Study on the PI/SPEEK nanofiber composite proton exchange membrane for fuel cells

Peng Wei 1,2, Dong Huang 1,2, Xi Li 1,2, Bensheng Zhu 3, Chuanbo Cong 1,2, Xiaoyu Meng 1,2a, Qiong Zhou1,2b*

1Department of Materials Science and Engineering, New Energy and Material college, China University of Petroleum-Beijing, Beijing 102249, People’s Republic of China
2Beijing Key Laboratory of Failure, Corrosion, and Protection of Oil/Gas Facilities, China University of Petroleum-Beijing, Beijing 102249, People’s Republic of China
3China Helicopter Research and Development Institute, Aviation Industry Corporation of China, Limited, Jingdezhen Jiangxi 333001, People’s Republic of China
a* xymeng800418@sohu.com, b* zhouqiong_cn@163.com

Abstract—Sulfonated poly ether ether ketone (SPEEK) can be selected as the candidate for proton exchange membrane (PEM) used in the fuel cell for its cheap price, great proton conductivity and stability. To further improve its performance, more SO3H were induced into SPEEK but would result in excessive swelling and losing its stability. Polyimide (PI) nanofibers have excellent mechanical properties and can be a supporter to improve stability. In this work, the PI nanofiber was put in the middle of the SPEEK to create the PI/SPEEK nanofiber composite membranes (NCMs). Its morphology of PI/SPEEK NCMs observed by SEM showed that PI nanofiber was almost in the middle of these NCMs. The proton conductivity and swelling ratio of 3%PI/SPEEK were 271.7 mS·cm⁻¹ and 20.0% at 60℃ and 100% RH, which is 29.6% higher and 90.4% lower than that of pristine SPEEK. It was intact after the single-cell test in the fuel cell and its power density was 199.1 mW·cm⁻², but for pure SPEEK there was some broken area on it. The reason was that PI/SPEEK can maintain the durability of the channels for the proton to transport and it can be attributed to an interaction at their interface of PI nanofiber and SPEEK. The 3%PI/SPEEK NCM will have a broad application prospect in PEM fuel cells.

1. Introduction
Proton exchange membrane fuel cells (PEMFCs) have fascinated considerable interests due to their great efficiency of energy conversion and environmental friend [1, 2]. The proton exchange membrane (PEM) was served as electrolytes for the protons to transport and prevent fuel permeability [2]. Sulfonated poly ether ether ketone (SPEEK) is an ideal PEM for its excellent strength and high proton conductivity. But sulfonic acid directly linked to the main chain makes it hard to form a continuous proton transport channel [3]. A common method to raise its proton conductivity was to introduce more sulfonic acid groups to the main chain but it will lead to excessive swelling [4]. Based on the above mentioned, it is important for high-performance PEM in PEMFC to equilibrate proton conductivity and stability [1].

A facile way to solve the above problem is to introduce inorganic polymer to form organic-inorganic nanocomposite PEM [5]. SiO2 [6-9], TiO2 [10-12], ZrO2 [13], g-C3N4 [14-16] were
incorporated into PEM to improve their performance. But it caused the accumulate of fillers, which degrades the performance. Under the magnetic field [17, 18] and electric field [19], the fillers can form aligned functional nanocomposite PEM with highly conductive well-aligned proton channels. If conductive proton channels can be formed in PEM, the proton conductivity will be improved. Based on this assumption, we found electrospinning can form long-range proton transport channels at micro and nanoscales [20]. Due to its versatility and easily scale-up, it has been extensively used in nanostructured PEM [21, 22].

Electrospinning nanofiber can be divided into two categories, one is easy to dissolve into chemical solvent and the other is chemical resistant [23]. For the dissolving one, polymers such as chitosan [24] or Nafion [25] used water as the solvent. And for the chemical-resistant one, the structure of the nanofiber must be stable and steady in the chemical solvent, such as Polyimides (PI) [26-29] and polybenzimidazoles (PBI) [30]. PI as an aromatic imide monomer are well known because of its higher mechanical strength, high chemical and thermal stability [28]. The ultrafine PI nanofibers prepared by electrostatic spinning have a large specific surface area and great durability, thus improving the performance of composite membranes [26]. On this basis, some researchers placed ultrafine PI nanofibers in the middle of SPEEK [31] or SPAES [32] for the efficient microbial electrolysis cell.

In our work, pyromellitic dianhydride (PMDA) and 4,4-oxydianiline (ODA) in the N, N-dimethylformamide (DMF) were used to form poly (amic acid) (PAA) solutions. Then the PAA solutions were electrospun into PAA ultrafine nanofiber when the DMF was evaporated. PI nanofibers were prepared by thermal imidization [26-29, 33]. Then the PI was placed into the center of the SPEEK, so the PI/SPEEK composite membrane was fabricated. For the great chemical stability of PI nanofibers, the PI/SPEEK membrane has high performance. Compared with pure SPEEK, PI/SPEEK had higher stability at high temperature with PI as the framework of the nanofiber composite membrane, and their proton channels will not collapse. And PI didn’t occupy the -SO₃H in the PI/SPEEK nanofiber composite membrane (NCM), its proton conductivity won’t decrease. Its proton conductivity was higher than that of pure SPEEK under high temperatures.

2. Materials and methods

2.1 Materials
Poly (ether ether ketone) (PEEK) powder was supplied by Victrex. PMDA and ODA were provided by Aldrich. Beijing Chemical Reagent Factory provided dimethyl sulfoxide (DMSO), DMF and H₂SO₄ (95-98 wt%) with no further purification.

2.2 Fabrication of x-PI/SPEEK NCMs
SPEEK and PI nanofiber was fabricated and can be seen in our previous work [34, 35]. SPEEK was dissolved in DMSO solution to acquire the clean solutions. PI (x=1%, 2%, 3% and 4%) nanofiber was placed in the middle of the SPEEK solution as displayed in Scheme 1, and the x-PI/SPEEK membrane was constructed after removing the DMSO solution at 80°C for 48 hours.

Scheme 1 The preparation method of PI/SPEEK NCMs
2.3 Characterization
The surface of PI nanofiber and the cross-sectional morphology of all NCMs were inspected by scanning electron microscope (SEM, SU8010). Its chemical structure was determined through Fourier Transform Infrared Spectroscopy (FTIR, Bruker Tensor II/Hyperion). The thermal stability of all membranes was analyzed by a thermogravimetric analyzer (TGA, TA Q5000). Mechanical stability was characterized through the machine (SHIMADZU, AGS-X). The test conditions and processing methods of IEC values, proton conductivity, $E_a$, swelling ratio (SR), water uptake (WU) and fuel cell performance are all the same compared with our previous work [34, 35].

3. Results and discussion

3.1 Cross-sectional morphologies of x-PI/SPEEK NCMs
The x-PI/SPEEK NCMs were prepared by the casting method mentioned above. To further explore the location of nanofiber in these NCMs, the cross-sectional morphology was observed after fracture in the liquid nitrogen through SEM as displayed in Fig. 1. These nanofibers were basically in the middle position of the nanofiber composite membrane. It was flat and there were no defects for the cross-sectional morphology of SPEEK. But for x-PI/SPEEK membranes, the PI nanofibers were pulled out from the SPEEK matrix due to their difference in mechanical performance. Most PI nanofibers even lay in the surface of the cross-sectional surface, leaving some holes in the SPEEK matrix. This phenomenon suggests that PI nanofibers did have excellent mechanical properties compared with the SPEEK matrix.

![Fig. 1 The cross-sectional morphologies of the membranes](image)

3.2 Thermal performance of x-PI/SPEEK NCMs
The thermal performances of the x-PI/SPEEK membranes were detected through TGA and can be seen in Fig. 2. There was only one disassemble step for the PI nanofiber, which occurred at 450°C and above. But for all the NCMs, it can be divided into three steps [36, 37]. The DMF evaporated below 200°C results in degradation at the first step. The fracture of SO$_3$H in SPEEK started to decompose at 200~350°C in the second step. The main chain of SPEEK and PI was decomposed at 450°C and above results in the third disassemble step. All membranes can be used at the service condition of PEM because there was no change in thermal stability for these NCMs after the PI nanofibers were incorporated in the SPEEK matrix.
3.3 Mechanical Properties of x-PI/SPEEK NCMs

Mechanical properties of x-PI/SPEEK NCMs at different conditions have been experimented and the outcome was depicted in Fig. 3 and Table 1. Yield strength (YS) and elongation at break (EB) of SPEEK were 45.9 MPa and 35.1% at dry state. As the increase of PI nanofiber incorporation content, YS and EB increased at the outset then declined. The YS and EB of 2%PI/SPEEK NCM were 53.7 MPa and 85.3%, and it was 17% and 143% higher than that of original SPEEK, respectively. PI could improve the stability of composite membranes after incorporating them into the SPEEK matrix at the dry state.

Table 1 Mechanical properties of x-PI/SPEEK NCMs

| Specimen     | YS (MPa) | EB (%) |
|--------------|----------|--------|
|              | Dry      | Wet (50℃) | Dry      | Wet (50℃) |
| SPEEK        | 45.9     | 16.0    | 35.1     | 142.6     |
| 1%PI/SPEEK   | 50.4     | 15.1    | 52.5     | 142.6     |
| 2%PI/SPEEK   | 53.7     | 16.6    | 85.3     | 85.3      |
| 3%PI/SPEEK   | 52.3     | 21.5    | 36.6     | 162.6     |
| 4%PI/SPEEK   | 48.4     | 19.6    | 14.4     | 62.4      |

PEM was used in hydrate conditions and high temperatures. So all membranes in 50℃ at hydrate conditions were tested. It has the same tendency as tested in dry conditions but different results. The YS of pristine SPEEK was 16 MPa, which is 65% lower than that of SPEEK at dry state. Absorbing excessive water can result in losing its usage in the PEM. However, the YS and EB of 3%PI/SPEEK...
were 21.5 MPa and 162.6%, which were 34% and 14% higher than that of pure SPEEK. PI nanofiber soaked in SPEEK solution could be selected as a potential candidate material for PEM.

### 3.4 WU and SR of x-PI/SPEEK NCMs

All sulfonic acids are on the side chain of SPEEK\[38\] can serve as transport sites for the protons to transport by Grothuss mechanism, and the water as vehicles for protons to transport by vehicle mechanism in PEM \[39, 40\]. IEC values mean the quantity of SO$_3$H in the SPEEK and more sulfonic acids mean high proton transportability but it would cause a high SR of NCM and low mechanical performance \[41\]. Therefore, it is important for PEM to have a proper SR and WU. IEC values of all NCMs are displayed in Table 2.

| Content of PI nanofibers (wt%) | 0     | 1     | 2     | 3     | 4     |
|-------------------------------|-------|-------|-------|-------|-------|
| IEC (mmol/g)                  | 1.654 | 1.589 | 1.588 | 1.554 | 1.524 |

The SR and WU of x-PI/SPEEK NCMs were detected and displayed in Fig. 4. For pure SPEEK, it has a higher sulfonated degree and its SR and WU reached 209% and 485% at 60℃ and 100% RH. As the increase of PI nanofibers in the SPEEK, their SR decreased from 50% to 20% at 60℃ and 100% RH and 3%PI/SPEEK have the lowest SR. The decreased tendency of SR and WU was nearly consistent. PI nanofibers acted as the framework in PEM had great stability would descend their change in SR and WU. 3%PI/SPEEK had the highest comprehensive performance and its SR was 20% and WU was 135%, which would satisfy the demand of PEM in the fuel cell.

![Fig. 4 SR (a) and WU (b) of the NCMs](image)

### 3.5 Proton conductivity of x-PI/SPEEK NCMs

It is crucial for the x-PI/SPEEK membranes to have higher proton conductivity because high proton conductivity means high power density. The proton conductivity of x-PI/SPEEK NCMs was tested range from 25℃ to 60℃ at 100% RH. All the NCMs were soaked at 100% RH for 24 hours for equilibration. Membranes were fixed on the homemade mold to test their proton conductivities through CHI 660E with the same procedure in 100% RH, as shown in Fig. 5a. The addition of PI nanofibers into the SPEEK would decrease the proton conductivity of the NCMs before 50℃. When the temperature reached 60℃, the proton conductivities of all NCMs were higher than that of the original SPEEK, which was 209.7 mS·cm$^{-1}$ at 60℃ and 100% RH. The proton conductivities of 1%PI/SPEEK, 2%PI/SPEEK, 3%PI/SPEEK and 4%PI/SPEEK were 226.4, 288.0, 271.7 and 252.8 mS·cm$^{-1}$ at 60℃ and 100% RH respectively, and it was better than that of original SPEEK at the same condition. The proton conductivity was confirmed by the content of sulfonic acids and the stability of proton transport channels, their synergistic effect determines the proton conductivity of the NCMs. Moreover, it can be attributed to an interaction at their interface of PI nanofiber and SPEEK could be proved by the FTIR part in the next chapter.
$E_a$ was applied to express the minimum energy for protons to transport and could be calculated as shown in Fig. 5b. The $E_a$ of pristine SPEEK was 24.7 kJ/mol, and it is almost near to the value [42]. The $E_a$ of 1%PI/SPEEK, 2%PI/SPEEK, 3%PI/SPEEK and 4%PI/SPEEK were 24.0, 23.8, 23.7 and 21.6 kJ/mol, respectively. The ability of proton transport is increased with the increase of PI nanofiber. Indeed, it can be attributed to an interaction at their interface of PI nanofiber and SPEEK, and it can decrease the value of $E_a$.

![Fig. 5 The curve of proton conductivity (a) and $E_a$ (b) of x-PI/SPEEK composite membrane changed with temperature](image)

3.6 Fuel cell test of x-PI/SPEEK NCMs

The fuel cell test was conducted at 60°C and 95% RH to test their performance. 3%PI/SPEEK was chosen to test single-cell performance for its high proton conductivity and stability. SPEEK was also tested for comparison, as displayed in Fig. 6a. The maximum current density of SPEEK and 3%PI/SPEEK is 338.9 and 332.5 mA·cm⁻² when the power density reaches maximum. But the maximum power density of SPEEK is 185.2 mW·cm⁻² and for 3%PI/SPEEK, it’s 199.1 mW·cm⁻². The addition of PI nanofibers into the SPEEK indeed increased fuel cell property according to the result of proton conductivity. This can be attributed to an interaction at their interface of PI nanofiber and SPEEK, which is favorable for the proton to transport in PEM. And PI nanofibers indeed can improve the stability of PI/SPEEK NCMs as displayed in Fig. 6, which are the photos of MEA (membrane electrode assembly) after the test. The outcome displayed that MEA made of SPEEK can’t stand in the test environment and there were some broken areas on it which are circled in Fig. 6b. But for MEA that is made of 3%PI/SPEEK as shown in Fig. 6c, it was intact after the test in the fuel cell. In a word, 3%PI/SPEEK has a better performance with the balance of the fuel cell performance and stability.

![Fig. 6 Fuel cell test (a) of SPEEK and 3% PI/SPEEK in fuel cell and photos of SPEEK (b) and 3%PI/SPEEK (c) after single-cell test in fuel cell](image)
3.7 FTIR spectra of SPEEK and x-PI/SPEEK NCMs

The vibration of C=C in benzene ring on SPEEK can be found at 1500 cm\(^{-1}\), which is stable during fabrication of membranes, was used for all band areas to normalize and the FTIR spectra were displayed in Fig. 7. The axial stretching and bending vibration of C-N-C were found at 1376 and 724 cm\(^{-1}\), respectively, which can be assigned to PI nanofibers and can be found in 4%PI/SPEEK. But there are no characteristic peaks in other composite membranes this is because the addition of 4% PI nanofibers to the SPEEK was excessive for the PI/SPEEK composite membrane. This phenomenon can also explain why 3%PI/SPEEK has the best comprehensive performance. The intensity of symmetric vibration of O=S=O, stretching vibration of S=O and S-O is increased with the addition of PI nanofibers. This can be attributed to an interaction at their interface of PI nanofiber and SPEEK [43].

![FTIR spectra of PI nanofibers and all NCMs](image_url)

Fig. 7 The FTIR spectra of PI nanofibers and all NCMs

4. Conclusions

The PI/SPEEK NCMs fabricated by immersing PI nanofibers to the SPEEK solutions were used in the PEM for the fuel cell. PI nanofiber was almost at the center of the PI/SPEEK NCM. The incorporation of PI nanofibers indeed has higher performance at high temperatures. PI/SPEEK NCM was intact during the fuel cell test. The PI nanofibers had excellent mechanical performance and would keep the stability of the channels for the protons to transport. Also, this can be attributed to an interaction at their interface of PI nanofiber and SPEEK. As a result, the PI/SPEEK NCM was an essential candidate used in PEM to balance proton conductivity and stability. And the PI/SPEEK NCM can be used in high-temperature PEM, filtration and separation, and so on.

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