OPEN ACCESS

1st International Electronic Conference on Materials
26 May - 10 June 2014

http://sciforum.net/conference/ecm-1

Article

Hypercrosslinked Sulfonated (poly ether ether ketone) Polyelectrolyte Membranes for Fuel Cells Applications

Nedal Abu-Thabit[1,*]

[1] Department of Chemical and Process Engineering Technology, Jubail Industrial College, Jubail Industrial City 31961, Saudi Arabia; E-Mail: abuthabit_nidal@yahoo.com

***** Author to whom correspondence should be addressed; E-Mail abuthabit_nidal@yahoo.com
Tel.: +966-13-*340 2356*

Received: 27 March 2014 / Accepted: 23 May 2014 / Published: 26 May 2014

Abstract

Sulfonated poly(ether ether ketone) (SPEEK), with excellent mechanical properties and chemical stability, is one of the promising polyelectrolyte membranes (PEMs) for fuel cells applications. However, the dimensional stability of SPEEK is reduced at certain degree of sulfonation (DS > 70%); and at operation temperatures above 60 $^{\circ}$C. One of the practical approaches for improving membrane integrity and dimensional stability is through formation of covalent crosslinks between SPEEK polymer chains. In this article, a simple and novel approach is introduced for enhancing the dimensional stability of SPEEK membranes through hypercrosslinking methodology. SPEEK membranes were hypercrosslinked with formaldehyde and the resulted membranes exhibited reduced water swelling and methanol permeability with negligible effect on the original proton conductivity.

Keywords: Sulfonated poly(ether ether ketone), polyelectrolyte membrane, hypercrosslinked polymer, fuel cells, proton conductivity.

---

1. Introduction

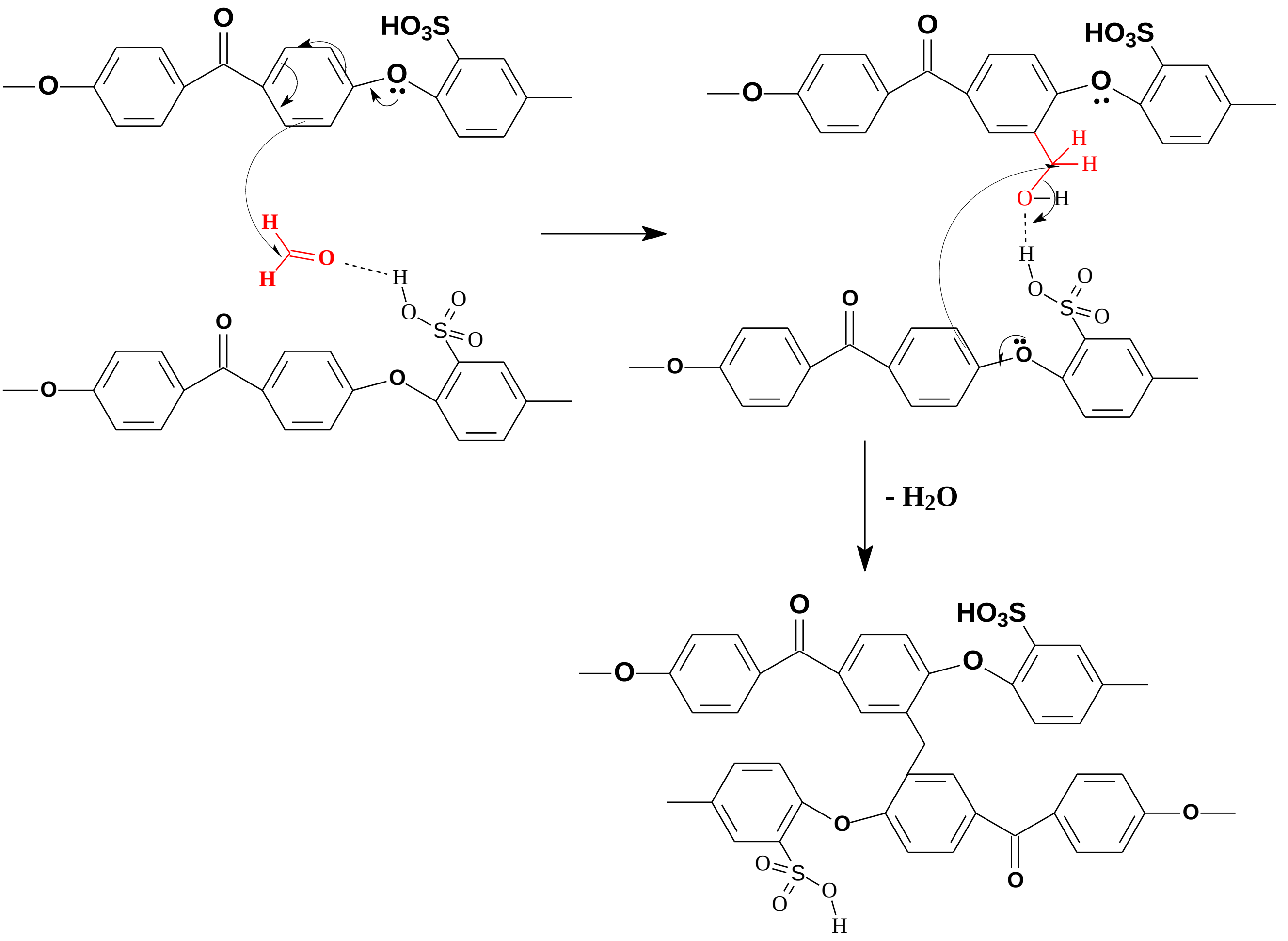
Fuel cell technology, which converts the chemical energy directly into electrical energy, is proposed as an alternative resource for generating energy with high efficiency and environmental compatibility [1]. One of the most attractive fuel cell categories is the polymer electrolyte membrane fuel cells (PEMFCs), such as direct hydrogen fuel cells, direct methanol fuel cells and alkaline fuel cells [2]. The polyelectrolyte membrane (PEM) serves as a conductor for protons and a barrier for fuel, oxidant and electrons. The state-of-the-art used PEMs are perfluorosulfonic acid membranes (e.g. Nafion series, DuPont) [3]. Nafion ionomer membranes are known for their excellent proton conductivity and chemical stability. However, their high cost, high fuel permeability, poor mechanical and chemical stabilities at elevated temperatures, are considered serious drawbacks and restrict the PEMFCs from worldwide commercialization. To overcome these shortcomings, new membranes have been investigated and proposed as alternative ionomers for both low and high temperature PEMFCs.

Sulfonated poly(ether ether ketone) SPEEK is one of the most studied PEMs for application in hydrogen and direct methanol fuel cells [4]. SPEEK membranes possess number of interesting features such as, high thermal stability, high mechanical strength, low methanol permeability and moderate proton conductivity. The proton conductivity of SPEEK membranes can be increased by increasing the number of pendant sulfonic acid moieties per polymer repeating unit, which is known as degree of sulfonation (DS). Nonetheless, when the DS exceeds 70%, the water uptake values increase dramatically, especially at temperature above 60 °C, which lead to poor mechanical properties of the highly swollen membranes. Different approaches have been employed to enhance the dimensional stability and water swelling properties of SPEEK membranes having DS > 70% for possible operation at temperatures ≈ 100 °C. These approaches include, blending [5-7], covalent crosslinking [8-10] and ionic crosslinking [11, 12].

Covalent crosslinking can be achieved by thermal treatment and formation of $–SO_2-$ bridges [13], *via* esterification reactions [9], by addition reactions and *via* Friedel-Crafts (F-C) reactions [14]. F-C reactions have been employed for synthesis of various hypercrosslinked polymers with controllable porosity [15]. Recently, Rhoden et al. employed F-C reactions as a strategy for crosslinking SPEEK membranes [16]. The formation of crosslinked covalent bonds between SPEEK polymeric chains (DS = 96%) was achieved by using benzenedimethanol (BDM) as a crosslinking agent in the presence of tiny amount of zinc chloride as Lewis acid catalyst. The crosslinked membranes exhibited enhanced chemical, mechanical and thermal properties, while significantly reducing the water uptake, swelling ratio and methanol permeability. The formed covalent crosslinks reduced the water swelling and improved the dimensional stability of the crosslinked SPEEK membranes at temperatures between 80 and 100 °C, without significant loss of proton conductivity. The overall fuel cell performance was close to that of Nafion.

In the current study, SPEEK (DS = 90%) was crosslinked by using formaldehyde (FA) as crosslinking agent. The crosslinking parameters were optimized and the resulted membranes were characterized in terms of water swelling, ion-exchange capacity, methanol permeability and proton conductivity.

Figure 1 Illustration of the crosslinking reaction between formaldehyde and SPEEK polymeric chains.



2. Results and Discussion

2.1. Membrane preparation and crosslinking

SPEEK membranes were crosslinked by using formaldehyde as illustrated in figure 1. The crosslinking reaction was achieved without use of any external catalyst. As depicted in figure 1, self-catalyzed Friedel-Crafts analog reaction is proposed in two step procedure. In the first step, the strongly ionizable sulfonic acid groups (Pka < 1) function as internal acid catalyst in the F-C hydroxyalkylation reaction. This will produce the hydroxymethyl substituted benzene ring. In the second step, sulfonic acid groups also catalyze the dehydration reaction and consequent formation of carbocation center for the subsequent F-C alkylation. As a result, the polymeric chains are crosslinked through one methylene bridging carbon.

2.2. Water Uptake

Table 1 lists the properties of the prepared crosslinked membranes with different SPEEK/FA compositions. For effective crosslinking, 35-40 wt. % formaldehyde has to be used. At this point, water uptake values was reduced by ≈ 30% at room temperature, and reached a value of ≈ 1000 % at 80 °C. Although, the water uptake values at 80 °C are still high, the crosslinked membranes are totally insoluble in boiling water (T=100 °C). This result proves the successful crosslinking reaction between SPEEK and FA at temperatures between 120 and 150 °C.

Table 1 List of crosslinked SPEEK membranes with different weight percentage of formaldehyde

Entry	Membrane Code	Ratio (wt. %) FA : SPEEK	Water Uptake (%)		IEC (meq./ g)	Proton Conductivity (S/cm)
			25 °C	80 °C		
1	SPEEK-90	0 : 100	685	∞[a)]	2.32	0.14
2	CL-15-SPEEK-90	15 : 85	672	∞[a)]	2.30	0.14
3	CL-25-SPEEK-90	25 : 75	283	1870	2.24	0.13
4	CL-35-SPEEK-90	35 : 65	220	1212	2.12	0.12
5	CL-40-SPEEK-90	40 : 60	210	990	2.0	0.11

[a)] Membrane is soluble above 60 °C.

2.3. Proton conductivity and ion-exchange capacity (IEC) of the crosslinked membranes

Ion-exchange capacity is an important property for membranes intended to be used as PEMFCs. Membranes with high IECs are expected to transport protons effectively through the available conducting ionic sites by proton hopping mechanism. Sulfonic acid-based PEMs, with high acidity and high ionization power, are one of the best choices in this area. Crosslinking reactions have strong effect on the IECs of the crosslinked membranes, especially in cases where the sulfonic acid groups are utilized as crosslinking sites for formation of covalent crosslinks. In the current study, the crosslinking reaction used is based on F-C alkylation and sulfonic acid groups are not expected to participate in such reaction, except by acting as acid catalyst for steps 1 and 2 (figure 1). As can be inferred from table 1, the IECs of the crosslinked membranes along with their proton conductivities were almost not affected.

2.4. Methanol Permeability

As shown in table 2, methanol permeability of the highly crosslinked membrane (CL-40-SPEEK-90) is lower than that of pristine SPEEK-90 membrane. This result could be attributed to the availability of crosslink points between the polymeric chains which reduce the hydrophilic domains and consequently hinders transportation of polar species such as methanol. In addition, methanol permeability of both SPEEK-90 and CL-40-SPEEK-90 is still lower than that of Nafion membrane. These results are important for PEMs to be considered for direct methanol fuel cell operation.

Table 2 Methanol permeability data for Nafion 117, SPEEK-90, and CL-40-SPEEK-crosslinked membrane.

Membrane Code	Methanol Permeability (cm^2/s)
Nafion 117	$6.80x\ 10^{-6}$
SPEEK-90	$1.85\ \ x\ 10^{-6}$
CL-40-SPEEK-90	$1.10\ x\ 10^{-6}$

3. Experimental

3.1. Membrane Preparation:

SPEEK polymers were dissolved in deionized (DI) water to form a final concentration of ≈ 5%. The required amount of FA crosslinker was added and the solution was stirred for 30 minutes. The prepared solutions were cast in Petri dishes and water was evaporated at 30 °C. Once water was evaporated, membranes were crosslinked by heating in oven at 120 °C for 1 hour, and then at 150 °C for one hour. The crosslinked membranes were immersed in DI water for 12 hours, then peeled off and submerged in 1.0 M HCl. After that, the crosslinked membranes were washed with DI water and stored for subsequent use.

3.2. Water Uptake (WU):

Initially, all membranes were dried at 100 °C until a constant weight was reached. A dried membrane sample with mass (m_{dry}) was equilibrated in water at the required temperature for 4 hours. Then, the membrane was removed from the water, quickly dry-wiped and the mass of wet membrane (m_{wet}) was determined. The water uptake values were calculated as follows:

$WU = m_{wet}/m_{dry} - 1$

3.3. Ion-Exchange Capacity (IEC):

The crosslinked membranes in the acid form were immersed in 1M NaCl solution for 24 h to liberate the H^+ ions. The released HCl was back titrated with 0.05M NaOH.

3.4. Proton conductivity and Methanol Permeability

Proton conductivity and methanol permeability of the selected membranes were determined following procedure described elsewhere [17].

4. Conclusions

The current study reports novel and simple approach for covalent crosslinking of SPEEK with high sulfonation degree. The resulted crosslinked membranes were insoluble in boiling water and exhibited improved characteristics such as reduced water uptake values, lower methanol permeability, with minimum effect on their proton conductivities.

References and Notes

1. Zhang, H.; Shen, P. K., Advances in the high performance polymer electrolyte membranes for fuel cells. *Chemical Society Reviews* **2012,** 41, (6), 2382-2394.
2. Zhang, L.; Chae, S.-R.; Hendren, Z.; Park, J.-S.; Wiesner, M. R., Recent advances in proton exchange membranes for fuel cell applications. *Chemical Engineering Journal* **2012,** 204, 87-97.
3. Liu, Y.-L., Developments of highly proton-conductive sulfonated polymers for proton exchange membrane fuel cells. *Polymer Chemistry* **2012,** 3, (6), 1373-1383.
4. Iulianelli, A.; Basile, A., Sulfonated PEEK-based polymers in PEMFC and DMFC applications: A review. *International Journal of Hydrogen Energy* **2012,** 37, (20), 15241-15255.
5. Abu-Thabit, N. Y.; Ali, S. A.; Zaidi, S.; Mezghani, K., Novel sulfonated poly (ether ether ketone)/phosphonated polysulfone polymer blends for proton conducting membranes. *Journal of Materials Research* **2012,** 27, (15), 1958-1968.
6. Swier, S.; Ramani, V.; Fenton, J.; Kunz, H.; Shaw, M.; Weiss, R., Polymer blends based on sulfonated poly (ether ketone ketone) and poly (ether sulfone) as proton exchange membranes for fuel cells. *Journal of Membrane Science* **2005,** 256, (1), 122-133.
7. Campagne, B.; David, G.; Améduri, B.; Jones, D. J.; Rozière, J.; Roche, I., Novel Blend Membranes of Partially Fluorinated Copolymers Bearing Azole Functions with Sulfonated PEEK for PEMFC Operating at Low Relative Humidity: Influence of the Nature of the N-Heterocycle. *Macromolecules* **2013,** 46, (8), 3046-3057.
8. Feng, S.; Shang, Y.; Wang, Y.; Liu, G.; Xie, X.; Dong, W.; Xu, J.; Mathur, V., Synthesis and crosslinking of hydroxyl-functionalized sulfonated poly (ether ether ketone) copolymer as candidates for proton exchange membranes. *Journal of Membrane Science* **2010,** 352, (1), 14-21.
9. Mikhailenko, S. D.; Wang, K.; Kaliaguine, S.; Xing, P.; Robertson, G. P.; Guiver, M. D., Proton conducting membranes based on cross-linked sulfonated poly (ether ether ketone)(SPEEK). *Journal of Membrane Science* **2004,** 233, (1), 93-99.
10. Zhang, Y.; Wan, Y.; Zhang, G.; Shao, K.; Zhao, C.; Li, H.; Na, H., Preparation and properties of novel cross-linked sulfonated poly (arylene ether ketone) for direct methanol fuel cell application. *Journal of Membrane Science* **2010,** 348, (1), 353-359.
11. Luu, D. X.; Kim, D., Strontium cross–linked sPEEK proton exchange membranes for fuel cell. *Solid State Ionics* **2011,** 192, (1), 627-631.
12. Xue, Y.; Fu, R.; Wu, C.; Lee, J. Y.; Xu, T., Acid–base hybrid polymer electrolyte membranes based on SPEEK. *Journal of Membrane Science* **2010,** 350, (1), 148-153.
13. Chen, J.; Maekawa, Y.; Asano, M.; Yoshida, M., Double crosslinked polyetheretherketone-based polymer electrolyte membranes prepared by radiation and thermal crosslinking techniques. *Polymer* **2007,** 48, (20), 6002-6009.
14. Hou, H.; Di Vona, M. L.; Knauth, P., Building bridges: Crosslinking of sulfonated aromatic polymers—A review. *Journal of Membrane Science* **2012,** 423, 113-127.

15. Xu, S.; Luo, Y.; Tan, B., Recent Development of Hypercrosslinked Microporous Organic Polymers. *Macromolecular rapid communications* **2013,** 34, (6), 471-484
16. Rhoden, S. L.; Linkous, C. A.; Mohajeri, N.; Díaz, D. J.; Brooker, P.; Slattery, D. K.; Fenton, J. M., Low equivalent weight Friedel-Crafts cross-linked sulfonated poly (ether ether ketone). *Journal of Membrane Science* **2011,** 376, (1), 290-301.
17. Abu-Thabit, N. Y.; Ali, S. A.; Javaid Zaidi, S., New highly phosphonated polysulfone membranes for PEM fuel cells. *Journal of Membrane Science* **2010,** 360, (1), 26-33.