Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A Novel Porous Sulfonated Poly(Ether Ether Ketones)-Based Multi-Layer Composite Membrane for Proton Exchange Membrane Fuel Cell Application

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Materials and chemicals

PEEK powder with Grade 450 was purchased from Victrex PLC, UK. Nafion PFSA polymer dispersion with the type of D520 (available acid capacity: >1.0 meq g^{-1}) was purchased from Dupont, USA. Gas diffusion electrodes (GDE) were supplied from Sunrise Power Co. Ltd., China. The Pt loading of cathode GDE and anode GDE was 0.5 mg Pt cm^{-2} and 0.3 mg Pt cm^{-2}, respectively. Both of them used the Nafion dispersion as a binder, and the mass ratio of Nafion/C was 0.7/1.0. Dimethylacetamide (DMAc) was purchased from Kermel Chemical Reagent Co., Ltd, Tianjin, China. Sulfuric acid (95-98%, AR) was also from Kermel Chemical Reagent Co., Ltd. Deionized water was homemade in the whole study.

Membrane characterization

Flourier Transformed Infrared Spectroscopy (FTIR)

The chemical structure of the membranes was characterized on a FTIR spectrometer (Bruker Tensor 27, Germany). Each spectrum was recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} in transmittance mode.

Mercury intrusion porosimetry

To investigate the relationship between the DBP addition and the initial cell performance of the SPEEK membranes, the porosity and the pore size distribution of SPEEK porous membranes prepared by VIPI method were characterized with mercury intrusion porosimetry (PoreMasterGT 60).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (STA449F3, NETZSCH, Germany) from 25 ^{o}C to 700 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere.

Scanning electron microscope (SEM) and transmission electron microscopy (TEM)

The surface and cross section morphology of the membranes were characterized using a scanning electron microscope (SEM, JSM 6360-LV). The cross section samples of the membranes were obtained through breaking the sample in the liquid nitrogen. Before SEM testing, all the samples were sputtered with a thin platinum layer under vacuum. The distribution of sulfonic acid (-SO_3H) in the membranes, stained with 0.5 M silver nitrate solution, was recorded by the high-resolution transmission electron microscopy (TEM, JEM-2100) in the thin slice sample forms.

Water uptake (WU) and swelling ratio

Water uptake (WU) and swelling ratio of the membranes were calculated based on the difference between wet and dry membrane samples in weight, length. Before the data was recorded, the membrane samples would be immersed in DI water from 25 ^{o}C to 65 ^{o}C for every 24 h. The percentage of water uptake is given by

$$WU = (W_{wet}\text{-}W_{dry})/W_{dry} \times 100\%$$

The linear swelling ratio is calculated following

Linear swelling ratio (%) = $(L_{wet}-L_{dry})/L_{dry} \times 100\%$

where W_{wet}, W_{dry}, L_{wet} and L_{dry} represent the weight and length of wet and dry membranes, respectively.

Proton conductivity

The proton conductivity was evaluated by electrochemical impedance spectroscopy (EIS) using a Solartron SI 1287 equipped with a potentiostat 1260 frequency response analyzer over a frequency range from 105 to 100 Hz at a voltage amplitude of 10 mV. Before the measurements, the membrane samples were cut into 1×3 cm^2 rectangles and were mounted in two point probe conductivity cells, putting in a temperature-controlled water bath during the measurement. The proton conductivity (σ) was measured at the desired temperature and was given by the formula:

$\sigma = l/RA$

where l (cm), R (Ω), and A denote the distance between the two electrodes, the resistance of membrane, and the cross-sectional area of the membrane sample, respectively.

SUPPORTING RESULTS

1.

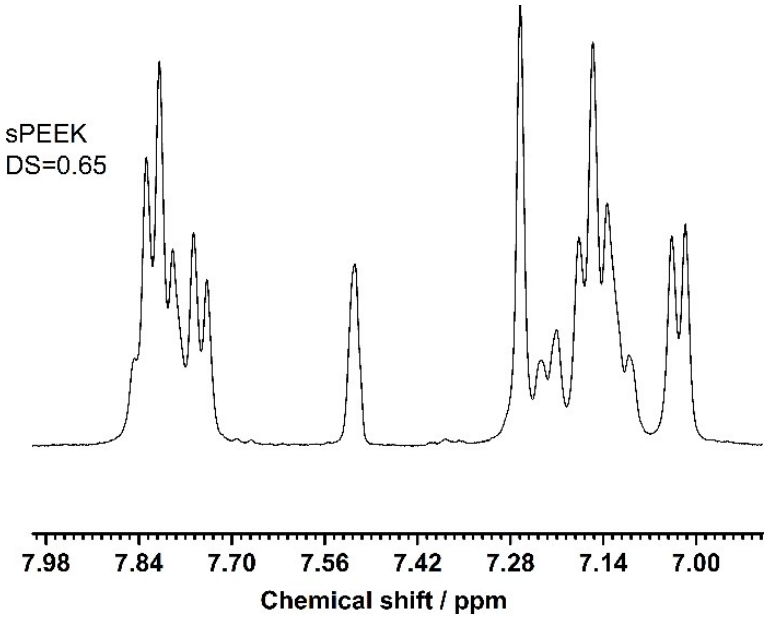

Figure S1. ^{1}H NMR spectra of sPEEK resin in DMSO-d_6

2.

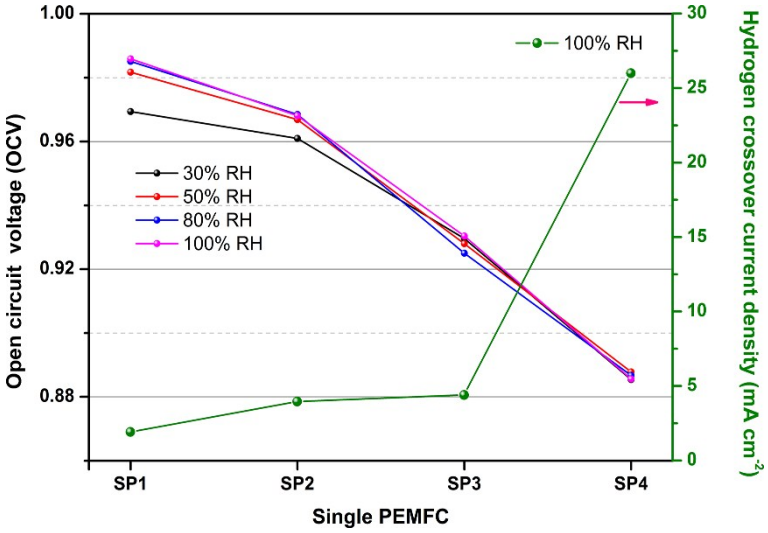

Figure S2. Comparable of OCV and hydrogen crossover current density of the sPEEK membranes.

3.

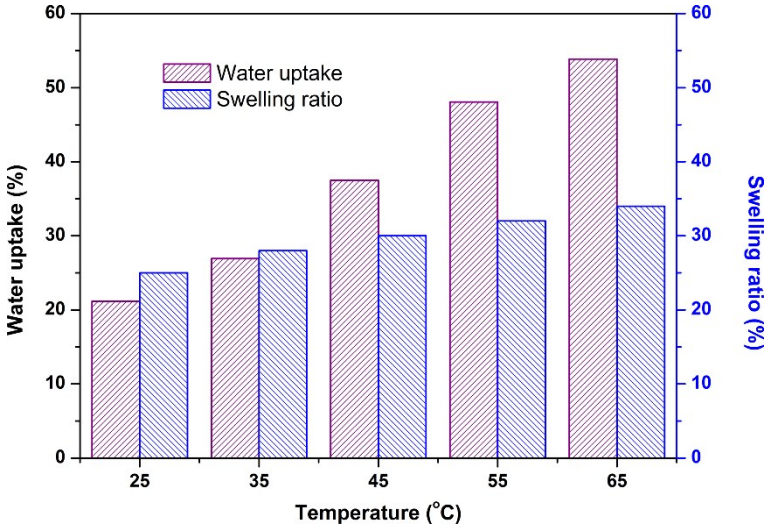

Figure S3. Water uptake and swelling ratio dependence of temperature for the SP3-NF.

4.

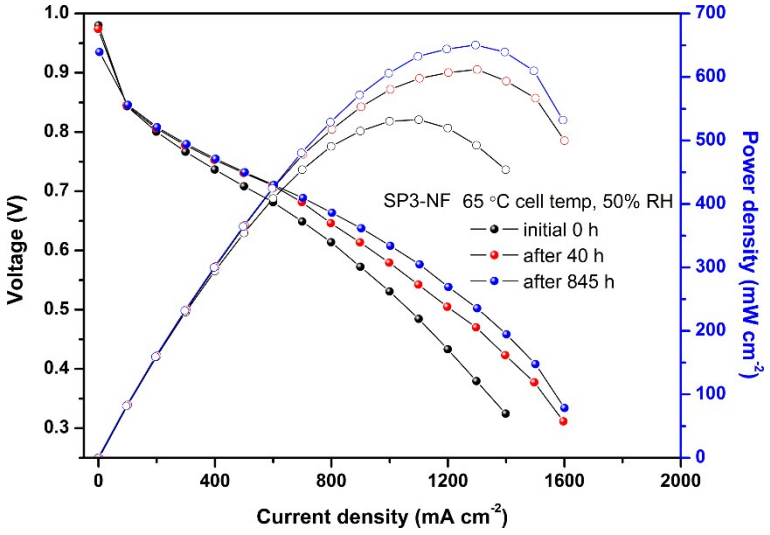

Figure S4. I-V performance and corresponding power density of MEA fabricated with SP3-NF composite membrane during stability tests at 65 °C and 50% RH.

5.

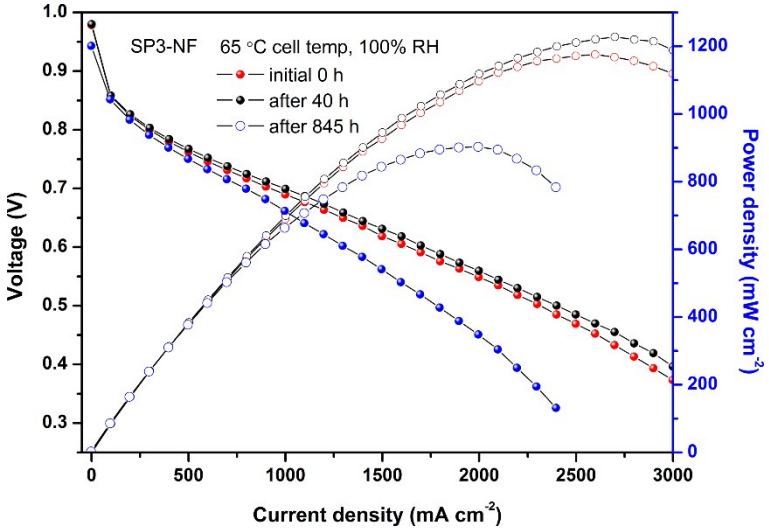

Figure S5. I-V performance and corresponding power density of MEA fabricated with SP3-NF composite membrane during stability tests at 65 °C and 100% RH.