Investigations of the *ex situ* ionic conductivities at 30°C of metal-cation-free quaternary ammonium alkaline anion-exchange membranes in static atmospheres of different relative humidities

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This article presents the first systematic study of the effect of relative humidity (RH) on the water content and hydroxide ion conductivity of quaternary-ammonium-based alkaline anion-exchange membranes (AAEMs). These AAEMs have been developed specifically for application in alkaline membrane fuel cells where conductivities of $> 0.01 \text{ S cm}^{-1}$ are mandatory. When fully hydrated, an ETFE-based radiation-grafted AAEM exhibited a hydroxide ion conductivity of $0.030 \pm 0.005 \text{ S cm}^{-1}$ at 30°C without additional incorporation of metal hydroxide salts; this is contrary to the previous wisdom that anion-exchange membranes are very low in ionic conductivity and represents a significant breakthrough for metal-cation-free alkaline ionomers. Desirably, this AAEM also showed increased dimensional stability on full hydration compared to a Nafion-115 proton-exchange membrane; this dimensional stability is further improved (no concomitant reduction in ionic conductivity) with a commercial AAEM of similar density but containing additional crosslinking. However, all of the AAEMs evaluated in this study demonstrated unacceptably low conductivities when the humidity of the surrounding static atmospheres was reduced ($\text{RH} = 33 - 91\%$); this highlights the requirement for continued AAEM development for operation in H_2/air fuel cells with low humidity gas supplies. Preliminary investigations indicate that the activation energies for OH^- conduction in these quaternary-ammonium-based solid polymer electrolytes are typically 2 – 3 times higher than for H^+ conduction in acidic Nafion-115 at all humidities.

1. Introduction

This paper significantly extends a previous study of the ionic conductivities at temperatures between 20 – 80°C of radiation-grafted alkaline anion-exchange membranes (AAEM), the OH^- -analogues of proton-exchange membranes (PEMs) such as Nafion[®] by Du Pont;¹ this earlier study was limited to the investigation of the conductivities of poly(tetrafluoroethylene-co-hexafluoropropylene), FEP = $-\text{[CF}_2\text{CF}_2\text{]}_n\text{-[CF(CF}_3\text{)CF}_2\text{]}_m\text{-}$, based AAEMs whilst submerged in water (*i.e.* fully hydrated). The main conclusions were:

- a) The conductivities of fully hydrated radiation-grafted AAEMs ($\lambda = 27 \pm 2$ water molecules per OH^- ion at room temperature) synthesised from 50 μm thick FEP precursor films did not perceptibly vary with degrees of grafting between 21 – 25%.
- b) Conductivities at 50°C of $0.022 \pm 0.003 \text{ S cm}^{-1}$ were demonstrated with these fully hydrated AAEMs ($84 \pm 2 \mu\text{m}$ thick), which correspond to 20% of the $0.104 \pm 0.008 \text{ S cm}^{-1}$ achieved with fully hydrated Nafion-115 PEM ($153 \pm 3 \mu\text{m}$ thick, $\lambda = 24 \pm 2$) at 50°C; therefore thinner membranes are mandatory for the AAEMs to minimise absolute resistances.
- c) The empirical activation energies for the AAEMs in the range 20 – 95°C, measured from empirical Arrhenius plots, are double those found for Nafion-115 ($12.6 \pm 0.6 \text{ kJ mol}^{-1}$

and $6.0 \pm 0.8 \text{ kJ mol}^{-1}$ respectively); therefore maximising the operating temperature of these AAEMs (*i.e.* improving thermal stability) will reduce the gap between the conductivities of AAEMs and Nafion PEMs.

This type of AAEM is of considerable interest in the field of fuel cells; a recent review describes in detail the advantages and disadvantages of this application of AAEM electrolytes² and so, for conciseness, these details will not be repeated. A significant problem with the above FEP-based AAEMs is the lack of physical strength; they tear easily and demonstrate critically poor durability when assembled in fuel cells. Subsequent breakthroughs in radiation-grafted AAEM technology and membrane electrode assembly fabrication (development of a novel alkaline electrode interface polymer), relevant to application in fuel cells, have been reported in two recent communications.^{3,4}

This article details the effect of relative humidity (RH) on ionic conductivities, water uptake properties and stability against excessive swelling of a variety of AAEMs at a temperature of 30°C; this includes measurements on a recently developed class of AAEM based on poly(ethylene-co-tetrafluoroethylene), ETFE = $-(\text{CH}_2\text{CH}_2)_n\text{-(CF}_2\text{CF}_2)_m\text{-}$, precursor films, that are substantially more durable than the FEP-based AAEMs.³ The primary aim of this investigation is to gain a physical insight into the currently unknown behaviour of quaternary-ammonium AAEMs under reduced humidity conditions. Ionic conductivity is the membrane property that directly affects fuel cell performance, whilst the

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humidities of the fuel and oxidant gases in H₂/air fuel cells are critically important operational parameters.

2. Materials and methods

2.1. Synthesis of alkaline anion-exchange membranes

The synthetic protocol for radiation-grafted AAEMs has been described in detail in reference¹ and will only be summarised here (Scheme 1); this methodology was chosen as it avoids the requirement of a final film formation step – preformed films are functionalised. Reverse osmosis (RO) water was used throughout this study. The fully fluorinated FEP or partially fluorinated ETFE films (both 50 µm thick and purchased from Goodfellow) were irradiated with a ⁶⁰Co γ-ray source (Defence Academy of the United Kingdom), Cranfield University, Shrivenham, UK) in air at a temperature of 23 ± 1°C to a total dose of 7 Mrad (dose rate of 0.04 Mrad h⁻¹) and stored at -37 ± 3°C until required. Vinylbenzyl chloride (VBC, Dow Chemicals) was stored in a refrigerator and used undiluted as the grafting monomer after being purged with nitrogen for 2 h and without removal of 4-*tert*-butylcatechol and nitromethane inhibitors. The degree of grafting (d.o.g., %) of the FEP/ETFE-g-poly(VBC) intermediate membranes were calculated as follows:

$$d.o.g. = \frac{m_g - m_i}{m_i} \times 100\% \quad (1)$$

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

These intermediate membranes were subsequently submerged in aqueous trimethylamine (Acros, 50% by mass) for 4 h to yield the desired quaternary ammonium exchange sites. After washing several times in water the resulting hydrophilic membranes (now as chloride-forms) were boiled in water for 1 h (to remove residual trimethylamine and to fully hydrate the membranes) and finally washed in water several more times. Final conversion to the alkaline-forms was conducted as follows: the membranes were submerged in aqueous potassium hydroxide (Fisher Scientific, 1.0 mol dm⁻³, at least 10 times excess) for 1 h with two changes of potassium hydroxide solution during this period to ensure complete ion-exchange (important to obtain maximum ion-exchange capacities). The resulting AAEMs were then soaked in water to remove any lingering / occluded potassium hydroxide species. The desired radiation-grafted AAEMs “as-synthesised” were stored in water until required and were not allowed to dry out at any point before measurements were conducted.

Nafion-115 was evaluated for benchmarking purposes and also to allow a link to previous conductivity and water uptake work in the literature. Nafion[®]-115 was subjected to the standard hydrogen peroxide and sulfuric acid pre-treatment before use.⁵ A thicker commercial quaternary ammonium type AAEM was also evaluated; the physical properties of this AAEM, which is of comparable thickness to Nafion-115 when both are fully hydrated, have been previously reported in detail.⁶ This AAEM also contains additional cross-linking (undisclosed proprietary information). Despite the lack of

Scheme 1 The synthetic methodology used to produce the ETFE- and FEP-based radiation-grafted alkaline anion-exchange membranes.

Table 1 The constant relative humidity (RH) solutions, and desiccant, used in this study. The relative standard deviations in the RH of the atmospheres produced with this technique are less than 2%.⁷

	<i>RH</i> _{30°C} (%)
H ₂ O(l)	100
KNO ₃ (aq, sat)	91
NaCl(aq, sat)	75
Mg(NO ₃) ₂ ·6H ₂ O(aq, sat)	52
MgCl ₂ ·6H ₂ O(aq, sat)	33
CaCl ₂ (s)	0

synthetic and chemical details regarding this ionomer, its inclusion in this study yields interesting and corroboratory information relating to conductivities and water uptakes (see Sections 3.3 and 3.4). Ion-exchange of this membrane to the alkaline form from the supplied Cl⁻ form was conducted using the same procedure as for the radiation-grafted AAEMs. The ETFE-AAEM (d.o.g. = 23.6 %, Scheme 1), FEP-AAEM (d.o.g. = 23.7 %), and crosslinked-AAEM are designated AAEM-E, F, and C respectively.

2.2 Determination of physical properties at each RH

The thicknesses (determined using an outside micrometer of 2 µm precision), areas, and masses of multiple samples of each membrane were recorded after equilibration for at least 7 days over either water, constant humidity solutions or a desiccant (Table 1)⁷ in sealed desiccators that had been placed in an oven set to 30 ± 1°C. Before these measurements were conducted the same properties were determined using the same samples but in the fully hydrated, labelled FH, form (*i.e.* “as-synthesised”: immediately after the water soaking / washing treatment that followed the aqueous KOH ion-exchange procedure). The re-hydrated properties were recorded when the fully dehydrated membranes (7 days over anhydrous CaCl₂(s)) were equilibrated in a RH=100% atmosphere for at least 7 days. All errors in this study relate to one sample standard deviation for multiple measurements over different samples of the same membranes.

The water uptakes for each membrane at each RH, WU_{RH} , were calculated using:

$$WU_{RH} = 100\% \times \frac{(m_{RH} - m_{0\%})}{m_{0\%}} \quad (2)$$

where m_{RH} is the mass at each RH and $m_{0\%}$ is the mass of the fully dehydrated membrane samples. The area increases,

$A_{inc,RH}$, and thickness increases, $t_{inc,RH}$, were calculated in the same fashion:

$$t_{inc,RH} = 100\% \times \frac{(t_{RH} - t_{0\%})}{t_{0\%}} \quad (4)$$

$$A_{inc,RH} = 100\% \times \frac{(A_{RH} - A_{0\%})}{A_{0\%}} \quad (3)$$

where t and A represent the ionomer thicknesses and areas respectively. The volume increases, θ_{RH} , were calculated in a slightly different way to be consistent with the widely reported values of this parameter for PEMs in the literature.^{8,9}

$$\theta_{RH} = 100\% \times \frac{(V_{RH} - V_{0\%})}{V_{RH}} \quad (5)$$

where V represents the volumes of the ionomer samples. The densities of each membrane at each RH, ρ_{RH} , were calculated as follows:

$$\rho_{RH} = \frac{m_{RH}}{V_{RH}} \quad (6)$$

The previously reported¹ standard back titration method was used to calculate the OH⁻ ion-exchange capacity of the fully dehydrated AAEM, $IEC_{0\%}$ / mol(OH⁻) g⁻¹. Similarly the equivalent ion-exchange capacity of Nafion-115, mol(H⁺) g⁻¹, can be determined. The ion-exchange capacities at each RH, IEC_{RH} , can then be calculated from this value and the ratio of the fully dehydrated mass / mass of the same sample of membrane at each RH:

$$IEC_{RH} = IEC_{0\%} \times \frac{m_{0\%}}{m_{RH}} \quad (7)$$

From these values, the concentration of OH⁻ ions (or H⁺ ions) in the membrane, [OH⁻] / mol dm⁻³, at each RH can be determined:

$$[OH^-]_{RH} = IEC_{RH} \times \rho_{RH} \quad (8)$$

Finally the water content, λ_{RH} , the number of water molecules per OH⁻ ion for AAEMs (or per H⁺ ion for Nafion-115), of each membrane at each RH was calculated using the equation:

$$\lambda_{RH} = \frac{WU_{RH}}{IEC_{0\%} \times 100\% \times MW_{water}} \quad (9)$$

where the molecular weight of water, MW_{water} , was taken as 18.015 g mol⁻¹.

2.3. Measurement of conductivities

The method for measuring the normal (through membrane) conductivities followed the impedance spectroscopy approach recently reported by Pozio *et al.*^{5,10} Impedance spectra were recorded with a Solartron 1260 frequency response analyser / 1287 electrochemical interface combination controlled by ZPlot v.1 software (Scribner Associates) with data analysis of

the Nyquist plots using ZView v.2 software (Scribner Associates); these plot Z_{im} vs. Z_{real} of the complex plane vector $Z(\omega) = R + j\chi$, where the resistance $R = Z_{real}$, the reactance $\chi = Z_{im}$, $\omega = 2\pi f$ (f is the frequency of the a.c. voltage perturbation), and $j = \sqrt{-1}$.

The AAEMs (or Nafion-115), cut to circular diameter = 1.39 cm, were pressed between two single-sided carbon-powder-coated carbon cloth electrodes (E-Tek: A-6 ELAT/SS/NC/V2, carbon only - no metal catalyst, thickness = 355 μ m, circular diameter $\phi = 1.13 \pm 0.02$ cm (area $A = 1.00 \pm 0.04$ cm²) with the powder side pressed to the membrane) at 150 ± 50 kg cm⁻² at 60°C for 3 min. After pressing, the resulting membrane electrode assemblies (MEAs) were stored in water for at least 12 h prior to conductivity measurements. The cell design, with circular graphite plates, is similar to that previously reported by Pozio (see Fig. 2 in reference 5), the only difference being that ELAT A-6 carbon cloth electrodes were used instead of Toray carbon paper. The conductivities of the fully hydrated membranes, σ_{FH} / S cm⁻¹, were measured with the cell assembly submersed in a beaker of water at controlled temperature so that all of the MEA was submerged; the gold jack plug (for electrical connection) were kept outside of the water.¹ The conductivities in the RH=100% to RH=33% range were conducted with the cell assembly suspended above (not in) the constant humidity solutions. RH=0% measurements were conducted with the cell assembly suspended above anhydrous CaCl₂(s); however, at RH=0%, with this cell design, the resistances and capacitances of all of the AAEM samples were such that it was not possible to measure the membrane resistances/conductivities with any confidence in the frequency range available on the instruments. Impedance spectra were recorded between frequencies $f = 1$ MHz – 1 Hz (7 steps per decade), 50 mV root mean squared voltage perturbation, and integration of the responses over 10 cycles. R_{tot} (the sum of the membrane, R_{mem} , and cell resistance, R_{cell}) was taken as the intercept with the x-axis (see Figure 2 in Reference 1). R_{cell} was determined by impedance measurements for a blank cell containing two ELAT A-6 electrodes pressed together in an identical manner to that described above (no membrane therefore forming an electrical short circuit). Nafion-115 MEAs were prepared in a similar manner to that above, with the following slight modifications: the MEAs were pressed at 135°C for 3 min and the MEAs were boiled in water for 2 h after preparation to ensure the expanded form was recovered after the hot pressing;⁵ this procedure was deliberately adopted to allow comparison with literature data. These acidic benchmark MEAs were also stored in water until required for impedance spectroscopy.

Conductivities, σ / S cm⁻¹, are calculated as below:

$$\sigma_{RH} = \frac{t_{RH}}{R_{mem,RH} \times A} \quad (10)$$

where t is the membrane thickness in cm (the values determined in section 2.2 at each RH were used), A is the electrode area in cm² and R_{mem} / Ω is the membrane resistance, at each RH, calculated from $R_{tot} - R_{cell}$.

3. Results and discussion

Fig. 1 The effect of relative humidity (RH) at 30°C on selected physical properties (see Section 2.2) for Nafion-115 (▽), AAEM-F (●), AAEM-E (◆), and AAEM-C (■). FH = fully hydrated and R = rehydrated after complete dehydration.

3.1. Nafion-115: Selected physical properties at 30°C

The values of WU , t_{inc} , A_{inc} , θ , λ , and ρ for all ionomers are presented in Fig. 1(a-d); the calculated values of IEC and $[H^+]$ are presented in Table 2. The thickness of Nafion-115 decreased from $153 \pm 3 \mu m$ when fully hydrated to $148 \pm 3 \mu m$ at $RH=100\%$ and then further reduced to $121 \pm 3 \mu m$ at $RH=0\%$; these values compare well with literature values (at room temperature) of $149 \pm 9 \mu m$ when fully hydrated and $124 \pm 2 \mu m$ when fully dehydrated.⁵ The thickness only recovered to $140 \pm 3 \mu m$ when re-hydrated at $RH=100\%$ (Table 3). This is consistent with current wisdom in that the

ionic cluster/channel nanostructure of Nafion membranes can only be re-formed on treatment in water at temperatures around $80^\circ C$;¹¹ hence, re-hydrating at $RH=100\%$ and $30^\circ C$ from fully dehydrated will yield a membrane with intrinsically different properties than a Nafion PEM that has been equilibrated at $RH=100\%$ directly from the fully hydrated, expanded, form.

This behaviour pattern is observed for Nafion for all of the properties investigated in this study. For example, the WU values decreased from $40 \pm 2 \%$ when fully hydrated (literature value 39 ± 2)⁵ to 29 ± 2 at $RH=100\%$, whilst the water content, λ , decreased from 24 ± 2 water molecules per

Table 2 The ion-exchange capacities and the concentration of conductive ion species for each ionomer at decreasing values of RH at 30°C.

	AAEM-F		AAEM-E		AAEM-C		Nafion-115	
	$10^3 \times IEC_{RH}$ / mol(OH) ⁻¹ g ⁻¹	[OH] / mol dm ⁻³	$10^3 \times IEC_{RH}$ / mol(OH) ⁻¹ g ⁻¹	[OH] / mol dm ⁻³	$10^3 \times IEC_{RH}$ / mol(OH) ⁻¹ g ⁻¹	[OH] / mol dm ⁻³	$10^3 \times IEC_{RH}$ / mol(H ⁺) ⁻¹ g ⁻¹	[H ⁺] / mol dm ⁻³
FH	0.72 ± 0.04	1.02 ± 0.08	0.74 ± 0.09	1.02 ± 0.12	0.89 ± 0.02	1.21 ± 0.05	0.66 ± 0.05	1.05 ± 0.09
RH=100%	0.75 ± 0.05	1.18 ± 0.11	0.76 ± 0.09	1.06 ± 0.13	0.92 ± 0.02	1.26 ± 0.04	0.72 ± 0.06	1.19 ± 0.10
RH=91%	0.84 ± 0.05	1.33 ± 0.11	0.82 ± 0.09	1.13 ± 0.14	0.97 ± 0.02	1.35 ± 0.04	0.81 ± 0.06	1.44 ± 0.12
RH=75%	0.93 ± 0.06	1.53 ± 0.14	0.90 ± 0.10	1.31 ± 0.16	1.04 ± 0.02	1.49 ± 0.05	0.86 ± 0.07	1.61 ± 0.14
RH=52%	0.98 ± 0.06	1.67 ± 0.15	0.95 ± 0.11	1.40 ± 0.17	1.09 ± 0.03	1.57 ± 0.06	0.88 ± 0.07	1.72 ± 0.15
RH=33%	1.00 ± 0.07	1.75 ± 0.15	0.98 ± 0.11	1.44 ± 0.18	1.11 ± 0.03	1.63 ± 0.05	0.90 ± 0.07	1.77 ± 0.15
RH=0%	1.04 ± 0.07	1.80 ± 0.16	1.03 ± 0.11	1.57 ± 0.20	1.14 ± 0.03	1.72 ± 0.06	0.93 ± 0.07	1.84 ± 0.16
Rehydrated at RH=100%	0.76 ± 0.05	1.27 ± 0.10	0.76 ± 0.09	1.07 ± 0.13	0.93 ± 0.02	1.28 ± 0.03	0.77 ± 0.06	1.35 ± 0.12

Table 3 The percentage of selected properties recovered on re-hydration at RH=100% for 7 days following full dehydration (RH=0%, 7 days) from an initial RH=100% humidified state.

	$X^a = t / \mu\text{m}$	$X^a = A / \text{cm}^2$	$X^a = V / \text{cm}^3$	$X^a = \lambda$	$X^a = \sigma / \text{S cm}^{-1}$
Nafion-115	95 ± 3	93 ± 2	88 ± 2	71 ± 6	85 ± 29
AAEM-F	96 ± 7	97 ± 2	93 ± 2	94 ± 5	89 ± 8
AAEM-E	100 ± 4	99 ± 2	99 ± 4	99 ± 4	89 ± 6
AAEM-C	99 ± 2	99 ± 1	98 ± 1	95 ± 3	82 ± 7

$$^a X = 100\% \times (X_{100\%, \text{rehydrate}} / X_{100\%, \text{initial}})$$

proton (literature value 22 ± 2)⁵ when fully hydrated to 17 ± 2 at RH=100%. However the values for WU and λ on re-hydration from fully dehydrated to RH=100% did not recover fully (20 ± 2 % and 12 ± 1 respectively, see Table 3 for more comprehensive data).

The values of $\theta_{FH} = 43 \pm 3$ %, $\rho_{RH} = 1.59 \pm 0.04$ g cm⁻³, $IEC_{0\%} = 0.93 \pm 0.07 \times 10^{-3}$ mol_{H+} g⁻¹ and $[H^+]_{FH} = 1.05 \pm 0.09$ mol dm⁻³ were observed for Nafion; these match literature values of 38 - 39 %^{8,9}, 1.6 ± 0.1 g cm⁻³, 0.93×10^{-3} mol_{H+} g⁻¹ (calculated from the reported equivalent weight of 1075 for Nafion-115)⁵ and 1.05 mol dm⁻³ respectively.^{8,9} This confirms that the methodologies adopted in this paper are reproducing previous data for Nafion-115.

3.2. Nafion-115: Conductivities at 30°C

The values of σ observed as functions of RH and λ are presented in Fig. 2(a-d). The first notable observation is that there is a significant decrease from $\sigma_{FH} = 0.093 \pm 0.008$ S cm⁻¹ to $\sigma_{100\%} = 0.075 \pm 0.014$ S cm⁻¹, which is concomitant with the decrease in λ described in Section 3.1. The conductivity was significantly reduced to less than 50% of the fully hydrated value when the RH was reduced to only 75%, whilst the conductivity collapsed to below 10^{-4} S cm⁻¹ on full dehydration (as previously observed by Wintersgill *et al.*).¹² For confirmation that the conductivities measured in this study match those in the literature, a plot of σ vs. λ was compared with the empirical equation for Nafion-117 developed by Springer *et al.*¹³ (Figure 2b) that has been generally verified in the literature.¹⁴

$$\sigma_{30^\circ\text{C}} = 0.005139 \times \lambda - 0.00326 \quad \text{valid for } \lambda > 1 \quad (11)$$

As can be seen there is a close match between this linear relationship and the conductivities determined in this study; it is the author's view that this linear response is quite simplistic for such a complex material and electrochemical property. Literature values for Nafion-117 of 0.06 S cm⁻¹ for $\lambda = 14$ at 30°C ^{14,15} and 0.105 S cm⁻¹ at $\lambda = 21$ ⁸ at ambient temperatures act as further corroboration. An important consideration is that Nafion-115 was the benchmark PEM in this study, whilst most literature values are for Nafion-117; there is increasing evidence in the literature that the conductivity of Nafion is a

function of membrane thickness (as well as the equivalent weight as expected).^{5,16} On rehydration to RH=100%, the conductivity does not fully recover with some Nafion-115 samples, whilst recovery is observed to be complete for other samples (as can be seen from the large value of sample standard deviation in Table 3); therefore no firm conclusions about this can be made without additional measurements.

3.3. AAEMs: Selected physical properties at 30°C

All relevant properties are presented in Fig. 1 and Table 2 and 3. As anticipated, the crosslinked AAEM-C exhibited lower levels of water uptake and swelling at higher humidities than the non-crosslinked AAEMs and Nafion-115 PEM as can be seen from the WU , λ , t , t_{inc} , A_{inc} , and θ measurements; this is a desirable trait as long as the added crosslinking does not decrease membrane conductivity (see Section 3.4). Within margins of error, the water uptake properties of AAEM-E, AAEM-F, and Nafion-115 cannot be clearly differentiated when submerged in water (fully hydrated forms). However, AAEM-F and AAEM-E show a trend towards higher water content (λ and WU) between RH=75 and RH=100% compared to Nafion-115. When fully hydrated, AAEM-F swells to a larger degree than Nafion-115 in term of thickness (t_{inc}) but to a lesser extent in terms of area (A_{inc}) at higher humidities; as a result, the volume increase parameter θ is similar for both membranes at RH=100% and when fully hydrated. The thickness increase parameter for AAEM-E is similar to Nafion-115 when both are submerged in water but A_{inc} (and therefore θ) is considerably less. Therefore, all of the AAEMs show improved area-dimensional-stability compared to Nafion-115 at the highest hydration levels. At intermediate humidity levels, differences in A_{inc} , t_{inc} and θ between the ionomers are not discernible (within margins of error), with the possible exception of greater area and volume increases for AAEM-E.

As anticipated, the densities for all membranes increase on dehydration. Nafion-115 has the highest density as it is a sulfonated fully fluorinated membrane with no C-H bonds. The AAEM-F is less dense: even though the precursor FEP is fully fluorinated, the grafting of VBC and subsequent amination introduces C-H bonds into the membrane. AAEM-E is less dense again as the ratio of C-H/C-F bonds is further increased (the ETFE precursor is only partially fluorinated). The crosslinked AAEM-C exhibits similar densities (within measurement precision) to AAEM-E indicating a comparable ratio of C-H to C-F bonds.

All three AAEMs studies show good recovery of their properties on rehydration to RH=100% (Table 3); recovery of volume and water content was significantly improved compared to Nafion-115.

Fig. 2 The relationship between conductivity, relative humidity and ionomer water content for Nafion-115 (▼), AAEM-F (●), AAEM-E (◆), and AAEM-C (■). FH = fully hydrated and R = rehydrated after complete dehydration. $\% \sigma_{FH,30}$ is the ratio of the conductivities at each RH compared to the conductivity at full hydration. The empirical $\sigma(\lambda)$ relationship for Nafion-117 is given in equation 11.

3.4. AAEMs: Conductivities at 30°C

When comparing the relationships between conductivity and humidity (Fig. 2), it is clear that all AAEMs behaved in a similar manner between $RH=33$ and $RH=100\%$ with AAEM-F exhibiting the best conductivities in this intermediate humidity range. However, as mentioned above, FEP-based AAEMs are physically brittle, unlike the ETFE analogues, and cannot currently be safely used in fuel cells.¹⁷ The conductivities of the AAEMs could not be determined at $RH=0\%$ due to limitations in instrumentation (as described in Section 2.3). When immersed in water both AAEM-C and -E showed significantly improved conductivities compared to AAEM-F (0.033 ± 0.002 , 0.030 ± 0.005 and $0.017 \pm 0.001 \text{ S cm}^{-1}$ respectively); these two low density AAEMs with restricted dimensional changes showed an impressive 32 – 35% of the conductivity exhibited by Nafion-115 when fully hydrated. The unusual behaviour of the two low density AAEMs when fully hydrated can clearly be seen in the plot of σ_{30} vs. λ (Fig. 2d); the sharp increase in conductivity when

fully hydrated is not seen for AAEM-F. This sharp increase occurs at lower water content for the crosslinked AAEM.

Ion mobilities, $\mu / \text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$, are related to both the conductivity and the concentration of the conductive species:

$$\sigma = \mu F [\text{OH}^-] \quad \text{or} \quad \sigma = \mu F [\text{H}^+] \quad (12)$$

where F is Faraday's constant ($= 96,485.3 \text{ C mol}^{-1}$). The ion mobilities of OH^- in the fully hydrated quaternary-ammonium-based AAEM were between 18 and 33% of the mobilities of H^+ in Nafion-115 ($\mu = 9.2 \times 10^{-8}$, 2.8×10^{-8} , 3.1×10^{-8} and $1.7 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Nafion, AAEM-C, AAEM-E and AAEM-F respectively). The lower conductivities in these solid ionomers is not due to a concentration effect as the concentration of the conductive species for all ionomers are similar (Table 2). Hence, it has been established that the conductivities in these AAEMs are controlled by the ion mobilities; this is in line with diffusion coefficient arguments presented by Agel *et al.*¹⁸ The OH^- mobilities in the low

density AAEMs (E and C) are similar, whilst the mobility of this conductive species in AAEM-F is tentatively lower.

3.5 Comparison to previous literature

There is a range of different anion-exchange membranes in the literature; these are either being developed for, or are suitable for, application in alkaline membrane fuel cells. An ammonium-type commercial anion-exchange membrane (AHA, Tokuyama, Japan; 240 μm in thickness in Cl^- anion form, $\text{IEC} = 1.15\text{--}1.25 \times 10^{-3} \text{ mol}(\text{OH}^-) \text{ g}^{-1}$) demonstrated a conductivity of 0.01 S cm^{-1} (undisclosed temperature) when submerged in aqueous KOH (1 mol dm^{-3}).¹⁹ Quaternary-ammonium-containing 1,4-diazabicyclo[2,2,2]octane-crosslinked epichlorohydrin AAEMs displayed conductivities of $0.01\text{--}0.05 \text{ S cm}^{-1}$ at 25°C when submerged in aqueous KOH solutions of various concentrations between $0.1\text{--}7.2 \text{ mol dm}^{-3}$.¹⁸ A quaternised cholomethylated polysulfone-Cardo AAEM exhibited a conductivity of 0.06 S cm^{-1} at 30°C when submerged in aqueous NaOH (1 mol dm^{-3}).²⁰

Another class of AAEM is the M^+OH^- -doped polymer electrolyte. Savadogo *et al.* showed that conductivities as high as 0.1 S cm^{-1} at 90°C in aqueous KOH ($> 1 \text{ mol dm}^{-3}$) were achievable using a KOH-doped poly(benzimidazole) AAEM;²¹ this is not a metal-cation-free system (see Section 3.6 for the importance of this). A conductivity of $0.0154 \pm 0.0018 \text{ S cm}^{-1}$ was obtained for fully hydrated KOH-doped chitosan AAEMs;²² this is a rare example in the literature where the conductivity measurements were conducted with an AAEM that was not submerged in aqueous alkali solution. The conductivity of this membrane collapsed to $10^{-7}\text{--}10^{-8} \text{ S cm}^{-1}$ at $\text{RH}=0\%$. An AAEM synthesised by doping a cross-linked poly(vinylalcohol)-co-poly(acrylic acid) copolymer with aqueous KOH (32 mass%) exhibited a high conductivity of 0.3 S cm^{-1} at 25°C .²³

A final class of AAEM is based on ionomers containing pyridinium exchange sites. An example of this has been reported by Zhuang *et al.*;²⁴ a conductivity of 0.008 S cm^{-1} at 25°C was obtained for a quaternised copolymer of 4-vinylpyridine and styrene.

It is difficult to directly compare the AAEM conductivities determined in this study to those in the literature as the vast majority report conductivity data of AAEMs that were submerged in aqueous hydroxide salt solutions. The particularly high conductivities of KOH doped polyelectrolytes is noted; the durability of this class of AAEM in fuel cells, however, requires more thorough investigation – would the incorporated KOH species remain in the ionomer when used in fuel cells where liquid water can be present? The manifest lack of conductivity data to date regarding metal-cation-free AAEMs clearly justifies the approach described in this article; this is especially true for data at reduced humidities.

3.6. Implications for application of AAEMs in fuel cells

The low conductivities under reduced relative humidity conditions are evident from Fig. 3 ($< 0.01 \text{ S cm}^{-1}$ at $\text{RH} < 91\%$). The conductivities of the AAEMs were more sensitive to humidity than Nafion-115 proton-exchange membrane. A key requirement for the polymer electrolyte in H_2/air fuel cells

(especially those for automotive power trains) is the ability to retain high ion conductivities at low humidities; humidifying the input gases adds significant complexity to the balance of plant and can consume a significant proportion of the energy output of the cells. The utilisation of the AAEMs evaluated in this study in H_2/air fuel cells supplied with low humidity gas supplies will not be successful, unless the AAEMs are fabricated sufficiently thin that the back transport of electrogenerated water leads to significant ionomer water uptake.

With respect to the anticipated application in fuel cells, it is important to recognise that the conductivity measurements in this study are *ex situ*. A recent *in situ* impedance spectroscopy study⁶ has been conducted where the commercial AAEM-C described above was evaluated in a H_2/O_2 fuel cell; this study demonstrated that the *in situ* resistance of this AAEM with $\text{RH}=100\%$ gas supplies was on average only double that of Nafion-115 of similar thickness (rather than the three times more resistive as predicted by the *ex situ* results presented in this article). Remarkably, this study also showed that AAEM-C exhibited notable drops in resistance at high current densities as water was electrogenerated at significant rates at the anode ($2\text{OH}^-(\text{membrane}) + \text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l/g}) + 2\text{e}^-$); this water is then consumed at the cathode, after backtransport, as a stoichiometric reactant ($\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l/g}) + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{membrane})$). Hence, *ex situ* conductivity measurements under static atmospheric conditions, such as those presented in this study, should only be considered as an initial guide to *in situ* ionomer resistances (under dynamic conditions).

Alkaline membranes can also be applied to direct alcohol fuel cells; recent studies have shown that in the specific absence of metal cations, AAEMs can be operated in direct methanol fuel cells with $< 95 \mu\text{V h}^{-1}$ cell voltage degradation rates;⁴ carbonation of the electrolyte ($\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$) was minimal despite the electrogenerated CO_2 at the anode and the inherent CO_2 component of the air supply at the cathode. As this class of fuel cell is typically supplied with aqueous alcohol solutions at the anode, the issue of poor conductivity at low humidities is negated. The permeability of alcohols through the ionomer is now an important consideration. AAEM-E and AAEM-C have been shown to exhibit significantly reduced methanol permeabilities compared to Nafion-115;^{17,6} this demonstrates the applicability of these membranes in direct alcohol fuel cells.^{3,17} A further advantage with using AAEMs in direct alcohol fuel cells arises when ethanol (a potentially carbon-neutral biofuel) is used as the fuel. Initial investigations in our laboratories indicate that the power density of a AAEM-based direct ethanol fuel cell exceeded that of a directly comparable direct methanol fuel cell containing the same AAEM. This is the reverse of what is observed with Nafion-based direct alcohol fuel cells (less power is produced with ethanol than with methanol). In-depth investigations into this phenomenon have now been initiated.

The power densities of AAEM-based direct alcohol fuel cells is currently poor unless additional alkali metal hydroxide is added to the aqueous alcohol fuel supply; this is clearly seen when comparing the performances of alkaline membrane direct methanol fuel cells with^{25,26} and without^{3,17} the addition

of KOH into the methanol supply (*cf.* a peak power density of 18 mW cm⁻² at 60°C with KOH (1 mol dm⁻³) in aqueous methanol (2 mol dm⁻³)²⁵ and a peak power density of only 2 mW cm⁻² at 60°C with KOH-free aqueous methanol (2 mol dm⁻³) and a lower resistance AAEM³). These poor performances are due to the use of fuel cell electrode architectures that have currently not been specifically optimised for solid alkaline fuel cells.^{6,17}

3.7. Determination of empirical activation energies

Activation energies, assuming Arrhenius behaviour, are calculated from the slope, *b*, of the linear regression of ln (σ / S cm⁻¹) vs (1000 / *T*) / K⁻¹ plots:

$$E_a = -b \times R \quad (13)$$

where *R* is the gas constant 8.314 J K⁻¹ mol⁻¹.¹ The activation energies at RH=100% of AAEM-F, E, C, and Nafion-115 were determined to be 15.1 ± 0.8, 17.1 ± 1.3, 18.9 ± 2.1, and 7.4 ± 3.2 kJ mol⁻¹ respectively by measuring the conductivities of these membranes at increasing temperatures between 30 and 60°C. A previous study observed that the activation energies for OH⁻ conduction in fully hydrated FEP-based AAEMs are more than twice that seen for H⁺ conduction in Nafion-115.¹

Caution is required in determining the activation energies for ion conduction in ionomers at lower humidities when using constant humidity (saturated salt) solutions. This is because the humidity above such salt solutions is a function of temperature (this function varies with salt species). Sudden changes in temperature will also cause transient drops in humidity as the atmosphere above the solutions heat up faster than the solutions themselves, which could cause some additional ionomer dehydration. Hence only tentative estimations of activation energies are reported. As expected, the activation energies of all ionomers increased at lowered humidities (ionic transport is restricted with reduced water contents). In the range RH=33 – 52%, activation energies of 21 – 32 kJ mol⁻¹ were observed for the AAEMs and 7 – 13 kJ mol⁻¹ were observed for Nafion-115. A better experimental methodology is clearly required; a new cell for future conductivity studies with flowing nitrogen of controlled humidity is therefore being designed in order that more accurate determinations of activation energies at low RH can be achieved.

Conclusions

The ETFE-based alkaline anion-exchange membrane (AAEM) exhibited reduced physical swelling than both FEP-based AAEMs and Nafion-115 proton-exchange membrane at 30°C when fully hydrated; this is desirable for application in polymer-based low temperature fuel cells. The normal (through membrane) OH⁻ conductivity of this AAEM was 0.030 ± 0.005 S cm⁻¹ when fully hydrated (*i.e.* 32% of the H⁺ conductivity of Nafion); this represents an impressive level of conductivity for a solid alkaline ionomer with no additional incorporation of metal hydroxide species. A commercial AAEM containing additional crosslinking reduces the water

contents and swelling further with no detrimental loss of ionic conductivity at full hydration. Unfortunately, all the AAEMs exhibited substantially lowered conductivities at lower relative humidities; this is undesirable for the anticipated application in alkaline membrane fuel cells where operation with low humidity gases is considered necessary; the case for development of AAEMs with conductivities that are less sensitive to humidity is therefore highlighted. Recovery of the physical properties on subsequent rehydration, after full dehydration, was superior for all the AAEMs compared to that for Nafion-115.

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