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Supporting Information

Highly proton conductive, dense polybenzimidazole membranes with low permeability to vanadium and enhanced H_2SO_4 absorption capability for use in vanadium redox flow batteries

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Fig. S1 UV-Vis absorbance *verse* mol% VO^{2+} in mixed VO^{2+} and VO_2^+ solution at 760 nm (total vanadium concentration = 0.1 M).

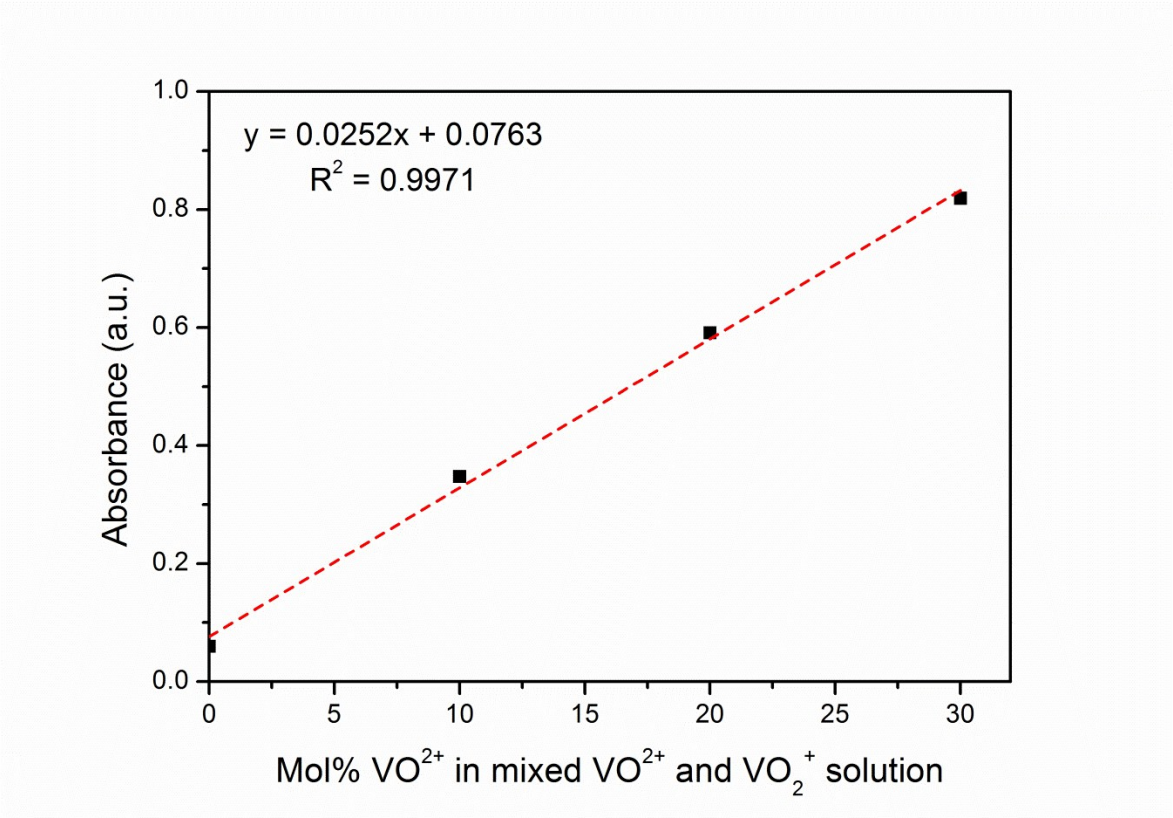


Fig. S2 Chemical structure of sulfonated poly(arylene ether sulfone) (BPSH-50).

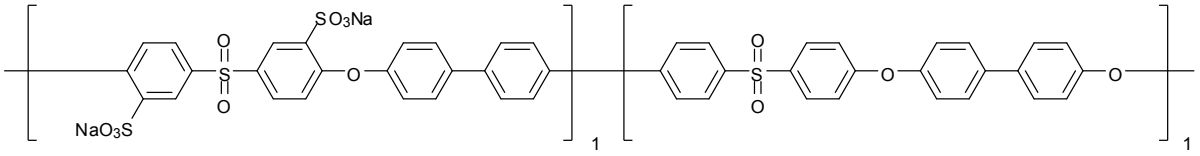
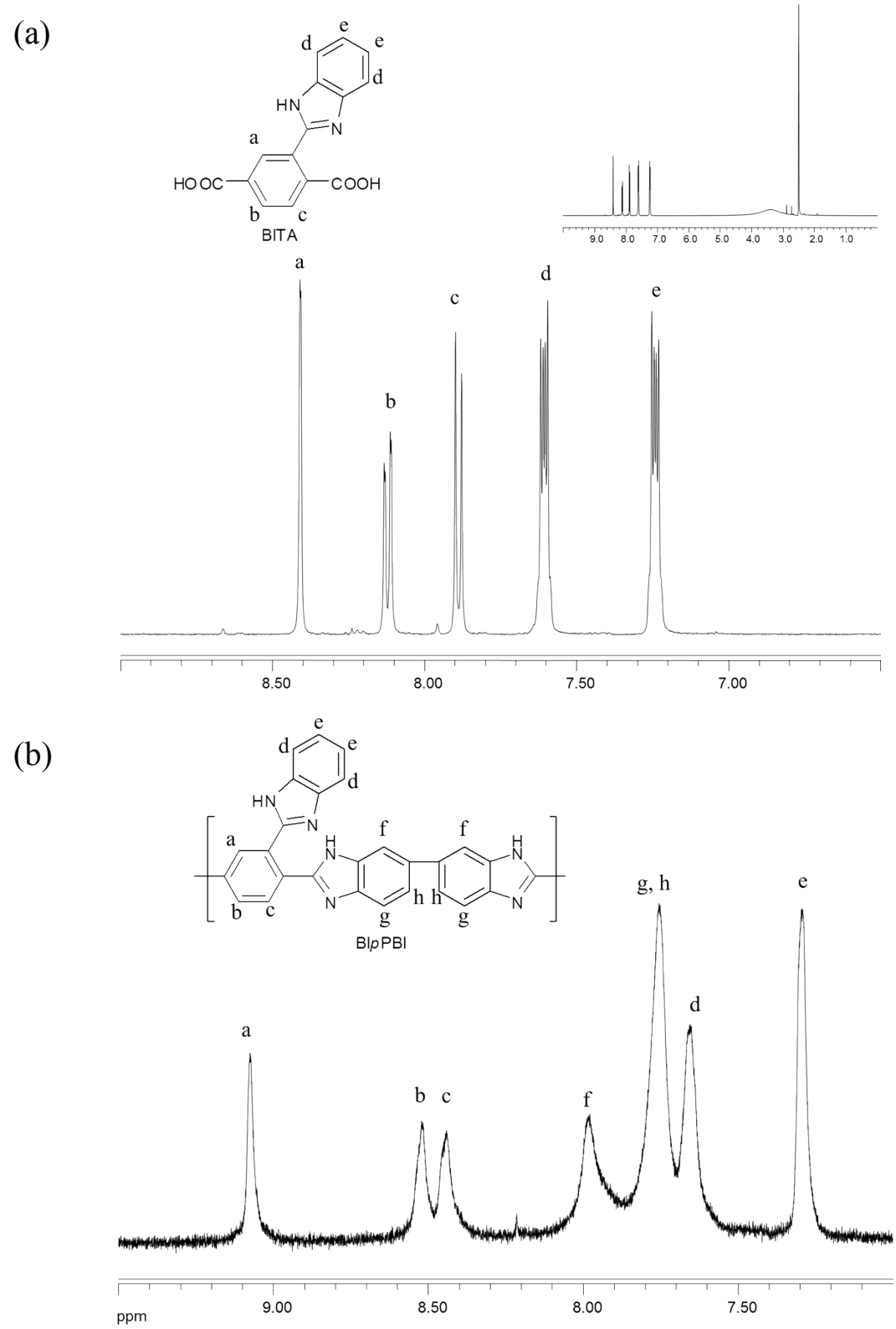


Fig. S3 (a) ^{1}H NMR spectrum of BITA, (b) ^{1}H NMR spectrum of BI*p*PBI, and (c) ATR-IR spectra of mPBI and BI*p*PBI



(c)

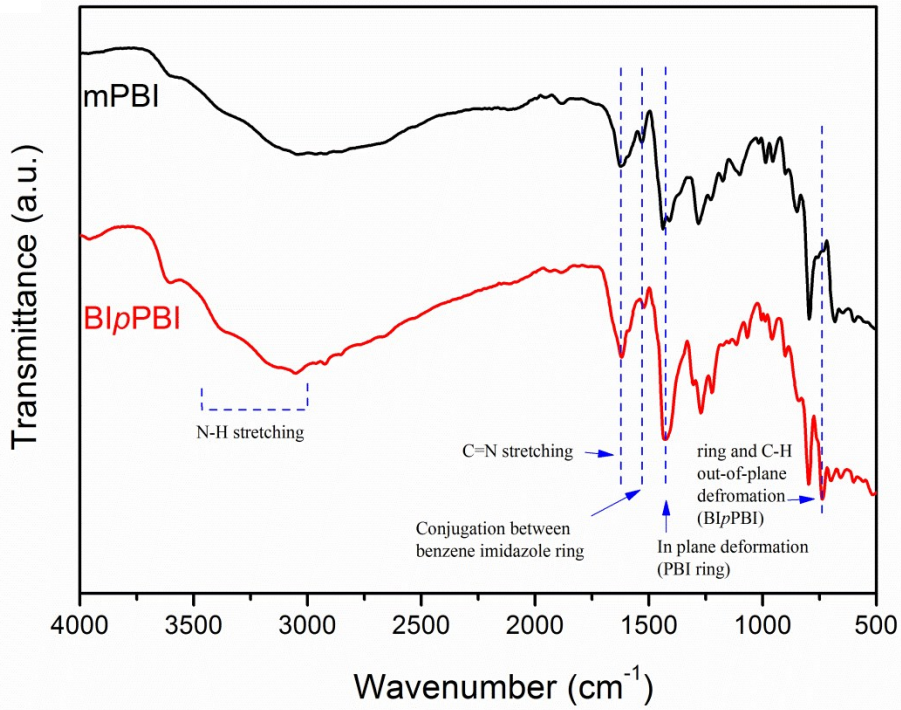
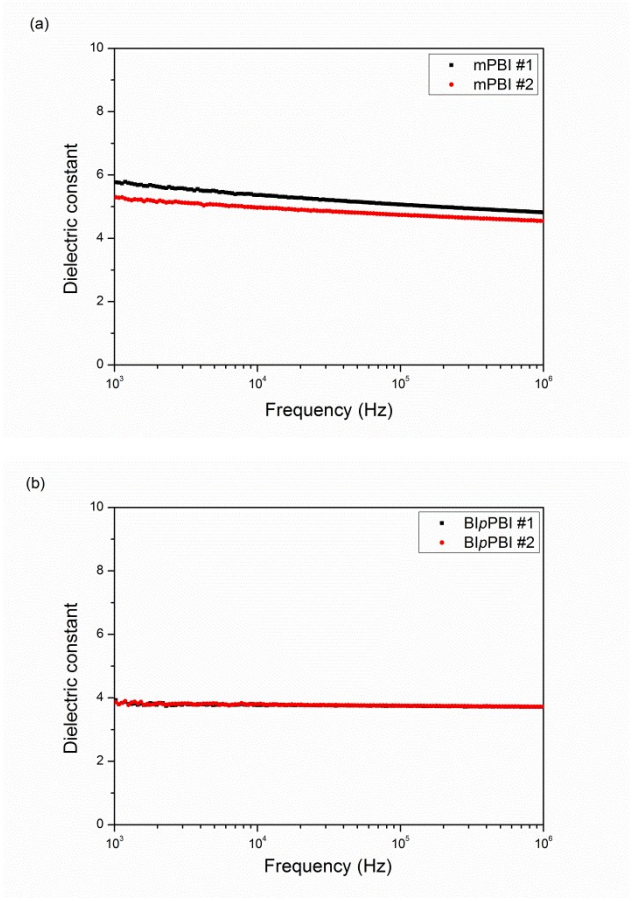

mPBI
BIpPBI
Transmittance (a.u.)
N-H stretching
C=N stretching
Conjugation between
benzene imidazole ring
In plane deformation
(PBI ring)
ring and C-H
out-of-plane
defromation
(BIpPBI)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig. S4 The dielectric constant of PBI membranes (a) mPBI (b) BI*p*PBI



Summary of the dielectric constant

	Sample	40 Hz	1 kHz	1 MHz
mPBI	1	6.04	5.70	4.82
	2	5.98	5.30	4.55
BI*p*PBI	1	3.70	3.93	3.71
	2	3.95	3.87	3.72

Fig. S5 Charge-discharge curves of VRFBs at various current densities with prepared membrane (a) Nafion 115 (b) mPBI (c) BI*p*PBI

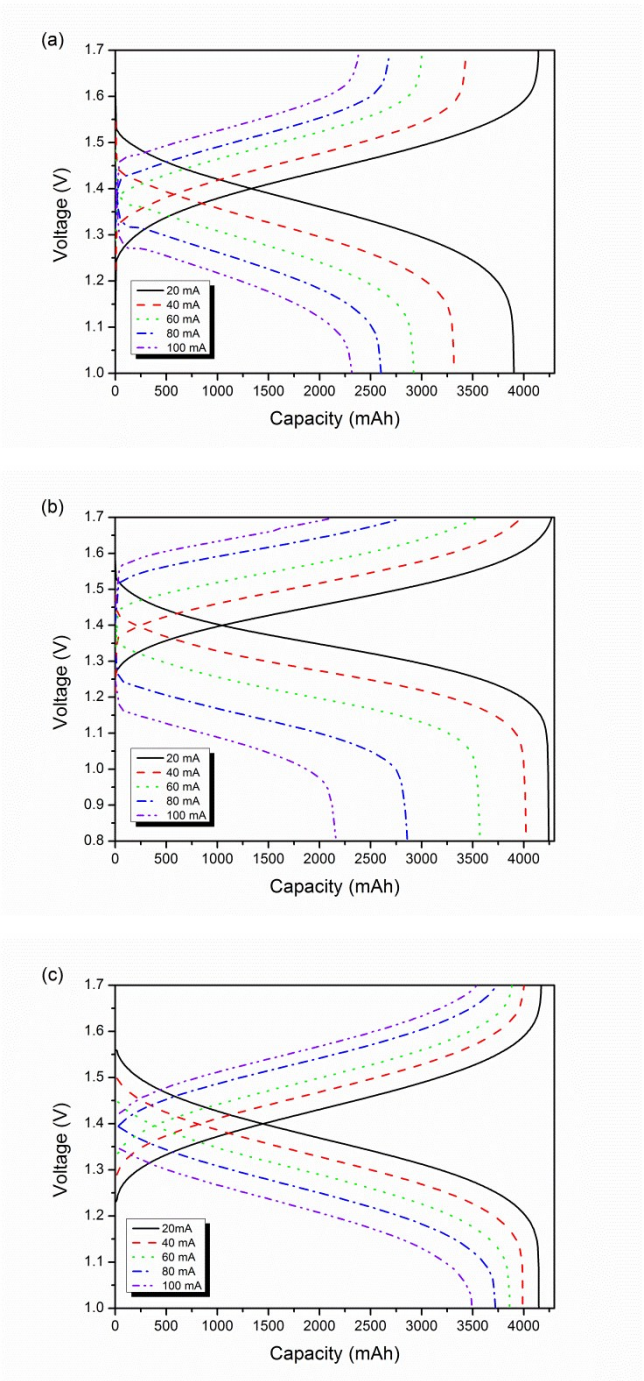


Fig. S6 Cycling test result of VRFB single cells with BIpPBI membrane at 120mA cm^{-2} for 500 cycle.

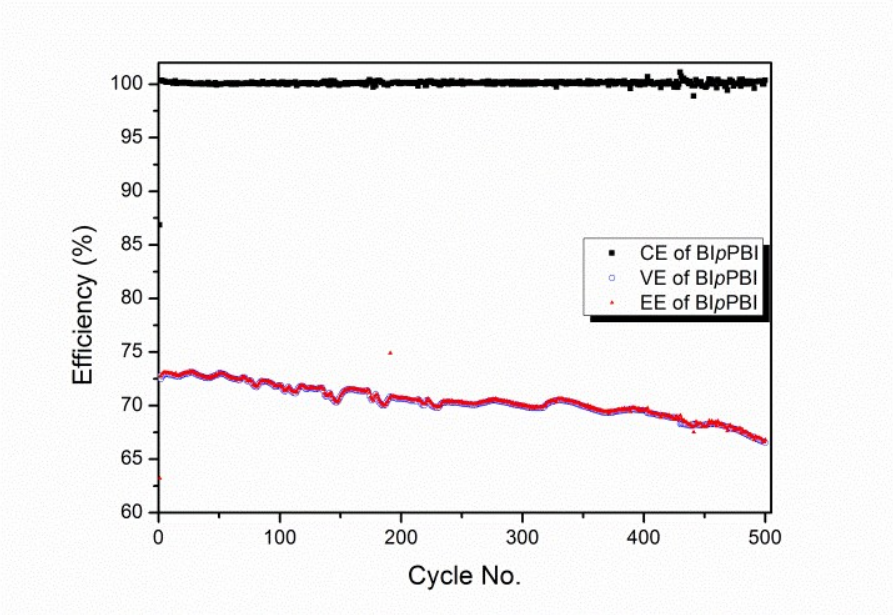


Fig. S7 Electrolyte volume change after the 200 cycling tests for VRFB cells assembled with (a) mPBI and (b) BI*p*PBI membranes.

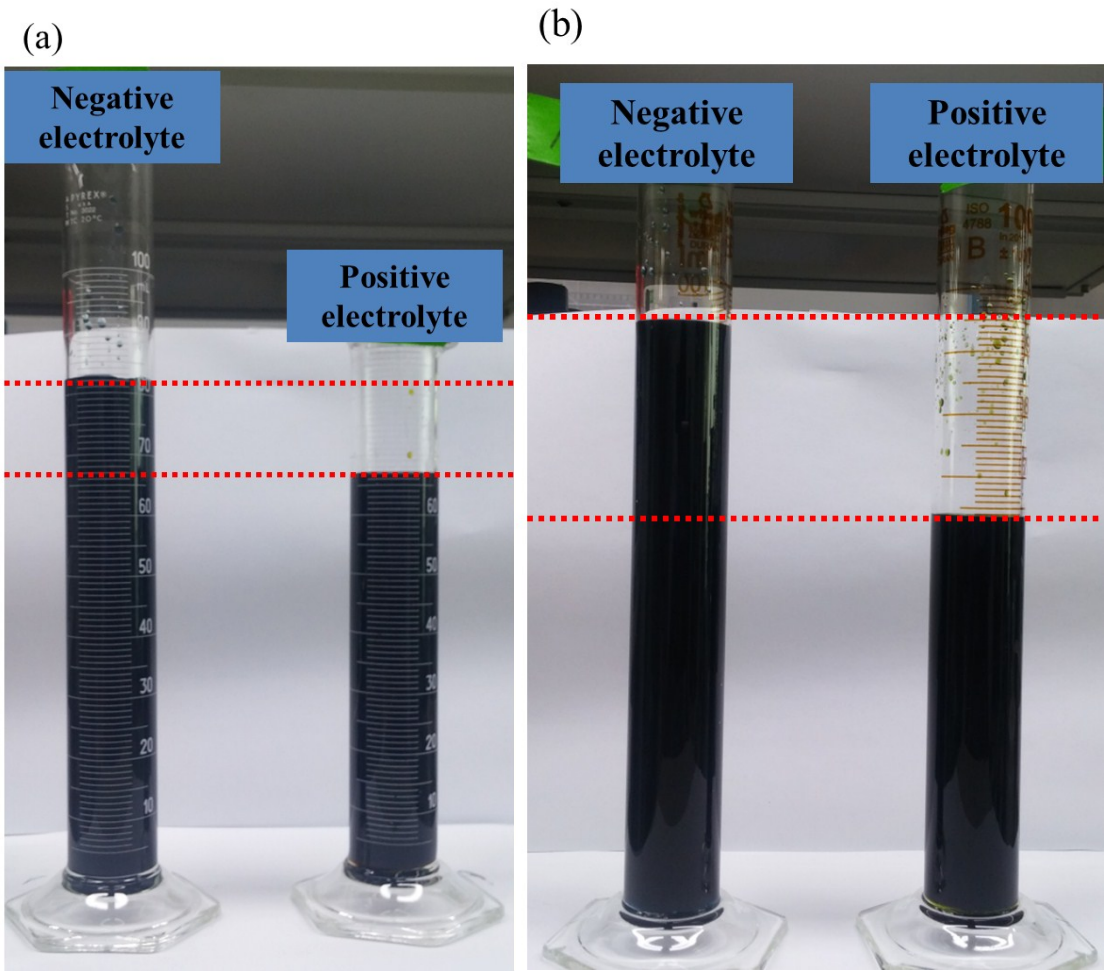


Fig. S8 Color change of the ex situ test solutions (0.1M VO_2^+/5M H_2SO_4) containing Nafion 115, BPSH-50, mPBI, and BI*p*PBI membranes over measuring time.

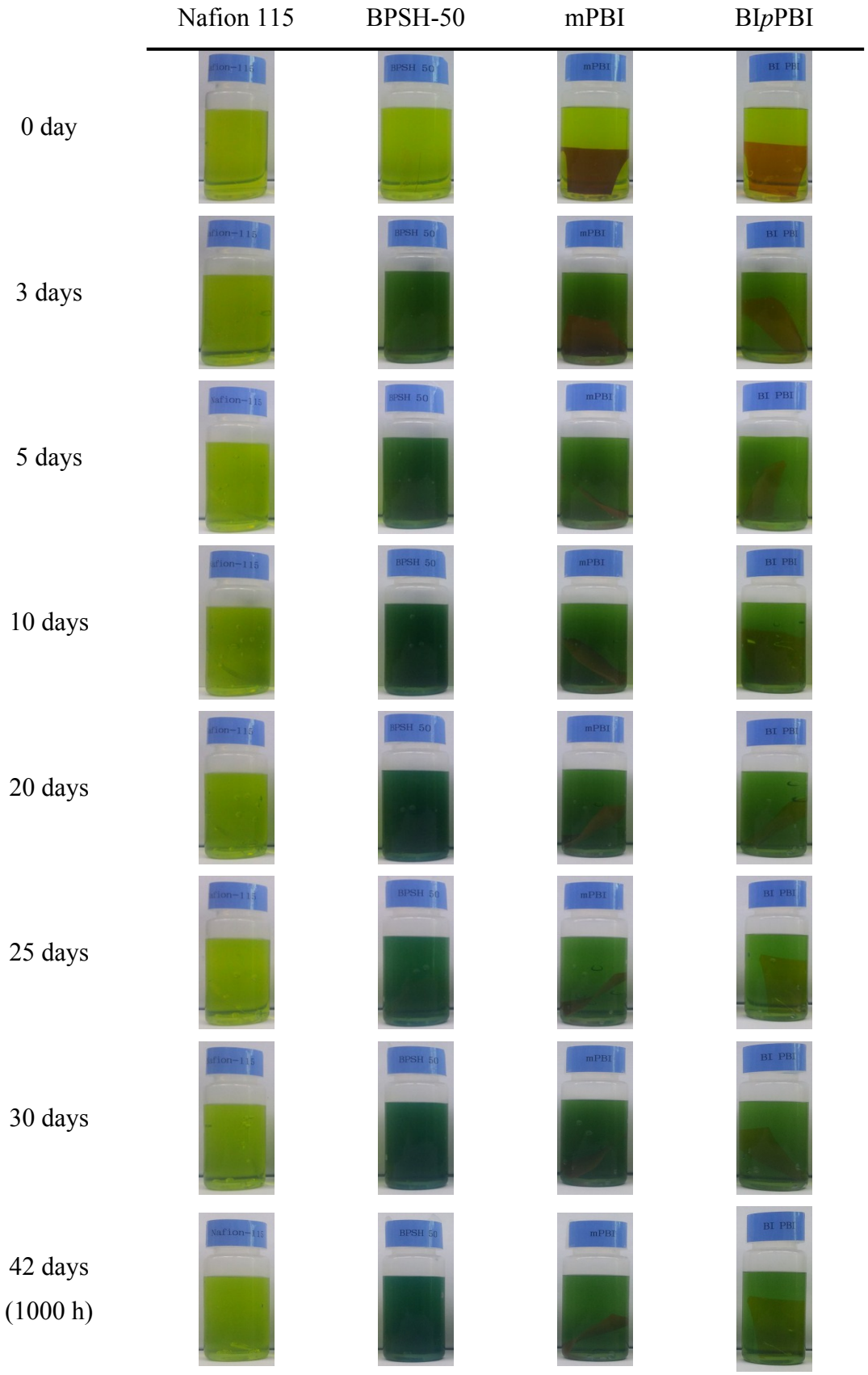


Fig. S9 SEM image of BI*p*PBI membranes : pristine (a : surface, a' : cross section), after 1000 h soaking test (b : surface, b' : cross section), and after 200 cycling test (c : surface, c' : cross section).