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Preparation and Characterization of Poly(vinyl alcohol)-based Anion Exchange Membranes

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Abstract

Anion exchange membranes (AEMs) play an important role in improving the performance and efficiency of anion exchange membrane fuel cells (AEMFCs). A sequence of composite anion exchange membranes (AEMs) consisting of poly(vinyl alcohol) (PVA) as a backbone polymer and different approaches for introducing functional groups has been prepared by a solution casting method. The performance of composite AEMs was evaluated using water uptake, swelling degree, and OH⁻ conductivity measurement. Composite AEMs consisting of quaternized poly(vinyl alcohol) (QPVA) and poly diallyldimethylammonium chloride (PDDA) acquired the highest hydroxide conductivity, water uptake, and swelling degree. This study demonstrates that the PVA-based AEMs has the potential for fuel cell application.

Introduction

Over the past decades, enormous attention has been devoted to proton exchange membrane fuel cells (PEMFCs) development because of their significant performance in comparison with other types of fuel cells. However, the development has been hampered by several issues, including considerable cost due to the use of a platinum catalyst in the electrode layer, fuel crossover, slow reaction kinetics in an acidic condition, and complicated water management [1], [2]. In order to resolve these issues, considerable attention has been evoked on anion exchange membrane fuel cells (AEMFCs). Since AEMFCs employ anion-exchange membranes (AEMs) as opposed to proton-exchange membranes, hydroxide transport emerges instead of a proton, which offers advantages as compared to the PEMFCs. These comprise the use of low-priced and non-noble catalysts, high oxygen reduction rate (ORR) in the cathode, low fuel permeability, and outstanding corrosion resistance in the alkaline condition [3], [4]. Therefore, AEMs contribute considerably to increase the performance and efficiency of AEMFCs [5].

Poly(vinyl alcohol) (PVA) is a low-cost polyhydroxy-type polymer that possesses exceptional film-forming properties, hydrophilic, and non-toxic. PVA has a high density of reactive chemical functional groups, which are favorable for cross-linking and chemical modification [6]. Furthermore, due to the high selectivity of water to alcohol, PVA has low methanol permeability and has the potential for alkaline fuel cell application [7], [8].

The anion exchange membranes were frequently prepared by dissolving KOH into the matrix of PVA membranes to provide charge carriers. Since KOH has a high solubility in water, fuel cells with this type of membrane are susceptible to lose conductivity arising from the loss of KOH [7].

In this research, we applied PVA as the main-backbone polymer. For converting PVA membrane to anion exchange membranes, we used three different approaches: (i) glycidyltrimethylammonium chloride (GTMAC) by quaternization of PVA, (ii) poly(diallyldimethylammonium chloride) (PDDA) by blending with PVA and (iii) combination

of both techniques. PDDA contains quaternary ammonium functional groups that are able to offer OH⁻ as charge carriers [9], [10]. Furthermore, the cyclic structures of PDDA establish large steric hindrance, obstructing functional groups' degradation through S_N2 nucleophilic substitution in an alkaline condition [11]. PDDA also has a hydrophilic and is eco-friendly.

In order to restrain membrane swelling and improve the chemical stability of the membrane, cross-linking of the polymer chains was introduced to the membrane preparation. The effect of different approaches for inducing ion-conducting functional charge was investigated in PVA-based AEMs preparation.

Methods

Polymers solution preparation

Four different samples with different ion-conducting sources were prepared (Table 1). First, 10 wt.% PVA (98-99% hydrolyzed, average Mw = 86,000-89,000 g mol⁻¹, Sigma-Aldrich) aqueous solution was prepared by dissolving PVA in ultra-pure water at 80°C with stirring.

QPVA was prepared as reported by [12]. Firstly, 5 g PVA was dissolved in 95 ml ultra-pure at 80 °C until obtaining a homogeneous clear solution. Then 10 ml of 2.0 M KOH solution (Merck) and 10 g glycidyltrimethylammonium chloride (GTMAC, ≥90%, Sigma-Aldrich) were added to the solution under continuous stirring for 4 h at 65 °C for PVA chains quaternization. Anhydrous ethanol (Merck) was added into the solution to acquire the precipitate and dried at 40 °C for 24 h. Finally, the white obtained QPVA particles were dissolved in ultra-pure water at 80°C with stirring to obtain 10 wt.% QPVA solution.

The aforementioned 10 wt.% PVA solution and 10 wt.% QPVA solution was then blended with poly(diallyldimethylammonium chloride) (PDDA, Mw = 400,000-500,000, 20 wt.% in H₂O) under stirring for 4 hours, resulting in PVA/PDDA and QPVA/PDDA with a weight ratio of 1:0.5, respectively.

Table 1 Composition of the samples

Sample names	Description
PVA	10 wt.% PVA solution
QPVA	10 wt.% QPVA solution
PVAPDDA	Blend of 10 wt.% PVA and 10 wt.% PDDA solution with a weight ratio of 1:0.5
QPVAPDDA	Blend of 10 wt.% QPVA and 10 wt.% PDDA solution with a weight ratio of 1:0.5

Swelling Degree

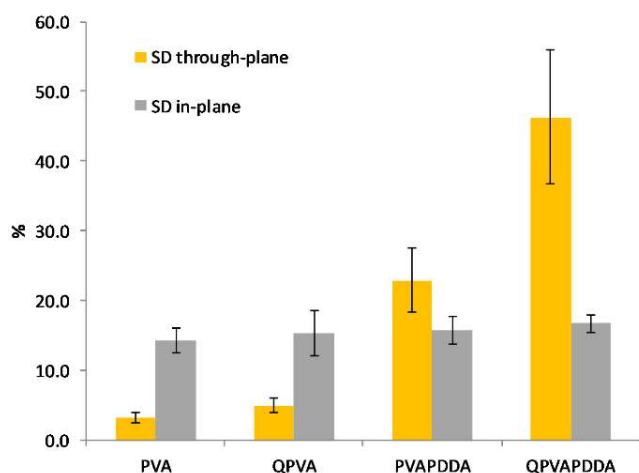


Figure 4. Swelling degree of membranes

Regardless of the fact that a certain amount of water in the membrane is required for OH⁻ conductivity, excessive water uptake can induce a severe swelling of the membrane. This excessive swelling can decrease the dimensional stability and possibly restricts the preparation of membrane electrode assembly (MEA) by reducing contact between the active layer of the electrodes and the membrane [15].

Pristine PVA is hydrophilic, easily damaged in water, and completely dissolved in hot water. Cross-linking treatment has restrained the swelling formation of membranes. However, small swelling still occurred in the chemical swelling process and changed the dimension afterward. This swelling was due to the water present in the source cross-linking solution (25 wt.% in H₂O).

In order to evaluate any change in area dimension and the thickness of membranes, the swelling degree (SD) of different PVA membranes are assessed. Figure 4 exhibits the SD through-plane (thickness) and SD in-plane (area) of the membranes. The SD through-plane of PVA membrane is 3.13% and increases with the order QPVA, PVAPDDA, and QPVAPDDA. The increase of SD through-plane is proportional to the increase of WU membranes. However, SD in-plane (area) of membranes only increases slightly with the same order. This implies that changes in membrane dimensions have a tendency towards through-plane than in-plane direction.

Membrane swelling also

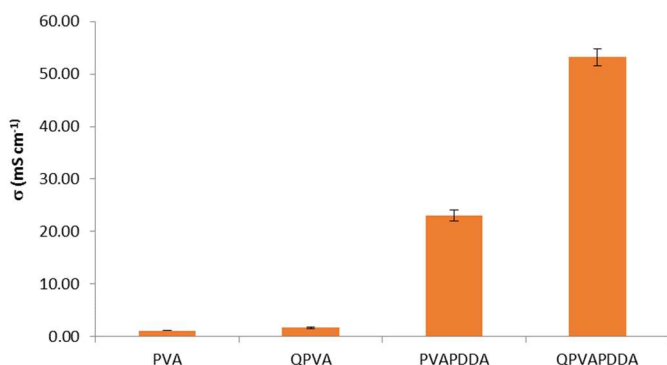
OH⁻ conductivity

Figure 5. Hydroxide conductivity of membranes

The OH⁻ conductivity is one of the most crucial attributes of AEMs and is strongly assigned to the performance of AEMFCs. Typically, the ionic conductivity of AEMs is strongly reliant on the number of quaternary ammonium groups present in the membrane, water uptake and morphology of membranes.

Figure 5 shows the OH⁻ conductivity of membranes. The conductivity of the pristine PVA membrane is really low (1.09 mS cm⁻¹) due to no exchangeable quaternary ammonium groups present in the membrane. Quaternization of PVA (QPVA) slightly increases the conductivity of the membrane to 1.71 mS cm⁻¹. This probably because the quaternary ammonium groups available in PVA chemical structure are not high. In order to increase the number of quaternary ammonium groups in the membrane, the amount of GTMAC should be increased in the quaternization process. However, excessive concentration of quaternary ammonium groups could deteriorate the mechanical strength of the membranes, due to excessive swelling or brittleness due to an intensive dryness [16]. PVAPDDA and QPVAPDDA membranes give much higher OH⁻ conductivity of 23.03 mS cm⁻¹ and 53.19 mS cm⁻¹, respectively. The increase of OH⁻ conductivity is comparative to the increase of WU membranes. These results prove that the ionic conductivity of AEMs is intensely dependent on the water uptake of membranes and PDDA contributed more to the number of quaternary ammonium groups present in the membrane. Combination of PVA quaternization and PDDA blend resulting highest OH⁻ conductivity of membranes. Interestingly, the OH⁻ conductivity of QPVAPDDA is much higher than the sum of conductivity of QPVA and PVAPDDA. This phenomenon is still not well understood, probably due to good I compatibility of QPVA and PDDA polymers.

Conclusion

Composite anion exchange membranes (AEMs) consisting of poly(vinyl alcohol) (PVA) as a backbone polymer and different approaches for introducing functional groups have been successfully prepared by a solution casting method. QPVA/PDDA composite AEMs acquired the highest hydroxide conductivity, water uptake, swelling degree through-plane and swelling degree in-plane of 53.19 mS cm⁻¹, 52.1 %, 46.3%, and 16.7%, respectively. This study demonstrates that the PVA-based AEMs have the potential for fuel cell application.

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References

- [1] Dai, W., Wang, H., Yuan, X., Martin, J. J., and Yang, D., "A review on water balance in the membrane electrode assembly of proton exchange membrane fuel cells," *Int. J. Hydrogen Energy*, vol. 34, no. 23, pp. 9461–9478, 2009, doi: 10.1016/j.ijhydene.2009.09.017.
- [2] Fang, J., Wu, Y., Zhang, Y., Lyu, M., and Zhao, J., "Novel anion exchange membranes based on pyridinium groups and fluoroacrylate for alkaline anion exchange membrane fuel cells," *Int. J. Hydrogen Energy*, vol. 40, no. 36, pp. 12392–12399, 2015, doi: 10.1016/j.ijhydene.2015.07.074.
- [3] Couture, G., Alaaeddine, A., Boschet, F., and Ameduri, B., "Polymeric materials as anion-exchange membranes for alkaline fuel cells," *Prog. Polym. Sci.*, vol. 36, no. 11,

- pp. 1521–1557, 2011, doi: 10.1016/j.progpolymsci.2011.04.004.
- [4] Wang, Y.-J., Qiao, J., Baker, R., and Zhang, J., "Alkaline polymer electrolyte membranes for fuel cell applications," *Chem. Soc. Rev.*, vol. 42, no. 13, pp. 5768–5787, 2013, doi: 10.1039/c3cs60053j.
- [5] Iravaninia, M. and Rowshanzamir, S., "Polysulfone-based Anion Exchange Membranes for Potential Application in Solid Alkaline Fuel Cells," *J. Renew. Energy Environ.*, vol. 2, no. 2, pp. 59–65, 2015.
- [6] Zhou, T., Zhang, J., Jingfu, J., Jiang, G., Zhang, J., and Qiao, J., "Poly(ethylene glycol) plasticized poly(vinyl alcohol)/poly(acrylamide-co-diallyldimethylammonium chloride) as alkaline anion-exchange membrane for potential fuel cell applications," *Synth. Met.*, vol. 167, no. 1, pp. 43–50, 2013, doi: 10.1016/j.synthmet.2013.02.008.
- [7] Xiong, Y., Fang, J., Zeng, Q. H., and Liu, Q. L., "Preparation and characterization of cross-linked quaternized poly(vinyl alcohol) membranes for anion exchange membrane fuel cells," *J. Memb. Sci.*, vol. 311, no. 1–2, pp. 319–325, 2008, doi: 10.1016/j.memsci.2007.12.029.
- [8] Susanto, H., Samsudin, A. M., Faz, M. W., and Rani, M. P. H., "Impact of post-treatment on the characteristics of electrospun poly(vinyl alcohol)/chitosan nanofibers," in *AIP Conference Proceedings*, 2016, vol. 1725, doi: 10.1063/1.4945541.
- [9] Zhang, J., Qiao, J., Jiang, G., Liu, L., and Liu, Y., "Cross-linked poly(vinyl alcohol)/poly(diallyldimethylammonium chloride) as anion-exchange membrane for fuel cell applications," *J. Power Sources*, vol. 240, pp. 359–367, 2013, doi: 10.1016/j.jpowsour.2013.03.162.
- [10] Samsudin, A. M., "PVA / PDDA / Nano-Zirconia Composite Anion Exchange Membranes for Fuel Cells," 2019.
- [11] Yuan, Y., Shen, C., Chen, J., and Ren, X., "Synthesis and characterization of cross-linked quaternized chitosan/poly(diallyldimethylammonium chloride) blend anion-exchange membranes," *Ionics (Kiel)*, vol. 24, no. 1173, p. 1180, 2018, doi: 10.1007/s11581-017-2280-x.
- [12] Jiang, X., Sun, Y., Zhang, H., and Hou, L., "Preparation and characterization of quaternized poly(vinyl alcohol)/chitosan/MoS₂ composite anion exchange membranes with high selectivity," *Carbohydr. Polym.*, vol. 180, no. October 2017, pp. 96–103, 2018, doi: 10.1016/j.carbpol.2017.10.023.
- [13] Liao, G. M., Yang, C. C., Hu, C. C., Pai, Y. L., and Lue, S. J., "Novel quaternized polyvinyl alcohol/quaternized chitosan nano-composite as an effective hydroxide-conducting electrolyte," *J. Memb. Sci.*, vol. 485, pp. 17–29, 2015, doi: 10.1016/j.memsci.2015.02.043.
- [14] Hari Gopi, K. and Bhat, S. D., "Anion exchange membrane from polyvinyl alcohol functionalized with quaternary ammonium groups via alkyl spacers," *Ionics (Kiel)*, vol. 24, pp. 1097–1109, 2018, doi: 10.1007/s11581-017-2272-x.
- [15] Feketeföldi, B. *et al.*, "Chitosan-Based Anion Exchange Membranes for Direct Ethanol Fuel Cells," *J. Membr. Sci. Technol.*, vol. 06, no. 01, pp. 1–9, 2016, doi: 10.4172/2155-9589.1000145.
- [16] Merle, G., Wessling, M., and Nijmeijer, K., "Anion exchange membranes for alkaline fuel cells: A review," *J. Memb. Sci.*, vol. 377, no. 1–2, pp. 1–35, 2011.