Supporting Information for

Triazole-rich 3D Metal-organic Framework incorporated solid electrolyte for superior proton conductivity and durability in fuel cells

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S1. Synthesis of SPEEK (Sulfonated Poly ether ether ketone)

SPEEK was synthesized by a previously reported procedure with by optimizing some conditions. At first 150 ml of concentrated sulfuric acid was added into a 4-neck glass reaction vessel. It was fitted with an overhead mechanical stirrer at set at 1200 rpm. Dried PEEK powder (10gm) was added in small portions into the container over the next 30 minutes. After dissolution of the powder, it was kept under stirring for 48 h at room temperature. Finally, the viscous solution was precipitated into chilled water and a white filament-like solid was obtained. It was washed repeatedly with water to neutralize the acid and oven dried for 24 h at 100°C. The Degree of sulfonation (DS) was determined by the formula using ^{1}H NMR spectroscopy as given in FIGURE S1.

$$\frac{n}{12-2n} = \frac{\Delta H_E}{\Sigma AHA,A^{'},B,B^{'},C,H} \qquad (S1)$$

$0 \leq n \leq 1$

Degree of Sulfonation (%) = n × 100

Where, n denotes the sulfonation number, ΔH_E is the calculated area of the NMR peak of hydrogen adjacent to SO_3H group signal and $\Sigma AH_{A,\ A',\ B,\ B',\ CD}$ is the total sum of the area of

NMR peak signals that corresponds to the other hydrogens in different chemical environment of the benzene ring, named $H_{A, A', B, B', C, D}$. The ratio between the number of H_E (n) and the all the others aromatic hydrogens (12 - 2n) per repeat unit is calculated from the ratio between the peak area of H_E signals, (ΔH_E). The degree of sulfonation obtained in this work is 70 %.

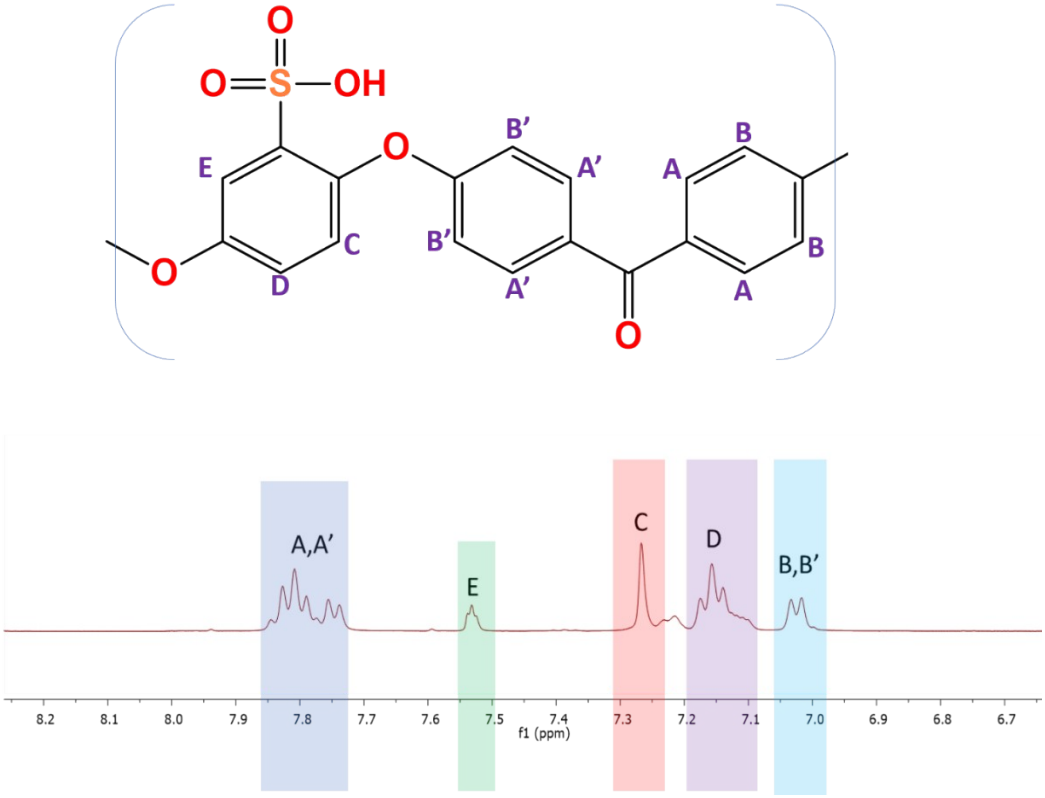
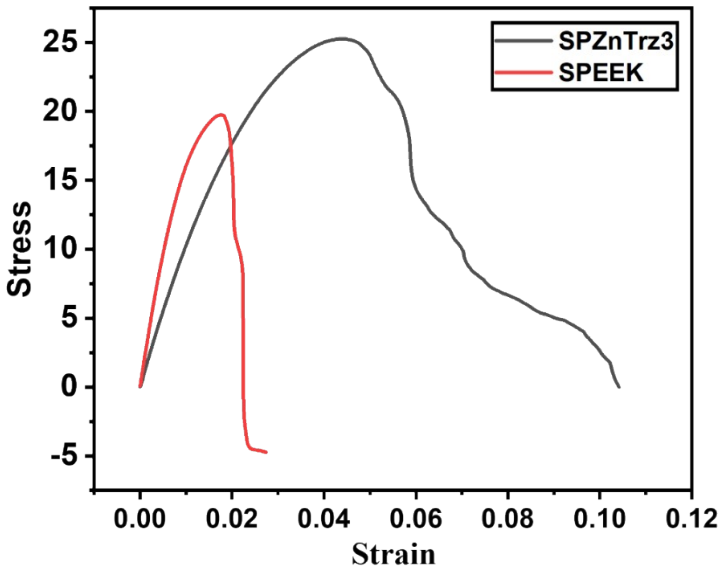


Figure S1: NMR spectrum of SPEEK



Mechanical Behavior

Figure S2: The stress-strain curve of SPEEK and SPZnTrz3 was obtained using the UTM (INSTRON 5kN Model 3365) machine.

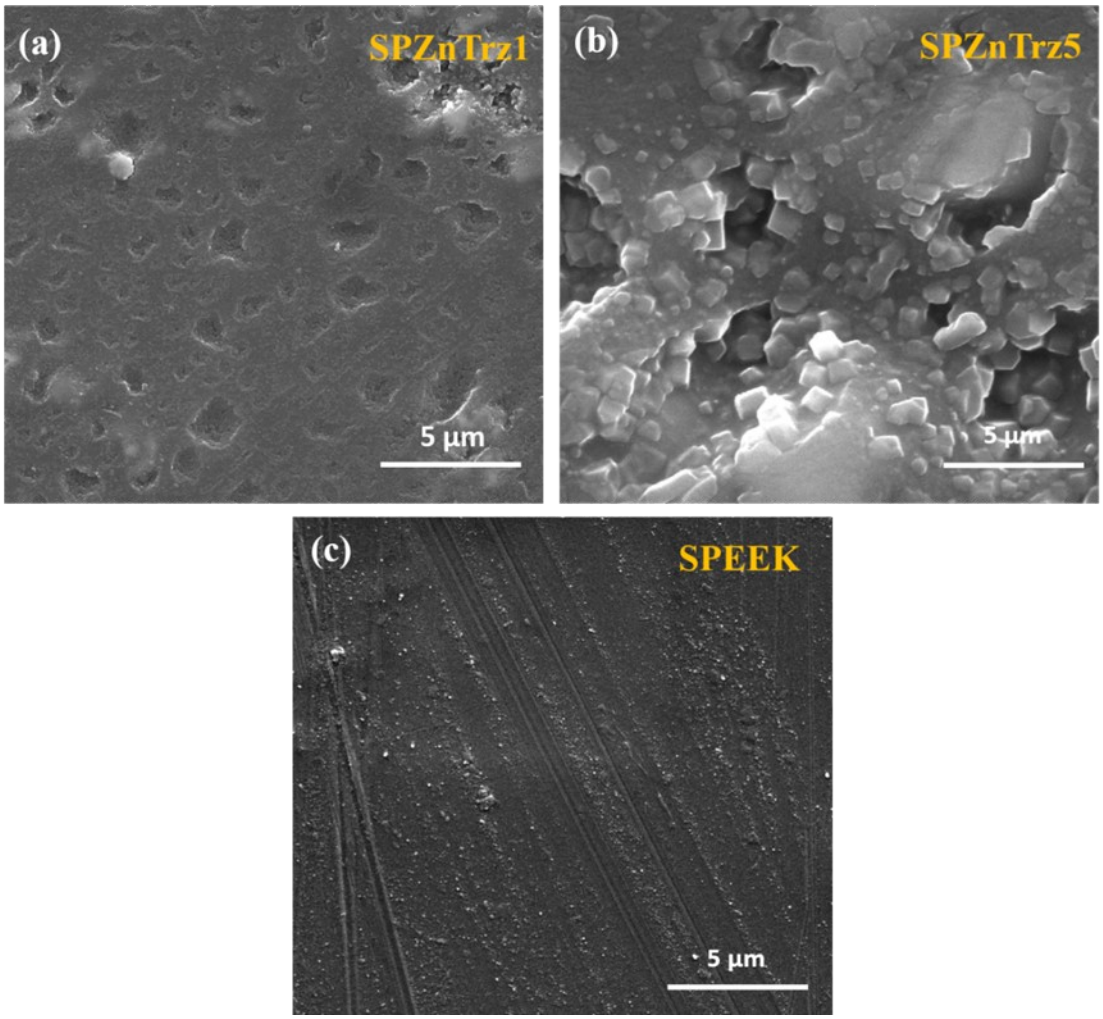


Figure S3: SEM images of SPZnTrz1(a), SPZnTrz5 (b), SPEEK (c).

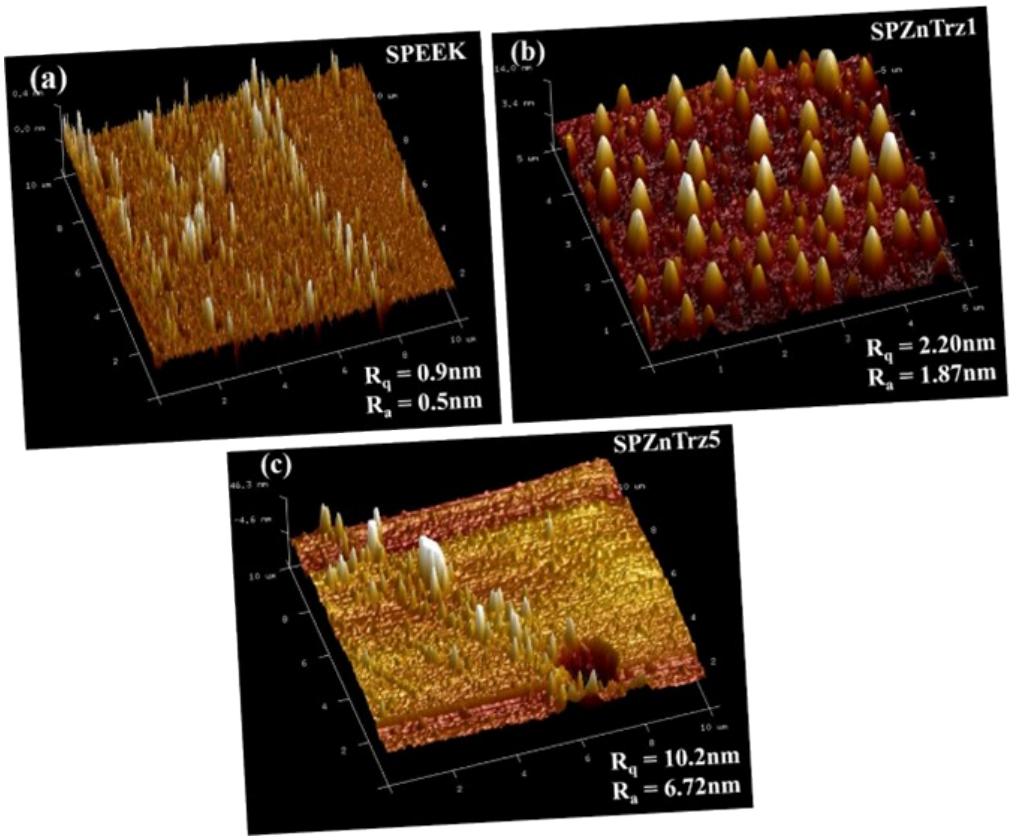


Figure S4: 3D AFM images of SPEEK(a), SPZnTrz1 (b), SPZnTrz5 (c).

S2. Water Uptake

Membrane water uptake was measured by weight change following a 24-hour immersion in deionized water at from 20-80 °C temp. range. Next, the samples' weights were determined, and the following formula was used to estimate the water uptake (WU):

$$WU(wt\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad \text{(S2)}$$

Where, W_{dry} and W_{wet} represent the membrane's measurements in the corresponding wet and dry circumstances.

S3. IEC

The ion-exchange capabilities were evaluated by acid-base titration using phenolphthalein indicator. To replace the H+ ions with sodium ions, the dried membrane samples were dipped in a 1M NaCl solution for 24 hours after the weight was recorded. The volume consumed was measured at the edge of the indicator's color shift when the solution containing the released

protons was titrated against NaOH (0.01 M) solution. The IEC of the membranes was then determined using the following formula:

$$IEC\ (mmol\ g^{-1}) = \frac{C_{NaOH} \times V_{NaOH}}{W_{dry}} \quad \text{(S3)}$$

where V_{NaOH} is the volume of NaOH solution consumed during the titration and C_{NaOH} is the titrant concentration. The final values were determined by averaging three measurements that were obtained simultaneously.

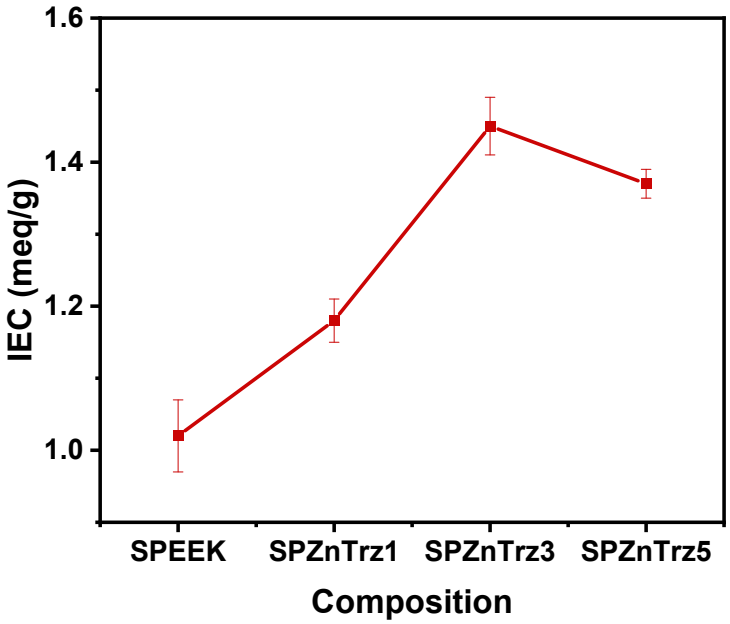


Figure S5: IEC graph of different membranes

S4. Swelling Ratio

The following equation was used to assess the difference in length between the initial dried membrane sample (L_{dry}) and the hydrated sample (L_{wet}) in order to determine the swelling ratio of the membrane at various temperatures:

$$SR\ (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times\ 100\% \quad \text{(S4)}$$

The final values of the test were determined by averaging three measurements that were obtained simultaneously.

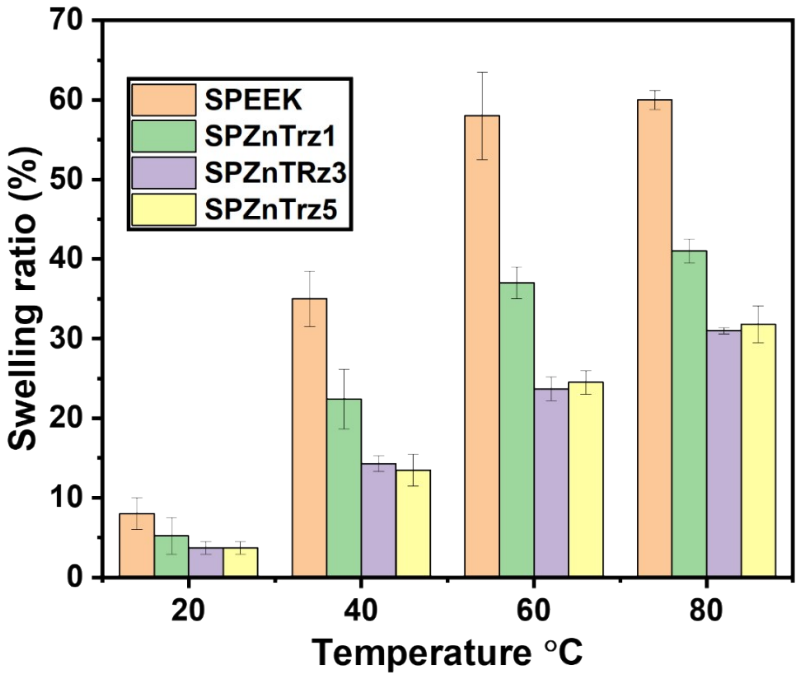


Figure S6: Swelling Ratio of the composite membranes with varying temperature.

S5. Oxidative Stability

To study the antioxidant stability of the membranes, the weight of the dried samples was measured and then dipped in aliquots of hydrogen peroxide catalysed with Fe^{2+} salt (3 wt.% H_2O_2 solution with 4 ppm Fe^{2+}), to create hydroxyl radical environment for 12 h at 60 °C. The residual weight percentage was noted after the treatment and the difference in weight was calculated and plotted.

S6. Proton Conductivity

Proton conductivity (σ) of the samples was determined using the alternating current impedance technique (EIS) of two electrode systems at various temperatures and relative humidity levels 50 % between 0.1 and 100 kHz. Firstly, the membranes were cut into square shapes of appropriate size and kept overnight in 1(M) H_2SO_4 solution. The membranes were wiped and air dried for 1 h and sandwiched between two steel electrodes and placed inside the cell as shown in FIGURE S7 equipped with heater, humidity and temperature sensors for conductivity measurement. The electrodes measure potential drop. The membranes resistances were measured at 30, 50, 65, 80, 100 ° C. To attain equilibrium and stability the cell was maintained for 20 mins at every measuring temperature before performing the EIS test. With the help of

the Metrohm Autolab Potentiostat/Galvanostat 2.0 (USA), the electrochemical characterization was completed, and the bulk resistance was noted from the Nyquist plots that were produced to calculate conductivity using equation 1.

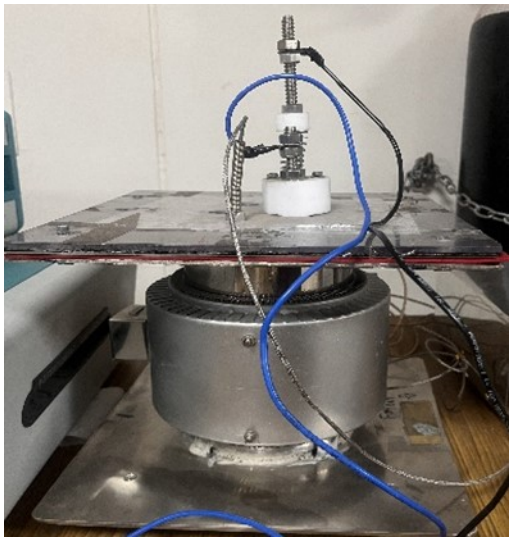


Figure S7: Conductivity cell used to generate Nyquist plots for proton conductivity of membranes by two probe method.

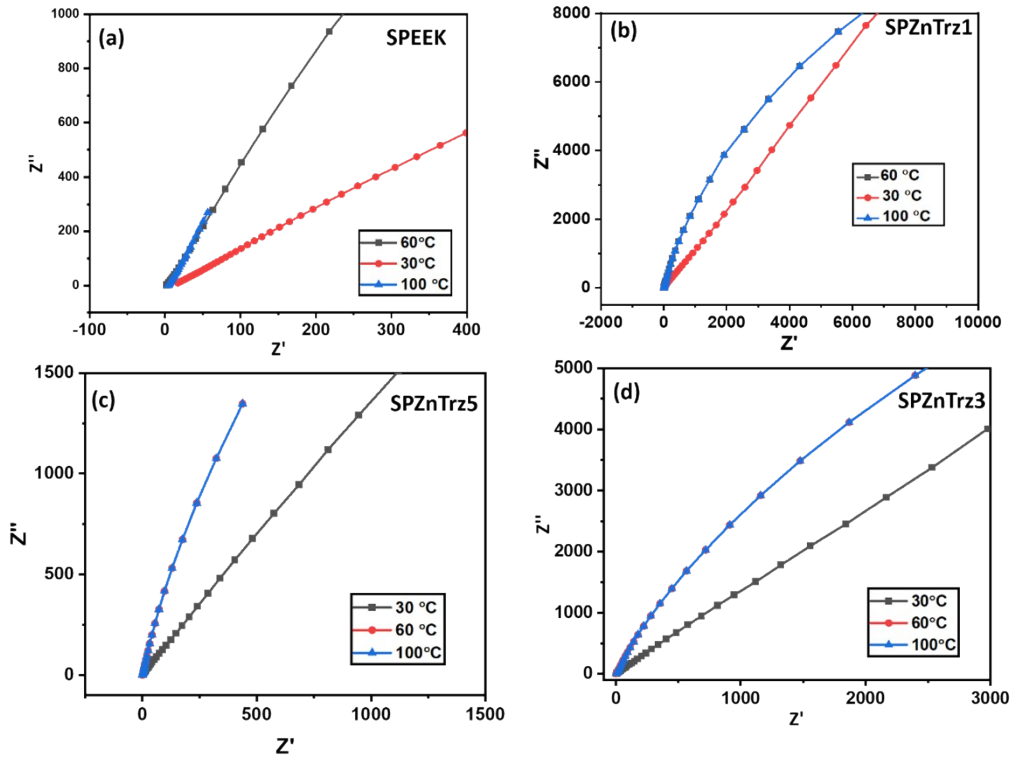


Figure S8: Nyquist plots obtained for membranes at different temperatures SPEEK (a), SPZnTrz1(b), SPZnTrz5(c), SPZnTrz3(d).

S7. PEMFC testing (Single cell)

Membrane electrode assemblies (MEAs) were prepared by brush coating of the catalyst ink slurry on a gas diffusion layer. Teflonised carbon cloth was used in our MEA. The catalyst ink was formulated using commercial DURA-LYST® ST1110 20% Platinum on Vulcan XC72. A measured amount of Pt/C catalyst was taken in a glass vial and wetted with small amounts of distilled water to prevent its burning by isopropanol. After few minutes, required amount of isopropanol was added into the vial and sonicated for 30 mins in an ultrasonicator bath whose temperature was maintained at 20 °C. Into the dispersed ink, 5 % Nafion solution was used as binder ionomer to promote adhesion to the carbon cloth layer and sonicated for another 20 mins and coated (0.25 mg/cm^2 on anode side and 0.5 mg/cm2 on the cathode side). After sufficient drying of the coated electrodes, a membrane was sandwiched between them and hot-pressed at 120 °C and 20 kg/cm^2 for 2 minutes to prepare the MEA. The MEA was fitted in a single cell assembly after activation as shown in FIGURE S9 and tested for performance and durability.

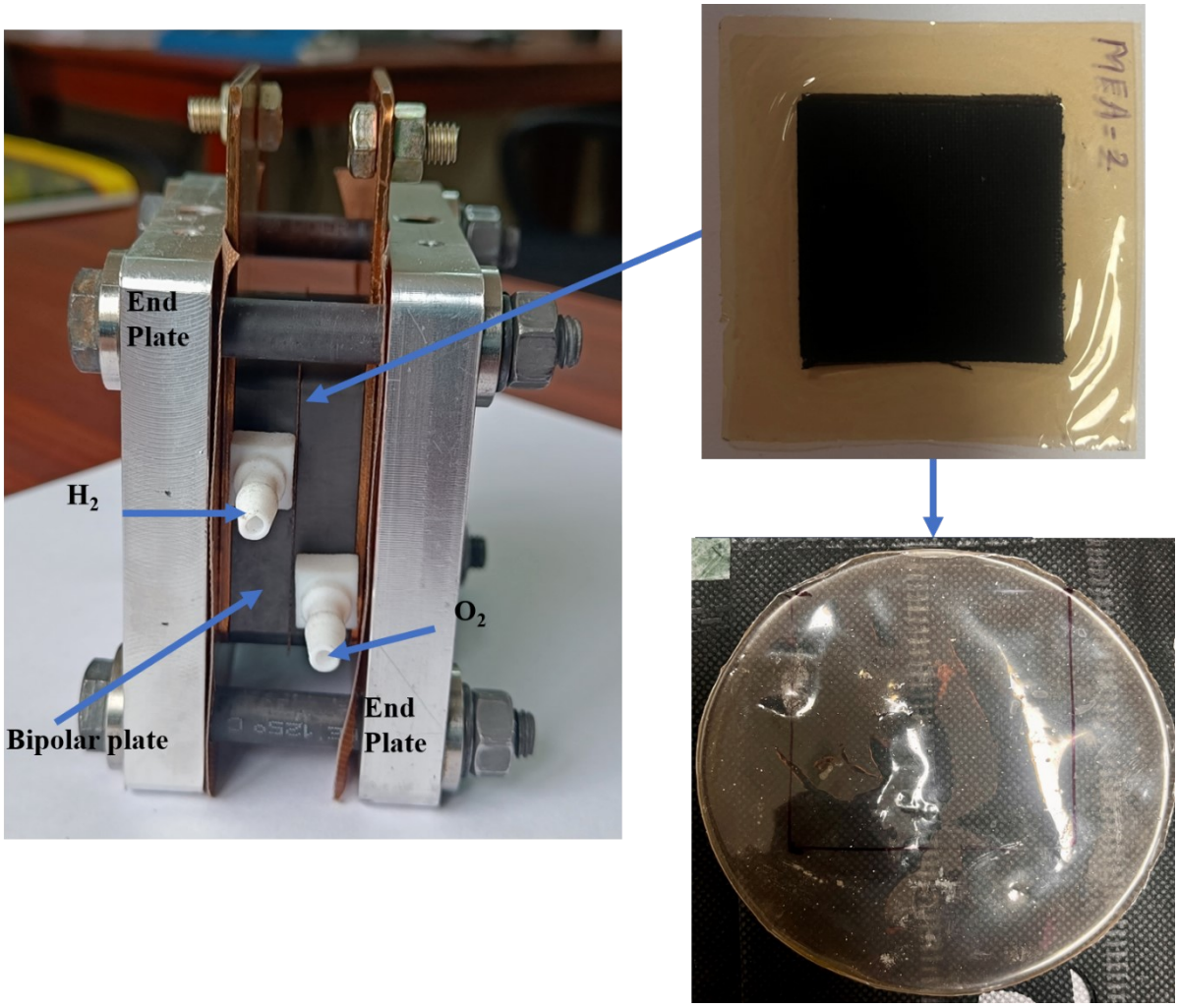


Figure S9: Single cell set up with H_2 and O_2 feed at 200 ml/min for MEA testing

Table S1: Comparative study of the developed composite membranes with recently published literatures.

Composite Membranes	**Conductivity (S cm^{-1})**	**Conditions**	**Power density ($mW \cdot cm^{-2}$)**	**References**
Nafion@D1020+ Sulfonated MOF 808	0.002	80°C, 35% RH	-	[1]
SPEEK/S-UiO-66@GO-10	0.01	100°C, 40% RH	-	[2]
Nafion-4PVIm (ATRP)	0.01 0.20	80°C,20%RH 100°C ,40%RH	210	[3]
Nafion + imidazole	0.04, 0.06	80°C-70%RH 100°C-70%RH	-	[4]
Nafion + imidazole functionalized mesoporous silica	0.007 0.0092	80°C -0%RH 100°C-0%RH	-	[5]
SPEEK + poly (ethylene glycol dimethacrylate-co-vinylimidazole)	0.03	30°C-100%RH	104.5 mW	[6]
Speek + ZIF-67	0.01	100°C	49.77	[7]
SP-$_3$PGO-5%	0.07	90 ℃, 100% RH	183.1	[8]
SPEEK/HPW@mGO	0.005	65 ℃, 40% RH	120.1	[9]
SPEEK@Ox-DBD-COF-SO_3H	3.87 × 10−3	90℃ ,98% RH	-	[10]
SPEEK/SMOF/TEA2.5	0.14	80 ℃,	-	[11]
PEEK/S-SiO2/MOF-5	3.69×10^{-3}	30℃	-	[12]
CCNF/SPEEK	0.05	20℃	-	[13]
SPEEK/ZMix (ZIF-8, ZIF-67)	0.02	100 °C	-	[14]
SPEEK/Zn-1H-1,2,4-Triazole based MOF (3 wt. %)	0.04	80°C, 50% RH	231 mW/cm^2	This work

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