



Fuel cell durability enhancement by crosslinking alkaline anion exchange membrane electrolyte

Yanting Luo^a, Juchen Guo^a, Chunsheng Wang^{a,*}, Deryn Chu^b

^a Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA

^b Sensors and Electron Device Directorate, U.S. Army Research Laboratory, Adelphi, MD, 20783, USA

ARTICLE INFO

Article history:

Received 22 November 2011

Received in revised form 21 December 2011

Accepted 5 January 2012

Available online 12 January 2012

Keywords:

Energy conversion

Fuel cells

Polymer electrolytes

s-IPN system

Crosslinking

ABSTRACT

Our previously investigated quaternized poly (methyl methacrylate-co-butyl acrylate-co-vinylbenzyl chloride) (QPMBV) AAEM (alkaline anion exchange membrane) showed exceptional fuel cell performance, yet the poor durability is still remained to solve. The focus of this research is to enhance the durability of QPMBV AAEM through monomer reselection and crosslinking, which increases T_g by 20 °C and decreases water uptake by 75%. The resulted AAEM can continuously work for 420 and 146 hrs in fuel cell without significant performance decline at 50 °C and 70 °C, respectively.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Alkaline anion exchange membrane fuel cell (AAEMFC) technology has been revived for applications in transportation and portable electronic devices due to the advantages of using non-noble metal catalysts [1], faster oxygen reduction in alkaline medium [2], and compact design [3]. In an AAEMFC, it is essential for OH⁻ conductive AAEM to have both high conductivity and superior durability in fuel cell working environment. Our previous QPMBV AAEM, synthesized by miniemulsion copolymerization, demonstrated promising fuel cell performance [4–6]. The maximum fuel cell power density could reach 180 mW cm⁻² and the fuel cell durability could last 48 hrs under 100 mA cm⁻² discharge current. From the previous studies, several insights can be drawn. Firstly, AAEM electrolyte could be synthesized from a bottom-up polymerization with designed hydrophobic and hydrophilic portion in polymer chains to serve mechanical support and conducting function, respectively. Also, the composition, the molecular weight (MW), and the glass transition temperature (T_g) of the copolymer could be adjusted to enhance the mechanical properties, i.e. the durability performance of AAEMFCs.

In the present communication, we focus on enhancing the durability of QPMBV by (1) increasing T_g and MW, and (2) crosslinking the copolymer. The increase in T_g was realized by eliminating butyl acrylate from monomers, which was a low T_g component. MW was further optimized through investigating binary copolymerization kinetics

after removal of butyl acrylate. The newly obtained poly (methyl methacrylate-co-vinylbenzyl chloride) (PMV) was crosslinked as a semi-interpenetrating network (s-IPN) to reduce water uptake. In an s-IPN, one polymer is locked into another crosslinked polymer matrix. The crosslinked polymer matrix gives mechanical support to the whole structure, while the polymer locked in provides functionality. Several s-IPNs including chitosan [7–9], poly (vinyl alcohol) [10–12], poly (arylene ether sulfone) [13], and poly (epichlorohydrin) [14] based AAEMs were widely investigated. Those s-IPNs demonstrated low water uptake and relatively high conductivity, yet no durability data on fuel cell were reported.

In our study, PMV copolymer was crosslinked into an s-IPN system, using DVB (divinylbenzene) as the crosslinker. DVB can be polymerized as a crosslinked rigid network due to its phenyl ring structure and the two vinyl groups on one ring. Therefore, poly (divinylbenzene) (PDVB) can hold the QPMV providing more mechanical support. A schematic structure of QPMV-PDVB s-IPN is shown in Fig. 1. The synthesis and crosslinking processes are detailed in the experimental section.

2. Experimental

2.1. Copolymerization

Miniemulsion was prepared by dispersing 30 g monomers (MMA: VBC = 90: 10 mol%) and 0.12 g hexadecane into 150 mL aqueous SDS (sodium dodecyl sulphate, 0.02 mol/L) solution by ultra-sonication. The polymerization was initiated by injection of initiator KPS (K₂S₂O₈ 2.5 mmol/L of the water phase) into the miniemulsion at 70 °C under nitrogen protection. The reaction was terminated after 4 hrs by

* Corresponding author. Tel.: +1 301 405 0352.

E-mail address: cswang@umd.edu (C. Wang).

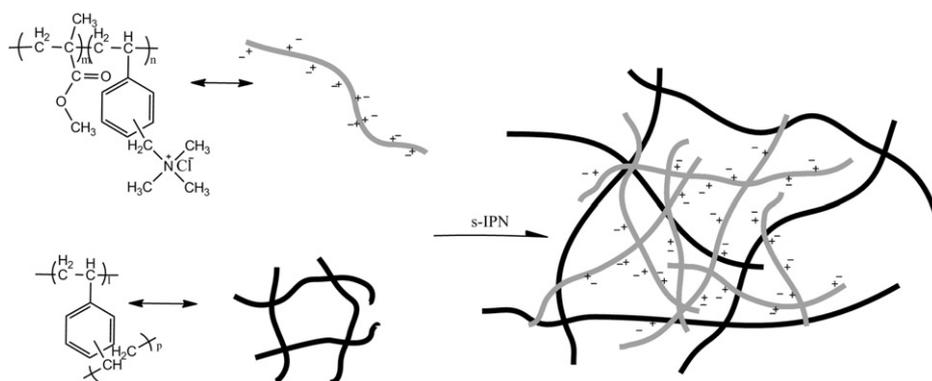


Fig. 1. Schematics of QPMV-PDVB AAEM.

quenching in ice bath. The copolymer was filtered and dried in vacuum overnight.

The resulted copolymer was characterized by $^1\text{H-NMR}$ (Proton nuclear magnetic resonance), GPC (Gel permeation chromatography), and DSC (Differential scanning calorimetry) according to the same procedure described in the previous work [5,6].

2.2. Crosslinking process and membrane preparation

The obtained PMV was dissolved in dimethylformamide (DMF) to form a 5 wt.% solution and quaternized with trimethylamine (Me_3N) for 2 hrs at 60°C by bubbling Me_3N into the solution while stirring. The obtained QPMV solution in DMF was then moved into a reflux condenser connected flask under nitrogen protection. A certain amount of DVB (0 to 10 wt.% of the QPMV) was added into the system. The crosslinking process was started by the initiator azobisisobutyronitrile (AIBN, 1.5 mmol/L of the DMF solution). The reaction was carried out at 60°C for 24 hrs when the solution became visually more viscous.

The QPMV was directly cast into a film on an aluminium plate inside a chamber under nitrogen environment at 60°C for overnight. The obtained membrane was further dried in vacuum oven at 60°C for 24 hrs, followed by soaking in 6 M KOH solution for overnight to exchange Cl^- to OH^- . The OH^- exchanged membrane was washed with DI water until pH of 7 was reached.

2.3. MEA fabrication

The slurry composed of PTFE/carbon black (35/65 wt.%) was first coated on carbon paper with a loading of approximately $0.2 \pm$

0.02 mg/cm^2 . The catalyst of Pt/C (60/40 wt.%) was dispersed in a dilute OH^- exchanged QPMBV solution in ethanol/ water mixture (50/50 vol.) by sonication. This catalyst dispersion was sprayed onto the processed carbon paper with the Pt loading of $0.4 \pm 0.05 \text{ mg/cm}^2$. Then the membrane was sandwiched by two 5 cm^2 catalyst loaded carbon papers using hot-press under the pressure of 2 atm at 60°C for 10 min to obtain the MEA for performance test. The assembling and testing condition was the same as in the previous study [6].

3. Results and discussion

3.1. Characterization of PMV

The ratio of MMA to VBC in PMV copolymer synthesized through miniemulsion copolymerization is 85:15 mol% as confirmed by $^1\text{H-NMR}$ (Proton nuclear magnetic resonance). GPC (gel permeation chromatography) test indicated that PMV copolymer has a very high molecular weight over $6 \times 10^6 \text{ g mol}^{-1}$, which is two times higher than that of the PMBV copolymer in our previous study [6]. DSC (differential scanning calorimetry) showed that the T_g of PMV was 105°C , which was 20°C higher than the previous PMBV copolymer with 10% butyl acrylate content [6].

3.2. Characterization of crosslinked QPMV-PDVB

The crosslinked QPMV-PDVB structure was confirmed by FTIR (Fourier transform infrared spectroscopy) as shown in Fig. 2. After quaternization and crosslinking, a broad peak from 3200 to 3700 cm^{-1} (intermolecular O—H stretching) [15] appeared in crosslinked sample indicated that the membrane changed from hydrophobic to hydrophilic. The three peaks in PMV at 3100 (C—H in aromatic ring of the VBC) [16], 2943 (C—CH₃ in MMA) [13], and 2800 (O—CH₃ in MMA) [17] cm^{-1} were merged in crosslinked QPMV-PDVB, which was attributed to two reasons. Firstly, the C—H structure was also in the aromatic ring of DVB, which enhanced the original intensity at 3100 cm^{-1} . Second, the quaternized QPMV-DVB would have the stretching vibrations of N—CH₃ at 2805 cm^{-1} [18]. Another noticeable enhanced peak intensity at 1600 cm^{-1} [19] was due to the conjugated C C stretching vibrations of the aromatic ring in DVB, which confirmed that the QPMV was crosslinked into the PDVB matrix. The presented FTIR results

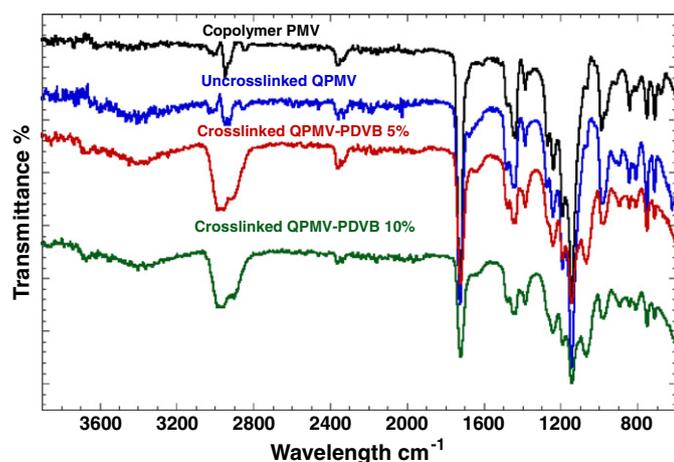


Fig. 2. FTIR spectra of PMV, uncrosslinked QPMV, and crosslinked QPMV-PDVB membranes.

Table 1
Properties of QPMV-PDVB AAEMs.

DVB crosslinker percentage	0%	5%	10%	
IEC (mmol g^{-1})	1.35	1.23	1.19	
Young's modulus ^a (GPa)	2.3	2.2	2.3	
Swelling ratio ^b	volume %	175.4	98.4	58.0
Water Uptake ^b	weight %	197.0	110.3	63.1

^a Membranes at room temperature and ambient environment.

^b Water saturated at room temperature.

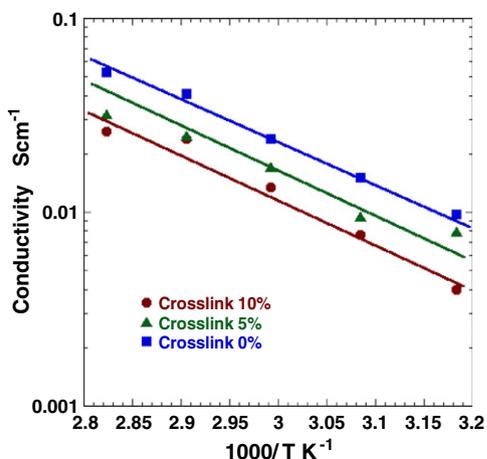


Fig. 3. Conductivities of QPMV-PDVB AAEMs.

are qualitative so that different DVB contents would not necessarily show difference in intensity. Therefore, QPMV-PDVB 5% and 10% showed similar spectra pattern.

3.3. Membrane properties of QPMV-PDVB AAEMs

After preparation of QPMV-PDVB AAEMs, the ion exchange capacity (IEC), Young's modulus, water uptake, and swelling ratio were measured and shown in Table 1. Crosslinking decreased the IEC of the membranes by around 0.1 mmol g^{-1} for 5% crosslinking and 0.15 mmol g^{-1} for 10% crosslinking. The Young's modulus of the obtained membranes was all above 2 GPa indicating a strong mechanical strength [1]. This was attributed to removing butyl acrylate component and crosslinking. Water uptake and swelling ratio of QPMV-PDVBs were measured after soaking the membranes in de-ionized water for 3 hrs at room temperature. Both water uptake and swelling ratio of the crosslinked membrane were reduced with the increase of the crosslinker concentration. This test demonstrated that s-IPN crosslinking was an effective strategy to control the water content in the membrane.

3.4. Conductivity of QPMV-PDVB AAEMs

Conductivity test was performed on the fuel cell test station under N_2 protection at 80% relative humidity (RH) using four-probe method. As shown in Fig. 3, although the conductivity of the two crosslinked

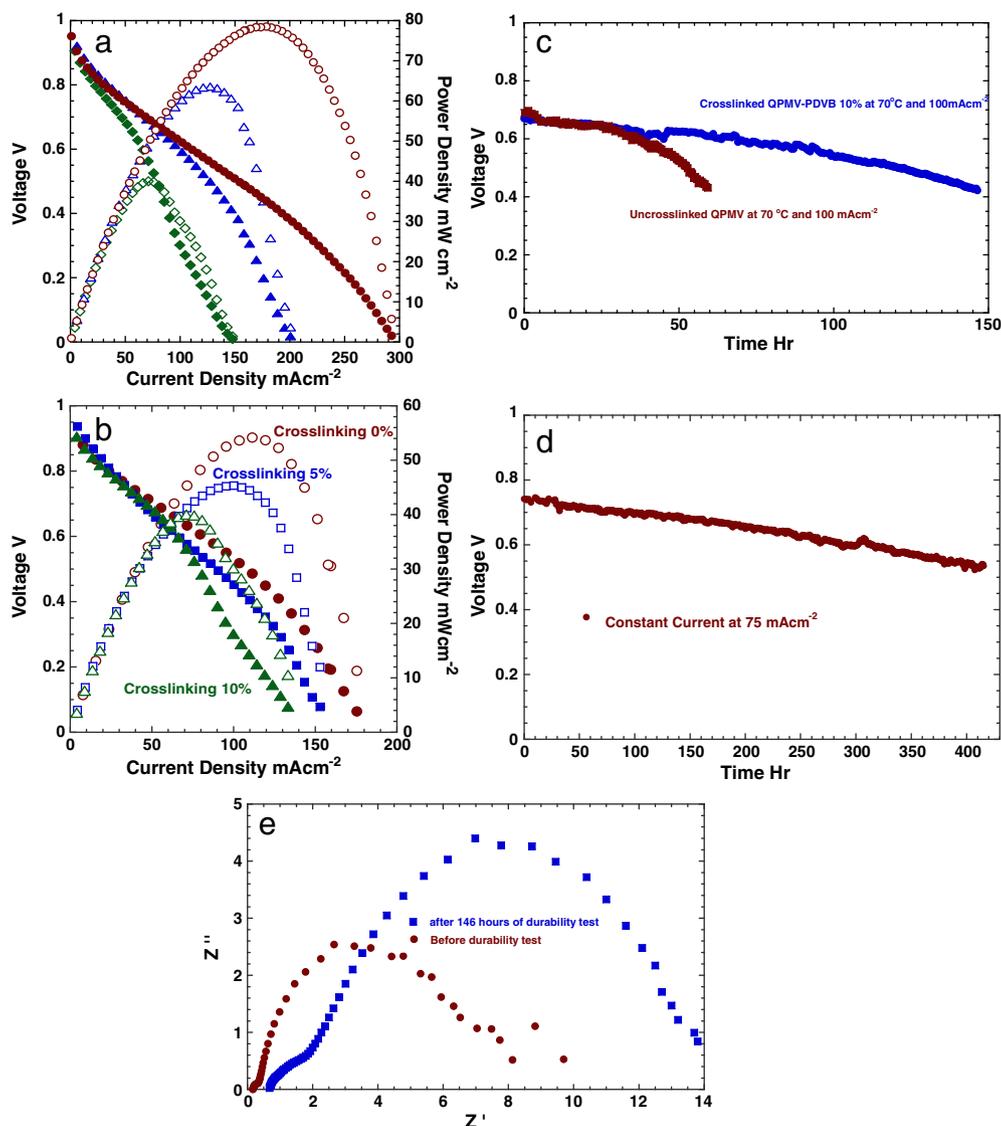


Fig. 4. (a) Polarization of 10% crosslinked QPMV-PDVB at different temperatures; (b) Polarization of various crosslinked AAEMs at 50 °C; (c) Durability tests of uncrosslinked QPMV and 10% crosslinked QPMV-PDVB AAEMs at 70 °C; (d) Durability test of 10% crosslinked AAEM at 50 °C; (e) Impedance test for crosslinked QPMV-PDVB 10% AAEM at 70 °C before and after the durability test.

AAEMs was lower than the un-crosslinked one, nevertheless the conductivity of both crosslinked membranes could reach $10^{-2} \text{ S cm}^{-1}$ above 50°C . The highest conductivity of the 5% crosslinked membrane could reach $2.5 \times 10^{-2} \text{ S cm}^{-1}$ at 80°C .

3.5. QPMV-PDVB AAEMs performance on fuel cell

The QPMV-PDVB AAEMs were tested on AAEMFC for both polarization and durability performance. Fig. 4(a) showed the polarization performance of the 10% crosslinked AAEM at different temperatures. It was shown that the delivered power density was improved with increased temperature. The best performance of the 10% crosslinked AAEM was at 70°C with a maximum power density of 80 mW cm^{-2} . This polarization performance was lower than the ones in our previous work [6]. It could be attributed to the much lower water-uptake of the crosslinked membranes. Fig. 4(b) showed the polarization performance of crosslinked AAEMs with different crosslinker percentage at 50°C . It illustrated that 10% crosslinked AAEM had the lowest power density, but it still could reach 46 mW cm^{-2} as its peak power density.

Due to its lowest water uptake, the 10% crosslinked QPMV-PDVB was used for the durability test. To compare the performances with our previous work, we conducted durability tests for both crosslinked 10% QPMV-PDVB and uncrosslinked QPMV membranes at 70°C and 100 mA cm^{-2} . The results in Fig. 4(c) showed that the uncrosslinked QPMV membrane could last 62 hrs on the fuel cell while the crosslinked QPMV-PDVB could run for 146 hrs. The 10% crosslinked QPMV-PDVB could approximately last three times longer than the membrane reported in our previous work under the same conditions. This largely improved durability can be mainly attributed to the improved mechanical strength due to crosslinking and removal of butyl acrylate. Moreover, the durability of the 10% crosslinked QPMV-PDVB membrane at 50°C and 75 mA cm^{-2} (slightly lower than the peak power density) could be further improved to 420 hrs (17.5 days) as shown in Fig. 4(d). Hoffman effect could be a possible reason for the gradually decreased performance. Also, it is possible that the platinum catalyst might catalyze water-shift reaction to generate H_2 and CO_2 from reaction of carbon and water, which would consume the OH^- in the AAEM during the durability test [20]. Furthermore, the impedance tests before and after the durability test for 10% QPMV-PDVB at 70°C are shown in Fig. 4(e). It indicated that not only the ohmic resistance was increased but the resistances at both anode and cathode were also increased, which were all accounted for the loss of voltage at the stable current density. The detailed mechanism is still under investigation.

4. Conclusion

Two effective strategies were used in this study to improve the durability of QPMBV membranes. The first strategy was to increase glass transition temperature and molecular weight by eliminating butyl acrylate from the monomers. The second method is to reduce the water uptake and swelling ratio by crosslinking to lock the functionalized QPMV into a PDVB polymer network. Crosslinking significantly enhanced the durability performance with minor sacrifice of power density. The fuel cell with crosslinked QPMV-PDVB AAEM could continuously work for 420 hrs at 50°C and 146 hrs at 70°C , which was eight and three times longer than that in our previous study, respectively.

Acknowledgements

The authors gratefully acknowledge the supports of this project by: 1. Office of Naval Research: N000140810717; 2. Army Research Lab: W911NF0920007; 3. Army Research Office: W911NF0910028.

References

- [1] S. Lu, J. Pan, A. Huang, L. Zhuang, J. Lu, PNAS 105 (2008) 20611.
- [2] N.J. Robertson, H.A. Kostalik IV, T.J. Clark, P.F. Mutolo, H.D. Abruna, G.W. Coates, Journal of the American Chemical Society 132 (2010) 3400.
- [3] R. Devanathan, Energy and Environmental Science 1 (2008) 101.
- [4] Y. Luo, J. Guo, C. Wang, D. Chu, Journal of Power Sources 195 (2010) 3765.
- [5] Y. Luo, J. Guo, C. Wang, D. Chu, ChemSusChem 11 (2011) 1557.
- [6] Y. Luo, J. Guo, C. Wang, D. Chu, Macromolecular Chemistry and Physics 212 (2011) 2094.
- [7] Y. Wan, K. Creber, B. Peppley, V. Bui, Journal of Membrane Science 284 (2006) 331.
- [8] Y. Wan, B. Peppley, K. Creber, V. Bui, E. Halliop, Journal of Power Sources 162 (2006) 105.
- [9] J. Wang, R. He, Q. Che, Journal of Colloid and Interface Science 361 (2011) 219.
- [10] J. Qiao, J. Fu, R. Lin, J. Ma, J. Liu, Polymers 51 (2010) 4850.
- [11] L. Lebrun, E. Silva, G. Pourcelly, M. Metayer, Journal of Membrane Science 227 (2003) 95.
- [12] E. Silva, L. Lebrun, M. Metayer, Polymers 43 (2002) 5311.
- [13] J. Zhou, M. Unlu, I. Anestis-Richard, P. Kohl, Journal of Membrane Science 350 (2010) 286.
- [14] C. Sollogoub, A. Guinault, C. Bonnebat, M. Bennjima, L. Akrou, J. Fauvarque, L. Ogier, Journal of Membrane Science 335 (2009) 37.
- [15] S. Feng, Y. Shang, G. Liu, W. Dong, X. Xie, J. Xu, V. Mathur, Journal of Power Sources 195 (2010) 6450.
- [16] J. Zhou, M. Unlu, J. Vega, P. Kohl, Journal of Power Sources 190 (2009) 285.
- [17] R. Paris, J. Fuente, J. Polym, Journal of Polymer Science, Part A1: Polymer Chemistry 45 (2007) 3538.
- [18] K. Wang, C. Luo, Zhou Xiao, Modern Instrumental Analysis of Polymer, 2nd ed. Tsinghua University Press, 2000.
- [19] Y. Choi, M. Kang, S. Moon, Journal of Applied Polymer Science 88 (2003) 1488.
- [20] X. Yu, S. Ye, Journal of Power Sources 172 (2007) 145.