Then it was mixed with 18.5 mL DMF and sonicated until the mixture became homogeneous. Then, homogeneous mixture was poured into Petri dish and put in a vacuum oven at 80°C for 20 h. After that, it was heated up to 160°C for 4 h under -0.9 bar. Finally, recasted Nafion membrane was removed from the dish and kept in deionized water.

Casting of MCC/NC Composite Membrane

First, 7.445 g Nafion solution 7.445 g was dried for 5-7 days. After that, 0.2127 g MCC was mixed with 5 mL DMF and sonicated for 2 h. Then, dried Nafion was mixed with 13.56 mL DMF and sonicated for 4 h. The MCC mixture and the dried Nafion mixture were mixed and sonicated until homogeneous solution was obtained. Then, it was poured into Petri dish and put in a vacuum oven at 80°C for 20 h. After that, it was heated up to 160°C for 4 h under -0.9 bar. Finally, recasted Nafion membrane was removed from the dish and kept in deionized water.

Fabrication of NCC/NF Composite Membrane

First, 7.445 g Nafion solution was dried for 5-7 days. After that, 0.2127 g NCC was mixed with 5 mL of DMF and sonicated for 2 h. Then, dried Nafion was mixed with 13.56 mL DMF and sonicated for 4 h. The NCC mixture and the dried Nafion mixture were mixed and sonicated until homogeneous solution was obtained. Then, it was poured into Petri dish and put in a vacuum oven at 80°C for 20 h. After that, it was heated up to 160°C for 4 h under -0.9 bar. Finally, recasted Nafion membrane was removed from the dish and kept in deionized water.

Membrane Pretreatment

Membranes was pretreated by soaking in boil deionized water for 10 min. After that it was treated by soaking in 5 wt% H₂O₂ at 80°C for 30 min and 1 M H₂SO₄ acid solution for 30 min. Finally, the membranes were cleaned in boil deionized water 3 times for 10 min and kept in DI water until use (Prapainainar *et al.*, 2017).

Size and Morphology Analysis

The size of MCC and NCC were investigated by scanning electron microscope (SEM) and using Transmission Electron Microscopy (TEM), respectively. After that, particle size of NCC was measured by ImageJ program. The morphology of recasted NF membrane, MCC/NF, and NCC/NF composite membranes were investigated by FEI QUANTA 450 scanning electron microscope (SEM) equipped with Oxford X-Max EDX detector.

Water Uptake (WU) Testing

Membrane samples were dried at 80°C in vacuum oven for 24 h. After that, dried membranes were weighted then soaked in deionized water at room temperature for 24 h. And it was weighted again to determine the value of wet weight. The value was used calculate %WU using Equation (1) (Prapainainar *et al.*, 2017).

$$\%WU = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100 \quad (1)$$

Solubility Testing

First, 50 mg of the dried membrane was added into 10 ml of 50:50 ratio of methanol - water solution and sonicated in ultrasonic cleaner for 1 h. The solution was filtered through No1 filter paper. Finally, the filtered solid was dried at 100°C until dry and weighted. The soluble percentage was calculated by use Equation (2) (Prapainainar *et al.*, 2017).

$$\% \text{ Soluble} = \frac{\text{weight of residue}}{\text{weight of membrane}} \times 100 \quad (2)$$

Ion Exchange Capacity (IEC)

First, 50 mg samples of treated membranes were immersed in 10 mL of 1 M NaCl for 24 h. The solution was titrated with NaOH 0.01M using phenolphthalein as an indicator to determine the amount of H⁺ in the solution. Finally, the IEC value was calculated by Equation (3) (Prapainainar *et al.*, 2017).

$$IEC = \frac{C_{NaOH} V_{NaOH}}{m_{dry}} \quad (3)$$

Chemical Degradation

The Fenton's reagent solutions were prepared by mixing between 200 ml of 5 wt% H₂O₂ and Fe₂SO₄ with 50 ppm concentration. The dried membrane was weighted and put into the Fenton's reagent solution for 48, 96, 144, and 192 h. The soaked membrane was dried in oven at 60°C for 24 h and weighted. The chemical degradation value was calculated by Equation (4) (Taechaboonsersak *et al.*, 2020).

$$\% W_{Residual} = \frac{W_{after \text{ Fenton test}}}{W_{before \text{ Fenton test}}} \times 100 \quad (4)$$

Methanol Permeability

The treated membrane was placed in a diffusion cell and sealed with gasket to prevent the leak. The cell was connected to 1 M methanol feed solution tank (2,000 mL) and deionized water tanks (250 mL). The pump was started at the feed side to saturate the system for 25 min. The pump at the permeate side was then started and 1 mL of liquid sample was collected at 5, 30, 60, and 90 min. Methanol permeability test was performed at 30, 50, and 70°C (Prapainainar *et al.*, 2017).

Results and Discussion

Size and Morphology Analysis

MCC particle size had an average length of 67.5*10³±13.9*10³ nm and average diameter of 13.7*10³±3.4*10³ nm as shown in SEM image in Figure 1. NCC from acid hydrolysis process of MCC was investigated by TEM. The shape of NCC as shown in Figure 2. The NCC particle size was measured by ImageJ program. It was found that the particle size of NCC was has an average length of 196.9±35.2 nm and average diameter of 13.8±4.2 nm. It was found that NCC particle size was smaller

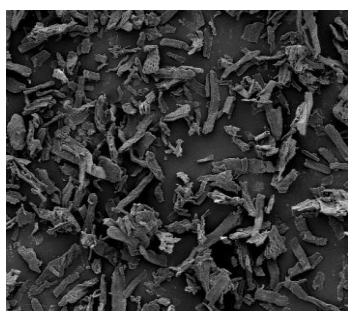


Figure 1. SEM images of MCC before hydrolysis process

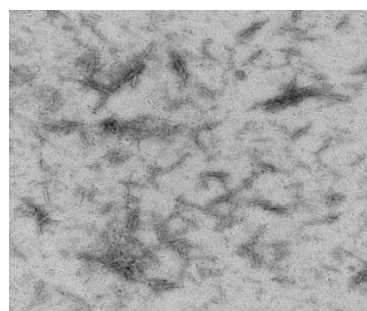


Figure 2. TEM images of NCC

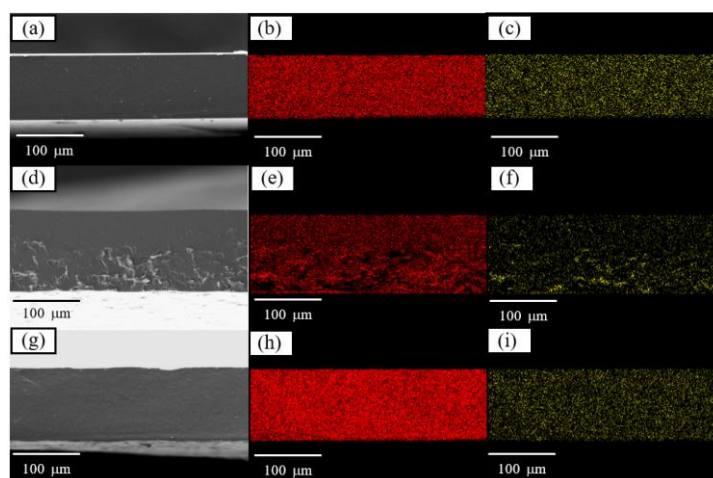


Figure 3. SEM images of cross-section of membranes (a) recasted NF, (d) MCC/NF, (g) NCC/NF and EDS mapping of membranes (b) F mapping of recasted NF, (c) O mapping of recasted NF, (e) F mapping of MCC/NF, (f) O mapping of MCC/NF, (h) F mapping of NCC/NF, (i) O mapping of NCC/NF

Table 1. The results of WU, solubility, and IEC of recasted Nafion membrane, MCC/NF and NCC/NF membranes

Membrane	%WU	%Soluble	IEC
recasted NF	18.72	0.37	0.96
MCC/NF	22.14	1.65	0.58
NCC/NF	27.33	1.27	0.54

than that of MCC after acid hydrolysis process of MCC.

Membranes Characterization

Membrane Morphology

The morphology of MCC/NF and NCC/NF membranes were characterized by SEM and EDS mapping as show in Figure 3. It can be seen that cross-section of NCC/NF membrane was better and smoother than MCC/NF membrane as shown in Figure 3(a, d, g). The EDS mapping images of fluoride mapping and oxygen mapping of NCC/NF membrane showed better dispersion than that of

MCC/NF membrane as shown in Figure 3(e)-(f) and (h)-(i) due to NCC particle has smaller size than that of MCC particle.

Ex-situ Test

Water uptake

The water uptake results of all membranes are shown in Figure 4(a) and Table 1. It was found that NCC/NF composite membrane showed higher water uptake than MCC/NF composite membrane. Both composite membranes have higher water uptake than that of recased Nafion membrane. The result of water uptake showed that using cellulose as filler for NF composite membrane can increase percentage of water uptake because cellulose contains many hydroxyl group (-OH). Cellulose have ability to form hydrogen bond with water molecules (Medronho *et al.*, 2012) due to hydrophilic of -OH. This can be helpful for proton transport.

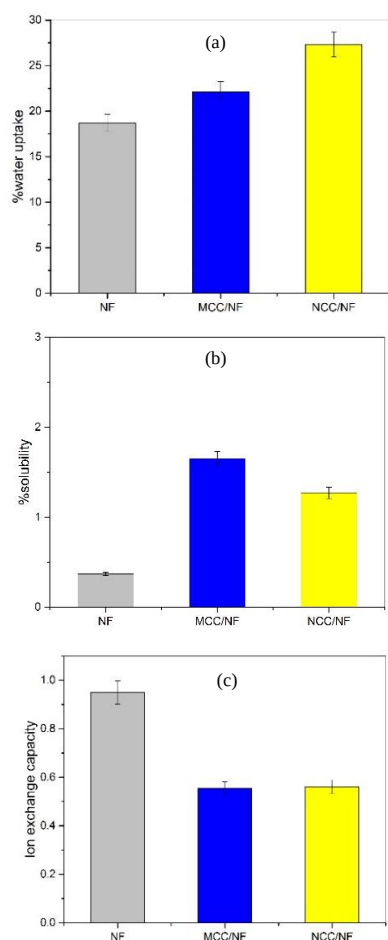


Figure 4. The results of (a) Water uptake (b) Solubility (c) IEC of recasted Nafion membrane, MCC/NF and NCC/NF membranes

Solubility Test

Solubility test was used to evaluate the chemical resistance of the membrane. The solubility of membrane should be less than 5% for proton exchange membrane (Moore and Martin, 1987). The solubility of MCC/NF membrane was higher than NCC/NF and recasted Nafion membranes as shown in Figure 4(b) and Table 1. Both composite membranes have less than 5% solubility. It was found that adding cellulose resulted in an increase of solubility. It referred to lower chemical resistance of membrane compared with recasted Nafion membrane.

Ion Exchange Capacity (IEC)

IEC can be used as indirect approximation of proton conductivity of membrane (Wu *et al.*, 2007). The IEC values of membranes are shown in Figure 4(c) and Table 1. It was found that recasted Nafion membrane has the highest IEC compared with

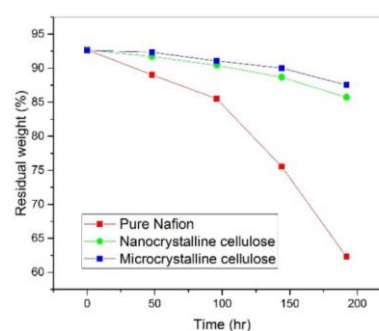


Figure 5. Chemical degradation results of recasted Nafion, MCC/NF, and NCC/NF membranes

MCC/NF and NCC/NF composite membranes. It was found that adding cellulose can decrease IEC due to lower concentration of acid group or sulfonic group (SO_3^-) of the composite membrane (Gadim *et al.*, 2016). Thus, the sulfonic group was important for proton movement. The IEC value of MCC/NF membrane was slightly higher than that of NCC/NF membrane.

Chemical Degradation

Chemical degradation of composite membranes were tested using Fenton's reagent to destroy organic compounds (Koppenol, 1993). The result of chemical degradation is showed in Figure 5. It was found that recasted Nafion membrane had higher chemical degradation than those of MCC/NF and NCC/NF membranes. It might be due to cellulose particles blocked hydrogen peroxide and hydroxyl radical from attacking the chain of Nafion.

Methanol Permeability

Methanol permeability refers to methanol crossover from anode to cathode sides. High methanol permeability causes loss the fuel. The results of MeOH permeability is shown in Figure 6. It was found that recasted Nafion membrane has higher MeOH permeability than NCC/NF and MCC/NF membranes as shown in Figures 6(a) and 6(b) for 1 M and 2 M, respectively at 30, 50, and 70°C. Adding cellulose into Nafion can reduce methanol permeability due to cellulose in composite membrane blocked methanol crossover and reduced methanol permeability in composite membranes (Xu *et al.*, 2018). The results of methanol permeability increased with increasing concentration of methanol. The permeability result showed that NCC composite membrane has higher MeOH permeability than that of MCC membrane. It may be due to NCC/NF composite membrane was smoother than MCC/NF composite membrane. Therefore, it was easy for MeOH crossover from anode to cathode sides.

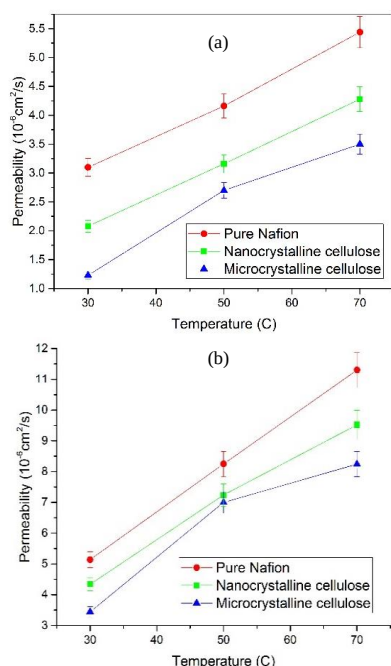


Figure 6. Methanol permeability results of recasted Nafion, MCC/NF and NCC/NF membranes (a) 1 M MeOH (b) 2 M MeOH at temperature of 30°C, 50°C, and 70°C

Conclusions

NCC was successfully extracted by acid hydrolysis to reduce the particle size of MCC. It was confirmed by TEM and SEM images. Recasted NF, MCC/NF, and NCC/NF composite membranes were casted by solution casting method from dried Nafion.

MCC and NCC composite membranes have MeOH lower permeability percentage, chemical degradation, and ion exchange capacity than that of recasted NF membrane. Both composite membranes have higher water uptake than that of recasted Nafion membrane. Moreover, recasted NF, MCC/NF and NCC/NF composite membranes have solubility less than 5%.

It was also found that chemical degradation and methanol permeability of MCC membrane were better than that of NCC. However, using NCC as a filler led to better dispersion of atom and water uptake percentage than those of MCC.

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Environment and Department of Chemical Engineering Department, Faculty of engineering, Kasetsart University.

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