Supporting information

Proton exchange membrane fabricated from chemically heterogeneous nonwoven with sandwich structure by the program-controlled co-electrospinning process

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EXPERIMENTAL SECTION

Materials. The SPFEK polymer used was obtained from the scale up production line of our laboratory, and the synthesis procedure has been published earlier. The structure of SPFEK is depicted in Fig. 1e. Poly(diallyldimethyl ammonium chloride) (PDDA, 20 wt% in water, molecular weight 100,000–200,000) and poly(styrene sulfonic acid, sodium salt) (PSS, molecular weight 500,000) was purchased from Alfa Aesar. Nafion 117 was supplied by DuPont chemical. Poly(ether sulfone) (PES) was purchased from Tianjin Shengtai chemical Plant, China. N,N-dimethylacetamide (DMAc), Hydrochloric acid, Sodium chloride, Ferrous sulfate heptahydrate, Sulfuric acid (95–97 %) and Hydrogen peroxide (30 wt%) were obtained from commercial sources.

Fabrication of Chemically Heterogeneous Nonwoven composed of bead-free SPFEK nanofiber and beaded PES nanofiber. The schematic of the custom-built electrospinning apparatus used to prepare nanofibrous nonwoven is shown in Fig. S1. The two needles were fixed on the same metal electrode to ensure that the same voltages were applied during the co-electrospinning process. A nonwoven contained both SPFEK nanofibers and PES nanofibers obtained on the collector by moving the metal electrode back and forth along a horizontal axis. The typical electrospinning parameters were as follows: 30% (w/v) SPFEK (IEC of 1.45 mmol/g) solution in DMAc and 20% (w/v) PES solution in DMAc were loaded into syringe A and syringe B, respectively. A voltage of 30 KV was applied between the metal electrode and the grounded collector. The distance between the two needles was fixed at 1 cm, the metal electrode moved back and forth at a speed of 1 mm/s along a horizontal axis 80 mm in length. A grounded aluminum plate (5 cm×9 cm)
served as the collector. The needle-to-collector distance was 18 cm. A syringe pump was used to squeeze out
the polymer solutions through the needles (inner diameter 0.45 mm). The duration of electrospinning process
was 5 h, and the squeezing speeds of the two polymer solutions were program-controlled independently. For
the first two hours, only SPFEK solution was squeezing out and its squeezing speed was fixed at 0.18 ml/h
for the whole 5 h. For the third hour, PES solution was co-electrospun as well as SPFEK solution, and the
speed of PES solution was controlled at 0.09 mL/h. For the last 2 h, PES solution was stopped squeezing out
and only SPFEK solution was kept squeezing out to finish the electrospinning process. A bench-top
hydraulic press was employed to preliminarily compact the chemically heterogeneous sandwiched nonwoven
with a pressure of 10 MPa at room temperature. The nonwoven was compacted with thickness reduced from
300 to 130 μm in 2 minutes. Fig. S2 shows the surface appearance of the nonwoven after compaction.

The LBL self-assembly of PDDA-PSS multilayer was carried out by alternate dipping of the pre-compacted
nonwoven in PDDA (10 mM) and PSS (10 mM) solutions at room temperature for 10 minutes. After each
dipping step, the nonwoven was washed with deionized water. The LBL self-assembly nonwoven with five
PDDA-PSS bilayers was finally washed with deionized water, followed by protonation treatment in 0.5 M
H2SO4 at 80 °C for 1 h, then washed again with deionized water and dried at 110 °C for 2 h.

At last, the nonwoven was immersed in mixture solvent of DMAc and water (V_{DMAc} : V_{water} = 10 : 90) at
room temperature for 3 minutes, wiped excess solvent on surface with filter paper, then compacted under a
pressure of 1 MPa at 100 °C for 3 h when the nonwoven was surrounded by four pieces of solid paper in 110
μm thickness as shown in Fig S4. The resulting yellowish transparent F-SPFEK membrane in a thickness of
110 μm was further dried in a vacuum oven at 110 °C for 10 h, immersed in 0.5 M H2SO4 at 80 °C for 1 h,
then washed and stored in deionized water.

**Membrane characterization.** F-SPFEK membrane was characterized in terms of ionic exchange capacity
(IEC), water uptake, swelling ratio, mechanical strength, oxidative stability, proton conductivity and fuel cell
performance. Measurements were also conducted on pretreated Nafion 115 (immersing for 30 min at 80 °C
each in 5 wt% H2O2, deionized water and 8 wt% H2SO4) and a homogeneous SPFEK membrane (IEC,
1.45 mmol/g) with a thickness of 120 μm cast directly from 10 wt% SPFEK solution in DMAc (dried at 80 °C
for 24 h in hot air circulation oven and further dried at 110 °C for another 10 h in vacuum oven).
The IEC of the membranes were determined by traditional titration using NaOH solution. The water uptake measurements were conducted by measuring the weight differences between fully hydrated membranes and vacuum dried membranes. The dry membranes were obtained under vacuum at 110 °C for 10 h. The water uptake was calculated according to the following Eq. 1:

$$\text{Water uptake} \, (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad \text{(Eq. 1)}$$

Here, $W_{\text{wet}}$ and $W_{\text{dry}}$ are weights of the fully hydrated and dry membranes, respectively.

Mechanical tensile strength was determined at 30 °C and 100% relative humidity by a universal test machine (Model: SANS-CMT, Shenzhen, China). The cross-head speed was set at 2 mm/min. The samples were prepared by cutting them into a dumbbell shape. Oxidative stabilities were investigated by immersing the membrane samples in Fenton’s reagent (2ppm FeSO4 in 3 wt% H2O2) at 80 °C for 1 h. The stabilities were evaluated by the reduction in mass. Proton conductivity measurements were performed using a Solartron electrochemical interface 1287 and 1255B instrument over the frequency range from 1 MHz to 100 Hz. Specimens of the membranes were soaked in deionized water for 24 h prior to the test. Each specimen was clamped between two gold electrodes and placed above liquid water in a thermocontrolled humidity chamber. Equilibration time at each temperature was fixed at 0.5 h.

A membrane–electrode assembly (MEA) with 4 cm² active area was used in the fuel cell tests. A single PEMFC cell was operated at 80°C in humidified H2 and O2 gases with no gas back-pressure. The polarization curves were measured using a fuel cell test station (Arbin Instruments, 160269). The power densities were calculated from the steady-state voltages and applied currents.

Notes and references

**Fig. S1** Schematic of the custom-built electrospinning apparatus for preparation of chemically heterogeneous sandwiched nonwoven

**Fig. S2** SEM image of nonwoven after pre-compaction

(a) SPFEK fibrous nonwoven

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(b) SPFEK fibrous nonwoven after LBL self-assembly

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**Fig. S3** Solubility of nonwovens before and after LBL self-assembly in DMAc at 100°C
Fig. S4 Nonwoven surrounded by four pieces of solid paper (110μm in thick).