Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ce-Mn bimetallic oxide doped SPEEK/SPPO blend composite membranes to induce high oxidative tolerance and proton conductivity for hydrogen fuel cells

Sk Miraz Hossain[a,1], Pratyush Patnaik[a,b,1], Suman Sarkar[a,b], Ritika Sharma[a,b], Uma Chatterjee[a,b,*]

[a]*Membrane Science and Separation Technology Division, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar, 364002, India*

[b]*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India*

[1]these authors contributed equally

Corresponding author: Uma Chatterjee (umac@csmcri.org, umac@csmcri.res.in)

SI 1: Characterization of SPEEK and SPPO by ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy

Bruker 500 MHz to spectrometer was used to record the ^{1}H NMR spectra. ^{1}H NMR spectra were recorded at 25 ^oC, using deuterated dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane (TMS) as the internal reference.

SI 2: Attenuated Total Reflection Infrared (ATR-IR) spectroscopies

The prepared PEMs were dried in a vacuum oven at 40 $^\circ C$ for 24 h and subjected to the ATR-IR analysis. The area of 3×6 cm^2 of membrane sample was taken for ATR-IR analysis. ATR-IR of the membranes were recorded on an instrument (Spectrum 2, Perkin Elmer) at room temperature. A Germanium crystal, fixed at a 45^o angle of incidence, which gave a penetration depth of ~1 µ in the chemical infrared region, was used for recording the ATR-IR spectra. ATR-IR spectra on 5 different positions were recorded.

SI 3: X-ray photoelectron spectroscopy (XPS) analysis

$CeMnO_x$ bimetallic oxide in powder form was dried at 70 °C for 12 h in vacuum. XPS was analyzed for O 1s, Ce 3d, and Mn 2p using Thermo Scientific Nexsa G2 Surface Analysis System (Voltage: 220–240 V– Frequency: 50 / 60 Hz).

SI 4: Wide-angle XRD of the $CeMnO_x$

Wide-angle XRD of $CeMnO_x$ nanostructure was determined in a powder XRD (Empyrean-PANalytical) instrument using a Cu Kα X-ray source operating at 40 kV and 20 mA with a scan rate of 0.033 ^{o}/min in the 2θ. θ range 5 ^{o} to 60 ^{o}.

SI 5: Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM) analyses of $CeMnO_x$ and PEMs

The surface morphology of the $CeMnO_x$ and composite PEMs was investigated in a field emission SEM (JEOL JSM-7100F) at an accelerated voltage of 15kV. AFM measurements of the composite PEMs were performed in semi-contact mode using a Ntegra Aura, (made by Nt-Mdt, Moscow) instrument at room temperature in air, employing "Nova" software for image analysis. Images were recorded from different areas of each sample. For AFM sample preparation, 10 mg of blend PEMs (SS-73 and SS-55) and composite membranes (SSM-73 and SSM-55) were dissolved in NMP (10 mL) each. After complete dissolution, the solution was deposited on freshly cleaved mica and kept for 12 h at room temperature in $CaCl_2$ filled desiccator fitted with the outlet to slowly remove the solvent while avoiding moisture contact. Next, the coated mica was dried in an oven at 60 °C under a vacuum for 12 h for AFM analysis. TEM images were obtained with a transmission electron microscope (JEM 2100, JEOL) operated at an accelerated voltage of 80 kV. For TEM analysis, 1 mg of $CeMnO_x$ was dispersed 4 mL isopropanol using an ultra sonicator, and the dispersed solution was carefully deposited on the carbon-coated copper grid (SPI Supplies, 300 mesh). The grid was then kept at a $CaCl_2$ filled desiccator fitted with an outlet for slow evaporation of the solvent and also to avoid moisture contact with the coated grid. Then the coated grid was heated at 80 ^{o}C under vacuum for 12 h for TEM analysis.

SI 6: Glass transition temperature (T_g) of the PEMs by DSC analysis

DSC measurements of the PEMs were carried out in a Netzsch DSC 204 F1 Phoenix instrument. The data were analyzed with the help of proteus 6.1.0d software. Cyclohexane and indium were used for the calibration of the temperature scale. Vacuum dried samples (20 mg) were heated from -80 ^{o}C to +180 ^{o}C at the rate of 20 ^{o}C/min. The samples were then quenched to -80 ^{o}C at a rate of 20 ^{o}C/min after keeping it for 1 min at +180 ^{o}C and then the second heating was performed at a heating rate of 20 ^{o}C/min. The first run in DSC was necessary to remove the trace of moisture and to the homogenization of the sample. Glass transition temperature (T_g) was recorded as the inflection point of the heat-capacity jump from the second heating curve.

SI 7: Thermal stability of the PEMs by Thermogravimetric analysis (TGA)

TGA analysis was carried out using a Netzsch TGA (TG209 F1 Libra) system. The membrane samples were heated from 30 ^{o}C to 500 ^{o}C under a nitrogen atmosphere at a heating rate of 10 ^{o}C/min. The data was analyzed with the help of proteus 6.1.0d software. The DSC measurements were carried out in a Netzsch DSC 204 F1 Phoenix instrument.

SI 8: Mechanical stability of the membranes by dynamic mechanical analyzer (DMA)

The mechanical stability of the PEMs was determined from DMA analysis. DMA analysis was carried out in a Netzsch DMA system. Samples were heated from 30 ^{o}C to 250 ^{o}C at a heating rate of 3 ^{o}C/min at a frequency 1Hz and a force of 1N. The mechanical property was determined from the storage modulus-temperature plot.

SI 9: Stress-strain property of the PEMs

Stress-strain property (stress and elongation at break) of membrane samples (2.5 cm long, 0.35 cm width 0.18 mm thick) was determined using ISO 527 S2 method in a Zwick Roell Z2.5 tester. The speed used for the measurement was 20 mm/min. The testXpert II-V3.5 software was used for data analysis. Measurements were carried out with 4–5 sample films in the water-swollen state, whose averages are reported. During measurements, the water content of the samples was maintained by placing wet tissue around the samples.

SI 10: Dye distribution study

The dye solution was prepared by dissolving 5 mg of the methylene blue dye powder in 20 ml of water. The prepared membrane samples of 4 cm^2 were dipped in a methylene blue dye solution for 6 h. After that, the membranes were washed with water multiple times and kept in water for 24 h to remove extra dye from the membrane surface. Digital images of the membranes were taken in water-wet state, and dye absorbed state.

SI 11: Determination of Water Uptake, Swelling Ratio, and extractable (%) of the PEMs

Three pieces of each type of membrane sample (size: 3 cm × 3 cm) were dried in a vacuum oven. Then dry weight (W_d) of these pieces was measured and put in DI water for 24 h. After that, by removing the surface water by filter paper, the wet weight (W_w) of the pieces was obtained. The following equation was used to calculate the WU value.

$$Water\ uptake\ (\%) = \frac{W_w - W_d}{W_d} \times 100 \qquad (S1)$$

For the determination of swelling ratio, the change of length of the membranes at dry state (L_d) and wet state (L_w) were measured and calculated by the following equation:

$$Swelling\ ratio\ (\%) = \frac{L_w - L_d}{L_d} \times 100 \qquad (S2)$$

SI 12: Determination of IEC of the PEMs

The IEC, defined as the ratio between the number of exchangeable ionic groups (equivalents) and the weight of dry membrane, was determined by the classical titration method. IEC of PEMs was measured by acid base titration method. Accurately weighted dry membranes were kept in 1 M HCl solution for 24 h then excessive HCl was washed off by DI water. After that, the membranes were put into 0.5 M NaCl solution to exchange the H^+ with Na^+. The amount of exchange H+ was titrated with 0.01 M NaOH solution using phenolphthalein indicator. At least three cycles of ion exchanging and regeneration were used to obtain a steady value. The averages of 4–5 cycles are reported here. IEC was calculated using the following eqn.:

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{Dry\ weight\ of\ PEM} \times \frac{V_{NaCl}}{V_{NaCl}^{'}} \qquad (S3)$$

Where C_{NaOH} and V_{NaOH} are the concentration and volume of NaOH, V_{NaCl} is the volume of NaCl in which the membrane was kept and $V_{NaCl}^{'}$ is the volume NaCl which was used for titration. Means if the PEM was kept in 50 ml of NaCl and if 10 ml of it was used for titration then the value of V_{NaCl} is 50 and the value of $V_{NaCl}^{'}$ is 10.

Fixed charge density (χ^m) was calculated from IEC and WU value using the following equation.

$$\chi^m = \frac{IEC}{WU} \times \rho_w \qquad (S4)$$

Where, ρ_w is the density of water.

Hydration number (λ_{hyd}) of the membranes was calculated as:

$$\lambda_{hyd} = \frac{10 \times WU}{18 \times IEC} \qquad (S5)$$

SI 13: Determination of the proton conductivity of the PEMs

The surface area resistance of PEMs was measured in a potentiostat/galvanostat (Vionic model, Metrohm Autolab BV, The Netherlands). The membranes were placed in between two in-house made acrylic plates coated with circular carbon electrodes (with 1 cm diameter having an effective area of 0.78 cm^2), which were kept in ultrapure water after conditioning in 0.5 M HCl for 12 h. Direct current (DC) and sinusoidal alternating currents (AC) were supplied to the respective electrodes for recording the frequency at a 1 $\mu A\ s^{-1}$ scanning rate within 1 MHz to 1 Hz. Membranesurface area resistance was measured from the Nyquist plot using the fit and simulation method. K^m was calculated by using the following equation,

$$K^m = \frac{\Delta x}{A \times R} \qquad (S6)$$

where Δx is the thickness of the wet membrane, R is the membrane resistance, and A is the effective membrane area.

SI 14: Activation energy (E_a) calculation

The E_a of the composite PEMs was calculated from their respective Arrhenius plots. The slope of the straight Arrhenius curve (b) was evaluated and the E_a was calculated using the following equation.

$$E_a = -b \times R \qquad (S7)$$

Where b is the slope and R is the gas constant (8.314 J/mol/K).

SI 15: Calculation of the $CeMnO_x$ crystallite size

The crystallite ssize of the $CeMnO_x$ nanocomposite was evaluated using the Debye-Scherrer equation mentioned below using XRD spectra.

$$D = \frac{K \times \lambda}{\beta \times COS\,\theta} \qquad (S8)$$

where D is the nanoparticles crystallite size, K is the Scherrer constant (0.98), λ is the X-ray wavelength (1.54), θ is angle of incidence of X-rays on the cystal surface, and β is the full width at half maximum (FWHM).

SI 16: Current density and power density calculations

The power density and current density was calculated using the following equations.

$$current\ density = \frac{I}{A} \qquad (S9)$$

$$power\ density = current\ density\ \times V \qquad (S10)$$

Where, I is the current produced using the membrane at a given potential V and A is the electrochemical active area of the fuel cell test station.

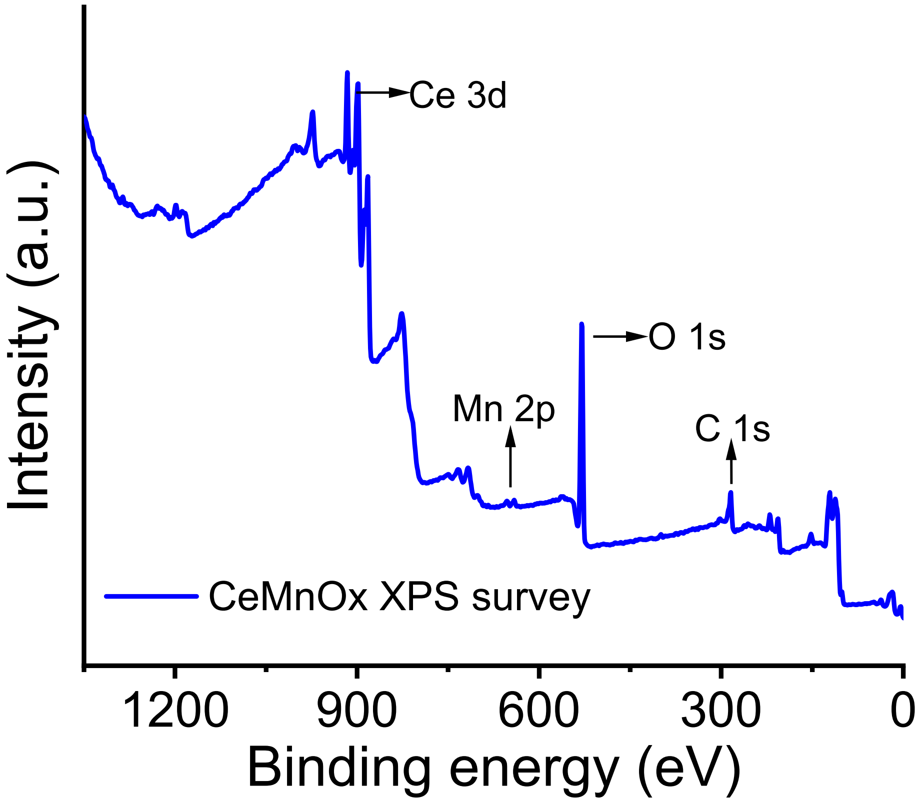


Figure S1 – XPS full scan of CeMnO_x.

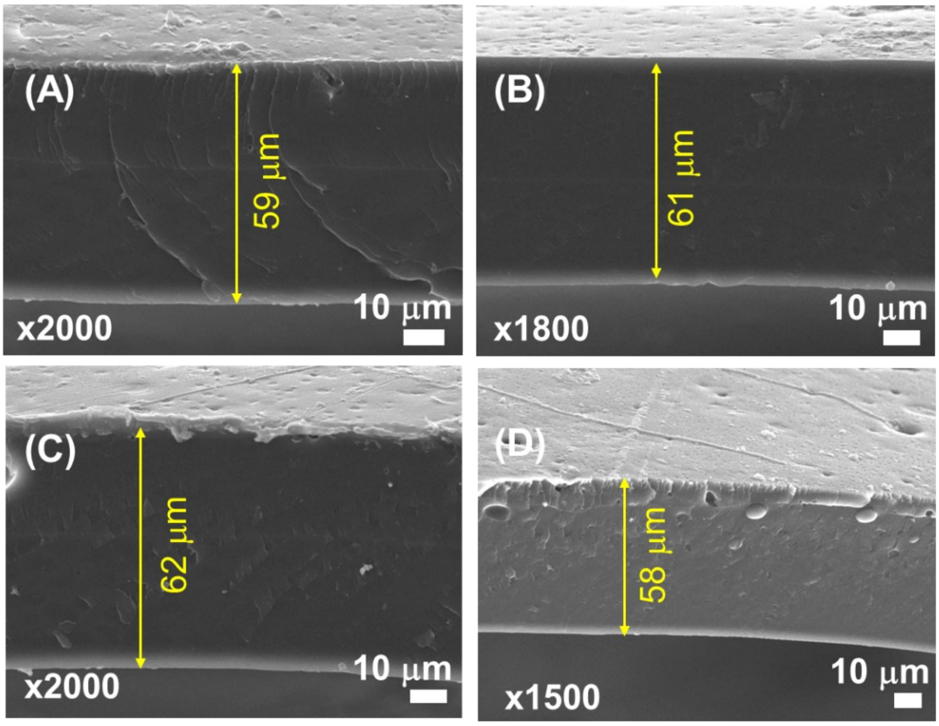
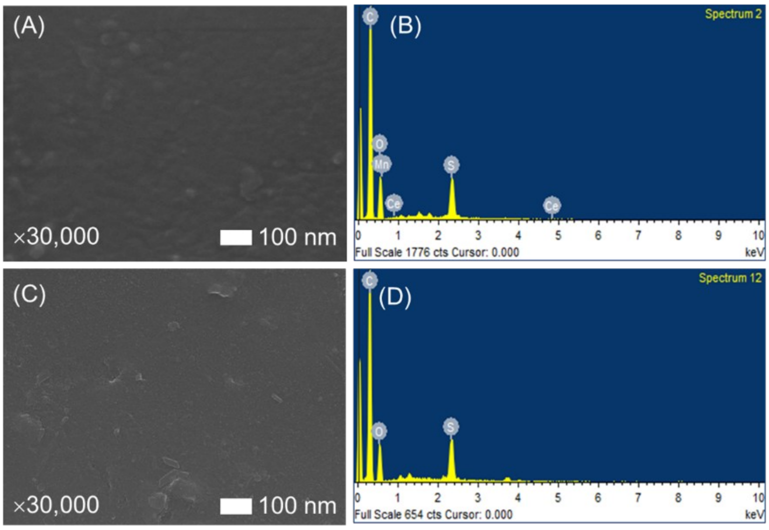
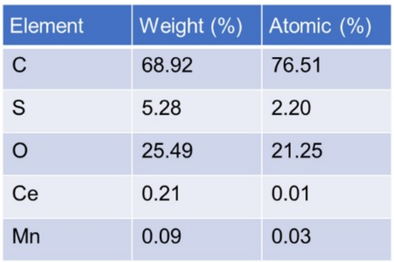


Figure S2 – Cross-sectional FE-SEM images of (A) SSM-55, (B) SSM-73, (C) SS-73, and (D) SS-55.

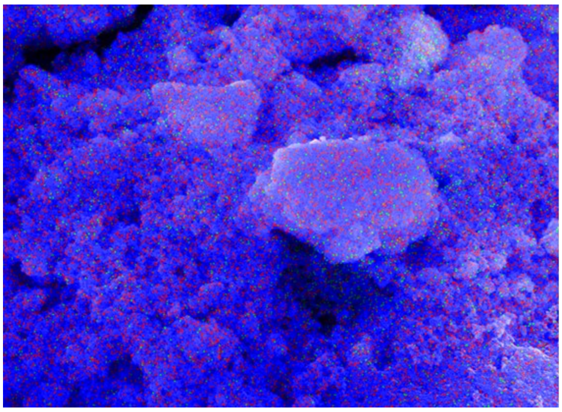




Element	Weight (%)	Atomic (%)
C	68.92	76.51
S	5.28	2.20
O	25.49	21.25
Ce	0.21	0.01
Mn	0.09	0.03

Element	Weight (%)	Atomic (%)
C	71.01	78.36
S	5.73	2.37
O	23.26	19.27
Ce	NA	NA
Mn	NA	NA

Figure S3 – Surface FE-SEM image and EDX elemental mapping of (A,B) SSM-73 and (C,D) SS-73.



Element	Weight (%)	Atomic (%)
O	34.06	80.44
Mn	4.26	2.93
Ce	61.68	16.63

Figure S4 – Weight percent and atomic percent of Ce, Mn, and O in CeMnO$_x$.

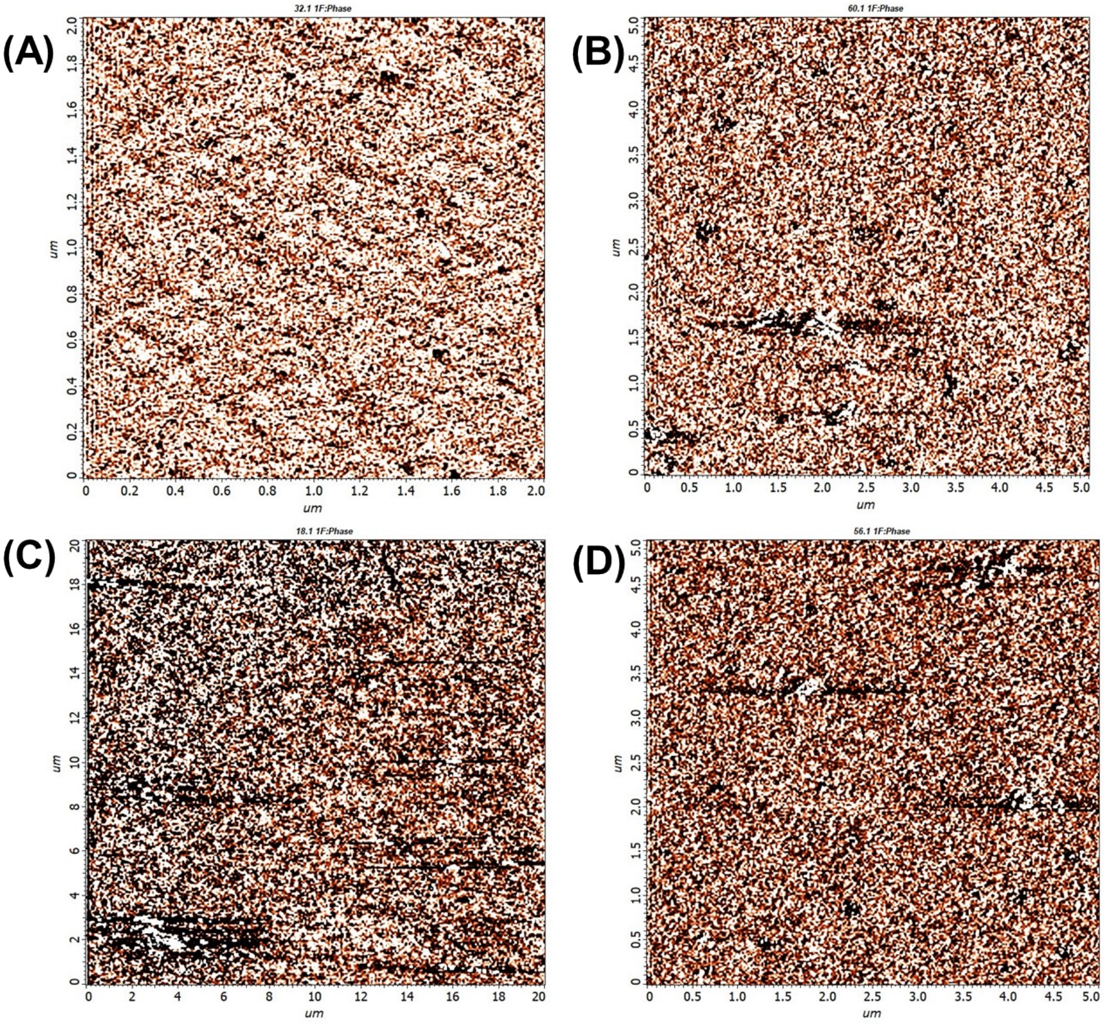


Figure S5 – AFM phase images for (A) SS-73, (B) SS-55, (C) SSM-73, (D) SSM-55.

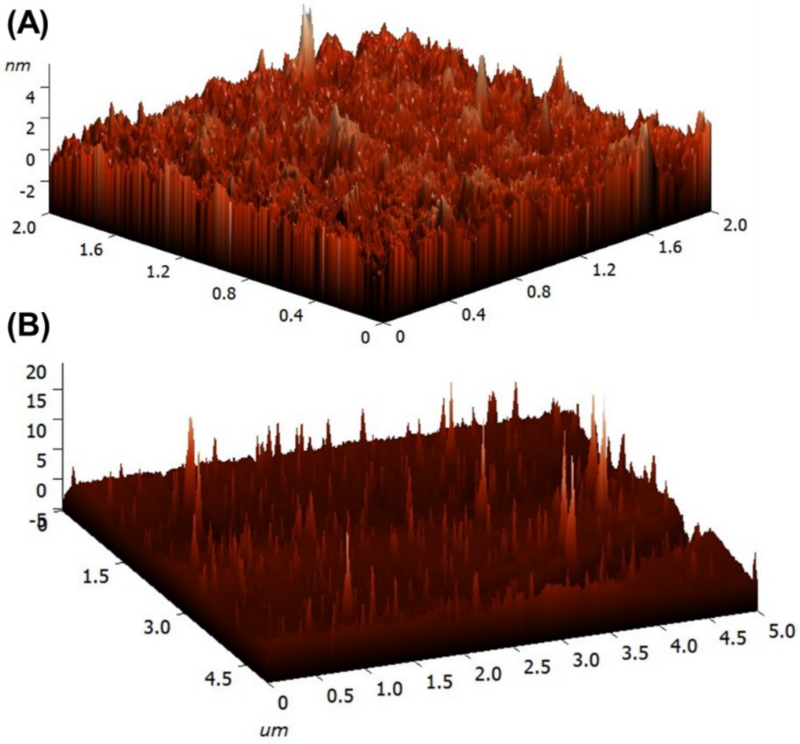


Figure S6 – AFM topological images for (A) SS-55 and (B) SSM-55.

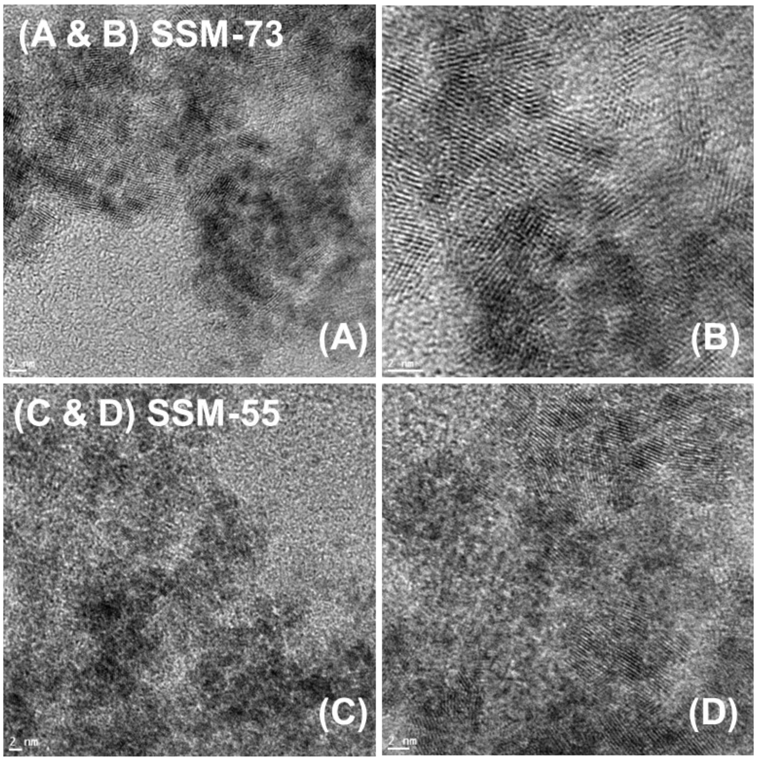


Figure S7 – TEM images of the composite PEMs (A,B) SSM-73 and (C,D) SSM-55.

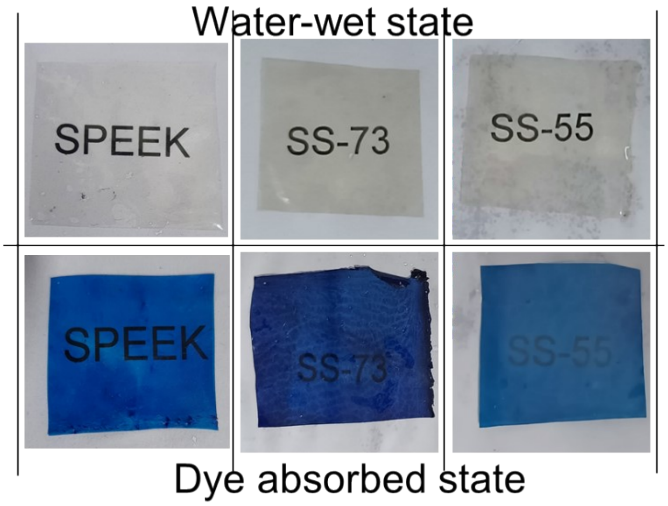
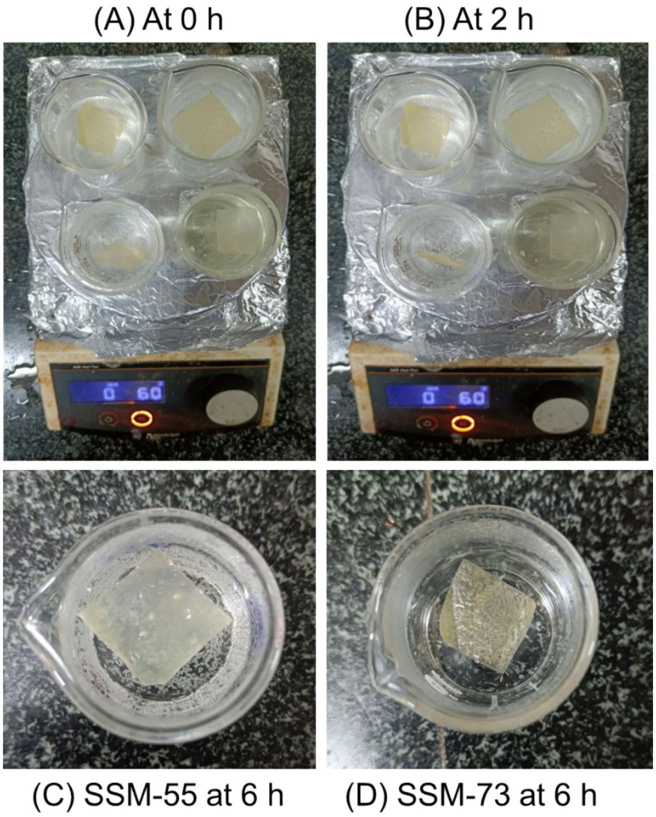


Figure S8 – Dye absorption test for SPEEK, SS-73, and SS-55.



(A) At 0 h

(B) At 2 h

(C) SSM-55 at 6 h

(D) SSM-73 at 6 h

Figure S9. Digital images of the prepared membranes at different time periods in Fenton's solution: (A) at 0 h, (B) at 3 h, and (C-D) at 6 h for SSM-55 and SSM-73.

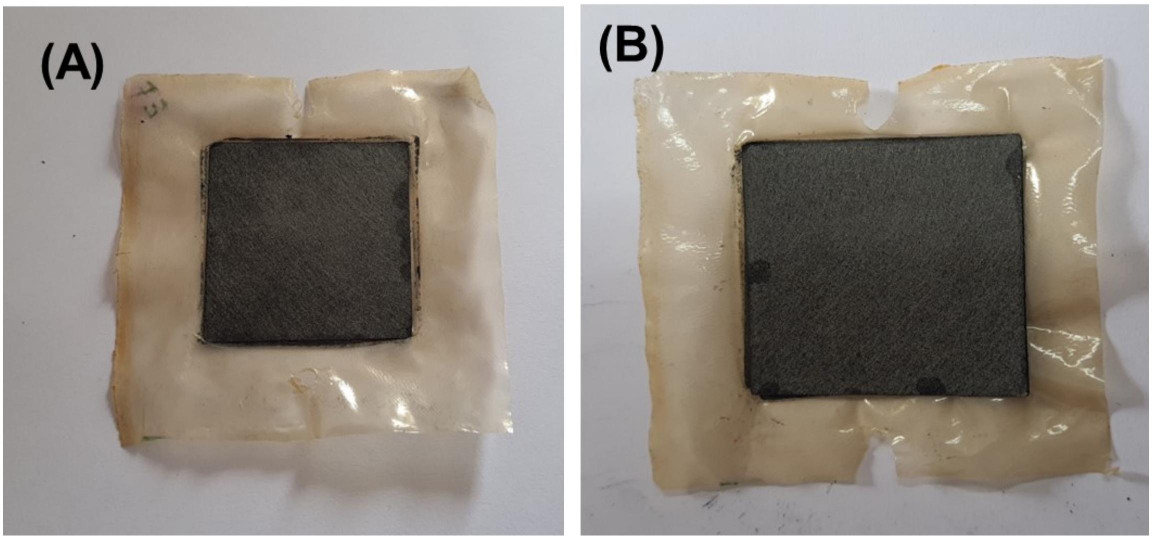


Figure S10 – MEA conditions after several PEMFC testing in FCT: (A) SSM-73 and (B) SSM-55.

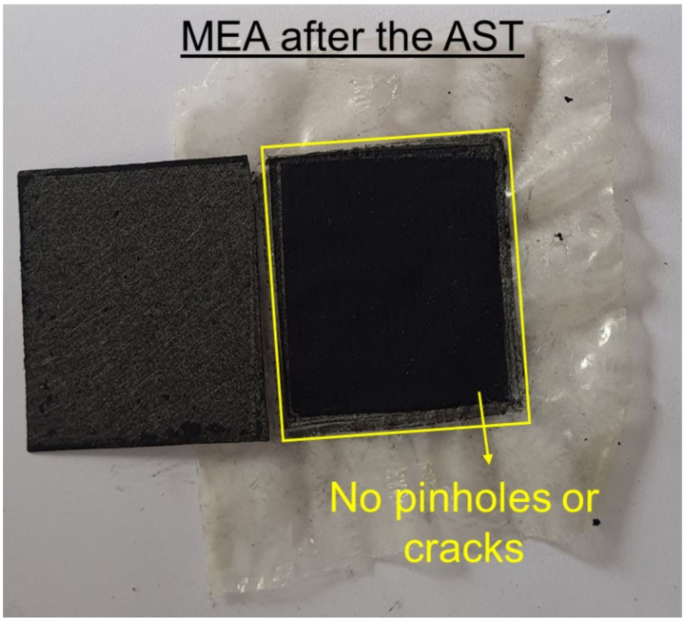


Figure S11 – Membrane condition after removing GDL from MEA after the durability test.

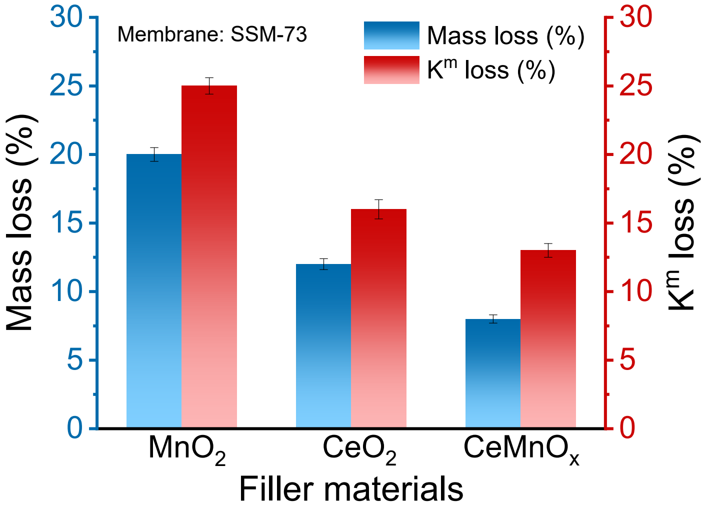


Figure S12 - Oxidative stability analysis using different filler materials.

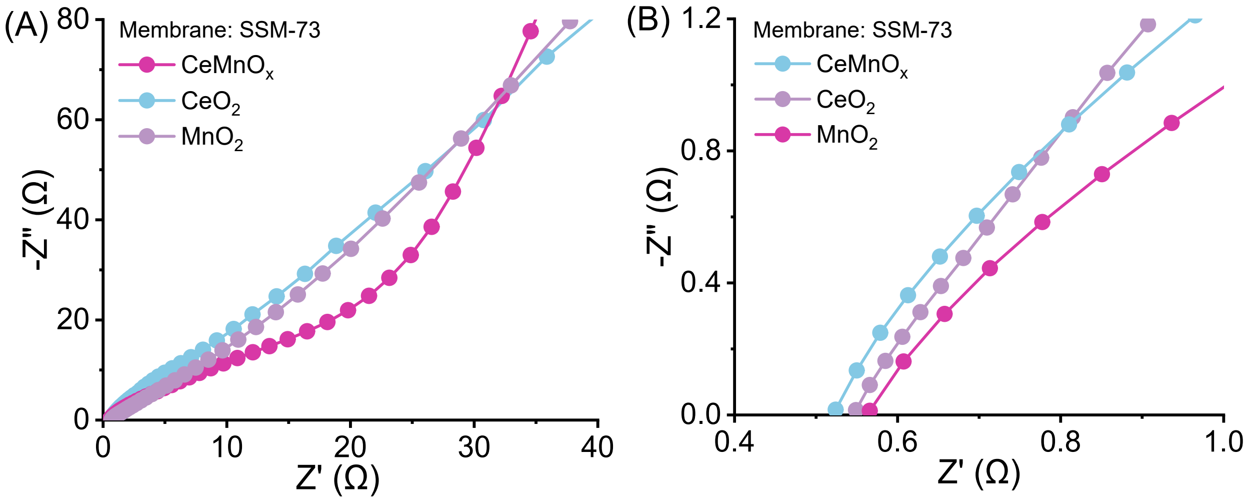


Figure S13 - (A) Nyquist plots and (B) magnified Nyquist plots of SSM-73 using different filler materials.

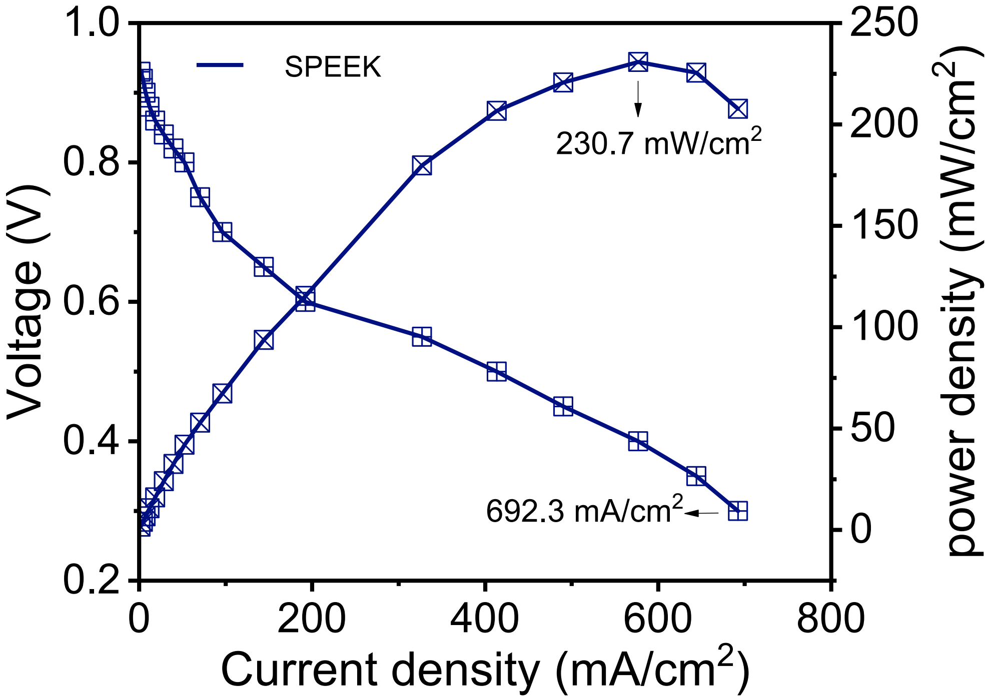


Figure S14 – PEMFC single cell performance of virgin SPEEK membrane at 75 °C and 100% RH.

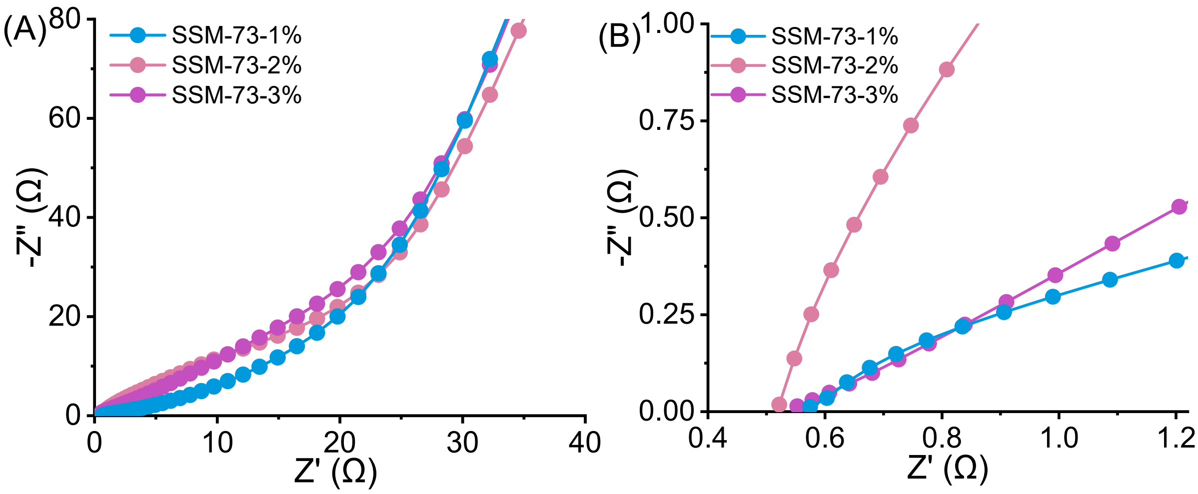


Figure S15 - (A) Nyquist plots and (B) magnified Nyquist plots of SSM-73 using CeMnO$_x$ filler with different loadings (w/w).

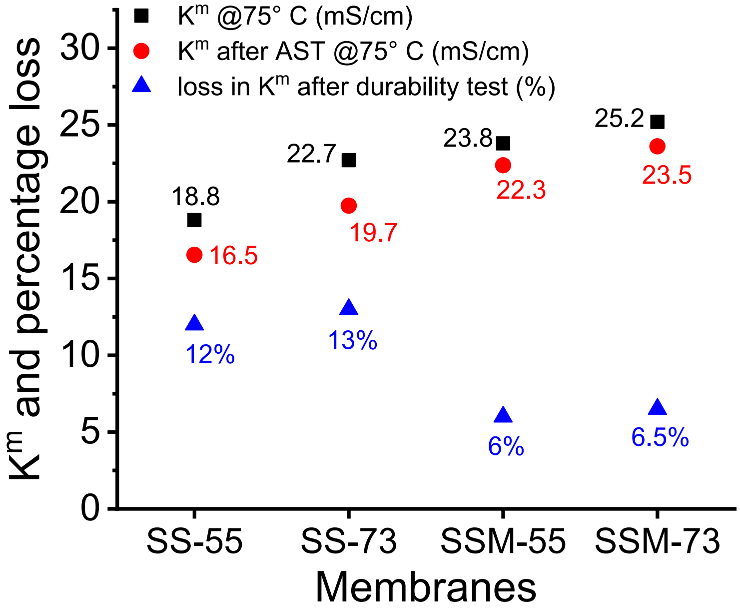


Figure S16 - Durability test in terms of K^m measurements after durability test.

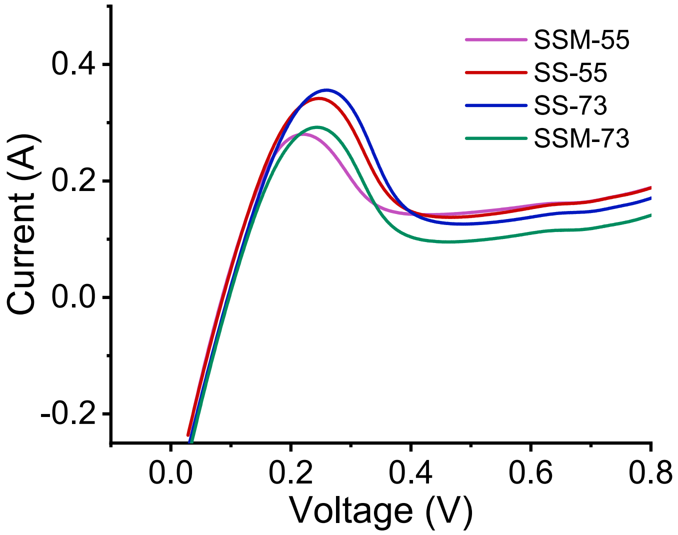


Figure S17 – Hydrogen crossover study using LSV for the prepared PEMs.

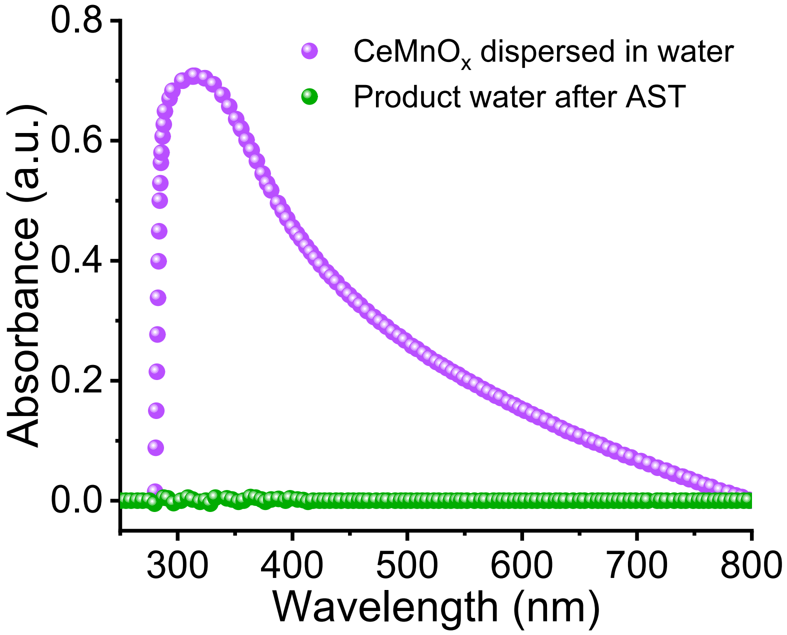


Figure S18: Comparative UV-vis spectra of product water collected during AST after 50 h with $CeMnO_x$ stock solution dispersed in water.

Table S1 – Preparation and abbreviation of PEMs with diverse SPEEK:SPPO ratio.

SPEEK (%)	SPPO (%)	PEM abbreviation	Phase miscibility (physical observation)
90	10	SS-91	Highly miscible
80	20	SS-82	Highly miscible
70	30	SS-73	Highly miscible
60	40	SS-64	miscible
50	50	SS-55	miscible

Table S2 - WU, K^m, and oxidative stability analysis of SSM-73 using different fillers.

Parameters	Filler materials in SSM-73		
	CeO_2	MnO_2	$CeMnO_x$
WU (%)	39.8	38.3	41.2
K^m (mS/cm)	14.6	14.3	15
Surface resistance (Ω)	0.55	0.56	0.52
Mass loss (%)	12	20	8
K^m loss (%)	16	25	13

Table S3 – Electrochemical properties and oxidative stability of the PEMs with diverse SPEEK:SPPO ratio.

Blend PEMs	WU (%)	K^m (mS/cm)	Fenton's test (for 2 h)		Remarks
			Mass loss (%)	K^m loss (%)	
SS-91	42.1	13.8	32	35	High WU and low OS
SS-82	39.4	13.3	25	26	High WU and low OS
SS-73	37.2	12.7	14	17	moderate WU and moderate OS
SS-64	36.7	11.1	11.5	13	moderate WU and moderate OS

SS-55	36.3	9.4	10	10	moderate WU and good OS

Footnote: *OS stands for oxidative stability.*