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Research article

Sulfonated poly (fluorenyl ether ketone nitrile) membranes used for high temperature PEM fuel cell

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A B S T R A C T

A series of sulfonated poly (fluorenyl ether ketone nitrile)s with different equivalent weights (EW) ranging from 681 to 369 g mequiv.$^{-1}$ were used to assemble a series of single proton exchange membrane fuel cells (PEMFC) in their turns. The mechanical strength and morphology of the copolymer were studied systematically. This paper mainly evaluated and compared their cell performance. The polarization curves showed that the prepared films have good performance at low temperature and high relative humidity. Due to the increase of temperature, dehydration seriously deteriorated the performance of the cell, especially for the membrane with high electron flow and low proton conductivity. However, at 100 °C, the cell performance of the membrane containing 441 g mequiv.$^{-1}$ was even better than that of Nafion@117 membrane. It could even be used at 125 °C. In the short life test, the output power density was stable at about 0.24 W•cm^{-2} within 24 h. These results show that our membranes were suitable for the applications of PEM fuel cell at high temperature.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical energy converters that can directly convert chemical energy into electrical energy. As a clean, quiet and efficient vehicle transport power supply, its potential application in electrochemical devices is more and more concerned [1, 2, 3]. At present, perfluorinated membrane, such as DuPont Nafion membrane, has become the main membrane of PEMFC due to its excellent performance [4]. However, these membranes still have many disadvantages, especially in large-scale applications, such as high cost, high methanol permeability and poor performance at operating temperature above 80 °C [5, 6, 7, 8]. In addition, it is necessary to increase the operating temperature to improve mass transfer, avoid catalyst poisoning and electrode immersion, improve efficiency and reduce the cost and complexity of the system [9, 10, 11]. Although some polyaryl heterocyclic compounds (such as polyimide, polybenzimidazole, polybenzoxazine, etc.) and organic-inorganic composite membranes have been successfully prepared, more membrane materials with low price, high proton conductivity and good mechanical strength

need to be developed, especially under high temperature operation conditions [9,12, 13, 14, 15, 16].

Sulfonated aromatic polymer is an ideal raw material for proton exchange membrane, which is easily synthesized from industrial monomers. In addition, its physicochemical properties can be easily adjusted by functionalizing monomers or modifying the final polymer. Therefore, as alternative proton exchange membrane, Sulfonated aromatic polymer has made significant progress in the synthesis [17, 18, 19, 20, 21]. In general, these sulfonated polymers require low equivalent (EW) to obtain high electrical conductivity [11]. Unfortunately, low water content usually leads to high water absorption and even loss of mechanical properties of membranes, but Sulfonated membrane crosslinking post-treatment can limit water absorption by sacrificing proton conductivity [12]. Therefore, it is necessary to maintain good proton conductivity and reduce water absorption to obtain high mechanical properties.

In the previous work [13], A series of sulfonated poly (fluorene ether ketone nitriles) with low EW were synthesized by one-step polycondensation from commercial raw materials. Different from the traditional sulfonated aromatic polymers, they have high proton conductivity

and low water uptake unexpectedly. In addition, they also show good thermal and chemical stability. These characteristics make it have broad application prospects in high temperature proton exchange membrane fuel cells. In this paper, a series of PEMFC membranes with different EW values were prepared on a large scale. The properties of the composites at 30–100 °C were evaluated and compared. In particular, PEMFC with membrane capacity of 441gmequiv.$^{-1}$ was selected as the model cell, and its performance and life at 125 °C were measured. As far as we know, this is the first time to study the high temperature cell performance of this kind of membrane. The purpose of this paper is to reveal the possibility of application of Sulfonated Poly (fluorene ether ketone nitrile) in high temperature PEMFC.

2. Experimental

2.1. Materials

According to the previous work [13], a series of sulfonated poly (fluorene ether ketone nitriles) with different EW (polymer **a-f**) were prepared on a large scale. Their molecular structures are shown in Figure 1. The EW of polymers **a-f** were 681, 569, 494, 441, 401 and 369 gmequiv.$^{-1}$, respectively, and the water remaining after TGA test and proton conductivity of the polymers were shown in Figures 2 and 3, respectively. N. N-Dimethylacetamide (DMAC) is purchased from commercial sources and can be used without further purification.

2.2. Preparation of polymer membrane

The polymer solution with a mass fraction of 5% (mass fraction) was cast on a glass plate in a dust-free environment, and then vacuum dried at 60 °C and 110 °C for 48 h to form membrane. And the thickness of all the membranes is about 175 μm.

2.3. Preparation of membrane electrode assemblies (MEAs)

MEAs are prepared with standard catalyst ink according to a known procedure [14]. Carbon supported platinum catalyst (0.5 mg•cm^{-2} Pt, Johnson Matthey platinum 40% on Vulcan XC-72R carbon) was used as anode and cathode of PEMFC. TGP-H-120 carbon paper (Toray) with thickness of 330 μm was used as gas diffusion medium (GDM). The procedure is the same as that described in reference 13.

2.4. Measurement

Mechanical tensile tests were performed on SANS-CMT at a rate of 1 mm•min^{-1} at 25 °C and 100% RH. The test was carried out on specimens with a size of 20 mm × 2 mm. The preparation steps of TEM samples are as follows: firstly, the membrane was dyed overnight in saturated lead acetate solution, then washed with water, and finally dried in vacuum at room temperature for more than 4 h. The morphology of the stained membranes was observed by transmission electron microscopy (TEM, FEI Tecnai G2 Spirit) at 120 kV. The effective area of MEA for fuel cell test was controlled at 4 cm^2. Single PEMFC was studied under the conditions of 100% relative humidity and 0 MPa back pressure using pure hydrogen
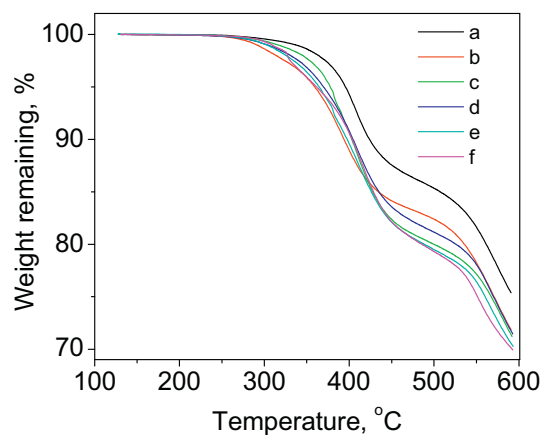

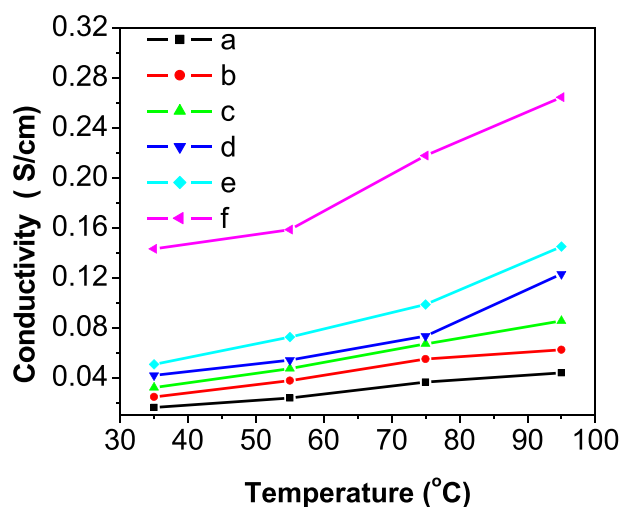
Figure 2. TGA curves of polymers **a-f**.

Figure 3. Proton conductivities of polymers **a-f** as a function of temperature.

and pure oxygen as reaction gases. In order to provide sufficient oxidant for the fuel, the gas flow rate was fixed at 1.5 times the stoichiometric ratio of hydrogen and twice the stoichiometric value of oxygen. On the fuel cell test-bed, the polarization curve is obtained by applying constant current at each point for 3 min (Arbin instruments, 160269).

3. Results and discussion

3.1. Mechanical strength of the wet membranes

Since proton exchange membrane fuel cells (PEMFC) usually operate at a certain humidity to obtain better power output, it is important to maintain the mechanical strength of the electrolyte membrane under humidification conditions. The mechanical strength of wet membrane **a-f** is shown in Figure 4. In general, under wet conditions, the electrolyte membrane becomes weaker due to the absorption of water as a plasticizer [15]. However, the maximum tensile strength of wet membrane **a-e** is still 18.0–41.5 MPa, and the elongation at break is 14.8–36.7%, depending on the EW value. In addition, the mechanical strength of the wet membrane **a-d** is even comparable to that of the crosslinked multi block sulfonated poly (aryl ether ketone nitrile) membrane measured at 30% RH [16]. In the literature [17], many membranes with tensile strength less than 15 MPa have been successfully applied to PEMFC and show good cell performance. Therefore, the tensile strength of **a-e** membrane is greater than 18 MPa, which indicates that the strength of **a-e** membrane is sufficient to meet the mechanical properties

Figure 1. Molecular structure of polymer **a~f**. polymer **a**, x = 0.4; polymer **b**, x = 0.5; polymer **c**, x = 0.6; polymer **d**, x = 0.7; polymer **e**, x = 0.8; polymer **f**, x = 0.9.

requirements of PEMFC. Small strain is also beneficial because the size of MEA should show little change under fuel cell operating conditions. Due to the high water uptake, the tensile strength of e membrane is very low and the elongation at break is very high [13].

3.2. Morphology

The hydrophilic hydrophobic microphase separation of PEM can limit the water absorption of ionomer membrane and promote proton transport. Therefore, the morphology of silver ion stained membrane d was studied by transmission electron microscopy (TEM) and compared with Nafion@117. In TEM images, the dark and bright areas represent hydrophilic and hydrophobic regions respectively. As shown in Figure 5, spherical ion clusters of relatively uniform size are dispersed throughout the membrane d, similar to Nafion@117. The results show that membrane d has good hydrophilic/hydrophobic microphase separation, which may hinder water swelling and facilitate proton transport. This partly explains the reasons for its low water absorption and high proton conductivity.

3.3. Single cell performance of membrane a-e and Nafion® 117

The effects of temperature and EW on the cell performance were investigated in detail. A series of polarization curves of membranes **a-e** at several operation temperatures between 30 and 90 °C at RH 100% were displayed in Figure 6. Since the water uptake of membrane **e** was too high at higher temperature (80.6% at 55 °C) [13], the performance of the cell is only evaluated at 30 and 40 °C. At 30 °C, the membrane e is superior to Nafion@117 with a maximum current density of 0.5 A · cm^{-2}. It also performs well at 40 °C. Therefore, PEMFC devices driven by membrane e can be started quickly at low temperature. Fast-start is also one of the important performance of fuel cell. When the operating temperature of membrane **a-d** increases from 30 °C to 90 °C, the average current density increases and the performance of the cell is improved. This can be explained by the increased catalytic activity in the liquid membrane as well as in the enhanced water transport [18]. The excessive liquid water accumulated in the pores of the gas diffusion layer and catalyst layer would increase the oxygen transport resistance and therefore reduce the cell performance [19]. Moreover, cell performance was also enhanced with the EW of membrane **a-d** decreasing from 681 to 441 g mequiv.$^{-1}$ due to the increase of proton conductivity [13]. The optimal operation temperature of all the prepared membranes was 90 °C, 15 °C higher than that of Nafion® 117.

Figure 4. Mechanical strength of wet membranes **a~f**.

For comparison, Figure 7 depicts the polarization curves of the membrane **a-d** at 90 °C and Nafion@117 at 75 °C (the best performance of Nafion@117). The maximum current density of **a-d** membrane is 0.65, 1.0, 1.02 and 1.25 A · cm^{-2}, respectively, while the current density of Nafion@117 is only 0.87 A · cm^{-2}. At 0.6 V, the current density of b, c and d is 0.27, 0.27 and 0.45 A · cm^{-2}, while that of Nafion@117 is only 0.25 A · cm^{-2}. It can be seen that although membrane **b** and membrane c are not as good as membrane **d**, they also have good cell performance. It should be noted that the cell performance of membrane **b**, **c** and **d** is better than that of Nafion@117. The results show that the membrane **b**, **c** and **d** can be used as proton exchange membrane and have good cell performance at 100 °C. Due to the special molecular structure containing nitrile group, high proton conductivity and low water absorption contribute to such excellent single cell performance.

Hydrogen crossover refers to the poor permeation of hydrogen through proton exchange membrane (PEM). High hydrogen crossover rate will lead to the decrease of open circuit voltage (OCV) and fuel efficiency, and even lead to pinhole formation and membrane degradation. Therefore, low hydrogen crossover is the first choice for fuel cell applications, and OCV is a good indicator of hydrogen transfer from the PEM to the cathode [18]. As shown in Figure 7, the OCV of membrane **a-d** and Nafion@117 are 1.0, 0.97, 0.97, 0.95 and 0.94 V, respectively. With the decrease of EW of these membranes, their OCV values decrease, indicating the increase of hydrogen exchange capacity. This result is consistent with that reported by Dai et al. [20]. This is because the water absorbed in the membrane has a great influence on the hydrogen transfer. With the decrease of EW, the higher the water absorption and the deeper the ionization. The cluster formed by hydrated ions of polymer can enhance the crossover of H$_2$ [22].

When the cell temperature rises to 100 °C, the maximum relative humidity can only reach 70% when the gas back pressure is 0 MPa. When the temperature of the cell is higher than the humidification temperature, the evaporation rate of liquid water in the cell is significantly accelerated, resulting in the drying of the membrane and the increase of proton transport resistance. Figure 8 shows that dehydration at 100 °C reduces the cell performance of all membrane **a-d**. Obviously, the negative effect of dehydration on cell performance inhibits the positive effect of accelerating the reaction rate due to the increase of temperature at 100 °C. The current density decreases from 1.0 A•cm^{-2} at 90 °Cto 0.3 A•cm^{-2} at 100 °C. All other membranes have similar effects. In addition, the lower the proton conductivity of the membrane, the lower the cell performance caused by dehydration. In other words, dehydration has little effect on the membrane with low EW and high proton conductivity, which is consistent with Dai's results [20]. Herein, membrane **d** still showed very good cell performance, even better than Nafion@117 at 75 °C and RH 100%, indicating that membrane **d** could be potentially used in PEMFC at much higher temperature (e.g. 100 °C).

High temperature operation can improve the allowable level of CO in the anode of fuel cell, accelerate the reaction rate of anode and cathode, and promote the water management of fuel cell system [23]. Therefore, the PEMFC with d-membrane is chose as the model cell at 125 °C. From 110 °C to 125 °C, as shown in Figure 9, the current density is 0.3, 0.2 and 0.15 A · cm^{-2}, respectively. The cell with Nafion@117 membrane can hardly output any power at 120 °C due to its low glass transition. In addition, the OCV of d membrane is still at a high level of 0.96 V at 125 °C, while that of Nafion@117 is only 0.85 V at 120 °C. That is to say, the d membrane is still in good condition at higher temperature, unlike SPEEK, which will puncture above 90 °C [24]. It means **d** membrane could be used in higher temperature proton exchange membrane if the dehydration problem could be overcome technically.

3.4. Short lifetime of PEMFC based on membrane d

The service life of membrane d is very important for its practical application, so it is evaluated and the results are shown in Figure 10. It
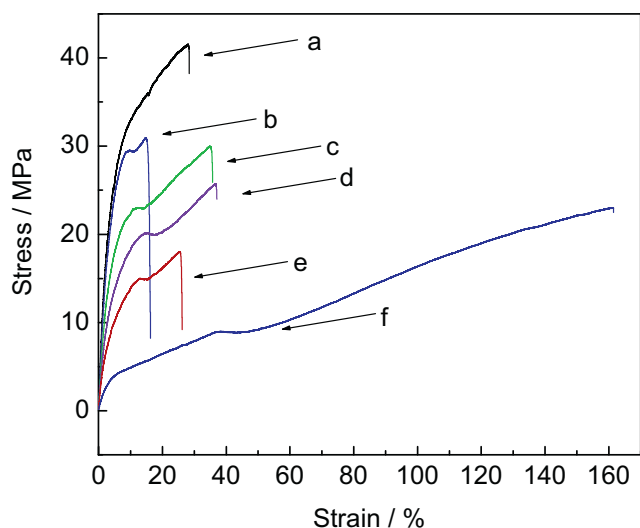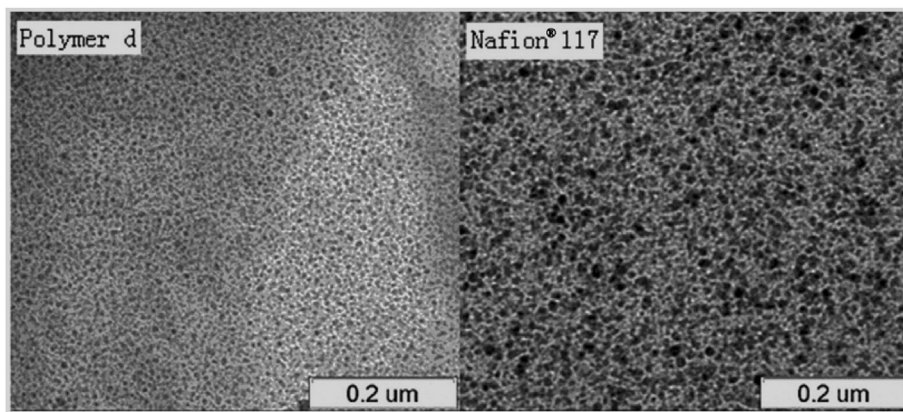
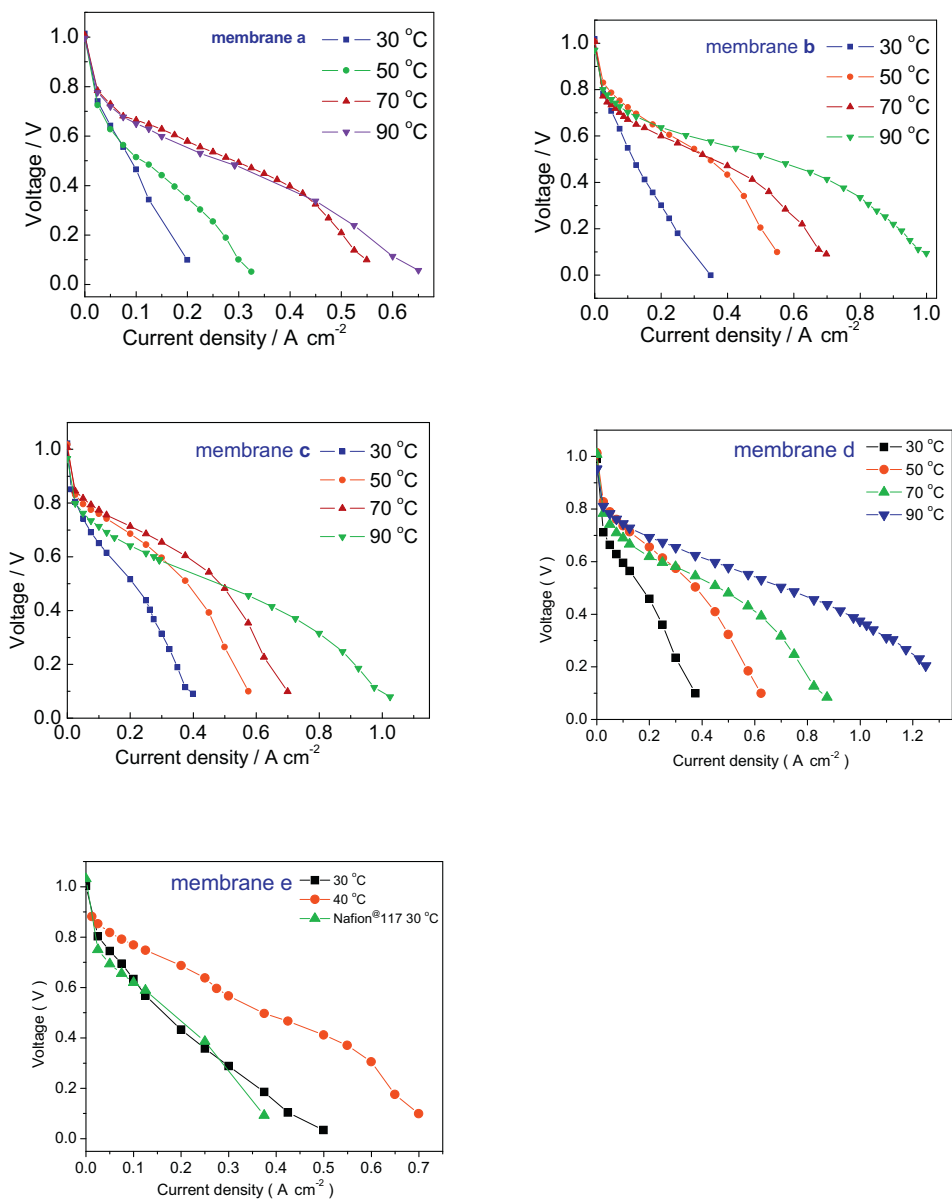**Figure 5.** TEM images of membrane **d** and Nafion® 117.

Figure 6. Polarization curves of fuel cell using membrane **a, b, c, d, e,** and Nafion® 117 as PEM. Operation conditions: 100% relative humidity (under 100 °C), 0 MPa gas back pressure, cell temperature and membrane as referred in the figure.
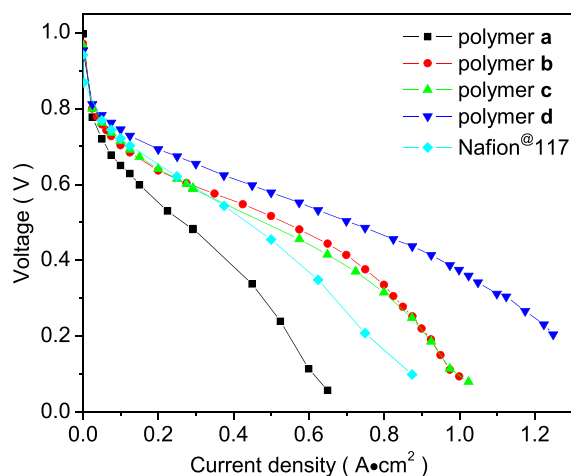
Figure 7. Polarization curves of fuel cell using membranes **a~d** and Nafion® 117 as PEM at the cell temperature of 90 °C for membrane **a~d** and 75 °C for Nafion® 117.
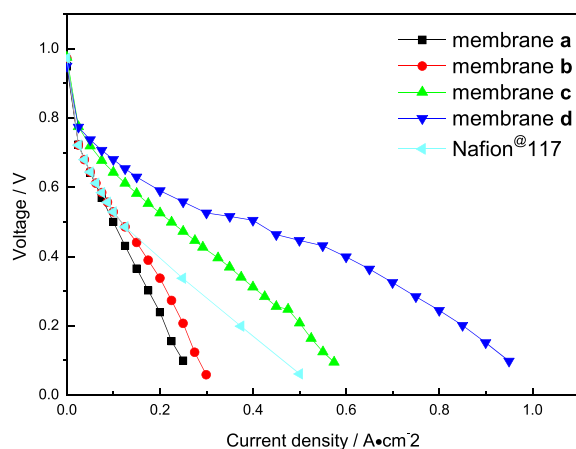

Figure 8. Polarization curves of PEMFC using membrane **a~d** and Nafion® 117 as PEM at the cell temperature of 100 °C, operation conditions: 70% relative humidity, 0 MPa gas back pressure.
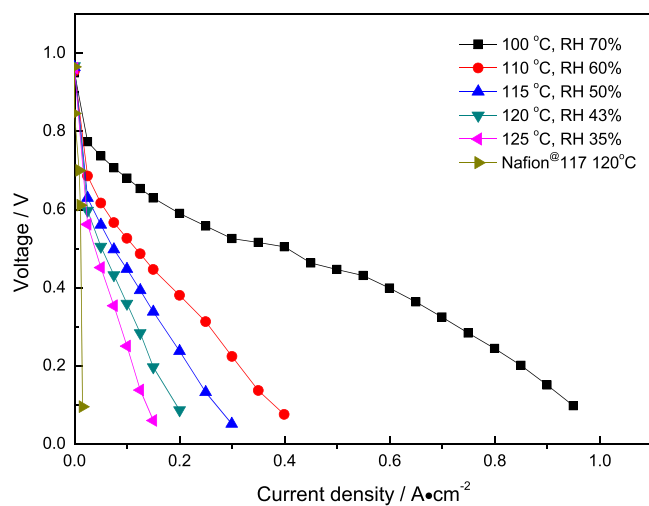

Figure 9. Polarization curves of PEMFC using membrane **d** and Nafion® 117 as PEM at the referred cell temperature, operation conditions: 0 MPa gas back pressure.
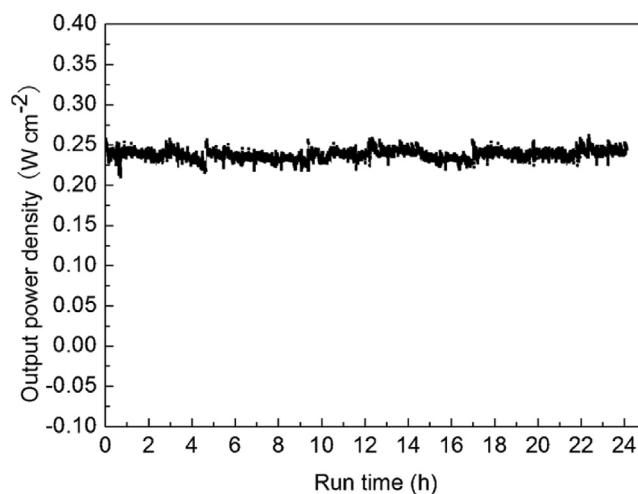

Figure 10. Lifetime measurement of PEMFC using membrane **d** as PEM, operation conditions: 100% relative humidity, 0 MPa gas back pressure and cell temperature of 90 °C.

can be seen that the single fuel cell can run successfully for 24 h at a constant voltage of 0.6V. In the life test, the output power density is stable at about 0.24W•cm^{-2}, and there is no attenuation even after 24 h. The stable output power indicates that the d membrane has no obvious degradation in such a short time. The experimental results show that the self-made polymer is durable in the actual operation of fuel cell.

4. Conclusion

A series of home-made membranes **a-e** exhibited good mechanical strength, and a clear hydrophilic–hydrophobic microphase separation morphology was observed in membrane **d**. The cell performance of membranes **a-d** was enhanced with increasing temperature from 30 to 90 °C. The best cell performance assembled from membranes **b-d** was much better than that from Nafion®117 membrane. When the cell temperature was raised to 100 °C, the cell performance became worse due to the dehydration. However, the cell performance from membrane **d** kept almost unchanged, which was even better than the best one from Nafion® 117. With increasing temperature from 110 to 125 °C, the highest current density decreased from 0.3 to 0.2 and 0.15 A•cm^{-2}, whereas the cell made from Nafion® 117 membrane hardly output any power at 120 °C. In the short-life time test, the output power density of membrane d is stable at about 0.24 W•cm^{-2} in 24 h, which proves that the film is suitable for the application of high temperature PEM fuel cell.

Declarations

Author contribution statement

Yingnan Zou: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mei Yang: Conceived and designed the experiments; Analyzed and interpreted the data.

Guoqing Liu: Contributed reagents, materials, analysis tools or data.

Chungang Xu: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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