NCNE-2020 Special Issue

J. Indian Chem. Soc.,
Vol. 97, July 2020, pp. 1025-1028

Synthesis and characterization of cellulose acetate based proton exchange membranes

Kosuri Praveena[a], Sandeep Dharmadhikari*[b], Ghoshna Jyoti[b] and Manivannan Ramachandran[a]

[a]Department of Chemical Engineering, National Institute of Technology Raipur, Raipur-492 010, Chhattisgarh, India

[b]Department of Chemical Engineering, SOS, Engg. and Tech., GGV, Bilaspur-495 009, Chhattisgarh, India

E-mail: dharmadhikarisandeep14@gmail.com

Manuscript received online 02 May 2020, accepted 08 June 2020

The proton exchange membranes (PEMs) were prepared using cellulose acetate (CA), orthophosphoric acid (OPA) and polyvinyl alcohol (PVA) and epichlorohydrin (ECH) as an active agent. Polyvinyl alcohol (PVA) was used as polymeric backbone for the synthesized PEMs. CA was used as a hydrophilic agent and OPA provided acidic matrix for the membranes. Polymeric membranes have minimal environmental effects and hence we focused on these membranes for fuel cell applications. These membranes were prepared by physical blending and casting methods. The cellulose acetate was dissolved in the required amount of pure acetone to form a solution and subsequently activated using ECH at 45°C for 6 h. Activated cellulose acetate and OPA was used in molar ratios of 1:1 and 1:2 in this study. PVA was added in the desired quantity. The approach allowed the membrane to have an excellent ion exchange capacity (IEC) and water uptake (WU) such as 1.14 meq/g and 11.83%, respectively.

Keywords: Proton exchange membrane, ion exchange capacity, swelling ratio, water uptake.

Introduction

The enhancement in the demand of power requirement makes the researchers to focus on the renewable energy sources. PEM fuel cells have a promising ability to convert electrochemical energy into power. They gained sufficient interest because of their high efficiency and low emissions of wastes. Essentially, the mechanism of PEM is to transfer the protons from anodic compartment to cathodic compartment. The PEM serves as a media to conduct electrons from anode chamber to cathode chamber in a fuel cell. It is a polymeric membrane prepared using different types of polymers[1,2]. Commercially available PEM is Nafion. Nafion is widely used proton exchange membrane due to its high mechanical, chemical, and thermal stability and proton conductivity. However, these Nafion membranes are lavish. Hence, several researchers explore the alternative to Nafion membranes for fuel cell applications. Fuel cell converts the energy with high efficiency and extremely low pollutant emission. PEM fuel cell consists of a polymeric membrane, which transports the protons from anode chamber to cathode chamber. The electrons generated in anode chamber travels through the external circuit of cell to cathode chamber and produce electricity. Hydrogen based fuel cell was charged through a field flow plates to the anode side, where hydrogen splits into H^+ ions and charged electrons. Hence, there's no change of emission of pollutants it is an eco-friendly way of production of energy. The key component of the fuel cell is PEMs, which may be polymeric membranes or acid base membranes. The products of these fuel cells are water from cathode chamber and electricity from the external circuit. To produce H^+ ions and negatively charged electrons fuel cell requires hydrogen which is costlier and it is difficult to produce hydrogen and also to store. Hence many of the fuel cells use H^+ ions producing gases such as methanol or gasoline etc., where direct methanol fuel cell gained success by using liquid methanol fuel[3]. But emission of CO is the noticeable disadvantage of the direct methanol fuel cell, which damages the platinum electrodes[4] and may decrease the efficiency of the fuel cell. In this study, we prepared a polymeric proton exchange membrane using cellulose acetate (CA) and epichlorohydrin as an active agent, orthophosphoric acid (OPA) and polyvinyl alcohol (PVA). The prepared membrane should be thin having high ion exchange capacity and water uptake.

Materials and method

Cellulose acetate (CA), epichlorohydrin (ECH), orthophosphoric acid (OPA) (85% extra pure), and polyvinyl alcohol (PVA) were purchased from Loba Chemie, India; acetone (purity 90%) was purchased from Merck, India; sodium chloride, hydrochloric acid, sodium hydroxide, phenolphthalein were purchased from Rankem, India.

Experimental

Activation process:

Cellulose acetate powder was dissolved in required amount of pure acetone to make the slurry. Epichlorohydrin was added to activate the cellulose acetate[1]. The activation process was conducted at a temperature of 50°C for 8 h. The epichlorohydrin was added in desired quantity to activate the cellulose acetate. The activation samples were left at room temperature for 5 h and in water bath for 7 h.

Phosphorization process:

The activated cellulose acetate solution was added with orthophosphoric acid solution in molar ratio of 1:1 and 1:2. Orthophosphoric acid solution also contained polyvinyl alcohol in the ratio of 1:2[2]. The reaction was conducted at a temperature of 45°C in a water bath for 12 h. The unreacted and excess orthophosphoric acid was removed by the successive washing with the distilled water. The whole solution was casted into the petri dishes up to mark to maintain the thickness of the membranes and allowed to cool at ambient temperature.

Characterization

Epoxy content determination:

The epoxy content of the epichlorohydrin activated cellulose acetate membrane was quantified by using back titration method[1]. The activated samples dipped in a 50 ml 0.1 *M* hydrochloric acid solution for at least 12 h with shaking at room temperature. The HCl molecules react and hydrolyze the epoxy ring of ECH. The left HCl solution was titrated in against 0.1 *M* NaOH solution. The epoxy content was determined using the eq. (1):

$$X = \frac{(V_1 - V_2)\times \mathrm{N}}{g} \quad (1)$$

where, X as mg equivalents of ECH per gram of sample, V_1 as NaOH volume in original sample, V_2 as NaOH volume in modified sample, g as weight of sample tested.

Water uptake:

Water uptake plays a crucial role in the IEC of PEM. Enhancement in water uptake leads to increase in the IEC. However, very higher water uptake in the membrane causes the dimensional mismatches[8] resulting excess of swelling and instability. Water uptake is measured by soaking the membranes in water for 24 h at ambient temperature. After that membrane was removed and cleaned with tissue to remove the adhered water molecules and the membrane was weighed. WU was estimated using eq. (2):

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \quad (2)$$

with W_w as weight of wet membrane, W_d as weight of dry membrane.

Swelling ratio:

The membrane was dipped in water for 24 h and measured the thickness of the membrane before and after soaking. The swelling ratio was estimated using eq. (3):

$$\text{Swelling ratio (\%)} = \frac{t_w - t_d}{t_d} \times 100 \quad (3)$$

where, t_w as thickness of wet membrane, t_d as thickness of dry membrane.

Thickness determination:

The thickness of the membrane was determined at different places in the membrane using digital screw gauge (Mituotoyo, Japan) and the average thickness value was calculated using eq. (4):

$$t_{avg} = \frac{t_1 + t_2 + t_3 + \ldots\ldots\ldots + t_n}{n} \quad (4)$$

where, t_{avg} as the average thickness, $t_1, t_2, t_3 \cdots, t_n$ are the thickness at different positions, n as number of positions.

Ion exchange capacity (IEC):

The ionic conductivity is directly correlated to the IEC of the membrane. IEC is determined by the acid base titration method[5]. A portion of membrane was dipped in 2 *M* NaCl

solution for 24 h. The solution was then titrated against 0.1 *M* NaOH solution. IEC was calculated using the formula reported in literature[2].

Results and discussion

Epoxy content of membrane:

By using back titration method epoxy content of a given membrane is calculated by eq. (1). The epoxy content is determined 3.849 meq/gm.

Thickness:

The thickness of the membrane M-1 (1:1) and M-2 (1:2) were 0.2838 mm and 0.2742 mm.

Water uptake:

M-1 and M-2 membranes were 1:1 and 1:2 molar ratios of cellulose acetate and orthophoshoric acid. The water uptake of M-1 and M-2 membranes was 9.02 and 11.85, respectively. Whereas the WU of Nafion 117 was measured as 20%. Fig. 1 shows the increase in water uptake with increasing the ratio between orthophosphoric acid and cellulose acetate. The maximum water uptake is obtained with the OPA content of 2 *N*. The enhancement in hydrophilicity is increased by the phosphoric group.

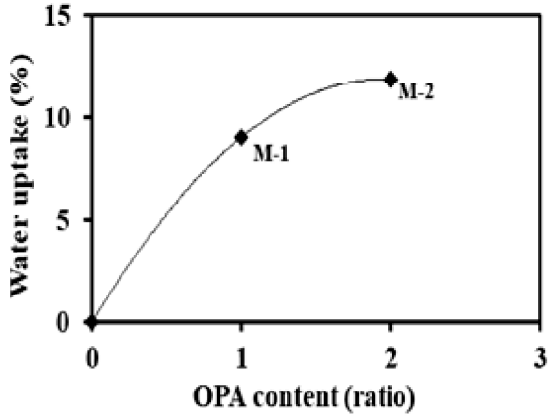

Fig. 1. Water uptake of M-1 and M-2 membrane vs different OPA content.

Ion exchange capacity:

The ratios of cellulose acetate and orthophoshoric acid in M-1 and M-2 membranes were 1:1 and 1:2. IEC of M-1 and M-2 were 0.94 meq/g and 1.14 meq/g. As the acid groups

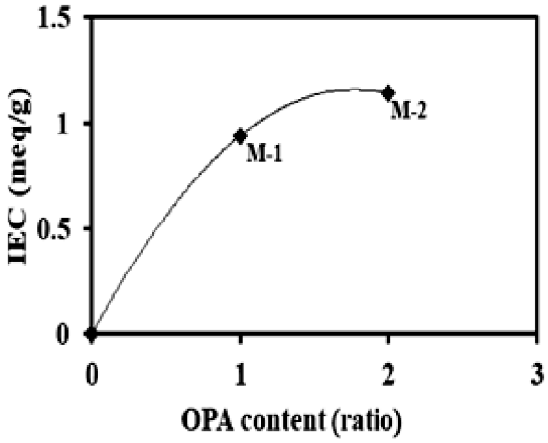

Fig. 2. IECs of M-1 and M-2 membrane vs different OPA content.

are increased the IEC also increased. Fig. 2 shows the increase in IEC with increasing the ratio between orthophosphoric acid and cellulose acetate whereas the IEC of the Nafion 117 is 0.91 meq/g which is showing low value compared to the synthesized membranes.

Swelling ratio:

The swelling ratios of M-1 and M-2 were 0.0899% and 0.1185%, respectively. Swelling ratios were found to be lesser than 5%, which is reasonable as reported in the literature[9]. Fig. 3 shows the increase in swelling ratio's with increasing the ratio between orthophosphoric acid and cellulose acetate.

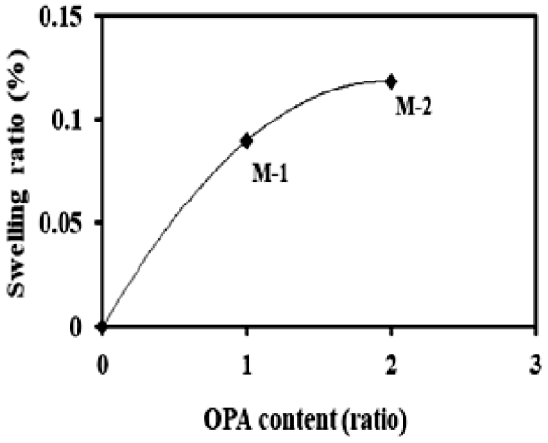

Fig. 3. Swelling ratios of M-1 and M-2 membrane vs different OPA content.

The characteristics of the synthesized membrane and commercial membrane is summarized in Table 1.

Table 1. Values of water uptake and IEC of synthesized membranes and Nafion-117

Sr. No.	Membranes	Water uptake (%)	IEC (meq/g)
1.	M-1	9.02	0.94
2.	M-2	11.85	1.14
3.	Nafion-117	20	0.91

Conclusion

The cellulose acetate based proton exchange membrane has been prepared using the blending and casting method. M-1 and M-2 shows water uptake of 9.02 and 11.85%, IEC of 0.94 and 1.14 meq/g and swelling ratios of 0.0899% and 0.1185%.

References

1. M. S. Mohy Eldin, M. H. Abd Elmageed, A. M. Omer, T. M. Tamer, M. E. Yossuf and R. E. Khalifa, *Int. J. Electrochem. Sci.,* 2016, **11**, 3467.
2. S. Dharmadhikari, P. Ghosh and M. Ramachandran, *J. Serb. Chem. Soc.,* 2018, **83**, 611.
3. S. Wasmus and A. Kuver, *J. Electroanal. Chem.,* 1999, **461**, 14.
4. R. Ianniello, V. M. Schmidt, J. Stumper, U. Stimming and A. Wallan, *Electrochim. Acta*, 1994, **39**, 1863.
5. S. Feng, Y. Shang, Y. Wang, G. Liu, X. Xie, W. Dong, J. Xu and V. K. Mathur, *J. Membr. Sci.,* 2010, **352**, 14.
6. G. Cacciola, V. Antonucci and S. Freni, *J. Power Sources,* 2001, **100**, 67.
7. C. K. Dyer, *J. Power Sources*, 2002, **106**, 31.
8. X. Lia, Y. Zhaoa, Z. Fenga, X. Xianga, S. Wanga, X. Xiea and V. K. Ramani, *J. Membr. Sci.,* 2017, **52**, 55.
9. W. Li, C. Gao, J. Guo, Y. Ren, X. Deng and Y. Liu, *Solid State Ion.,* 2015, **278**, 254.