

Devising ultra-robust mixed matrix membrane separator using functionalized MOF-Poly(phenylene oxide) for high performance vanadium redox flow battery[†]

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Supporting Information

Section S1

Degree of bromination

Extent of bromination occurred in poly(2,6-dimethylphenylene oxide) (PPO) was determined by calculating degree of bromination. ¹H-NMR is used for the determination of extent of bromination. Integral ratio of the peaks obtained in NMR is applied for the calculation of bromination.

The degree of bromination (DOB) was calculated from the peak intensity of bromomethyl and methyl group obtained in ¹H-NMR as shown below:

$$\text{DOB} = \frac{3 \times I_{CH_2}}{2 \times I_{CH_3} + 3 \times I_{CH_2}} \quad (\text{S1})$$

Where, I is the intensity of the peaks.

Section S2

Instrumental analysis

FT-IR spectra of dried sample were recorded by KBr technique with a spectrum GX series 49387 spectrometer in the range of 4000-400 cm⁻¹ in the range.

Thermal property of the Cd-MOF and membranes were studied by thermogravimetric analyzer (TGA) (NETZSCH TG 209F1 Libra TGA209F1D-0105-L) under a N₂ environment with 10 °C/min heating rate from 30-700 °C.

Scanning electron microscopy (SEM), gold sputter coatings on the desired beads samples were achieved between 0.1-1.0 Pa pressure. Micrographs were obtained at 10⁻³ to 10⁻² Pa EHT 15.00kV with 300V collector bias using Leo microscope.

Presence and homogeneous distribution of Cd in the Cd-MOF and in membrane phase were confirmed by EDX and elemental mapping studies using LEO VP1430.

Atomic force microscopy (AFM) studies of dried membrane samples were performed at 30 °C using NTEGRA AURA (NTMDT) instrument in semi contact mode SPM S-2 NSG 01tip with approx. 10 nm radius of curvature (natural frequency for the cantilever was 300 kHz).

Mechanical strength of the membrane samples (26 cm² rectangular pieces) was studied by using bursting strength tester machine model No. 807DMP (test techno consultants, Gujarat, India).

The 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.

Powder X-ray diffraction (PXRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) system equipped with Cu K α ($\lambda=1.54$ Å) radiation.

X-ray structural studies

Single crystals with suitable dimensions were chosen under an optical microscope and mounted on a glass fibre for data collection. Intensity data for as synthesized orange block crystal of Cd-MOF were collected using graphite-monochromated MoK α ($\lambda=0.71073$ Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 123.15 K. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were performed with SAINT¹ software. Absorption corrections to the collected reflections were accounted with SADABS² using XPREP.³ The structure was solved by direct method using SIR-97⁴ and was refined on F² by the full-matrix least-squares technique using the SHELXL-2014⁵ program package. All H atoms were placed in calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement

parameters using the SHELXL default. To give an account of disordered electron densities associated with solvent molecules, the “SQUEEZE” protocol in PLATON⁶ was applied that produced a set of solvent free diffraction intensities. Final cycles of least-squares refinements improved both the R values and Goodness of Fit with the modified data set after subtracting the contribution from the disordered solvent molecules, using SQUEEZE program. The crystal and refinement data for solvent free Cd-MOF is listed in Table S3.

Section S3

Membrane stabilities

Oxidative stability of AEMs and Nafion 117 were assessed under the treatment with Fenton’s reagent (3% peroxide solution in 3 ppm ferrous sulphate) at 80 °C temperature for 8 h, and percentage loss in weight and conductivity after the treatment were recorded.

Chemical stability of different AEMs and Nafion 117 were recorded under highly acidic environment (1.5 M VO²⁺ solution in 2.0 M H₂SO₄) for 3 months at room temperature (30 °C). The weight loss (%) was estimated by following equation.

$$\text{Weight loss (\%)} = \frac{W_{\text{untreated}} - W_{\text{treated}}}{W_{\text{untreated}}} \times 100 \quad (\text{S2})$$

Where $W_{\text{untreated}}$ and W_{treated} are the weight dry membrane sample before and after treatment.

Section S4

Methods for physical and chemical property measurement

The membrane was equilibrated in the DI water at room temperature for 24 h. The excess water on the surface of wet membrane was removed by tissue paper and weight of wet membrane (W_{wet}) determined. The wet sample was dried in vacuum oven at 80 °C and constant dry weight (W_{dry}) was recorded for the estimation of water uptake (WU):

$$WU (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (\text{S3})$$

Hydrophobic-hydrophilic nature of membrane was assessed by water contact angle measurement (optical tensiometer). Water drop (4 mL) was placed on the membrane surface using micro-syringe and contact angle was obtained (model DSA 100, Kruss).

Swelling ratio (SR) of the membrane was measured by immersed the membrane in water at 65°C for 12h using given equation; where L_{wet} and L_{dry} are the lengths of the wet and dry membranes,

$$SR (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \quad (S4)$$

Ion exchange capacity (IEC) of membrane samples was estimated by the acid base titration by following equation.

$$IEC = \frac{V_{HCl} \times C_{HCl}}{W_{dry}} \quad (S5)$$

Where C and V denote the concentration and volume of HCl. Measuring error of IEC is ± 0.01 meq/g.

Zeta Potential (ζ) of the membranes were measured at pH 7 using a Zeta Cad streaming current and zeta potential meter, CAD Instruments (France). The membranes were equilibrated with 1 mM KCl solution (pH=7) for overnight. Membranes (two membranes are sandwich using Teflon spacer) were then fixed in the cell of the instrument. The area of the each membrane is 5 cm x 2.5 cm. The steady-state zeta potential values were recorded with a 1 mM KCl electrolyte solution.

The ionic conductivity for different prepared amphoteric ion exchange membrane samples was measured by impedance spectroscopy. In-plane ionic conductivity of different membrane samples was determined 0.1M NaOH using four-electrodes AC impedance potentiostat/galvanostat frequency response analyzer (Eco Chemie, B.V. Utrecht, The Netherlands Auto Lab, model PGSTAT 302N) over $1-10^6$ Hz frequency range. The membrane sample was sandwiched between two stainless steel circular electrodes (area: 0.13 cm^2). Direct current (dc) and sinusoidal alternating currents (ac) were applied to the respective electrodes and frequency was recorded at $1 \mu\text{A/s}$ scanning rate.

The permeability of VO^{2+} ions was tested on a diffusion cell, as shown in Figure S14. The permeability of vanadium ion (VO^{2+}) across the different membranes were measured in a two-compartment permeability cell separated by membrane sample (7.0 cm^2). Compartment (I) was filled with VOSO_4 (1.0 M) solution in 2.0 M H_2SO_4 (35.0 cm^3), while compartment (II) was filled with MgSO_4 (1.0 M) in 2.0 M H_2SO_4 (35.0 cm^3). Both compartments were stirred

continuously. MgSO_4 was used to neutralize the ionic strengths in both compartments to minimize the osmotic effects. After certain time interval, sample of compartment II, was analyzed for VO^{2+} concentration by UV-vis spectrometer. The permeability of the vanadium ion (P) was calculated by following equation.

$$P = \frac{V L d C_t}{S C_o dt} \quad (S6)$$

Where, L is the membrane thickness, V is the solution volume in compartment I and II, S is the effective membrane area, C_o is the initial VO^{2+} concentration in compartment I, and C_t is the VO^{2+} concentration in compartment II at time (t).

Section S5

Calculation of efficiencies

The Columbic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) were calculated using following equations.

$$CE(\%) = \frac{\int I_d dt}{\int I_c dt} \times 100 \quad (S7)$$

$$VE(\%) = \frac{\int V_d dt}{\int V_c dt} \times 100$$

$$EE(\%) = CE \times VE \quad (S9)$$

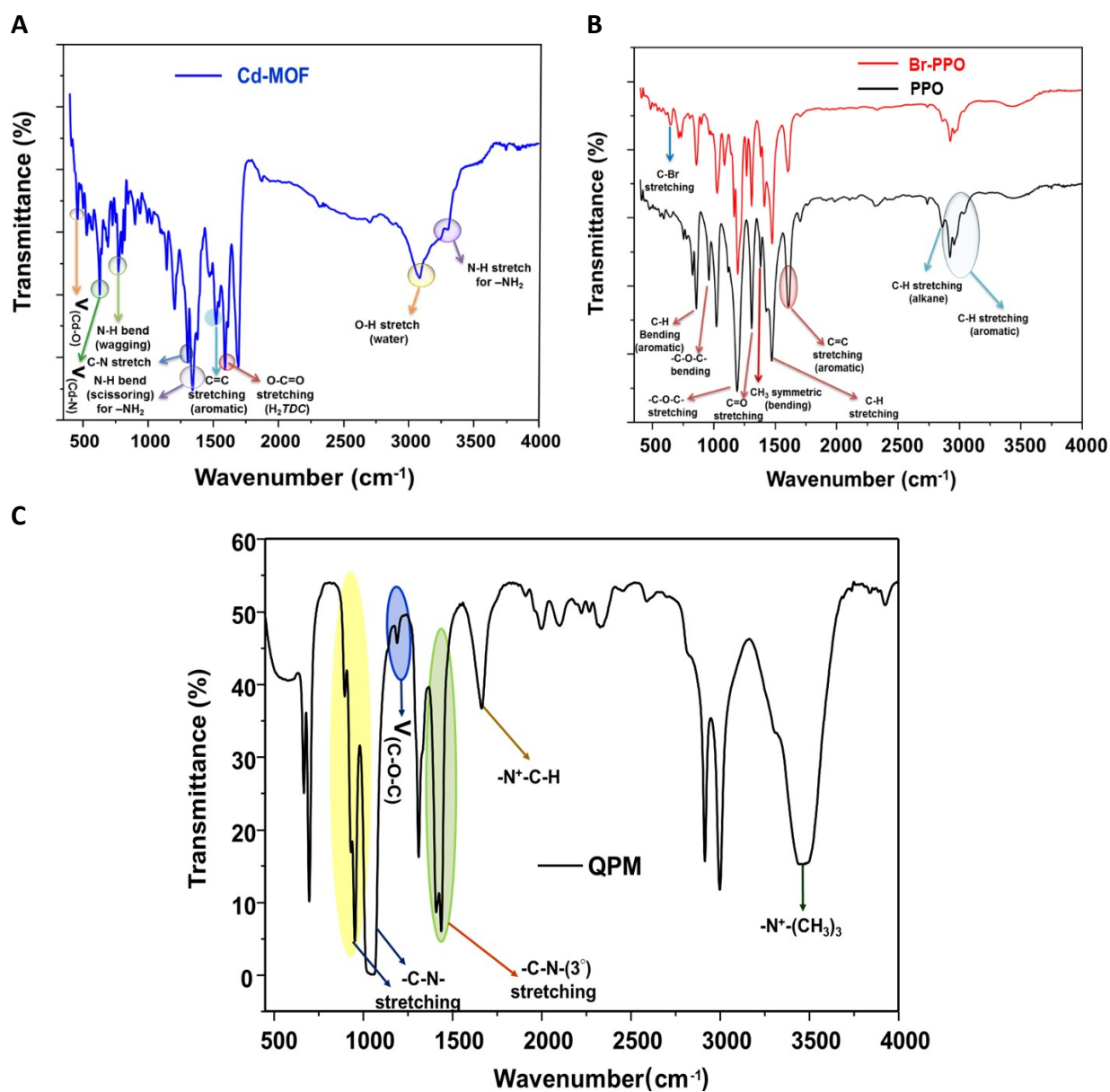
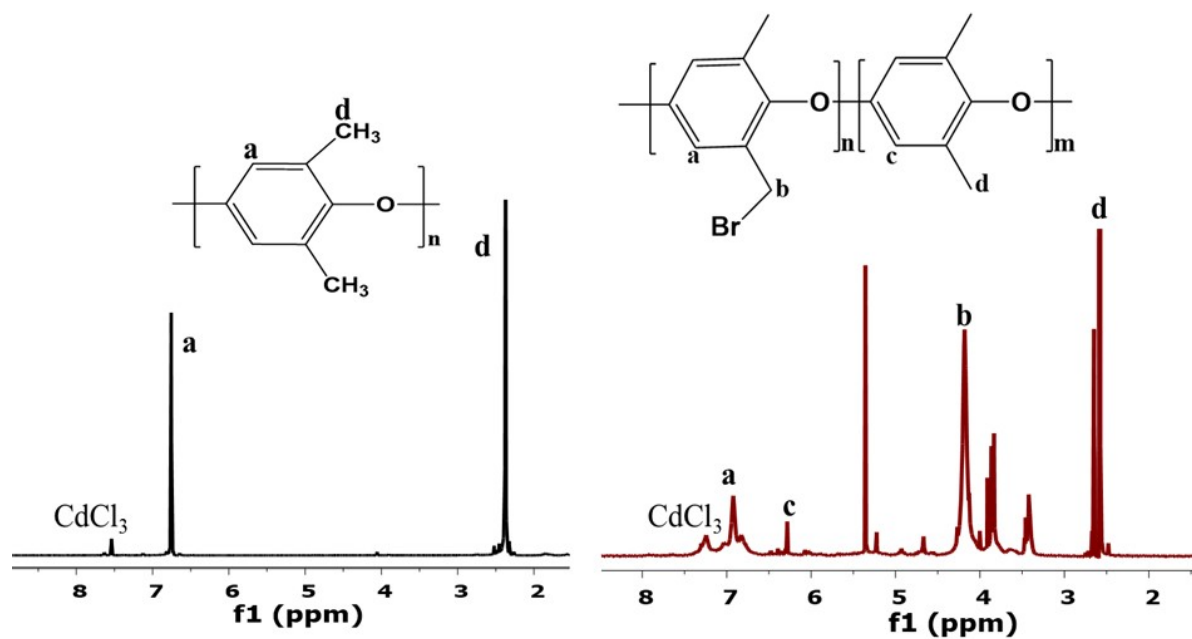


Fig. S1 FT-IR spectra of: (A) Cd-MOF; (B) PPO, and BrPPO; (C) **QPM**

A



B

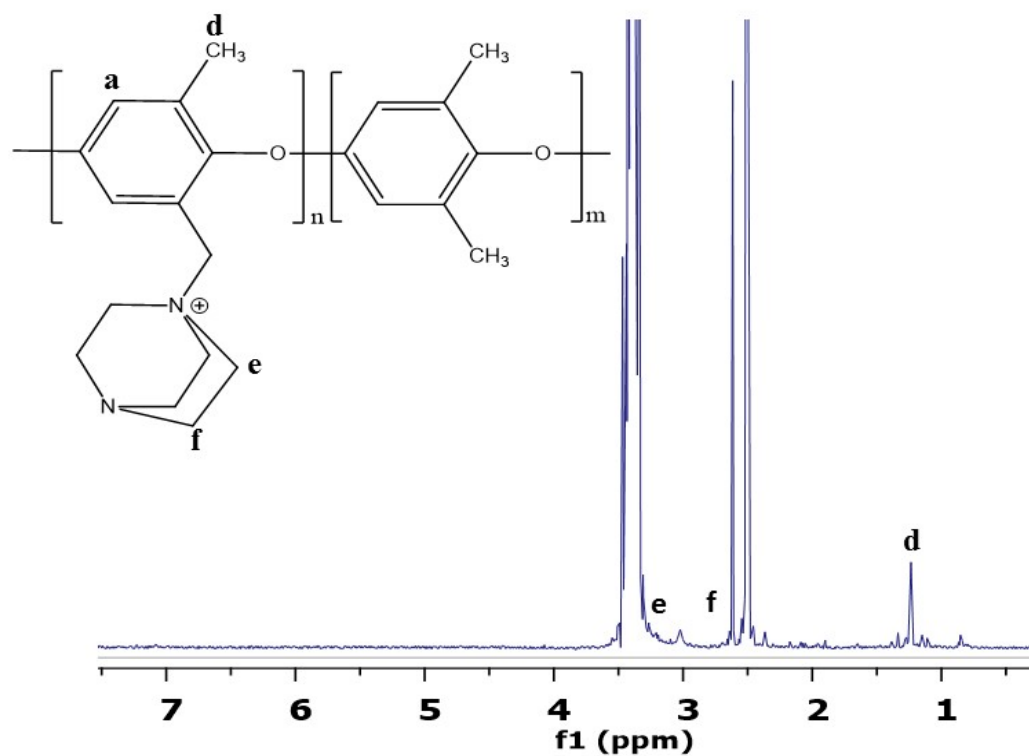


Fig. S2 ^1H -NMR of spectra of (A) PPO, and BrPPO, and (B) pristine QPM membrane.

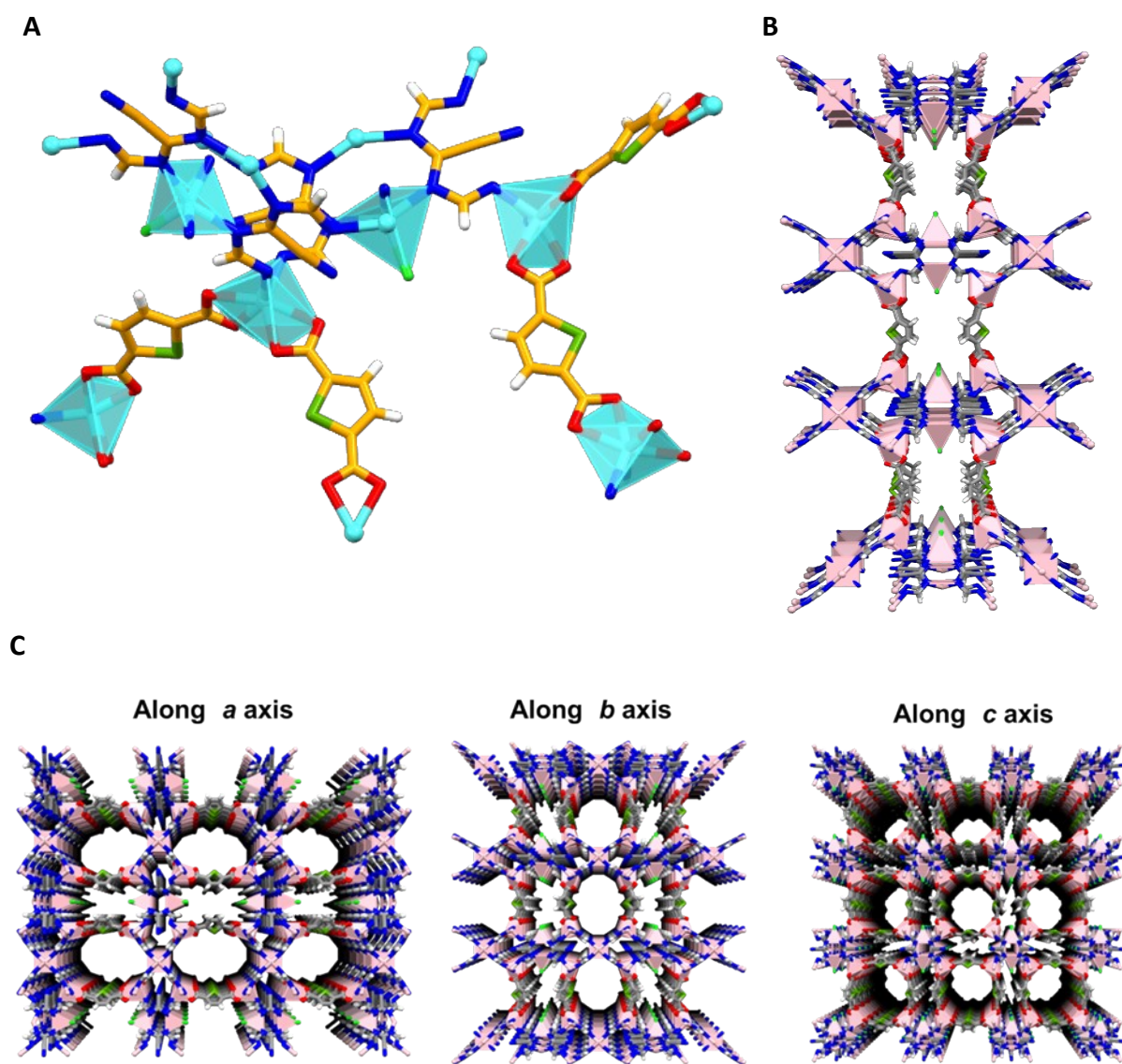
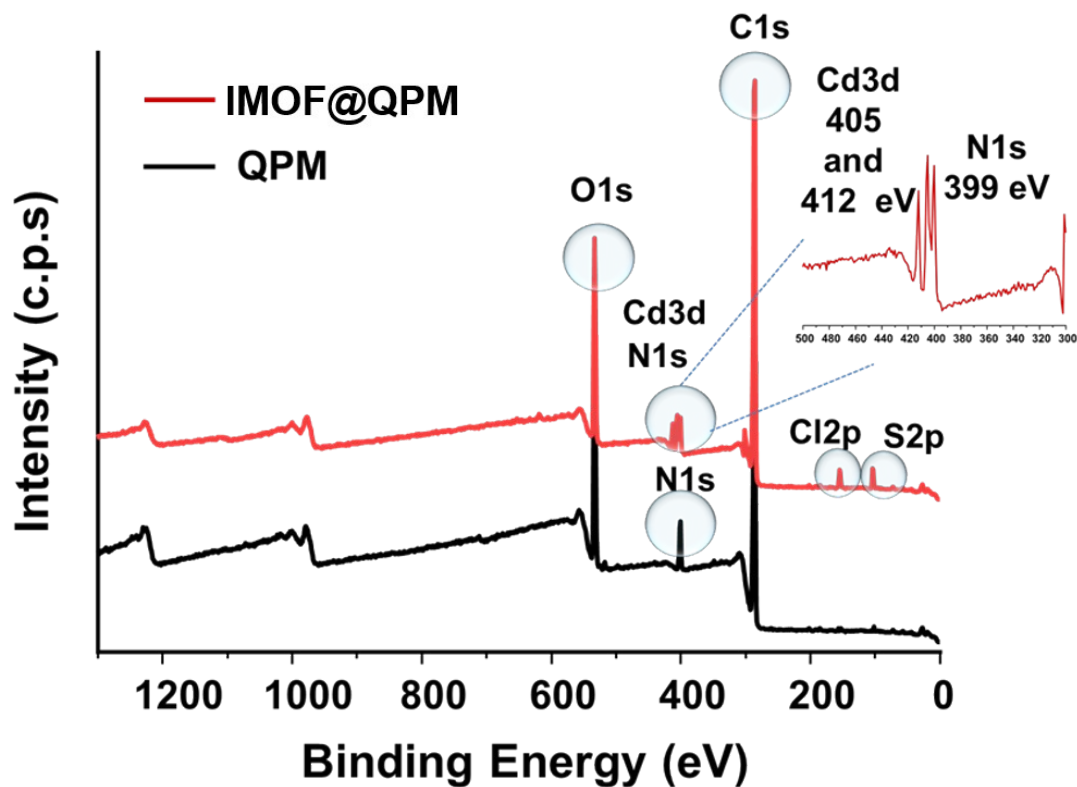


Fig. S3 (A) Coordination environment of Cd-MOF. (Color code: C: yellowish orange, H: white, N : blue, O : red, Cd : cyan, S : dark green, Br ; green) (B) Cd-Ad octahedral cages with infinite secondary building units along crystallographic *b* direction. (C) Pore views of the framework along three directions. (for B,C,D color code: C: dark grey, H: white, N : blue, O : red, Cd : pink, S : dark green, Br ; green)

A



B

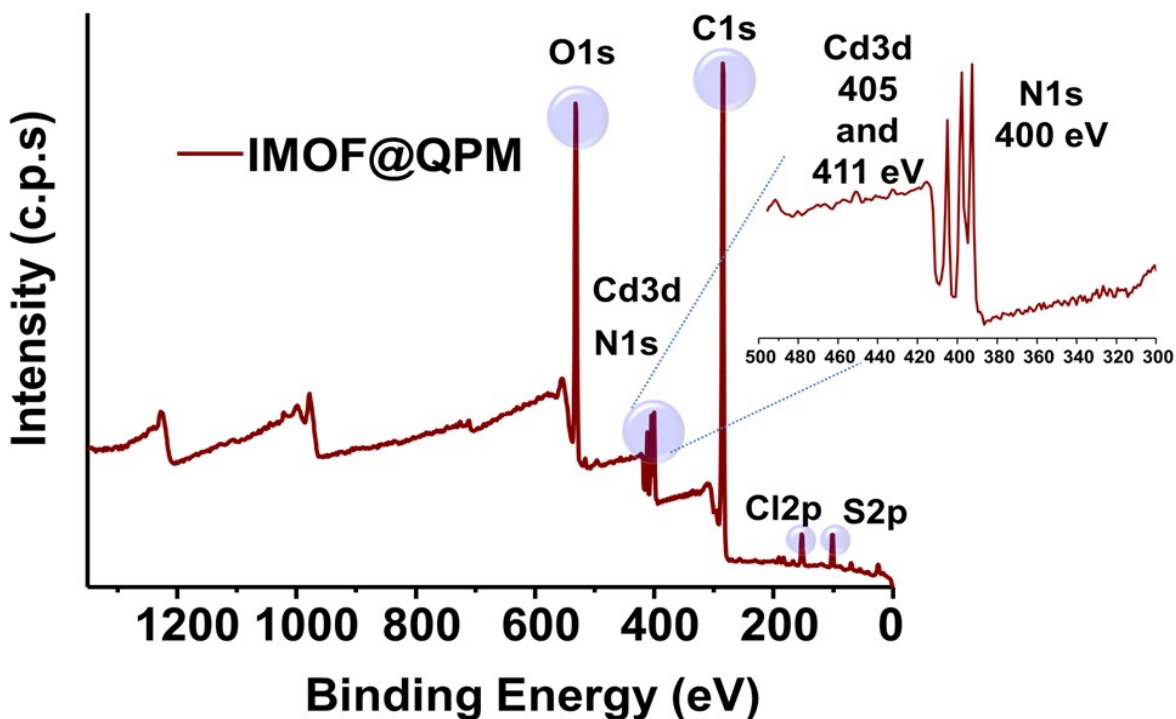


Fig. S4 Complete XPS survey spectra of C1s, N 1s, O 1s, Cd 3d, S 2p, Cl 2p for IMOF@QPM and QPM. (B) Complete XPS survey spectra of IMOF@QPM after 800 charge-discharge cycle performance.

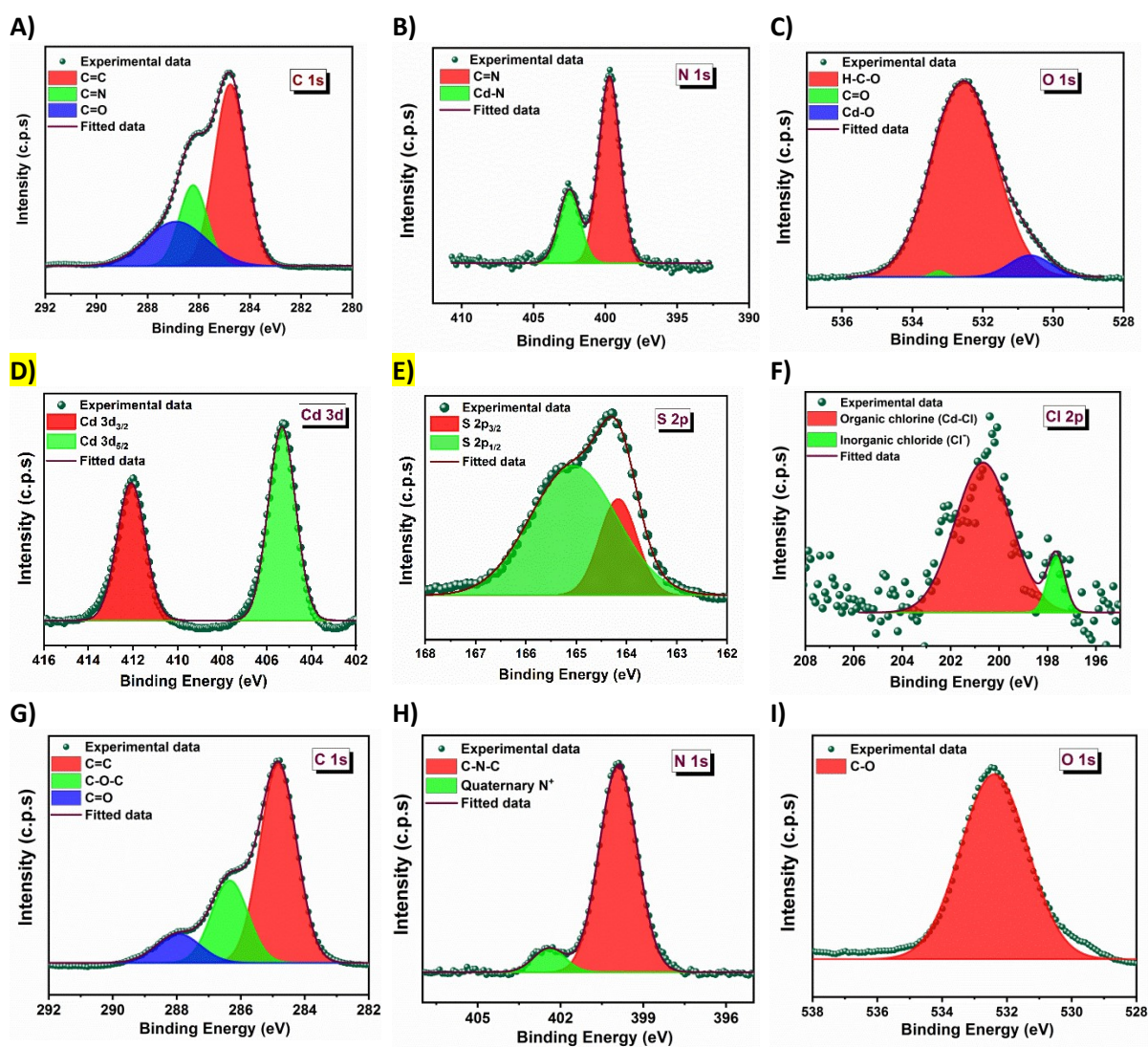


Fig. S5 (A-F) XPS spectra of C1s, N 1s, O 1s, **Cd 3d**, **S 2p**, Cl 2p for IMOF@QPM; (G-I) C1s, N 1s, O 1s for QPM.

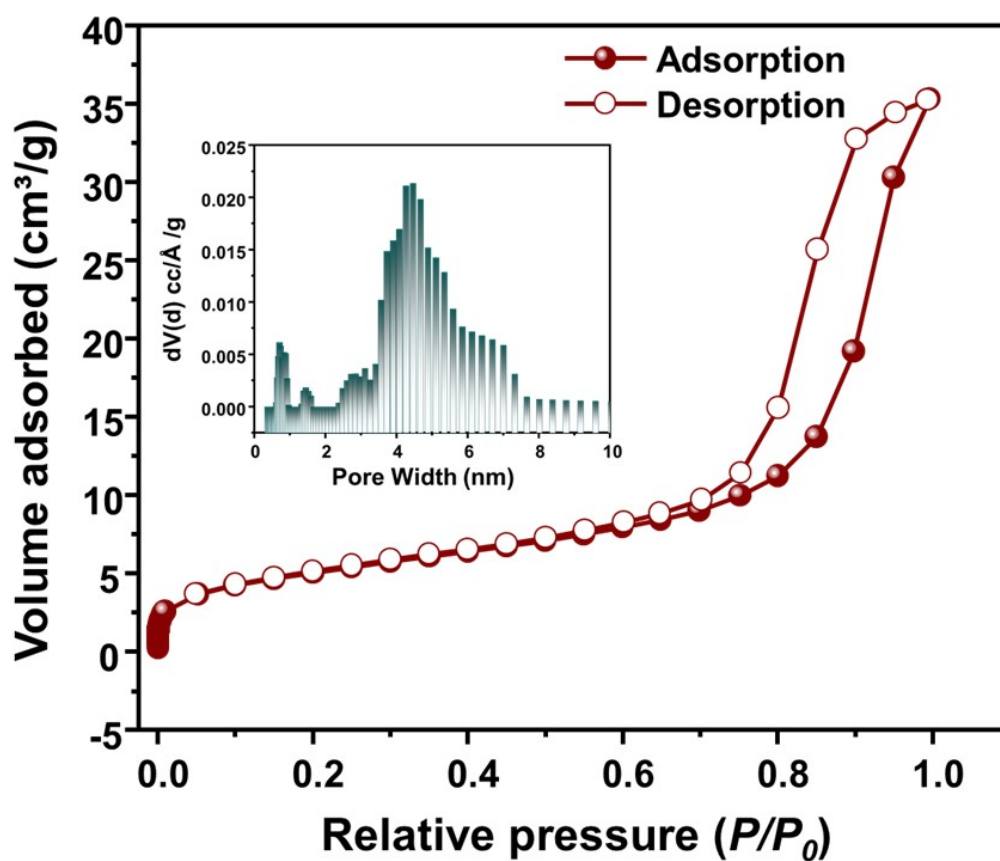


Fig. S6 N_2 adsorption-desorption isotherm and inset showing pore-size distributions of Cd-MOF.

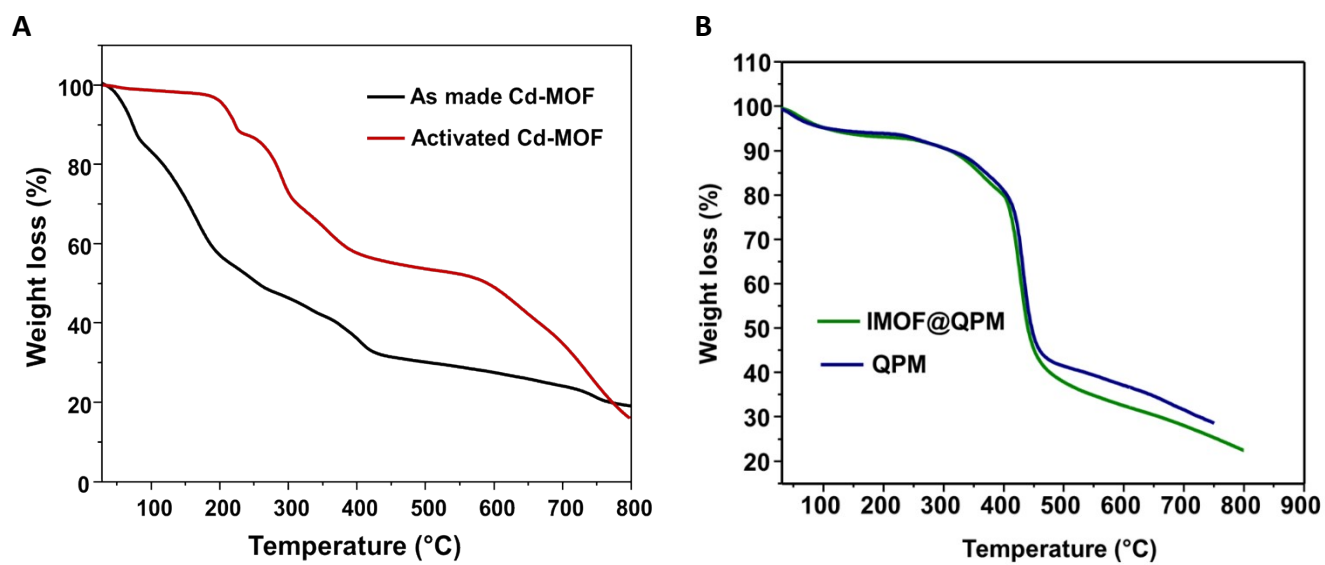
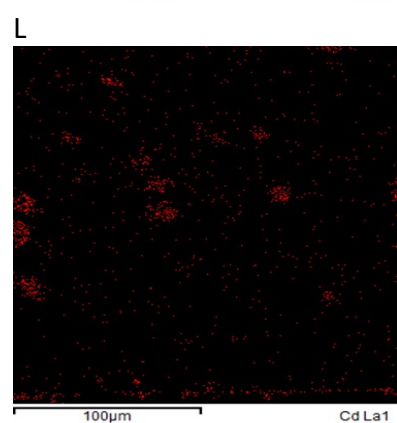
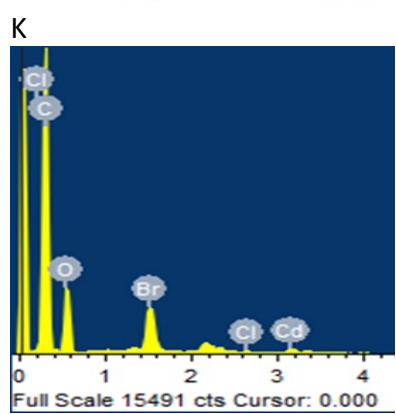
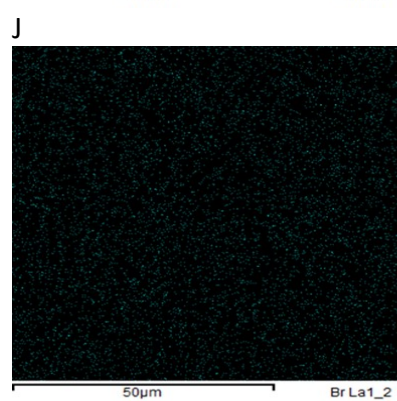
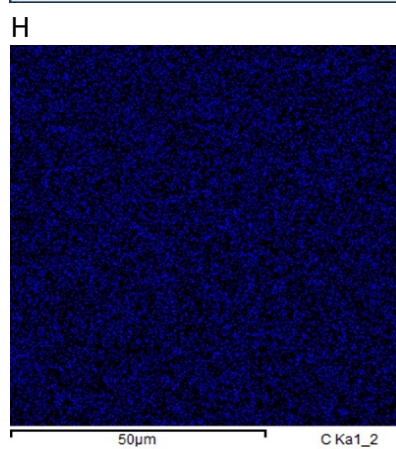
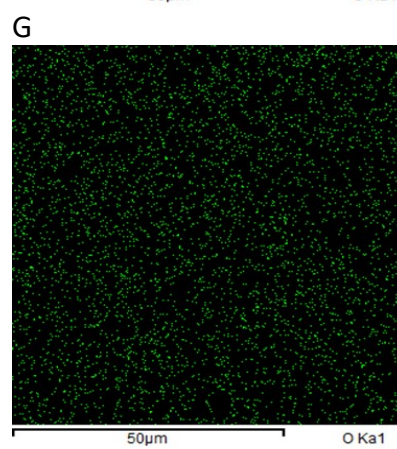
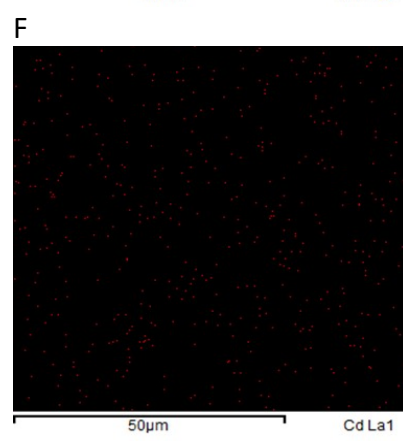
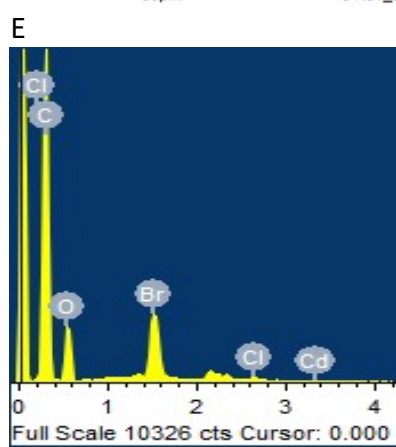
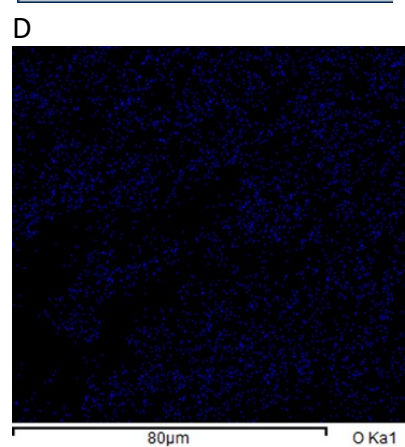
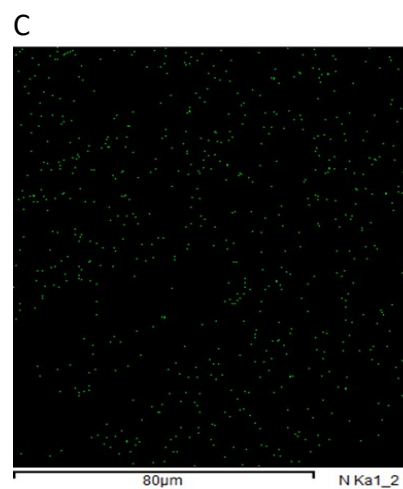
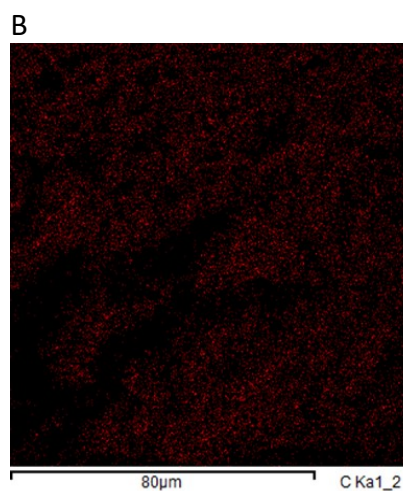
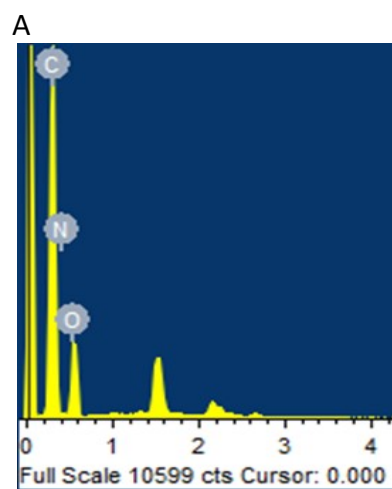


Fig. S7 TGA curves of: (A) As made and activated Cd-MOF (B) QPM and IMOF@QPM membranes.



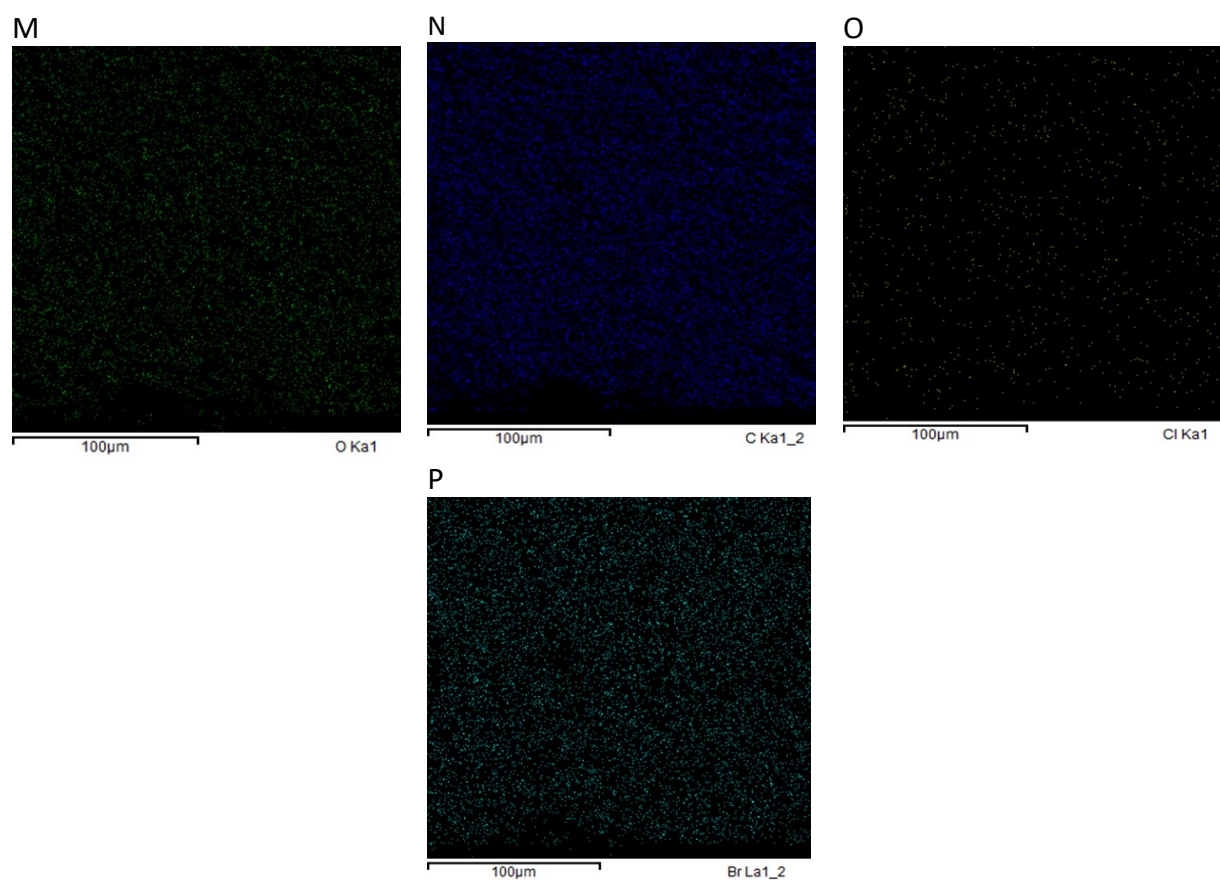


Fig. S8 (A-D) EDX spectra and elemental mapping of pristine QPM membrane; (E-J) EDX spectra and elemental mapping of surface for IMOF@QPM membrane; (K-P) EDX spectra and elemental mapping of cross-section for IMOF@QPM membrane.

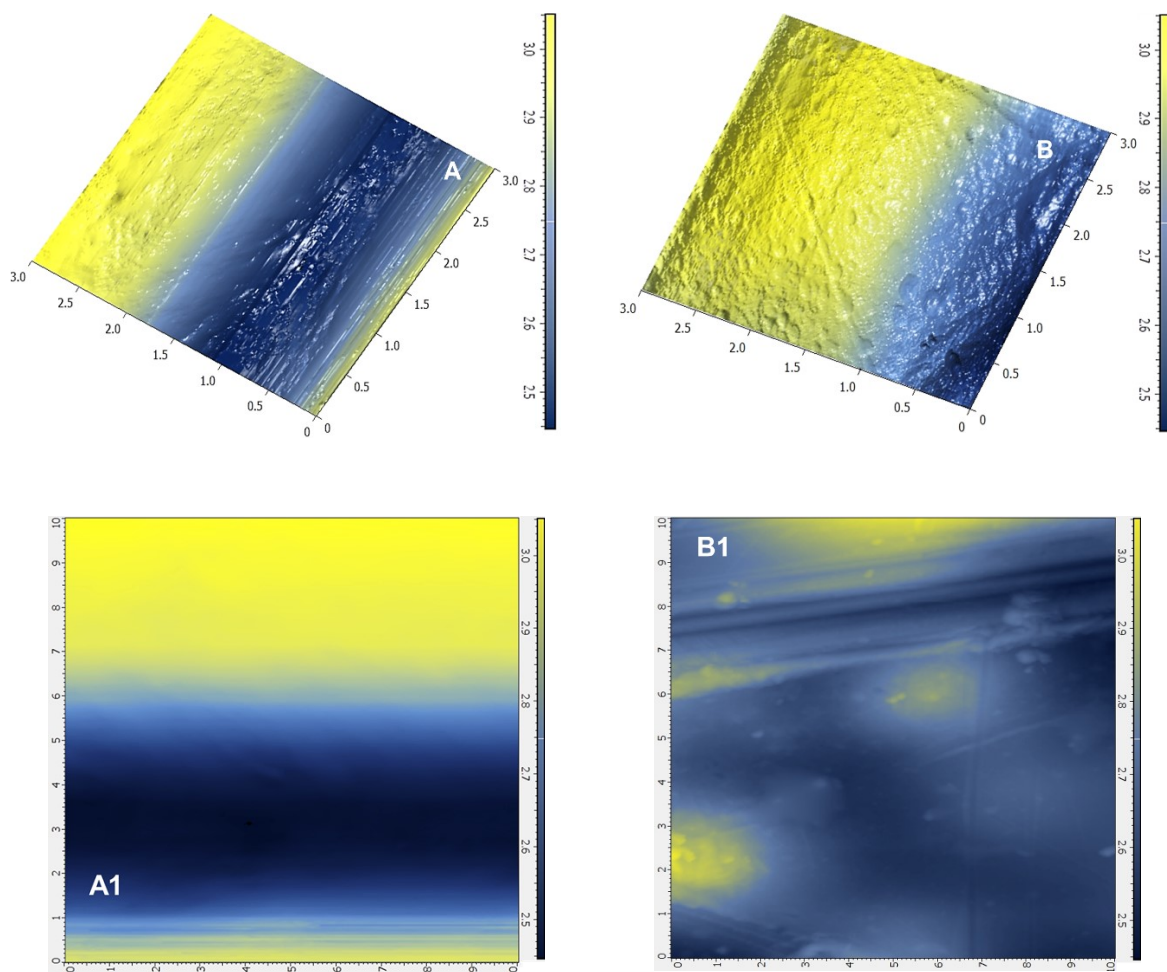


Fig. S9 AFM heights of: (A) QPM; (B) IMOF@QPM membranes, and phase images (A1) QPM (B1) IMOF@QPM membranes.

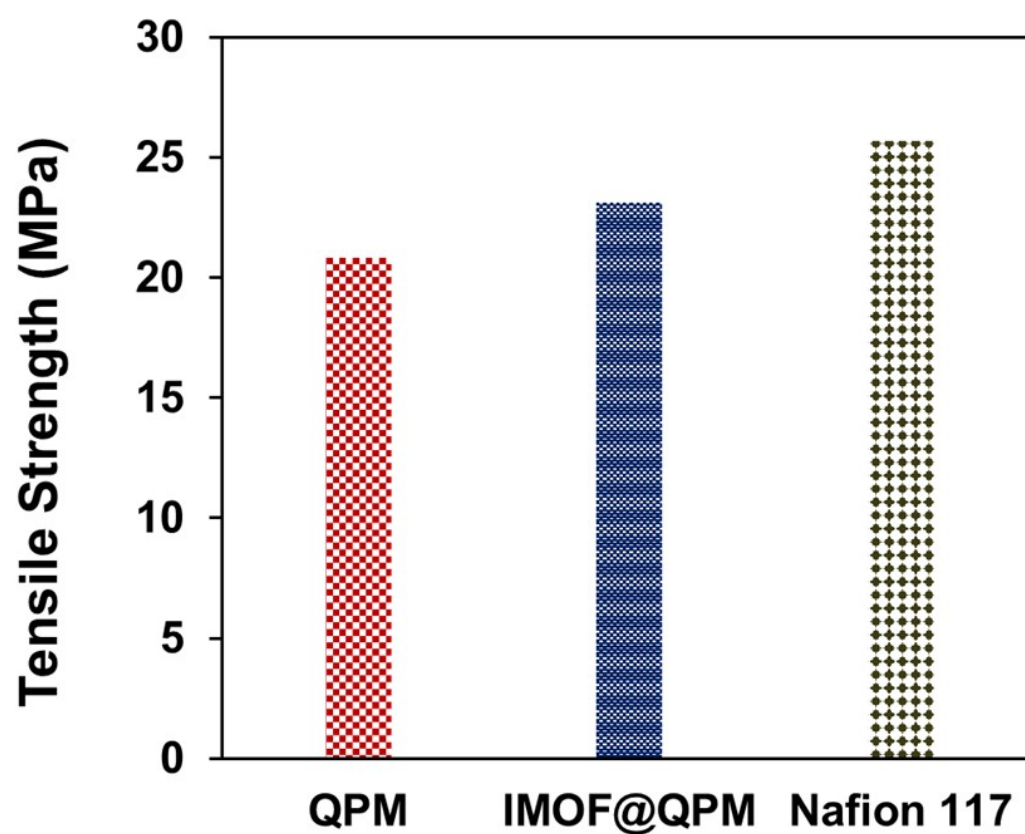


Fig. S10 Tensile strength of QPM, IMOF@QPM, and Nafion 117 membranes.

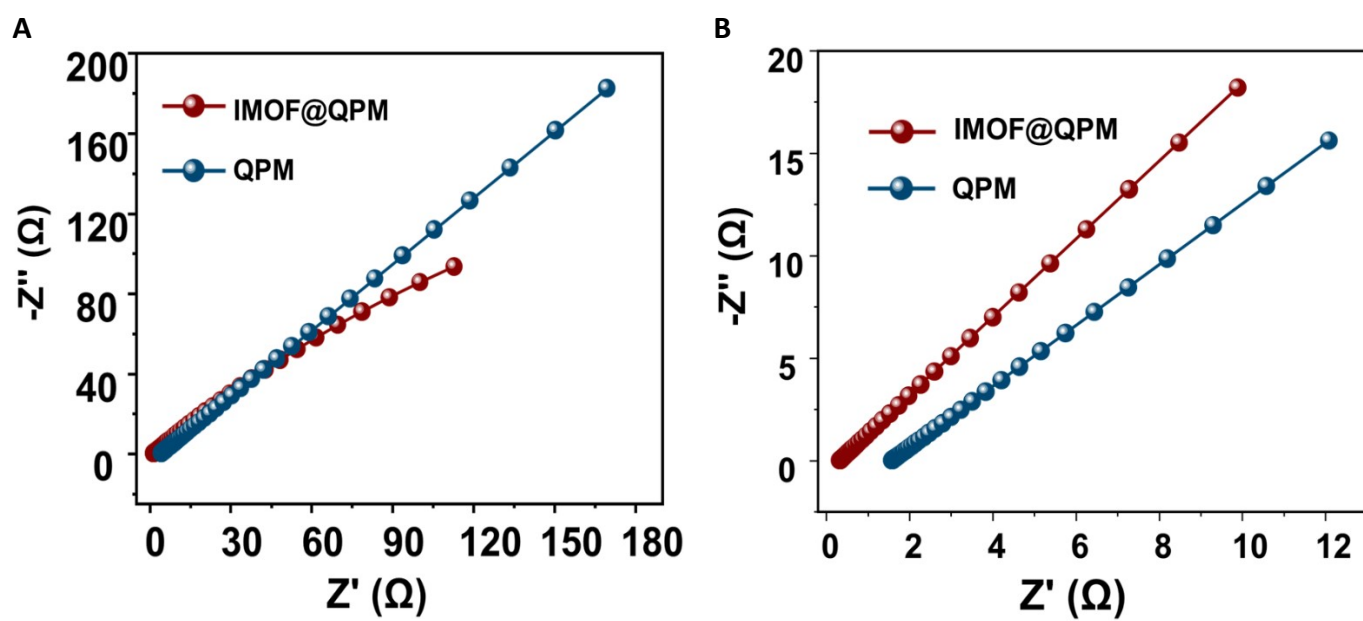


Fig. S11 Nyquist plot of (a) QPM and IMOF@QPM membranes at 30 °C; (b) QPM and IMOF@QPM membranes at 80 °C.

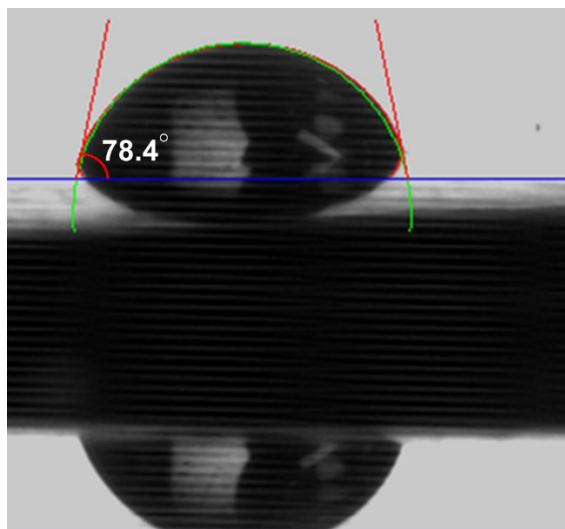
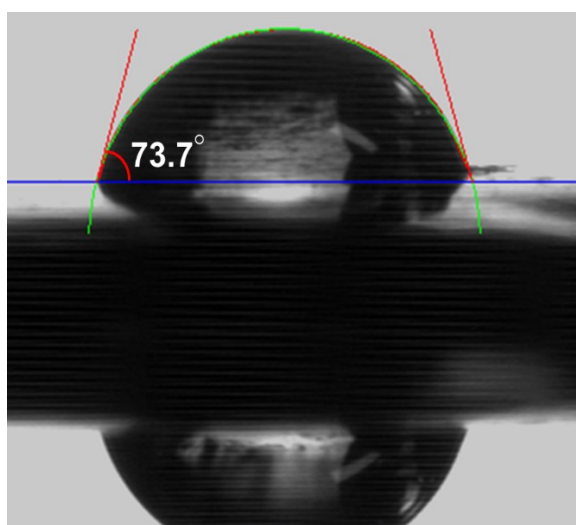
A**B**

Fig. S12 Contact angle of pristine and modified membrane (QPM and IMOF@QPM)

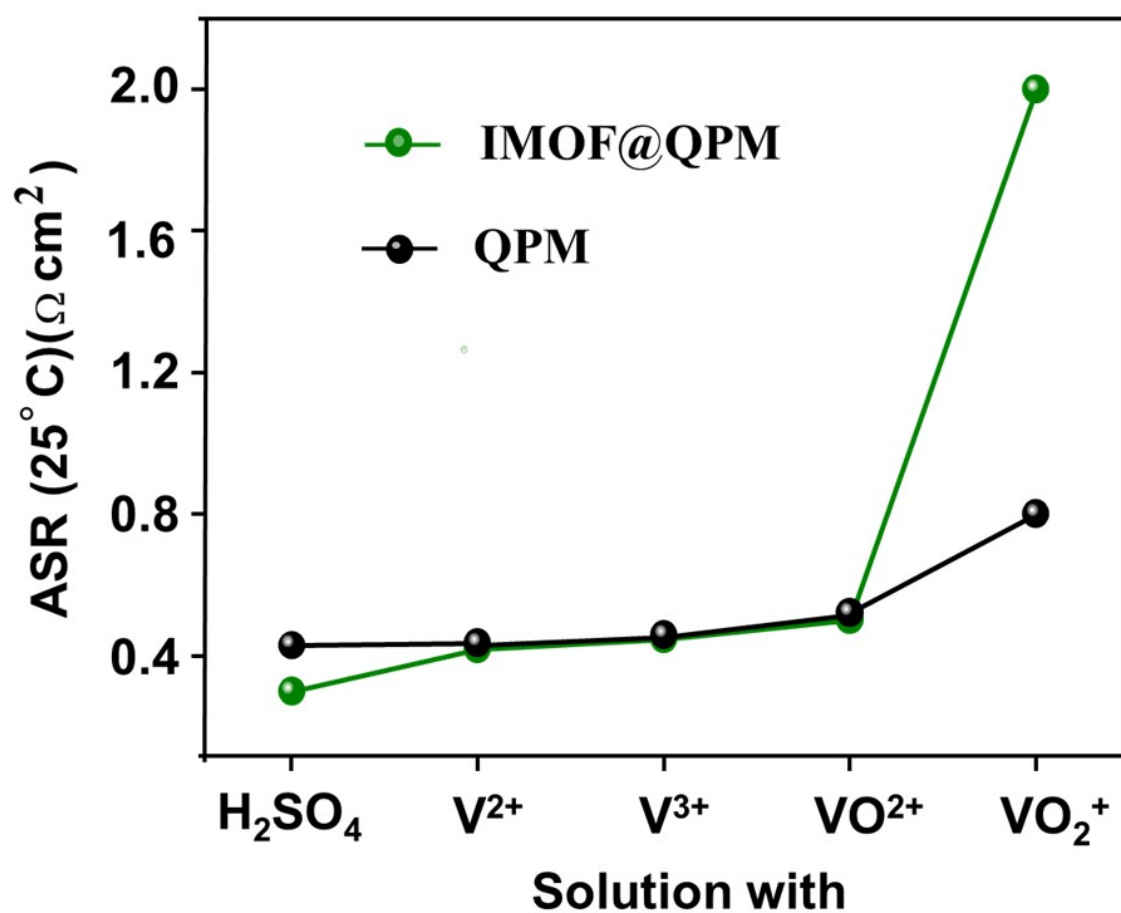


Fig. S13 ASR values for QPM and IMOF@QPM membranes in different electrolyte solutions.

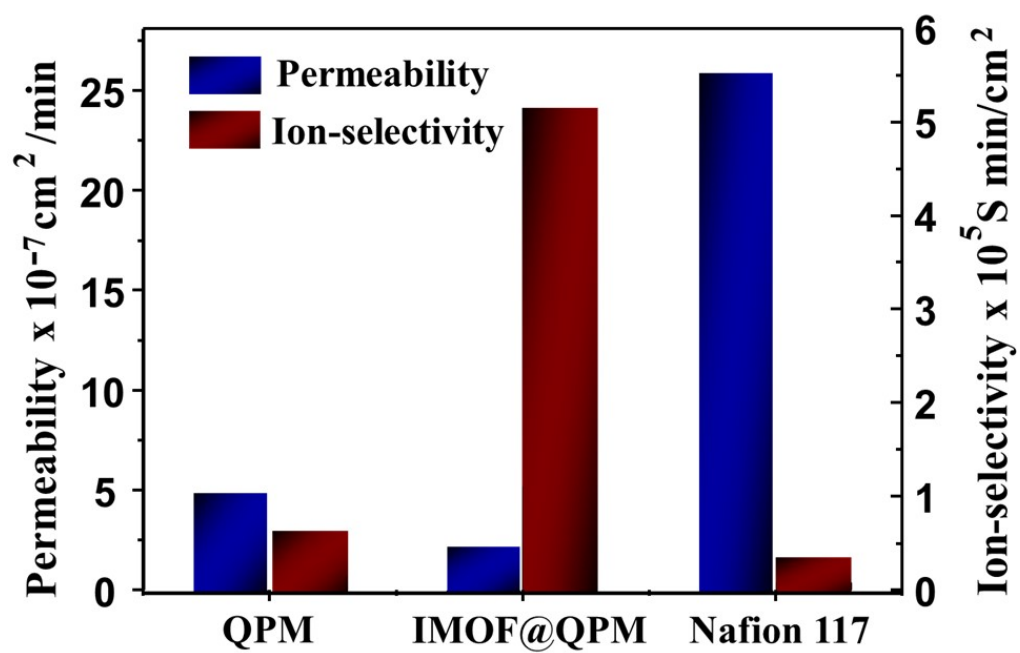


Fig. S14 VO_2^+ permeability and ion-selectivity of studied membranes.

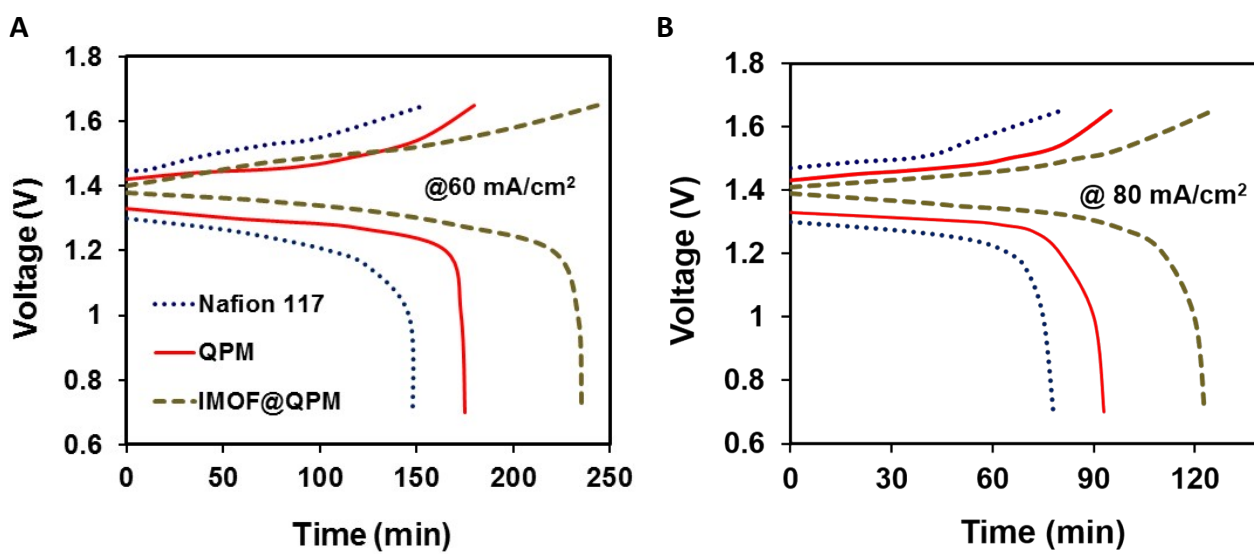


Fig. S15 Charge-discharge curves for Nafion117, QPM, and IMOF@QPM membranes at 60 and 80 mA/cm² current densities.

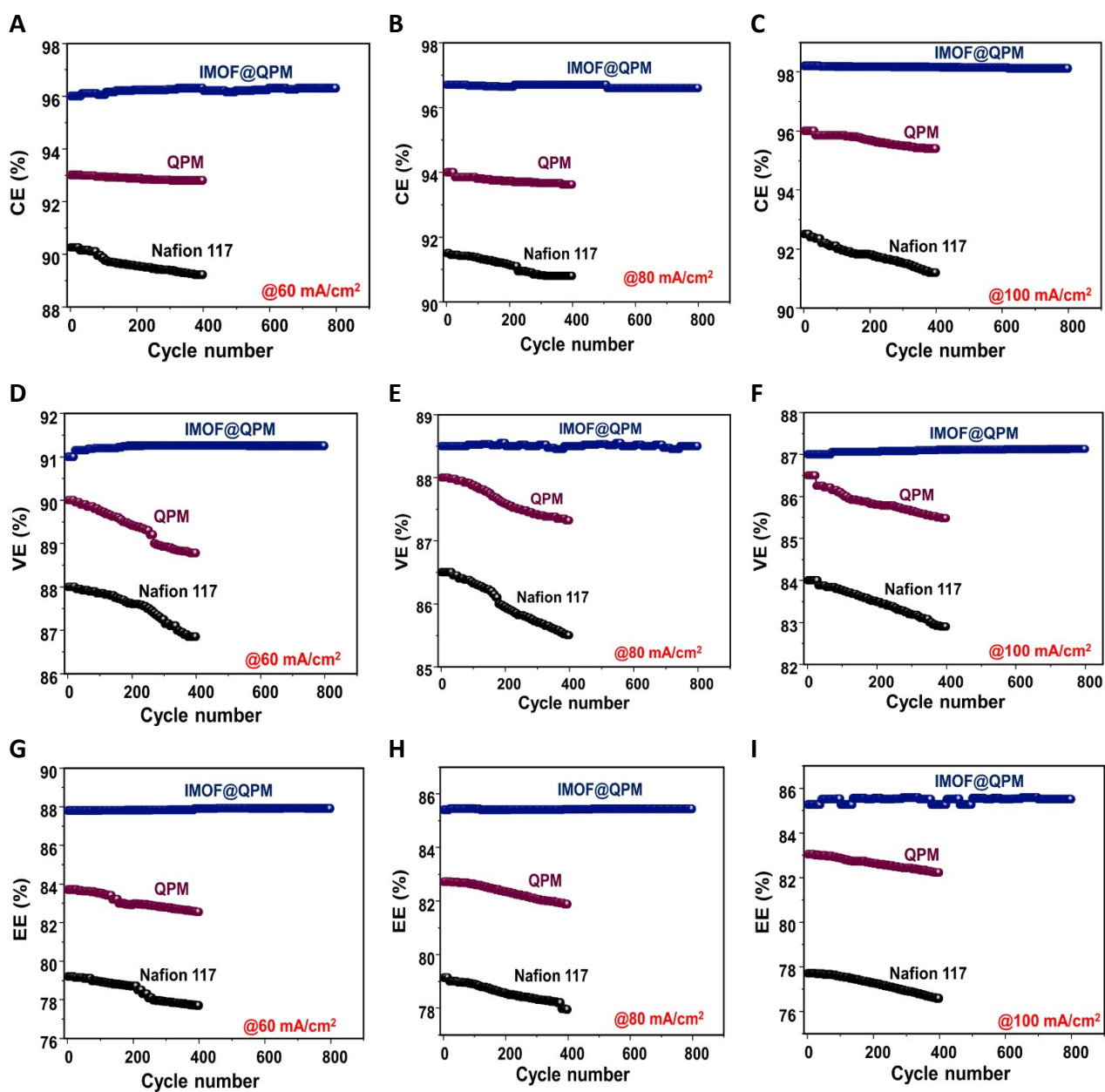


Fig. S16 Comparison of CE, VE, and EE for IMOF@QPM, QPM and Nafion 117 membranes at different current densities (60-100 mA/cm²).

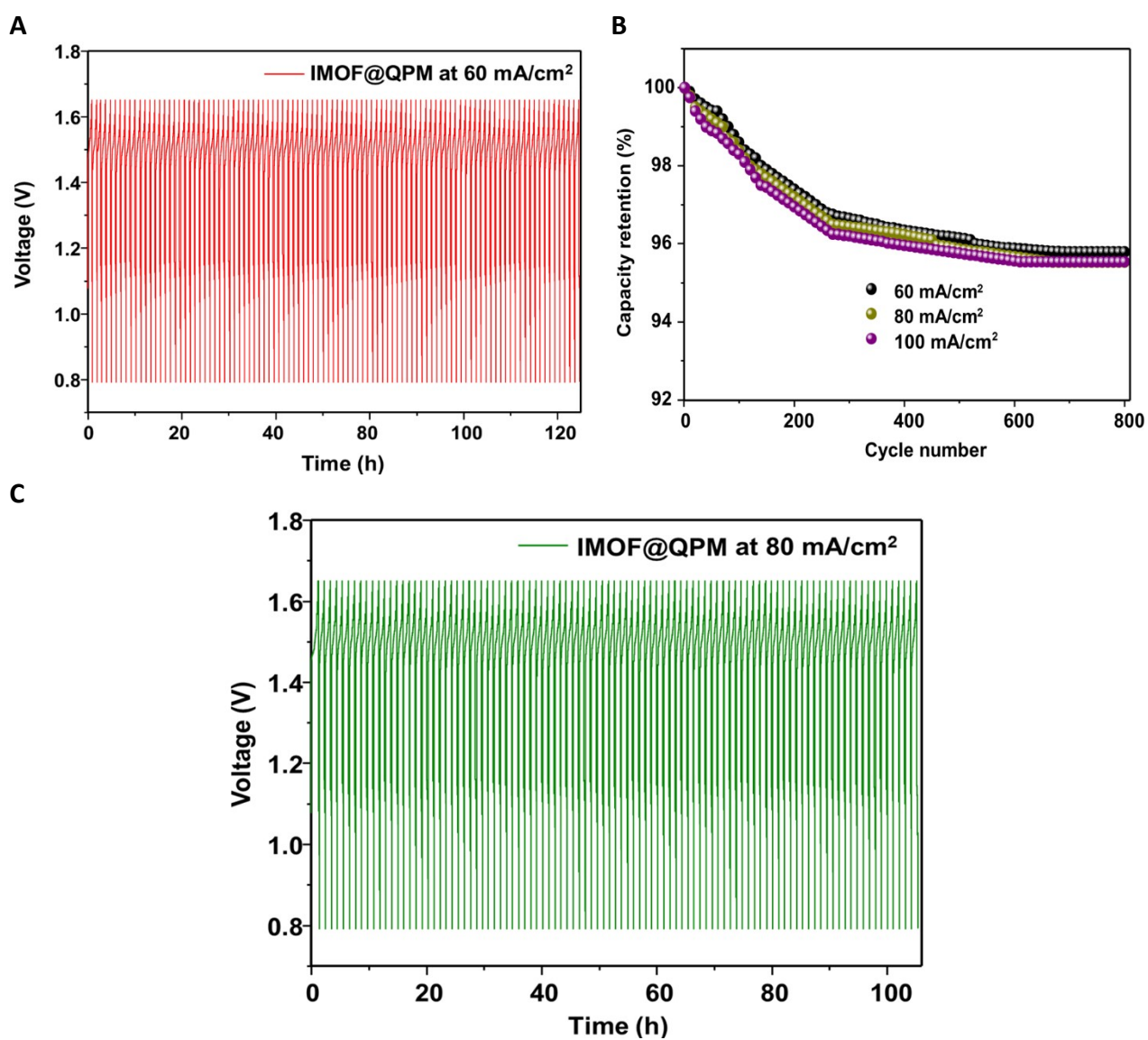


Fig. S17 (A&C) VRFB charge-discharge 100 cycles at 60 and 80 mA/cm² current density and (B) capacity retention (%) performance comparison at 60, 80, 100 mA/cm² of IMOF@QPM.

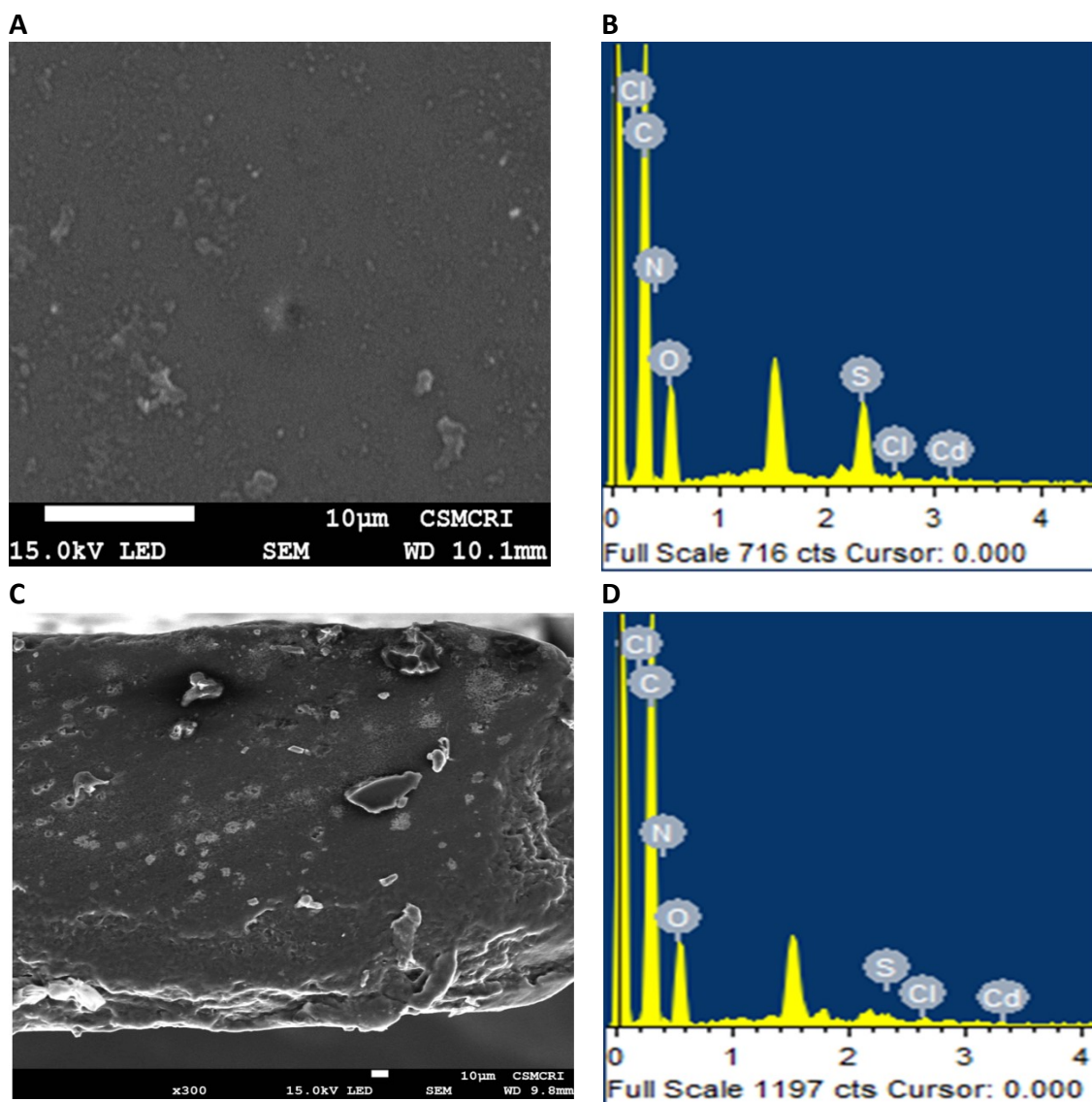


Fig. S18 SEM of (A&C) IMOF@QPM (Surface and cross-section) and EDX spectra of (B&D) IMOF@QPM (Surface and cross-section) after 800 VRFB charge-discharge cycles

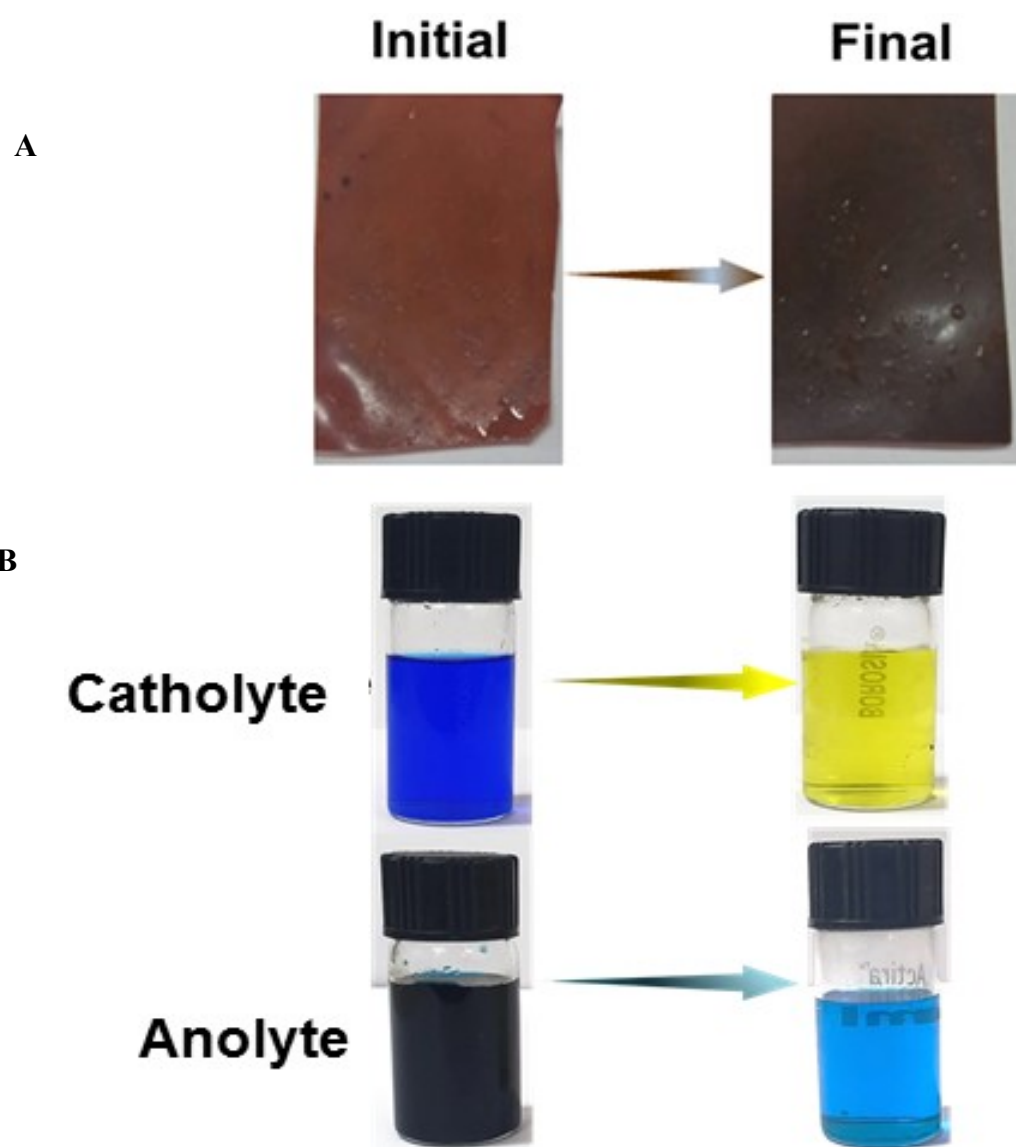


Fig. S19 Photographs showing the effect on membrane (IMOF@QPM) and electrolyte solution before and after VRFB performance.

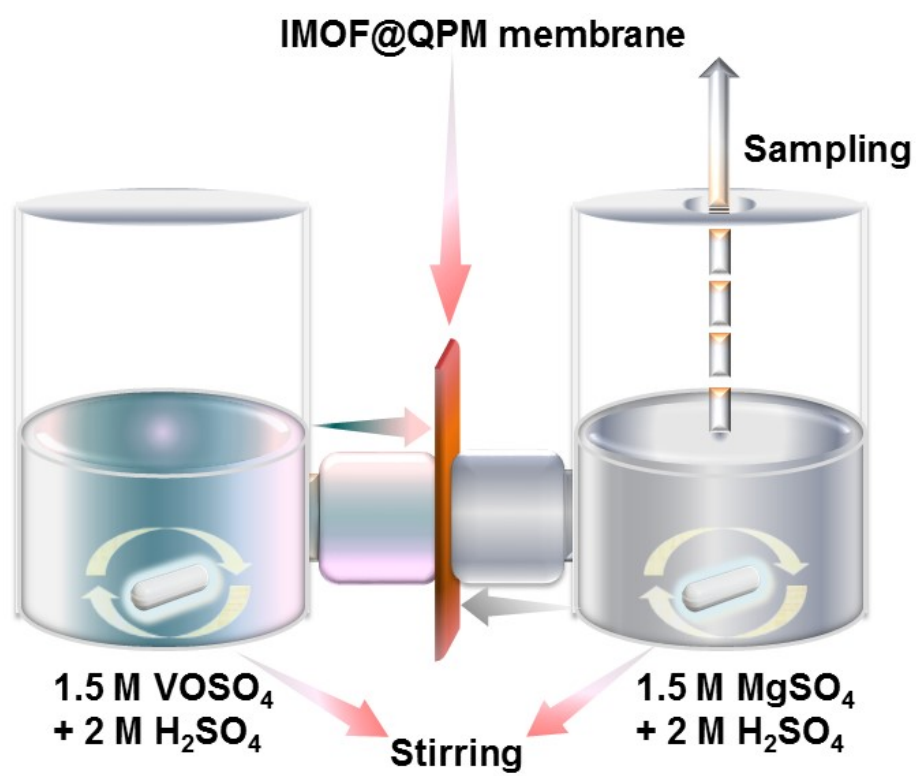


Fig. S20 The typical two-compartment diffusion cell for measuring VO^{2+} permeability.

Table S1. Oxidative and chemical stability of different membranes in terms of percentage weight (Wt) and conductivity (κ^m) loss values after treatment.

Membrane	Oxidative stability		Chemical stability			
			VO ²⁺		VO ₂ ⁺	
	Wt loss (%)	κ^m loss (%)	Wt loss (%)	κ^m loss (%)	Wt loss (%)	κ^m loss (%)
QPM	2.35	1.83	1.52	1.46	1.47	1.42
IMOF@QPM	1.39	1.25	1.03	1.13	0.99	1.09
Nafion 117	2.27	1.39	0.75	0.98	0.73	0.95

Membrane	Thickness (μm)	Current densities (mA/cm^2)	Active area (cm^2)	CE (%)	EE (%)	Cycles	Ref.
Nafion/(UiO-66-NH ₂ @PWA)	144	40	14	85.24	81.7	100	7
Nafion/TiO ₂ nanotubes	39	50	13.5	~97.1	~91.5	-	8
S/UiO-66-OH	57	50	-	98.9	91.4	100	9
SPEEK/MOF-801	50	120	-	99.2	80.2	700	10
SPEEK/MOF-808	50	120	-	98.2	84	800	10
Nafion/S-U66-3	52	80	1.77	93.9	85	1000	11
Nafion/SiO ₂	204	60	36	< 94	< 74	100	12
Nafion-D-AMH-3	180	40	12	97.4	83.4	100	13
Nafion-NdZr	22.3	40	-	~96	~76	200	14
Colloidal silicalite-Nafion	120	60	2	-	77	-	15
Im-bPPO	-	40	-	~98	~76	-	16
Nafion-ZrNT	150	40	9	97.5	78.5	100	17
PBI/Nafion	25	100	49	99	78.1	-	18
CLGO/Nafion	~50	80	9	97	86	180	19
Nafion/SPEEK	100	50	5	97.6	83.3	300	20
Nafion-(NKF _s @PWA)	120	40	14	86.77	80.24	100	21
IMOF@QPM	150	100	4	98	~ 87	800	This work

Table S2. Performance comparison of the modified QPM membranes for VRFB application.

Table S3. Table 1 Crystal data and structure refinement for Cd-MOF.

Identification code	Cd-MOF
Empirical formula	C ₁₀ H ₄ Cd _{1.5} Cl _{0.5} N ₅ O ₄ S
Formula weight	476.58
Temperature/K	123.15
Crystal system	Tetragonal
Space group	P4 ₂ /mmc
a/Å	17.3681(17)
b/Å	17.3681(17)
c/Å	18.6120(19)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	5614.3(10)
Z	8
ρ _{calc} /g/cm ³	1.1276
μ/mm ⁻¹	1.281
F(000)	1812.6
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.18 to 56.9
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	57816
Independent reflections	3824 [R _{int} = 0.0823, R _{sigma} = 0.0561]
Data/restraints/parameters	3824/0/111
Goodness-of-fit on F ²	0.891
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0935, wR ₂ = 0.2690
Final R indexes [all data]	R ₁ = 0.2396, wR ₂ = 0.3506

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