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Electronic Supplemental Information

The reaction between Nafion sulfonyl fluoride precursor membrane and 1,4–dimethylpiperazine does not yield reliable anion–exchange membranes.

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Additional Experimental Details

Membrane Synthesis and Handling

A **Nafion–SO_2F** membrane (Nafion® PFSA resin R–1100 purchased from Alfa Aesar UK as 50 μm thick extruded films, equivalent weight (EW) 1100 [equivalent to a CEC = 0.91 meq g^{-1}] when converted to the proton–exchange form, product code 46324) was cut into small pieces (total mass in the range 2 – 4 g depending on the batch) and placed into a N_2–purged glass pressure vessel containing a magnetic stirrer bar (vacuum dried at 80 °C for 2 h) that contained a large excess of N_2–purged (20 min) **14DMP** (98% purchased from Sigma–Aldrich, product code D179302–100G). The **14DMP** containing the **Nafion–SO_2F** was quickly re–purged with N_2 for 5 min and the vessel was then sealed under a blanket of N_2. The reaction was left to proceed at room temperature for 144 h with stirring. Variations in **Nafion–SO_2F** + **14DMP** reaction times (3 – 503 h) and temperatures (room temperature, 60 °C and 80 °C) were used to produce the different batches of final **Nafion–DMP(F^-)** membranes. Work up involved removal of the excess **14DMP**, copious washing of the resulting transparent brown membrane with water, and then storage of the membranes in water until required for characterisation. In some cases (see relevant Figure captions), toluene was used to wash the membranes in order to study select membranes that had not been exposed to water.

Ion–exchange of the as–synthesised **Nafion–DMP(F^-)** membranes to the various other anion forms were conducted by immersion of the membranes in excess aqueous solutions containing the desired anions (at least 1 mol dm^{-3} concentrations) over at least 1 d (with at least 2 replacements of the solution over this time period) followed by soaking over at least 1 day in Grade I (18.2 MΩ cm) deionised water (with at least 3 changes of water over this time period). For an example involving conversion to the Cl^- form: An as synthesized **Nafion–DMP(F^-)** was immersed in aqueous NaCl (1 mol dm^{-3}) for 3 d at room temperature with 2 changes of solution in the 3 d period followed by soaking in water over 3 d with more than 6 changes of water over this period). Despite this, the continuous presence of traces of F^- anions (even after long term storage in water [with multiple changes]), that were not present in the pristine 18.2 MΩ cm water that was used to soak the membranes, was observed using ion–chromatography (Dionex ICS5000).

Vibrational Spectroscopy

FT–Raman spectra were recorded on a Perkin–Elmer System 2000 FT–Raman/near–IR spectrometer with a laser power of 1435 ± 5 mW and wavelength of 1064 nm and a resolution of 4 cm^{-1}. Samples were directly mounted in the beam in glass vials under ambient conditions. The spectra of the highly coloured AEMs (Cl^-–form) were recorded with a trace of water in the vials to prevent the laser burning the samples. Note: **Nafion–DMP(F^-)** membranes were so dark in colour when synthesised at elevated temperatures that analysis using Raman spectroscopy became impossible (quality spectra could not be recorded over the severe fluorescence). FTIR spectroscopy was carried out upon a Agilent Cary 640 FTIR spectrometer. Spectra were recorded on RH = 0% desiccator dried AEM samples: ATR spectra were recorded using a Specac Mk II Golden Gate attachment containing a Diamond 45° ATR window and a Sapphire anvil. The scan range was 4000–600 cm^{-1} with a resolution of 4 cm^{-1} and with averaging over 64 repeat scans.

Determination of Ion–Exchange Capacities (IEC)

Anion–exchange capacity Cl^- titrations (AEC).
The anion–exchange capacities of the Cl^- form AEMs were measured using chloride precipitation titrations on a Metrohm 848 Titrino plus autotitrator with Ag–Titrodes. Firstly, multiple samples of each AEM were treated in aqueous KCl (1.0 mol dm^{-3}) for at least 1 day (with at least 3 replacements of the solution in this time period) to ensure the anions in the AEM were fully exchanged to Cl^-. After thorough washing with deionised water (Grade I) at room temperature, the AEM samples dried for at least 4 days in a RH = 0% desiccator that contained anhydrous $CaCl_2$ as desiccant. The dried AEMs samples were weighed and each sample of AEM was immersed in aqueous $NaNO_3$ (50 cm^3, 2 mol dm^{-3}) for at least 24 h in separate polypropylene pots (glass would have risked a potential halide and analytical interference).

After addition of aqueous HNO_3 (3 cm^3, 2 mol dm^{-3}), the solutions, still containing the membrane samples, were titrated with aqueous $AgNO_3$ (0.02000 ± 0.00006 mol dm^{-3}) titrant. The titration endpoint was determined from the maximum gradient of the Ag titrode voltage *vs.* titrant volume plot and this endpoint corresponds to the amount of Cl^- anions in the AEM samples (1:1 titration). The IECs of 3 replicate samples of each AEM were measured. The IEC(Cl^-) / mmol g^{-1} values were calculated using:

$$AEC(Cl^-) = \frac{EP \times 0.0200}{m_d} \quad (1)$$

where EP / cm^3 was the determined end point, 0.0200 was the concentration / mol dm^{-3} of aqueous $AgNO_3$ titrant and m_d / g was the dry mass of each membrane sample (in the Cl^-–form).

Cation–exchange capacity titrations (CEC)

The CEC of the membranes were measured using an acid–base titration method on a Metrohm 848 Titrino plus autotitrator with a pH glass electrode. Firstly membrane samples were converted into the H^+ form by submerging them in aqueous HCl (1.0 mol dm^{-3}) for 24 h with 5 replacements of the solution being made during the time period to ensure full conversion. The samples were then thoroughly rinsed with 18.2 MΩ cm water; each sample was then placed in a polypropylene pot containing 20 cm^3 aqueous NaCl (0.1000 ± 0.0001 mol dm^{-3}). The samples were left stirring at 150 rpm overnight to allow the H^+ ions to be driven from the membrane into solution. The titrand solutions, still containing the membrane samples, were then titrated with aqueous KOH (0.1000 ± 0.0001 mol dm^{-3}) titrant. The endpoint was determined from the maximum in the gradient of the pH *vs.* titrant volume plot, which gives the amount of H^+ ions in solution. The membrane samples were then dried over anhydrous $CaCl_2$ for one week (relative humidity = 0%). The CEC(H^+) / mmol g^{-1} values were calculated using:

$$CEC(H^+) = \frac{EP \times 0.1000}{m_d} \quad (2)$$

where EP / cm^3 was the determined end point, 0.1000 was the concentration / mol dm^{-3} of aqueous KOH titrant and m_d / g was the dry mass of each post–titration membrane sample.

Additional Experimental Results

FT–Raman spectroscopy

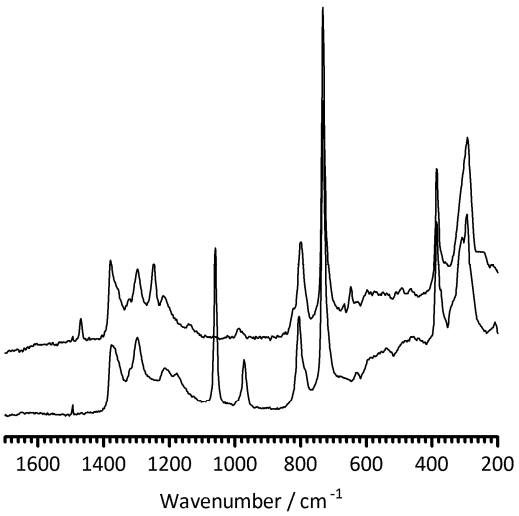

Fig. ESI1 The FT–Raman (in the diagnostic range 1600 – 200 cm^{-1}) spectra of Nafion sulfonyl fluoride precursor membranes (**Nafion–SO_2F**, top) and Nafion–117 proton–exchange membrane (**Nafion–SO_3H**, bottom). For presentational purposes, the spectra were normalised to the strong band at 732 cm^{-1} (symmetrical CF_2 stretch)[1] that is present in both spectra and were then stacked.

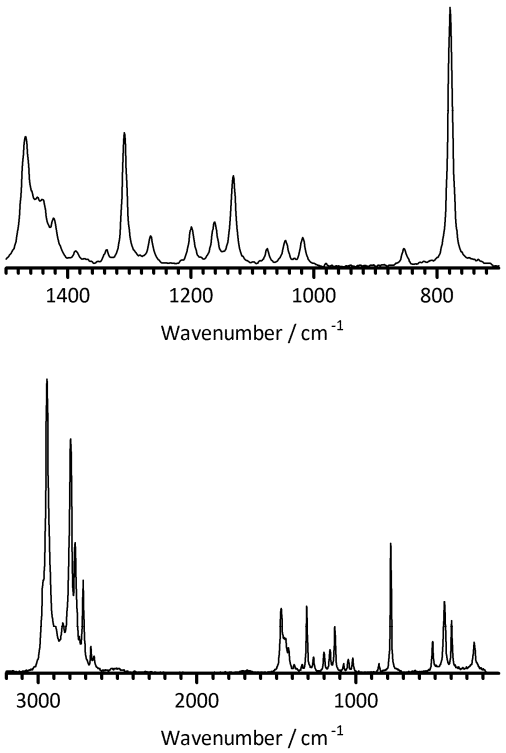

Fig. ESI2 The FT–Raman spectrum of 1,4–dimethylpiperazine (**14DMP**) at different wavenumber ranges.

FTIR spectroscopy

The FTIR spectra of the precursor **Nafion–SO_2F** membrane are shown in Figure ESI3 and are assigned according to prior spectroscopic studies.[1,2] The broad band at 2380 cm^{-1} in the transmission spectrum is a C–F overtone band, whilst the weak band at 2705 cm^{-1} is due to the SO_2F group. The sharp band at 1468 cm^{-1} is the asymmetric O=S=O stretch of the –SO_2F functional group. The very strong bands at 1200 and 1148 cm^{-1} are due CF_2 asymmetric stretches. The strong band at 985 cm^{-1} is either due to –CF_3 groups or the C–O–C ether stretch. The twin peaks at 823 and 796 cm^{-1} are assigned to S–F stretching vibrations.

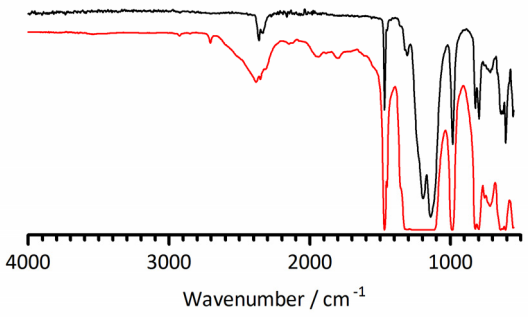

Fig. ESI3 The FTIR ATR spectrum (black) and transmission spectrum (red) of **Nafion–SO_2F**.

The FTIR spectra of the membrane synthesised by the reaction of **Nafion–SO_2F** and **14DMP** at 80 °C and 240 h is given in Figure ESI4. The asymmetric O=S=O (–SO_2F functional group) at 1468 cm^{-1} has decreased in intensity (apparent in the ATR spectrum) and indicates reaction of the –SO_2F groups. There is

also evidence of –C–H stretches and –O–H stretches in the bands above 2700 cm^{-1}. Additional bands at 1671, 1397, 1058, and 907 cm^{-1} are now evident (the 1058 cm^{-1} band is also present as a symmetric $–SO_3^-$ stretch in the FTIR spectrum of **Nafion–SO_3H**).

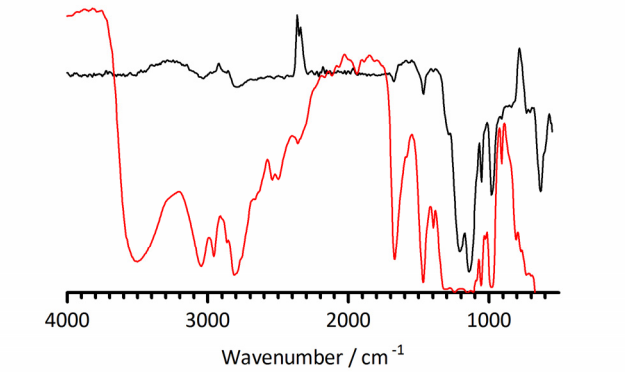

Fig. ESI4 The FTIR ATR spectrum (black) and transmission spectrum (red) of the dark brown membrane synthesised by the reaction of **Nafion–SO_2F** and **14DMP** at 80 °C and 240 h. For the work–up, the membrane was thoroughly washed in toluene, rather than water, and dried in a vacuum oven (only exposed to atmospheric moisture, whilst handling).

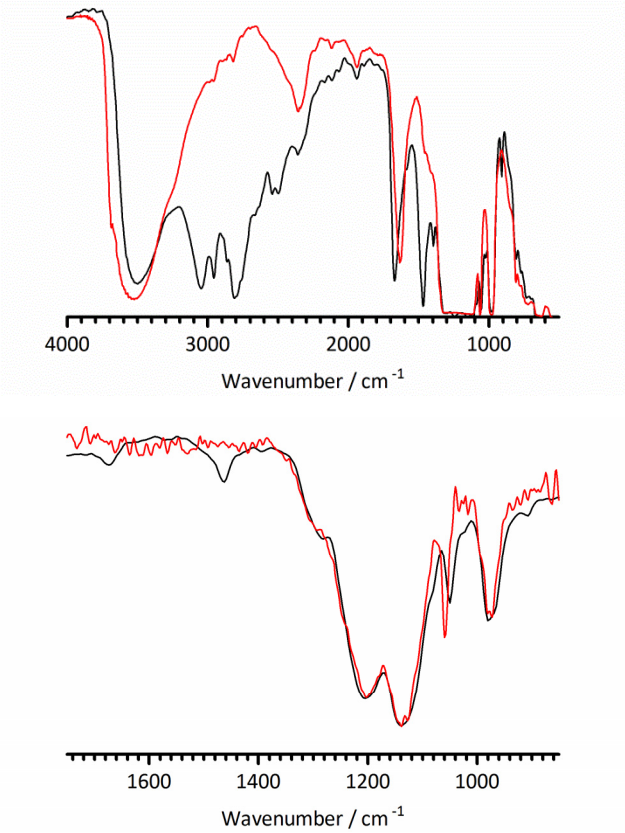

Fig. ESI5 The FTIR spectra of the same membrane as in Figure ESI4 before (black) and after (red) submersion in aqueous KOH (1 mol dm^{-3}) for 7 d at room temperature. Top = transmission and bottom = ATR .

Figure ESI5 shows result of immersing of the **Nafion–SO_2F/14DMP** reacted membrane in aqueous alkali. There is significant evidence of loss of C–H bonds as well as all remaining $–SO_2F$ groups. The band at 1671 cm^{-1} is shifted to 1630 cm^{-1} on alkali treatment. This represents strong evidence of some form of alkali induced change in the membrane.

Solid State NMR Data[3]

The NMR spectra of the **Nafion–SO_2F** and the **Nafion–DMP(F^-)** membrane synthesised at 80 °C and 240 h were collected. The ^{19}F spectra (Figure ESI6) show the expected intense signal at δ_F = –126 and high frequency shoulder, which are due to the backbone $C\underline{F}_2$s. The signal at δ_F = –84 is due to the $–C\underline{F}_2O–$ and $–CF_3$. The signals at δ_F = –149 and 143 are from the $C\underline{F}$–O fluorine nuclei in the side chains and backbone respectively. The S–F signal at δ_F = 40 disappears on reaction with the **14DM** suggesting reaction. The δ_F = –117 due to the $–C\underline{F}_2S–$ merges with the $C\underline{F}_2$ signal on reaction.

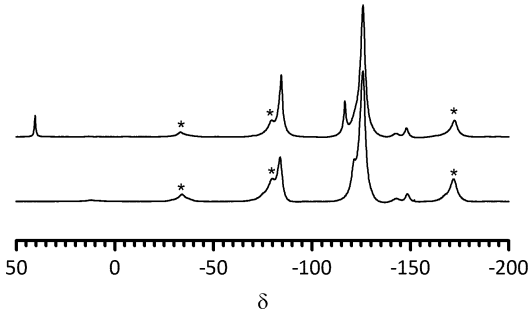

Fig. ESI6 The ^{19}F solid state magic angle spinning NMR spectra (direct polarisation, spin rate 13 kHz, Varian VNMRS 400 spectrometer, $CFCl_3$ shift reference, no decoupling) of the same membrane as in Figure ESI4. * = spinning side bands.

The two signals at δ_C = 53 and 44 in the ^{13}C NMR spectrum of **Nafion–DMP(F^-)** in Figure ESI7 are consistent with $–C\underline{H}_2N$ and $N–C\underline{H}_3$ carbons, respectively These are very close to the δ_C = 46 and 55 observed for **14DMP**. There is no sign of the additional signal splitting expected on quaternisation of 1 of the nitrogens or the δ_C = 36 signal that is predicted (Chemdraw Ultra version 11) for a $–C\underline{H}_3$ carbon bound to a the $N^+–SO_2CF_2–$ nitrogen.

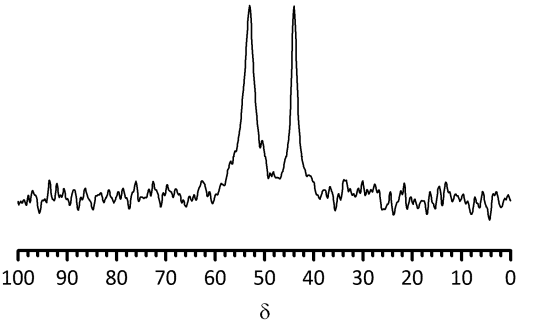

Fig. ESI7 The $^{13}C\{^1H\}$ solid state magic angle spinning NMR (cross polarisation, spin rate 6.8 kHz, Varian VNMRS 400 spectrometer, tetramethylsilane shift reference) spectrum of the same membrane as in Figure ESI4. As expected, no signals observed for the sulfonyl fluoride precursor membrane.

References to the ESI

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2 S. A. Perusich, *J. Appl. Polym. Sci.*, 2011, **120**, 165; A. J. Greso, R. B. Moore, K. M. Cable, W. L. Jarrett and K. A. Mauritz, *Polymer*, 1997, **38**, 1345.
3 Q. Chen and K. Schmidt–Rohr, *Macromolecules*, 2004, **37**, 5995.