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Electronic Supplementary Information: Non-fluorinated pre-irradiation-grafted (peroxidated) LDPE-based anion-exchange membranes with high performance and stability

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This document contains addition figures in support of the main article.

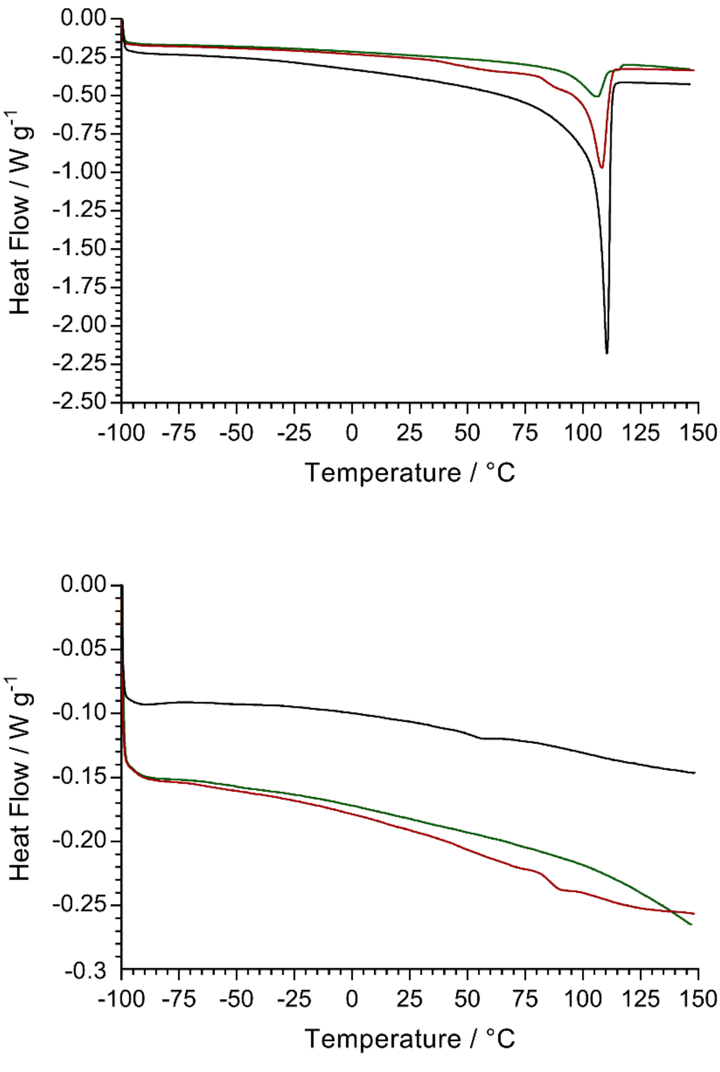

Figure S1 (Top graph) Differential scanning calorimetry (DSC) data for the pristine LDPE (black – bottom plot), the intermediate LDPE-*g*-poly(vinylbenzyl chloride)(100 kGy) intermediate membrane (red – middle plot), and the final LDPE-AEM(100 kGy) (green – top, least intrense plot). (Bottom graph) DSC data for the pristine ETFE (black – top plot), the intermediate ETFE-*g*-poly(vinylbenzyl chloride)(30 kGy) intermediate membrane (red – bottom plot), and the final ETFE-AEM(30 kGy) (green – middle plot). This is uncorrected raw data (*i.e.* not normalised) from the 2nd heating cycle. A heating rate of 10°C / min was used.

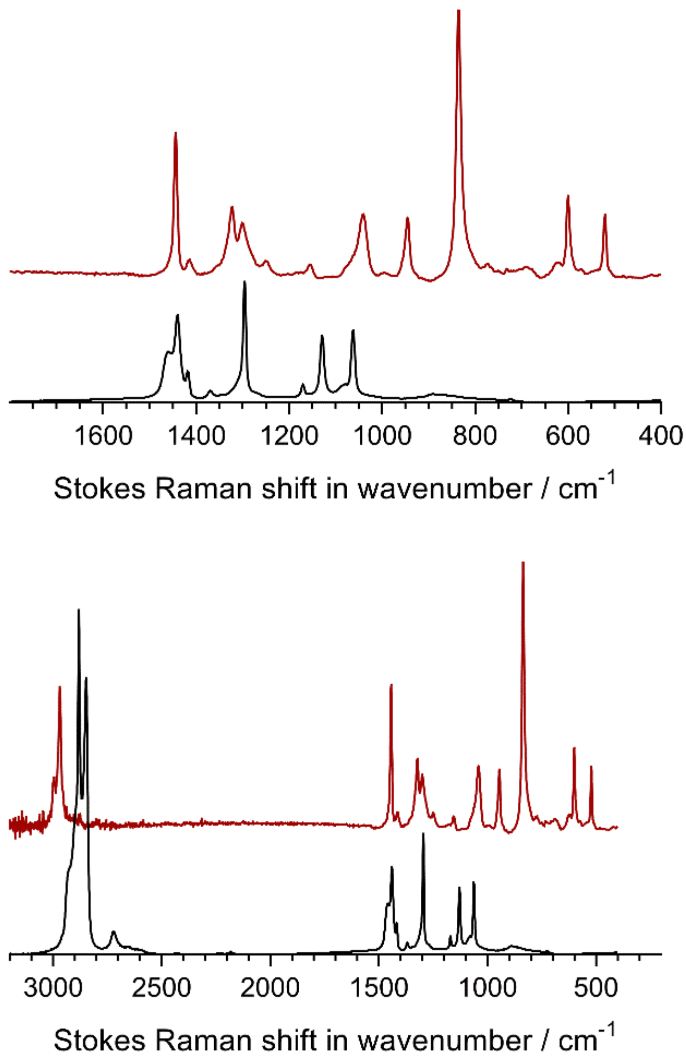

Figure S2 The Raman spectra of the pristine LDPE (black) and ETFE (red) precursor films used to make the radiation-grafted anion-exchange membranes (RG-AEM) in this study: (left) wavenumber range of most diagnostic value; (right) full wavenumber range.

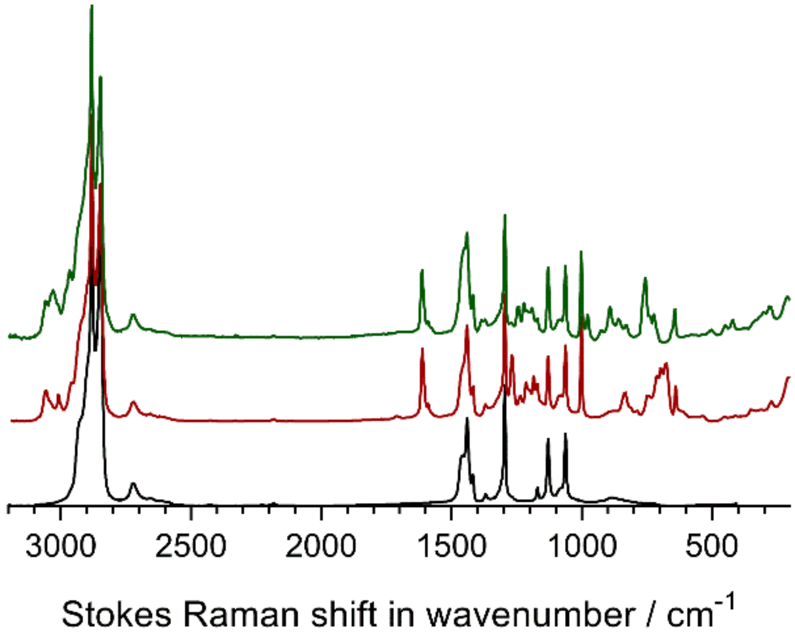

Figure S3 The Raman spectra of the precursor LDPE film (bottom), the LDPE-*g*-poly(VBC) intermediate film (middle) and the LDPE-AEM(100 kGy) (top). All RG-AEMs were in the Cl^- anion form. The spectra were recorded with a 532 nm (green) laser. All spectra were normalised to the intensity of the 1130 cm^{-1} peak to aid visual comparison.#

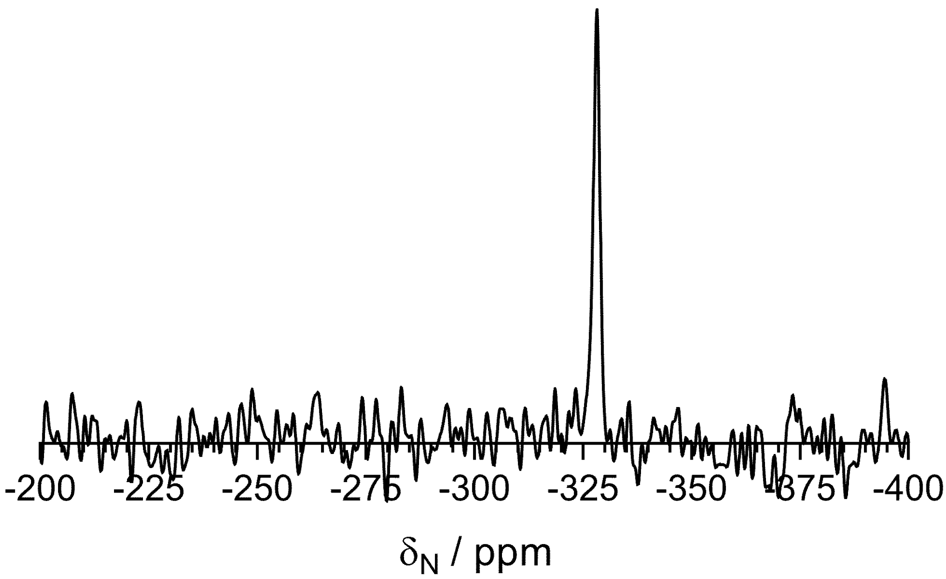

Figure S4 The ^{15}N solid-state NMR of the LDPE-AEM(100 kGy) in the Cl^- anion form. Nitromethane was used as the shift reference. Magic angle spinning rotation rate = 8 kHz.

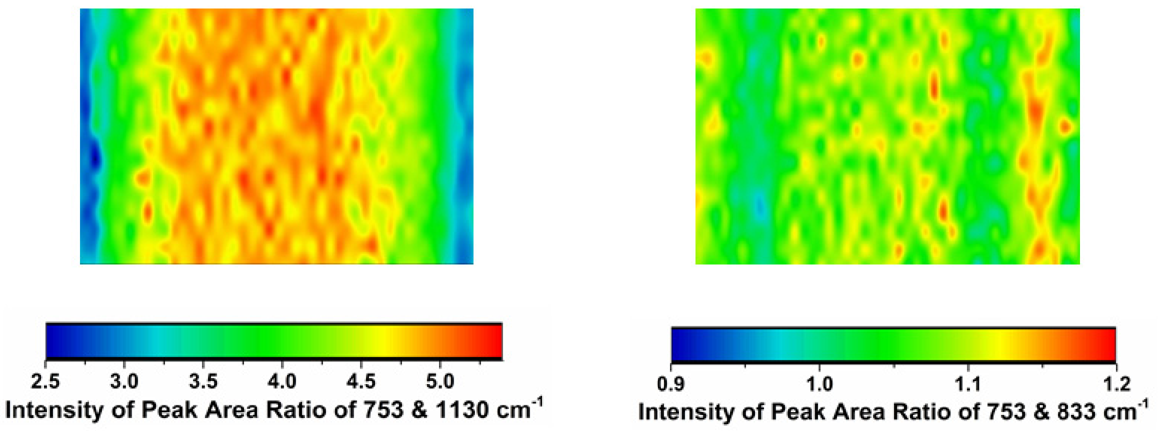

Figure S5 The Raman micrographs showing the trimethylammonium distributions in the RG-AEMs: (left) 753 cm^{-1} (relates to the trimethylammonium group) *vs.* 1130 cm^{-1} (relates to the LDPE backbone) gives an indication of the level of amination distribution through the cross-section of LDPE-AEM(100 kGy); (right) 753 cm^{-1} *vs.* 833 cm^{-1} (relates to the ETFE backbone) gives an indication of the level of amination distribution through the cross-section of ETFE-AEM(30 kGy). The laser was used was of λ = 532 nm.

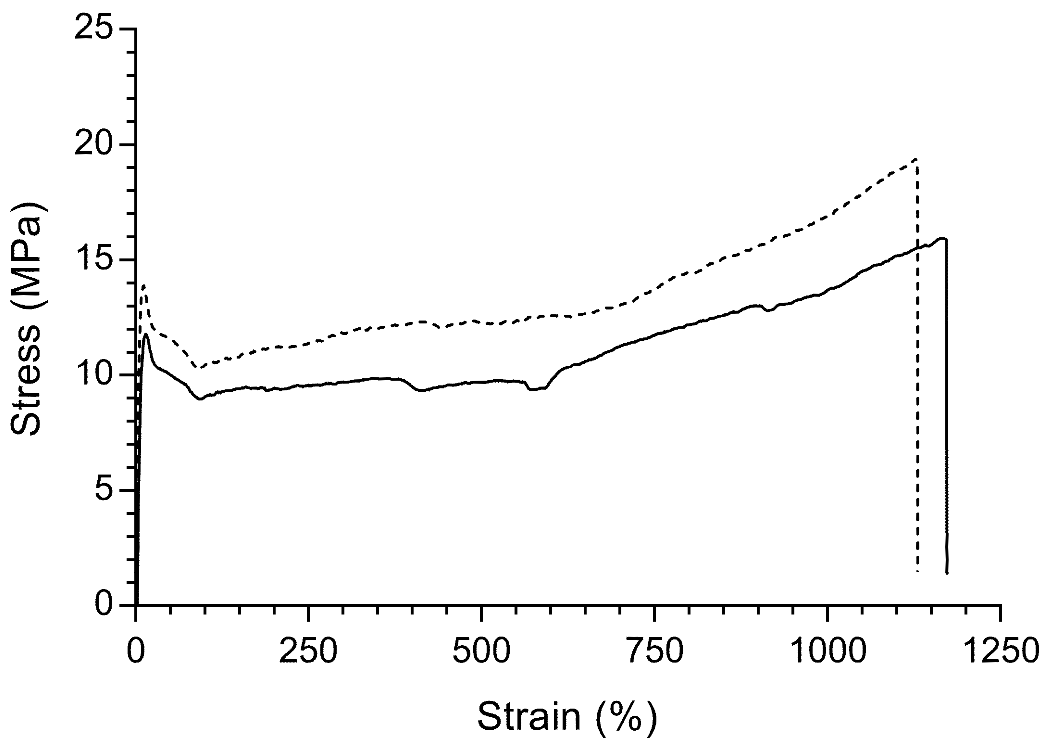

Figure S6 Tensile stress-strain curves for the precursor LDPE before (solid) and after (dashed) exposure to 100 kGy electron-beam absorbed dose.

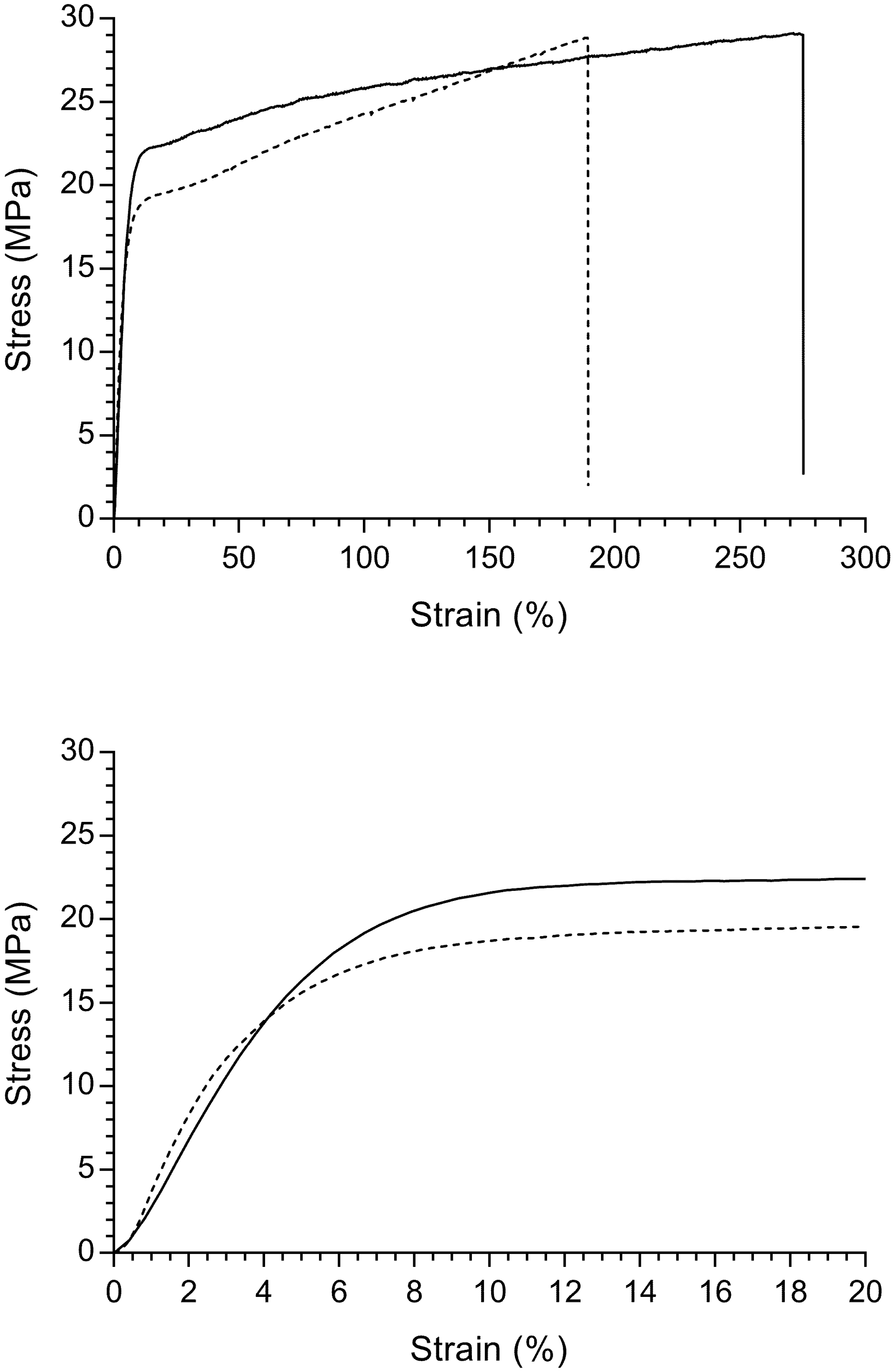

Figure S7 Tensile stress-strain curves for LDPE-AEM(100 kGy) (solid) and ETFE-AEM(30 kGy) (dashed), where the RG-AEMs were in the Cl^- anion forms (dehydrated).

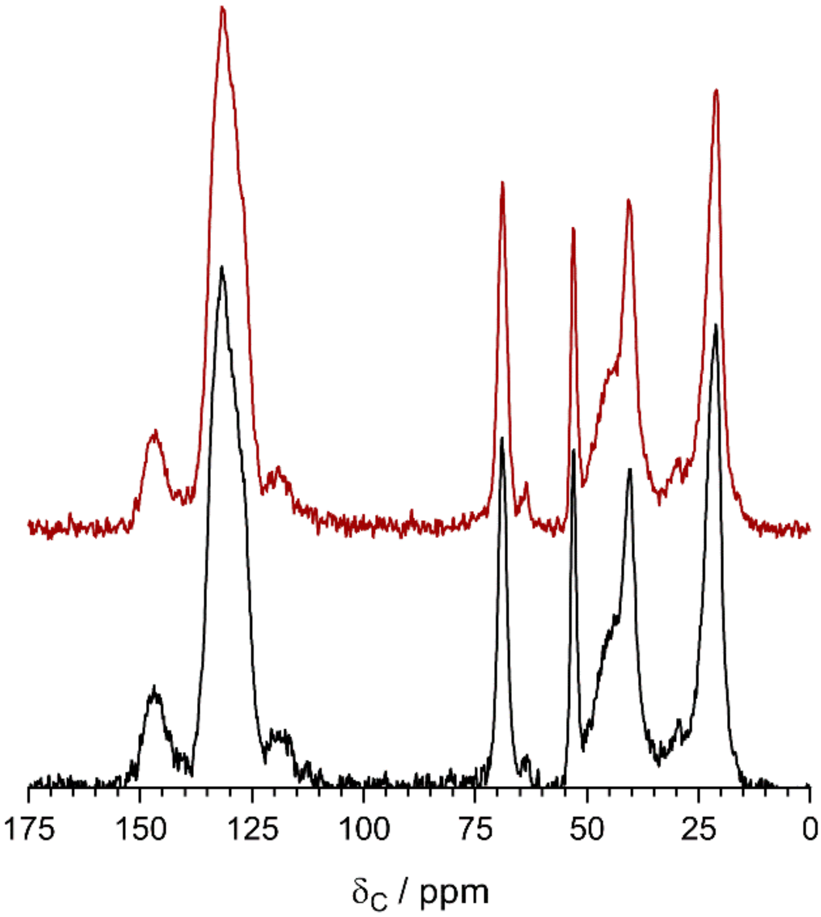

Figure S8 The ^{13}C solid-state NMR of the ETFE-AEM(30 kGy) before (bottom spectra) and after ageing in aqueous NaOH (1 mol dm^{-3}) 80°C for 7 d (top spectra). Tetramethylsilane was used as the shift reference. Magic angle spinning rotation rate = 10 kHz. The NMR spectra were normalised to the δ = 22 ppm to aid visual comparison.

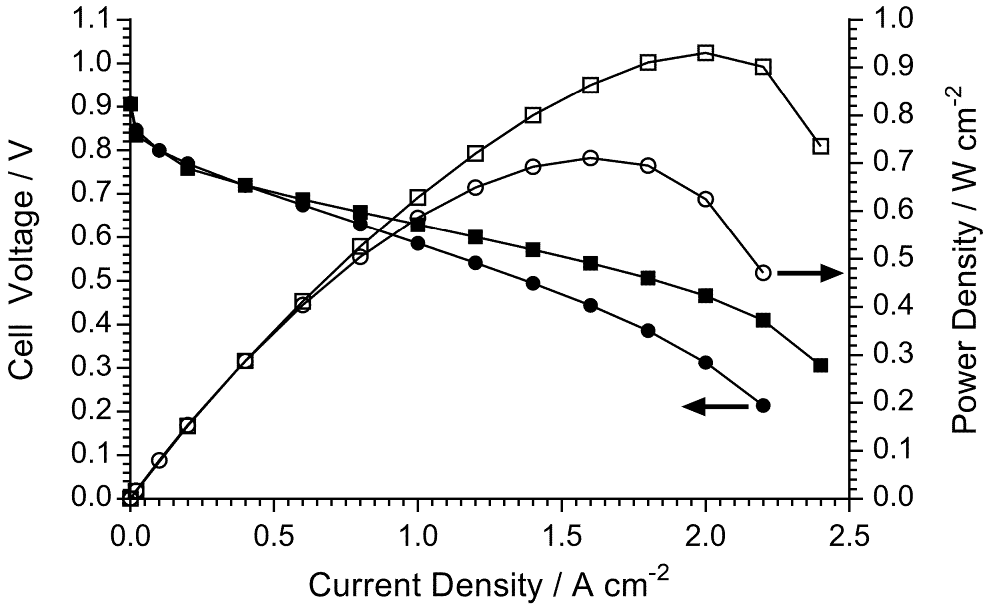

Figure S9 The beginning-of-life H_2/O_2 AEMFC performance of the LDPE-AEM(100 kGy) with a Ag/C (0.8 mg cm^{-2}) cathode at 60°C (●,○) and 80°C (■,□): PtRu/C(50%wt Pt and 25%wt Ru) anodes (0.4 mg_{Pt} cm^{-2} loading). The 1.0 SLPM (RH = 100%) gas supplies were not pressurised.

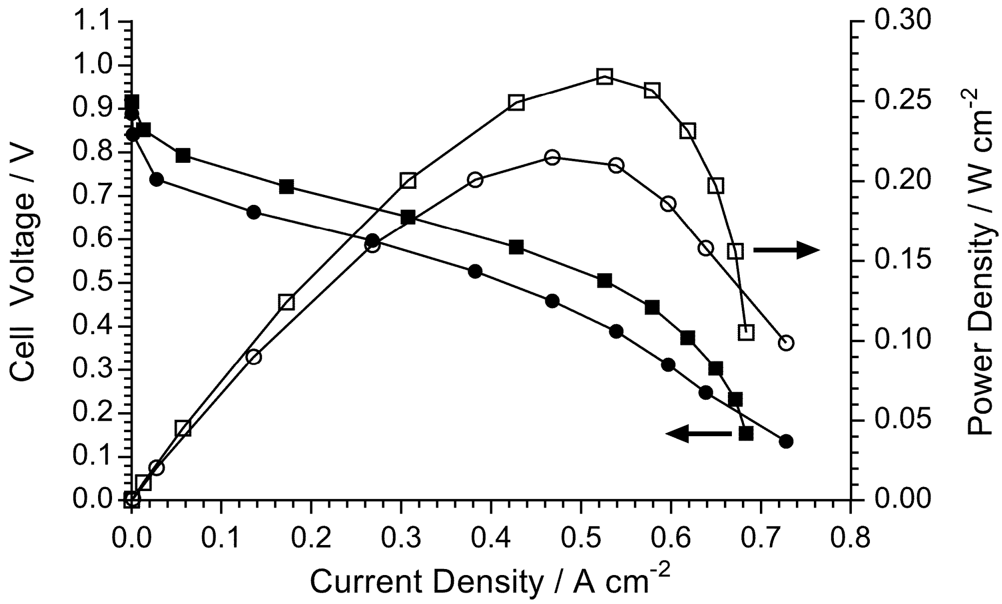

Figure S10 The beginning-of-life H_2/O_2 AEMFCs performances with an ETFE-AEM (60 µm hydrated thicknesses) at 60°C with Ag/C (40%wt Ag, 0.8 mg_{Ag} cm^{-2}) (●,○) and Au/C (40%wt Au, 0.8 mg_{Au} cm^{-2}) (■,□) cathodes: PtRu/C(50%wt Pt and 25%wt Ru) anodes (0.4 mg_{Pt} cm^{-2} loading). The same ETFE-AEI powder was used as for the other AEMFC tests in this study. The 1.0 SLPM supplies were not pressurised: the dew point temperatures for the Ag/C test were 59°C and for the Au/C test were 57°C.

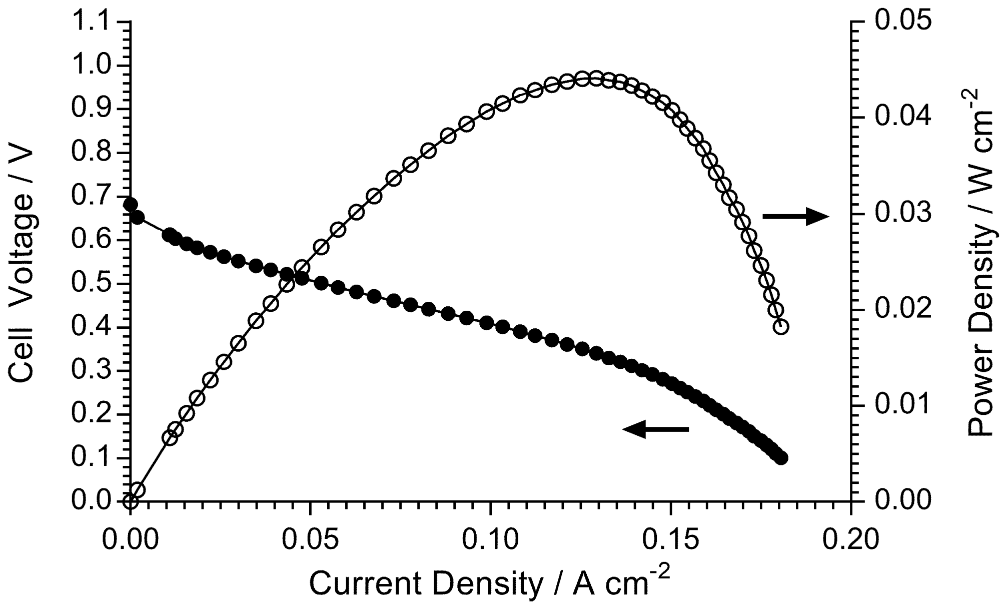

Figure S11 H_2/O_2 AEMFC performance with an ETFE-AEM (60 µm hydrated thicknesses) at 60 °C with a metal-free XC-72 Carbon (100%wt C, 0.4 $mg_C cm^{-2}$) cathode along with a PtRu/C(50%wt Pt and 25%wt Ru) anode (0.4 mg_{Pt} cm^{-2} loading). The 1.0 SLPM supplies were not pressurised: the dew point temperatures for the test were 60 °C (RH = 100%).

Table S1 A summary of the tensile mechanical properties of the pre- and post-degraded LDPE-AEM(100 kGy) and ETFE-AEM(30 kGy).

	Stress at break /MPa	**Elongation at break (%)**	**Young's modulus / MPa**
LDPE-AEM(100 kGy)	29.3	276	386
ETFE-AEM(30 kGy)	28.9	189	412
Degradated LDPE-AEM (60 °C)	23.4	337	141
Degradated ETFE-AEM (60 °C)	24.1	128	334
Degradated LDPE-AEM (80 °C)	23.2	293	143
Degradated ETFE-AEM (80 °C)	20.4	15.7	332