**Electronic Supplementary Information (ESI)**

# Polyoxometalate Coupled Graphene Oxide-Nafion Composite Membrane for Fuel Cell Operating at Low Relative Humidity

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**Characterizations**

*PW-mGO Characterization*

Fourier-transform infrared (FT-IR) spectra was performed on the Agilent Cary 600 FT-IR spectroscopy equipped with an auto-sampler (over 6000 scans) with a resolution of 4 cm$^{-1}$ in the range from 4000 to 400 cm$^{-1}$. Thermogravemetric analysis (TGA) analysis was carried out by thermogravimetric analyzer (Rigaku, TG 8120) from 25 to 1000 °C at a heating rate of 10 °C per minute in air atmosphere. Cyclic voltammetric (CV) measurements were performed with a Biologic potentiostat/galvanic with a three-electrode cell configuration using Pt wire, Ag/AgCl saturated electrode, and glassy carbon (3 mm, φ) as counter, reference and working electrodes, respectively in 1 M $H_2SO_4$. The electrode ink was prepared by dispersing 5mg of sample in 125 μL of isopropyl alcohol and 125 μL of DI water adding 10 μL of 5 wt% Nafion solutions (Aldrich) was added finally. A glassy carbon (GCE) working electrode was polished in diamond solution and 0.05 μM of $Al_2O_3$ paste before coating the ink on the surface of a GCE. Then, 3 μL of well dispersed ink was dropped on the surface of glassy carbon, and dried at room temperature in order to form a uniform thin film of catalyst. All CV measurements were recorded using a potential window between -0.75 and -0.25 V at different scan rates.

*Membrane characterization*

Water uptake (WU) of samples was determined by drying membranes in the oven at 80 °C and the membranes were then soaked in DI water for 24 h at room temperature. WU was calculated by the following Equation (1).

$$WU\ (\%) = \frac{W_{swollen} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

Where, $W_{swollen}$ is the weight of the membrane that was soaked in water for 24 h and $W_{dry}$ is the weight of dry membrane.

Ion exchange capacity (IEC) was investigated by an acid-base titration using phenolphthalein as indicator. The samples were dried in the oven at 80 °C and the membranes were then immersed in 2 M NaCl solution for 24 h so that the H$^+$ of membrane could be exchanged with Na$^+$. The solution was finally titrated with 0.001 M NaOH. IEC value was calculated according to Equation (2)

$$\text{IEC} = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \qquad (2)$$

Where, IEC was the ion exchange capacity (mmol g$^{-1}$), $V_{NaOH}$ was the added volume of NaOH at the equivalent point (mL), $C_{NaOH}$ was the concentration of NaOH (M) and $W_{dry}$ is the weight of dry membrane.[1]

The proton conductivity of the membranes was measured in the longitudinal direction with a four-probe method using membrane conductivity cell (Bekktech) with gas flowing options. Membrane sample with area of 1 cm x 3 cm was assembled in the cell, in contact with two platinum electrodes placed at a fixed position. The potentiostat is set to apply specific voltages between two Pt electrodes and resulting currents were measured. The resistance (R) is derived from the slope of the line that connects the data points. The membrane conductivity as a function of relative humidity percentages (RH %) at 80 °C was determined according to the Equation (5).

$$\sigma = \frac{L}{R \times W \times T}$$

(5)

Where, $L = 0.425$ cm is the fixed distance between two Pt electrodes; $R$ is the membrane resistance in $\Omega$; $W$ is the width of the sample in cm and $T$ is the thickness of the membrane in cm.

To verify the reduction of ohmic resistance of composite membranes, the ohmic resistance was determined according to Eq. (6)[2,3]

$$E = E_0 - b \log i - Ri$$

(6)

Where, $E$ and $i$ are the measured cell potential and current. $E_0$ is defined by Eq. (7), $b$ is the Tafel slope, and $R$ accounts for the linear variation of overpotential with current density primarily due to ohmic resistance. The exchange-current density ($i_0$) of the oxygen-reduction reaction was calculated by Eq. (7)

$$E_0 = E_r + b \log i_0$$

(7)

Where, $E_r$ is the thermodynamically reversible cell potential.[2,3] The electrode kinetic parameters derived from Eq. (6) and Eq. (7) of recast Nafion, NRE-212, and Nafion/PW-mGO composite membranes at 80 °C under ~100% RH were listed in Table S2.

*Fabrication of membrane electrode assembly and fuel cell performance evaluation.*

The PEFCs performance of composite membranes was evaluated by making membrane electrode assemblies (MEAs). Gas diffusion layers (GDL) (SGL, thickness = 0.27mm) were used as the backing layers. For the cathode catalyst layers, 40 wt% Pt/C catalysts (Johnson Matthey)

were mixed with 30 wt % Nafion ionomer and isopropyl alcohol and the slurry was then ultrasonicated for 60 min. The resultant slurries were coated onto GDL. For anode catalyst layer, 40 wt % Pt/C was dispersed in isopropyl alcohol and 7 wt % of Nafion and the slurry was coated in a similar manner. Catalyst loading on both the anode and cathode was kept at 0.5 mg cm$^{-2}$. The active area for the PEFCs was 5 cm$^2$. A thin layer of Nafion ionomer was applied to the catalyst surface of both the electrodes. MEAs were obtained by sandwiching the membrane between the cathode and anode followed by its hot-compaction under a pressure of 30 kg cm$^{-2}$ at 130 °C for 2 min. MEAs were coupled with Teflon gas-sealing gaskets and placed in single-cell test fixtures with parallel serpentine flow-field machined on graphite plates. The PEFCs was maintained at ca.100% RH by passing hot and wet hydrogen and oxygen gases to its anode and cathode sides, respectively, at a flow rate of 300 sccm through a mass flow controller. After establishing and equilibrating the desired humidity level, measurements of cell potential as a function of current density were conducted galvanostatically. The polarization data are collected point by point and 1 min is given to the system to come to steady state. The reproducibility of the data was ascertained by repeating the experiments at least twice. All the MEAs were evaluated in PEFCs under atmospheric pressure.
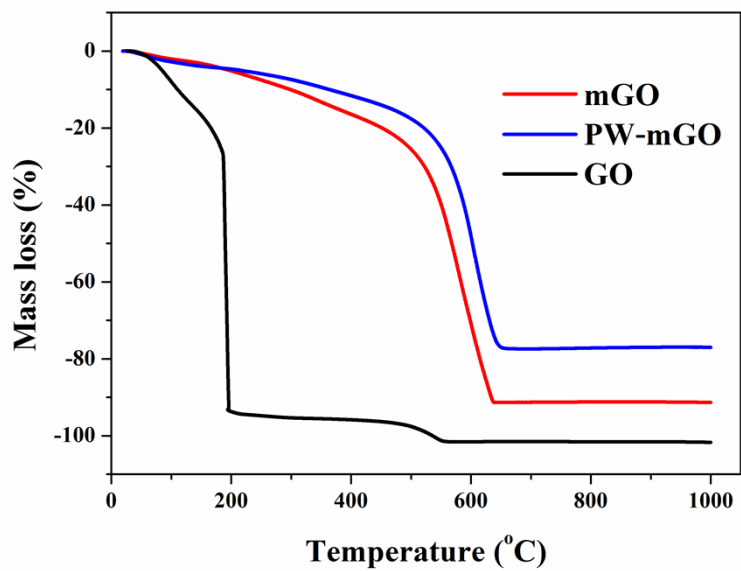
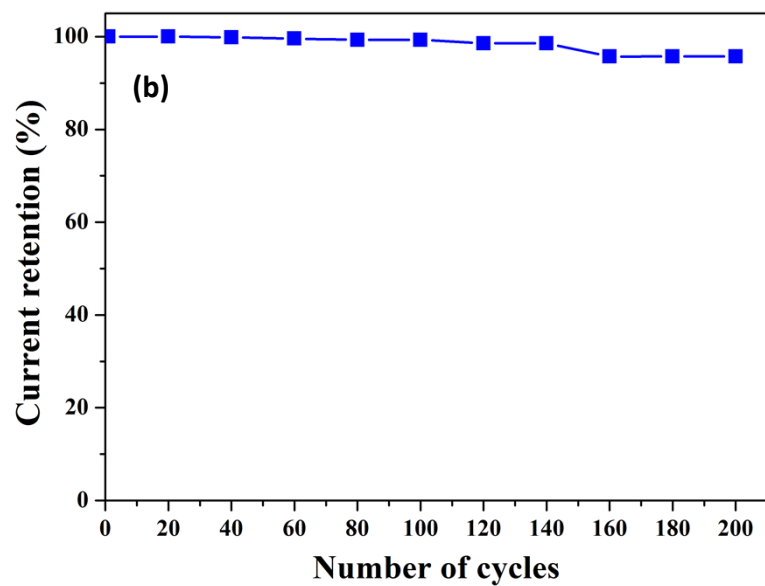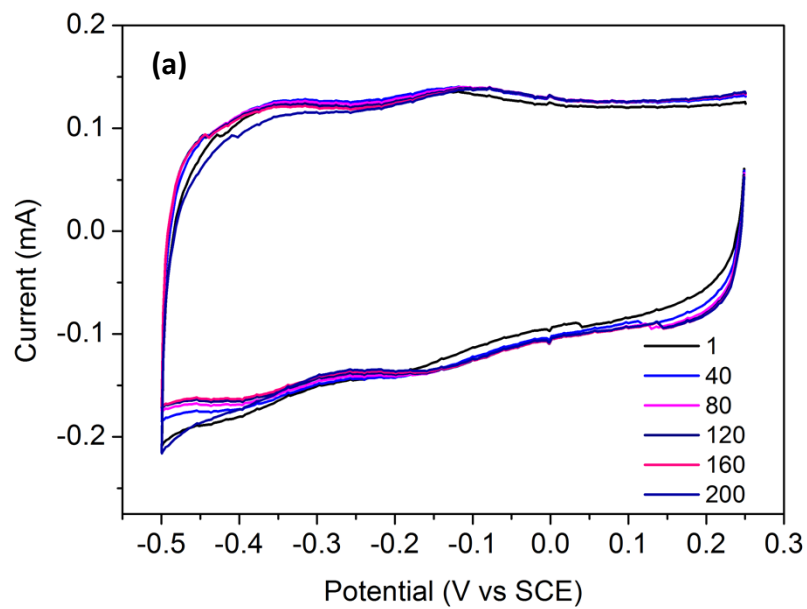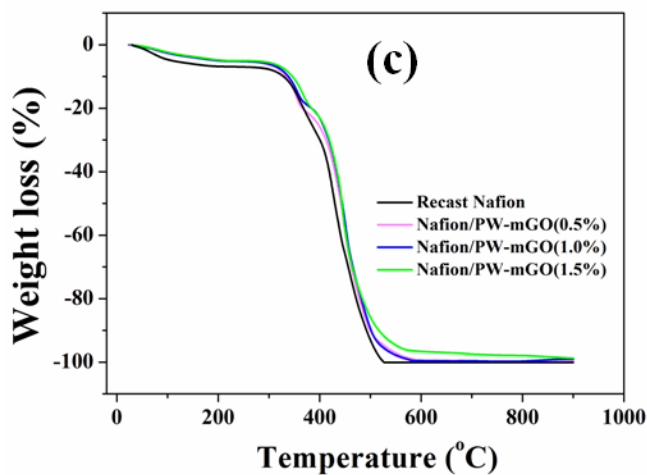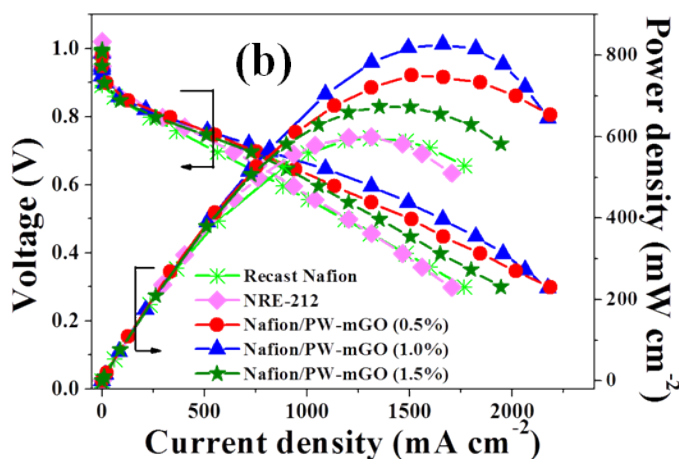**Fig. S1**. Thermograms of GO, mGO and PW-mGO carreid out in air atomsphere.

**Fig. S2**. (a) The CV stability test of PW-mGO nanohybrid coated on glassy carbon electrode for 200 cycles at a scan rate of 50 mVs$^{-1}$ in 1 M H$_2$SO$_4$ electrolyte, (b) The current decay of the 1st reduction peak as the cycle number.
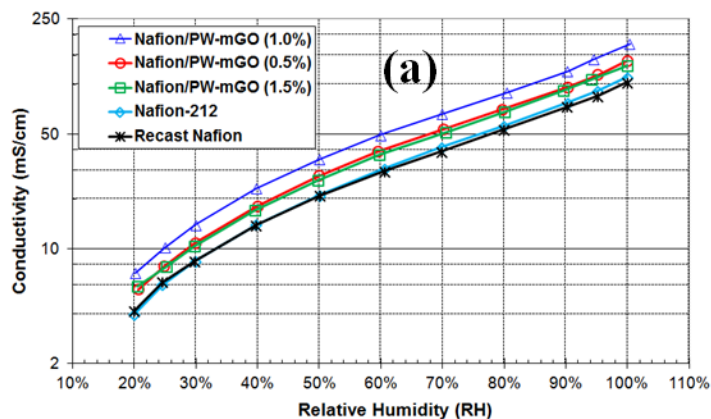
**Fig. S3.**
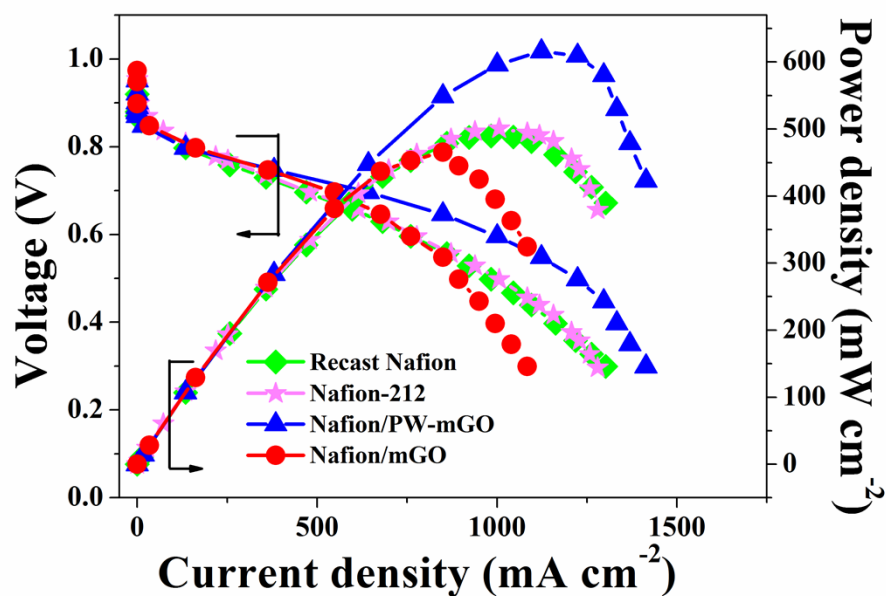


Optimization of PW-mGO filler in Nafion membranes based on (a) proton conductivity analysis measured at 80 ºC and (b) polarization plot operated under 100 %RH at 80 ºC. (c) thermogravimetric analysis traces of Nafion-mGO/PW composite membranes.

**Fig. S4**. Polarization and power density plots of Nafion -212, recast Nafion, Nafion/mGO and Nafion/PW-mGO under 100%RH at 100 $^{o}$C.
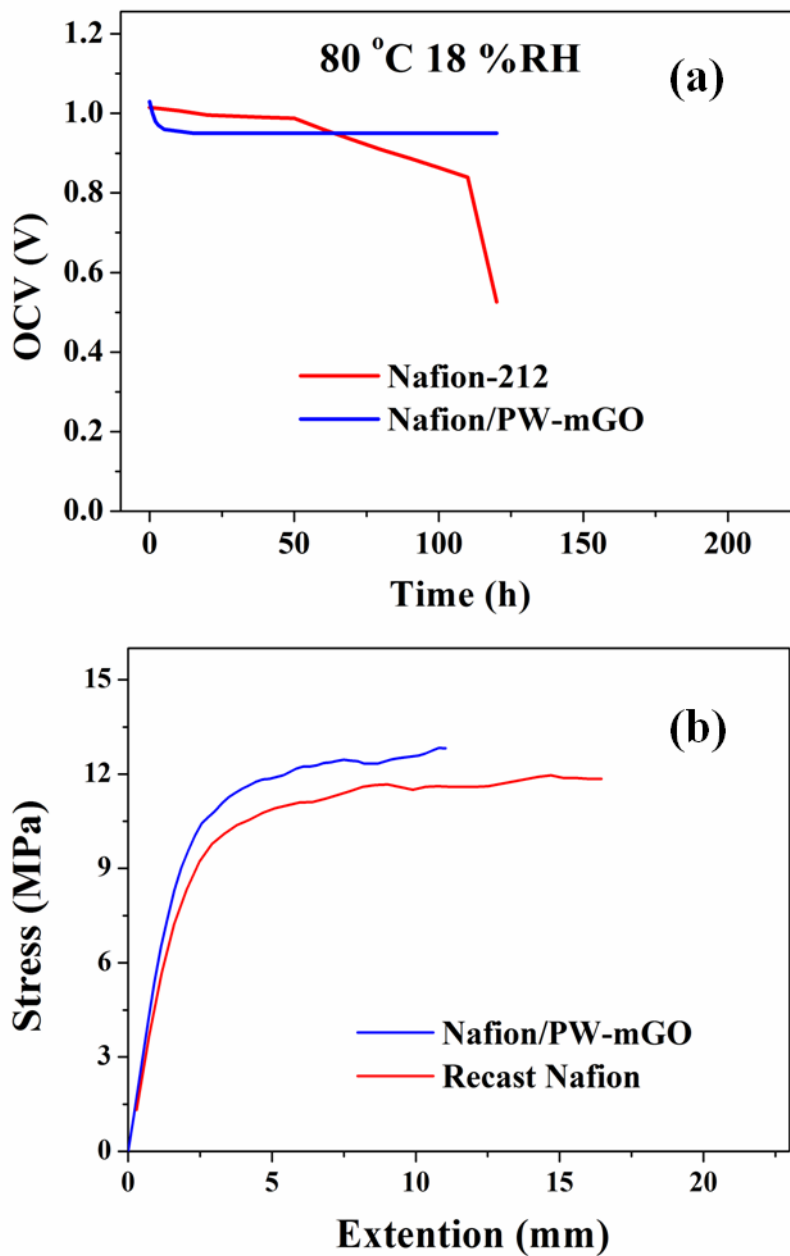
**Fig. S5**. (a) Durability studies under 18 %RH at 80 °C and (b) mechanical properties of Nafion/PW-mGO composite membranes.

**REFERENCES**

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