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# COMPARATIVE STUDY OF ANION EXCHANGE MEMBRANES PREPARED BY BROMINATED POLYPHENYENE OXIDE POLYMERS

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ABSTRACT

This research was designated to find out the solution for solving energy shortage problems of globe. There were three different brominated polyphenyleneoxide(BPPO) membranes such as 45% BPPO membrane, 35% BPPO membrane and 30% BPPO membrane that were prepared by dissolving BPPO polymer in dimethyl formamide (DMF) with the assistance of magnetic stirrer. Moreover, the prominent functional groups of each BPPO membranes were identified by Fourier Transform Infrared (FT IR) spectroscopy that informs the presence of distinct C-Br stretching band at 1019.66 $cm^{-1}$. The Ion-Exchange Capacity (IEC) value of each membrane was determined by Mohr titration method where as 45% BPPO membrane gave 1.42 $mmolg^{-1}$ IEC value which is a suitable result for Anion Exchange Membrane (AEM) and this value was highr than other two BPPO membranes. The resistance values of membranes were investigated by Multi-Meter that was related the conductivity of membranes and the swelling ratio, the solubility of each membrane were detected by dipping membranes in various solvents.

Key Words: Brominated polyphenylene oxides, Ion-exchange capacity, Anion exchange membrane, solubility, SEM, FT-IR

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# INTRODUCTION

Poly (p-phenylene oxide) or poly (p-phenylene ether) (PPE) is a high-temperature themoplastic. It is rarely used in its pure form due to difficulties in processing. It is

mainly used as blend with polystyrene, high impact styrene –butadiene copolymer or polyamide. While it was one of the cheapest high-temperature resistant plastics, processing was difficult and the impact and heat resistance decreased with time. Mixing it with polystyrene in any ratio could compensate for the disadvantages. In the 1960s, modified PPE came into the market under the trademark.

PPE is an amorphous high-performance plastic. The glass transition temperature is 215°C but it can be varied by mixing with polystyrene. Through modification and incorporation of fillers such as glass fibers, the properties can be extremely modified. PPE blends are used for structural parts, electronics, household and automotive items that depend on high heat resistance, dimensional stability and accuracy. They are also used in medicine for sterilizing instruments made of plastic.

Alkaline fuel cells (AFCs, hydrogen-fuelled cells with an alkaline liquid electrolyte such as KOH(aq)) are the best performing of all known conventional hydrogen–oxygen fuel cells operable at temperatures below 200ºC. This is due to the facile kinetics at the cathode and at the anode; cheaper non-noble metal catalysts can be used (such as nickel and silver), reducing cost. McLean et al. gave comprehensive review of alkaline fuel cell technology. The associated fuel cell reactions both for a traditional AFC and also for an AMFC are:

Anode : $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Overall: $2H_2 + O_2 \longrightarrow 2H_2O$

## Aim

The aim of this research is to study the ion-exchange capacity, resistance and the solubility of different brominated ratios of BPPO polymer membranes.

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## Methods and Materials

### Material

Poly(2,6-dimethyl-1,4-phenylene oxide)(PPO), Dimethyl Formamide (DMF) and 1-Bromo-2,5 Pyrrolidinedione (NBS) were purchased from local market, Mandalay in Myanmar. Ethanol and deionized water were distilled for purification. Sodium hydroxide and chloroform were directly used from analytical grade.

### Methods

1. Fourier Transform Infrared Spectroscopy (FT-IR)
2. Water Uptake and Swelling Ratio Measurement by comparing the wet and dry weights of the membranes
3. Ion Exchange Capacity (IEC) by Mohr titration method
4. Resistance Measurement by Multi meter
5. Scanning Electron Microscopy (SEM)

### Procedure for 45%, 35% and 30% brominated polyphenylene oxide membranes



Firstly, 0.25 g of 45% brominated sample was placed in round-bottomed flask and 15 mL of dimethyl formamide (DMF) was added. The mixture was stirred with the help of magnetic stirrer at 80° C for 24 hours. After the mixture was dissolved in DMF, it was poured into petri dished and dried in oven for 24 hours. Finally, 45% brominated polyphenylene oxide membrane was obtained. Similarly, the same procedure was done for 35% and 30% brominated poly phenylene oxide membranes.

Figure 5 45% brominated polyphenylene oxide memembrane

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**Characterization**

**Determination of Resistance of Brominated Polyphenylene Oxide Membrane**

Resistance of brominated polyphenylene oxide membranes was determined by Multimeter at the Department of Physics, University of Mandalay.


Figure 1 Multi -meter



**Determination of thickness of membrane**

The thickness of brominated polyphenylene oxide membranes were determined by Micrometer at the Department of Physics, University of Mandalay.


Figure 2 Micrometer

**Determination of Solubility of Membrane**

The solubility of each membrane was measured by immersing the membranes in 1.0 M sodium hydroxide solution, chloroform, ethanol, distilled water and water for 24 hours.

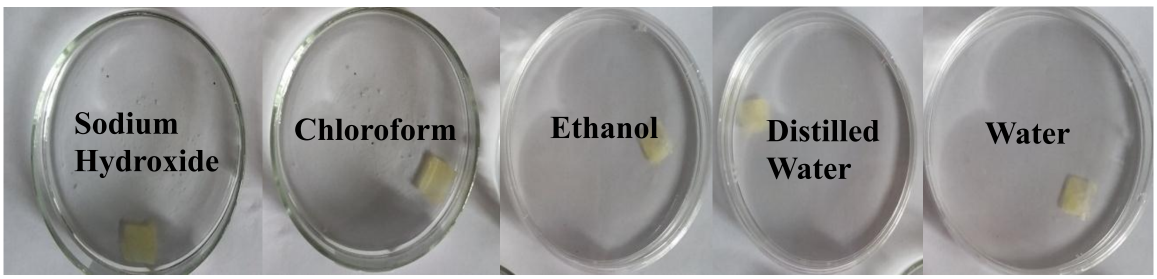



Figure 3 Determination of Solubility of Membrane

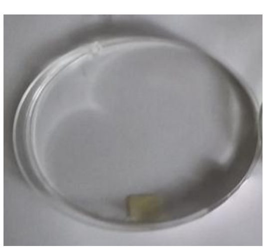


**Identification of Brominated Polyphenylene Oxide Membrane by Fourier Transform Infrared Spectroscopy**

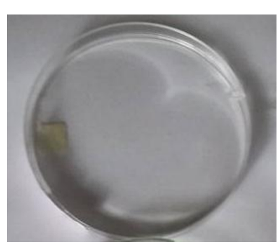
Brominated polyphenylene oxide membranes were identified by Fourier Transform Infrared Spectroscopy at Department of Chemistry, Monywa University.

**Determination of Water Uptake (WU) and Swelling Ratio**

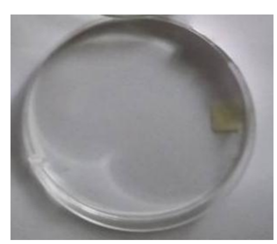
The water uptake of brominated polyphenylene oxide membrane was measured by weight differences between the wet and dry weight of membrane. The membranes were soaked in water for 24 hours.



45% brominated membrane



35% brominated membrane



30% brominated membrane

Figure 4

## Measurement of Ion Exchange Capacity (IEC)

Ion exchange capacity (IEC) was determined by a back titration method derived from Slade and Varcoe. The membranes were soaked in 1.0 M sodium hydroxide solution to exchange the bromide ion for hydroxide. And then the membranes were washed with deionized water and again dipped into this sodium hydroxide solution. After rinsing the membranes until neutral, they were dried in vacuum and immersed into 10 ml of 0.01M hydrochloric acid. After soaking a day, the acid was titrated with 0.01M sodium hydroxide. The ion exchange capacity of each membrane was calculated by the following equation:

IEC = $C_{HCl}V_{HCl} - \ / m_{dry}$

Where C is the concentration of acid or base, V is the volume of the acid or base, and $m_{dry}$ is the dry weight of the membrane after ion exchange.



## RESULTS AND DISCUSSION

### Determination of resistivity value of 45% brominated membrane

**Table 1 The resistivity value of 45% brominated membrane before and after immersing in various solvents**

| Solvents | Resistivity values before immersing in solvents | Resistivity values after immersing in solvents |
|---|---|---|
| Sodium Hydroxide | 6.0 MΩ | 4.5MΩ |
| Ethanol | 6.0 MΩ | 84.5MΩ |
| Chloroform | 6.0 MΩ | 40.3MΩ |
| Distilled Water | 6.0 MΩ | 45.2MΩ |
| Water | 6.0 MΩ | 44.5MΩ |

According to the experimental result, the resistivity value of 45% brominated membrane immersing in sodium hydroxide responds the excellent value of 4.5 MΩ that is suitable for conductor. In other solvents such as ethanol, chloroform, distilled water and water, it was found that the resistivity values of 45% brominated membrane after immersing the solvents are higher than before.

**Determination of resistivity values of 35% brominated membrane**

**Table 2 The resistivity values of 35% brominated membrane before and after immersing in various solvents**

| Solvents | Resistivity values before immersing in solvents | Resistivity values after immersing in solvents |
|---|---|---|
| Sodium Hydroxide | 9.5 MΩ | 8.2 MΩ |
| Ethanol | 9.5 MΩ | 8.8MΩ |
| Chloroform | 9.5 MΩ | 52.9MΩ |
| Distilled Water | 9.5 MΩ | 49.5MΩ |
| Water | 9.5 MΩ | 49.5MΩ |



Similarity, the resistivity value of 35% brominated membrane immersing in sodium hydroxide responds the excellent value of 8.2 MΩ and 8.8 MΩ in ethanol that are suitable for conductor. In other solvents such as ethanol, chloroform, distilled water and water, it was found that the resistivity values of 35% brominated membrane are higher than that of the values before immersing in various solvents.

**Determination of resistivity values of 30% brominated membrane**

**Table 3 The resistivity values of 30% brominated membrane before and after immersing in various solvents**

| Solvents | Resistivity values before immersing in solvents | Resistivity values after immersing in solvents |
|---|---|---|
| Sodium Hydroxide | 9.6 MΩ | 10.3 MΩ |
| Ethanol | 9.6 MΩ | 9.6 MΩ |
| Chloroform | 9.6 MΩ | 12 MΩ |
| Distilled Water | 9 .6 MΩ | 64.8 MΩ |
| Water | 9.6MΩ | 60.7 MΩ |

The resistivity value of 30% brominated membrane immersing in sodium hydroxide responds the resistivity value of 10.3 MΩ , 9.6 MΩ in chloroform, 12 MΩ in distilled water and 64.8 MΩ in distilled water and 60.7 MΩ in water that point out the resistivity values of 30% brominated membrane are lower than their original value
before immersing in the solvents.

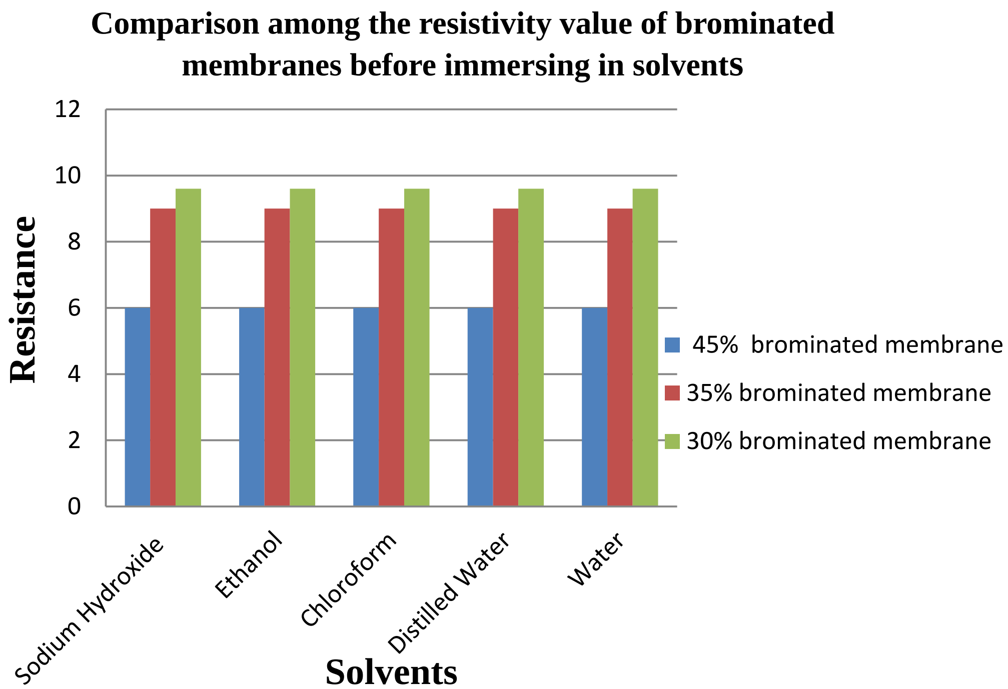



figure 5 Resistivity values of brominated membranes before immersing in solvents



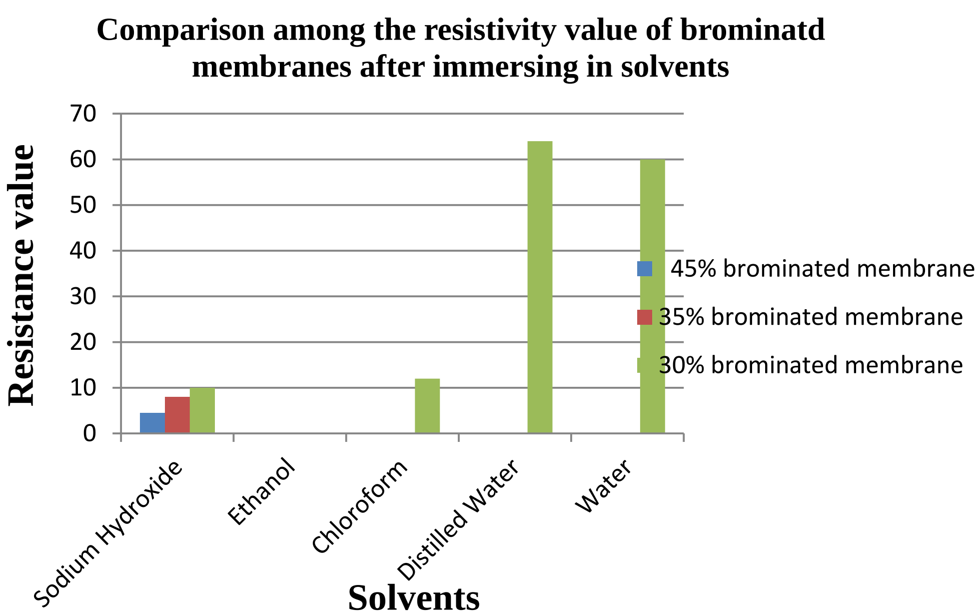



Figure 6 Resistivity values of brominated membranes after immersing in solvents

### Determination of thickness and swelling ratio of 45%, 35% and 30% brominated membrane

From the result, it was found that 45% brominated membrane immersing in sodium hydroxide shows the highest swelling ratio but the membrane dissolves in ethanol solution where its swollen ratio cannot be measured. Consequently, 35% brominated membrane immersing in distilled water shows the highest swelling ratio compared with other solvents. In addition to 30% brominated polymer membrane, it was found that 30% brominated membrane immersing in distilled water shows the highest swelling ratio.



### Determination of Ion Exchange Capacity

**Table 4 The ion exchange capacity value of membrane**

| Membrane | IEC($mmolg^{-1}$) |
|---|---|
| 45% brominated membrane | 1.48 |
| 35% brominated membrane | 1.22 |
| 30% brominated membrane | 1.05 |

The ion exchange capacity (IEC) value is shown in table. The IEC represents the ion exchange capacity group in the membranes, and the IEC values can strongly interrelate to the water uptake, swelling ratio and hydroxide conductivity of the AEMs. Among the three membranes, 45% brominated membrane has the highest IEC value of 1.48 $mmolg^{-1}$showing that this membrane has the greater number of ion exchange groups that is reliable to the higher percent of bromination to the polymer polyphenylene oxide.

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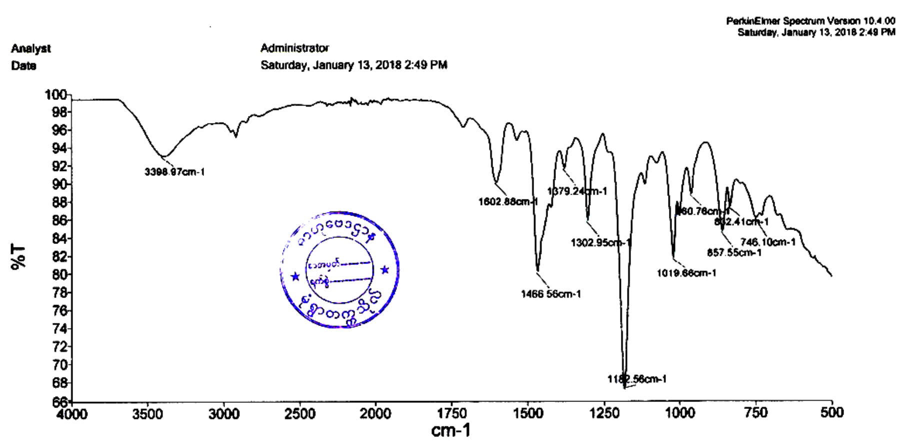
The water uptake (Wu) value was found to be a reasonable amount associated with the IEC values.35% brominated membrane has the less amount of water content (50%). Wu values of 45% brominated membrane and 30% brominated membrane were found to be (67 %) and (64%), respectively. We found that the modified chitosan membrane has a great thermal stability under boiling water. The water uptake and swelling ratio of three membranes were also mentioned. The influence of water uptake and swelling ratio of the membranes correspond to the hydroxide conductivity of the membrane. Wu value is measured by the weight difference between the wet and dry weight of the membrane. These values indicate that 45% BPPO membrane has a good performance in the application of the membranes. The ionic exchange capacity (IEC) value is reliable to the capacity of membrane which may influence the power of AEMs in fuel cell application. The higher value of the water uptake and swelling ratio provide the greater power of hydroxide conductivity. We found that 45% BPPO membranes have moderate amount of water content and swelling ratio. These results provides the great performances of AEM membranes that are suitable for the application of membrane associated with the ion exchange capacity.



## Identification of Brominated Polyphenylene Oxide Membrane by Fourier Transform Infrared Spectroscopy

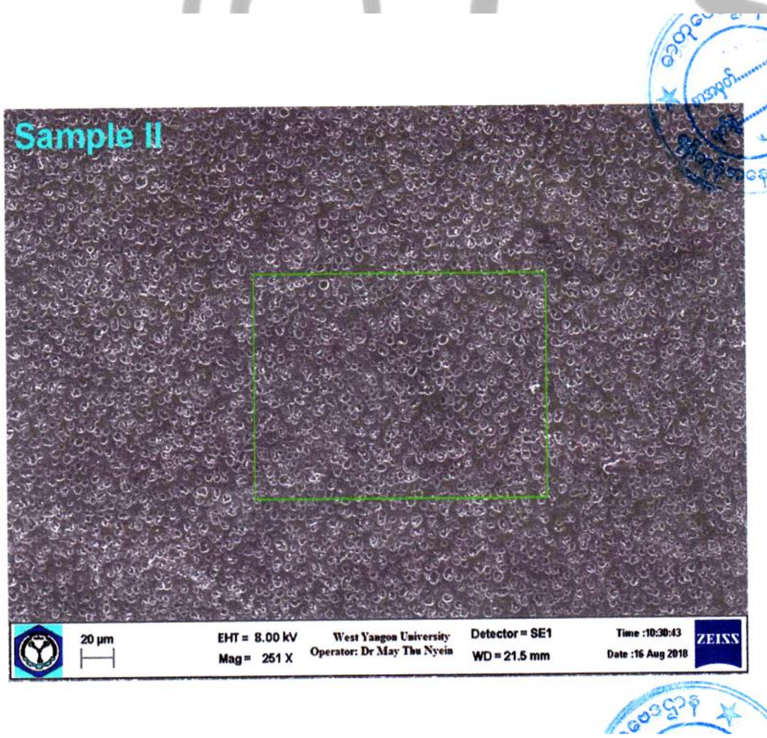


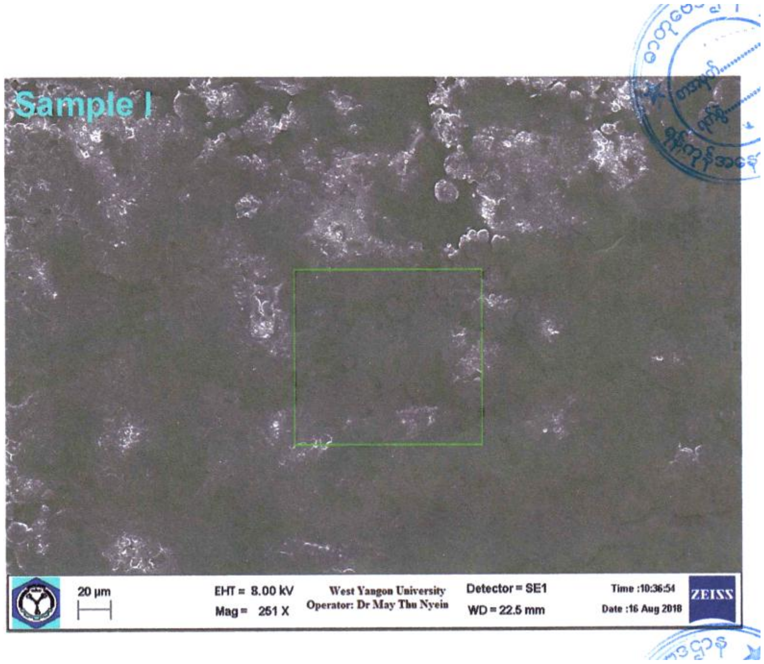

| Sample Name | Description | Quality Checks |
|---|---|---|
| Sample 1 | Sample 1 By Administrator Date Tuesday, January 09 2018 | The Quality Checks give rise to a Weak Bands warning for the sample. |

Figure 8 FT IR spectrum of brominated membran

From the FT IR assignment, the peak at 3398.97 cm$^{-1}$ displays the N-H stretching frequency of amine group which may be due to the solvent DMF. The band which appears at 3005.10 cm$^{-1}$ indicating the presence of C-H stretching frequency of unsaturated hydrocarbon and 2902.50 cm$^{-1}$, 2842.24 cm$^{-1}$ point out the C-H stretching frequencies of saturated hydrocarbons. The peak which appears at 1602.88 cm$^{-1}$ corresponding to the C=C ring skeleton of phenyl group. The other peaks at 1466.56 cm$^{-1}$, 1379.24 cm$^{-1}$ and 1302.95 cm$^{-1}$ displays C-H bending vibration of methyl groups. Moreover, 1019.66 cm$^{-1}$ indicates the presence of C-Br stretching vibration of brominated methyl groups. The band which appears at 960.76 cm$^{-1}$ indicates the C-H bending vibration group.

**SEM Analysis of 45%, 35% and 30% Brominated polyphenylene oxide**






According to SEM analysis, the morphology of 45% BPPO is rough and seems to be brittle where as 35% and 30% polymer membranes appear a little smoother than 45% BPPO membrane.



## CONCLUSION

In this research work, the three different brominated ratios of polyphenylene oxide (BPPO) membranes were firstly prepared by using DMF solvent with the use of magnetic stirrer. Moreover, the prominent stretching frequencies of membranes were determined by FT-IR that informs 1019.66 $cm^{-1}$ corresponding to C-Br bond of brominated polymer and the morphology of the BPPO membranes were compared by SEM spectroscopy that displays the appearance of 45% BPPO membrane was severe in smooth. In addition, the ion exchange capacity measurement informs that 45% BPPO membrane gives 1.48 $mmolg^{-1}$ which is in agreement with the AEM membrane that can be used for fuel cell as well as this value was higher than 35% and 30% BPPO membranes. The resistance of the membranes was determined by Multimeter at the department of Physics, Mandalay University where as 45% brominated (BPPO) membrane shows the suitable value of 6

MΩ before immersing in 1M NaOH solution as well as it shows 4.5 MΩ after immersing in 1M NaOH solution. Furthermore, the swelling ratio of 45% BPPO membrane indicates unexpected elongation at break that informs the more ion exchange group corresponds to greater swelling ratio and high solubility. This research would be one of the informations that provides to innovate the AEM fuel cell technology.

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