

## Novel high-performance nanohybrid polyelectrolyte membranes based on bio-functionalized montmorillonite for fuel cells applications

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### Experimental

*Materials.* Chitosan (molecular weight 280,000 g/mol, degree of deacetylation 83%) was supplied by Fluka. Acetic acid and methanol were obtained from Merck. K-10 montmorillonite (MMT) clay was purchased from Fluka and used as unfunctionalized MMT. Deionized water (purified with Milipore<sup>TM</sup>) was used in this work. Nafion<sup>®</sup> 5%wt solution in water and low molecular weight alcohols was acquired from E.I. DuPont de Nemours Company for membrane formation. Nafion<sup>®</sup> 117 membranes, from DuPont were used as the reference membrane. All analytical-grade reagents from commercial sources were used without further purification.

*Modification process of MMT.* Modification of MMT with chitosan was carried out according to a previously reported method.<sup>7</sup> Briefly, 1 g of MMT was dispersed in 50 ml of deionized water and definite amount of chitosan was separately dissolved in 1%v/v acetic acid aqueous solution. Both mixtures were then poured in an Erlenmeyer flask and stirred at 60°C for 48 h. After heating treatment, the mixture was centrifuged, and then washed with acetic acid solution and water. Finally, the product was dried in an air circulating oven at 60°C for 6 h and then was ground and kept in a glass capped bottle for subsequent usage.

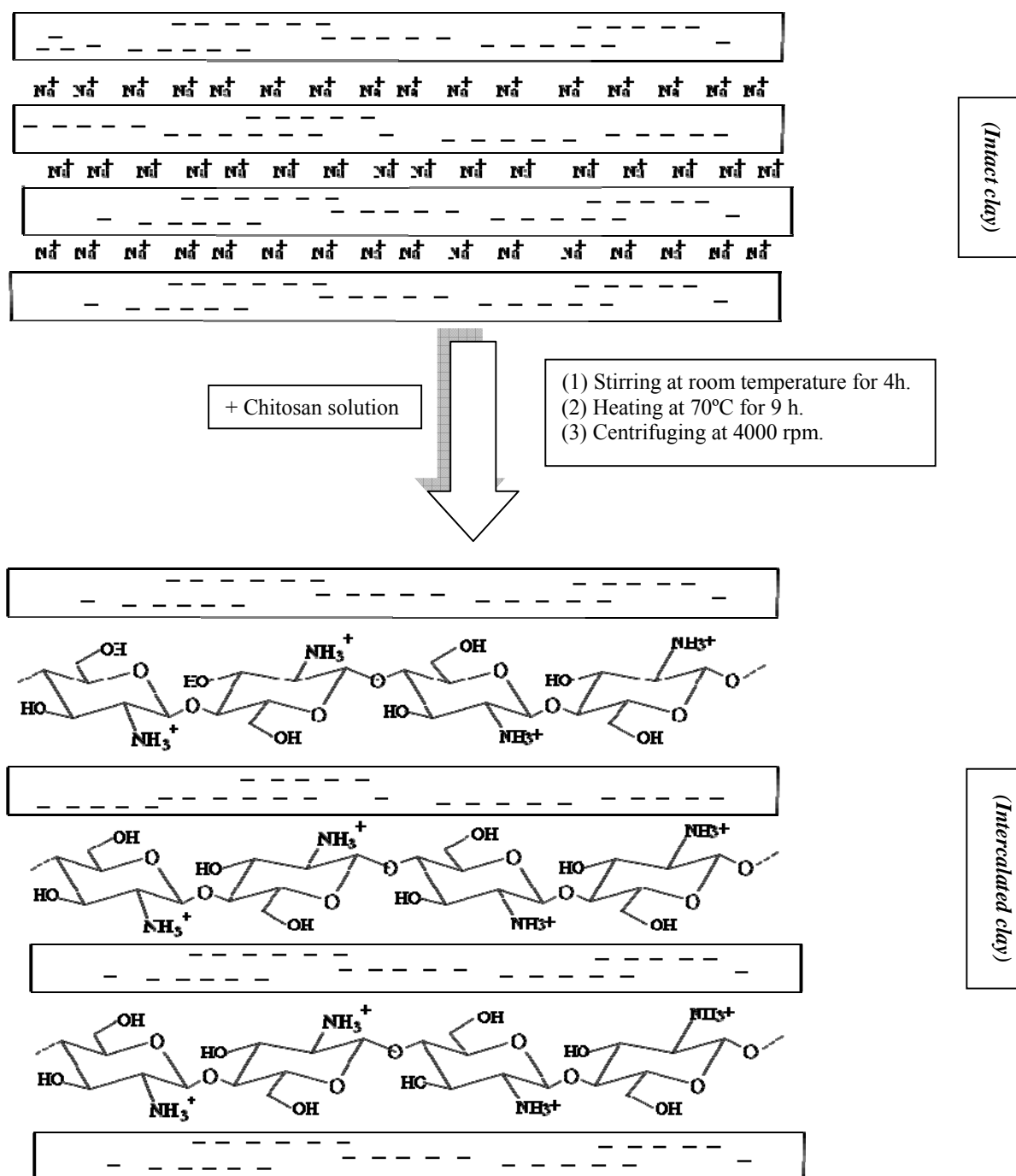
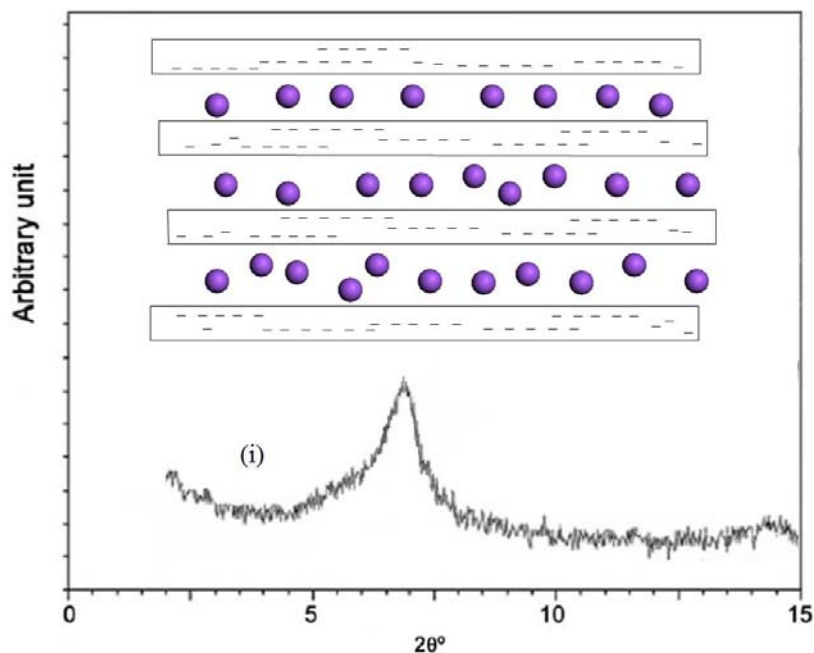


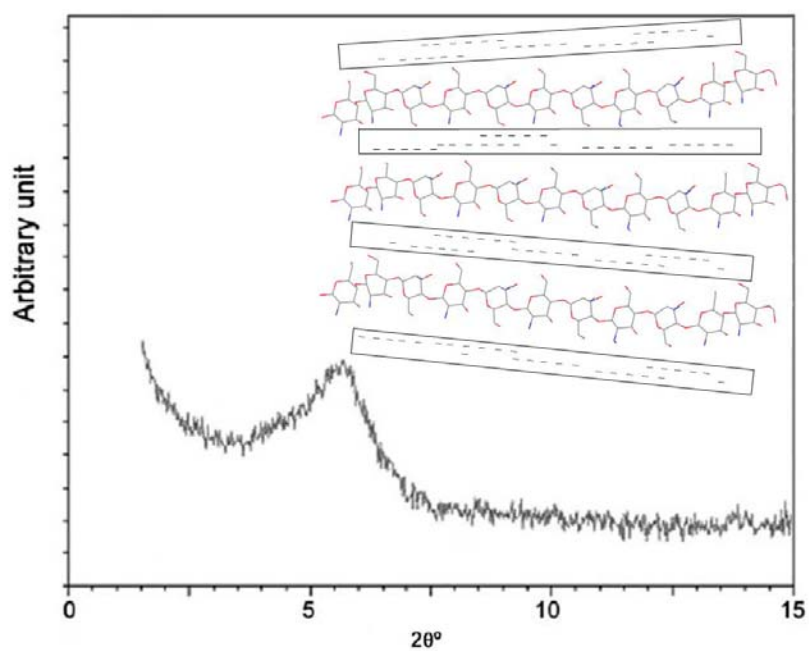
Figure S1. Schematic representation of montmorillonite modification with chitosan.

*Membrane preparation.* BMMT at various loading weights (1, 2, 3, 5 and 10 wt%) was suspended in Nafion<sup>®</sup> solution at 25°C and stirred for 2.5 h. The resultant mixtures were ultra-sonicated for five successive 30min intervals and concentrated in a rotary evaporator. The viscose solutions were cast on glass plates and incubated at 25°C overnight and then dried at 70°C for 8 h. Finally, fabricated membranes were annealed at 120°C for 12 h. Subsequently, prepared membranes were modified by boiling in hydrogen peroxide (3 vol%, for 30 min), then were washed several times and boiled for 1 h in deionized water. Subsequently, membranes were boiled in sulfuric acid for another hour and washed several times with deionized water. Nafion<sup>®</sup>117 membranes were modified through the same modification procedure.

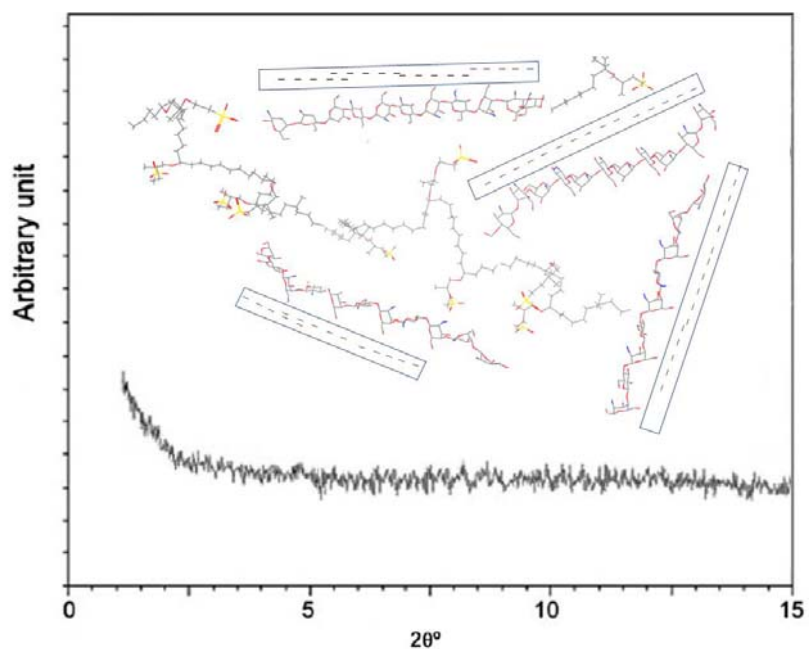
*X-Ray diffraction.* Dispersion of MMT particles in the membranes were detected by XRD (SIEMENS XRD-D5000 diffractometer, Cu-K $\alpha$ ). The scanning diffraction angle,  $2\theta$ , was less than 15°.



**Figure S2.** a) Schematic structure of silicate nanosheets with Na<sup>+</sup> ions and XRD pattern of unmodified MMT.

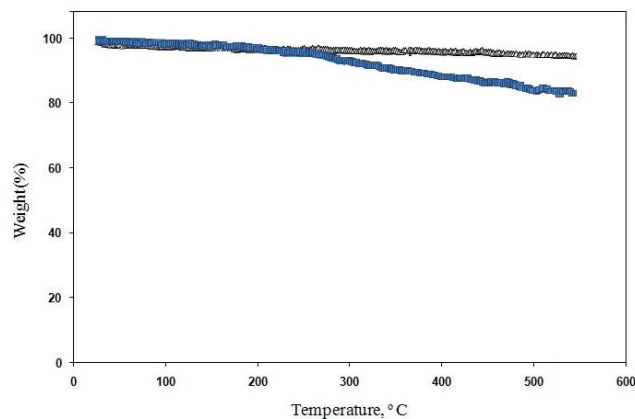


**Figure S2. b)** Schematic structure of silicate nanosheets with chitosan biomacromolecules and XRD pattern of chitosan modified MMT (BMMT).

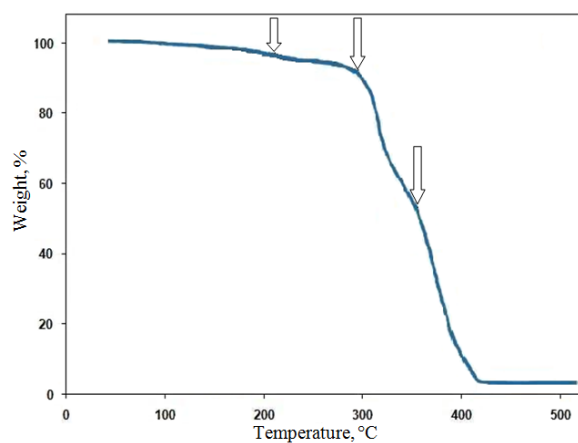


**Figure S2. c)** Schematic representation of nanohybrid Nafion<sup>®</sup>/BMMT with exfoliated structure and its XRD pattern.

*Thermogravimetry analysis.* The degradation process and the thermal stability of the MMT, BMMT and obtained nanohybrid membranes were investigated by TGA (Perkin-Elmer Pyris1). The approximately 10-20 mg of fully dried samples were characterized with a heating rate of 10 °C per minute.



**Figure S3. a)** TGA plots of unmodified MMT (white triangles) and Bio-modified MMT (blue rectangular).



**Figure S3. b)** TGA plot for Nafion<sup>®</sup>/BMMT nanohybrid; the degradation points has been shown.

**Table S1.** Thickness of dry Nafion<sup>®</sup>/BMMT (N/BMMT) nanohybrid membranes.

Sample	BMMT loading weight (%)	Membrane Thickness (μm)
N/ BMMT-0%	0.0	60
N/ BMMT-1%	1.0	55
N/ BMMT-2%	2.0	58
N/ BMMT-3%	3.0	56
N/ BMMT-5%	5.0	59
N/BMMT10%	10.0	55
Nafion <sup>®</sup> 117	-	178

Thickness was reported as mean values of at least three samples for each composition; Standard variation not exceeded than 10%.

*Water/methanol swelling measurements:* To study swelling behavior of fabricated membranes, dried samples were first soaked in deionized water and methanol separately at room temperature for a day, and then quickly weighed in different time intervals after carefully removing excess water or methanol with filter papers, and immersed back in the liquid. The mentioned process was repeated several times until no further weight gain was observed. Finally, the swelling ratio was calculated using the following equation:

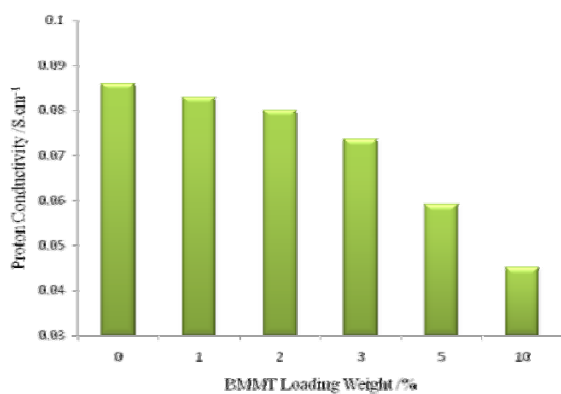
$$\text{Swelling ratio (\%)} = \frac{W_{sw} - W_{dry}}{W_{dry}} \times 100$$

where,  $W_{sw}$  and  $W_{dry}$  are the weights of membranes in the swelled and dried states, respectively.

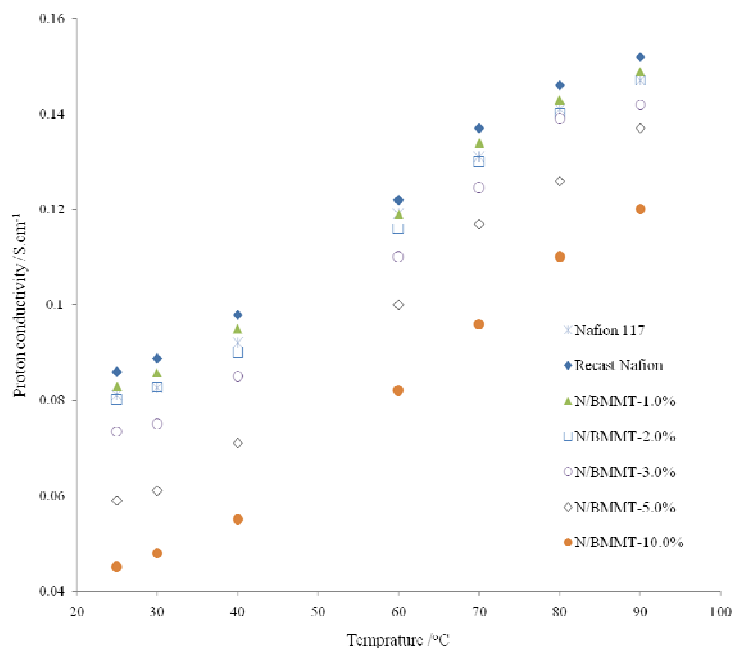
**Table S2.** Water/methanol uptake of N/BMMT-2wt% and Nafion<sup>®</sup> 117 in 1 and 5M methanol solutions at room temperature.

Sample	Methanol Concentration (M)	Methanol Uptake (%)	Water Uptake (%)	Water to Methanol Uptake Selectivity
Nafion <sup>®</sup> 117	1.0	36.4	32	0.88
Nafion <sup>®</sup> 117	5.0	48.2	32	0.66
N/BMMT-2wt%	1.0	38.3	35.5	0.93
N/BMMT-2wt%	5.0	42.5	35.5	0.84

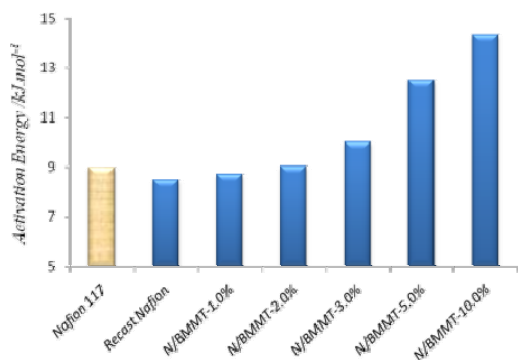
*Proton conductivity measurements:* Conductivity was calculated from the equation of  $\sigma = L \cdot R^{-1} \cdot A^{-1}$ , where  $L$ ,  $A$  and  $R$  is membrane thickness, cross-sectional area of membranes and resistance. Before proton conductivity measurements, conductivity cell was set into a humidity chamber at 25-90°C and 95% relative humidity (RH) at least for 3 h.



**Figure S4. a)** Effect of BMMT loading weights on proton conductivity of Nafion<sup>®</sup>/BMMT nanohybrid membranes.



**Figure S4. b)** Effect of temperature on proton conductivity of Nafion<sup>®</sup>/BMMT at different BMMT loading weights.



**Figure S5.** Proton conduction activation energies of Nafion<sup>®</sup>/BMMT membranes at different BMMT loadings.

*Methanol permeability:* Methanol permeability was measured via a dual compartment glass diffusion cell, wherein the membrane sample separated a methanol solution from a pure water solution. The rise in concentration of the methanol was measured by gas chromatography as a function of time, and methanol diffusion coefficient was determined



using following equation:

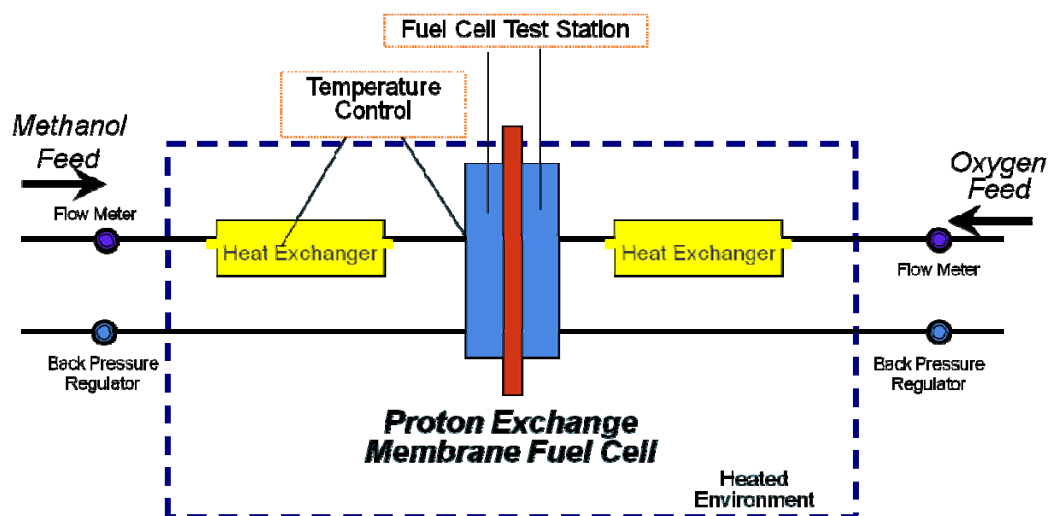
$$P = \frac{1}{C_A} \left( \frac{\Delta C_{B(t)}}{\Delta t} \right) \left( \frac{L \cdot V_B}{A} \right)$$

where,  $P$  is the methanol diffusion permeability of the membrane,  $C_A$  is the concentration of methanol in cell A,  $\Delta C_B/\Delta t$  is the slope of the molar concentration variation of methanol in the cell B as a function of time,  $V_B$  is the volume of each diffusion reservoir,  $A$  is the membrane area and  $L$  is thickness of the membrane.

*Membrane electrode assembly (MEA) and single cell DMFC test:* The MEAs were prepared via catalyst decaling and painting methods as our previous studies.<sup>4</sup> Pt and Pt/Ru-black (purchased from Johnson–Matthey) were used as catalysts at anode and cathode sides, respectively. The catalysts were mixed with 5 wt% Nafion<sup>®</sup> solution and several drops of glycerol (obtained from Merck) as the suspension/painting agent. The prepared suspension was brushed directly ( $4 \text{ mg cm}^{-2}$ ) onto dry membranes, and then hot-pressed to increase the contact area between the catalyst layer and membranes. Prepared MEAs were boiled in a dilute solution of sulfuric acid, and washed several times with distilled water.

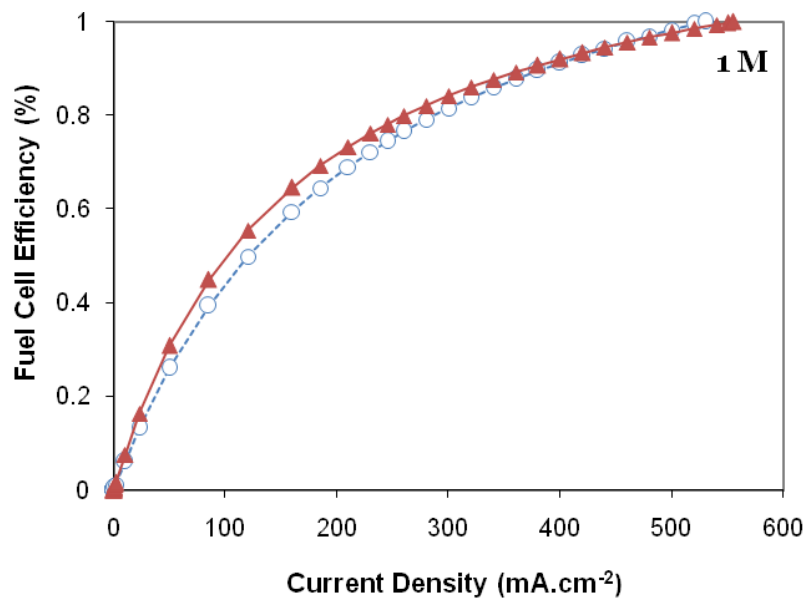
The DMFC was made according to our previous reports.<sup>4</sup> The TGP-H-120 Toray was employed as the gas diffusion layers and silicon rubber was used to seal internal sections. The performance of single cell DMFC was measured using two methanol concentrations (1 and 5M) and air flow in the anode and cathode sides at 70°C. Methanol was fed to the anode side at 20 psi back pressure for 1 h. Air was introduced at the cathode side with gradual increase to 20 psi, and the cell was allowed to run for 30 min before data collection. All single cell tests were conducted at least for three times, and obtained results were presented as the mean values.

For methanol crossover measurements, humidified nitrogen was fed to cathode side at 70°C, and the fuel cell was performed until a limiting current occurs. This limiting current obtained at the open circuit condition indicates the oxidation current of methanol crossover from anode to cathode.

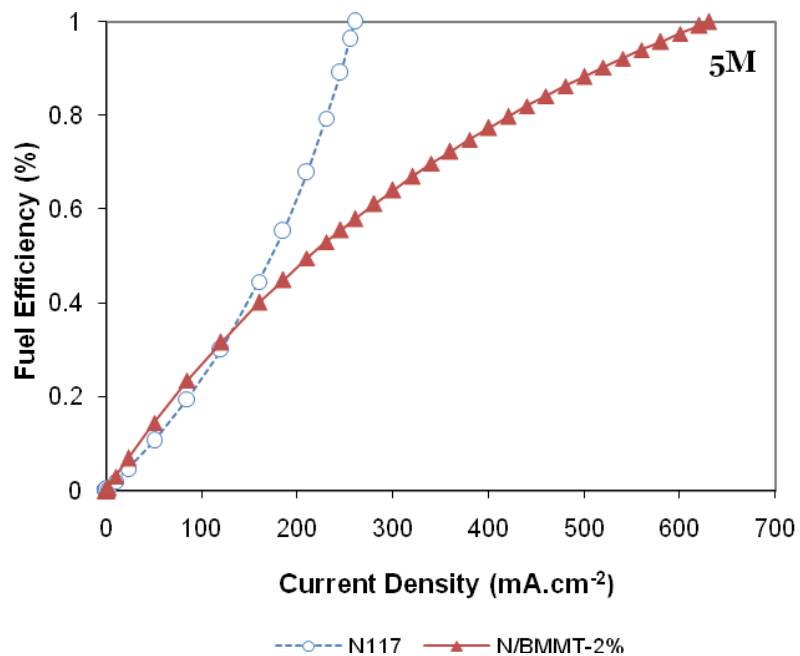


**Figure S6.** Schematic diagram of direct methanol fuel cell testing system.

As also mentioned in the manuscript, methanol permeation through polyelectrolyte membranes leads to catalyst poisoning at cathode, hindrance of oxygen reduction, reduced fuel efficiency and fuel loss. Fuel efficiency,  $\eta_{Fuel}$ , was calculated using methanol crossover results via following equation:  $\eta_{Fuel} = I / (I + I_C)$  ref. Thermodynamic efficiency,  $\eta_{Therm}$ , is defined as the ratio of Gibbs free energy change per mole of methanol,  $\Delta g$ , to enthalpy change per mole of methanol,  $\Delta h$ . The fuel efficiency results at two different methanol concentrations for nanohybrid and Nafion<sup>®</sup> 117 membranes have been displayed in Figure S7.



**Figure S7. a)** A comparison between fuel efficiency of nanohybrid and Nafion<sup>®</sup>117 membranes at 1M methanol concentration.



**Figure S7. b)** A comparison between fuel efficiency of nanohybrid and Nafion<sup>®</sup>117 membranes at 5M methanol concentration.

The voltage efficiency of fuel cell,  $\eta_{Volt}$ , is determined as ratio of the real operating voltage,  $V_{Cell}$ , to theoretical maximum voltage,  $V_{Th}$ , of fuel cell. Accordingly, real efficiency of fuel cell,  $\eta_{Real}$ , is obtained the combination of fuel efficiency, thermodynamic efficiency, and voltage efficiency:  $\eta_{Real} = \eta_{Fuel} \cdot \eta_{Therm} \cdot \eta_{Volt}$ . In this work, the methanol crossover current density and real efficiency of the DMFC were performed depend on methanol concentration and membrane types. The results of real efficiency assessment of fuel cell at two different methanol concentrations for Nafion<sup>®</sup>117 and N/BMMT-2% membranes have been displayed in Fig. 2 ((c) and (d)). As seen, in the case of Nafion<sup>®</sup>117, efficiency is dramatically decreased from 17% to 11% as methanol concentration is increased from 1 to 5M, and current density at the maximum efficiency is decreased as well. However, in the case of nanohybrid membrane overall efficiency is enhanced from 21% to 24% with increasing methanol concentration, which is owing to the effective role of BMMT in reduction of methanol crossover through designed nanohybrid membrane.