Boosting dimensional stability and proton conductive of proton exchange membrane by introducing SO₃H-UiO-66 coated nanofibers

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Abstract. In this work, we fabricated cross-linked pre-oxidized polyacrylonitrile nanofibers (PPNF) coating SO₃H-UiO-66 coated (named SU6@PPNF), which was introduced into sulfonated poly (ether ether ketone) SPEEK to produce membrane with superior proton conductivity, dimensional stability and mechanical properties under hydrated condition. The membrane displays a maximum power density of 172.1 mW cm^{-2} under 100% RH and 60 ℃, which is an increase of 12.2% compared with primary membrane.

1 Introduction

Proton exchange membrane fuel cell (PEMFC) is a significant electric supply technology because of their excellent energy density and environmental friendliness. [1] Among them, PEM is a key component requiring excellent proton conductivity, dimensional stability and mechanical strength. Increasing the concentration of proton conductive groups (e.g., -SO₃H) of membranes can improve proton conductivity.[2] However, excess proton conductive groups would weaken the dimensional stability and mechanical strength, leading to a degradation or even failure for the fuel cell. Therefore, the development of PEM with great conductivity, dimensional stability and mechanical properties is essential for high-performance PEMFC.

The sturdy fibers that building the 3D network in ionomer like steel bars can restrict water absorption, thus improving the dimensional stability and mechanical properties. Acid-functionalized fibers have been proven to build continuous acid-rich layers at the fiber-ionomer interface, which is a significant strategy to boost the efficiency of proton transmission.[3] Metal organic framework (MOF) has regular structure and adjustable groups by changing the ligand, which is beneficial to adjust the groups of fiber according to desired properties when MOF is coated on fibers.[4] MOF-coated fibers can not only functionalize the fiber without occupying the functional sites on the fiber, but also maintain the inherent solvent resistant and mechanical properties of the fibers.[5]

Herein, SU6 is coated on the surface of cross-linked pre-oxidized polyacrylonitrile nanofibers (PPNF) to construct a firm structure with rich proton conducting groups and named SU6@PPNF. SU6@PPNF is incorporated into SPEEK and then the -SO3H is condensed at the interface of them, which provides an efficient channel for proton conduction. The effect of the -SO₃H condensation layer on the proton conduction is verified by comparing the membrane doped with SU6 and PPNF respectively.

2 Materials and Method

2.1 Preparation of SU6@PPNF

PPNF was prepared by oxidizing PAN nanofibers, which was obtained through electrospinning. SU6@PPNF was prepared by hydrothermal reaction. 3.08 mmol of zirconium (IV) chloride and 2.9 mmol of 2-sulfoterephthalic acid monosodium were dissolved in solvent consisting of 18 ml deionized water (DI) and 12.6 ml acetic acid to obtain mixed solution. After vigorous stirring, PPNF was poured into the aforementioned solution and reacted at 80 degrees centigrade for 1 day. The final products were dried at room temperature and named SU6@PPNF.

2.2 Manufcture of SU6@PPNF-SPEEK

13 wt. % SPEEK/DMSO solution was produced by dissolving 0.66 gram of SPEEK in 4 milliliter DMSO solution at 60 ℃. Then, 4 ml SPEEK/DMSO was casted in mold and dried at 80 degrees centigrade for 60 hours to prepare primary SPEEK membrane. PPNF nanofiber and SU6@PPNF nanofiber were flatted on the petri dish with 2 ml SPEEK/DMSO solution, then another 2 ml

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SPEEK/DMSO solution was uniformly covered on nanofibers.SU6@PPNF.

3 Results And Discussion

3.1 Structure characteristics of SU6-PPNF

SU6@PPNF was prepared by a three-step method, and the morphology of fibers was characterized by SEM and STEM. As show in Fig. 1a, the covered layer of SU6 is very dense, and the average diameter of SU6@PPNF is increased to 450 nm. Additionally, SU6@PPNF still maintains a three-dimensional network, which also reflects the excellent structural stability of the PPNF. As can be seen from Fig. 1b, combining with TEM and elemental analysis of nitrogen (red), sulfur (yellow) and zirconium (green), it can be clearly observed that the nanoscale SU6 is coated on the surface of PPNF. These results preliminarily prove the successful preparation of SU6@PPNF.
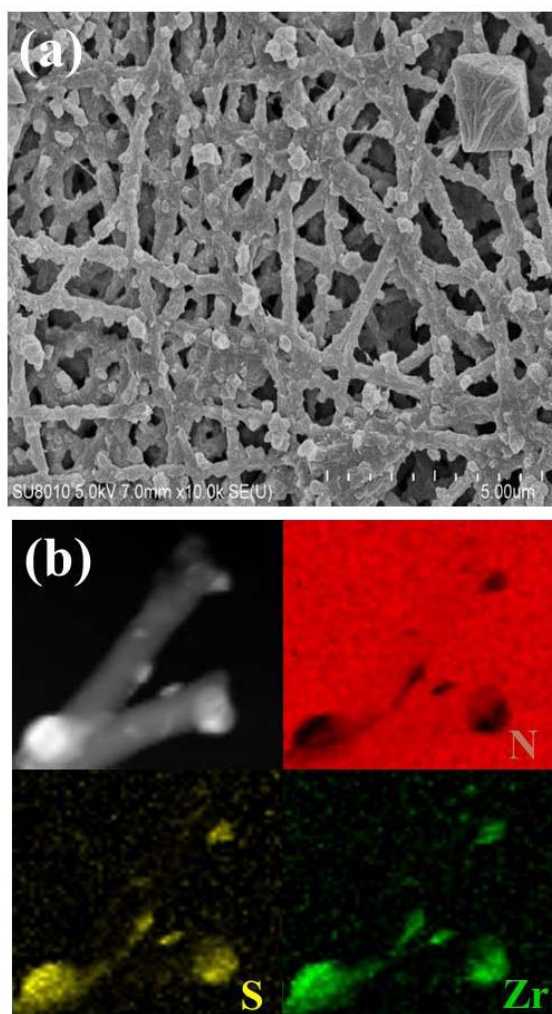

Fig. 1 (a) SEM images of SU6@PPNF, (b) STEM image and lemental elemental analysis of SU6@PPNF.

The structure of fibers was characterized by FTIR (Fig. 2a) and XRD (Fig. 2b). The bands at 2857 cm^{-1} and 1454 cm^{-1} are the stretching vibration of CH$_2$-, whith is weakening of asymmetrically deformed vibration of CH$_3$- (Fig. 2a). These indicate the saturated C-H bonds are replaced by a large number of unsaturated double bonds and ketonic.[6] Additionally, the intensity of the stretching vibration peak assigned to cyano-group at 2242 cm^{-1} is weakened, and the stretching vibration assigned to the aromatic heterocycle C=N occurs at 1598 cm^{-1}. These results also represent that PAN nanofibers are pre-oxidized. After SU6 is coated on PPNF, symmetrically stretching vibration peak attributes to S=O, asymmetrically stretching vibration peak of S=O attribute to carboxylate peaks appearing at 1229 cm^{-1}, 1179 cm^{-1} and 1409 cm^{-1}, respectively.[7] These results further prove that SU6 has been successfully coated on the surface of PPNF. According to fig. 2b, PPNF had an XRD pattern that is consistent with the literature. Obviously, the in-situ growth weakens the crystallization behavior of SU6,[8] and the diffraction peaks attributable to SU6 at 2Theta=6.0°, 7.4°, 8.5° are still observed in the XRD pattern of SU6@PPNF. Above results prove the successful preparation of SU6@PPNF.
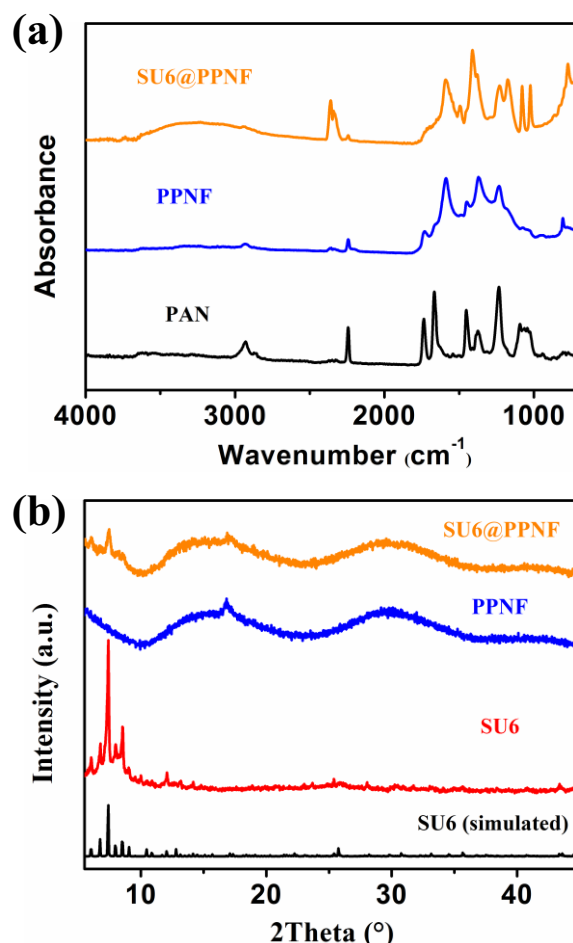

Fig. 2 (a) FTIR patterns and (b) XRD patterns of PAN, PPNF and SU6@PPNF

3.2 Morphology characterization of membranes

Fig.3 is cross-sectional SEM image of membranes. The cross-section of SPEEK was smooth and isotropic (Fig. 3a). In the cross-sectional SEM of PPNF-SPEEK, there are obvious morphological differences between PPNF nanofibers and SPEEK, but there is no obvious defects at the interface between them (Fig. 3b). Additionally, the

cross-section of PPNF was nearly circular (the high magnification image shows in upper right of Fig. 3b) and the diameter of PPNF is around 100-200 nm, which matches up the diameter of PPNF in Fig. 1b. SU6@PPNF was compatible with SPEEK (Fig. 3c) and the diameter of SU6@PPNF witch introduced in SPEEK was consistent with SU6@PPNF in Fig. 1. These results indicate that PPNF and SU6@PPNF also has excellent SPEEK compatibility and DMSO tolerance.
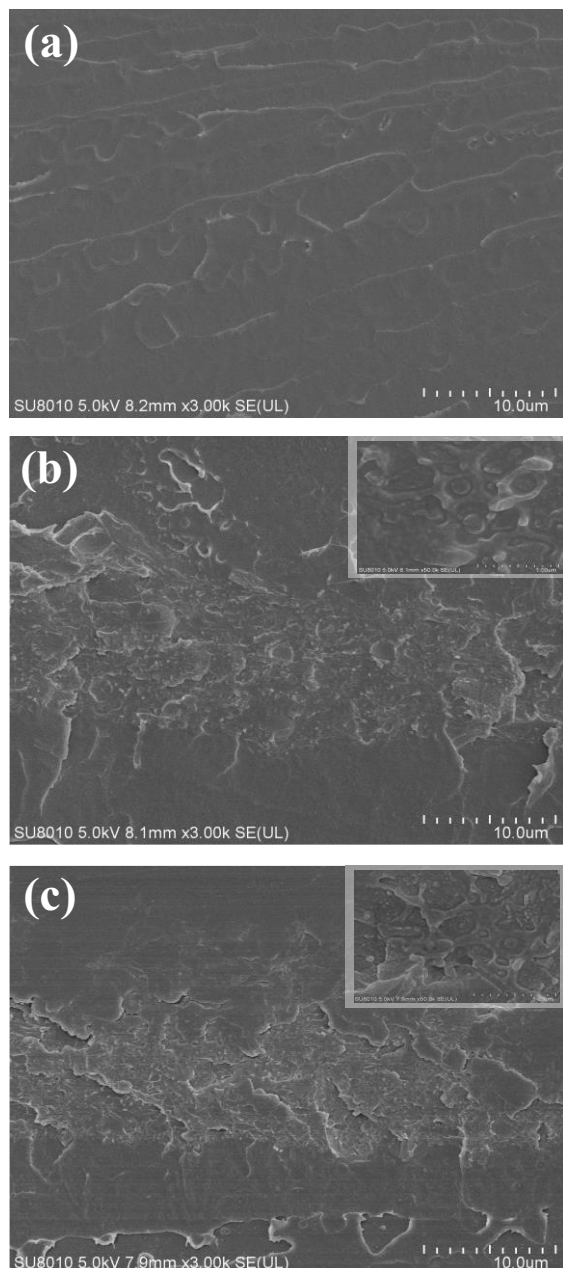

Fig. 3 SEM cross-section images of (a) SPEEK, (b) PPNF-SPEEK, (c) SU6@PPNF-SPEEK.

3.3 Structure characteristics of SU6-PPNF

Water can assist proton conduction, but it also compromises the dimensional stability and mechanical properties.[9] In hydrated status, PEM is prone to degradation, rupture and puncture, so it is crucial to enhance dimensional stability and the mechanical property. The swelling ratio of PPNF-SPEEK membrane

is 22.5 % at 60 °C, which is dramatically lower than that of SPEEK (Fig.4a). Such a low swelling rate of PPNF-SPEEK owes to the three-dimensional network of PPNF and the excellent compatibility between SPEEK and PPNF. Thus, PPNF can significantly inhibit the swelling of membrane. Based on the exceptional properties of PPNF, SU6@PPNF-SPEEK with hydrophilic SU6 also exhibits excellent dimensional stability. At 60 °C and 100 % RH, the area swelling of SU6@PPNF-SPEEK is only 69.1% of SPEEK. These results reveal that incorporating PPNF and SU6@PPNF nanofibers into SPEEK is an effective solution to improve the dimensional stability of membranes.
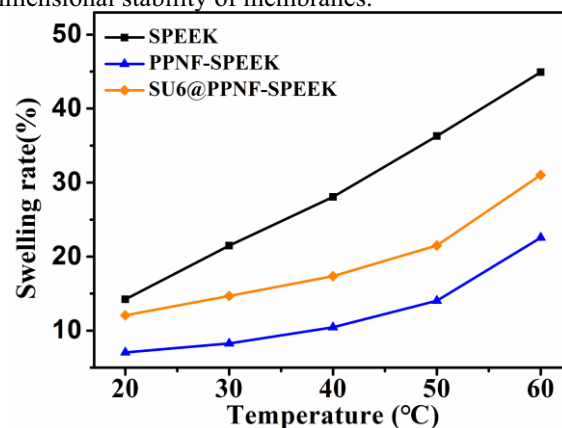

Fig. 4 SEM cross-section images of (a) SPEEK, (b) PPNF-SPEEK, (c) SU6@PPNF-SPEEK.

3.4 Proton conductivity and water uptake

Proton conductivity is a vital parameter to assess PEM performance. Fig. 5a is the temperature-dependent conductivity of membranes at hydrated condition and all conductivities was positively correlated with temperature. The conductivity of SPEEK-based membranes was even better than commercial Nafion 117 at 60 °C under hydrated condition. The conductivity of PPNF-SPEEK at 60 °C was 127.2 mS·cm^{-1}, which was 21.6% lower than SPEEK. The decrease in conductivity of the proton exchange membrane was undesirable. Therefore, SU6@PPNF was prepared and incorporated into SPEEK. The proton conductivity of SU6@PPNF-SPEEK increased to 154.6 mS·cm^{-1}. Combining results of conductivity and water uptake of SU6-SPEEK indicated that SU6 enhances conductivity by increasing the content of proton carriers reason (Fig. 5a and Fig. 5b). Otherwise, the excellent compatibility of SU6@PPNF and SPEEK can build continuous -SO3H condensation layer at the interface between them.[10-12] To prove the effect of -SO$_3$H condensation layer on conductivity, SU6-PPNF-SPEEK was prepared by incorporating the same proportion of SU6 and PPNF into SPEEK, simultaneously. The conductivity and water absorption of the SU6-PPNF-SPEEK were significantly lower than that of SU6@PPNF-SPEEK although they have similar components (Fig. 5a and Fig. 5b). There was still an inert area in SU6-PPNF-SPEEK with insufficient proton carriers and proton donors. These results indicate that the -SO3H condensation layer at the interface of SU6@PPNF and SPEEK can effectively improve the

efficiency of proton conduction. (The schematic image of the proton conduction of SU6@PPNF-SPEEK was shown in scheme 1).
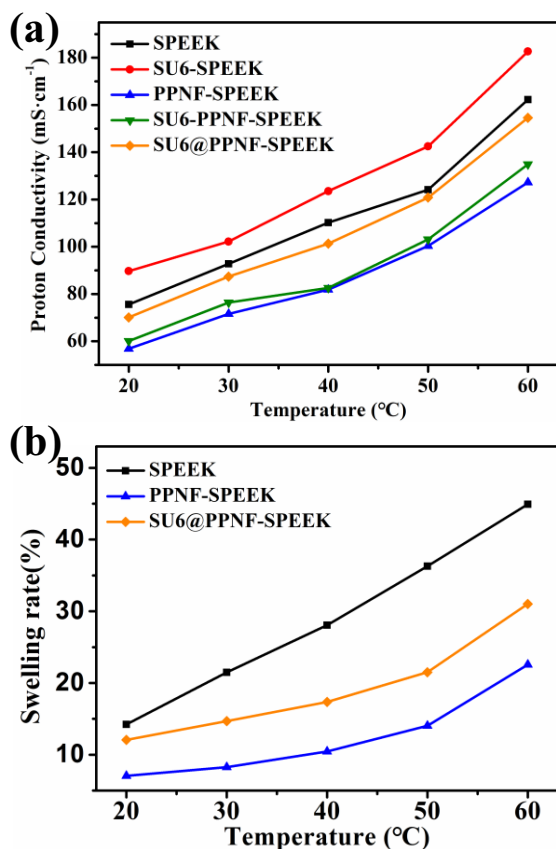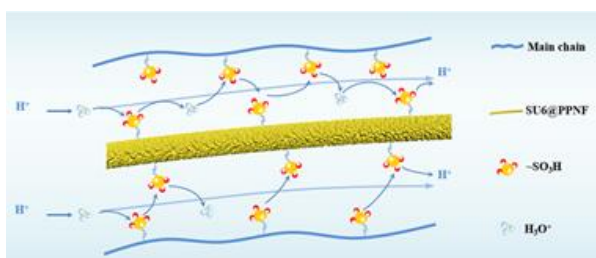

(a)

(b)

Fig. 5 (a) Proton conductivity, (b) water uptake of pristine SPEEK and SPEEK composite membranes.

Scheme 1 Schematic image of proton transport of SU6@PPNF-SPEEK

3.5 Fuel cell performance

Considering the excellent comprehensive performance of SU6@PPNF-SPEEK, we prepared the membrane electrode assembly of SU6@PPNF-SPEEK for fuel cell performance testing. The MEA of Nafion 117 and primary SPEEK was characterized as comparisons. Before the test, all cells were activated under fully hydrated conditions at 60 ℃ for 8 hours. The maximum current density and power density of SPEEK are better than Nafion 117, which is 526.4 mA·cm^{-2} and 150.3 mW·cm^{-2} (Fig. 6). The maximum current density and power density of SU6@PPNF-SPEEK was 576.4 mA·cm^{-2} and 172.1 mW·cm^{-2}. The excellent cell

performance of SU6@PPNF-SPEEK was attributed to the following reasons: (i) -SO3H condensation layer along SU6@PPNF promotes proton conductivity; (ii) the excellent dimensional stability of SU6@PPNF-SPEEK reduces the probability of separation of the catalytic layer from the membrane. These show that SU6 coated PPNF can effectively improve fuel cell performance.
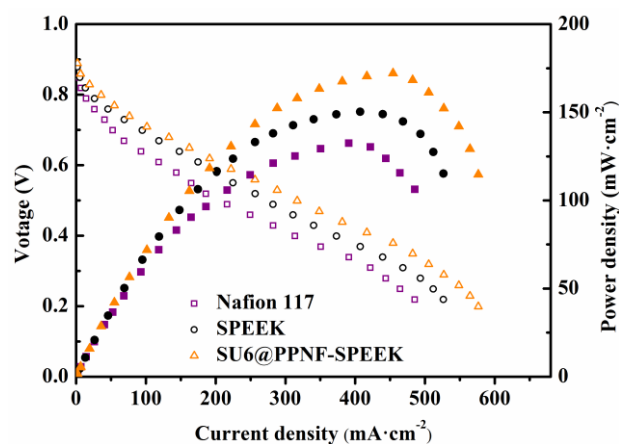

Fig. 6 Hydrogen fuel cell performance.

4 Conclusions

To summarize, the cross-linked PPNF was sulfonated by SU6. The membrane with high conductivity, fabulous dimensional stability and wonderful mechanical property was produced by incorporating SU6@PPNF into SPEEK. By comparing the conductivity of SU6@PPNF-SPEEK and SU6-PPNF-SPEEK, it revealed that the -SO3H condensation layer at the interface of SU6@PPNF and SPEEK is crucial to enhance the efficiency of proton conduction. Therefore, SU6@PPNF could balance the dimensional stability and electrochemical performance of the membrane, and its maximum power was 172.1 mW cm-2 under fully hydrated conditions at 60 ℃. This work provided a novel strategy for enhancing membranes dimensional stability and mechanical strength without reducing electrochemical performance.

Aknowledgements

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