Supporting Information

Special tailoring of copper-pyromellitic acid complex with sulfonated poly(ether ether ketone) to form composite membrane for polymer electrolyte fuel cells

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[#]*Contributed equally to this work.*

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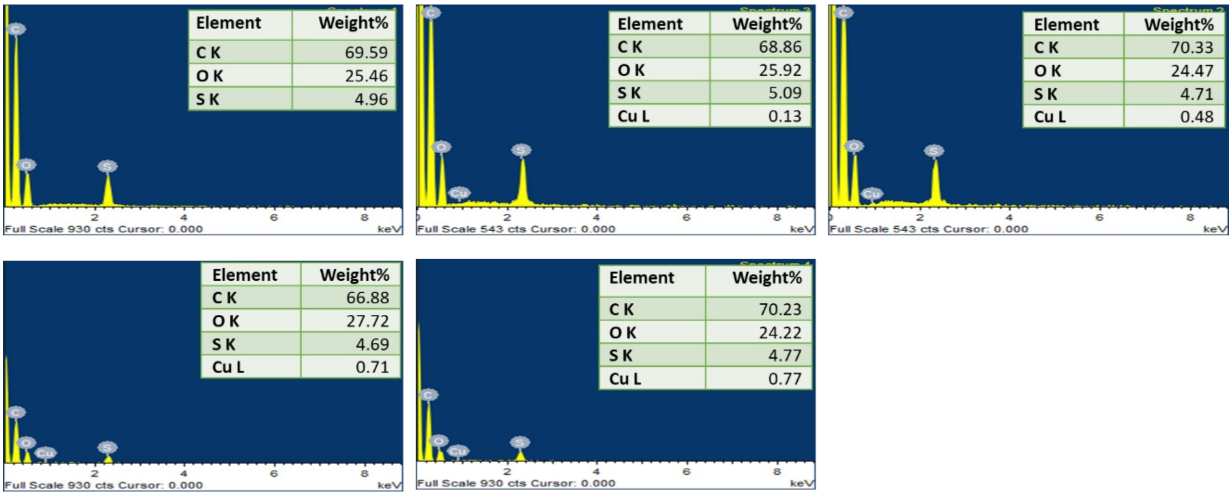


Figure S1: *EDAX analysis of (a) sPEEK, (b) sPEEK/Cu-PMA-0.25 wt.%, (c) sPEEK/Cu-PMA-0.5 wt.%, (d) sPEEK/Cu-PMA-0.75 wt.%, and (e) sPEEK/Cu-PMA-1 wt.%.*

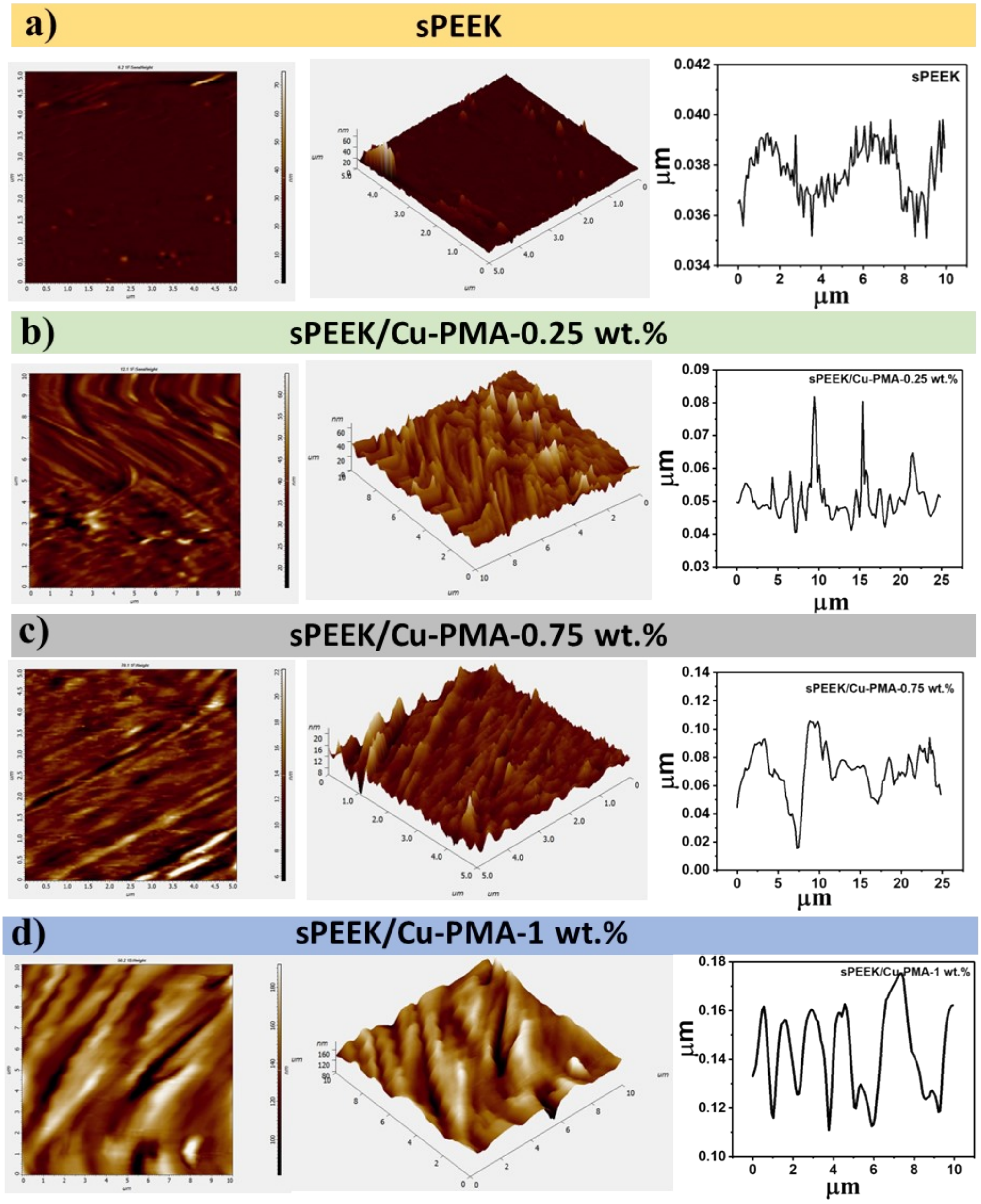


Figure S2. *AFM analysis of (a) sPEEK, (b) sPEEK/Cu-PMA-0.25 wt.%, (c) sPEEK/Cu-PMA-0.5 wt.%, (d) sPEEK/Cu-PMA-0.75 wt.%, and (e) sPEEK/Cu-PMA-1 wt.%*

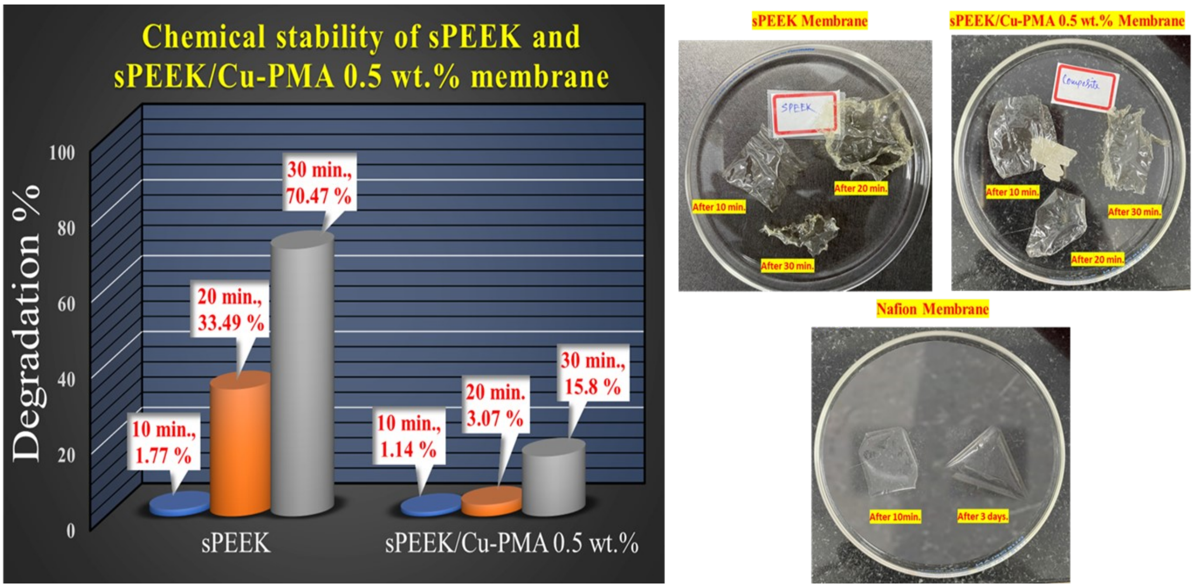


Figure S3: a) *Chemical stability of sPEEK and sPEEK/Cu-PMA-0.5 wt.% composite membrane and b) Optical images of sPEEK, Nafion 212 and sPEEK/Cu-PMA-0.5 wt.% composite membrane at regular time intervals.*

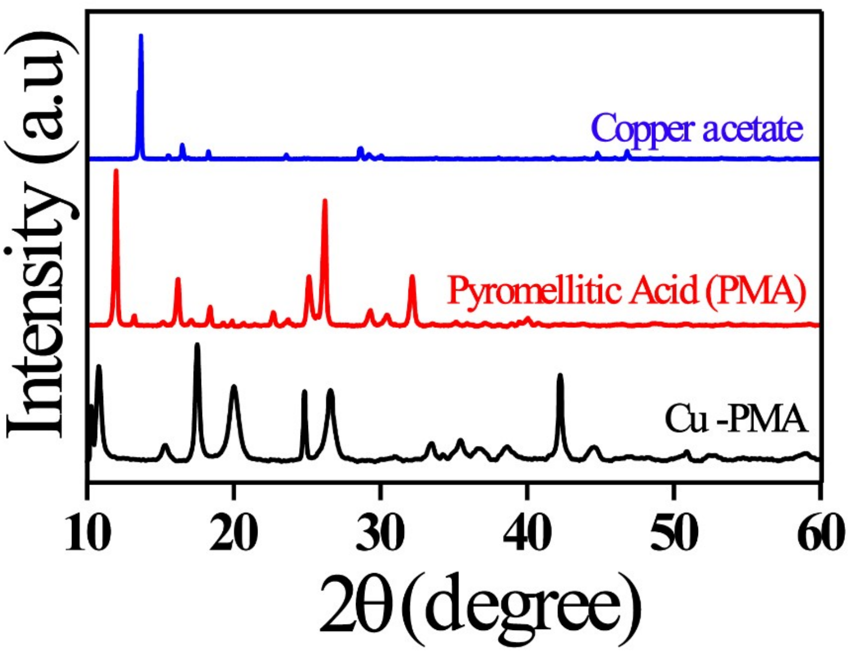


Figure S4. *Comparative XRD patterns of the as-prepared sPEEK, sPEEK/Cu-PMA-0.25 wt.%, sPEEK/Cu-PMA-0.5 wt.%, sPEEK/Cu-PMA-0.75 wt.%, and sPEEK/Cu-PMA-1 wt.% composite membranes.*

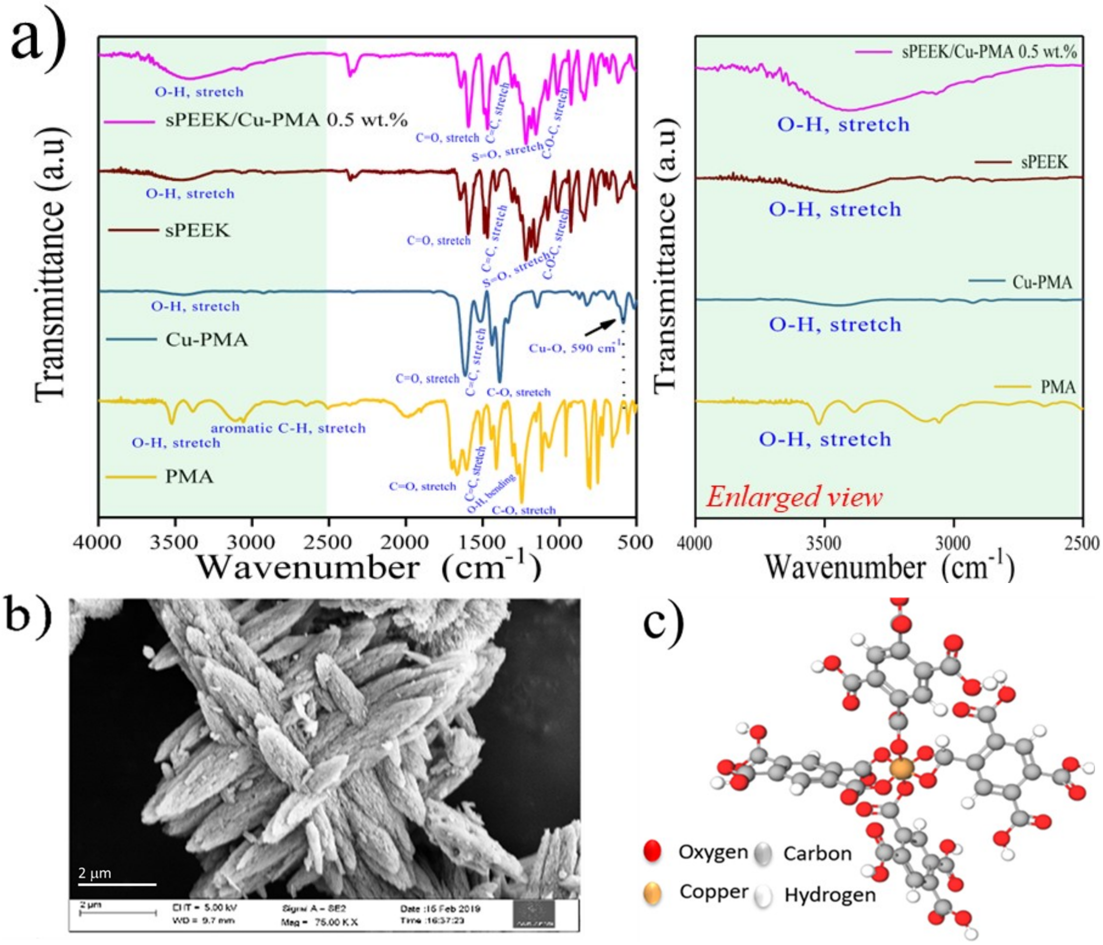
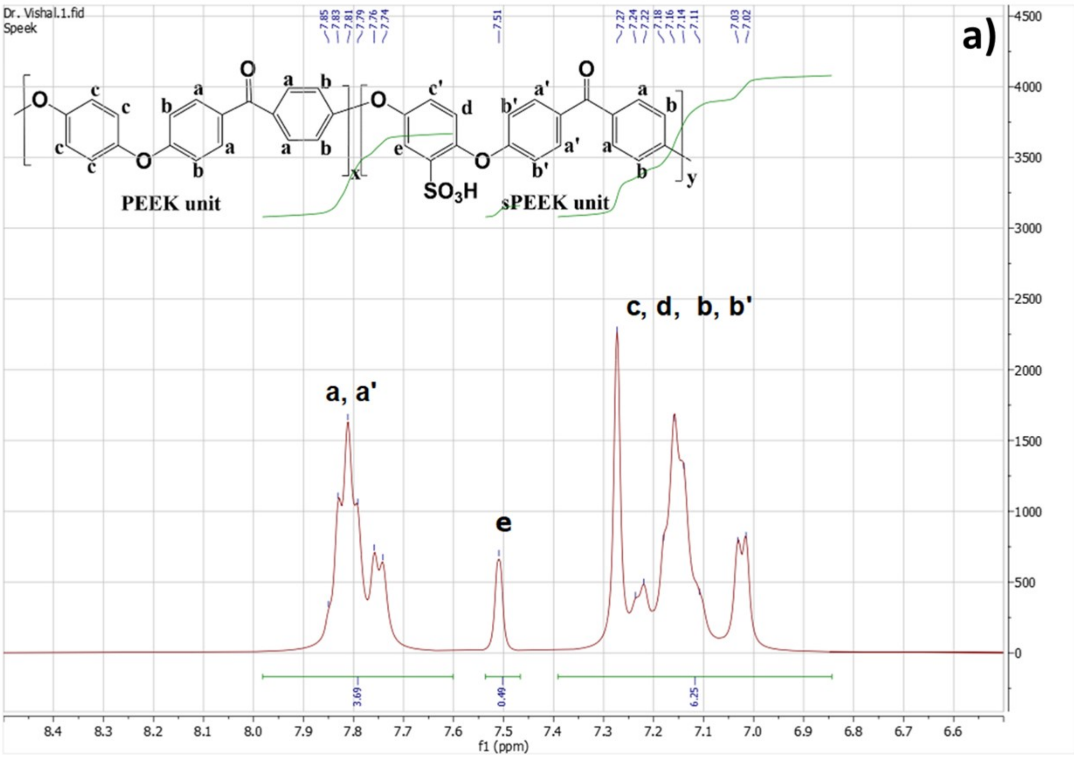


Figure S5. a) *Comparative FT-IR spectra of pyromellitic acid, Cu-PMA, sPEEK and sPEEK/Cu-PMA-0.5 wt.% membrane, enlarged view is green shaded region of fig. a, b) SEM image of Cu-PMA, and c) Proposed structure for Cu-PMA complex.*



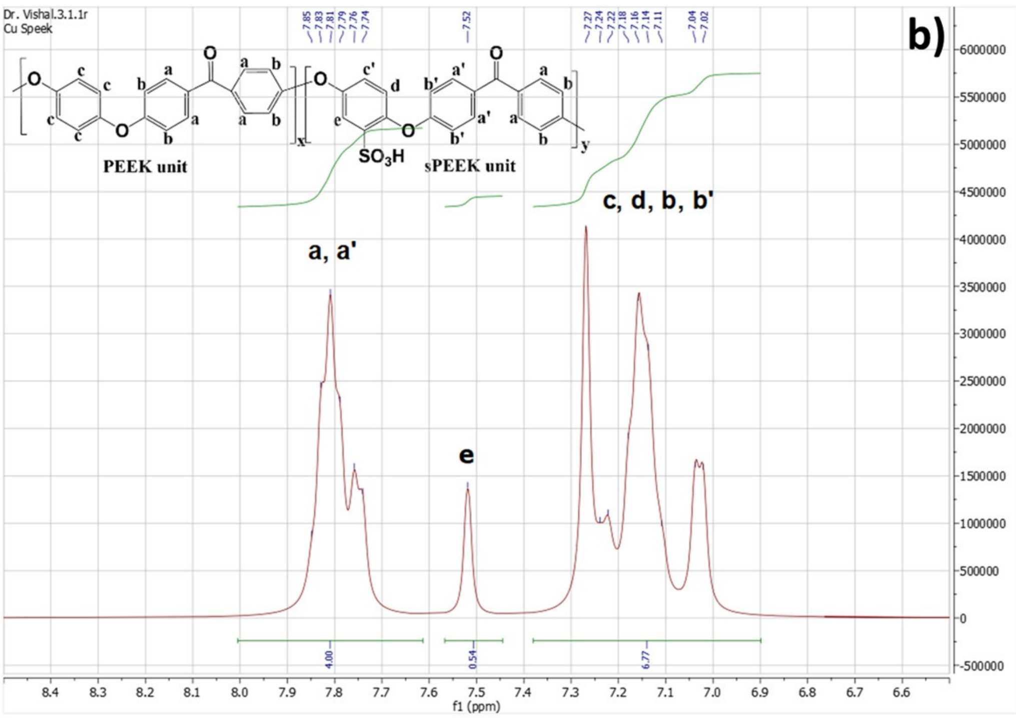


Figure S6. *a, b)* ^{1}*H-NMR spectra of sPEEK (top), and sPEEK/Cu-PMA-0.5 wt.% composite membrane (bottom), respectively.*

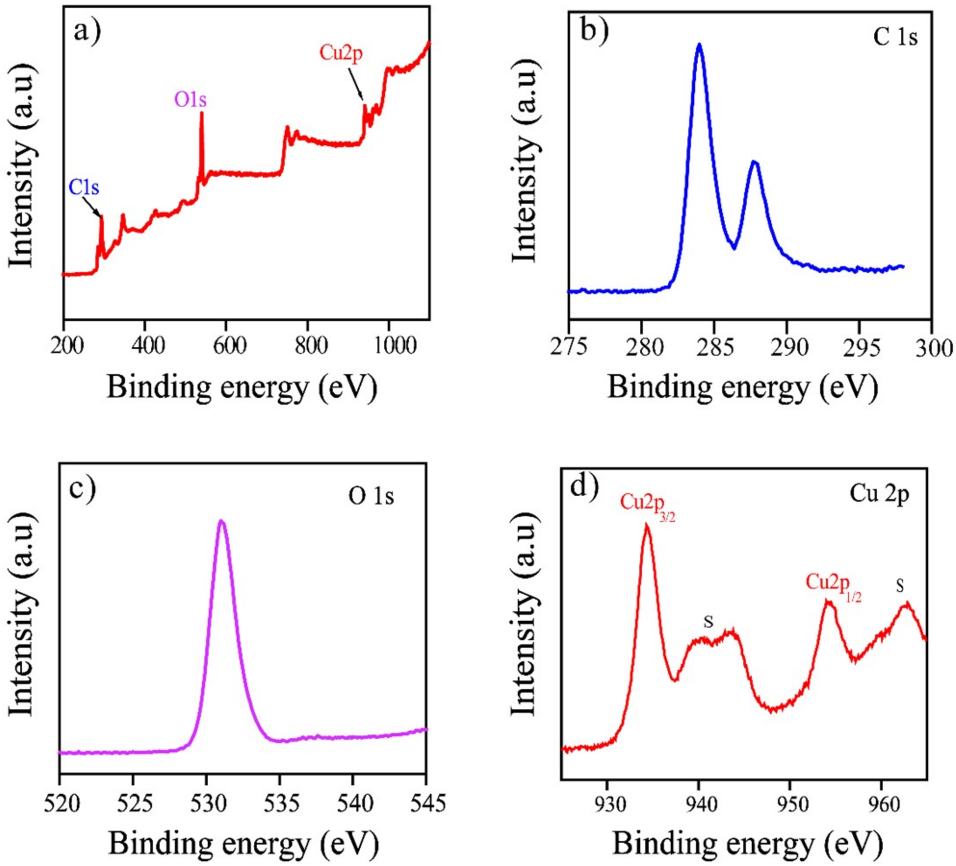


Figure S7: *a) Survey spectrum of Cu-PMA, high resolution XPS of b) C1s, c) O1s, and d) Cu2p.*

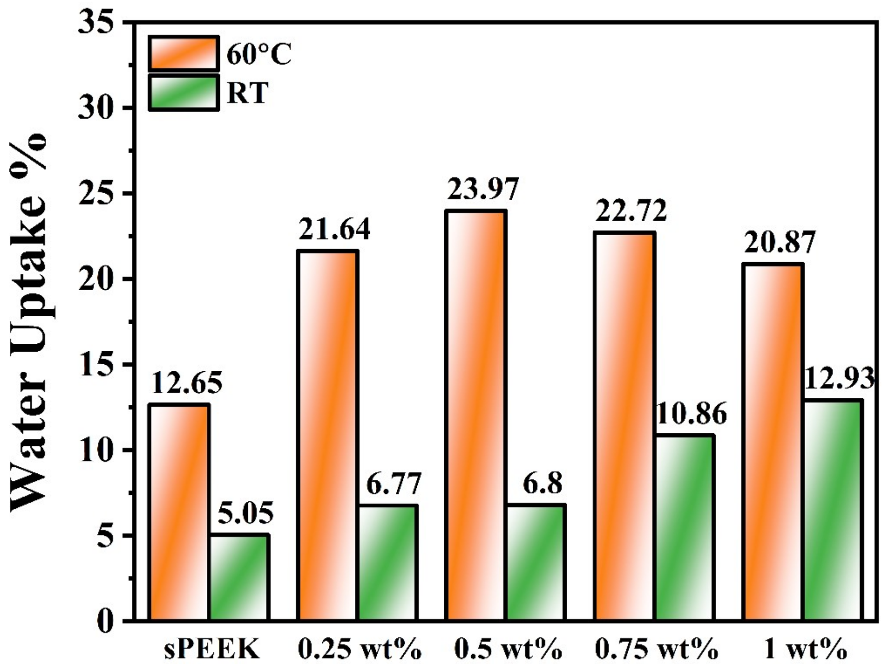


Figure S8. *Comparative water uptake results for the as-prepared sPEEK, sPEEK/Cu-PMA-0.25 wt.%, sPEEK/Cu-PMA-0.5 wt.%, sPEEK/Cu-PMA-0.75 wt.%, and sPEEK/Cu-PMA-1 wt.% composite membranes at room temperature (RT) and 60 ºC temperature.*

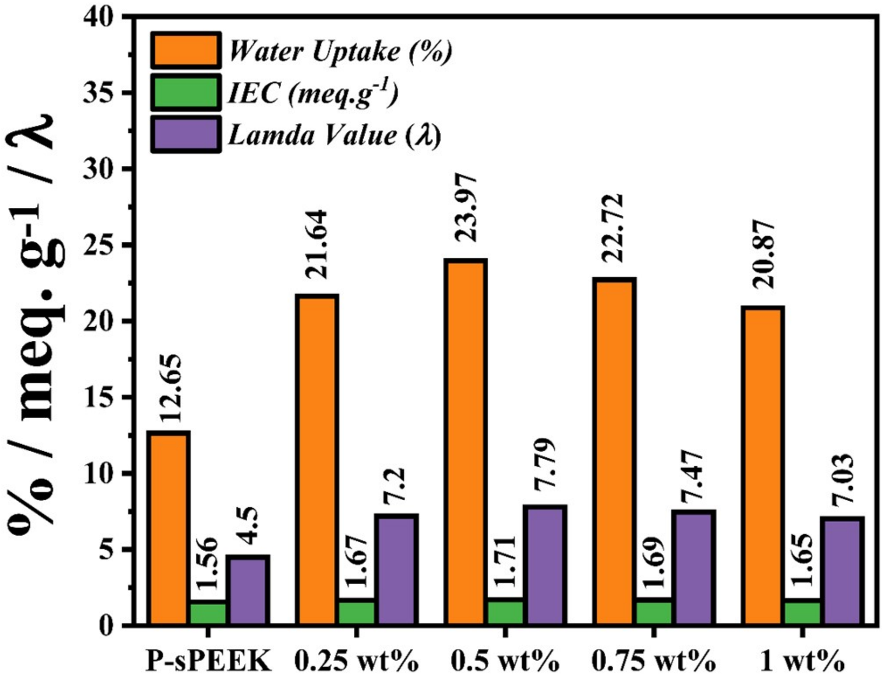


Figure S9. *Water uptake, IEC, and Lambda value for the as-prepared sPEEK, sPEEK/Cu-PMA-0.25 wt.%, sPEEK/Cu-PMA-0.5 wt.%, sPEEK/Cu-PMA-0.75 wt.%, and sPEEK/Cu-PMA-1 wt.% composite membranes.*

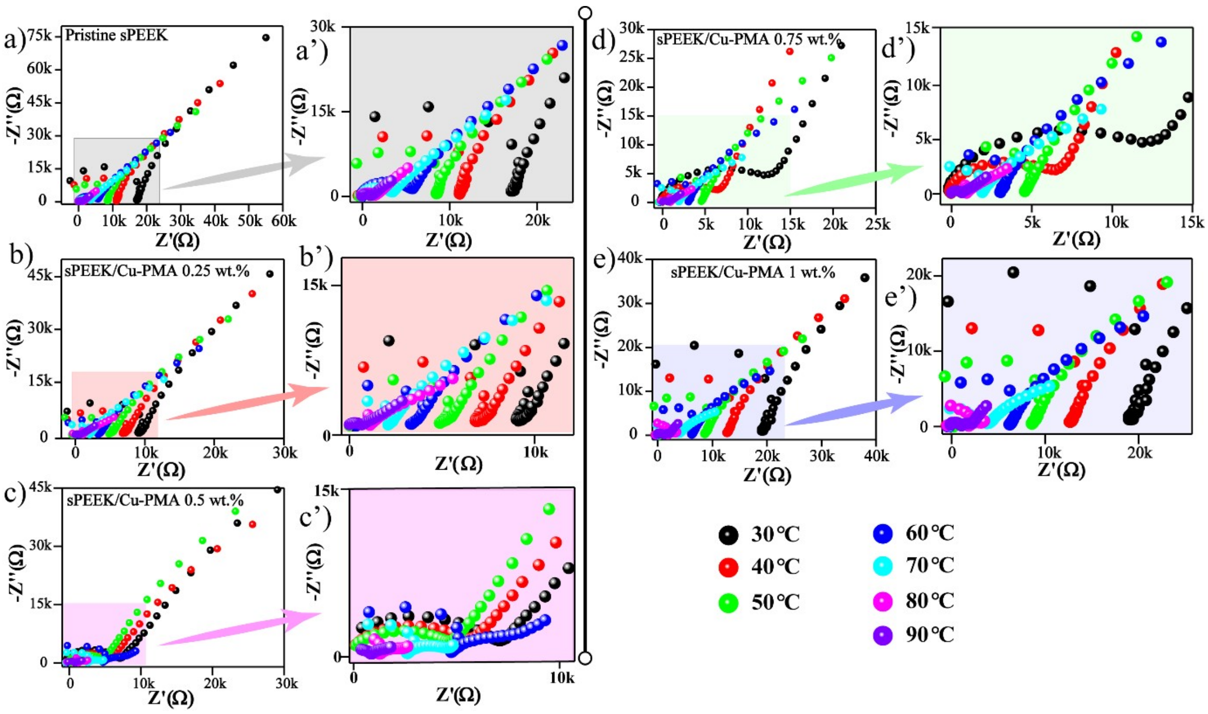


Figure S10. *(a-e) EIS plots of as-prepared sPEEK, sPEEK/Cu-PMA-0.25 wt.%, sPEEK/Cu-PMA-0.5 wt.%, sPEEK/Cu-PMA-0.75 wt.%, and sPEEK/Cu-PMA-1 wt.% composite membranes recorded at different temperatures of 30 – 90 ºC, and at 98% RH. (a'-e') are corresponding magnified plots marked with different colours.*

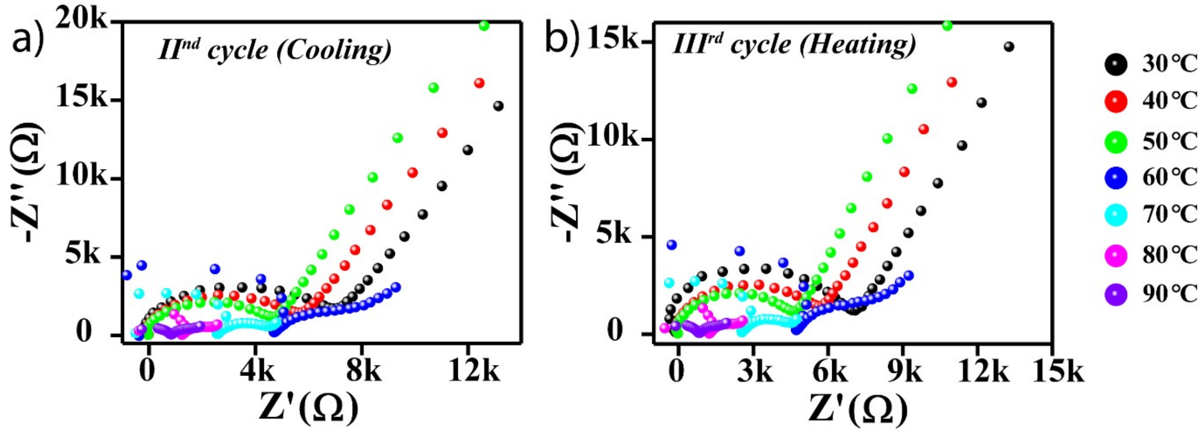


Figure S11. *EIS plots of sPEEK/Cu-PMA-0.5 wt.% composite membrane recorded for the stability assessment. EIS plot for the Ist cycle (Heating) is shown in Figure S10c, and subsequent IInd and IIIrd cycles of the cooling and heating is shown here a and b, respectively.*

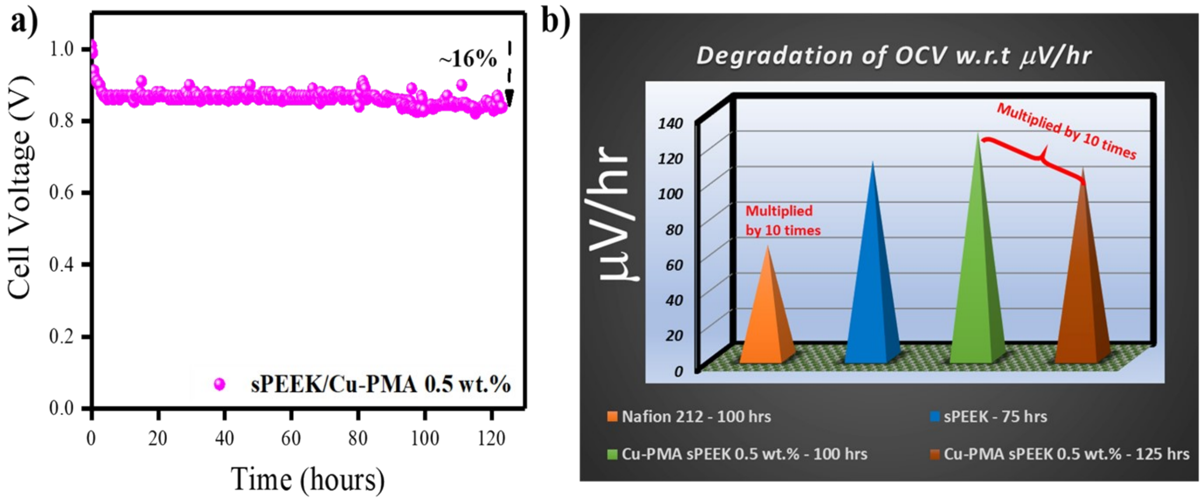


Figure S12: *a) Durability test result of OCV measurement as function of time for sPEEK/Cu-PMA 0.5 wt.% composite membrane-based MEA for 125 hrs. Conditions: Anode and Cathode side -commercial Pt/C electrodes, Pt-loading- 0.5 mg-Pt/cm^2 at anode and cathode side, respectively; Active area: 7.0 cm^2, Cell temperature- 80 °C, Relative humidity: 30 % RH at both side, Gases – Pure hydrogen (100 mL/min) and air (150 mL/min) as a fuel and oxidant at anode and cathode side, respectively. b) Measured degradation rate for Nafion 212, sPEEK, sPEEK/Cu-PMA 0.5 wt.%, sPEEK/Cu-PMA 0.5 wt.% based MEA's after the durability test. Please Note: In Figure b, Y-axis values of Nafion 212 and Cu-PMA/sPEEK-0.5 wt.% 100 hrs and 125 hrs are of 10x, to show the differences and variations with respect to each other.*

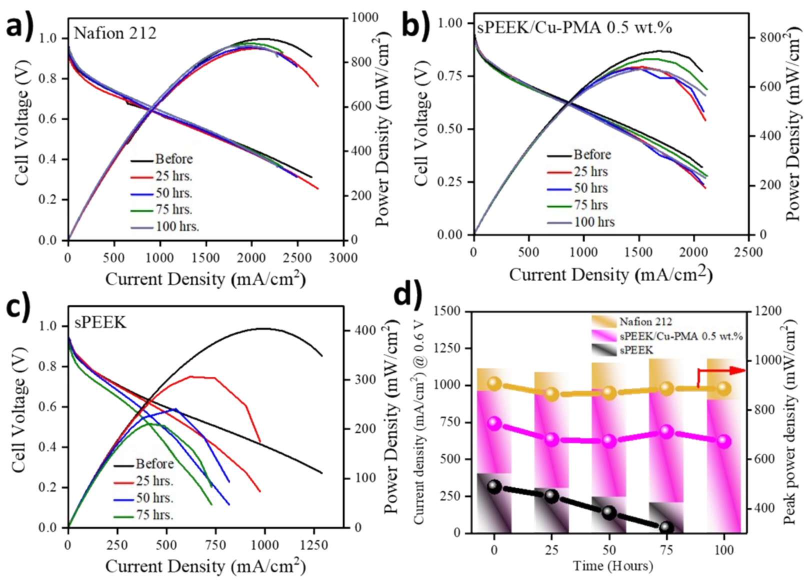


Figure S13: *Polarisation curves recorded during OCV degradation test. Polarisation curves for a) Nafion 212-based MEA after 0, 25, 50, 75, and 100 hrs of test, b) sPEEK/Cu-PMA-0.5 wt.%-based MEA after 0, 25, 50, 75, and 100 hrs test, c) sPEEK-based MEA after 0, 25, 50, and 75 hrs test. d) Comparison of current density @ 0.6 V and peak power densities of sPEEK, sPEEK/Cu-PMA-0.5 wt.% and Nafion 212 based MEA's after 0, 25, 50, 75, and 100 hrs test.* *<u>Conditions:</u> Anode and Cathode side -commercial Pt/C electrodes, Pt-loading- 0.5 mg-Pt/cm^2 at anode and cathode side, respectively, Active area: 7.0 cm^2, Cell temperature- 60 °C, Relative humidity: 90 % RH at both side, Gases – Pure hydrogen (1.2 Stio.) and oxygen (3.5 Stio.) as a fuel and oxidant at anode and cathode side, respectively.*

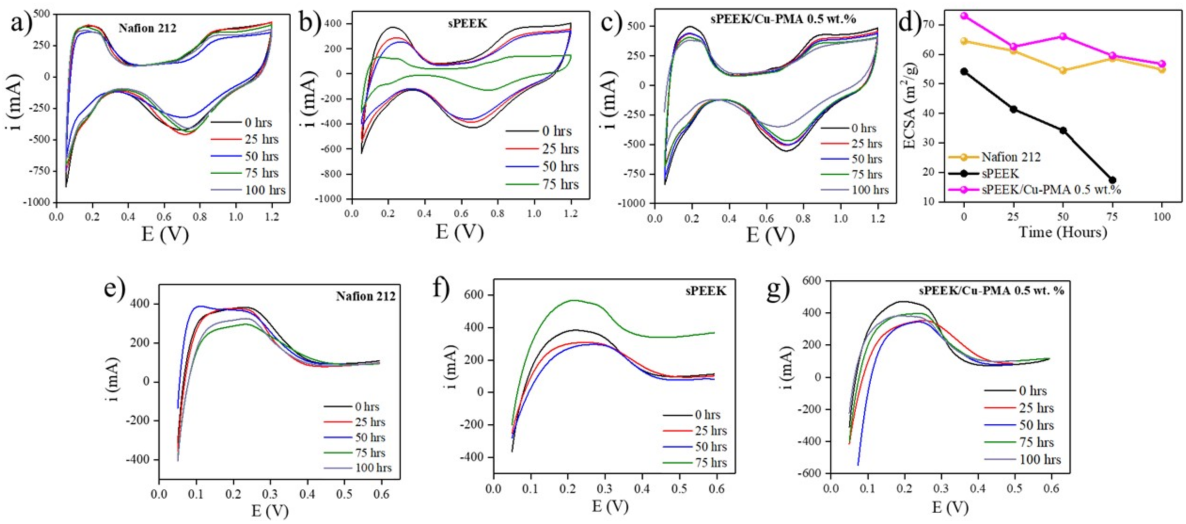


Figure S14: *a-c) Solid-state cyclic voltammogram for Nafion 212, sPEEK, sPEEK/Cu-PMA-0.5 wt.% based MEAs respectively, after regular time intervals during OCV degradation test. d) Change in electrochemical active surface area w.r.t time. e-g) H_2 cross-over study for Nafion 212, sPEEK, sPEEK/Cu-PMA-0.5 wt.% based MEAs respectively. Both the measurements were done at scan rate of 50 mV/s.* *<u>Conditions:</u> Anode and Cathode commercial Pt/C electrodes, Pt-loading- 0.5 mg$_{-Pt}$/cm^2 at both sides, Active area: 7.0 cm^2, Cell temperature- 60 °C, Relative humidity: 90 % RH at both sides, Gases – Pure hydrogen (100 mL/min), on Anode, and nitrogen (300 mL/min) on cathode side.*

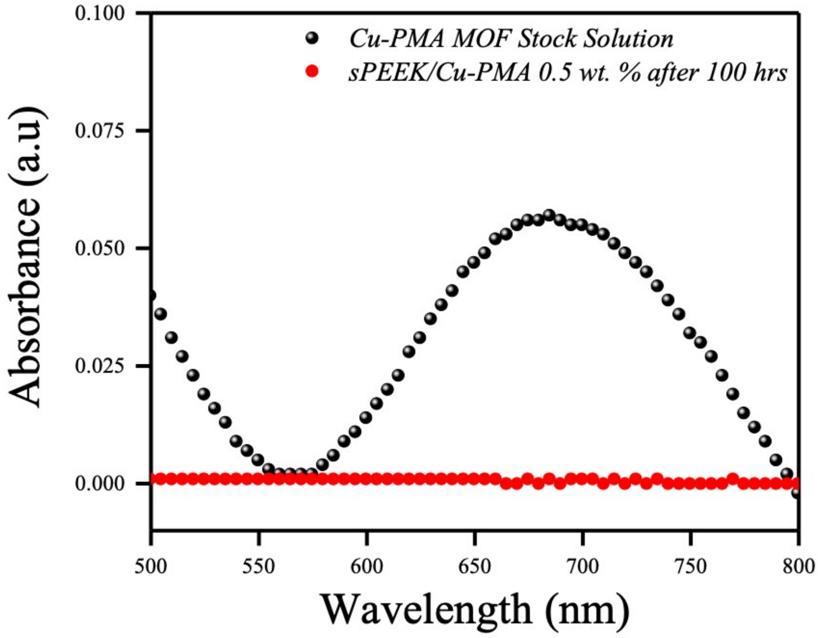


Figure S15: *Comparative UV-vis spectra of product water collected during OCV stability test of sPEEK/Cu-PMA-0.5 wt.% - based MEA after 100 h, and compared with the standard stock solution of Cu-PMA.*

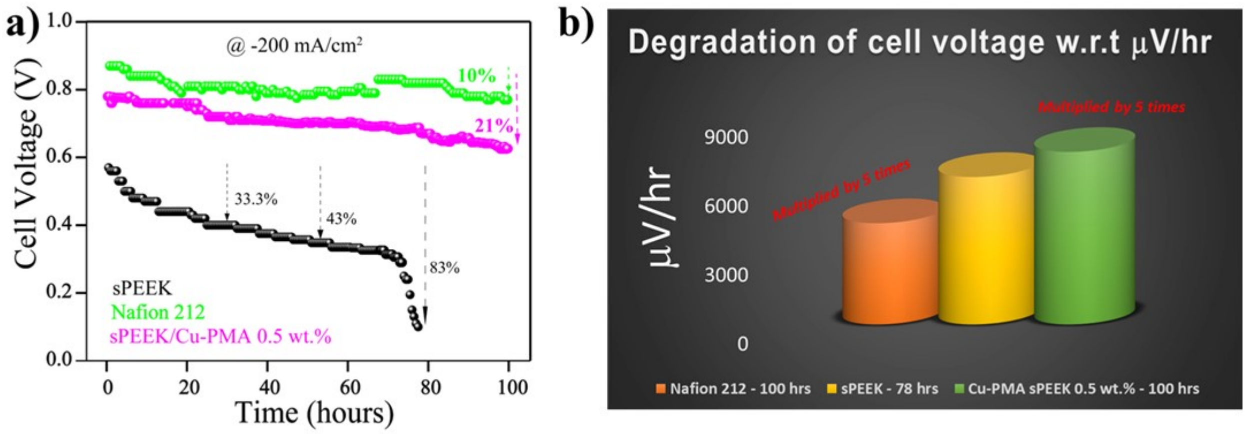


Figure S16: *a) Constant current discharge test as function of time for MEA's of sPEEK, sPEEK/Cu-PMA-0.5 wt.% composite membrane, and Nafion 212 at constant discharge rate of 0.2 A/cm^2. Conditions: Anode and Cathode side -commercial Pt/C electrodes, Pt-loading- 0.5 mg$_{-Pt}$/cm^2 at anode and cathode side, respectively, Active area: 7.0 cm^2, Cell temperature- 60 °C, Relative humidity: 50 % RH at both side, Gases – Pure hydrogen (100 mL/min) and oxygen (150 mL/min) as a fuel and oxidant at anode and cathode side, respectively. b) Measured degradation rate for Nafion 212, sPEEK, sPEEK/Cu-PMA 0.5 wt.% based MEA's. Please Note: In Figure S17b, Y-axis values of Nafion 212, and Cu-PMA/sPEEK-0.5 wt.% are of 5x, to show the differences and variations with respect to each other.*

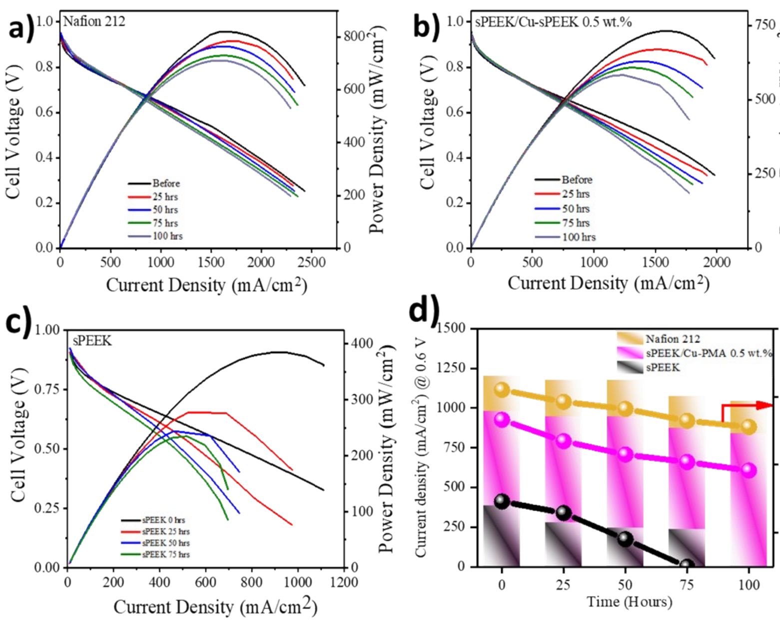


Figure S17: *Polarisation curves for the MEAs during the constant current discharge rate test (discharge current is 0.2 A/cm²) as function of time.*

Polarisation curves for a) Nafion 212-based MEA's after 0, 25, 50, 75 and 100 h of test, b) sPEEK/Cu-PMA-0.5 wt.% -based MEA after 0, 25, 50, 75 and 100 h of test, c) sPEEK-based MEA after 0, 25, 50, and 75 hrs of test. d) Observed current density @ cell voltage of 0.6 V and peak power densities from the polarisation curves presented in (a-c) for the Nafion 212, sPEEK/Cu-PMA 0.5 wt.% and sPEEK based MEA's. Conditions: Anode and Cathode side -commercial Pt/C electrodes, Pt-loading- 0.5 mg-$_{Pt}$/cm² at anode and cathode side, respectively, Active area: 7.0 cm², Cell temperature- 60 °C, Relative humidity: 90 % RH at both side, Gases – Pure hydrogen (1.2 Stio.) and oxygen (3.5 Stio.) as a fuel and oxidant at anode and cathode side, respectively

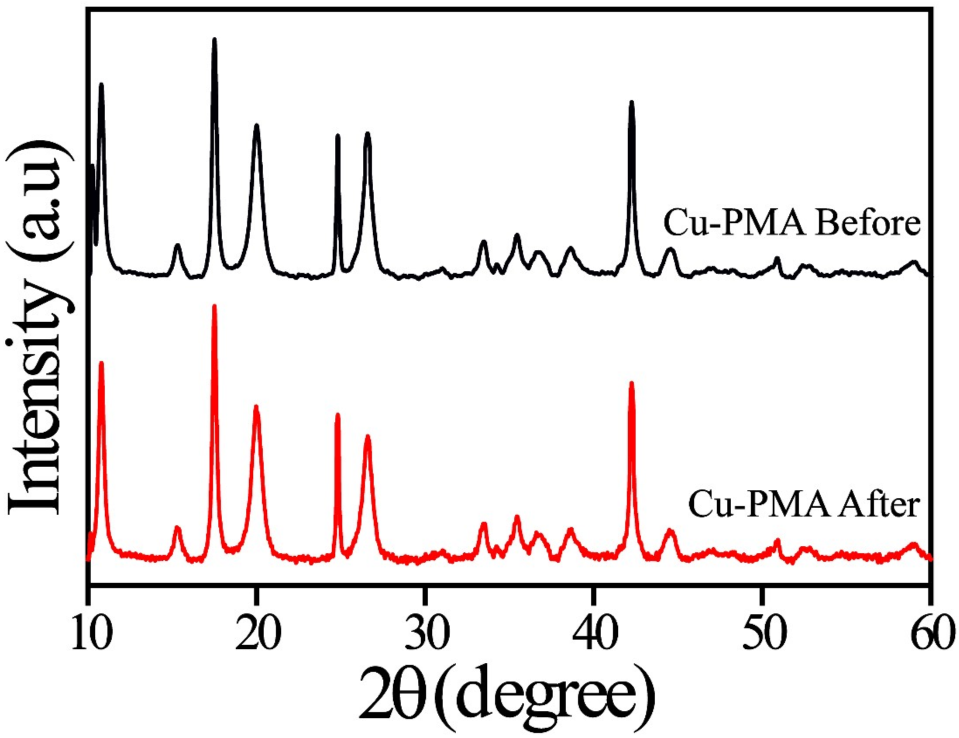


Figure S18. *Comparative p-XRD diffraction pattern of Cu-PMA before and after stability test.*

Figure S19: *Snapshot of sPEEK/Cu-PMA-0.5 wt.% composite membrane-based MEA.*

<u>Table S1:</u> *Comparative list of the properties and fuel cell performance of the as-prepared sPEEK/Cu-PMA composite membrane with the literature reports*

S. No	Membrane	Filler loading (%)	Conductivity (mS/cm)	Conductivity @ conditions		Pt-catalyst loading (mg/cm^2)	Fuel cell performance		Fuel cell performance @ condition		Ref.
				Temp. (°C)	RH%.		Current density (mA/cm^2) @ 0.6 V	Maximum power density (mW/cm^2)	Temp. (°C)	RH%.	
1.	**sPEEK**	**--**	**100.5**	**90**	**98**	**0.5**	**488.57**	**404.11**	**60**	**90**	**This work**
2.	**sPEEK/Cu-PMA-0.25 wt.%**	**0.25**	**124.6**	**90**	**98**	**0.5**	**660.3**	**476.17**	**60**	**90**	**This work**
3.	**sPEEK/Cu-PMA-0.5 wt.%**	**0.50**	**161.4**	**90**	**98**	**0.5**	**960.14**	**748**	**60**	**90**	**This work**
4.	**sPEEK/Cu-PMA-0.75 wt.%**	**0.75**	**137.8**	**90**	**98**	**0.5**	**564.5**	**427.61**	**60**	**90**	**This work**
5.	**sPEEK/Cu-PMA-1wt.%**	**1**	**131.9**	**90**	**98**	**0.5**	**564.6**	**446.02**	**60**	**90**	**This work**
6.	**Nafion 212**	**--**	**101.20**	**90**	**98**	**0.5**	**1203**	**906.56**	**60**	**90**	**This work**
7.	10CE/sPEEK	10	242	80	100	0.3	790	474	80	100	[1]
8.	sPEEK/TpPa−SO_3H-20	20	443.6	60	95	--	--	--	--	--	[2]
9.	SP-BCZO-7.5	7.5	30	90	--	0.5	--	574	60	100	[3]
10.	sPEEK/ZMix	1	29	100	--	--	--	--	--	--	[4]
11.	PA-C-sPEEK-Im-20	20	39	130	30	0.7	600$^{\$}$	209	130	30	[5]
12.	sPEEK/sGNR (0.1wt. %)	0.1	63.45	60	100	0.5	840	660	60	100	[6]
13.	Nafion 212	--	76.34	60	100	0.5	1132	900	60	100	[6]
14.	sPEEK/n-BuOH	--	314	80	90	--	--	--	--	--	[7]
15.	sPEEK/PCAS-15	15	38	80	100	--	--	--	--	--	[8]
16.	sPEEK/SSLM 5%	5	184	90	95	--	--	--	--	--	[9]
17.	sPEEK/2-AGO	2	11.32	120	20	--	--	--	--	--	[10]
18.	sPEEK/DGO-5	5	3	120	20	0.25	698.6$^{\$}$	162.1	120	#	[11]
19.	sPEEK/TPA	--	95	100	90	--	--	--	--	--	[12]
20.	sPEEK/WO_3	50	19	100	100	--	--	--	--	--	[13]
21.	sPEEK/sCNT	5	124	90	100	--	--	--	--	--	[14]
22.	sPEEK/PVA@GO-NF10	10	70	90	100	--	--	--	--	--	[15]
23.	sPEEK/PSSA-CNT		87	80	95	--	--	--	--	--	[16]
24.	sPPEK/SGNF	0.5	104	80	95	--	--	--	--	--	[17]
25.	sPEEK/PIL/PA	--	45	160	--	--	--	--	--	--	[18]
26.	sPEEK/SGO	5	55	80	30	--	--	--	--	--	[19]
27.	sPEEK/FPAPB/Fe_3O4-FGO	5	11.13	120	20	--	--	--	--	--	[20]
28.	sPEEK/CeO_2-ATiO_2	2	17.06	60	20	0.3	371	117	60	100	[21]
29.	sPEEK/QNPAES-6 wt.%	6	30.4	90	20	0.3	1180	560	60	100	[22]

$^{\$}$ Maximum current density at Maximum Power Density, #Anhydrous conditions,

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