Supporting Information

Copper-trimesic acid metal-organic framework incorporated sulfonated poly(ether ether ketone) based polymer electrolyte membrane for direct methanol fuel cells

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The Cu-TMA formation was confirmed by following characterization techniques. Powder X–ray diffraction (PXRD) analysis was carried out using Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation of wavelength 1.54 Å. FT-IR spectra of Cu-TMA particles and SP/CT-MOF-3 composite membrane were analyzed using Nicolet IR 860 Spectrometer (Thermo Nicolet Nexus-670). Thermo-gravimetric analysis (TGA) for pristine sPEEK and SP/CT-MOF-3 was carried out using NETZSCH STA 449F3 TGA-DSC instrument in the temperature range between 30°C and 900°C at a heating rate of 5°C min^{-1} with nitrogen purged at 60 ml min^{-1}.

Surface morphology of Pristine sPEEK and SP/CT-MOF-3 membranes was studied using TESCAN MIRA3 LMU Field Emission Scanning Electron Microscope (FE-SEM). The mechanical properties of the above membranes were examined using universal testing machine (UTM) (model: ZWICK/Roell,146500) with an operating head-load of 1 kN. Stress-strain curves were derived from the measurement to confirm the stability of the membranes. Topology images for pri

stine sPEEK and its composite membrane were taken by tapping mode atomic force microscopy (AFM, PicoSPM–Picoscan 2100, Molecular Imaging, USA).

Acid-base titration is carried out for the membranes to determine the ion exchange capacity (IEC) [1]. In brief, the required weight of dry membrane was soaked in 50 ml of saturated 3N NaCl solution for 24 h to exchange the H^+ ions present in the membrane with Na^+ ions. 10 ml of the the exchanged acidic solution was titrated against 0.01 N NaOH with phenopthalein as indicator to notice colourless solution to pale pink. The IEC was determined using the relation.

$$IEC = \frac{Volume\ of\ NaOH\ \times Normality\ of\ NaOH}{Dry\ weight\ of\ the\ sample} meq.\ g^{-1} \qquad (1)$$

The water sorption was measured by the mass difference between the wet and the dry membranes [2]. In brief, the membrane samples were dried in vacuum oven to remove adhered moisture in the sample and then weighed. The samples were immersed in the sorption chamber (filled with de-ionized water) and retained for 24 h till the equilibrium is attained. Samples were then taken out and surface sorbed to remove water and sorbed weight was noted and finally the water sorption is measured considering the weight difference of the membrane in dry and sorbed conditions as follows.

$$Water\ sorption\ = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (2)$$

Proton conductivity for the membranes was analyzed by four probe AC impedance analysis [3]. The membrane samples were cut into required dimension, and clamped in a BekkTech conductivity Cell interfaced with the four platinized probes. The cell was placed in a ESPEC humidification chamber for the required humidity (98 %). Four probes of the cell

were connected to a potentiostat (SP-150) to derive impedance spectra and the conductivity of the membrane in relation to temperature was determined by resistance by following relation.

$$Conductivity\ (\sigma) = \frac{L}{R\,A}$$

(3)

where R is the resistance from the real axis intercept ($Z′$) of the impedance spectra, L is the probe distance (0.425 cm) in the conductivity cell, A is cross-sectional area of the membrane.

Activation energy for proton transport (σ) for all the membranes is determined using Arrhenius plots by the following relation.

$$(\sigma) = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)$$

(4)

Where σ_0 is pre-exponential factor, E_a is activation energy, R is universal gas constant and T is temperature.

2.5. Methanol permeability for the membranes

Methanol permeability for pristine sPEEK and SP/CT-MOF membranes were analyzed using diffusional cell mode experiments carried out at 25°C [4]. The test membranes were clamped between two Teflon compartments in which first compartment is filled with 50 ml of 2M methanol and the second one with water of similar quantity. Methanol diffuses through the membrane in relation to time (0-8 h) towards water compartment due to concentration gradient and methanol concentration in water compartment is measured by gas chromatography (Thermo scientific Trace GC-700) equipped with flame ionization detector (FID). Methanol permeability for the membranes are calculated from the following relation.

$$P = \frac{k_2 \times V_2 \times L}{(C_1 - C_2) \times A}$$

Where P is permeability of the membrane, k_2 is the slope of the concentration profile derived from water compartment, V_2 is the volume of liquid in water compartment, C_1, C_2 are the concentrations of methanol in compartment 1 and 2 respectively. L, A are thickness and area of the test membranes.

$$\textit{Electrochemical selectivity } (S\, s\, cm^{-3}) = \frac{\textit{Proton conductivity } (S\, cm^{-1})}{\textit{Methanol permeability } (cm^2\, s^{-1})}$$
(6)

4 cm² active area membrane electrode assemblies (MEA) based on the aforesaid membranes were fabricated as per our earlier reports[4] .In brief, the ionomer (Nafion-isopropyl alcohol) mixture was layered as binder on anode Pt-Ru/C (catalyst loading of 2 mg cm⁻²) and cathode Pt/C (catalyst loading of 2 mg cm⁻²) to achieve a proper triple phase boundary. The prepared membrane was placed between the anode and cathode during hot pressing at 80 ℃ with 20 kg cm⁻² pressure for 2 min to form a MEA. It is to be noted that different membrane electrode assemblies (MEAs) were prepared by placing the membranes of pristine sPEEK, SP/CT-MOF-1, SP/CT-MOF-2 and SP/CT-MOF-3 in between anode and cathode. The MEA prepared was tested by assembling it in a standard fuel cell fixture with single channel serpentine flow field machined on graphite plate (supplied by Fuel Cell Technologies, US). 2M aqueous methanol solution was passed at a flow rate of 2 ml min⁻¹ to the anode and oxygen was considered at a flow rate of 300 ml min⁻¹ to the cathode. The MEAs were tested using a electronic load Model-LCN4-25-24/LCN 50-24 from Bitrode Instruments (US). Cell was conditioned in galvanostatic mode and then polarized to measure the cell potential in relation to current density for the DMFC power output. Finally, stability tests for MEAs comprising pristine sPEEK and SP/CT-MOF-3membranes were carried out in

OCV condition wherein methanol cross-over will be maximum to notice the variation in OCV with time for 55 h.

References

1 D. Xu, G. Zhang, N. Zhang, H. Li, Y. Zhang, K. Shao and M. Han, *J. Mater. Chem.*, 2010, **20**, 9239-9245.

2 G. Rambabu and S. D. Bhat, *Chem. Eng. J.*, 2014, **243**, 517-525.

3 G. Rambabu and S. D. Bhat, *J. Memb. Sci.*, 2018, **551**, 1-11.

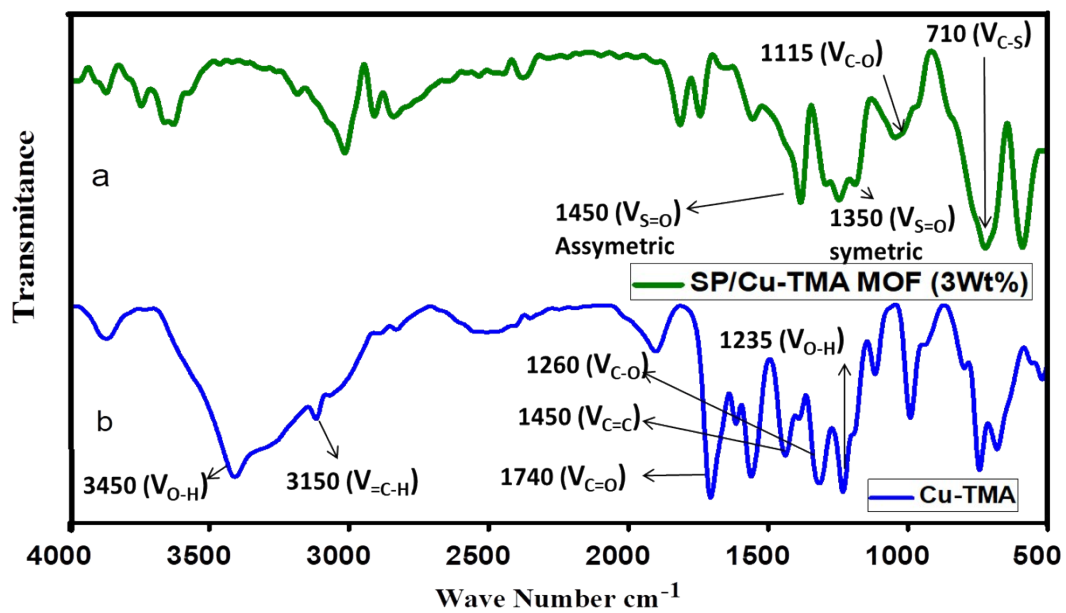4 G. Rambabu, N. Nagaraju and S. D. Bhat, *Chem. Eng. J.*, 2016, **306**, 43-52.

Figures

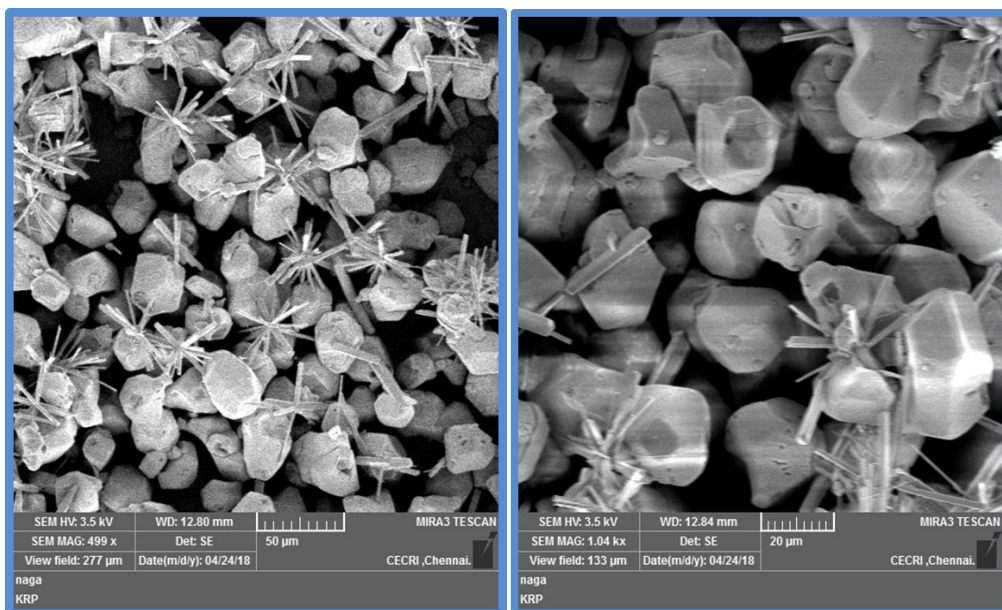**Fig. S1**. FT-IR spectra for (a) SP/Cu-TMA Composite membrane and (b) Cu-TMA MOF .

Fig. S2 SEM images for Cu-TMA MOF.