Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Radiation-induced grafting of a butyl-spacer styrenic monomer onto ETFE: synthesis of the most alkali stable radiation-grafted anion-exchange membrane to date

Julia Ponce-González,* Imad Ouachan, John R. Varcoe, and Daniel K. Whelligan
Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK

Electronic Supplementary Information

Radiation-activation of the precursor ETFE films

For the preparation of all the radiation-grafted anion-exchange membranes (AEM) in this study, poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films of 25 µm (supplied by Nowofol Kunststoffprodukte GmbH, Germany) were first irradiated in air (containing O_2) using a 4.5 MeV Dynamatron Continuous Electron Beam Unit (STERIS Synergy Health, South Marston, UK). The absorbed were doses were controlled by the number passes (10 kGy per pass). The films employed in this study were exposed to a total of 40 kGy absorbed dose. After irradiation and transport back to Surrey in dry-ice, films were stored in a freezer at -40 °C until the monomer grafting step was performed.

Chemicals and materials

Vinylbenzyl chloride monomer (VBC, mixture of *meta*- and *para*-isomers, containing 700 – 1100 ppm nitromethane Friedel-Crafts inhibitor and 50 – 100 ppm 4-*tert*-butylcatechol polymerisation inhibitor), 1-octyl-2-pyrrolidone wetting agent and *N*-methylpyrrolidine (**MPY**, 97%) were purchased from Sigma-Aldrich (UK). All chemicals were used as received. Ultra-pure water (UPW) used was of resistivity = 18.2 MΩ cm.

Instrumentation

High-resolution NMR spectra were obtained on a Bruker 500 MHz spectrometer. ^{1}H NMR spectra were referenced to TMS = 0 ppm. All NMR data is presented as follows: chemical shift (δ) in ppm, multiplicity, coupling constants (J / Hz), and integration.

GC-MS was carried out on an Agilent Technologies 7890A GC system connected to an Agilent Technologies 5975C inert XL EI/CI mass selective detector (MSD) operating in EI mode and the conditions were as follows: injection volume = 1 µL, injection temperature = 250 °C, column = Agilent HP-5MS (30 m × 0.25 mm), oven temperature gradient = 30 °C between 0 – 10 min and then 30 – 250 °C ramp (20 °C min^{-1}) between 10 – 21 min.

Preparation of the 4-Butyl-spacer monomer (C4-monomer)

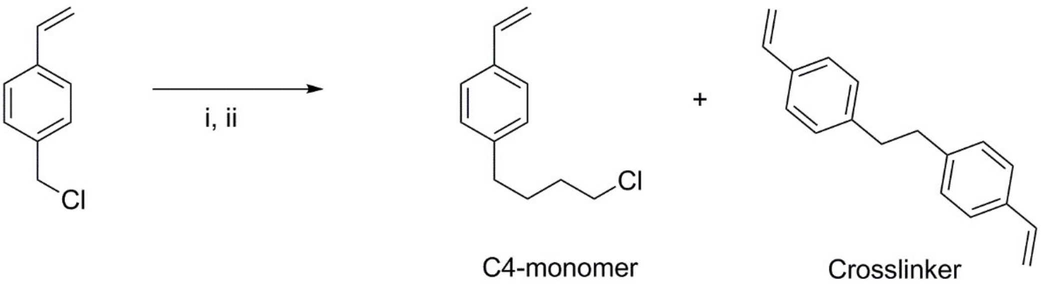


Fig. S1 Outline of the synthesis of C4-monomer: i) Mg, dry ether, 0 °C; ii) 1-bromo-3-chloropropane, Li_2CuCl, dry THF, 0 °C.

The butyl-spacer monomer (C4-monomer) was prepared in one step reaction between 4-vinylbenzyl chloride and 1-bromo-3-chloropropane according to the method described by Seki and co-workers.[1] 4-Vinylbenzyl chloride was added dropwise to a mixture of Mg turnings (2.76 g, 115 mmol) in dry diethyl ether (52 mL) at 0 °C. Once the addition was finished, the mixture was stirred at room temperature for 1 h. LiCl (0.084 g, 2.0 mmol), anhydrous $CuCl_2$ (0.133 g, 0.10 mmol) and 1-bromo-3-chloropropane (50 mL, 500 mmol) were dissolved in THF (90 mL) in a separate flask, degassed and added to the Grignard reagent solution via syringe. The reaction mixture was stirred under N_2 at room temperature overnight. After quenching with 10 mL methanol, the resulting suspension was filtered and concentrated under reduced pressure. The resulting oil was dissolved in diethyl ether and washed with water. The organic phase was dried over anhydrous $MgSO_4$ and concentrated to yield a yellow oil that was purified by distillation at reduced pressure (0.09 mbar, 125 °C) to yield 4CVBC as a mixture containing 2% crosslinker (11.98 g, 60 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): C4-monomer: δ 7.34 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 11, 17.5 Hz, 1H), 5.71 (d, J = 17.5 Hz, 1H), 5.20 (d, J = 11.0 Hz, 1H), 3.55 (d, J = 6.5 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 1.80 (m, 4H); GCMS (EI) 17.0 min, m/z = 117 (100 %, $CH_2CHPhCH_2^+$), 194 (16 %, $M(^{35}Cl)^+$), 196 (5 %, $M(^{37}Cl)^+$). [Crosslinker (1,2-bis(4-vinylphenyl)ethane) ^{1}H NMR peaks (not listed but shown in spectra in Figure S2, below) match those described in the literature;[2] GCMS (EI) 21.7 min, m/z = 117 (100 %, $CH_2CHPhCH_2^+$), 234 (20 %, M^+), 235 (4 %, M^+)].

Optimised grafting procedure

For the grafting step with VBC monomer, a mixture containing 71.25 mL of deionized water, 0.75 mL of 1-octyl-2-pyrrolidone, and 3 mL of VBC (4 %vol of grafting mixture) was purged with nitrogen for 30 min at room temperature in a Schlenk tube. Following this, one pre-irradiated ETFE film sample (size *ca.* 13 cm × 13 cm) was taken from the freezer, weighed (m_o) and placed in the mixture in the Schlenk tube. The mixture was then purged for another 2 h and the tube was connected to the Schlenk line before immersing it in an ultrasound bath preheated to 70 °C. After 6 h of sonication at 70 °C (35 kHz and 30% of the instruments 750 W maximum power), the grafting mixture was discarded and the membrane was washed with toluene and sonicated at 70 °C for 5 min. The **ETFE-polyVBC** grafted film was finally dried in a vacuum oven at 70 °C for 4 h and weighed (m_{graft}) in order to determine the Degree of Grafting (DoG).

$$DoG\ (\%) = \frac{m_o - m_{graft}}{m_o} \times 100$$

For the C4-monomer grafted films (**ETFE-polyC4**), the exact same procedure was applied but with a 5 %vol dispersion of monomer in the grafting mixture.

Optimised amination procedure (yielding the anion-exchange membranes)

The grafted intermediates were rolled and placed into Schlenk tubes. A mixture of MPY (15 %vol) in UPW was added and the tube was heated in a water bath with stirring: 60 °C for 6 h for the **ETFE-polyVBC** and 70 °C for 24 h for the **ETFE-polyC4**. The resulting AEMs were thoroughly washed with UPW and heated in water at 60 °C for 1 h. The as-synthesised AEMs were then treated with aqueous NaCl (1 mol dm^{-3}) for 2 h (changing the ion-exchange solution 2 times during this period) and then washed thoroughly with UPW. The final Cl^--forms of **C1-AEM** and **C4-AEM**, were stored in UPW until required for further analysis or testing. For the experiments on the determination of the optimal amination conditions, the same procedure was applied but with changes in amine concentration and reaction times.

Raman spectroscopy and microscopy

A DXR Raman microscope (Thermo Scientific) was used in this study, with a λ = 532 nm (10 mW) excitation laser focused through a confocal microscope. As well as the recording of Raman spectra of various films and membranes on the surface, the microscope mode was used to map the different components of (through thickness) cross-sectional samples of the (desiccator dried) AEMs. A 50× objective was used yielding a laser spot diameter of a theoretical minimum of 1 μm. Spectra were collected using the Thermo Scientific OMNIC™ Software with the use of the Array Automation function. The cross-sectional area maps of the AEMs were recorded with sample-stage step sizes of 1 μm in the *x* and *y* directions (with the *y* direction being the cross-sectional thickness direction in this study); the vertical *z* displacement was fixed. A single spectrum at each sampling point (each pixel in the Raman maps) was recorded with a spectral range of 3350 – 350 cm^{-1} with averaging of 4 acquisitions per spectrum (10 s per acquisition).

Water uptake (WU) and Swelling degree (SD)

AEM(Cl^-) samples were removed from the storage UPW and excess surface water was removed by dabbing the surfaces of the samples with filter paper. The hydrated masses (m_{hyd}), area (A_{hyd}), and thicknesses (T_{hyd}, measured using a digital micrometer) were speedily recorded (to avoid dehydration on prolonged exposure to the atmosphere that typically has a relative humidity RH < 100 % in the laboratories). The AEM samples were subsequently dried in a vacuum oven at 50 °C for 15 h, after which the dry masses (m_{dry}), area (A_{dry}), and thicknesses (T_{dry}) were recorded. All measurements were repeated on n = 4 samples of each AEM(Cl^-). The WU and SD values were then calculated using the following equations:

$$WU(\%) = \frac{m_{hyd} - m_{dry}}{m_{dry}} \times 100 \qquad SDxy\ (\%) = \frac{A_{hyd} - A_{dry}}{A_{dry}} \times 100 \qquad SDz\ (\%) = \frac{T_{hyd} - T_{dry}}{T_{dry}} \times 100$$

Ion-exchange capacity (IEC)

The dehydrated AEM(Cl^-) samples collected directly from the WU measurements above were individually immersed into aqueous $NaNO_3$ (2.4 mol dm^{-3}, 20 cm^3) solutions for 5 h. The solutions, still containing the AEM samples, were then acidified with aqueous HNO_3 (2.0 mol dm^{-3}, 2.0 cm^3) and titrated using analytical grade aqueous $AgNO_3$ (20.00 ± 0.06 mmol dm^{-3}) solution. A Metrohm 848 TitrinoPlus autotitrator equipped with a Ag-Titrode was used for the titrations. The IEC (mmol g^{-1}) was calculated from the end-point (E_p / cm^3) using the following equation:

$$IEC\ (mmol\ g^{-1}) = \frac{E_p\ (cm^3)\ \times\ 0.02\ (mol\ dm^{-3})}{m_{dry}\ (g)}$$

The number of water molecules per cationic group (λ) was calculated according to the following equation:

$$\lambda = \frac{WU}{\left(IEC\ (mmol\ g^{-1}) \times 18\ (g\ mmol^{-1})\right)}$$

Ion-conductivity

Samples (n = 3) of each AEM(Cl^-) were taken directly from the AEM(Cl^-)s that were stored in UPW after synthesis. The Cl^- conductivities of fully hydrated AEM samples were measured using a Solartron 1260/1287 combination controlled by ZPlot (Scribner Associates, USA). Impedance spectra were collected over a frequency range of 0.3 Hz–100 kHz (10 mV *a.c.* amplitude) with the samples mounted in a 4-probe BekkTech BT-112 test cell (supplied by Alvatek, UK) that was submerged in UPW at controlled temperatures. Ionic resistance values were extracted from the low frequency *x*-axis intercept. The in-plane conductivities (σ / S cm^{-1}) were then calculated using the following equation:

$$\sigma = \frac{d}{R \times w \times t}$$

where d is the distance between the Pt voltage sense wires (0.425 cm), and *w* and *t* are the width and thickness of the AEM samples, respectively.

Mechanical testing

The room temperature tensile mechanical properties of the AEMs were measured using a mechanical testing instrument (Instron® 5500 series single column testing system). Membrane specimens (6 cm × 1.5 cm) were stretched at a constant rate (2 mm min^{-1}) until failure. The tensile stress *vs.* strain data was used to estimate the ultimate tensile strength and the elongation (strain) at break for each sample.

***Ex situ* alkali tests**

Samples of each AEM(Cl^-) (*ca.* 10 × 10 cm) were immersed in aqueous KOH (1 mol dm^{-3}) solutions, purged with N_2 for 1 h (to minimise the O_2 and CO_2 contamination of the solutions) and immediately sealed in polypropylene plastic bottles. These sealed bottles were placed in an oven at 80 °C for 28 d. The KOH-aged AEMs were then re-exchanged to the Cl^- forms with aqueous NaCl (1 mol dm^{-3}) and UPW treatment as described above. IEC values were determined using the same methods as described above. Other experiments (spectroscopic, elemental analysis *etc.*) were conducted on the alkali aged AEMs as required (details given below).

Elemental Analysis

Elemental Analyses were performed at the Warwick Analytical Service. In order to evaluate the variation of N or Cl content on the alkali-aged AEM samples, the %loss was calculated according to the formula (%N, %C, and %Cl are %mol values):

$$\%loss(N/C) = 100 \times \left(1 - \frac{[\%_N / \%_C]_{post-aged}}{[\%_N / \%_C]_{pre-aged}}\right) \qquad \%loss(Cl/C) = 100 \times \left(1 - \frac{[\%_{Cl} / \%_C]_{post-aged}}{[\%_{Cl} / \%_C]_{pre-aged}}\right)$$

Solid-state NMR

Solid-state NMR spectra on the pre- and post-alkali-aged AEMs (and their pre-aminated grafted precursors) were collected at the University of Durham. The ^{13}C and ^{15}N magic-angle spinning spectra were obtained on a Varian VNMRS spectrometer (^1H resonance = 400 MHz). To record spectra of the AEMs, the samples were dried in a relative humidity RH = 0% desiccator to remove excess water. Chemical shifts (δ) are reported in ppm *vs.* the relevant shift references (tetramethylsilane and nitromethane for ^{13}C and ^{15}N, respectively). Other collection parameters are given in the relevant figure captions.

Fuel cell testing

Membrane-electrode assembly (MEA) preparation: The catalysed gas diffusion electrode (GDE) method was used for fabricating the AEMFC electrodes. Prior to formulation of the electrocatalyst ink, a previously synthesised ETFE-based radiation-grafted anion-exchange ionomer (AEI) powder, containing (non-spacer, C1-type) benzyltrimethylammonium functional groups and with an IEC = 1.26 ± 0.06 mmol g^{-1}, was ground with a pestle and mortar for 10 min. This powder was synthesised via the radiation-grafting of VBC onto an ETFE powder (Fluon Z8820X, supplied by AGC Europe) with subsequent amination using TMA [Poynton *et al.*, *J. Mater. Chem. A*, 2014, **2**, 5124]. For the cathode GDE, Pt/C (Alfa Aesar, Johnson Matthey HiSpec 4000, 40%wt Pt) and AEI powder (20%wt of the total solid mass) were mixed together with 1 cm^3 water and 9 cm^3 propan-2-ol. The ink was then homogenised with ultrasound for 30 min. The cathode catalyst ink was sprayed onto a Toray TGP-H-60 carbon paper gas diffusion substrate (Alfa Aesar, non-teflonated) and dried in air. For the anode GDEs, PtRu/C (Alfa Aesar, Johnson Matthey HiSpec 12100, 50%wt Pt and 25%wt Ru) catalyst was used as catalyst instead. The geometric surface areas of all GDEs were 5.0 cm^2 and the Pt loadings for the anodes and cathodes were all 0.40 ± 0.02 mg_{Pt} cm^{-2}(geometric).

All electrodes and AEMs were immersed in aqueous KOH solution (1 mol dm^{-3}) for 1 h and then washed in water (to remove all excess KOH ions) before assembly between two graphite plates using 5 N m torque (no prior hot-pressing of the membrane electrode assembly (MEA) was used: the lamination of the electrodes to the AEM occurs *in situ*). Each MEA consisted of an anode, cathode and the AEM under test.

Fuel cell performance data collection: An 850e fuel cell test station (Scribner Associates, USA) was used for testing. The fuel cell temperature was controlled at either 60 °C, 70 °C or 80 °C. H_2 and O_2 gas feeds were supplied to the anode and cathode, respectively, with flow rates of 1 dm^3 min^{-1} (SLPM) with no back-pressurisation: both gas feeds contained 10 ppm CO_2 by the time they had been piped to the fuel cell testers. The gas relative humidities employed were 68 %, 84 % and 92 % for 60 °C, 70 °C and 80 °C, respectively. The MEAs were activated by controlling the cell voltage at 0.5 V during cell heating with retention of this cell voltage until a steady current density was observed. Beginning-of-life AEMFC performance data were collected under controlled galvanostatic discharge steps where data (at each current density) was only recorded once the potentials had stabilised.

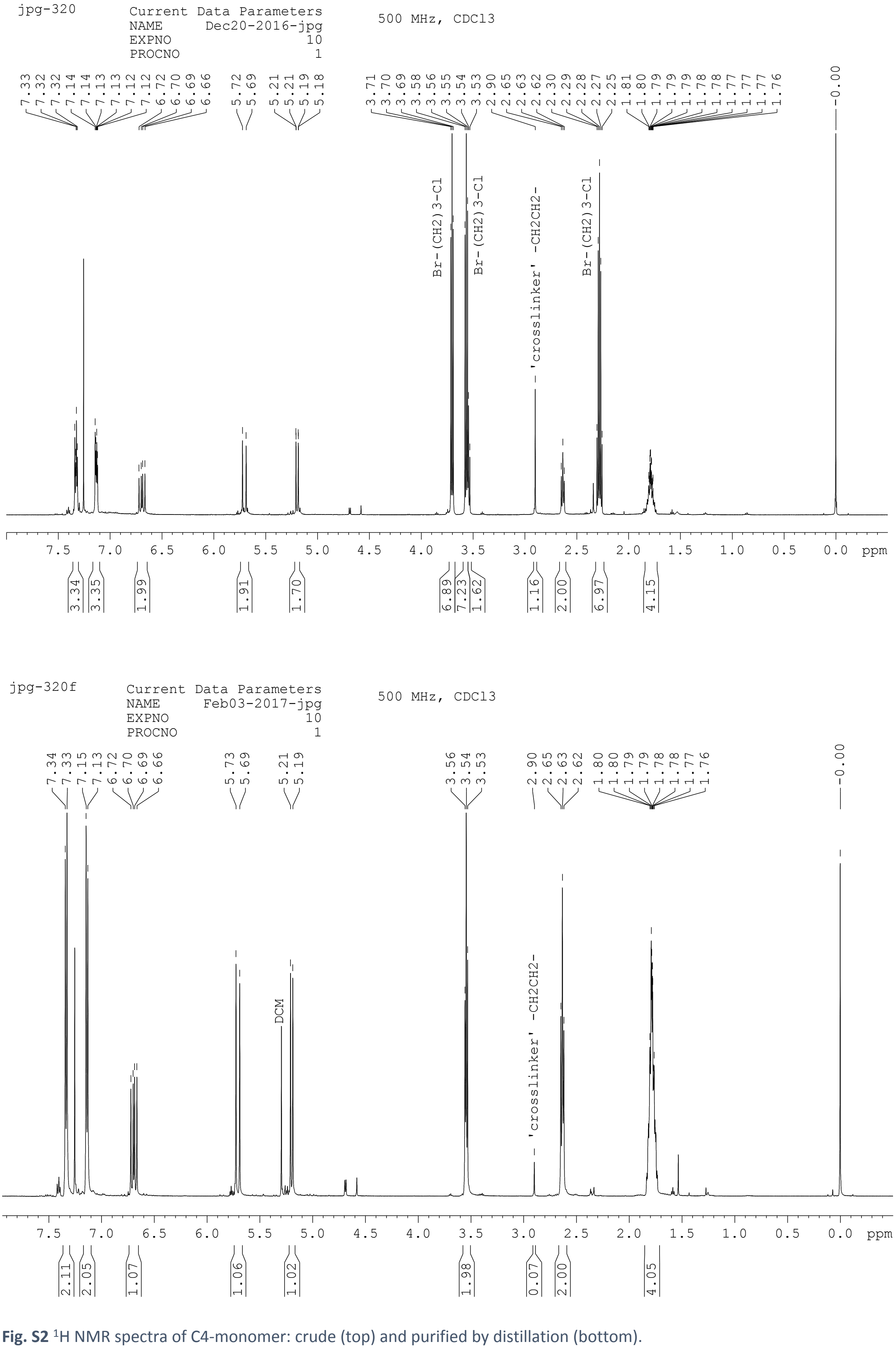


Fig. S2 ^{1}H NMR spectra of C4-monomer: crude (top) and purified by distillation (bottom).

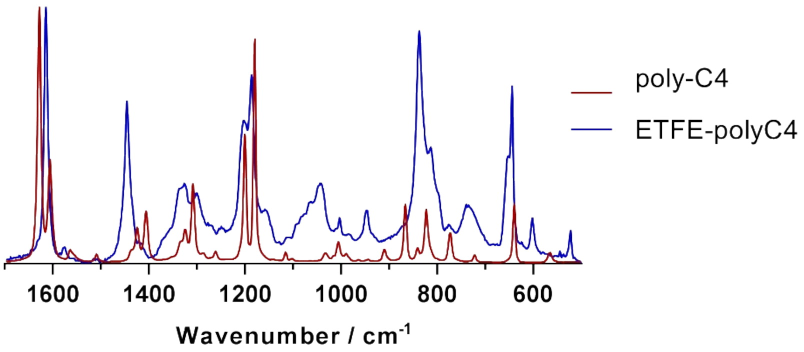


Fig. S3 Raman spectra of C4-monomer homopolymer (dark red) and ETFE-polyC4 (blue). Laser λ = 532 nm.

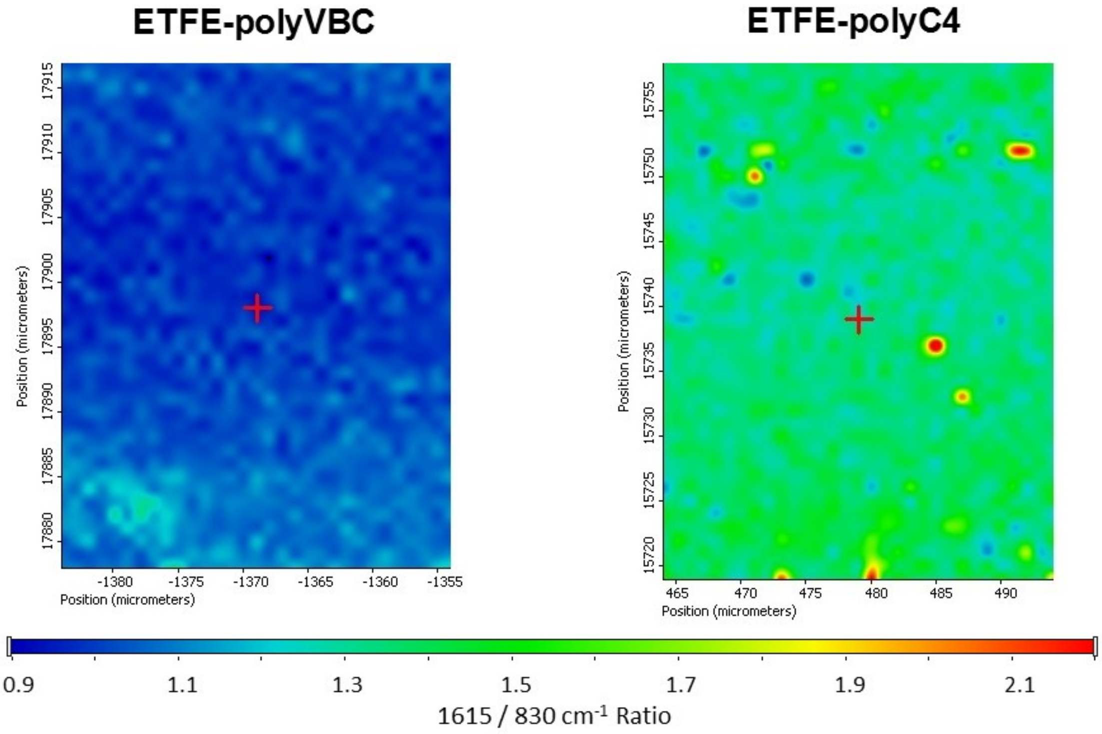


Fig. S4 2D cross-sectional Raman maps of both (pre-aminated) grafted membranes. Laser λ = 532 nm. The numbers on the scale-bar represent the band area ratio of the 1615 cm^{-1} / 830 cm^{-1} (aromatic ring / ETFE moieties): note the intrinsic intensity of the 1615 cm^{-1} band is different for the different monomers so this Raman map data does not indicate higher levels of grafting with the C4-monomer (this data is just an indication of grafting homogeneity through the membrane cores).

Table S1 Data from the optimisation study for the amination of ETFE-polyVBC using *N*-methylpyrrolidine (MPY). All AEMs were prepared from the same batch of ETFE-polyVBC intermediate (83% degree of grafting).

Temperature / °C	MPY concentration in UPW (%$_{vol}$)	Amination time / h	IEC / mmol g^{-1}
60	50	24	2.06 ± 0.06
60	20	24	1.99 ± 0.04
60	10	24	1.91 ± 0.02
60	20	16	2.02 ± 0.03
60	20	6	2.07 ± 0.01
60	15	6	2.09 ± 0.06

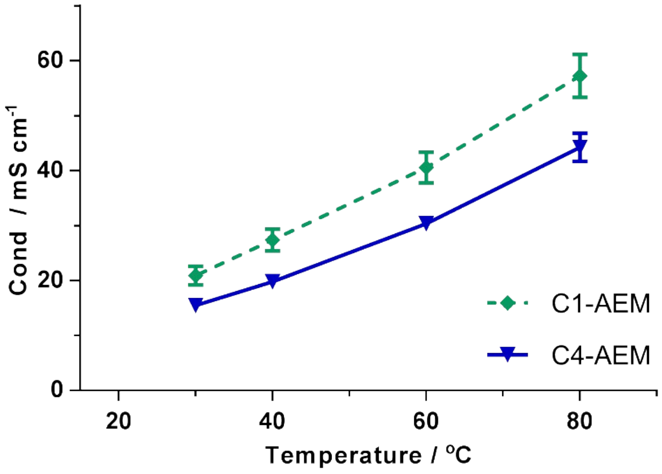


Fig. S5 Cl$^-$-anion conductivities (4-probe, in-plane, measured in water) for both AEMs. Errors bars are from repeat measurement on n = 3 samples of each AEM.

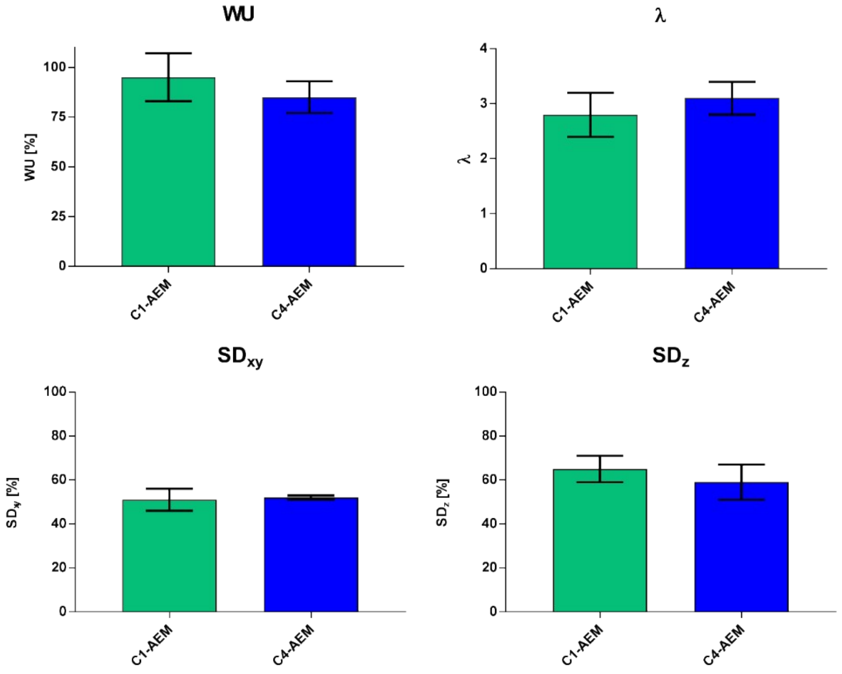


Fig. S6 Graphical comparision of the key properties of both AEMs.

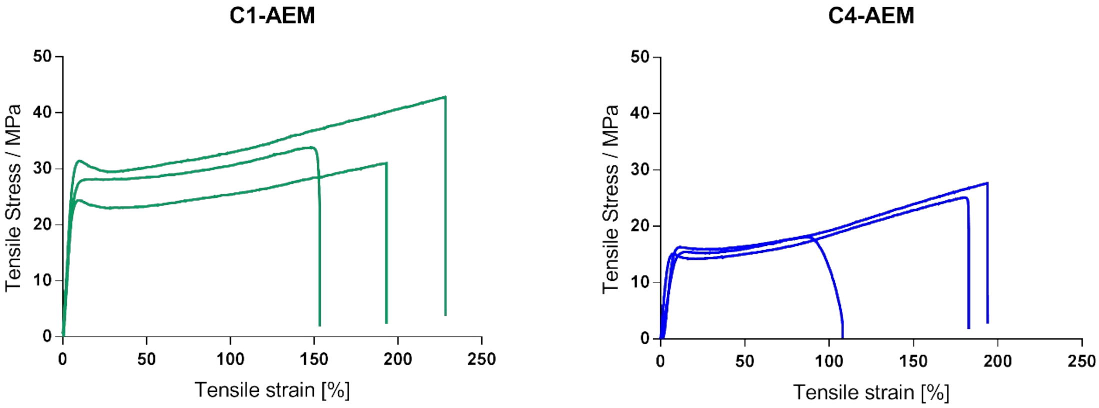
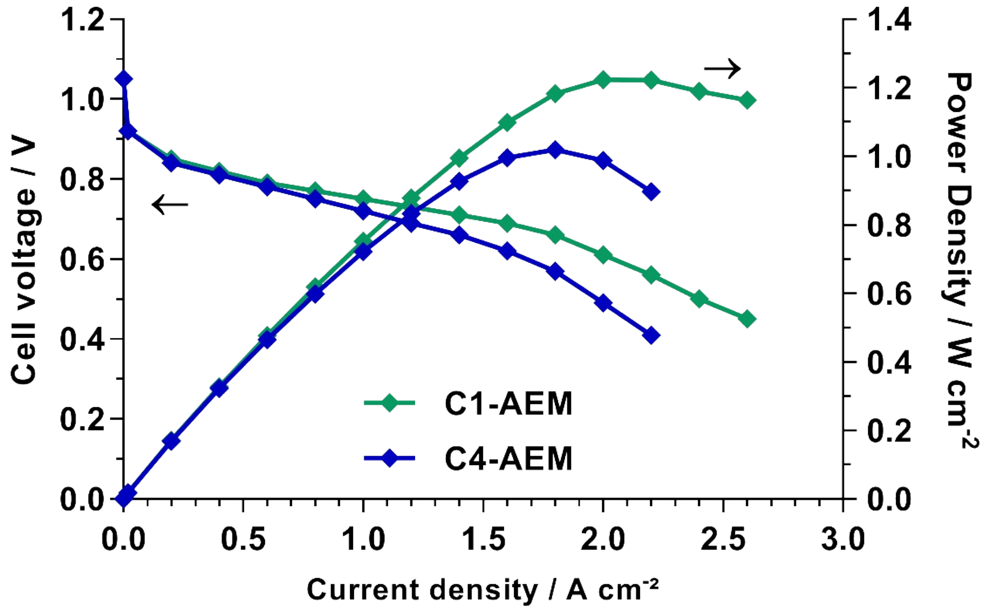


Fig. S7 Tensile stress-strain curves obtained at room temperature with n = 3 samples of each AEMs.

Table S2 Tensile mechanical properties of both AEMs (extracted from the data in Figure S7 above).

	C1-AEM	**C4-AEM**
Young modulus / MPa	5.0 ± 0.9	2.7 ± 0.7
Stress at break / MPa	34 ± 8	23 ± 5
Elongation at break (%)	190 ± 40	154 ± 58



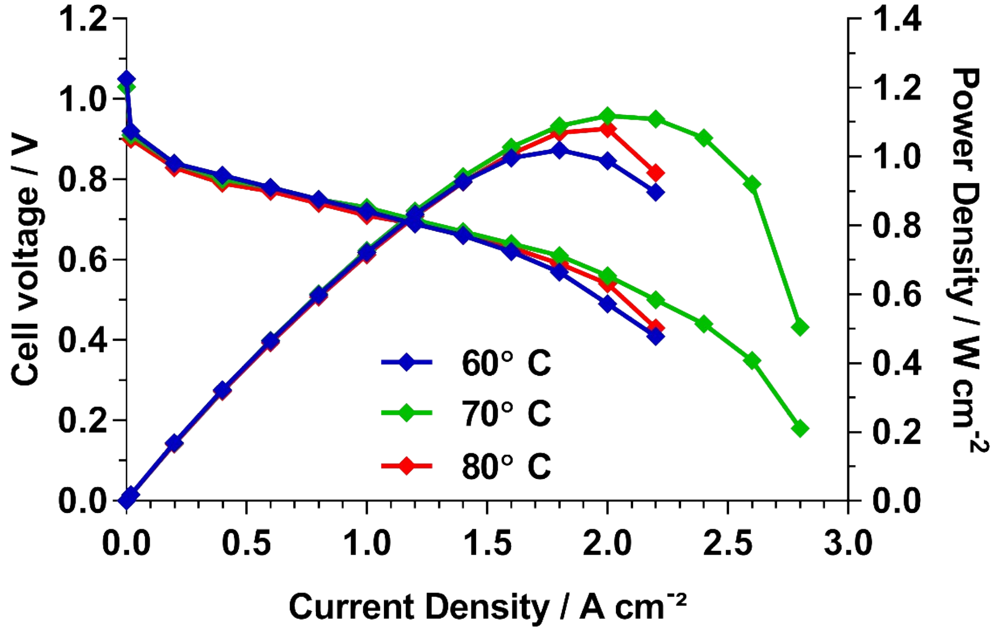
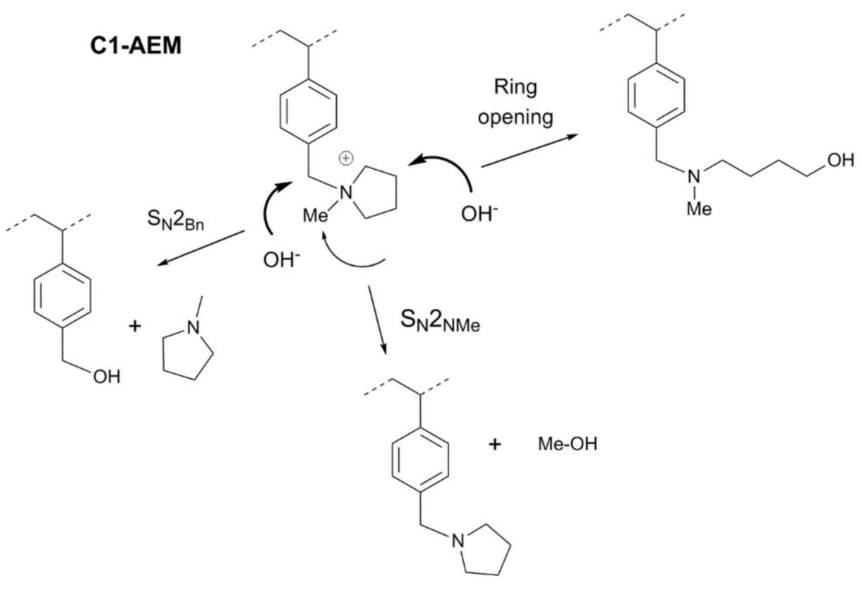


Fig. S8 Beginning-of-life H_2/O_2 AEMFC performances: (top) with both AEMs at 60 °C and (bottom) with **C4-AEM** at different temperatures (bottom). PtRu/C anodes and Pt/C cathodes (all 0.4 mg_{Pt} cm^{-2} loadings). All gases supplied at 1 SLPM. The gas relative humidities employed were 68 %, 84 % and 92 % at 60 °C, 70 °C and 80 °C, respectively.

C1-AEM



C4-AEM

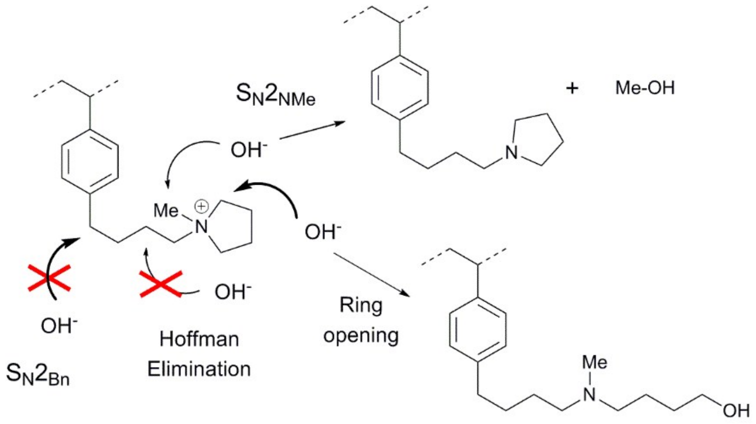


Fig. S9 The alkali degradation mechanisms for **C1-AEM** and **C4-AEM** that were discussed in the main paper.

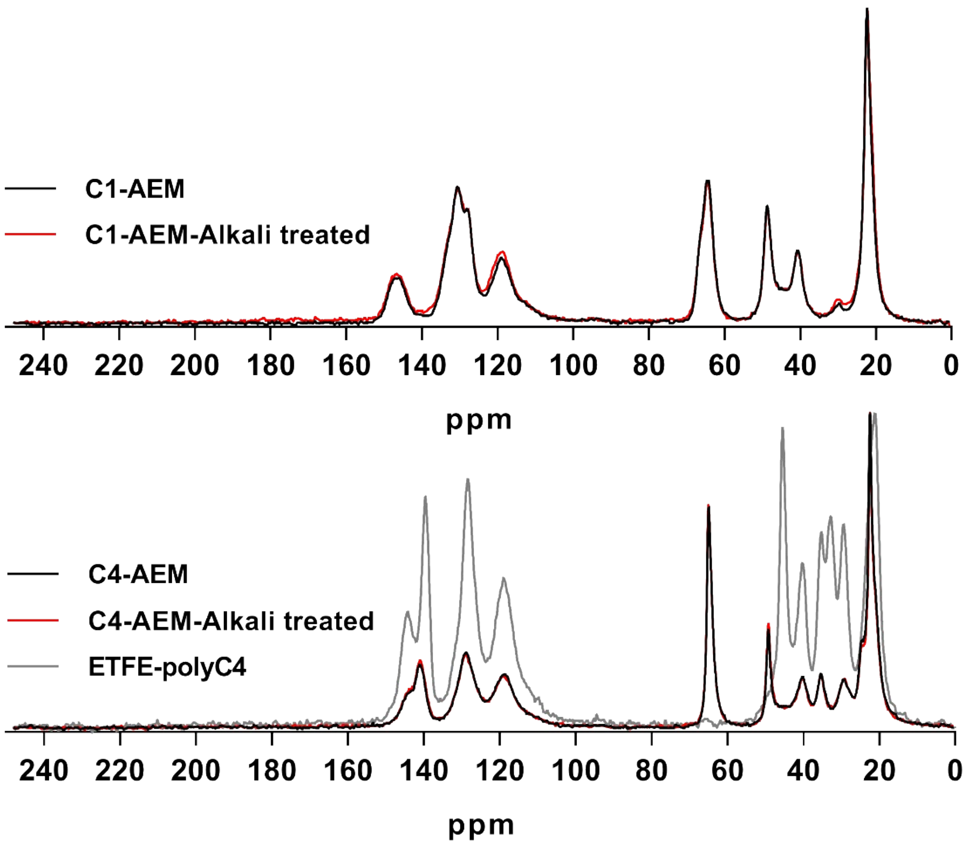


Figure S10 ^{13}C SS-NMR spectra of the AEMs before (black) and after the alkali treatment (red) in aqueous KOH (1 mol dm^{-3}) at 80 °C for 28 days. The spectrum of ETFE-polyC4 is plotted in grey (bottom panel). All spectra have been normalized to the intensity of the $\delta = 22$ band (corresponding to the methylene CH_2 groups in the ETFE backbone) for visual comparison.

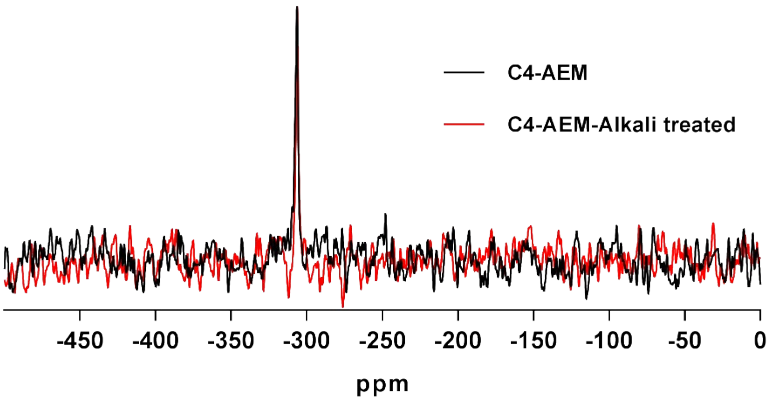


Figure S11 ^{15}N SS-NMR spectra of the before and after alkali treatment.