Int. J. Electrochem. Sci., 15**(2020)** 8190 – 8199, doi: 10.20964/2020.08.17

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Study on Synthesis and Characterization of Anion Exchange Membrane Based on Poly (Vinyl Alcohol) modified by free-radical polymerization

*Nguyen Van Thuc**, *Nguyen Thi Cam Ha*, *Nguyen Huu Tho*

Faculty of Chemistry, VNU-University of Science, 19 Le Thanh Tong, HoanKiem, Hanoi, Vietnam
*E-mail: nguyenvanthuc@vnu.edu.vn

Received: 4 March 2020/ *Accepted:* 29 April 2020 / *Published:* 10 July 2020

In this study, poly(vinyl alcohol) (PVA) has been modified by free-radical polymerization (PVA-PVA). The formation of products were confirmed by nuclear magnetic resonance spectra (^{13}C NMR). The anion exchange membranes based on modified PVA were fabricated in this work. The ionic conductivity, ion-exchange capacity, water uptake of membranes as a function of alkaline concentration and the thermal stability of electrolyte were studied. The obtained membranes have good conductivity (>1 mS/cm), high anion exchange capacity (>2 mmol/g), and stable at over 100°C, meeting the criteria for the anion-exchange membrane for alkaline fuel cell.

Keywords:Poly(vinyl alcohol), membrane, conductivity, fuel cell, polymerization.

1. INTRODUCTION

Currently, the alkaline fuel cell has been increasing concerns because of the development of new exchang e membranes of hydroxyl anion, separating two electrode regions. The anion exchange membranes are recognized to be more effective thanproton exchange membranes in alkaline fuel cell application. The membrane effective featuresare higher energy conversion efficiency, less corrosion, and more economical catalyst materials. In addition, the alkaline fuel cell uses the anion exchange membrane that is more preeminent than normal alkaline fuel cell because of blocking cation movement [1], suppressing carbonate precipitation, reducing fuel loss, and increasing specific energy density. Previous studies indicated that hydroxyl anion exchange membranes based on poly (vinyl alcohol) (PVA) displayed good performances in term of ionic conductivity, anion exchange capacity. Moreover, the manufacturing process is much more simple with using waterasthe solvent during fabrication [2-4]. However, the application of PVA-based membranes hasstill faced several challenges which need to overcome such as the high water absorption capacityleads to the reduction of the membrane durability. In order to address the aforementioned issue, the exchanging membrane is fabricated based on the denatured PVA or the incorporation of PVA with other polymers which have different characteristics which could enhance the fundamental properties as well as optimize the performance in order to benefit for the practical application of anion exchange membrane [2,4]. On that basis, the researching team focused on synthesis and characterization denatured PVA-based anion exchange membranes which could fulfill the basic requirements for fuel cell application.

2. EXPERIMENTAL

2.1. Chemical

PVA (98%), M_w = 16000 (Acros); benzoyl peroxide: $C_{14}H_{10}O_4$ (≥ 99%) (AR - China); KOH (Merck).

2.2. Modified poly (vinyl alcohol)

In the study, PVA was modified by the free radical reaction with benzoyl peroxideas an initiator in order to create polymer molecules with spatial structure according to the following diagram 1:

$$(C_6H_5COO)_2 \xrightarrow{T\sim100^oC} 2\,C_6H_5COO^{\bullet}$$

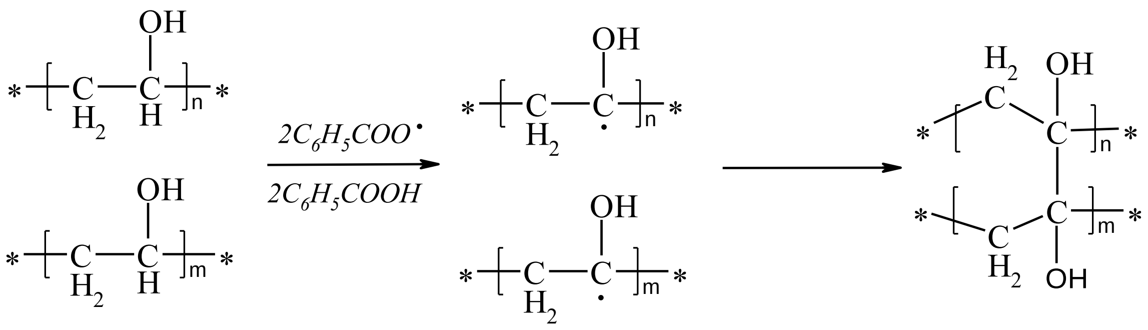


Diagram 1

Successful in circuiting PVA is demonstrated by the results of nuclear magnetic resonance spectroscopy ^{13}C (Figure 1) recorded on Avance 500 nuclear magnetic resonance device (Bruker, Germany).

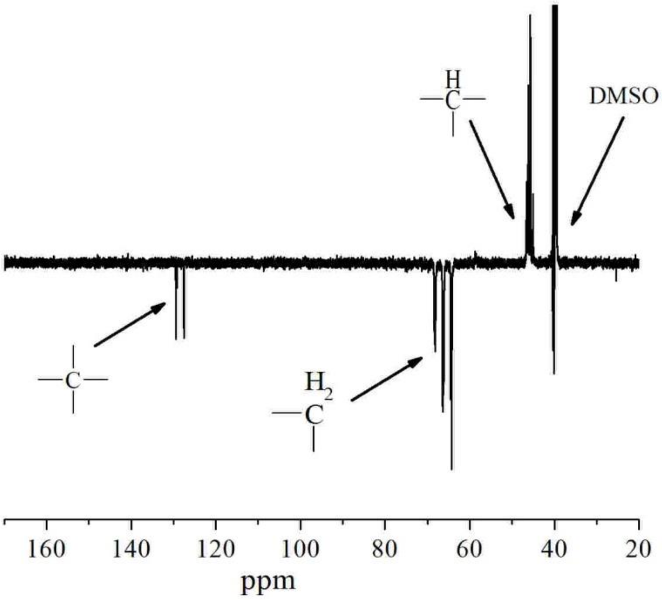


Figure 1. 13C-NMR spectrum of modified PVA(PVA-PVA).

Figure 1 shows the appearance of a ^{13}C spectral signal in the region of ~ 130 ppm chemical shift, which is characteristic of the signal of quaternary carbon atoms. This proves that the coupling process between PVA molecules has been done in diagram 1. The study on the PVA that was denatured by gamma irradiation [5] also showed the result of PVA circuit coupling which is similar to diagram 1.

2.3. Fabrication of membrane

Table 1. Components in the fabrication process of membrane

No	Membrane	Mass of 10% solution [PVA-PVA] – H_2O, gram	Mass of KOH, gram
1	PVA-PVA-0KOH	10,03	0.00
2	PVA-PVA-0.1KOH	11.06	0.11
3	PVA-PVA-0.2KOH	10.12	0.20
4	PVA-PVA-0.25KOH	10.20	0.25
5	PVA-PVA-0.30KOH	9.86	0.29
6	PVA-PVA-0.35KOH	9.93	0.35
7	PVA-PVA-0.40KOH	10.32	0.41
8	PVA-PVA-0.45KOH	9.68	0.44
9	PVA-PVA-0.50KOH	10.21	0.51

Anion exchange membrane based on modified PVA (PVA-PVA) is synthesized by procedure described below: A 10% solution of modified PVA (PVA-PVA) is added by different amounts of KOH. The mixture was stirred at 90°C for 90 minutes, resulting in PVA-PVA-xKOH/H_2O mixture (table 1). Anionic exchange PVA-PVA-xKOH is created from PVA-PVA-xKOH/H_2O solution by bar coating technique and dried in vacuum at room temperature.

2.4. Material characterizations

The specific conductivity of anion exchange membrane is measured via electrochemical impedance spectroscopy on an AUTOLAB 30 (Netherlands). The specific conductivity of anion exchange membrane is calculated by the equation (1) [1,2]:

$$\chi = \frac{l}{R \cdot S} \qquad (1)$$

Where χ, l, R, S are specific conductivity of the membrane, film thickness, membrane area, and membrane resistance, respectively.

Ion exchange capacity (IEC) is one of the important characteristics of the exchange membrane. The anion exchange capacity of membrane is determined by the titration method for determining OH- group existing inside the membrane by the solution of HCL. Anion exchange capacity is determined by the number of millimoles OH- corresponding to 1 gram of membrane [10]. In this study, the ion exchange capacity (IEC) of the membrane is determined by back titration. IEC values (mmol / g) were calculated using the following equation (2) [1, 2]:

$$IEC = \frac{n_{HCl}(1) - n_{HCl}(2)}{m_{dry}} \times 1000 \qquad (2)$$

n_{HCl} (1): the amount of HCl (in moles) before dipping the film

n_{HCl} (2): the amount of HCl (in moles) after dipping the film

m_{dry}: the weight of dry film (g)

The water uptake of anion exchange membranes (W_u,%) is determined by the difference in mass of the dry film and the mass of the membrane after 24 hours immersion in ionized water. The value of Wu is determined by the equation (3) [1,2,6]:

$$W_u(\%) = \frac{m_{\mathrm{wet}} - m_{dry}}{m_{dry}} \times 100 \qquad (3)$$

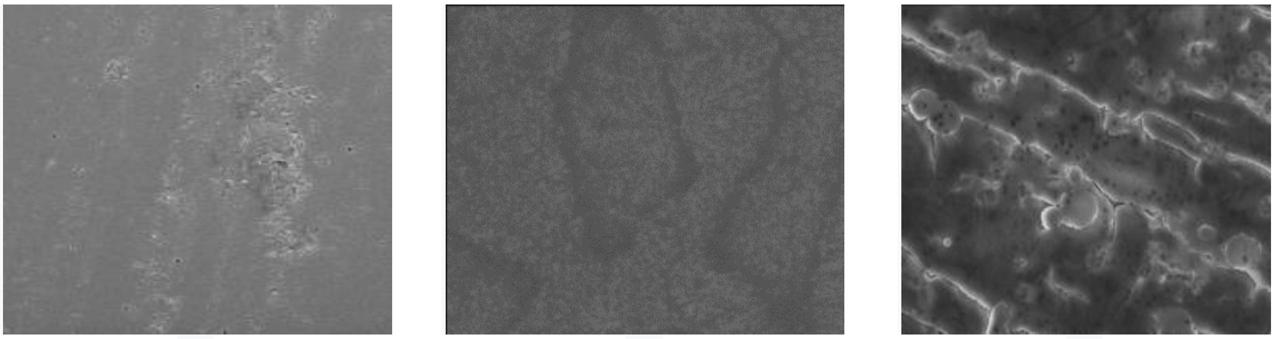
m_{wet} - weight of membrane after immersion, m_d - initial mass of dry film.

Morphology of membranes are characterized by scanning electron microscopy (SEM) by using SEM-JEOL-JSM 5410LV, 10 kV, working distance 8-19 mm, maximum zoom x 200.000 times

Thermalgravimetric analysis (TGA) was used to determine phase transition temperature by using SETARAM Labsys TG of the Department of Chemistry - VNU, University of Science. Samples are scanned from room temperature to 800oC and with heating rate was 10°C/min under the air-flow.

3. RESULTS AND DISCUSSION

Surface morphologies of the original PVA, PVA-PVA materials, and anion exchange membrane based on modified PVA (PVA-PVA) are displayed in Figure 2



(a) (b) (c)

Figure 2.SEM graphs at 200 000 times magnification (scale bar represents 4 µm) of membrane on based PVA (a), PVA-PVA(b) and PVA-PVA-0,25gKOH (c).

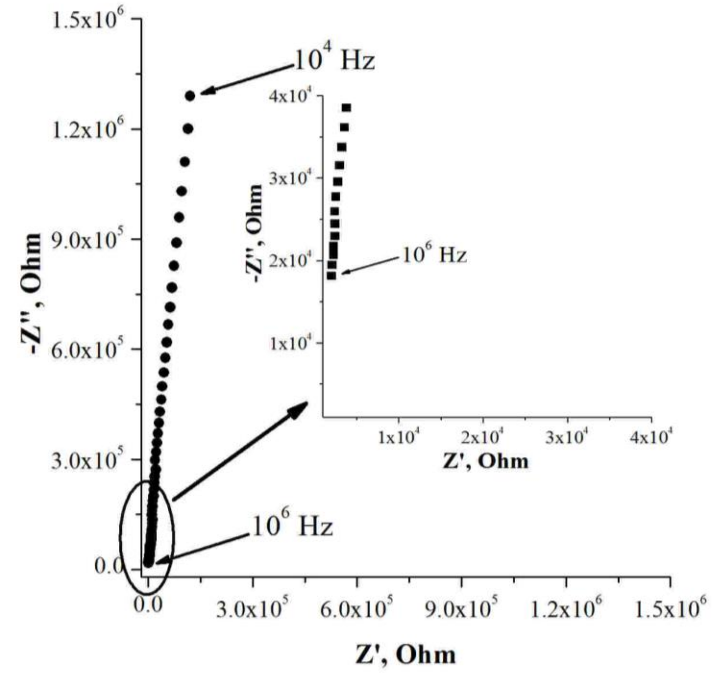


Figure 3a. Impedance spectroscopy of the anion exchange membrane PVA-PVA-0.25gKOH

As can be seen from Figure 2, the fabricated film based-on the original PVA shows a round granular surface. In contrast, the surface of PVA grafted is smoother (no more grain shape as the original PVA). This could be a good evidence for the successful coupling of PVA. Surprisingly, surface cracking could be observed from SEM image of PVA-PVA-0.25g KOH film. That was the cause by addition of KOH and some moisture making the film less durableandmore prone to breakage.

The specific ionic conductivity of the membrane was investigated by impedance spectroscopy [7-9]. Figure 3a shows the impedance spectrum of the membrane (PVA-PVA-0.25g KOH) which has the common shape for anion exchange film.

Figure 3b shows the equivalent circuit model for electrochemical impedance spectroscopy, corresponding to the spectrum in figure 3a. The circuit contains 2 basic elements, the resistor R, which represents for the bulk resistance of film, and the capacitance C representing the double layer of electrode [9]:

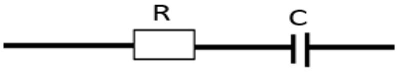


Figure 3b. Equivalent circuit model for electrochemical impedance spectroscopy of membranes

Based on the results of the total impedance spectrum and equivalent circuit, the resistance of the anion exchange membrane and the specific conductivity of the membrane is determined.

The resistance was extracted by fitting the equivalent circuit model then used to calculate the specific ionic conductivity based on equation 1. Figure 4 shows the results of the film's specific conductivity depend on the amount of the KOH at the fabrication step.

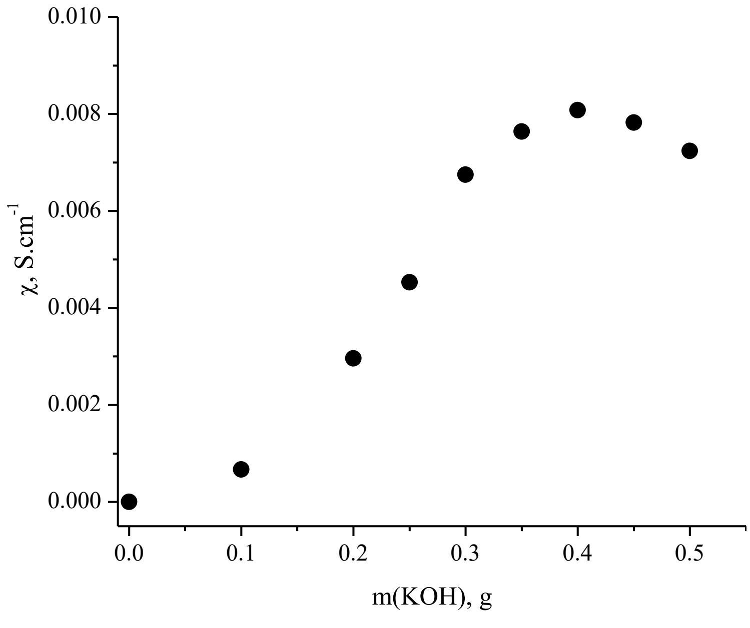


Figure 4. Conductivity of anion exchange membranes PVA-PVA-xKOH depending on KOH concentrations (x)

As displayed in figure 4, the specific ionic conductivity of membranes is strongly dependent on the content of KOH. Without KOH, the film acts as an insulator. When adding KOH, the specific conductivity of the membrane increased significantly and reached a peak at the initial KOH amount of about 0.4 g. This phenomenon could be explained by the increase in ion concentration when adding KOH. However, after that point, the moreadded KOH amount the lower ionic conductivity. It could be attributed to the reduction of the ion mobility of the KOH because the membrane is dry. Our result is competitive with previous work, which recorded the ionic conductivity of PVA-KOH-H_2O based polymer is approximately 10^{-3} S.cm^{-1} [10, 11]. In addition, the conductivity of anion exchange membrane based on the modified PVA by gamma irradiation method has a higher value of 0.34 S.cm^{-1} [5]

Another important characteristic of the anion exchange membrane is the anion exchange capacity determined by back titration in this work. The relation between anion exchange capacity values on the initial mass of KOH is displayed in Figure 5. It shows that the anion exchange capacity of PVA-PVA-xKOH membrane increases with the content of KOH. However, the experimental data is smaller than the calculated theoretical value which could be explained by the following reasons: the film is not completely dry, and the water absorptivity is high, so the mass of water needs to be involved when calculating the mass of the film. Part of the KOH could not be diffused into the environment containing HCl due to its being inside the polymer's structure or creating molecular bonds with the polymer structure.

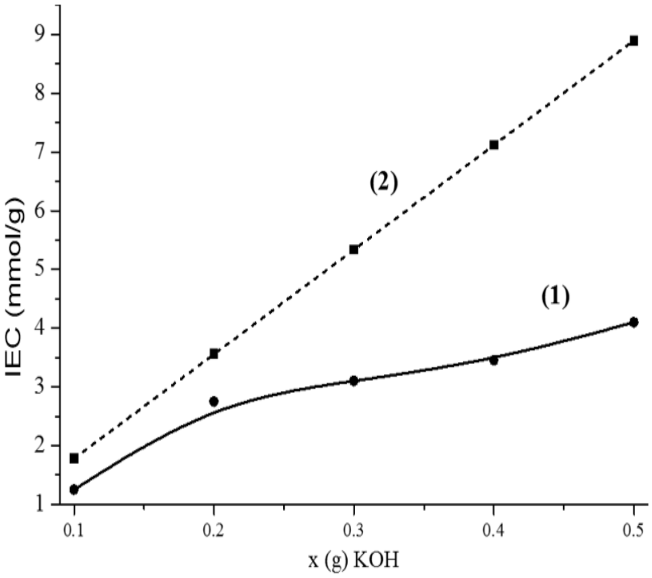


Figure 5. Anion exchange capacity of membranes PVA-PVA-xKOH depending on KOH concentrations (x) (1) Results obtained by back titration (2) The concentration of KOH in 1g of the membrane with the assumption of absolute dry film

The water inside of the membrane can provide the environment for OH^- transport that increases the ionic conductivity of the membrane but excessive water uptake will result in reduced mechanical strength and reduced lifetime of the membrane. Therefore, the water content is an important parameter that needs to be balanced to optimize membrane performance. Research on water uptake of manufactured PVA-PVA-xKOH membranes is displayed in figure 6

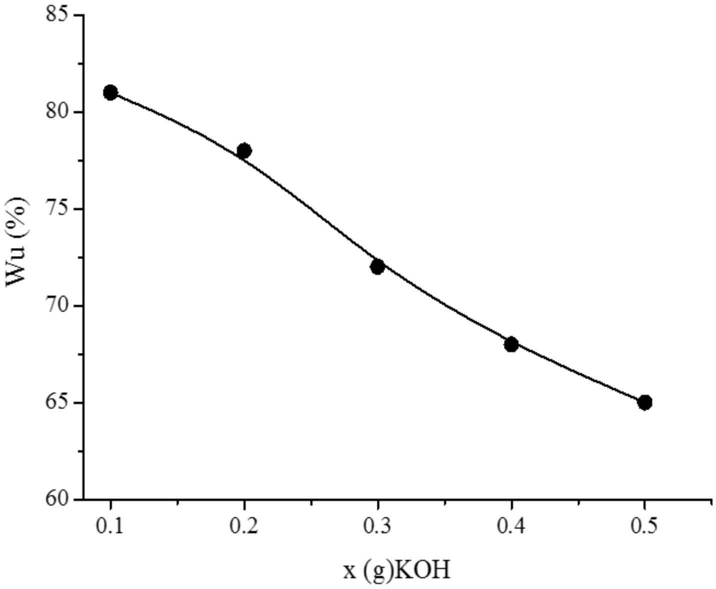


Figure 6. Water uptake of membranes anion exchange PVA-PVA-xKOH depending on KOH concentrations (x)

The results show that the water uptake of PVA-PVA-xKOH based membrane decreases when the increasing initial concentration of KOH. The decrease in water uptake capacity of the membrane can be explained by the fact that the amount of KOH in the membrane diffused into the water environment during the determination of water uptake. The nature of the network structure determines the membrane's ability to water uptake. The cross-linking network inhibits excessive expansion, reducing the free space in the circuit structure results in reduced water uptake and increased stability of membranes. Therefore, the water uptake value of our membrane is not higher than the previous work of Fu et.al. [2] in which, anion exchange membrane was synthesized from original PVA.

The achieved results show that based on PVA-PVA was denaturated, the anion exchange membrane has higher or similar properties to some previous studies on anion exchange membrane system (Table 2). However, the film fabrication method in this study is simpler and easier to implement.

Table 2. Anion exchange membranes based on PVA for fuel application

Anion exchange membranes	Specific conductivity (mS/cm)	IEC (mmol/g)	Water uptake (%)	Ref**.**
PVA-PVA-0.4KOH	8.05	3.25	65	This work
PVA-PVA-0.5KOH	6.89	3.83	68	This work
PVA-KOH	0.473			[2]
PVA-PVP-KOH	2			[2]
PVA- 6MKOH	12			[3]

PVA-ionic liqid	3-8			[12]
PVA-[DimL][OH]	7.3-14.8	1.05-1.35	68-107	[13]
PV/CS-HDT	3.56-4.26 (at 40°C)	0.28-0.58		[14]
PV-HDT/CS-TPTZ	3.06-3.55 (at 40°C)	0.23-0.46		[14]
PVA-PBI	> 10		>70	[15]

Another important characteristicof the anion exchange membrane is temperature stability, which is crucial. Thermalgravimetricanalysisof PVA-PVA-0.5gKOH film is displayed in Figure 7.

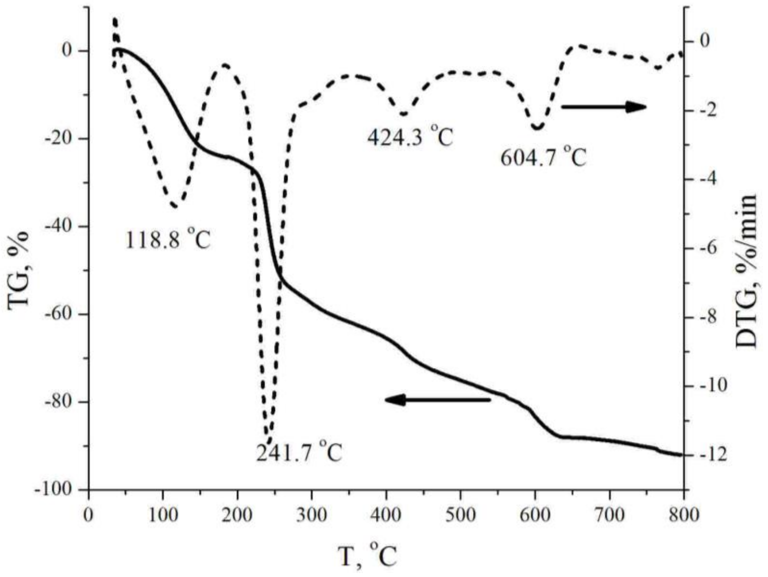


Figure 7. TGA and DTG curvens for the anion exchange membrane PVA-PVA-0.5g KOH

From room temperature to a temperature of 150°C, the weight loss around 25% (with exothermic peaks of the TGA locate at 118.8°C), implying the high content of water present in the sample. PVA decomposition process begins at around 200°C through various stages which are similar to the TG curve for PVA in the previous study of Merler et.al. [10]. Thus, the anion exchange film based on PVA-PVA-0.5gKOH could operate at temperature around 100°C, meeting the required thermal durability of the membrane for alkaline fuel cells.

4. CONCLUSION

By using free radical reaction, PVA has been modified and successfully created anion exchange membrane based on PVA denaturation. The modified membrane displays moderate specific ionic conductivity (> 1mS/cm), high anion exchange capacity (> 2mmol / g), and stable with temperature over 100°C, responding to the criteria of the exchanging membrane for the application in alkaline fuel cell. The effect of the KOH content t to the specific conductivity value, anion exchange capacity, and water uptake has been investigated, the optimum point is reached at 0.4 grams KOH added. Nevertheless, high water uptake still is an issue that needs to be overcome to find the optimum balance between specific ionic conductivity and the mechanical strength of the membrane.

ACKNOWLEDGEMENTS
This research is funded by the Vietnam National University, Hanoi (VNU) under project number QG.17.14

References

1. D. J. Kim, C. H. Park, and S. Y. Nam, *Int. J. Hydrogen Energy*, 41 (2016) 7649.
2. J. Fu, J. Qiao, H. Lv, J. Ma, X.-Z. Yuan, and H. Wang, *ECS Transactions*, 25 (2010) 15.
3. D. L. Zugic, I. M. Perovic, V. M. Nikolic, S. L. Maslovara, and M. P. MarcetaKaninski, *Int. J. Electrochem. Sci.*, 8 (2013) 949.
4. A. Jikihara, R. Ohashi, Y. Kakihana, M. Higa, and K. Kobayashi, *Membranes (Basel)*, 3 (2013) 1.
5. I. Stosevski, J. Krstic, N. Vokic, M. Radosavljevic, Z. K. Popovic, and S. Miljanic, *Energy*, 90 (2015) 595.
6. J. Wang, R. He , Q. Che, *J. Coll. and Int. Sci.*, 361 (2011) 219
7. M. Elangovan and S. Dharmalingam, *Int. J. Hydrogen Energy*, 41 (2016) 8595.
8. S. Vengatesan, S. Santhi, S. Jeevanantham, and G. Sozhan, *J. Power Sources*, 284 (2015), 361.
9. L. E. Shmukler, N. Van Thuc, and L. P. Safonova, *Ionics*, 19 (2013) 701.
10. G. Merle, M. Wessling, and K. Nijmeijer, *J. Memb. Sci.*, 377 (2011) 1.
11. N. J. Robertson, H. a T. Kostalik, T. J. Clark, P. F. Mutolo, H. D. Abruna, and G. W. Coates, *J. Am. Chem. Soc.*, 132 (2010), 3400.
12. N. Kakati, J. Maiti, G. Das, S. H. Lee, Y. S. Yoo, *Int. J. Hydrogen Energy, 40 (2015), 7114*
13. D. Wang, Y. Wang, J. Wang∗, L. Wang, *Polymer*, 170 (2019), 31.
14. K. H. Gopi, V. M. Dhavale, S. D. Bhat, *Material Science for Energy Tecnologies*, 2 (2019), 194.
15. D. Herranz, R. Escudero- Cid, M. Montiel, C. Palacio, E. Fatas, P. Ocon, *Renewable Energy*, 127 (2018), 883