Supporting Information

Side-chain-type Anion Exchange Membranes for Vanadium Flow Battery: Properties and Degradation Mechanism

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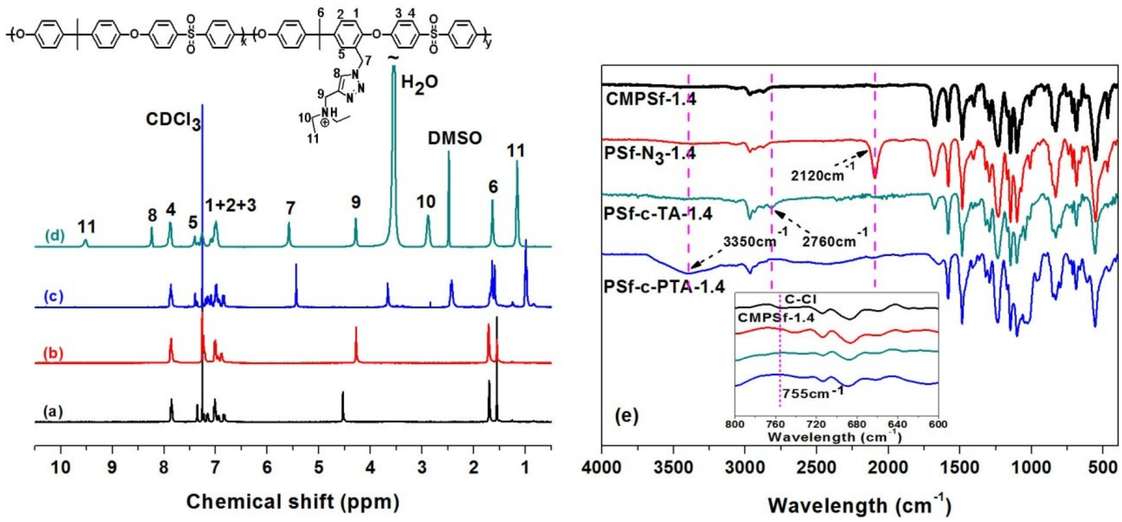


Figure S1. ^{1}H NMR spectra of (a) CMPSf-1.4, (b) PSf-N_3-1.4 and (c) PSf-c-PTA-1.4 copolymers in $CDCl_3$, and (d) PSf-c-PTA-1.4 membrane after protonating in DMSO-d_6 and (e) corresponding ATR-IR spectrum.

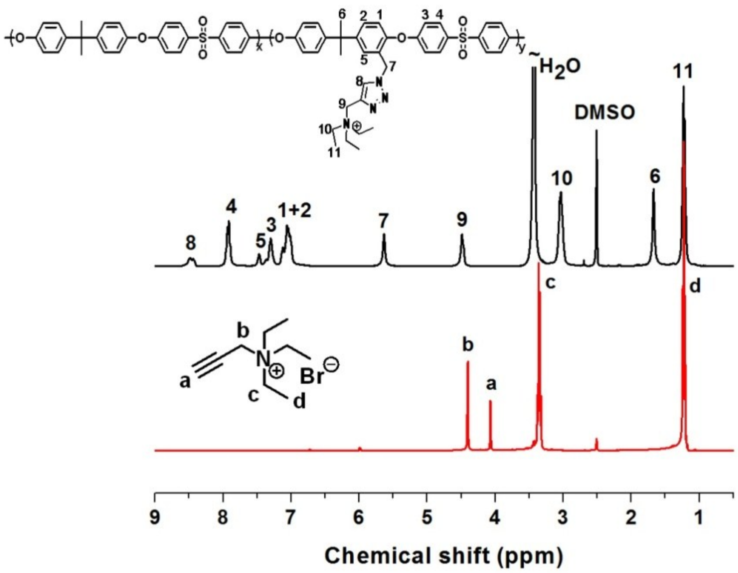


Figure S2. ^{1}H NMR spectra of TEPA salt and PSf-c-QA-1.2 copolymer in the bromine from in DMSO-d6.

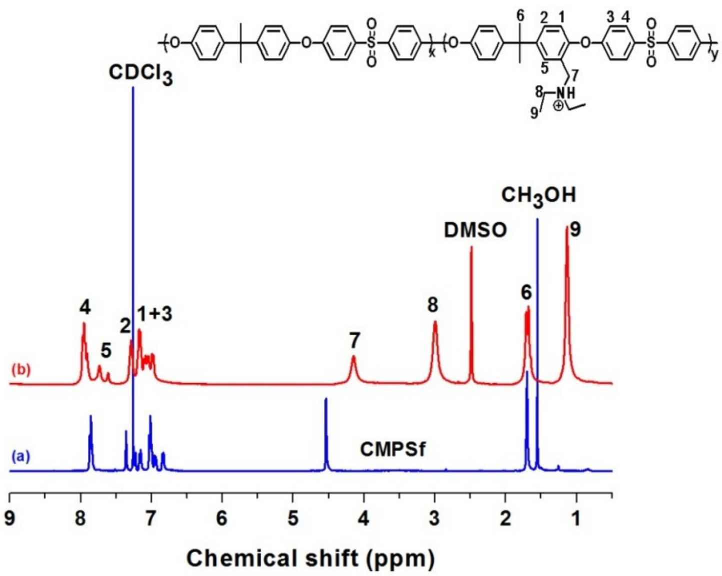


Figure S3. ^{1}H NMR spectra of (a) CMPSf-1.4 and (b) PSf-PTA-1.4 copolymer in $CDCl_3$.

Table S1. Solubility of membranes before and after protonation[a]

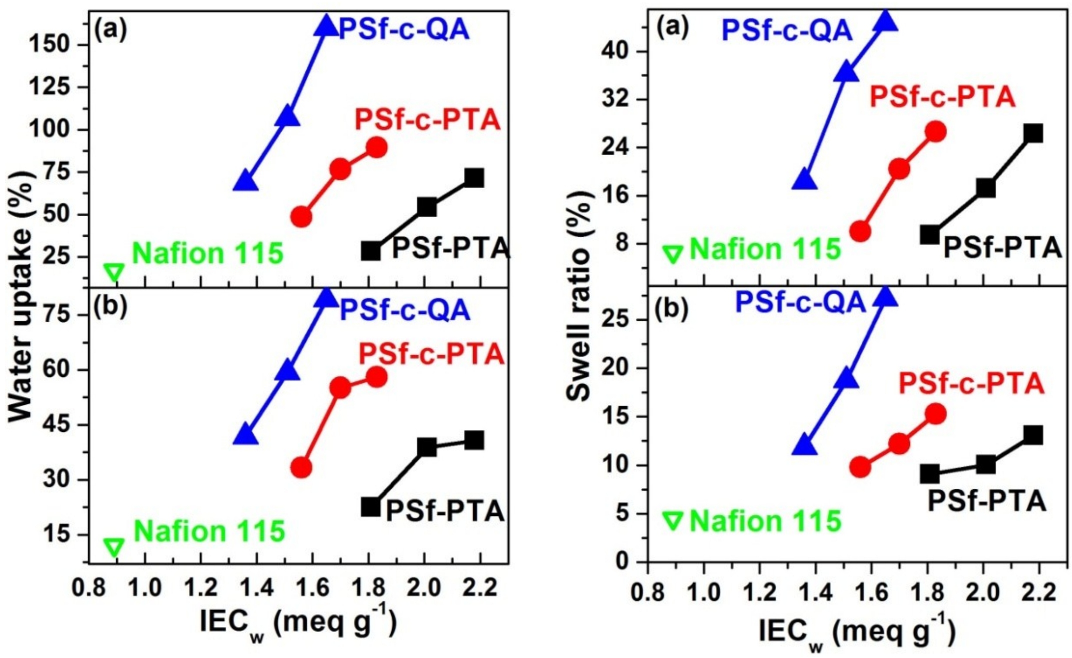
Membrane	PSf-PTA-1.4		PSf-c-PTA-1.4		PSf-c-QA-1.2	
	Before	After	Before	After	Before	After
THF	—	—	—	—	—	—
Acetone	—	—	—	—	—	—
Chloroform	+	—	+	—	—	—
DMF	+	+/—	+	+/—	+	+/—
NMP	+	+/—	+	+/—	+/—	+/—
DMSO	+/—	+	+/—	+	+	+
H_2O	—	—	—	—	—	—

[a] The AEMs immersed in 0.5 M H_2SO_4 for 48 h; [b] +, soluble; —, insoluble; +/—, partially soluable.

Table S2. Water uptake and swelling ratio of the prepared AEMs at 20 °C

Sample	IEC_W[a] (meq g^{-1})	WU[b] (wt%)	WU[c] (wt%)	SR[b] (%)	SR[c] (%)
PSf-PTA-1.2	1.81	28.4	22.5	9.5	9.1
PSf-PTA-1.4	2.01	54.3	38.8	17.2	10.0
PSf-PTA-1.6	2.18	71.4	40.7	26.3	13.1
PSf-c-PTA-1.2	1.56	48.6	33.3	10.1	9.8
PSf-c-PTA-1.4	1.70	76.7	55.1	20.5	12.2
PSf-c-PTA-1.6	1.83	89.6	58.1	26.7	15.3
PSf-c-QA-1.0	1.36	68.6	41.8	18.3	11.9
PSf-c-QA-1.2	1.51	106.7	59.3	36.3	18.7
PSf-c-QA-1.4	1.65	160.0	79.2	44.6	27.2
Nafion 115	0.89	17.2	12.1	6.6	4.5

[a] meq g^{-1}, AEMs in sulfate or hydrogen sulfate ion form, and calculated from ^1H NMR spectra. [b] wt%, measured in deionized water at 20 °C. [c] Measured in 0.5 M H_2SO_4 at 20 °C.



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igure S4. Water uptake and swell ratio of membranes in (a) Water and (b) 0.5 M H_2SO_4 at 20 °C as a function of IEC.

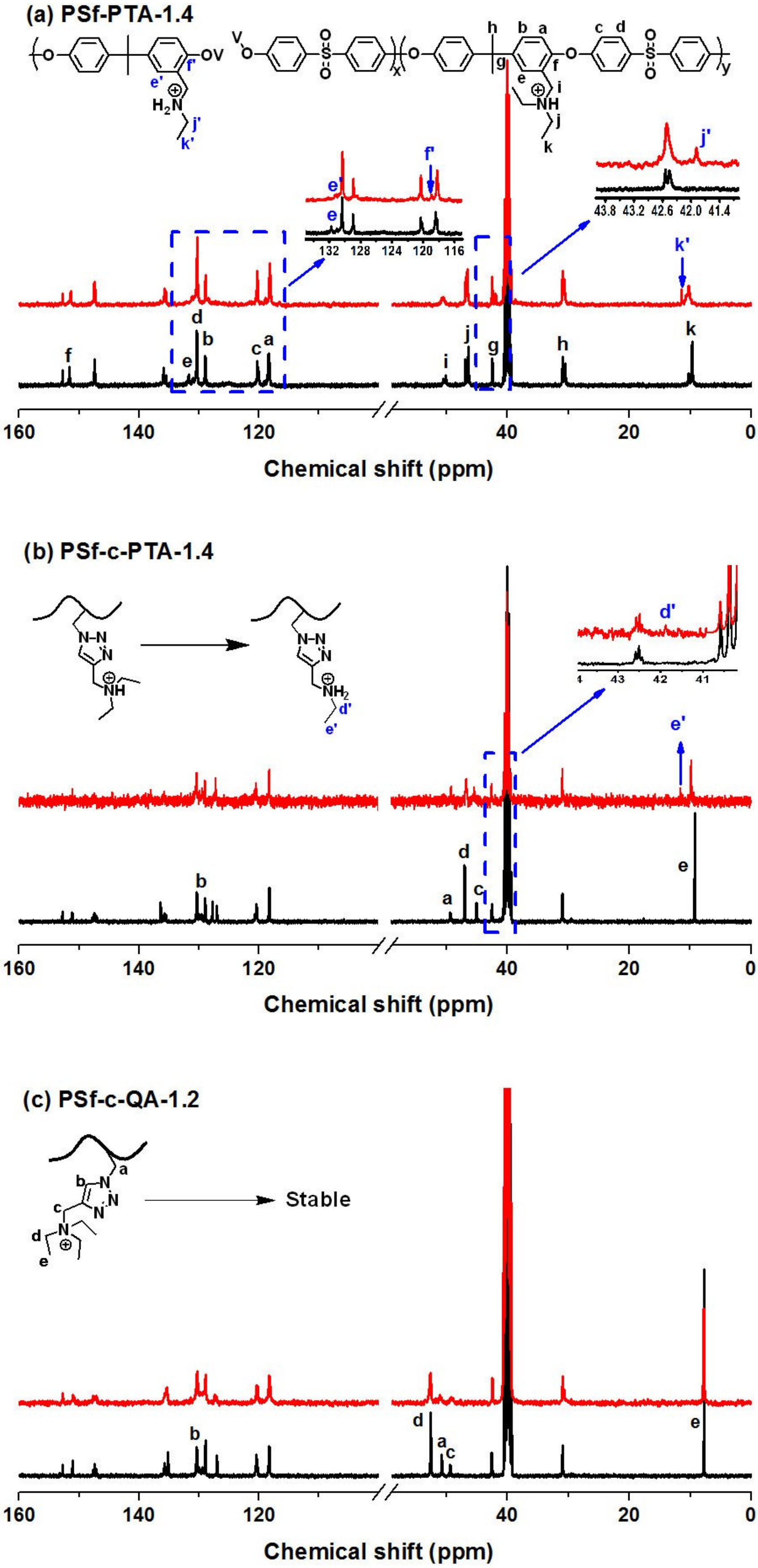

Figure S5. ^{13}C NMR spectra of AEMs before (black) and after (red) exposure to 1.5 M VO_2^+ [V(V)] in 3 M H_2SO_4 at 40 °C for 30 days.

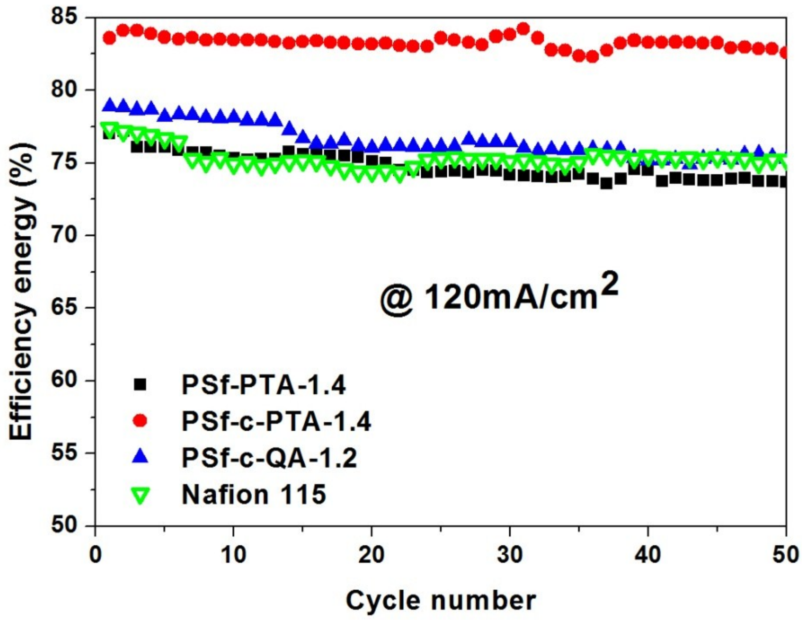

Figure S6. Cycling performance for VFBs assembled with the prepared AEMs and Nafion 115 at a current density of 120 mA/cm^2.

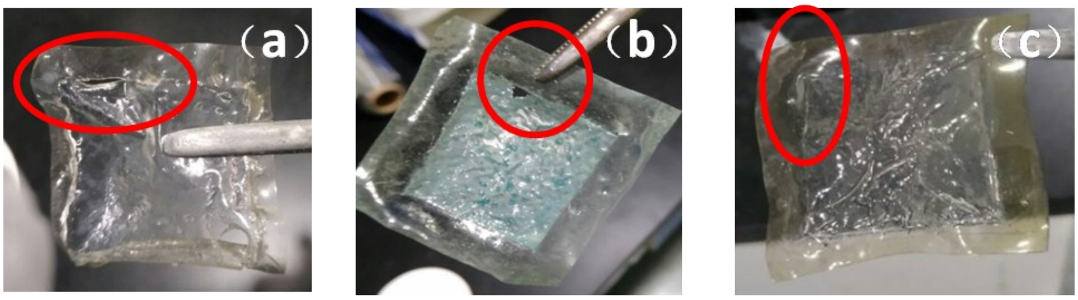

Figure S7. Images of AEMs after long-term charge-discharge cycles testing: (a) PSf-PTA-1.4, (b) PSf-c-PTA-1.4 and (c) PSf-c-QA-1.2.

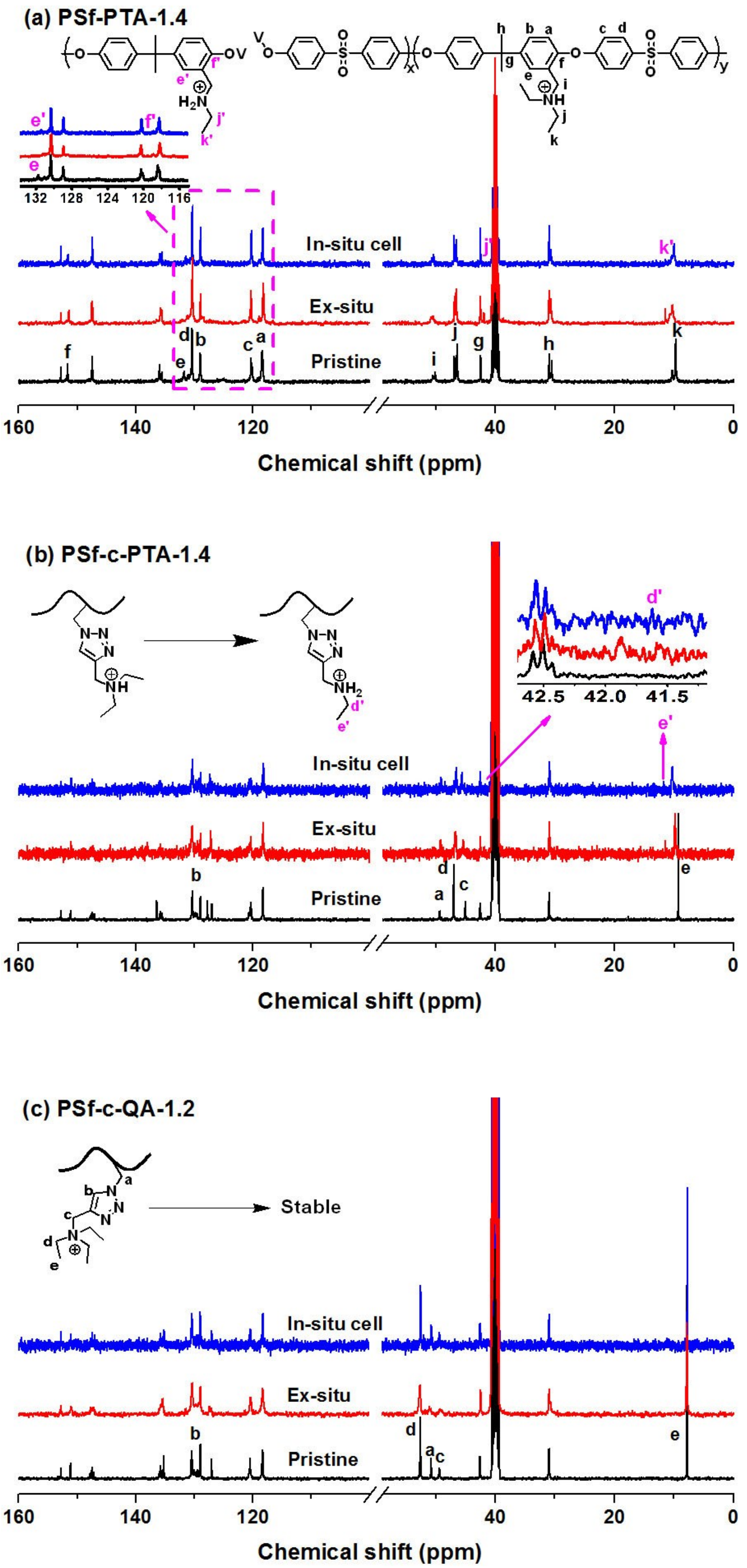

Figure S8. ^{13}C NMR spectra of pristine membranes (black), after 1.5 M VO_2^+/3M H_2SO_4 at 40 °C for 30 days (red) and in situ VFB durability testing (blue).

Table S3 Properties of reported AEMs for VFBs

sample	cations	IEC_W[a] (meq g^{-1})	WU[b] (wt%)	Area resistivity [Ω cm^2]	Ref.
Nafion 115	sulfonate	0.89	32.1	0.95	1
QAPPEK-5	trimethylammonium	1.64	24.7	0.88	2
PyPPEKK-4	pyridinium	1.55	16.5	0.6	3
VBC-co-St-co-HEA	trimethylammonium	1.18	40.2	1.9	4
QADMPEK-3	trimethylammonium	1.75	18.8	0.49	5
QBPPEK80	trimethylammonium	1.53	23.8	0.58	6
CMPSF-72	imidazolium	1.51	3.3[c]	1.22	7
CMPSF-0.9	4,4′-bipyridinium	1.54	11.9	0.18	8
PSf-TA-1.4	triethylammonium	2.01	29.6	1.3	this work
PSf-c-TA-1.4	triethylammonium	1.70	36.7	0.6	this work
PSf-c-QA-1.2	tetraethylammonium	1.51	53.0	0.5	this work

[a] Calculated from ^1H NMR spectra, meq g^{-1}. [b] Measured at room temperature in water, wt %. [c] Swelling, measured at room temperature in water, %.

Table S4 Mechanical Properties of AEMs at 20 °C

Sample	Tensile strength (MPa)		Elongation at break (%)	
	dry[a]	wet[b]	dry[a]	wet[b]
PSf-PTA	41.6	33.0	12	23.4
PSf-c-PTA	32.5	20.7	8.0	23.3
PSf-c-QA	20.2	13.7	5.6	27.4

[a]At 40% RH.[b]At 95 % RH.

References

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