Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplemental Information (ESI): The first anion-exchange membrane fuel cell to exceed 1 W cm^{-2} at 70 °C with a non-Pt-group (O_2) cathode

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Experimental Procedures

Chemicals and materials

ETFE film (12.7 µm thickness) was purchased from Polyflon Technology Limited (UK). Vinylbenzyl chloride monomer (VBC, 97%, mixture of 3- and 4-isomers) was used without removal of the inhibitor (50–100 ppm tert-4-butylcatechol and 700–1100 ppm nitromethane) and was supplied by Sigma-Aldrich (caution – potential mutagen). 1-Octyl-2-pyrrolidone (dispersant) and aqueous trimethylamine solution (TMA, 45%wt) were also purchased from Sigma-Aldrich. Reagent grade toluene and propan-2-ol were supplied by Fisher Scientific (UK). All chemicals were used as received and the ultra-pure water (UPW) used was of 18.2 MΩ cm resistivity.

Radiation grafting (peroxidation) of VBC onto ETFE

The ETFE-based radiation-grafted anion-exchange membrane (ETFE-AEM) was prepared from pre-formed ETFE film using the pre-irradiation grafting in air method (peroxidation) that has been previously reported.[1] The ETFE film was subjected to high dose rate e^--beam irradiation in air using a 4.5 MeV Dynamatron Continuous Electron Beam Unit (STERIS Synergy Health, South Marston, UK) with absorbed doses controlled by the number passes (10 kGy per pass). The ETFE film was exposed to a 30 kGy absorbed dose. As the irradiation step is performed in air, immediate reaction of the radicals that are formed on radiolysis, with O_2 molecules in the air leads to the creation of peroxide groups on the polymer chains in the films. The peroxidated ETFE film can then act as a solid-state free-radical initiator for the subsequent graft polymerisations (see below). After irradiation, the films were transported back to the laboratory in dry ice and they were then stored in a freezer at −40 °C.

For the grafting step, the e^--beam-treated film (15 × 15 cm in area) were immersed in aqueous mixtures containing VBC (5%vol) and 1-octyl-2-pyrrolidone dispersant (1%vol) in glass vessel. The grafting mixtures were then purged with N_2 for 2 h before the vessels were sealed and heated at 70 °C for 3 h. After the grafting reactions were complete, the film were removed from the solution and thoroughly washed with toluene: this process is employed to remove excess unreacted VBC and any traces of surface-bound VBC homopolymer that may be present. The resulting intermediate VBC-grafted films were subsequently dried at 70 °C for 5 h in a vacuum oven to remove all traces of solvent. The degree of grafting (DoG, %) of the intermediate membranes was calculated as follows:

$$\mathrm{DoG} = \frac{m_g - m_i}{m_i} \times 100\% \qquad \text{(S1)}$$

where m_g is the mass of grafted sample and m_i is the initial mass of the irradiated films.

Amination to form the ETFE-AEM (in the Cl^- anion form)

The intermediate grafted film was then submerged in the aqueous TMA (45%wt) at ambient temperature for 24 h, before being washed with UPW and subsequently heated in fresh UPW: this procedure was adopted to remove any excess TMA. Final assurance of the Cl^- anion form of the ETFE-AEM was achieved using ion-exchange whereby the AEM was submerged in aqueous NaCl (1 mol dm^{-3}) for 15 h with one change of NaCl solution during this period. The resulting RGAEM was then soaked in water to remove any excess Na^+ and Cl^- co- and counter-ions (such that the only Cl^- anions present were those that charge balance the covalently bound cationic benzyltrimethylammonium groups). The as-synthesised ETFE-AEM was stored in UPW until required and were not allowed to dry out at any point before other measurements were conducted.

RG-AEM(Cl^-)s characterisation

As a standard procedure, we always characterise our RG-AEMs, for select properties, in the Cl^- anion forms before they have been exposed to any high or low pH environments that may subtly change their properties (e.g. minor degradations) and to eliminate any CO_2 adsorption interference processes (that may occur with $HCO_3^-/CO_3^{2-}/OH^-$ form RG-AEMs). This aids routine determinations of gravimetric water uptake (WU), through-plane swelling (TPS), ion-exchange capacity (IEC), and anion conductivities (σ) that are significantly more repeatable and reliable. The determinations of IEC, WU, TPS, and Cl^- anion conductivities were exactly as described in ref 1 (and will not be repeated here).

Raman spectro-microscopy (quality assurance of cross-sectional graft homogeneity)

The DXR Raman microscope (Thermo Fisher Scientific) used contained a λ = 532 nm (8 mW) excitation laser focused through a confocal microscope. The microscope mode was used to map the different chemical components through a cross-sectional sample of the ETFE_AEM (desiccator dried). A 50 × objective was used yielding a theoretical minimum (Airy disk) laser spot diameter 0.7 µm. Spectra were collected using the OMNIC^{TM} software with the use of the Array Automation function. The cross-sectional area maps of the RG-AEM samples were recorded with sample-stage step sizes of 1 µm in the x and y directions (with the x direction being the cross-sectional, through thickness direction in this study); the vertical z displacement was fixed. A single spectrum at each sampling point was recorded with a spectral range of 3350 – 350 cm^{-1} with averaging of 2 acquisitions per spectrum (10 s per acquisition).

Mechanical testing

The tensile mechanical properties of base films and AEMs were measured using a Instron® 5500 Series Single Colum Testing Systems mechanical testing instrument. In this test, a membrane specimen (6 cm × 1.5 cm) was stretched at a constant rate (10 mm min^{-1}) until breakage. The stress vs. strain data was used to determine the ultimate strength and elongation of the films at break.

Anion-exchange membrane fuel cell (AEMFC) assembly and testing

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 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 was the AEI powder used in previous studies[1,2] and was synthesised via the radiation-grafting of VBC onto an ETFE powder (Fluon Z8820X, supplied by AGC Europe) with subsequent amination using TMA. For the non-Pt cathode GDE, Ag/C (BASF Fuel Cell Inc, 40%wt Ag on Vulcan XC-72) 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, PTFE treated) and dried in air. For the Pt-cathode GDE, Pt/C (Johnson Matthey UK, HiSpec 4000, 40%wt) was used as the electrocatalyst. For all anode GDEs, PtRu/C (Johnson Matthey UK, HiSpec 12100, 50%wt Pt and 25%wt Ru) catalyst was used as electrocatalyst. The geometric surface areas of all GDEs were 5.0 cm^2 and the total metal loading for the anode GDEs was 0.6 mg/cm^2, while the metal loadings for the cathode GDEs were either 0.4 mg_{Pt} cm^{-2} or 1.0 mg_{Ag} cm^{-2}.

All AEI-containing GDEs and ETFE-AEM samples were immersed in aqueous KOH solution (1 mol dm^{-3}) for 1 h followed by a thorough washing with water (to remove all excess K^+ and OH^- ions). The cathode and anode GDEs and AEM to be tested were then immediately assembled between two graphite plates to 4 N m torque with no prior hot-pressing of MEAs. An 850e fuel cell test station (Scribner Associates, USA) was used for controlling the parameters during the testing. The dew-points for the anode/cathode gas supplies were 66 °C/66 °C for the 70 °C single-cell testing (all relative humidities (RH) reported were calculated from the gas dew points and cell temperatures). All followers (heated lines between the fuel cell tester and the fuel cell fixture) were set at the same temperatures as the gas dew points. The H_2, O_2, and CO_2-free air gas feeds were supplied at a 1 dm^3 min^{-1} flow rate with no back-pressurisation (the H_2 was supplied to the anodes of the AEMFCs). The MEAs were activated by controlling the cell voltage at 0.5 V during cell heating from room temperature to the final 70 °C temperature and then retaining this cell voltage until the current density had stabilised. AEMFC activation involves removal of any CO_3^{2-} and HCO_3^- traces from the MEAs that may have formed on assembly of the fuel cell fixtures (after the anion-exchange polymer electrolyte components of the MEAs were converted to the OH^- forms). AEMFC performance data were collected under galvanostatic discharge (data points recorded when the potential had stabilised). The internal ohmic resistances were estimated using the 850e internal current interrupt method.

Raman Micrographs

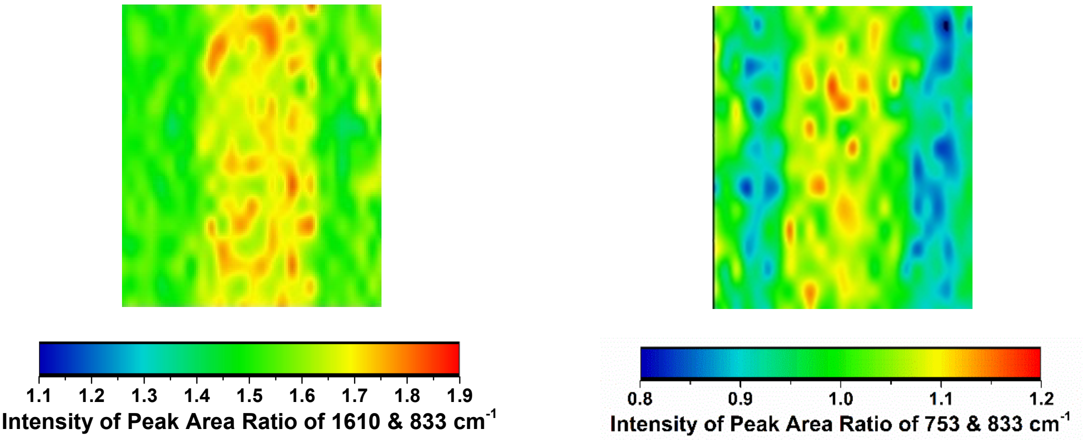

Figure S1 The Raman micrographs showing the cross-sectional distributions of the poly(vinylbenzyltrimethylammonium chloride) grafts through a cross-section (x-axis = through-plane direction) of the ETFE-AEM. The laser was used was of λ = 532 nm. Spatial resolution was 0.7 μm and the spectral resolution was 6 – 8 cm^{-1}. The size of the cross-sectional maps was 22 × 30 μm.

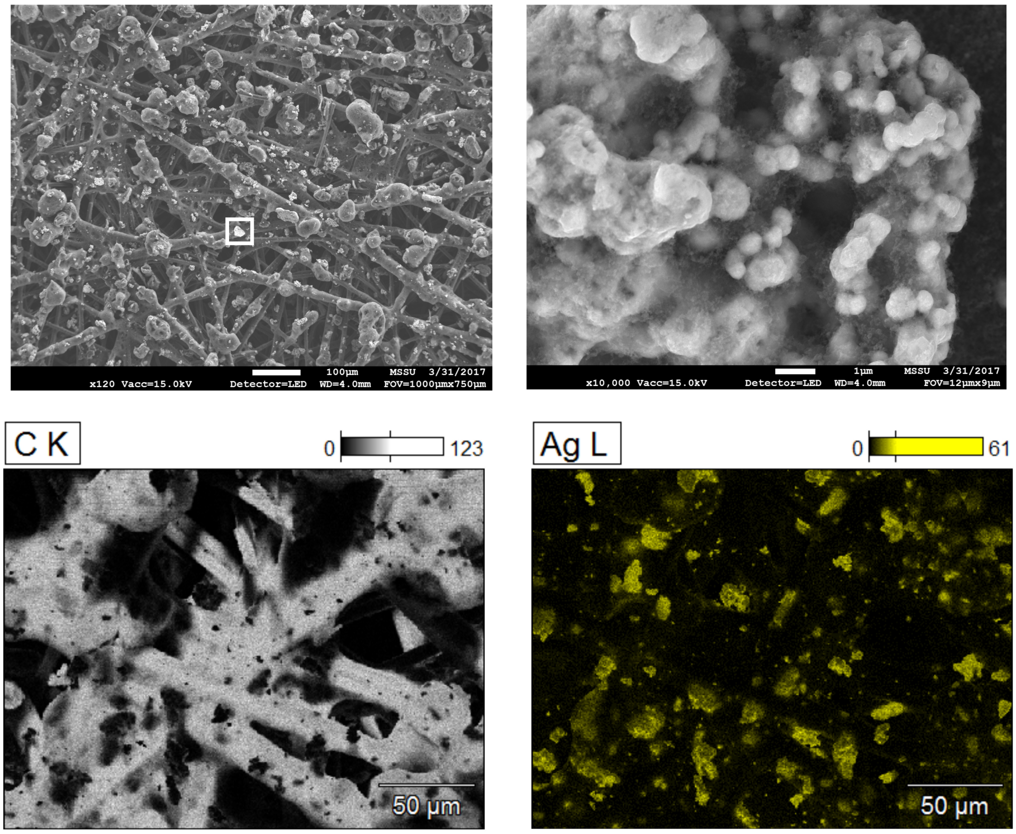

Figure S2 SEM (top row) of the Ag/C(40%wt.) cathode: (left) = 150× magnification and (right) = 10,000× magnification. EDX map data (bottom row) of the same electrode.

Acknowledgements and raw data access

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References to the ESI

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