Electronic Supplemental Information (ESI)

High performance aliphatic-heterocyclic benzyl-quaternary ammonium radiation-grafted anion-exchange membranes

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Table S1 Summary of the gravimetric water uptakes (WU), ion-exchange capacities (IEC), and through-plane conductivities of all of the radiation-grafted AEM synthesised (Cl^- forms) from the 50 μm ETFE precursor.

AEM	Amine	Water Uptake[a,b]	IEC_{QN}	IEC_{total}	IEC_{QN} after aqueous KOH treatment (1 mol dm^{-3} 60°C, 28 d)	Thickness[a,b]	$\sigma_{TP\ Cl}$ [a] (25° C)
		%	mmol g^{-1}	mmol g^{-1}	mmol g^{-1}	μm	mS cm^{-1}
PVB-TMA	Trimethylamine	49 ± 4	1.820 ± 0.002	–	1.268 ± 0.003	110	14 ± 2
PVB-MPRD	1-Methylpiperidine	82 ± 3	1.638 ± 0.014	–	1.356 ± 0.013	106	16.9 ± 1.6
PVB-MMPH	4-Methylmorpholine	57 ± 2	1.642 ± 0.011	–	0.798 ± 0.014	93	13.0 ± 0.6
PVB-MPY	1-Methylpyrrolidine	62.6 ± 1.3	1.655 ± 0.013	–	1.363 ± 0.009	115	20 ± 2
PVB-MPZ	1-Methylpiperazine	9.2 ± 0.9	0.642 ± 0.017	1.08 ± 0.07	0	74	0
PVB-DMPZ	1,4-Dimethylpiperazine	38.6 ± 1.3	1.236 ± 0.009	1.481 ± 0.012	0.5877 ± 0.0007	90	5.4 ± 0.5

[a]Fully hydrated AEMs, [b]Room temperature.

Table S2 %Loss of IEC_{QN}, as well as %loss of Cl/C and N/C molar ratio (extracted from the elemental analysis) for the downselected AEM samples after the *ex situ* alkali treatment (aqueous KOH, 60°C, 28 d, concentrations shown in table).

AEM	IEC_{QN} loss KOH (1 mol dm^{-3})	Elemental Analysis Cl/C loss KOH (1 mol dm^{-3})	Elemental Analysis N/C loss KOH (1 mol dm^{-3})	Difference (Cl/C loss – N/C loss) KOH (1 mol dm^{-3})	IEC_{QN} loss KOH (6 mol dm^{-3})
PVB-TMA	30 %	31 %	16 %	14 %	–
PVB-MPRD	17 %	19 %	6 %	13 %	28%
PVB-MPY	18 %	18%	6 %	12 %	25%

Table S3 Estimated laboratory-scale production cost of the three most alkali-stable AEMs with a basic comparison to the bulk price of select commercially available ion-exchange membranes.

Ion Exchange Membrane	Price, £ / m^2
Fumasep® FAA-3-PK-130	490
Nafion™ N115	375-525
Surrey PVB-TMA	240
Surrey PVB-MPRD	320
Surrey PVB-MPY	330

* Currency conversion rates taken on 2nd August 2016. The price of Surreys' AEMs were estimated solely on the cost of starting materials, reactants and e-beam facility access costs using the typical quantities purchased and used during this study (all supplied on the lab-scale, non-bulk, basis).

Table S4 Comparison of the Cl^-- and OH^--conductivity data of the three down-selected AEMs (in this article) with current state of the art of polymeric anion-exchange membranes.

AEM	Reference (see footnote)	Hydration level	Temperature / °C	σ_{Cl^-} / mS cm^{-1}	σ_{OH^-} / mS cm^{-1}
PVB-MPRD	This work	95% RH	30	10 ± 1	64 ± 2
			60	–	111 ± 1
PVB-MPY	This work	95% RH	30	12 ± 1	71 ± 2
			60	–	126 ± 2
PVB-TMA	1	95% RH	30	5.4 ± 1.9	–
AEM-2.9	2	95% RH	60	–	106
AEM-3.2	2	95% RH	60	–	138
HMT-PMBI	3	Fully hydrated	25	7.5 ± 0.4	10.0 ± 1.2[a]
aQAPS-1.27	4	Fully hydrated	30	–	53.9[b]
Q-PS_{100}-*b*-$PVBC_{167}$	5	95% RH	30	36.6	–
T25NC6NC5N	6	Fully hydrated	Room temp.	34 ± 3	99 ± 5
60PPOFC6NC6	7	Fully hydrated	Room temp.	16 ± 1	46 ± 4
C6D60	8	Fully hydrated	Room temp.	–	43
BPI (74.6 % DOG)	9	Fully hydrated	20	–	71
C-HPPES-4/1	10	Fully hydrated	30	–	76.7 ± 0.9
DMDPM-QTB	11	Fully hydrated	30	–	43.4

[a] Membranes exposed to ambient CO_2. [b] Through-plane measurements.

References to Table S4

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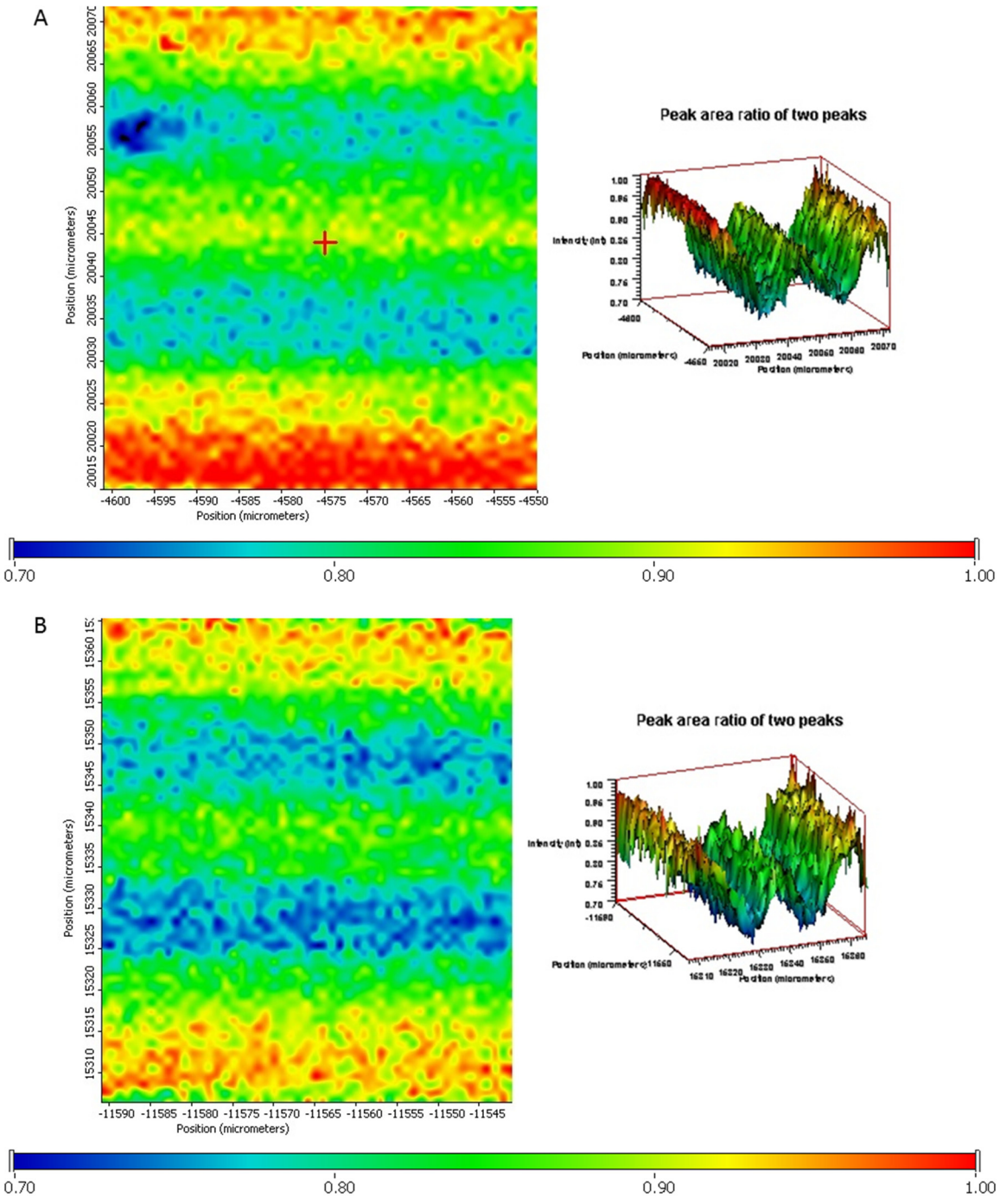

Figure S1 Cross-sectional Raman spectral maps recorded across additional 50 × 60 µm^2 sample areas of the ETFE-g-VBC intermediate film used in this study (the y-direction is from one surface of the membrane to the other). For these supporting maps, a λ = 532 nm (10 mW power) laser was used. Data points collected every 1 µm steps in both the x-y directions.

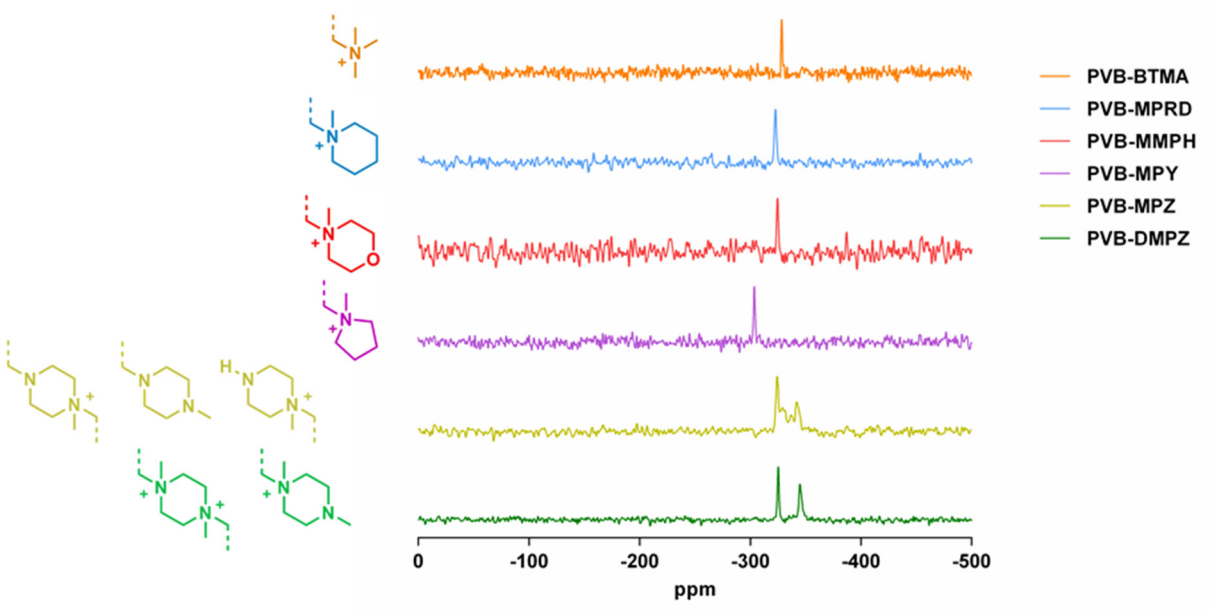

Figure S2 ^{15}N Solid state NMR of the AEMs with the different head groups (chemical connections possibilities also shown).

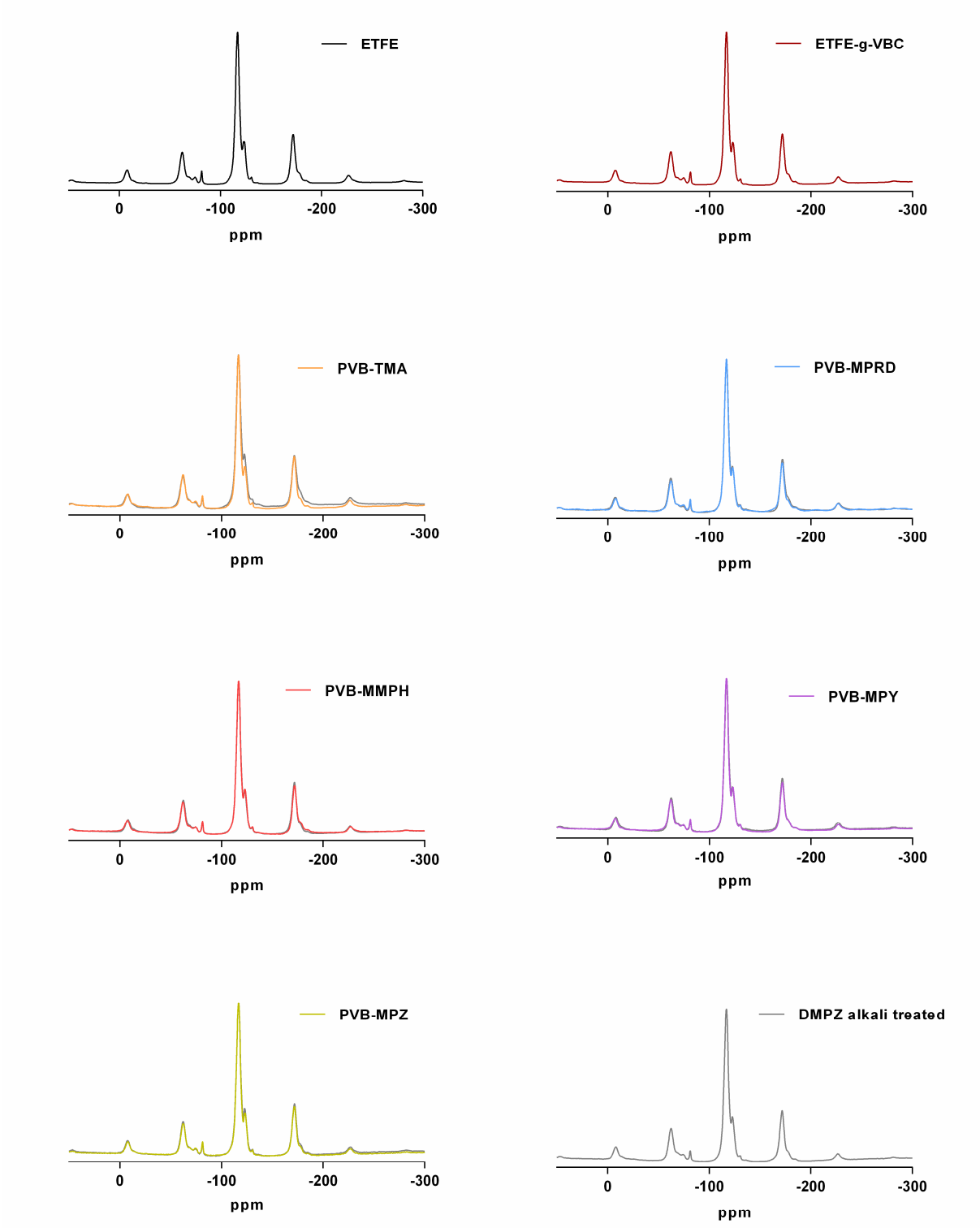

Figure S3 ^{19}F Solid state NMR spectra of the ETFE precursor film (50 µm thick), the intermediate VBC grafted ETFE film (ETFE-g-VBC), and the AEMs with different head groups. The grey solid lines correspond to alkali treated (aqueous KOH, 1 mol dm^{-3}, 60 °C, 28 d) AEM samples.

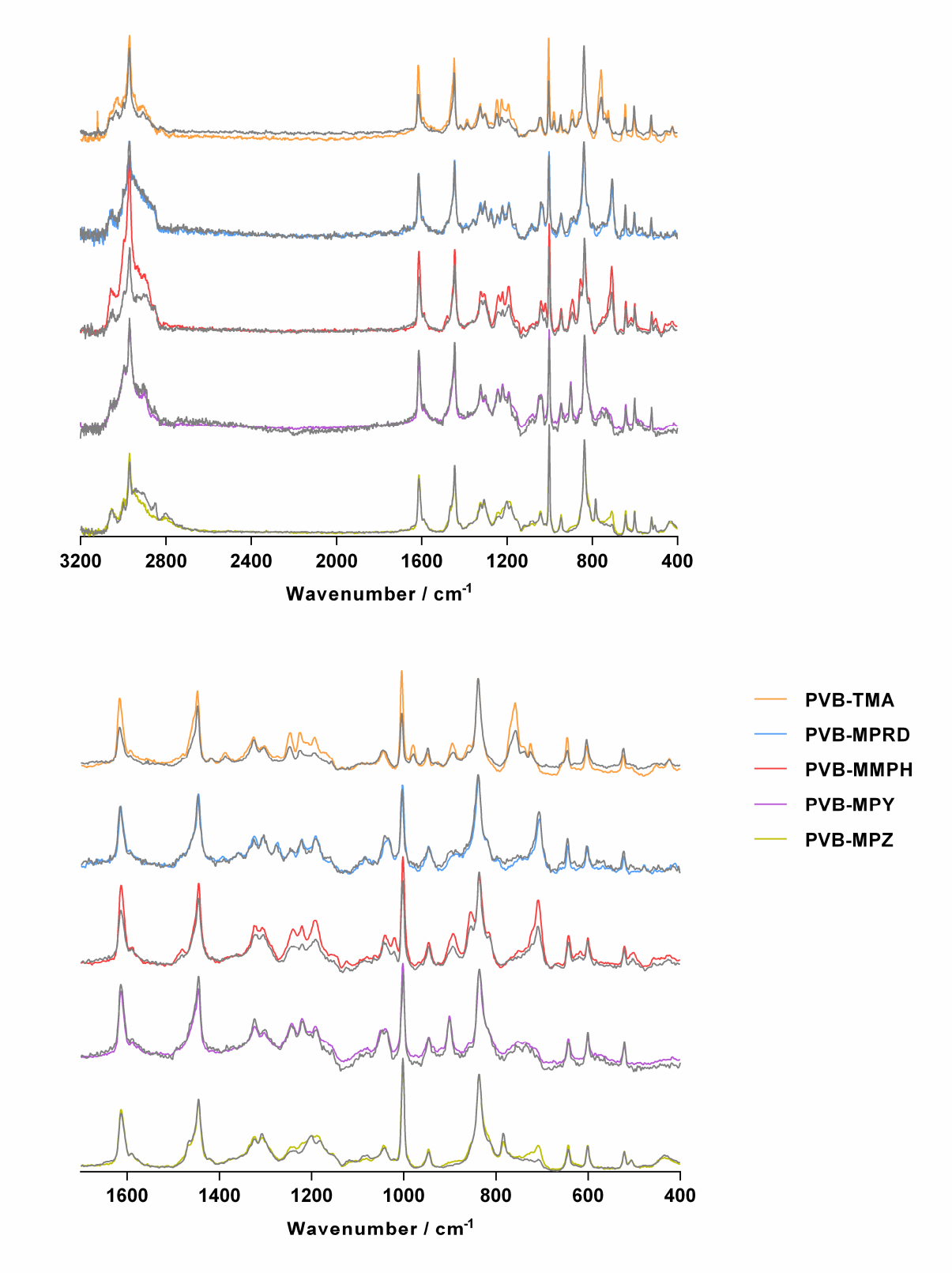

Figure S4 Raman spectra of the samples of the various AEMs with different head groups. Spectral windows from 3200 to 400 cm^{-1} (top) and 1700 to 400 cm^{-1} (bottom). The grey solid lines correspond to alkali treated (aqueous KOH, 1 mol dm^{-3}, 60 °C, 28 d) AEM samples. All spectra have been normalised to the intensity of the 830 cm^{-1} band (assigned to the CF_2 groups in the ETFE polymer backbone) to aid visual comparison.

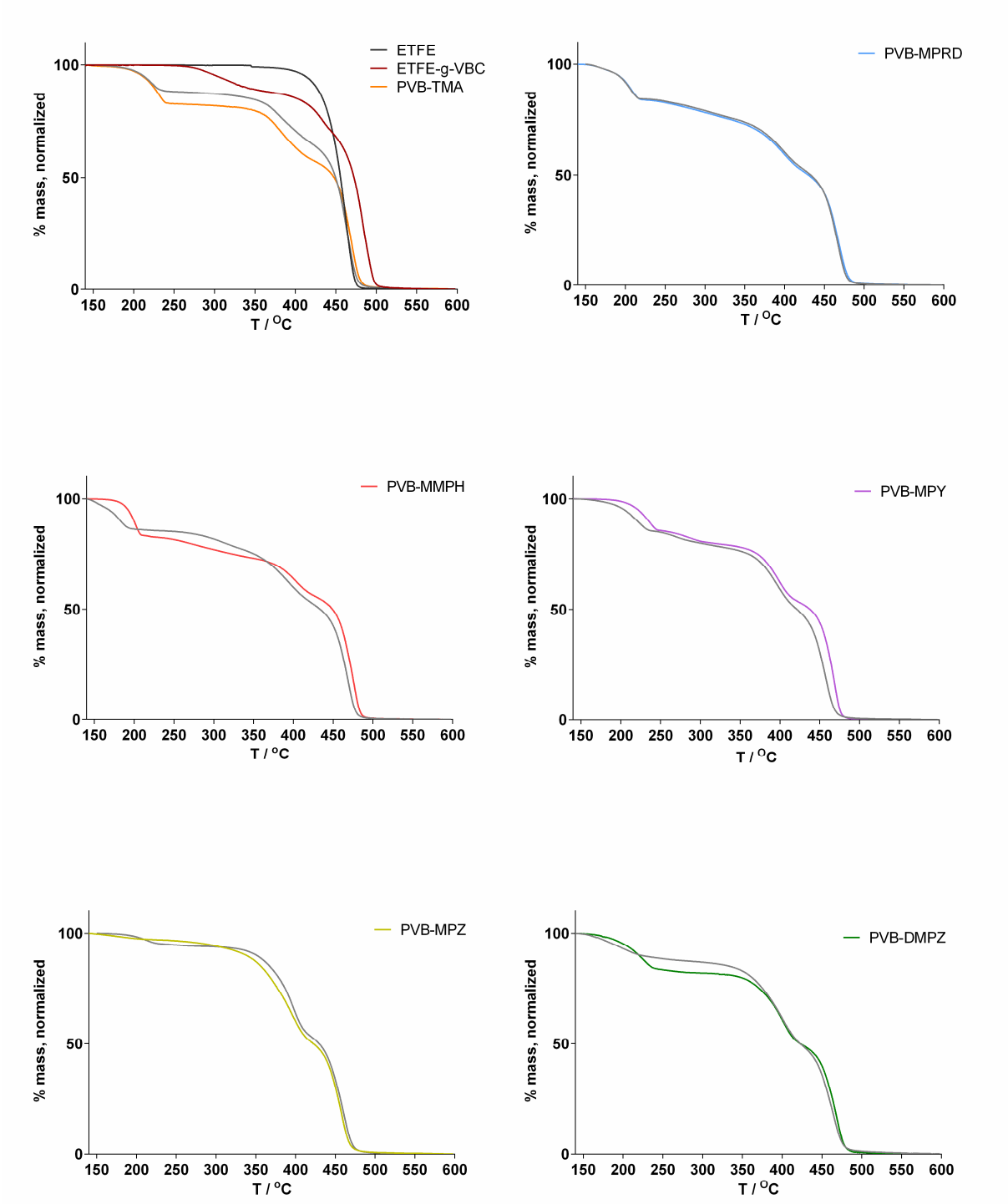

Figure S5 Thermogravimetric analysis of the ETFE, ETFE-g-VBC and the AEMs with different head groups. In the thermograms of the AEMs, the grey solid lines correspond to alkali treated (aqueous KOH, 1 mol dm^{-3}, 60°C, 28 d) AEM samples. Data recorded under a N_2 atmosphere from room temperature to 600 °C at a heating rate of 5 °C min^{-1}. All curves are shown from 140°C and have been normalised for visual comparison purposes (mass at 140°C normalised to 100% and residual mass at 600°C normalised to 0%).

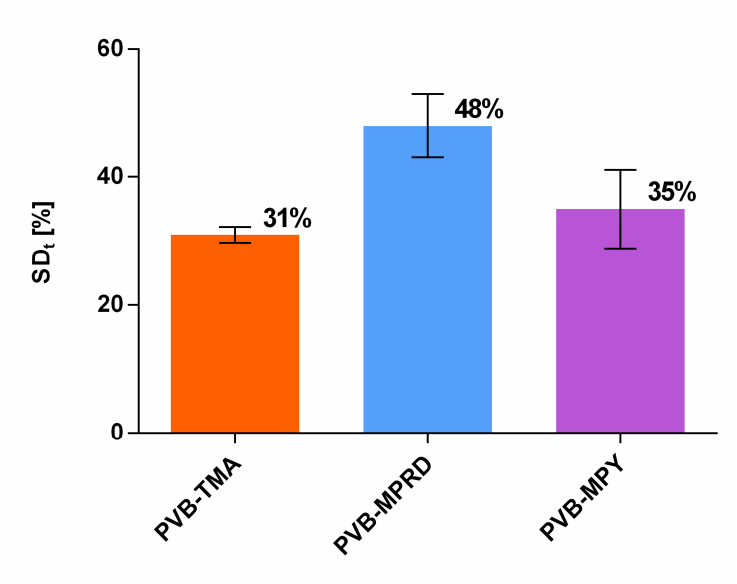

Figure S6 The through-plane Swelling Degree (SD_t) at room temperature for the down-selected PVB-TMA, PVB-MPRD and PVB-MPY AEMs in the chloride form.

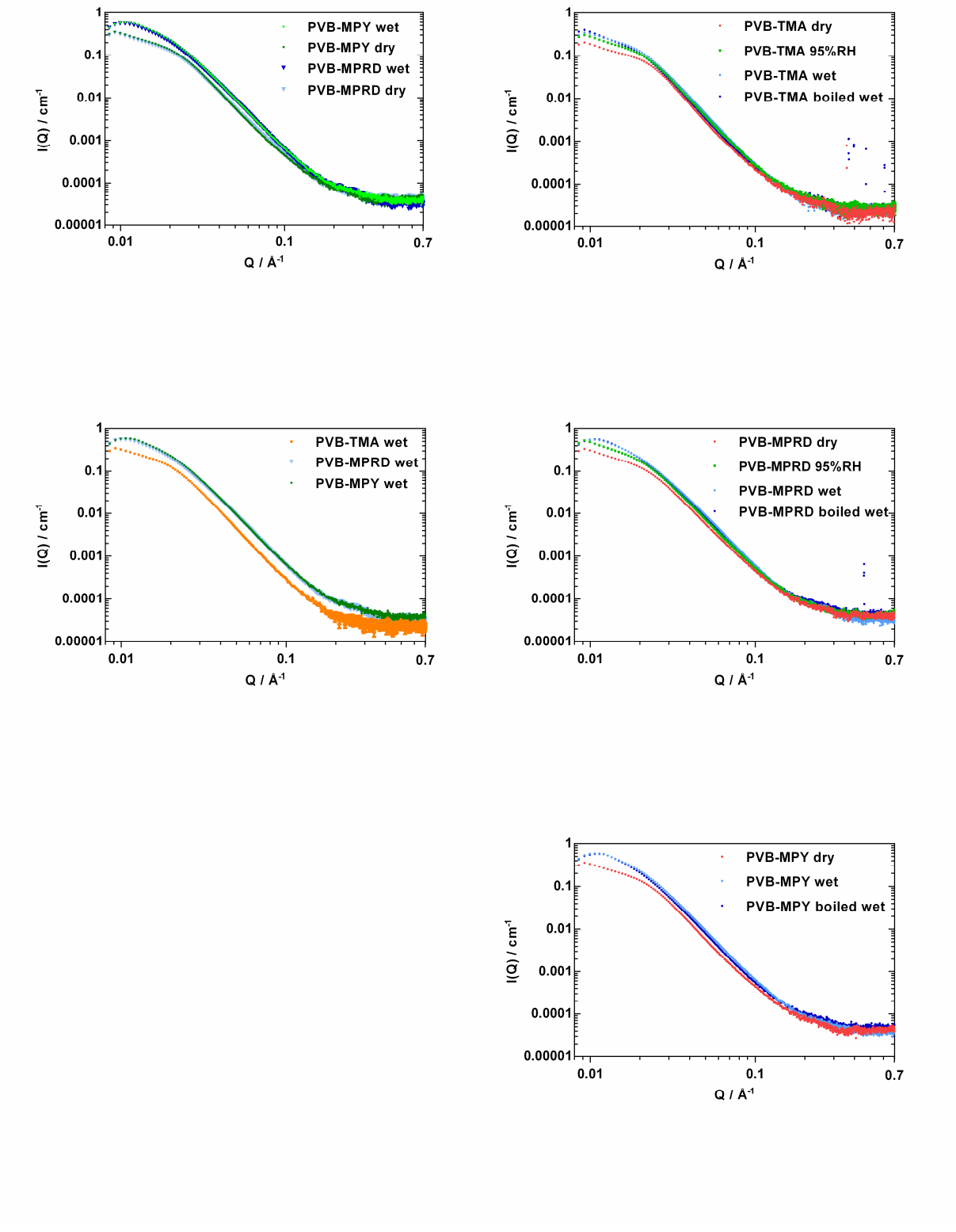

Figure S7 SAXS profiles collected for PVB-TMA, PVB-MPRD and PVB-MPY AEMs at 60 °C in dry atmosphere, 95% RH and wet atmospheres: the latter either just soaked in water (wet) and after been boiled (boiled wet). The PVB-TMA data was taken from the SAXS study in ref. 1 of Table S4.

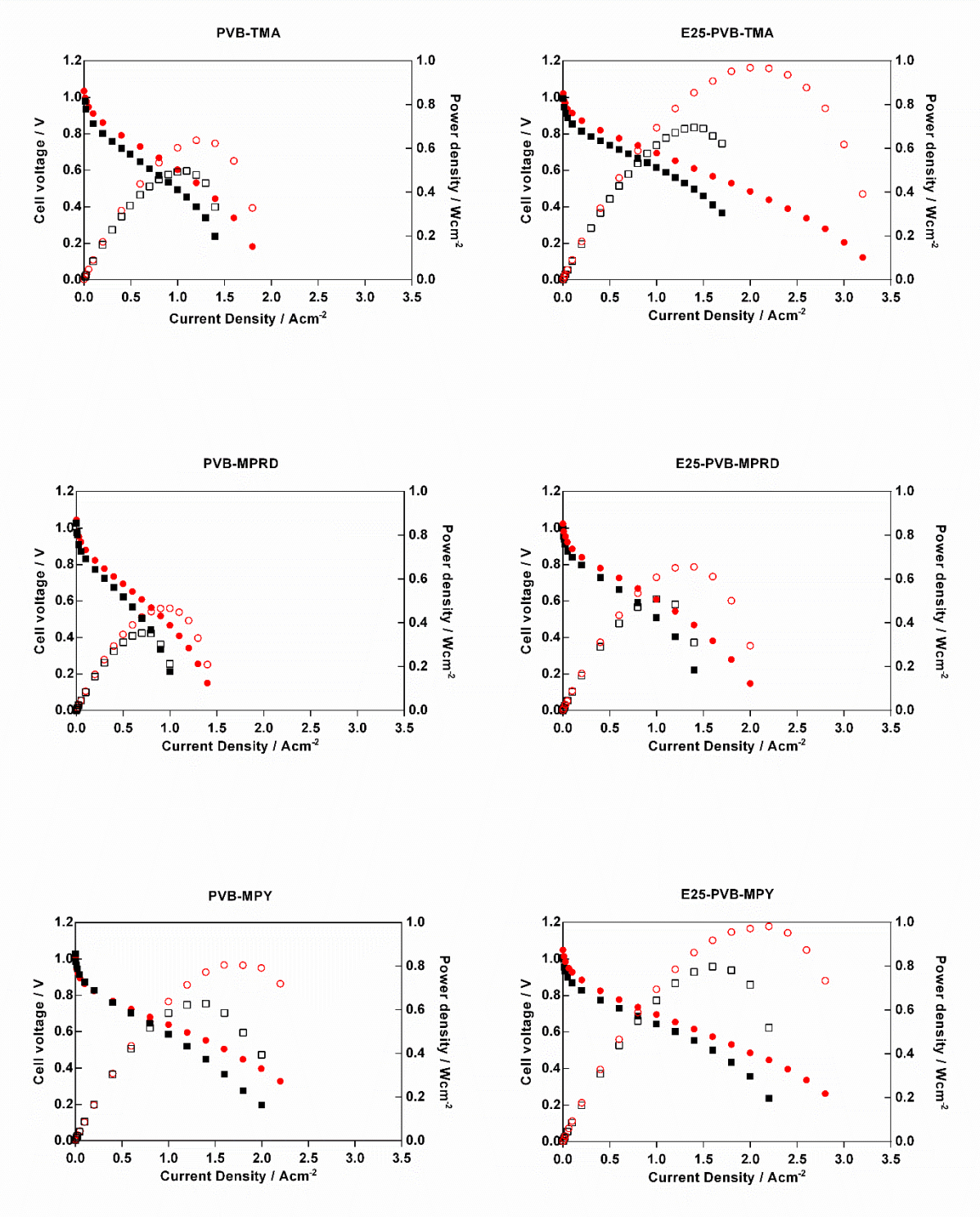

Figure S8 H_2/O_2 cell performances measured at 60°C PVB-TMA/MPRD/MPY AEMs (made from 50 µm ETFE – left) and E25-PVB-TMA/MPRD/MPY AEMs (made from 25 µm ETFE – right) membrane-electrode assemblies with both no back-pressurisation (black squares) and with 0.1 MPa pressurisation (red dots) of the fully humidified gas streams. PtRu/C(60%$_{w/w(metal/C)}$) anode and Pt/C(60%$_{w/w}$) cathode catalysts of 0.4 mg cm^{-4} metal loadings were used alongside the Wuhan University aQAPS polysulfone alkaline ionomer (20%$_{w/w}$ ionomer loading).