Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Towards Neat Methanol Operation of Direct Methanol Fuel Cells: A Novel Self-Assembled Proton Exchange Membrane

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Experimental section

Materials

Monomers, trimesic acid (TA) and 2,4-diaminobenzenesulfonic acid (DAS), and triphenylphosphite (TPP) as catalyst are purchased from Sigma Aldrich and used as received without further purification. Lithium chloride (LiCl) were purchased from Sigma Aldrich and dried at 100 ^oC in vacuum oven for 24 hrs before use. N-methyl-2-pyrrolidone (NMP) was distilled from P_2O_5, and pyridine (Py) was distilled from KOH. Nafion 117 membrane was purchased from Dupont Co. (USA), with a dry thickness of 0.177 mm.

Synthesis of Hyperbranched Sulfonated Polyamides

TPP (1 mL), NMP (4 mL) and pyridine (3 mL) were added into a mixture of trimesic acid (TA) (2m mmol), 2,4-diaminobenzenesulfonic acid (DAS) (2n mmol) and LiCl (0.4 g). The mixture was kept stirred under argon atmosphere at 100 ^oC for 2 hrs. After the reaction was completed, the mixture was cooled to 70 ^oC and 100 mL cold methanol was added. White precipitate was obtained by filtration and the pure products were collected upon continuous washing with methanol and deionized water for several times. The products were dried at 100^oC under a reduced pressure for 12 hrs.

Preparation of Hyperbranched Sulfonated Polyamide membranes

Membranes were prepared via a solution-cast technique using dimethylacetamide (DMF) as a solvent. The dried polymers were first uniformly dissolved in DMF to form 2wt. % solutions. The solutions were then casted onto glass plates, and left to dry at 80 °C. The dried membranes were removed from the glass plates and further dried at 100 °C under vacuum overnight. The prepared membranes were immersed into 1 M HCl at room temperature for 12 hrs, and then washed with ultrapure water repeatedly until the pH of the solutions became to 7. The average thicknesses of the membranes were measured to be in the range of 80-100 μm in a dry state.

Measurements and Characterizations

For characterization of the polymers, ^{1}H NMR spectra were taken on a Bruker AV300 NMR spectrometer using DMSO-d_6 as solvent at room temperature (RT) to confirm the structures of polymers. FTIR spectra of the polymers were recorded on a Shimadzu IR Prestige-21. Thermal analysis of the membranes was tested by using thermo gravimetric analysis (TGA), with TA Instruments Q500, at 10.00°C/min ramp up to 600°C, under nitrogen atmosphere. Cross-section images of the membranes were investigated by field emission scanning electron microscopy (SEM, JEOL JSM-6701F, Japan). Tapping mode AFM was performed with a Digital Instruments Multimode Atomic Force Microscope.

The thickness of each membrane sample was measured by a digital micrometer and repeated three measurements to give the average values. The tensile strength and elongation at break of the membranes at wet state were measured according to ASTM D882, REF ASTM using Instron 5544 at room temperature with an elongation rate of 1.00 mm min^{-1} and sensitivity set at 40%. The oxidative stability of membrane was tested by immersing the membranes into a Fenton's reagent (3 ppm $FeSO_4$ in 3% H_2O_2 solution) at 80 °C. The oxidative stability was represented by the retained weight (RW) of membranes after treatment for 1 hr and the expended time (t) of the membranes to dissolve into the Fenton's reagent.

To measure the water uptake, methanol uptake and volume dimensional swelling, the membranes were first immersed in ultrapure water or methanol at room temperature overnight. Then the membranes were removed, wiped the surface water with a clean tissue paper and quickly measured weight and volume. The membranes were then dried at 80 °C in a vacuum oven for 12 hrs and recorded the weight and volume immediately. The water uptake (WU) was calculated as follows:

$$\mathrm{WU} = \frac{\left(\mathrm{W_{wet,w}} - \mathrm{W_{dry}}\right)/\mathrm{M_{H_2O}}}{\mathrm{W_{dry}}}\left(mmol/g\right) \quad (1)$$

where $\mathrm{W_{wet,w}}$ and $\mathrm{W_{dry}}$ are the weights of wet (in water) and dry membranes, respectively, and $\mathrm{M_{H_2O}}$ (g/mmol) represents the molecular weight of water.

The methanol uptake (MU) was calculated as follows:

$$\mathrm{MU} = \frac{\left(\mathrm{W_{wet,m}} - \mathrm{W_{dry}}\right)/\mathrm{M_{MeOH}}}{\mathrm{W_{dry}}}\left(mmol/g\right) \quad (2)$$

where $\mathrm{W_{wet,m}}$ and $\mathrm{W_{dry}}$ are the weights of wet (in methanol) and dry membranes, respectively, and $\mathrm{M_{MeOH}}$ (g/mmol) represents the molecular weight of methanol.

Volume dimensional swelling (VS) of the membranes were calculated as:

$$\mathrm{VS} = \frac{\mathrm{V_{wet.w}} - \mathrm{V_{dry}}}{\mathrm{V_{dry}}} \times 100\% \quad (3)$$

where $\mathrm{V_{wet.w}}$ and $\mathrm{V_{dry}}$ are the volumes of wet(in water) and dry membranes, respectively.

Ion exchange capacity (IEC) of the membrane was determined using a titration method. The dried membrane (0.1- 0.2 g) were first immersed in 100 mL of 1M NaCl solution for at least 48 hrs to convert H^+ of the $-SO_3H$ to Na^+ completely. The contents of H^+ released from the membrane was measured by titration with 0.01M NaOH solution using phenolphthalein as an indicator. IEC was reported as the average of two measurements and calculated by the following equation:

$$\mathrm{IEC}=\frac{\mathrm{V(mL)}\times \mathrm{C(M)}}{\mathrm{W(g)}}\left(\mathrm{mmol/g}\right) \tag{4}$$

where V(mL) and C(M) are the volume and concentration of NaOH, respectively. W(g) is the weight of dry membrane.

The values of "methanol molecules per proton" (MPP) of the membranes were calculated as:

$$\mathrm{MPP}=\frac{\mathrm{MU}}{\mathrm{IEC}} \tag{5}$$

where MU is the methanol uptake (mmol/g) of a membrane.

Proton conductivity of the membrane was measured using a four-probe method by electrochemical impedance spectroscopy (EIS) using a Zahner potentiostate-galvanostatate electrochemical workstation model PGSTAT over a frequency range of 1Hz-4MHz with the oscillating voltage of 5mV. Before test, the membranes were immersed in 1 M HCl for 12 hrs to activation, and then washed with deionized water until PH to 7. The test was carried out at the temperature from 25 to 80 ^{o}C and 100% relative humidity. Proton conductivity was calculated from the impedance data according to the follow equation:

$$\sigma=\frac{d}{Rtw} \tag{6}$$

where σ is the proton conductivity (S/cm), *d* is the distance between the electrodes, *t* and *w* are the thickness (cm) and width (cm) of the membranes, respectively. *R* is the resistance (Ω) associated with the ionic conductivity of the membranes from the impedance data.

Fuel cell test

4.0 mg/cm^2 PtRu/C (40 wt%, of Pt and Ru atomic ratio of Pt to Ru=1:1) and 1.8 mg/cm^2 Nafion (5 wt% Nafion solution) were dispersed in an aqueous solution of isopropyl alcohol with ultrasonic treatment. After the suspension was uniformly dispersed, we sprayed it onto carbon paper to form the anode. The cathode was formed by spraying 4.0 mg/cm^2 of Pt/C (40 wt% Pt, 1.8 mg/cm^2 Nafion as a binding agent) onto carbon paper. A Nafion 117 membrane (thickness 175 μm) or BXL-15 membrane (80 μm) was sandwiched between the anode and the cathode during the fuel cell assembling as demonstrated in Figure S6. Hot-pressing was not carried on because the MEA with E-HBM cannot be properly hot-pressed since the molecule structure and thermal properties of E-HBM are substantially different from that of the Nafion ionomers used as a binder in the catalyst layers. That's the main reason of the relatively poor performances of the DMFC devices in the present work. Other than the electrodes and PEM, a passive DMFC includes a fuel reservoir and anode/cathode current collectors. Polycarbonate was selected as the fuel reservoir material, and the gold-electroplated 316 L stainless steel meshes were used as the current collectors. Polarization tests were performed on an Arbin Fuel Cell Test System (Arbin Instruments Co., US) at 25 ℃.

Methanol permeation measurement

Methanol permeation measurements were carried out in a methanol permeation cell of DMFC configuration as shown in Figure S6. Differently from a DMFC, the humidified air in the cathode of a DMFC is replaced by humidified argon in the methanol permeation cell and electro-oxidation reaction of methanol takes place at the cathode catalyst layer (Pt/C) at a rate determined by methanol permeability through the PEM. The anode side (PtRu/C) of the methanol permeation cell acts as both reference electrode and counter electrode due to electro-reduction of protons, which transfer from the cathode to the anode driven by applied voltage, to hydrogen could provide a stable reference potential.

Linear sweep voltammetry (LSV) measurements for the oxidation of methanol permeating through of E-HBM membranes and Nafion 117 membrane exposed to 1 M, 3M and 6 M methanol solutions are conducted using a CHI 660D electrochemistry workstation. The sweeping rate was set to be 1 mV/s in the voltage rage of 0.1-0.95 V.

Steady oxidation current densities of the permeated methanol through of E-HBM membranes and Nafion 117 membrane exposed to 1 M, 3M, 6 M and 15 M methanol solutions are conducted using a CHI 660D electrochemistry workstation by setting the voltage at 0.9 V for 5 min. Chronoamperometry curves of methanol permeating through the E-HBM2, E-HBM3 and Nafion membranes exposing in 1 M, 3 M, 6 M and 15 M methanol solutions at 0.9 V are displayed in Figure S7 and the current density values at 5 min are recorded as the steady oxidation current densities of the permeated methanol.

Table S1. Precursor ratios, excess TA, molecular weight and oxidative stabilities of the N-HBM and E-HBM membranes.

	m:n ratio	Excess TA (%)	Molecular weight		Oxidative stability	
			M_n[a] (10^4 g mol^{-1})	PDI	RW(%)	t(hr)
N-HBM	0.67:1	0	-	-	-	-
E-HBM1	1.11:1	65.67	10.31	1.46	-	-
E-HBM2	1.05:1	56.72	15.32	1.24	96.2	16
E-HBM3	1.02:1	52.24	21.32	1.14	96.5	16.5

[a] Measured at room temperature using DMF as the solvent and polystyrene as the standard.

Table S2. Proton conductivity and methanol permeation current density @ 0.9V of Nafion and E-HBM membranes in 15M methanol solution at 25 ^{o}C.

	Proton conductivity ($S\ cm^{-1}$)	Methanol permeation current density @ 0.9V (A/cm^2)
Nafion 117	0.0304	0.565
E-HBM2	0.0424	0.124
E-HBM3	0.0371	0.229

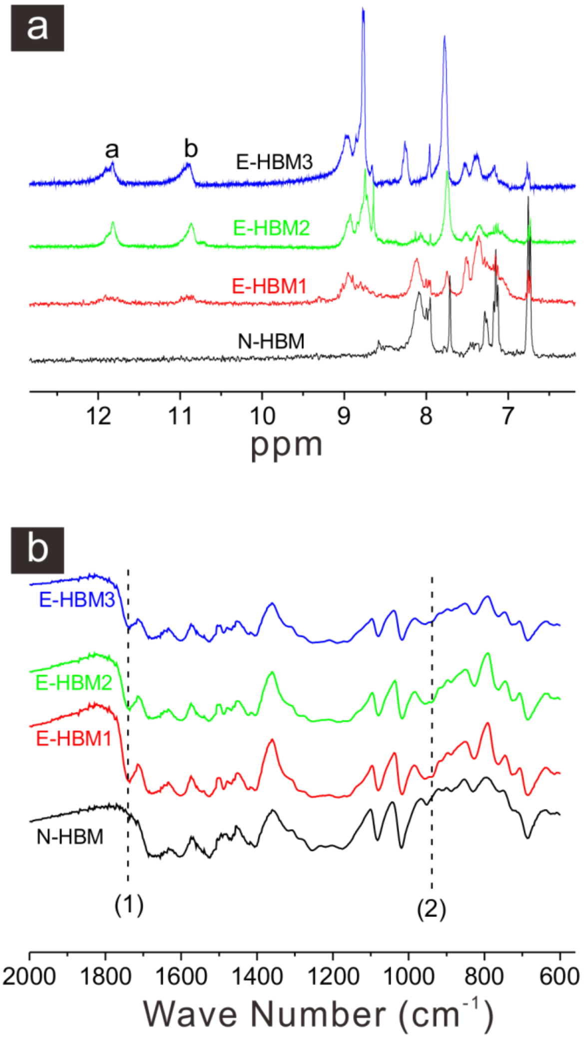

Figure 1. Characterizations of E-HBM compounds (a) The ^{1}H NMR spectra of N-HBM, E-HBM1, E-HBM2 and E-HBM3; (b) The FTIR spectra of N-HBM, E-HBM1, E-HBM2 and E-HBM3.

The distinct resonances at 11.8 ppm (a) and 10.9 ppm (b) in the 1H NMR spectra of E-HBMs (Figure S1a) are attributed to the hydrogen atoms of the two –COOH groups on the end dicarboxyphenyl group. The successful end-capping of E-HBMs is also evidenced from the FTIR spectra shown in Figure S1b. The stretching bands of C=O in –COOH at 1740 cm-1 as peak (1) and bending vibrations of O-H in –COOH at 945 cm-1 as peak (2) are readily identifiable in the FTIR spectra of E-HBMs.

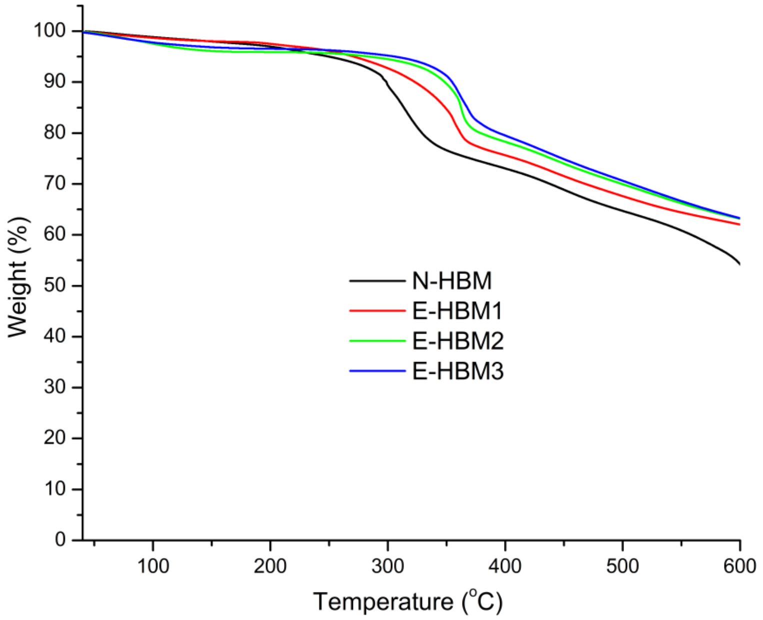

Figure S2. Comparison of TGA spectra of N-HBM, E-HBM1, E-HBM2 and E-HBM3 compounds.

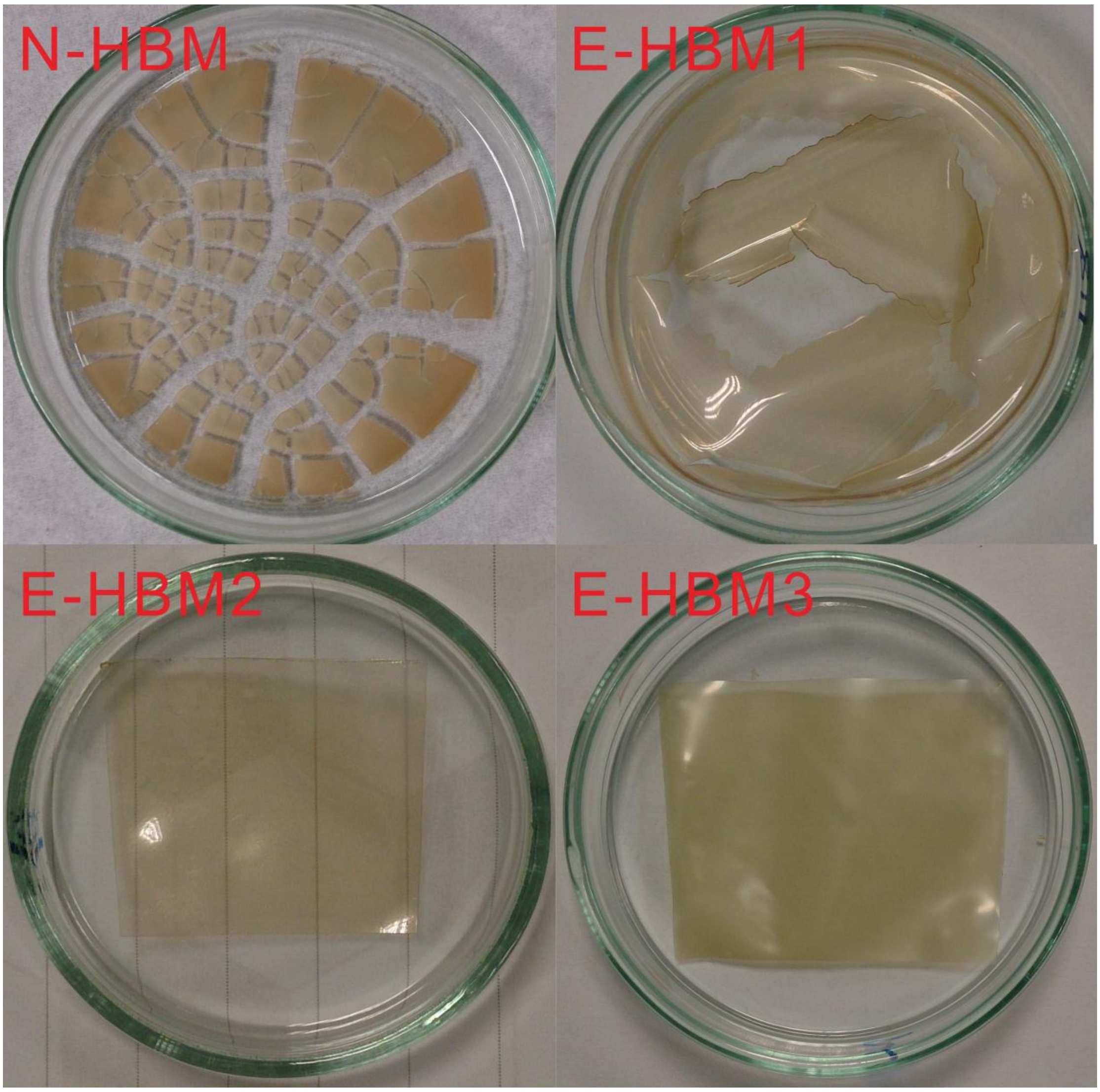

Figure S3. Photos of membranes made from N-HBM, E-HBM1, E-HBM2 and E-HBM3.

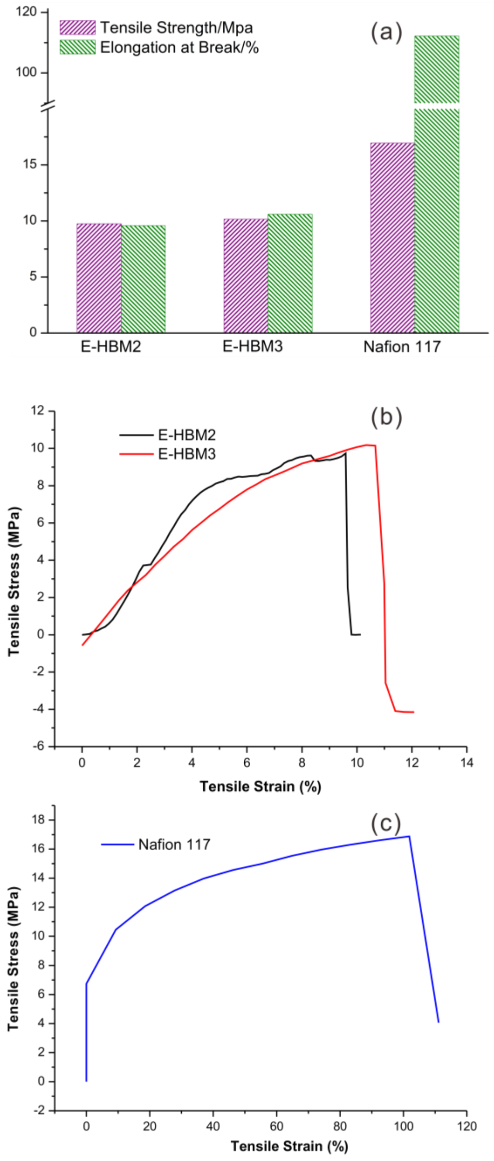

Figure S4. Tensile strengths and elongations at break and the stress-strain curves of E-HBM2, E-HBM3 and Nafion 117 membranes in wet state.

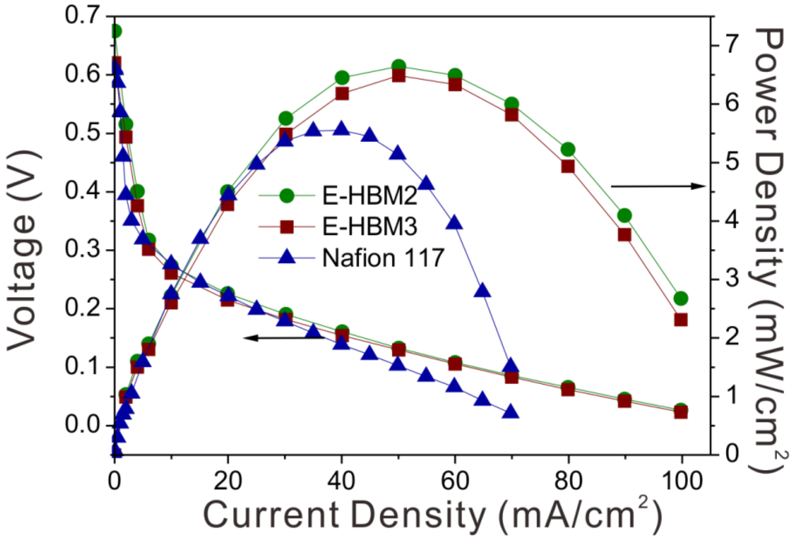

Figure S5. Polarization curve comparison of the passive DMFCs using the E-HBM2, E-HBM3 and Nafion 117 membranes as electrolytes with a 3M methanol solution.

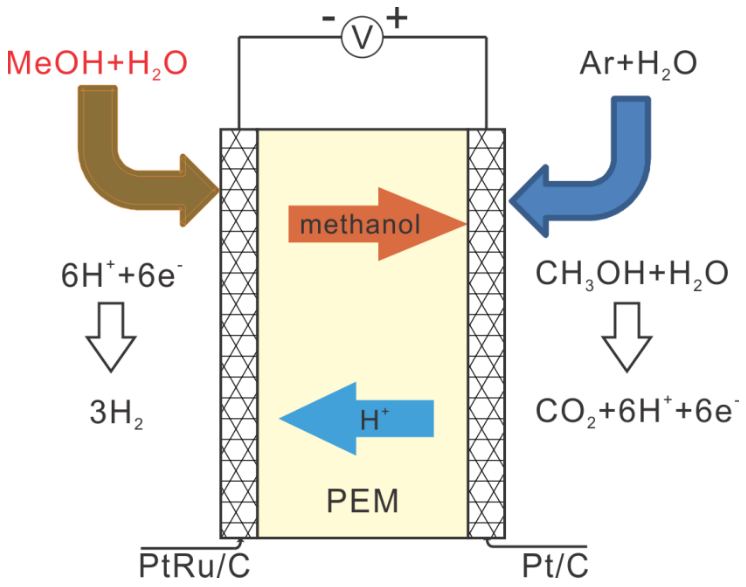

Figure S6. Schematic demonstration of methanol permeation measurement in a PEM cell of DMFC configuration.

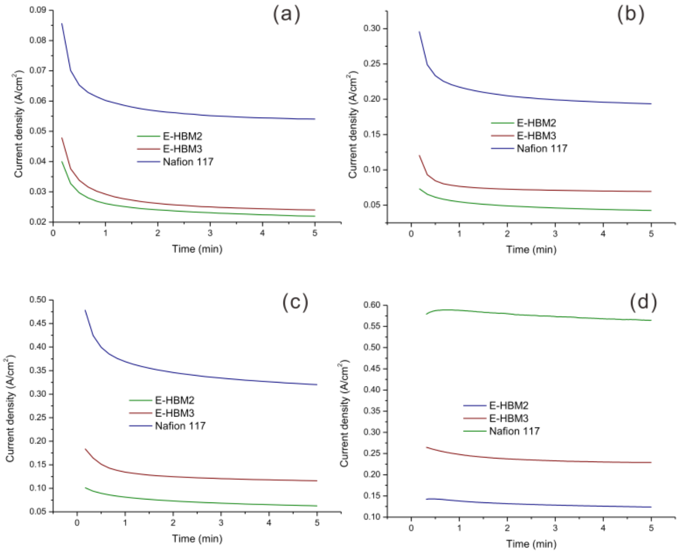

Figure S7. Chronoamperometry curves of methanol permeating through the E-HBM2, E-HBM3 and Nafion membranes exposing in (a) 1 M, (b) 3 M, (c) 6 M and (d) 15 M methanol solutions at 0.9 V.