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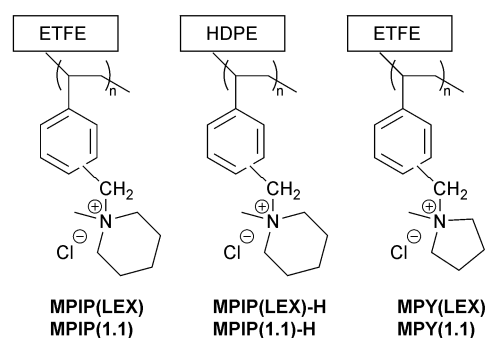
Radiation-grafted anion-exchange membranes for CO₂ electroreduction cells: an unexpected effect of using a lower excess of *N*-methylpiperidine in their fabrication

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Section A: RG-AEMs made with different chemistries (head-group and precursor polymer film)

To see if the different amination methods yield similar water content trends with different RG-AEM chemistries, the following RG-AEMs were made (Scheme S1):

1. MPIP-based RG-AEMs were fabricated from electron-beamed HDPE films¹ [designated MPIP(LEX)-H and MPIP(1.1)-H] using similar procedures to the ETFE-based MPIP(1.1) and MPIP(LEX) but with the following modifications: The HDPE films (Goodfellow, 12 μm thick) were irradiated to 100 kGy total dose in air and the VBC grafting step was conducted at 50 °C and 4 h.
2. ETFE-based RG-AEMs were fabricated from ETFE-g-poly(VBC) membranes (DoG = 73 %) using the same procedures but where *N*-methylpyrrolidine² was used in the amination step [designated MPY(LEX) and MPY(1.1)] instead of *N*-methylpiperidine. The *N*-methylpyrrolidine solutions used to make MPY(LEX) and MPY(1.1) were now pH = 13.1 and 12.0, respectively, which were more alkaline than those of the *N*-methylpiperidine solutions used to make MPIP(LEX) and MPIP(1.1) at pH = 12.4 and 11.6, respectively,



Scheme S1 The chemistries of the RG-AEMs discussed in Section A of this ESI document. Their key properties are presented in Table S1 below.

The successful amination of the ETFE-g-poly(VBC) intermediate membranes with *N*-methylpyrrolidine was confirmed by the disappearance of the 1267 cm⁻¹ -CH₂Cl peak seen in the Raman spectra of the ETFE-g-poly(VBC) and the appearance of the expected MPY-derived peak at 900 cm⁻¹.² The Raman spectra of MPIP(LEX)-H and MPIP(1.1)-H were the expected superposition of poly(vinyl-*N*-benzyl-*N*-methylpiperidinium chloride)-derived peaks and HDPE-derived peaks.

The key properties of these different chemistry RG-AEMs are compared to MPIP(1.1) and MPIP(LEX) in Table S1 below. With the same head-group (MPIP), the HDPE-based RG-AEMs (MPIP(LEX)-H and MPIP(1.1)-H) show the same trend in λ(H₂O) as the ETFE-benchmarks (MPIP(1.1) and MPIP(LEX)), where the LEX-variants have statistically higher water contents than the 1.1-variants. A drop in IEC was also seen with MPIP(1.1)-H compared to MPIP(LEX)-H, as was seen between MPIP(1.1) and MPIP(LEX). A switch in precursor film type (from partially-fluorinated semi-crystalline ETFE to non-fluorinated semi-crystalline HDPE) maintained the observed water content differences between analogous RG-AEMs made using the two different amination methods.

Table S1 Key *ex situ* properties³ of the Cl⁻-form of RG-AEMs made from HDPE + *N*-methylpiperidine or ETFE + *N*-methylpyrrolidine. Errors are sample standard deviations from measurements on n = 3 samples of each RG-AEM

| | MPIP(LEX) | MPIP(1.1) | MPIP(LEX)-H | MPIP(1.1)-H | MPY(LEX) | MPY(1.1) |
|------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Precursor polymer film | 25 μm thick ETFE | | 12 μm thick HDPE | | 25 μm thick ETFE | |
| DoG of grafted precursor (%) | 73 | | 84 | | 73 | |
| IEC / mmol g ⁻¹ | 1.80 ± 0.01 | 1.71 ± 0.03 | 1.59 ± 0.09 | 1.36 ± 0.16 | 1.92 ± 0.04 | 1.83 ± 0.02 |
| Thickness (dry) / μm | 47 ± 2 ^a | 50 ± 2 ^a | 14 ± 2 ^a | 14 ± 2 ^a | 47 ± 2 ^a | 46 ± 2 ^a |
| Thickness (hydrated) / μm | 62 ± 2 ^a | 59 ± 2 ^a | 17 ± 2 ^a | 16 ± 2 ^a | 62 ± 2 ^a | 61 ± 2 ^a |
| TPS (%) | 32 ± 6 ^b | 18 ± 6 ^b | 22 ± 8 ^b | 16 ± 7 ^b | 31 ± 1 ^b | 33 ± 4 ^b |
| AS (%) | 38 ± 3 | 24 ± 3 | 23 ± 8 | 13 ± 3 | 38 ± 2 | 31 ± 1 |
| WU (%) | 77 ± 1 | 33 ± 3 | 57 ± 7 | 27 ± 4 | 50 ± 5 | 47 ± 7 |
| λ(H ₂ O) | 23 ± 1 ^b | 11 ± 1 ^b | 20 ± 3 ^b | 11 ± 2 ^b | 15 ± 2 ^b | 14 ± 2 ^b |

^aErrors are sample standard deviations or 2 μm (the minimum accuracy of the micrometer), whichever is the largest. ^bCalculated propagated errors.

Previous work² with RG-AEMs of comparable IECs fabricated using thicker 50 μm thick ETFE (from the same supplier) indicates that MPIP(LEX) would also be expected to show a higher WU and $\lambda(\text{H}_2\text{O})$ than MPY(LEX), and this is the case here. As the MPY head-groups are lower relative molecular mass compared to the MPIP head-groups, this also means that the MPY-based RG-AEMs will intrinsically have a higher IEC than the MPIP-based RG-AEMs when made from the same ETFE-g-poly(VBC) intermediate membranes:² this is what is observed (e.g. when comparing the IECs of MPY(LEX) to MPIP(LEX)). However, a switch from MPIP head-group chemistry to MPY, whilst using the same batch of ETFE-g-poly(VBC) intermediate membrane, does show a different water content trend when comparing the two amination methods: the differences in $\lambda(\text{H}_2\text{O})$ between MPY(LEX) vs. MPY(1.1) are now minimal (despite the small drop in IEC with MPY(1.1)). The origins of the differing behaviour (cf. MPIP chemistry), such as *N*-methylpyrrolidine being smaller than *N*-methylpiperidine or its solutions being more alkaline, will need to be investigated in more detail in a future study.

Section B: Further CO₂RR test data with MPIP(1.1)-B3 and MPIP(LEX)-B3

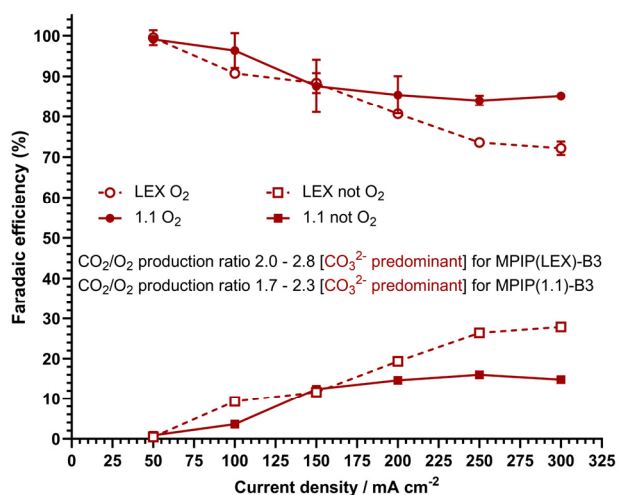


Fig. S1 Anode data for the room temperature galvanostatic CO₂RR cell tests on MPIP(1.1)-B3 and MPIP(LEX)-B3 (2.25 cm² geometric electrode area). The cathode was Ag-based supplied with 30 mL min⁻¹ dry CO₂. The anode was IrO₂-based supplied with aqueous KHCO₃ (0.1 mol dm⁻³) supplied at 40 mL min⁻¹. Error bars are from $n = 3$ repeat cell tests with different samples of each AEM.

Section C: Treatment of electron-beamed ETFE (pre-grafted) with the two *N*-methylpiperidine solutions that were used to make MPIP(1.1) and MPIP(LEX)

A possible source of the differences between MPIP(LEX) and MPIP(1.1) could be degradation of the core ETFE constituent due to a combination of the effect of the high energy electron-beam (causing bond scission and radical/peroxy based side reactions) and exposure to aqueous *N*-methylpiperidine of differing concentrations and pH. To probe this, e⁻-beamed (non-grafted) ETFE was exposed to the different *N*-methylpiperidine solutions at 60 °C (the solutions that were used to fabricate the MPIP-based RG-AEMs). TGA data indicates a lack of significant differences between e⁻-beamed ETFE treated using the different amination methods (Figure S2).

The ¹³C NMR spectra (Figure S3 left) show that there may be a subtle change between the pre-treated and the amine-treated e⁻-beamed ETFE films but there are no detectable differences between the two e-beamed ETFE films treated with the different amine solutions. The ¹⁹F NMR spectra (Figure S3 right) show no discernible differences between all three e⁻-beamed ETFE films (pre- and amine-treated).

Raman analysis of the three e⁻-beamed ETFE films is shown in Figure S4. This also indicates that there is a difference between the pre- and the post-treated films (but that there is no significant difference between the two different 60 °C *N*-methylpiperidine treated films). Note for ETFE, variations in intensities of the bands in the range between 1000 – 1425 cm⁻¹ can be due to changes in crystallinity, so this data indicates both amination conditions used are affecting the crystallinity of the ETFE substrate to an equal extent.

On top of the observation above, showing that HDPE-based RG-AEMs exhibit differing water contents when fabricated with the two different amination methods (MPIP(LEX)-H and MPIP(1.1)-H in Table S1 above), all of this evidence suggests that the origin of the intrinsically different water contents when using two different amination treatments is not down to significant chemical changes in the ETFE constituent of the RG-AEMs.

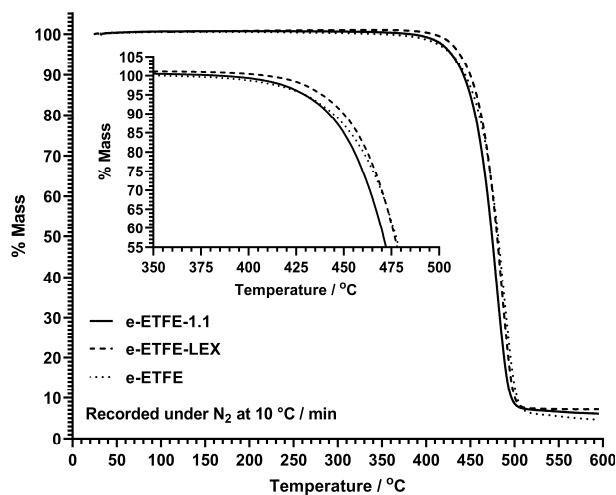


Fig. S2 Thermogravimetric analysis (TGA) of the electron-beamed (pre-grafted) ETFE before and after treatment at 60 °C with the two *N*-methylpiperidine solutions used to make MPIP(LEX) and MPIP(1.1).

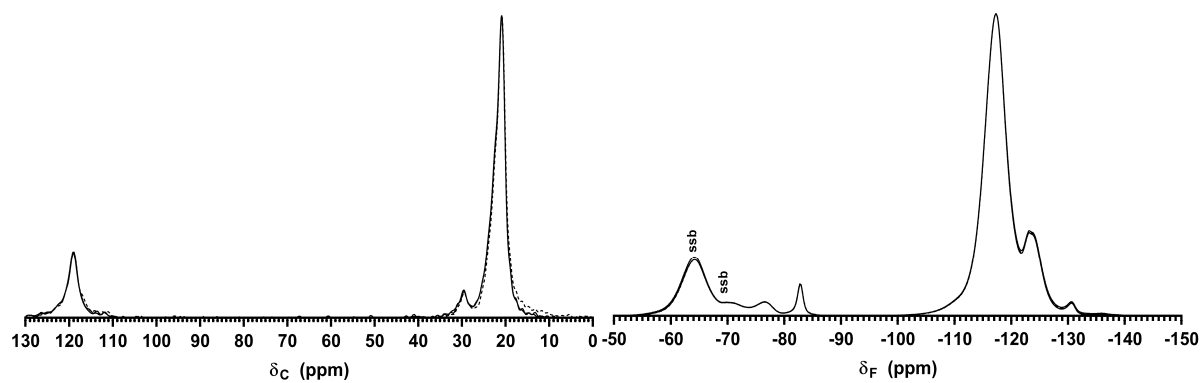


Fig. S3 The ^{13}C (left) and ^{19}F solid-state NMR of e-beamed (40 kGy) ETFE (dashed) and e-beamed ETFE treated at 60 °C with the two *N*-methylpiperidine solutions used to make MPIP(LEX) and MPIP(1.1) (superimposed solid lines). ssb = spinning sideband.

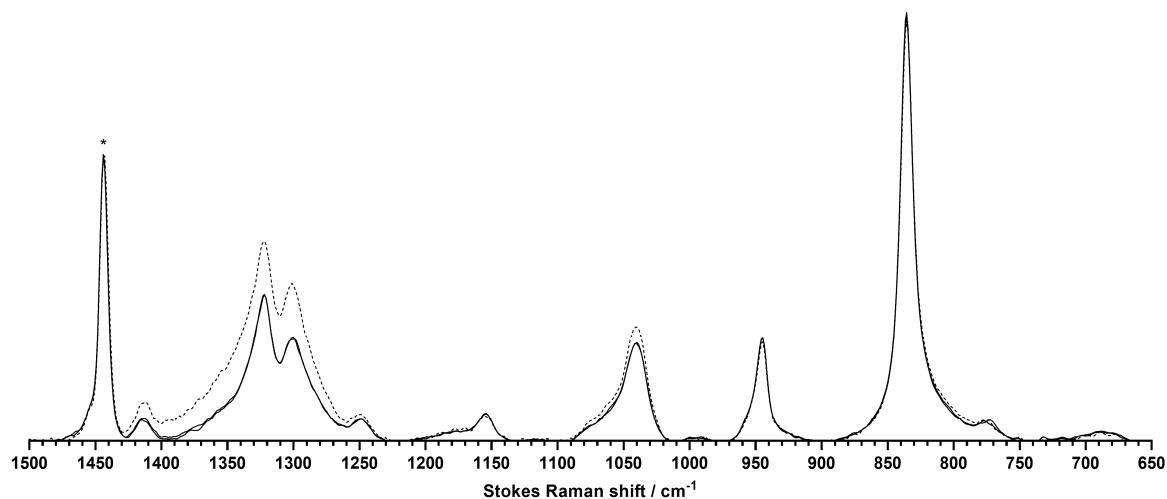


Fig. S4 The Raman spectra ($\lambda = 785$ nm line laser, $20\times$ NA = 0.40 objective) of e $^{-}$ -beamed (40 kGy) ETFE (dashed) and e $^{-}$ -beamed ETFE treated at 60 °C with the two *N*-methylpiperidine solutions used to make MPIP(LEX) and MPIP(1.1) (superimposed solid lines). Each spectrum is an average of $n = 5$ spectra recorded on random surface locations. * Spectra normalised to the 1443 cm^{-1} peak to aid visual comparison.

Section D: Amination of ETFE-g-poly(VBC) with *N*-methylpiperidine in both aqueous KOH and in ultrapure water.

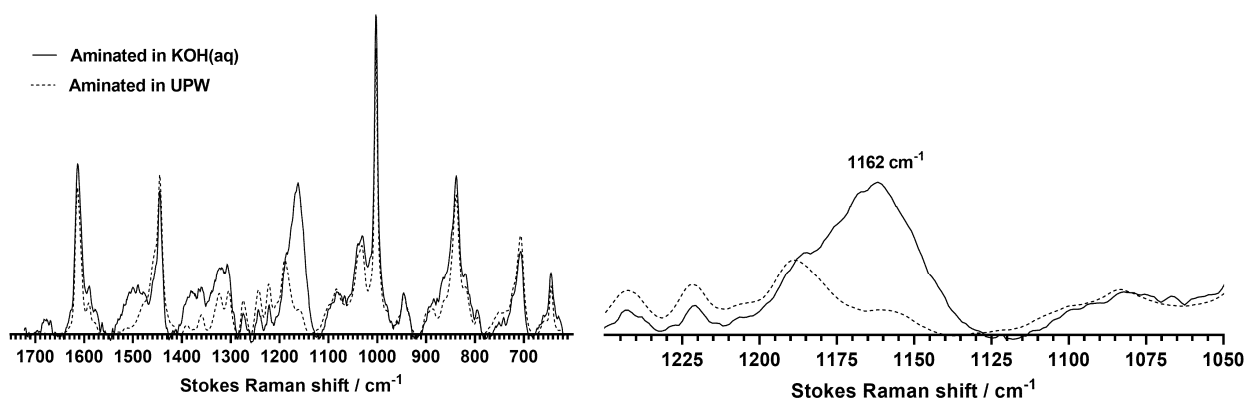


Fig. S5 The Raman spectra ($\lambda = 785$ nm line laser, $20\times$ NA = 0.40 objective) of ETFE-g-poly(VBC) after amination at 60 °C with *N*-methylpiperidine (LEX) in both aqueous KOH (1 mol dm⁻³) and UPW.

References to the ESI

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- 2 J. Ponce-González, D. K. Whelligan, L. Wang, R. Bance-Soualhi, Y. Wang, Y. Peng, H. Peng, D. C. Apperley, H. N. Sarode, T. P. Pandey, A. G. Divekar, S. Seifert, A. M. Herring, L. Zhuang and J. R. Varcoe, *Energy Environ. Sci.*, 2016, **9**, 3724.
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