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Enhanced performance of sulfonated poly (ether ether ketone) membranes by blending fully aromatic polyamide for practical application in direct methanol fuel cells (DMFCs)

Cuicui Li [1], *Zehui Yang* [1], *Xupo Liu* [1], *Yunfeng Zhang* *, *Jiaming Dong*, *Quan Zhang*, *Hansong Cheng*

Sustainable Energy Laboratory, Faculty of Materials Science and Chemistry, China University of Geosciences Wuhan, 388 Lumo RD, Wuhan 430074, China

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ABSTRACT

The high dimensional swelling has been considered as one of the most important issues for obstructing sulfonated poly (ether ether ketone) (SPEEK) membrane with high IEC value as an excellent performance proton exchange membrane (PEM) for direct methanol fuel cell (DMFC) application. Here, we present a facile way to overcome the issue via blending the fully aromatic polyamide (*fa*-PA) into SPEEK membrane. The Influence of the *fa*-PA on the key properties of the fabricated *fa*-PA/SPEEK composite membranes (*fa*-PASPs) was systematically investigated. As the promising dimensional stability of the *fa*-PA, the *fa*-PASPs display excellent dimensional stability both in water and methanol aqueous solution. In addition, the *fa*-PASPs exhibit uniform and smooth morphology due to the same fully aromatic polyamide backbones as SPEEK and strong hydrogen bonding interactions between *fa*-PA and SPEEK with significantly reduced methanol crossover. The remarkable cell performance at high methanol concentration up to neat methanol was significantly obtained, suggesting that the prepared *fa*-PASPs are suitable for using as PEMs in direct methanol fuel cells application.

Introduction

As the consumption of the fossil fuels (coal and oil), the development of new energy storage and conversion techniques has attached an increasing attention all over the world [1–3]. Proton exchange membrane fuel cells (PEMFCs) technique has been considered as one of the most efficient solution to solve the energy and environmental problems due to the high efficiency, environmentally friendly and the wide potential applications, e.g. transportation, stationary and portable electronics [4–6]. Proton exchange membrane (PEM) plays a vital role in transporting protons and blocking electrons and fuels from cathode to anode during the fuel cell operation. Therefore, key properties of high proton conductivity, good thermal, chemical and mechanical stability and low fuel crossover are required for a proton exchange membrane [7]. Moreover, the dimensional stability both in water

* Corresponding author.
E-mail address: zhangyf329@gmail.com (Y. Zhang).

[1] These authors contributed equally to the work.

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and fuel aqueous solutions (methanol and formic acid et al.) has to be considered because the high dimensional swelling of PEM will result in the shedding of catalyst from PEM, finally leads to poor cycle life of fuel cells [8,9]. Perfluorosulfonic acid ionomer membranes, represented by Nafion, possess these attributes, but they are still adversely affected by dimensional stability in the fuel aqueous solution, especially in methanol aqueous solution and serious fuel permeation, hindering their potential application in high methanol concentration DMFCs. As an alternative to Nafion, non-fluorinated acid ionomer membranes have been widely developed [10].

Sulfonated poly (ether ether ketone) (SPEEK) has been considered as one of the most potential alternatives because of its high mechanical strength, excellent chemical stability and low cost [11,12]. The high proton conductivity of the SPEEK based PEMs was always obtained at a high ionic exchange capacity (IEC) value. Unfortunately, the high IEC level will lead to significant dimensional swelling of the SPEEK membranes, giving rise to poor performance of fuel cells. Therefore, great efforts have been made to solve the problem by using cross-linking [13–15], organic/inorganic composite membranes [16] or polymer blends technologies [17]. Polymer blends have been widely applied for solving the dimensional swelling problem of the SPEEK because the advantages of the polymeric filler can be combined into SPEEK membrane for achieving additive promising performances. Meanwhile, the related properties of the mechanical strength, thermal and electrochemical stabilities, fuel permeability and proton conductivity can also be significantly improved [18]. However, the major challenge for developing the polymer blends is the polymer incompatibility since it largely dictates the formation of phase separation during the membrane fabrication process [19,20]. The induced phase separation can form the porous morphology, leads to severe fuel permeation [21]. To the best of our knowledge, polymer compatibility can be enhanced by the strong interactions such as acid-base, ion-dipole, or hydrogen bonding [14,22,23]. In the previous works, polybenzimidazole (PBI) [18] and sulfonated polyimide (SPI) [24] have been blended with SPEEK membrane because these materials possess the polar groups of the imidazole ring or the imide ring, which is beneficial for constructing the acid-base and hydrogen bonding interactions with sulfonic acid groups, O atoms and C=O groups of SPEEK.

Recently, the fully aromatic polyamides (*fa*-PA) have been paid great attentions to their application in proton exchange membrane fuel cells [25–27] or alkaline polymer electrolyte fuel cells [28–32] due to their superior thermal, chemical and mechanical stability, good machinability and low cost. Several experimental results in our previous works demonstrate that the sulfonated polyamide (SPA) based PEMs possess excellent water and fuel dimensional stability comparing to the Nafion and SPEEK membranes [1,25,27,33,34]. In the present work, the fully aromatic polyamide was therefore proposed as filler incorporated into SPEEK membrane to fabricate *fa*-PA/SPEEK composite membranes (*fa*-PASPs) to solve the dimensional swelling problem of neat SPEEK membrane. A series of the *fa*-PASPs with different content of *fa*-PA were thus prepared and the influence of the *fa*-PA content on the related properties of the *fa*-PASPs, such as mechanical strength, water uptake, dimensional swelling, proton conductivity and methanol permeation, was systematically investigated. Remarkably, the water and fuel dimensional swelling of the *fa*-PASPs was largely reduced at both room temperature and 80 °C. The *fa*-PASPs membrane with the *fa*-PA content of 40 wt% shows dimensional swelling of 8.2% and 5.69% in water and methanol aqueous solution, respectively, which are much lower than that of Nafion 117 (31.38% and 17.8%) at 80 °C. The highest power density of the DMFC assembled by the *fa*-PASPs membrane was obtained at a high methanol concentration of 10 M, which is still much higher than the highest value of Nafion 117 at a low methanol concentration of 1 M. Furthermore, the mechanical strength and methanol permeability of the *fa*-PASPs were also largely improved. We show that the blending of the fully aromatic polyamide strategy is important for blocking methanol crossover of the SPEEK membrane to toward neat methanol operation of DMFCs with an enhanced electrochemical performance.

Experimental

Materials

M-phenylene diamine (MPDA, Adamas Reagent, Ltd.), 4, 4′-(9-fluorenylidene) dianiline (BFA, Sigma-Aldrich) and isophthalic acid (IPA, Sigma-Aldrich) were dried at 100 °C under vacuum for 24 h. Lithium chloride (LiCl) (Sigma Aldrich) was dried at 180 °C under vacuum for 24 h. Poly (ether ether ketone) (PEEK, Victrex, Grade 381G) was received from Victrex PLC (England). Pyridine (Py, Shanghai Lingfeng Chemical Reagent Co., Ltd.) was purified by distillation from CaH_2 prior to use. Triphenyl phosphite (TPP, Sinopharm Chemical Reagent Co., Ltd.), dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd), methanol (Sinopharm Chemical Reagent Co., Ltd) and *N*-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd.) was used as received without further purification.

Synthesis of fully aromatic polyamide (*fa*-PA)

The *fa*-PA was synthesized according to the procedure reported by Kiran et al. [34]. A mixture of BFA (1.7598 g, 5 mmol), MPDA (0.540 g, 5 mmol), IPA (1.6952 g, 10 mmol) and LiCl were dissolved in 24 ml NMP, 6 ml Py and 6 ml TPP. The solution was heated to 100 °C and kept at the temperature for 24 h under stirring (Scheme 1). After reaction, the mixture was cooled to 70 °C and then precipitated into 200 ml cold methanol. The *fa*-PA was obtained by filtration upon continuous washing with methanol and ultrapure water. The white *fa*-PA was finally dried at 80 °C in a vacuum oven for 24 h, the yield is above 90%.

Sulfonation of PEEK

The procedure for sulfonation of PEEK was described by Liu et al. [35]. 20 g of PEEK was added into 200 ml of 98% H_2SO_4 at 50 °C for 8 h. After reaction, the mixture was poured into ice cold water under stirring and left it for 12 h. The sulfonated PEEK (SPEEK) was finally collected via vacuum filtration and washed with deionized water until the pH became neutral and then dried under reduced pressure at 100 °C for 12 h for further use.

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