Supplementary Information

Side Chain Engineered Ether-Free Polybenzimidazole Membranes with Enhanced Proton Transport and Stability for PEM Water Electrolysis

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SI-1. Determination of physicochemical and electrochemical parameters of the membrane

Water uptake: 2.0 × 2.0 cm^2 membranes piece was vacuum dried for 24h and weighed in its dry condition. The dry membrane was then immersed in distilled water for the next 24h to absorb the maximum water possible. The water uptake was calculated using equation:

$$WU\ (\%) = \frac{W_{Wet} - W_{Dry}}{W_{Dry}} \times 100$$

Here, W_{Wet} & W_{Dry} are the wet and dry weight of membranes.

Swelling ratio of membranes was measured in terms of change in volume of membrane under wet and dry conditions and calculated using following equation:

$$Sr\ (\%) = \frac{V_{Wet} - V_{Dry}}{V_{Dry}} \times\ 100$$

Where, V_{Wet} and V_{Dry} are the wet and dry volume of membrane samples respectively.

Ion exchange capacity describes the amount of exchangeable ionic groups induced per unit dry of membrane weight. For IEC, 2 × 2 cm^2 membrane pieces with known dry weight were immersed in 0.1M HCl for 24h for complete protonation. Afterwards, membrane pieces were removed from HCl solution washed thoroughly with D.I water to remove extra H^+ ion and equilibrated in 0.1M NaCl for 24 h under the similar environmental conditions and the equilibrated solution was titrated against 0.01 M NaOH solution using phenolphthalein as

indicator to measure the amount of Na^+ liberated in the solution, the endpoint was detected by visualizing the appearance of pale pink color. Three replications of exchanging and regeneration were carried out to gain steady value. The IEC is calculated from below equation:

$$IEC\ (meq\ g^{-1}) = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}}$$

Where V_{NaOH} is the volume of NaOH consumed, C_{NaOH} is the concentration of NaOH solution, and W_{dry} is the dry weight of the membrane sample. The average of the three cycles is mentioned here.

The degrees of sulfonation of prepared membranes were calculated using equation :

$$DOS\ (\%) = \frac{\frac{I_{SO_3H}}{G_{protons}}}{\frac{I_{SO_3H}}{G_{protons}} + \frac{I_{Ar.H}}{T_{Ar.H}}} \times 100$$

Where I_{SO_3H}, integral value of -SO_3H chain, $G_{protons}$ is the number of protons grafted, $I_{Ar.H}$ and $T_{Ar.H}$ are integral values and total number of aromatic protons, respectively.

The impedance was measured by sandwiching membrane samples (2 cm × 2 cm) between the electrodes and applying DC and sinusoidal AC at a scanning rate of 1 μA s^{-1}. The specimen's resistance (R) at room temperature was assessed using Nyquist plots that made use of fit and simulation approaches. The κ^m of the prepared PEMs was assessed using the following equation:

$$\kappa^m(S\ cm^{-1}) = \frac{L(cm)}{R(\Omega) \times A(cm^2)}$$

Where, L (cm) is thickness, and A (cm^2) is the effective area of the membrane.

The E_a for the AEMs 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.

$$E_a = -b \times R$$

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

The degradation rate of membranes were calculated using equation:

$$R_d(mV\ h^{-1}) = \frac{V_f - V_i}{t}$$

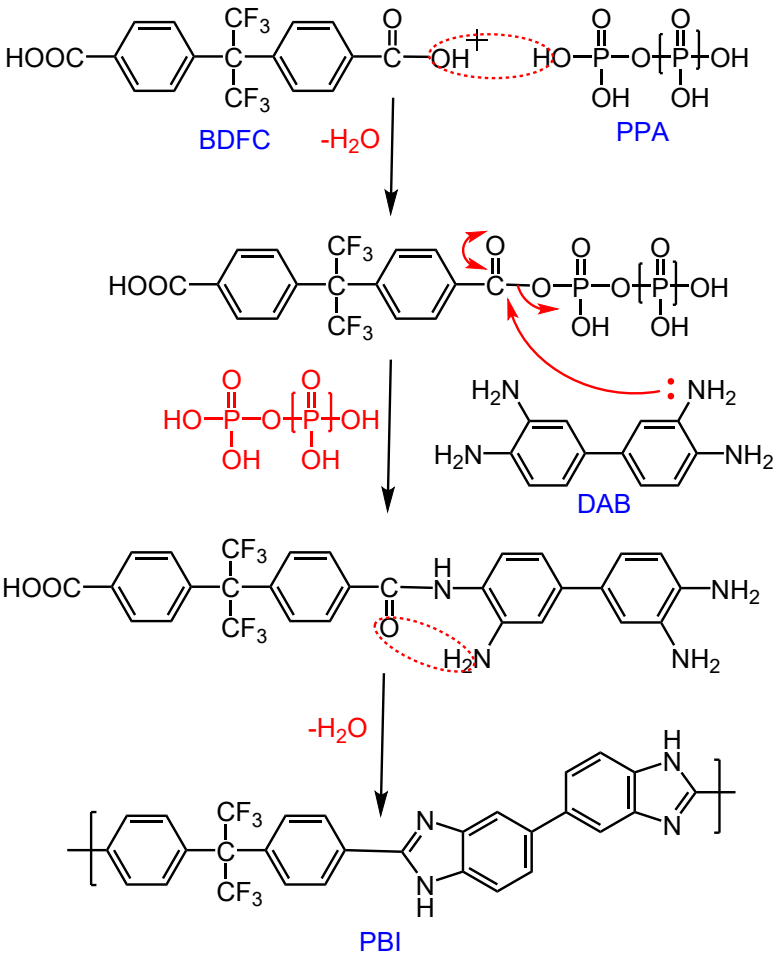
$V_f = final\ cell\ potential$

$V_i = initial\ cell\ potential$

$t = operation\ time$

Membrane	FPBI (mmol)	NaH (mmol)	Butane sultone (mmol)
FPBI-g-BS-21	1.77	8.33	3.67
FPBI-g-BS-43	1.77	8.33	7.34

Table S1. Varying the concentration of grafting of butane sultone on FPBI



Scheme S1. Mechanism of synthesis of polybenzimidazole polymer.

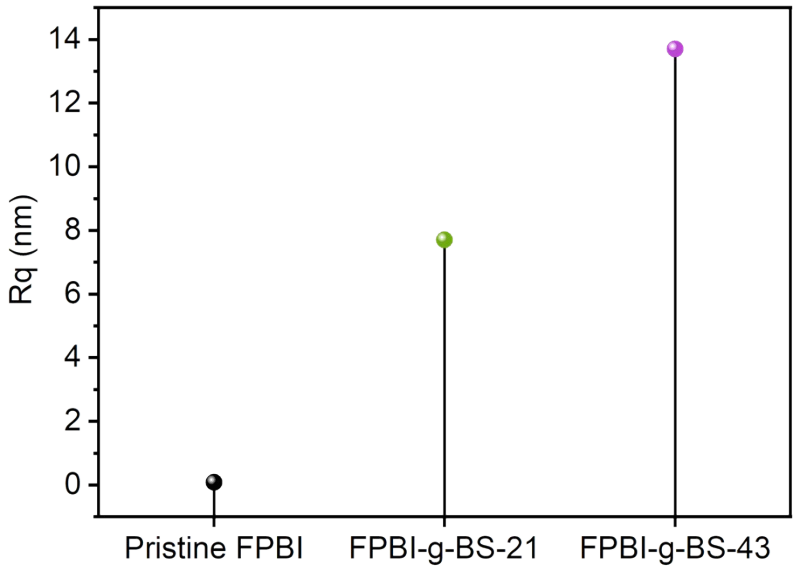


Figure S1. Root-mean square (Rq) roughness of fabricated membranes.

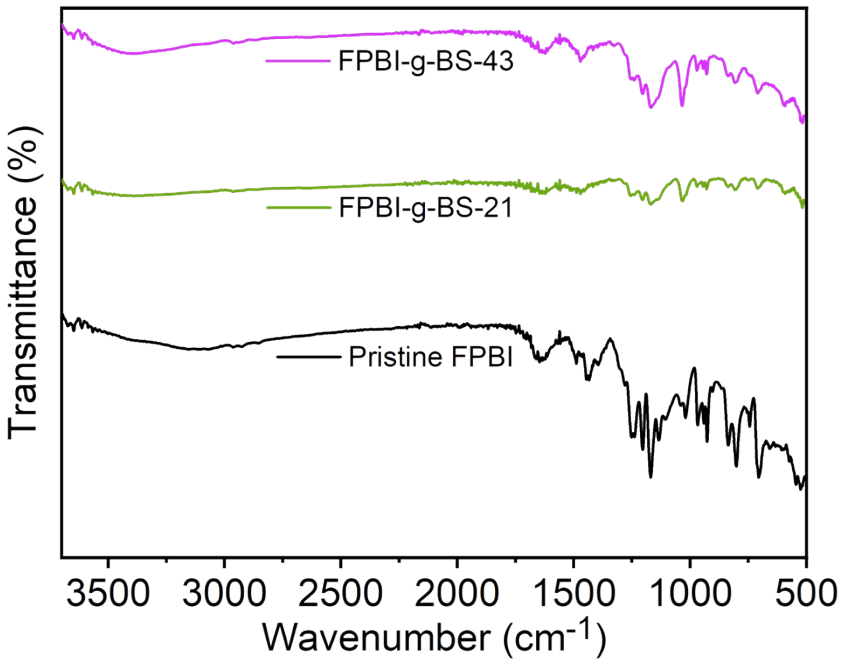


Figure S2. FTIR spectra of membranes after experiment of oxidative stability.

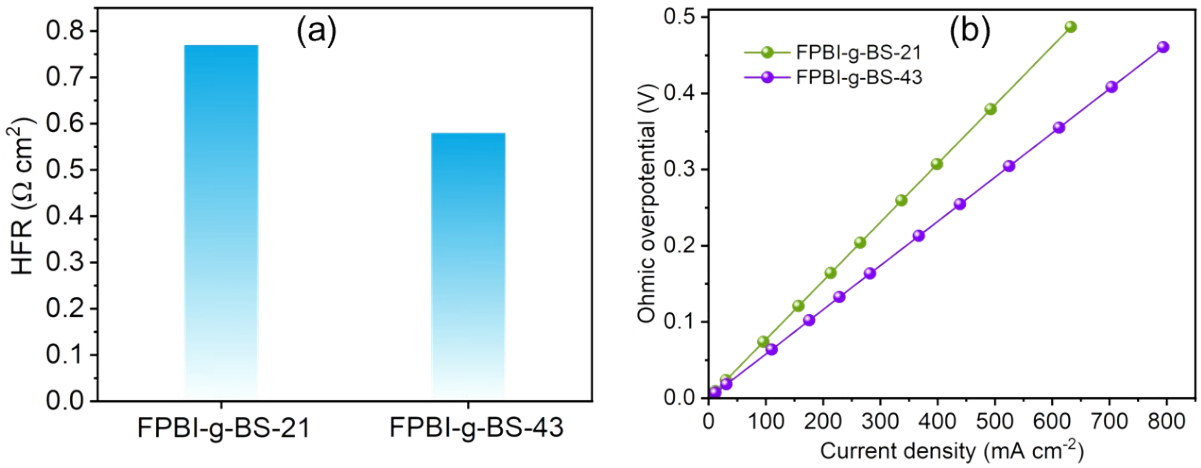


Figure S3 (a) High frequency resistance (HFR) and (b) ohmic overpotential analysis of fabricated membranes.

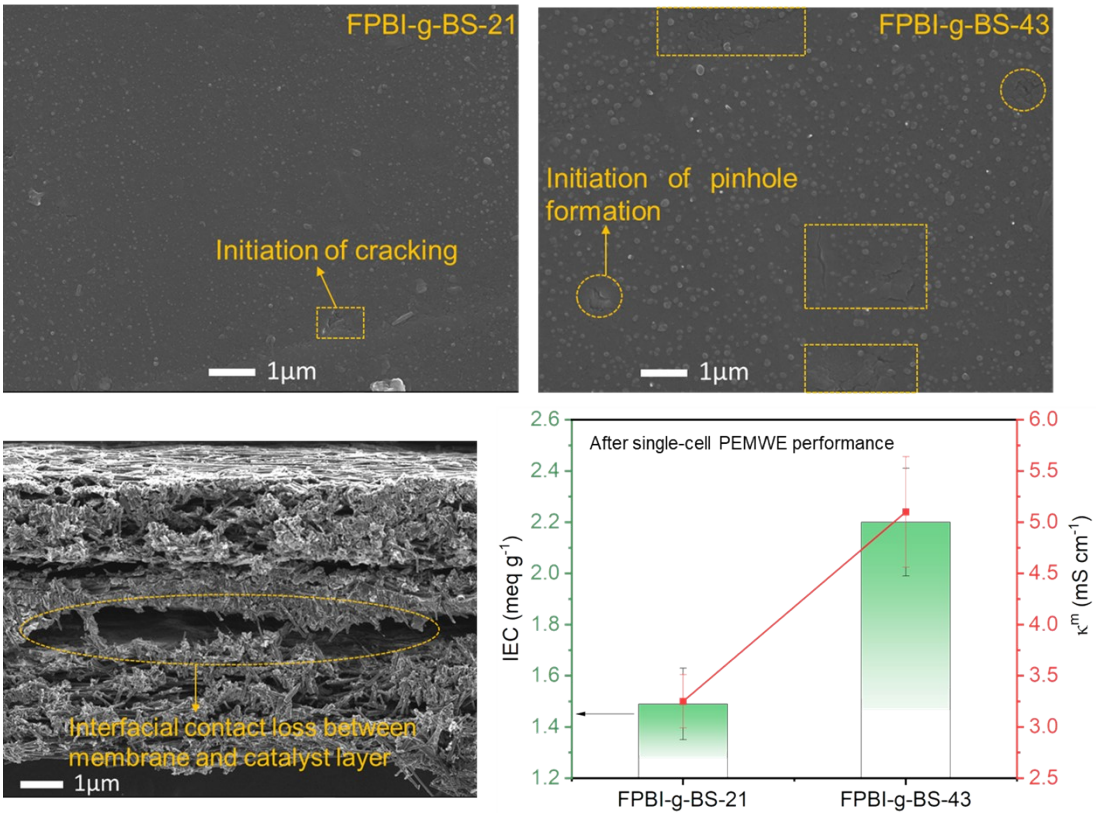


Figure S4. Post analysis of designed membranes: surface and cross-sectional images using FE-SEM techniques and electrochemical properties (IEC and κ^m).

Reference:

1. Mishra, S., Upadhyay, P., Sharma, J., Kumar, P., & Kulshrestha, V. Materials Today Chemistry, 47, 2025, 102822.