Supporting Information

A high-performance anion exchange membrane based on bi-guanidinium bridged polysilsesquioxane for alkaline fuel cell application

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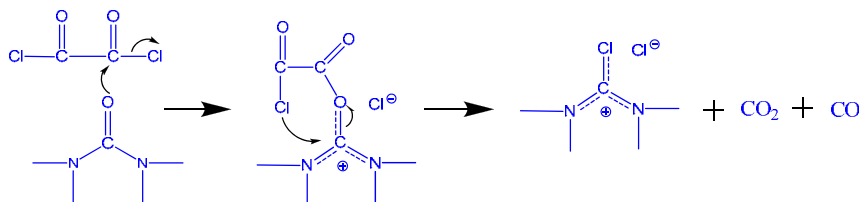E-mail: zhanghm@dicp.ac.cn (H. Zhang); zhfx2003@hotmail.com (F. Zhang)

Experimental Section

Materials

3-Chloropropyl trimethoxysilane was provided by Zibo Linzi Qiquan Industrial Trade Co. Ltd. Oxalyl chioride was purchased from Sinopharm Chemical Reagent Co. Ltd, and purified by distilling immediately before use. 1,1,3,3-tetramethylurea, dichloromethane (CH_2Cl_2) and acetonitrile were all analytical grade, provided by Aladin Reagents and stored over 4 Å molecular sieves. PTFE with a porosity of 90% was provided by Shanghai Dagong New Materials Co. Ltd. Other chemicals were all used as received without further purification.

Synthesis of 1,6-bi (1,1,2,3,3-tetramethylguanidine) hexane (BGH)

Under a nitrogen atmosphere, oxalyl chioride (15 g, 118.2 mmol) was added slowly at 0   to 20 mL CH_2Cl_2 solution of 1,1,3,3-tetramethylurea (9.7 g, 83.5 mmol) in a

round bottom flask. After reacting at 60 for 2 h, CH_2Cl_2 was evaporated under reduced pressure, and a solid product (Vilsmeyer salt) resulted (yield: 98%). Actually the above Vilsmeyer salt producing reaction has been widely reported in the literature; its mechanism is proposed as follows.

In the next step, Vilsmeyer salt was dissolved with 20ml acetonitrile at 0 , to which triethylamine (8.45 g, 83.5 mmol) and 1,6-diaminohexane (4.40 g, 37.9 mmol) were added slowly, and refluxed at 90 for 18 h. After cooling to room temperature, 300ml NaOH (5 mol L^{-1}) was added under vigorous stirring; the organic phase was extracted with dichloromethane（4 × 40 ml） and dried over anhydrous $MgSO_4$, filtered and evaporated to remove the solvent, triethylamine and other byproducts. A yellow viscous liquid was obtained，which is named BGH (yield: 55%; this is low because of product loss during extraction and filtering).

Synthesis of bi-guanidium bridged silsesquioxane (BGBS)

Under a dry nitrogen atmosphere, 3-chloropropyltrimethoxysilane (5.96 g, 3 mmol) was added into the above obtained BGH (3.32 g, 1 mmol), and reacted at 80 for 48 hours. After the mixture was cooled to room temperature, the excess of 3-chloropropyltrimethoxysilane was removed by distillation under pressure to give BGBS as a highly viscous brownish oil (yield: near 100%).

Preparation of BG-BPS /PTFE hybrid anion exchange membrane

Under a nitrogen atmosphere, BGBS (5 g) was dissolved in ethanol (5 g) with sonication for 0.5 h; a PTFE film was cleaned with ethanol and soaked in this solution for 8 hours at room temperature. Then the PTFE film was taken out, flattened on a stainless steel plate and dried at 40 in the open air for 20 h and 80 for 48 h, during which the hydrolysis and gellation of BGBG occurred. The resultant hybrid

membrane was soaked in 0.1M NaOH aqueous solution for 48 h for alkalization. The thickness of the membrane is 40 ± 3 μm.

It should be noted that methoxysilane hydrolysis can be catalyzed by either an acid or a base [1, 2]. Here in our case, the guanidinium cations have strong basicity and therefore can catalyze the hydrolytic reaction. Such catalytic effect and the prolonged thermal treatment can probably insure complete hydrolysis of BGBS.

Membrane characterizations

^{1}H-NMR analysis

The BRUKER DRX400 spectrometer was used to obtain the ^{1}H NMR spectra. CDCl$_3$ was used as the solvent and tetramethylsilane as the internal standard.

ATR-FTIR analysis

The JASCO FT-IR 4100 spectrometer with an ATR accessory containing a Ge crystal was used to record FTIR spectra for the membrane samples. All spectra were recorded in the wave numbers ranging from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

Water uptake measurements

A membrane sample was weighed and soaked in DI water at 20　for 12 h. Then, the sample was taken out, wiped with tissue paper quickly, and weighed again. Water uptake (WU) was calculated as WU $= (W_s - W_d) / W_d \times 100$ %, where W_d and W_s are the weights of the sample before and after swelling, respectively.
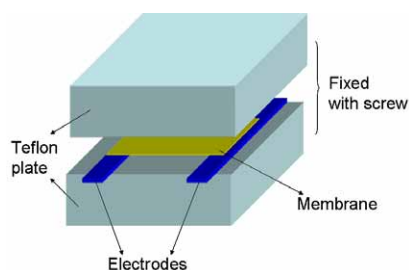
Swelling ratio (SR) measurements

A membrane sample with known dimensions was immersed in water at 20 ℃ for 12 h. After removing the surface liquid with filter paper, the sample was measured again for its dimensions. The SR was calculated as SR $= (l_s - l_d) / l_d \times 100$ %, where l_d and l_s are the lengths of the sample before and after swelling, respectively.

Ionic exchange capacity (IEC) measurement

A membrane strip was soaked into 100 mL of 0.01 M $NaNO_3$ solution for 24 h to undergo an ionic exchange process. The chloride ions released from the membrane was determined by a titration with 0.01 M $AgNO_3$ using K_2CrO_4 as an indicator. The IEC value (mmol g^{-1}) can be calculated from $IEC = V \times 0.01/W$, where V is the volume of $AgNO_3$ (ml) consumed for titration, and W is the weight of the dry membrane (g).

Ionic conductivity measurements

Electrochemical impedance spectroscopy was employed for ionic conductivity measurements using the normal four-point probe technique on an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK) over the frequency range from 1 mHz to 500 kHz. A membrane sample (2×4 cm^2) was soaked 48 h in DI water and rinsed copiously, and then fixed with the two ends contacting the electrodes on a Teflon cell as schematically shown below.

The cell was placed in DI water for measurement. The impedances were measured for three times after equilibrating for at least 30 min at a given temperature. The ionic conductivity (σ) was calculated from the following equation:

$$\sigma = \frac{L}{RWd}$$

where R is the obtained membrane resistance, L the distance between the electrodes (here 2 cm), W and d are the width (here 2 cm) and thickness of the sample, respectively.

Thermal gravimetric analysis (TGA)

Thermal stability of the membranes was analyzed using TGA/DTA (Pyris Diamond TGA/DTA) system over a temperature ranging from 50 to 800 ºC at the heating rate of 2ºC min^{-1} in nitrogen atmosphere.

Fuel cross-over studies

Take methanol as an example. A membrane sample was sandwiched between the two compartments of an in-house made diffusion cell. The left compartment（Part A） was filled with 70 ml 0.5 M methanol, and the right（Part B） with 70 ml DI water. Magnetic stirrers were used in both compartments to avoid concentration polarization. The effective area of the membrane, i.e. the area exposed to the solution was 1.13 cm^2. Samples from the right compartment were collected every 5 min, whose methanol concentrations were measured as follows. Methanol was oxidized by potassium permanganate in the presence of dilute sulfuric acid (25 %); the oxidization product (formaldehyde) was heated with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) in the presence of concentrated sulfuric acid such that an intense violet-red color appeared. Next, the concentration of methanol was calculated from a pre-plotted standard curve between the concentration of methanol and the absorbance of the colored solution at 566 nm. For methanol permeability calculation, an assumption was made that the change of methanol concentration in the left compartment is negligible. The relationship between methanol concentration in the right compartment and time could be described by Fick's diffusion law as:

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t))$$

Where C_A and C_B are the methanol concentrations in the left and the right compartments, respectively; V_B is the volume of the right compartment; A is the membrane area; P is the methanol permeability; L is the thickness of the membrane.

Preparation of PSIm/PTFE membrane

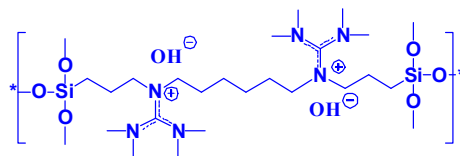For comparison purpose, an imidazolium-functionalized polystyrene/PTFE (or PSIm/PTFE) membrane was prepared as follows. A microporous PTFE sheet (9.5×9.5 cm^2, of the same origin as that used for BG-BPS/PTFE fabrication) was cleaned with ethanol, and then impregnated with a mixture consisting vinylbenzyl chloride (monomer, 3 ml), divinylbenzene (cross-linker, 0.3 ml), benzyl peroxide (initiator, 0.04 g) and isopropanol (wetting facilitator for PTFE, 2 ml); after 2h impregnation, the PTFE sheet was taken out, extended and flattened on a cleaned glass plate, covered with another glass plate, and heated at 110℃ overnight. This resulted in polymerization and cross-linking of the vinylbenzyl chloride monomer inside the PTFE matrix; the membrane was delaminated from the substrates with the aid of sonication and then soaked in aqueous 1-methylimidazole (10% by volume) at 50℃ for 72 h. Finally, the membrane was treated with 0.5 M NaOH (aq.) for alkalization.

Fuel cell performance evaluation

The membrane electrode assembly (MEA) was fabricated by hot-pressing the anode, the cathode, and the fabricated membrane together (membrane between the two electrodes) at 90 ℃ and 1 MPa for 2 min. The Pt/C (Tanaka, 46.1% Pt content) loading in the anode and the cathode were both 1 mg cm^{-2}. Nafion was used as the catalyst binder in both electrodes with a loading of 0.38 mg cm^{-2}. The active area of MEA was 5 cm^2. The MEA was mounted in a 5×5 cm test fixture containing graphite blocks with serpentine flow channels and gold-coated current collector plates. Single cell was operated at 40 ℃, and the cell performance was measured at a fuel (1 M NaBH$_4$ + 3 M NaOH) flow rate of 10 mL min^{-1} and an oxygen flow rate of 150 mL min^{-1}.

Theoretical IEC calculation

IEC is defined as the mole number of ion exchange groups per gram of dried membrane. The theoretical IEC was estimated from the following structure as the approximate repeat unit of the gel.
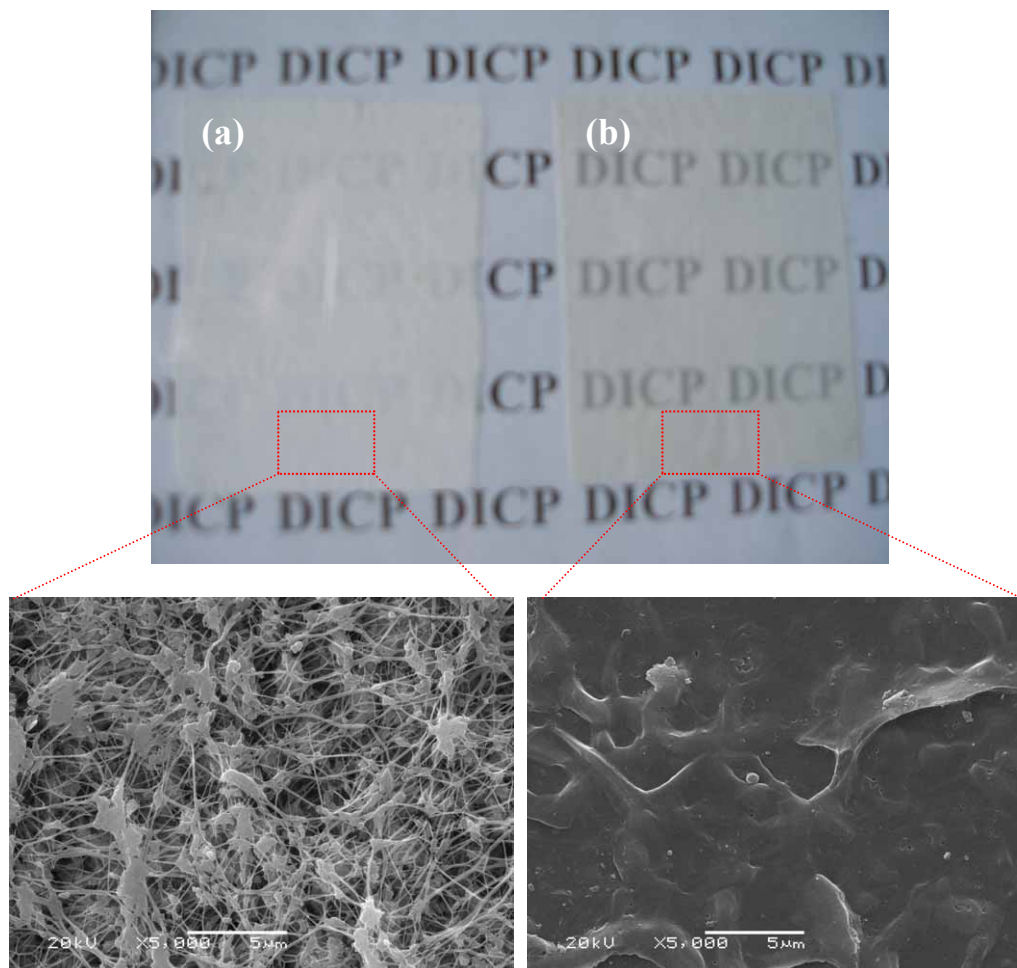

$$IEC = \frac{\dfrac{(0.71 - 0.422)g}{582 g/mol} \times 2}{0.71 g} = 0.00139 mol/g = 1.39 mmol/g \text{ , where } 0.71 \text{ and } 0.422$$

denote the mass (in gram) of the composite membrane (after prolonged vacuum drying) and pure PTFE sample, respectively, 582g/mol is the molecular weight of the gel repeat unit, and "2" denotes two cations in each repeat unit.

References

1. Y. Abe, T. Gunji, *Prog. Polym. Sci*. 29, 2004, 149.

2. K. A. Smith, *J. Org. Chem.* 51, 1986, 3827

Figures

Fig. S1 Electronic photographs (upper panel) and surface SEM (lower panel) of pure
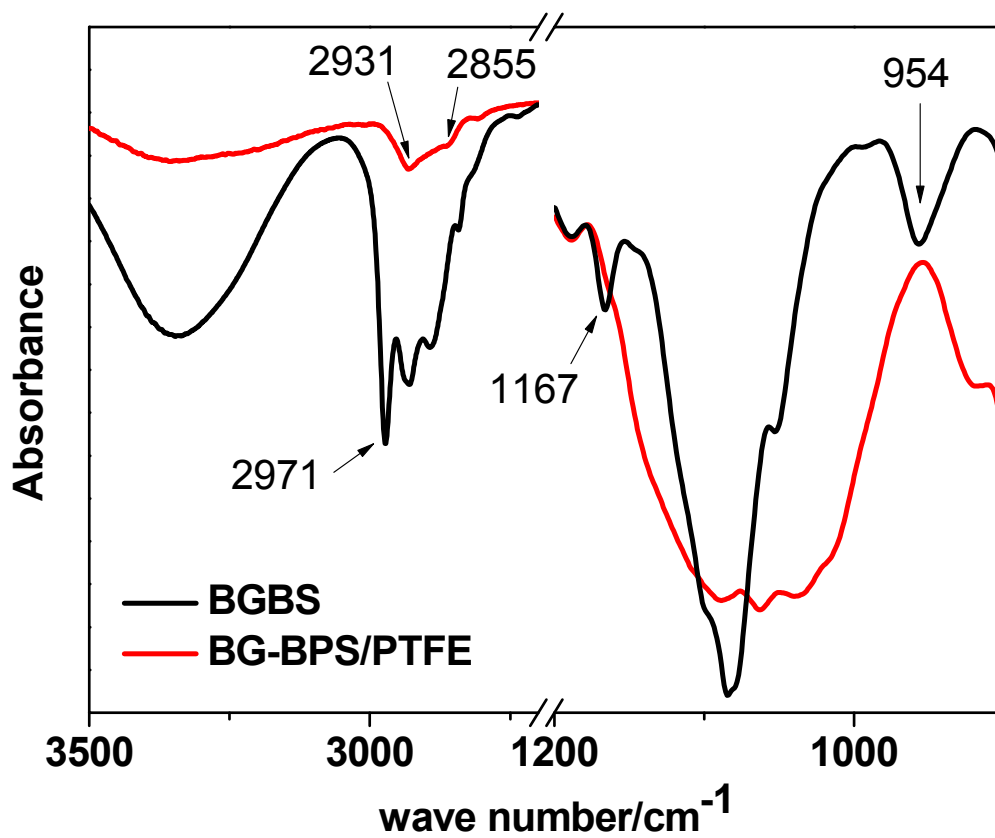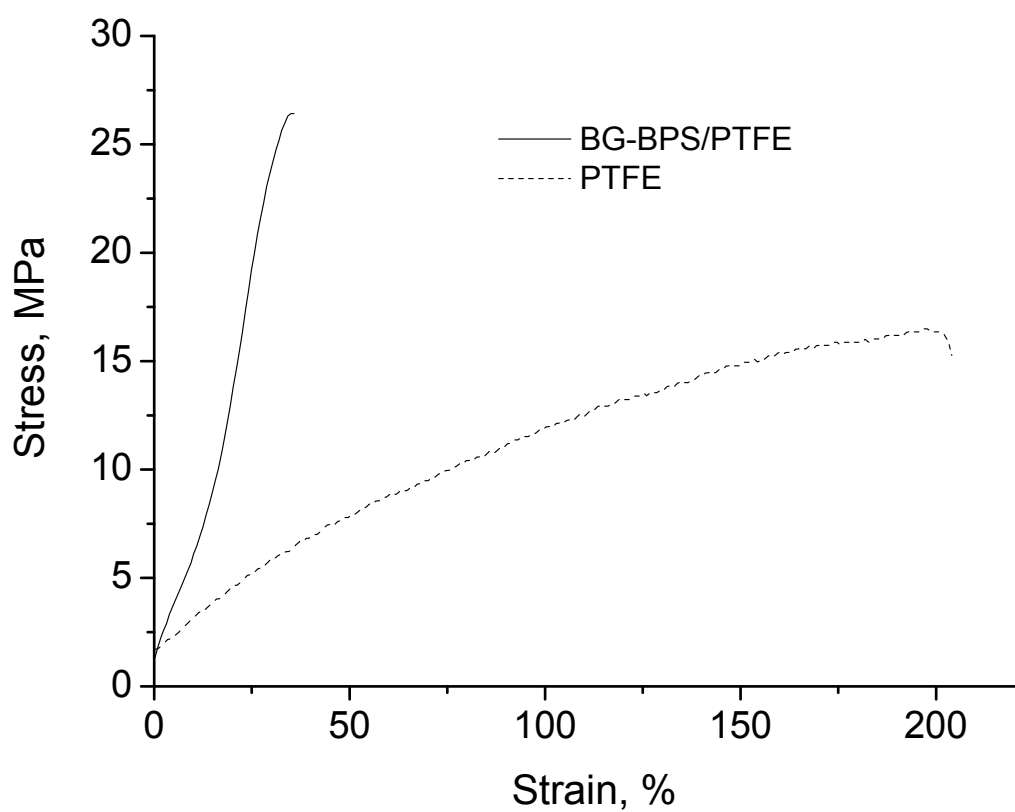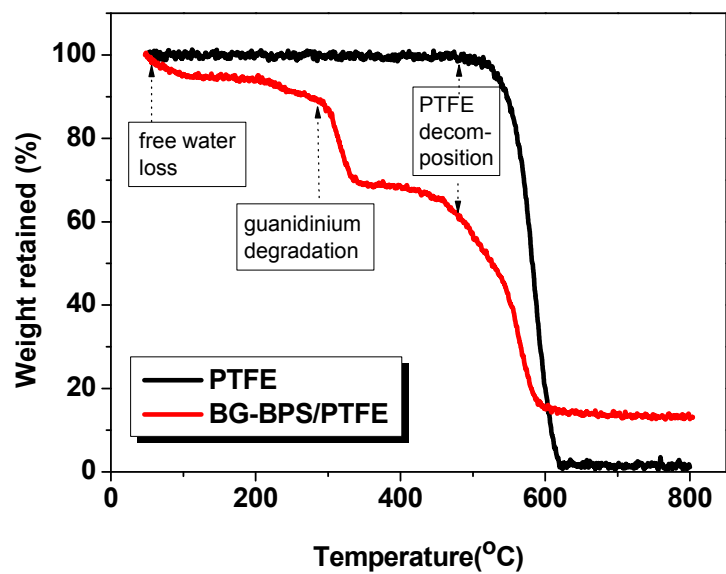PTFE film (a) and BG-BPS/PTFE membrane (b)

Fig.S2 FTIR spectra monitoring the BG-BPS/PTFE membrane synthesis process

Fig.S3 Tensile stress-strain curves for the BG-BPS/PTFE membrane and the pristine

PTFE membrane

Fig. S4 TGA curves for the BG-BPS/PTFE membrane and pure PTFE