

Experimental

Preparation of SSM with zeolite film

All chemicals were purchased from Sigma-Aldrich and used directly without further purification unless otherwise specified. Porous stainless steel mesh (SSM) with the size of 2.5 cm×2.5 cm was sequentially dipped into 1 vol. % 3-mercaptopropyl trimethoxysilane solution in ethanol for 15 min and 1.6 wt. % TPA- silicalite-1 nanocrystal suspension in double deionized water (DDI, Millipore Milli-Q Purification System) for 30 s, followed by drying at 373 K for 15 min. The processes of dipping into suspension and drying were repeated for 2 times to obtain the seeded SSM.

Silicalite-1 (Sil-1) and ZSM-5 films were grown on the seeded SSM via hydrothermal process. Sil-1 synthesis solution was prepared via adding drop by drop 3.4 ml of tetraethyl orthosilicate (TEOS) into the mixture of 1.9 ml of 1 mol·L⁻¹ tetrapropylammonium hydroxide (TPAOH) aqueous solution and 68.5 ml of DDI water, followed by stirring at room temperature for 24 h to produce a clear and homogeneous synthesis solution with the molar ratio of 80 TEOS: 10 TPAOH: 20,000 H₂O. In a typical ZSM-5 synthesis, 160 µl of TPAOH and 0.066 g of NaOH (BDH) were dissolved in 60 ml of DDI water. Then aluminum hydroxide fresh-prepared via the reaction of Al₂(SO₄)₃·18H₂O (0.22 g) and excessive ammonia (General) was added little by little into the basic solution, followed by the slow addition of 1.48 ml of TEOS. The obtained emulsion was stirred at room temperature for 24h to produce a clear and homogeneous synthesis solution with the molar ratio of 40 TEOS: 4 Al(OH)₃: 1 TPAOH: 10 NaOH: 20,000 H₂O. The seeded SSM was positioned vertically in a Teflon holder. The holder with the seeded SSM and Sil-1 (or ZSM-5) synthesis solution were transferred into Teflon-lined stainless-steel autoclave and hydrothermal-treated at 403 K for Sil-1 (or 423 K for ZSM-5) for 48 h to grow Sil-1 (or NaZSM-5) film on SSM. SSM with NaZSM-5 film was calcined in air at 823 K for 12 h to remove structure directing agent from channels of NaZSM-5 film. Then SSM with calcined NaZSM-5 film was ion-exchanged with 0.5 mol·L⁻¹ NaNO₃, KNO₃ and NH₄NO₃ solutions at room temperature for 3 times with 3 hours for each time, respectively, followed by calcination again in air at 673 K for

12 h to obtain SSM with calcined HZSM-5 film.

Preparation of SSM with double-layered zeolite film

ZSM-5 film was grown on SSM with as-synthesized Sil-1 film via template-free hydrothermal synthesis and ion-exchange processes to prepare SSM with ZSM-5/Sil-1 double-layered film. Template-free ZSM-5 synthesis solution was prepared by adding 14g of Ludox SM-30 into the mixture of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (0.58 g), NaOH (1.5 g) and DDI water (48.2 g). ZSM-5 synthesis solution stirred at room temperature for 24 h and the holder with SSM with as-synthesized Sil-1 film were transferred into Teflon-lined stainless-steel autoclave and hydrothermal-treated at 453 K for 16 h to grow NaZSM-5 film. SSM with NaZSM-5/Sil-1 film was ion-exchanged with $0.05 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ solution at room temperature for 3 times with 3 hours for each time to prepare SSM with HZSM-5/Sil-1 film.

Preparation of confined PFSA-zeolite composite membrane

Commercial 10 wt. % Nafion resin suspension in water was diluted into 5 wt. % suspension with DDI water. The Nafion precursor was prepared by mixing 5 wt. % Nafion resin suspension and 1,2-propanediol (1:2, volume ratio). Nafion precursor was casted into SSM with zeolite film on a clean glass dish, followed by vacuum drying at 353 K to remove solvents. The casting and vacuum drying processes were repeated to obtain confined PFSA-zeolite composite membrane.

Membrane-electrode assembly

Porous stainless steel plates coated with gold layers were used as current collectors and gas diffusion layers. They were brushed with the slurry containing 20% Pt on Vulcan XC-72 (BASF Fuel Cell) and 10% Nafion resin suspension (1:4, weight ratio), followed by drying at 353 K for 1 h to obtain electrodes with Pt loading of $0.5 \text{ mg} \cdot \text{cm}^{-2}$. Confined PFSA-zeolite composite membrane was hot-pressed between two pieces of porous stainless steels with Pt/C catalyst layers at 403 K under 10 MPa pressure for 3 min to prepare membrane-electrode assembly. For comparison, standard fuel cell was also prepared by hot-pressing Nafion 117 membrane (E-Tek) between two pieces of Teflon-treated carbon clothes with microporous carbon layers brushed with Pt/C catalyst layers.

Characterization

SEM images of SSM with zeolite film were made using a JEOL JSM-6300F field-emission scanning electron microscope. Olympus BX41 Microscope with fluorescence accessories was used to observe integrity of confined PFSA-zeolite composite membrane. DSC curves of recasted Nafion and confined PFSA-zeolite composite membranes in compressed air from room temperature to 573 K (ramp rate: 5 K·min⁻¹) were measured using a TA Q1000 differential scanning calorimeter. The samples were pre-dipped into DDI water overnight. Before measurement, the samples were wiped with weighing paper to remove water drops on surface and cut into small pieces with the size of 2 mm×2 mm. SEM images with EDX line scan and EDXS of confined PFSA-Sil-1 composite membrane were recorded in a JEOL JSM-6300 scanning electron microscope equipped with high-sensitive energy dispersive X-ray detector. ToF-SIMS mapping images of confined PFSA-Sil-1 composite membrane were made by an ION-TOF GmbH TOF-SIMS V spectrometer equipped with 25 keV Bi₃⁺ cluster ion source that has an average pulsed current of 0.1 pA. The sample was fixed on Si wafer with double sided carbon conductive tape.



Fig. S1 Photographs of (a) confined PFSA-zeolite composite membrane and (b) corresponding MEA.

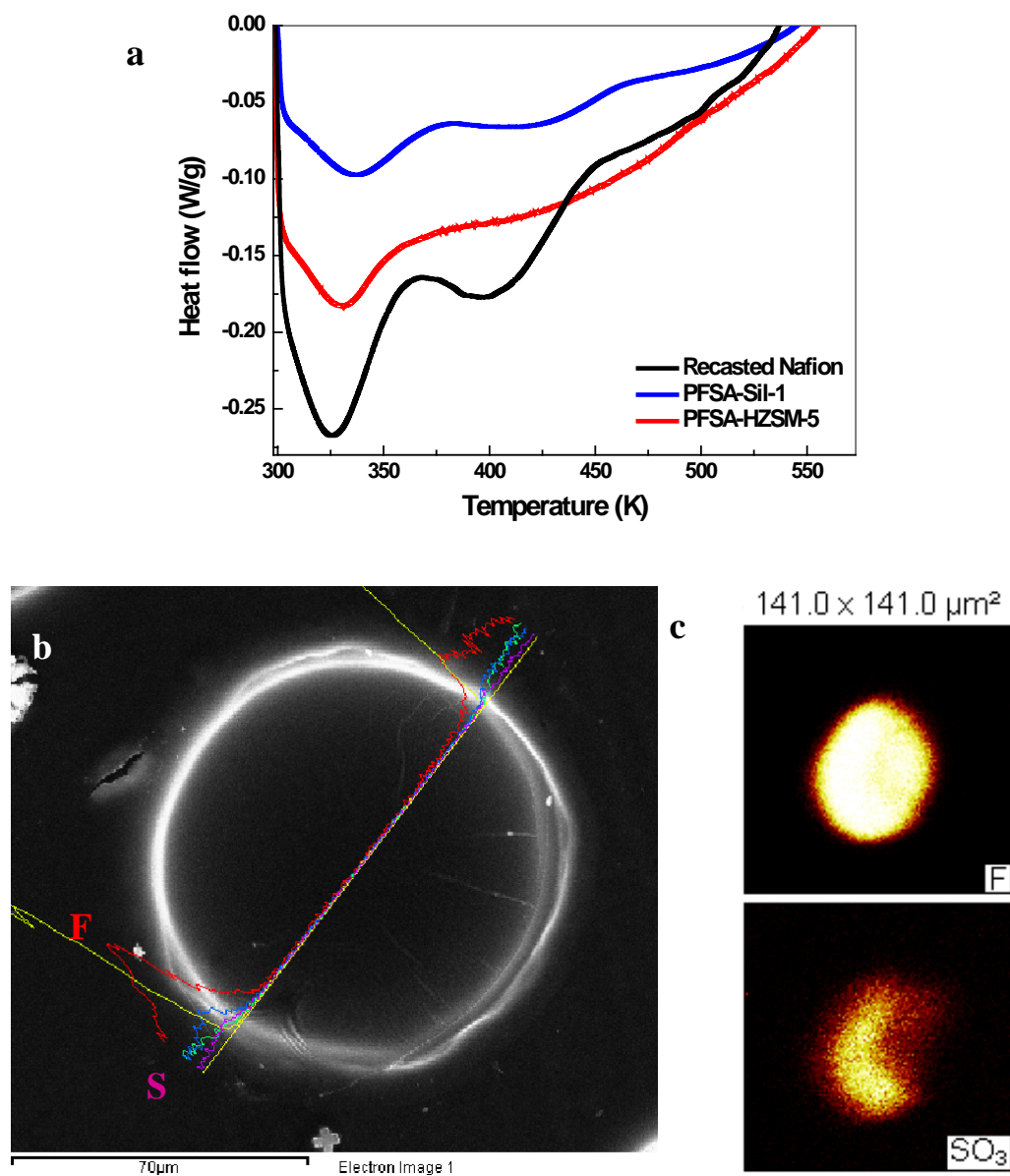


Fig. S2 (a) DSC curves of recasted Nafion, PFSA-Sil-1 and PFSA-HZSM, (b) SEM image with EDX line scan and (c) ToF-SIMS mapping image of PFSA-Sil-1.

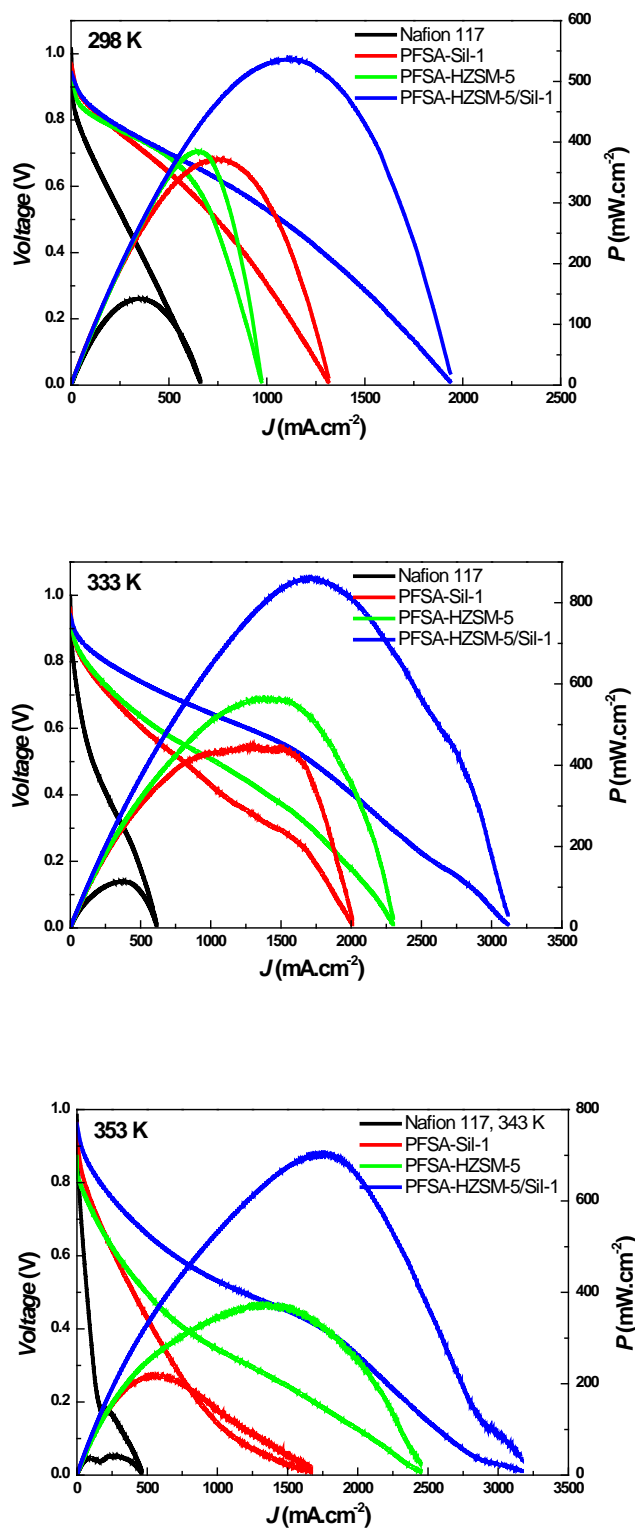


Fig. S3 Performance curves of all cells at 298, 333 and 353 K.