# Polyvinylidene fluoride based modified membranes for hydrogen generation by direct seawater electrolysis and proton exchange membrane fuel cell

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#### S-1. Physiochemical characterization

#### 1.1. Water uptake (WU) and ion-exchange capacity (PEC)

To determine the water uptake (WU), a  $2.0 \times 2.0 \text{ cm}^2$  membrane sample was vacuum dried for 24 hours and subsequently weighed in its dry state. The dry membrane was then immersed in distilled water for 24 hours to achieve maximum water absorption. Water uptake was calculated using the following equation: <sup>1,2,3,4</sup>:

$$WU (\%) = \frac{\Delta W}{W_{Dry}} x \ 100; \ \Delta W = W_{Wet} - W_{Dry}$$

Here, the mass of the membrane piece in a wet and dry state is abbreviated as  $W_{Wet} \& W_{Drv}$  respectively

Water uptake (WU) and proton exchange capacity (PEC) are complementary parameters that are proportionally dependent on each other. PEC quantifies the extent of exchangeable ionic sites (expressed in milliequivalents) per unit dry membrane mass, which is related to the density of sulfonic acid groups (-SO<sub>3</sub>H) within the membrane. A higher PEC generally indicates a greater density of -SO<sub>3</sub>H groups. The PEC of QuinoCEM-X (X = B, 0.15, 0.25) membrane samples was determined using a simple neutralization titration method at  $28 \pm 2^{\circ}$ C. Membrane samples (2.0 x 2.0 cm<sup>2</sup>) were soaked in 50 mL of 0.1 N HCl for 24 hours to convert all ionic sites to their H<sup>+</sup> form. Subsequently, the membranes were immersed in 50 mL of 0.1 N NaCl solution for an additional 24 hours to exchange Na<sup>+</sup> ions with H<sup>+</sup> ions in the membranes. The amount of H<sup>+</sup> released was quantified by titrimetric analysis using 0.1 M NaOH with phenolphthalein as the indicator. PEC was calculated using the following equation: <sup>1,2,3,4</sup>:

$$PEC = \frac{V \times C_{NaOH}}{W_{Dry}}$$

where V,  $C_{NaOH}$  and  $W_{Dry}$  are the titrant volume, concentration of NaOH solution (0.1M) and dry weight of membrane sample respectively

A remarkable balance between WU and PEC is crucial not only for maintaining membrane stability but also for enhancing performance in applications. This balance facilitates ionic mobility through the membrane while providing adequate abrasion resistance.

#### **1.2.** Ionic Conductivity (κ<sub>m</sub>)

The ionic conductivity of the prepared membranes was measured using AC impedance spectroscopy. The membranes were pre-equilibrated in a 0.1 M NaCl solution for 24 hours. QuinoCEM-X (X = B, 0.15, 0.25) membranes were then placed within an in-house manufactured acrylic assembly equipped with stainless-steel circular electrodes of 1.0 cm<sup>2</sup> area. These electrodes were immersed in a 0.1 M NaCl solution, serving ,as the conducting medium. An AC signal was applied to the electrodes, and the impedance was recorded over a frequency range of 10<sup>6</sup> to 1 Hz at a scan rate of 10<sup>-6</sup> A s<sup>-1</sup>, generating a Nyquist plot. The resulting data were fitted to an appropriate model to determine the membrane resistance. The conductivity of the membrane was calculated using the following formula<sup>1,2,3,4</sup>:

$$Km(S\ cm^{-1}) = \frac{L\ (cm)}{R\ (\Omega)x\ A(cm^2)}$$

Here, L is membrane thickness corresponds to distance between the electrodes, R is the resistance obtained, and A is the effective area of the SS-electrode.

# S-2 Detailed procedure for sample preparation and configurations of instruments employed for analysis

S-2.1. The chemical structure was investigated using JEOL RESONANCE ECZ600R 1H-NMR spectrometer at 600MHz frequency in a single pulse after dissolving QuinoCEM-X (X= B, 0.15, 0.25) co-polymer in deuterated -dimethyl sulfoxide (DMSO). PerkinElmer FT-IR spectrometer was used to examine the functional groups. The KBr-pallet method was employed to prepare the sample and transmission spectra is generated in range 4000-400 cm<sup>-1</sup>. The membrane of  $110 \pm 10 \mu m$  thickness semi-hydrated state was used get the desired spectra of CEMs.

**S-2.2.** Topographic imaging and composite dispersibility in the membrane were evaluated through semi-contact mode (SC mode) using an Ntegra Aura AFM instrument, AFM probe with micro fabricated cantilever operated at ambient temperature and open-air environment at

50 scans per minute over an effective area of 4  $\mu$ m<sup>2</sup>. Before characterization, the membrane film was kept at 60°C in vacuum oven for 48h.

Field-emission scanning electron microscopy (FE-SEM) was used to probe the surface and cross-sectional morphology of QuinoCEM-X (X= B, 0.15, 0.25) membranes. The sample were prepared by parallelly rupturing the membranes in liquid  $N_2$ . Before analysis, Au-sputtering was performed to induce electrical conduction. Surface and cross-section images show that these membranes are dense in nature and no internal porous channel are formed.

**S-2.3.** The tensile properties and stress-strain curve was evaluated from the results obtained using universal testing machine (UTM) Zwick Roell BT-FR2.5<sup>TH</sup>.40 at  $25 \pm 2^{\circ}$ C and at a stable crosshead speed of 2.0 mm per minute. Sample was prepared by cutting the membranes in long strips of dimension length x breadth (5.0 cm x 0.5 cm) and transitioned between the clutches of UTM device, the force/stress inhomogeneity was maintained by modulating the dimensions carefully.

#### S-3 Calculating the membrane potential and transport number of membranes:

The static transport number ( $\tau$  (H<sup>+</sup>)) of the designed polyelectrolyte membrane signifies preferential mobility of counter-ions through the charged membrane matrix w.r.t to its co-ion. The  $\eta_{mem}$  was measured in an indigenously designed bi-compartment acrylic material assembly whose overall volume capacity is 140 cm<sup>2</sup>. In this assembly, the membrane of dimension 5.0 x 5.0 cm<sup>2</sup> with an effective area of 15.5 cm<sup>2</sup> was transitioned and the compartments were filled with 0.01M and 0.1M electrolyte solutions (NaOH). The potential difference generated across the membrane was probed using MECO, 81K-TRMS connected to the reference calomel electrode. The t<sub>+</sub> was calculated from the equation <sup>[5,6]</sup>:

$$\tau_{H+} = \frac{\frac{nF \times \eta_{mem}}{RT \times ln \frac{C^{1}}{C^{2}}} + 1}{2}$$

Here, n = 1 (for uni-univalent ionic charge), (F) represents Faraday's constant (96,485 C mol<sup>-1</sup>), (R) is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), and (T) is the system temperature during the study (25°C, 298 K).



S-4 The 'H NMR spectrum of the Quino-PVDF sample was analyzed to determine the degree of grafting. Based on the integration of the relevant peaks, the calculated degree of grafting for Quino-PVDF was found to be 11%, indicating successful functionalization of the polymer backbone.



S-5 The <sup>13</sup>C NMR spectrum of SQuino-PVDF



S-6 UV-vis Spectra of Quino-PVDF and SQuino-PVDF



S-7 XRD Spectra of PVDF, QuinoCEM-B and QuinoCEM-0.25

Element	$\lambda \Lambda / a : a = b + 0 /$	Atomaia 0/	Spectrum 1
Element	vveignt%	Atomic%	QuinoCEM-B
СК	39.98	51.04	<b>e</b>
0 K	4.14	3.97	
FK	55.52	44.81	
SK	0.37	0.18	P
Totals	100.00		0 1 2 3 4 5 6 7 8 9 10 Full Scale 1231 cts Cursor: 0.000 keV
Element	Weight%	Atomic%	Spectrum 2
СК	38.20	49.34	QuinoCEM-0.15
0 К	2.49	2.41	•
FK	58.76	47.98	
SK	0.55	0.26	<b>P</b>
Totals	100.00		0 1 2 3 4 5 6 7 8 9 10 Full Scale 1205 cts Cursor: 0.000 keV
Element	Weight%	Atomic%	
СК	52.19	63.25	QuinoCEIVI-0.25
0 K	4.76	4.33	
FK	41.24	31.60	
SK	1.81	0.82	
Totals	100.00		0 1 2 3 4 5 6 7 8 9 10 Full Scale 984 cts Cursor: 0.000 keV

S-8: The Energy Dispersive X-ray (EDX) Spectrum of QuinoCEM-B, QuinoCEM-0.15, and QuinoCEM-0.25 Membranes Reveals a Correlation Between Nafion Content and Sulfur Weight Percentage, With the Highest Content Observed in QuinoCEM-0.25.



S-9: AFM analysis was conducted to study the surface roughness and phase distribution of fabricated membranes - QuinoCEM-B (a, a'), QuinoCEM-0.15 (b, b'), and QuinoCEM-0.25 (c, c'). The roughness of the surface was measured in terms of root mean square roughness (Sq) and average roughness (Sa). The investigation revealed that as the Nafion content increased, the dark and light regions converged, leading to a stable low-range ion conduction tortuous path.



S-10: Water Contact angle of PVDF film.



S-11: (a) The TGA of QuinoCEM-0.25 and QuinoCEM-B, and (b) Stress-Strain Curve (UTM analysis) of QuinoCEM-B, QuinoCEM-0.15, and QuinoCEM-0.25 Membranes.



S-12: Electrochemical Impedance Spectroscopy (EIS) plots illustrating dynamic ionic conductivity at diffrent temperatures for (a) QuinoCEM-0.25, (b) QuinoCEM-0.15, and (c) QuinoCEM-B.



*S-13: (a) and (b) showing the vapor water electrolysis performance of QuinoCEM-0.15 and QuinoCEM-B respectively at temperatures of 30°C and 80°C with varying RH.* 



S-14: The liquid water comparison graph of QuinoCEM-0.25 and Nafion-117 membranes at 80°C in deionized (DI) water clearly demonstrates the superior performance of the QuinoCEM-0.25 membrane. Under the same testing conditions, the Nafion-117 MEA achieves a current density of 320 mA cm<sup>-2</sup> at 1.8 V, which is notably lower than that of the QuinoCEM-0.25 membrane. In contrast, the QuinoCEM-0.25 membrane outperforms Nafion-117, delivering a current density of 402 mA cm<sup>-2</sup> at 1.8 V, indicating its enhanced electrochemical performance.



S-15: Electrochemical Impedance Spectroscopy (EIS) plots of the ohmic resistance ( $R_{ohmic}$ ) for QuinoCEM-0.15, QuinoCEM-0.25, and Nafion-212 demonstrate the trend in ohmic resistance as QuinoCEM-0.15 > QuinoCEM-0.25 > Nafion-212



S-16: polarization curve of QuinoCEM-B membrane.



S-17: Tafel slope at  $i < 100 \text{ mA cm}^{-2}$  from the experimentally recorded polarization data



S-18: FE-SEM images of the gas diffusion layer (GDL) are provided in two conditions: (a) prior to fuel cell analysis and (b) post fuel cell analysis. The FE-SEM images illustrate the presence of contaminants on the GDL after fuel cell operation, indicating potential issues such as residue formation or material degradation that occurred during the testing process.



S-19: Elemental analysis of gas diffusion layer (GDL) revealing the presence of (a) Carbon (C), (b) Oxygen (O), (c) Sulfur (S), (d) Platinum (Pt), and (e) Fluorine (F).

Table S-1: presents the physicochemical comparison between the commercial Nafion-117 membrane and the QuinoCEM-0.25 membrane. This comparison highlights key properties such as ion exchange capacity (IEC), water uptake, proton conductivity ( $k_m$  (×10<sup>-3</sup>) Scm<sup>-1</sup>) providing a comprehensive evaluation of the performance differences between these two materials in electrochemical applications.

Membrane	Water Uptake (%)	<i>IEC (meq</i> $g^{-1}$ <i>)</i>	$k_m$ (×10 <sup>-3</sup> ) Scm <sup>-1</sup>
QuinoCEM-0.25	27.0	1.00	11.8
Nafion-117	25.0	0.88	14.0



S-20:(a) and (b) represent the cyclic voltammetry (CV) curves of the Nafion 212 and QuinoCEM-0.25 membranes, respectively, highlighting their electrochemical behavior. (c) shows the linear sweep voltammetry (LSV) curves comparing the hydrogen crossover characteristics of the QuinoCEM-0.25 and Nafion 212 membranes.

Table S-2: Calculated values of electrochemical active surface area (ECSA) in  $cm^2/mg$  and double layer capacitance (Cdl) in  $F/cm^2$  for the tested membranes.

Membrane	ECSA (Cm <sup>2</sup> mg <sup>-1</sup> )	Double layer capacitance (mFcm <sup>-2</sup> )
Nafion-212	14.2	0.041
QuinoCEM-0.25	14.0	0.035



*S-21: (a) Illustration depicting the effective membrane area directly exposed to the gas phase, (b) The membrane condition following vapor electrolysis.* 



Water droplets

S-22: Digital Images of Membrane Electrode Assembly (MEA), specifically QuinoCEM-0.25, post fuel cell performance analysis.



S-23: Digital images of QunioCEM-B and QunioCEM-0.25 membranes.

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