Investigations of Conductivity in FEP-Based Radiation-Grafted Alkaline Anion-Exchange Membranes

Robert C. T. Slade and John R. Varcoe*

Chemistry, The University of Surrey, Guildford GU2 7XH, United Kingdom.

Tel: +44 (0)1483 682616   Fax: +44 (0)1483 686851

*Author for correspondence: E-mail: j.varcoe@surrey.ac.uk

A series of radiation-grafted alkaline anion-exchange membranes (AAEMs) with degrees of grafting (by mass) in the range 20 – 26% were produced and characterised. Conductivities (from impedance spectroscopy) up to $0.023 \pm 0.001 \text{ S cm}^{-1}$ at $50 \pm 1^\circ\text{C}$ were demonstrated, which are between 20 – 50% of values for the commercial acid-form membrane Nafion®-115 ($\sigma = 0.045 \pm 0.004$ (65°C) – 0.104 ± 0.008 ($50 \pm 1^\circ\text{C}$) S cm^{-1} , depending on the level of hydration (10 and 23 water molecules per sulfonate group respectively)). This significant result clearly indicates the suitability of these AAEMs for application in fuel cells at temperatures below the widely accepted alkaline membrane thermal stability limit of 60°C . Statistical analysis of the results of ion-exchange capacity and conductivity studies on the AAEMs indicate the presence of heterogeneity in the grafting levels within the AAEMs and suggest that more synthetic optimization work is required. The empirical activation energies (Arrhenius behaviour assumed) for the hydroxide ion migration in the AAEMs ($12.6 \pm 0.6 \text{ kJ mol}^{-1}$ at the 95% confidence level) is twice the value for proton migration found for fully hydrated Nafion®-115 ($6.0 \pm 0.8 \text{ kJ mol}^{-1}$) and shows that hydroxide ion mobility is more strongly temperature dependant.

Keywords: Radiation-Grafting, Alkaline Membrane, Fuel Cell, Conductivity, Impedance Spectroscopy

1. Introduction

There has been considerable recent interest in clean air technologies for power generation for both stationary and mobile applications. Fuel cell technologies are at the forefront of the effort towards green and sustainable energy generation. For mobile applications, the emphasis has been placed on lower temperature types ($< 150^{\circ}\text{C}$) including hydrogen fuelled (overall reaction: $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$) alkaline fuel cells (AFCs) and proton-exchange-membrane fuel cells (PEMFCs), and the direct methanol fuel cell (DMFC) (overall reaction: $\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$) [1,2]. DMFCs are of primary interest in the field of mobile devices (*e.g.* laptop computers), due to ease and speed (instantaneous) of refuelling and the large volumetric energy density of the liquid methanol fuel. Such low temperature portable DMFCs are expected to be the first type of fuel cells to be commercially available on a wide scale and in the hands of general consumers.

There is extensive worldwide research being conducted on replacement proton exchange membranes (PEMs) [3] and electrocatalysts for DMFCs [4]. The main problems with current generation PEMs (such as Nafion® produced by DuPont) are high methanol permeabilities (from anode to cathode), which result in wasted fuel and low power densities in DMFCs [5], and high cost. In the low $p\text{H}$ regime inherent with PEMs, the oxygen reduction reaction is electrokinetically slow resulting in high cathode activation overpotentials (a significant cause of power loss in PEMFCs). The anodic electrooxidation of methanol ($6e^-$ reaction) is also an inherently sluggish reaction at low $p\text{H}$, which reduces the performances of DMFCs even further and leads

to the necessity for unsustainable high loadings of complex and expensive catalysts (*e.g.* Pt/Ru of approximately $2 - 4 \text{ mg cm}^{-2}$ metal loadings).

The application of *alkaline anion-exchange membranes* (AAEMs) in fuel cells is a radical step that potentially allows the achievement of enhanced performances in hydrogen-fuelled (especially with the use of reformed hydrogen containing CO contaminant, a significant Pt catalyst poison at low *pH*) and direct liquid methanol fuelled fuel cells. AAEMs potentially remove several of the problems associated with traditional aqueous potassium hydroxide electrolyte alkaline fuel cells, principal among them destructive carbonate/hydrogen carbonate precipitation at the electrodes. The issues, advantages and challenges with the use of AAEMs in fuel cells have been comprehensively detailed in a recent review [6] and will not be repeated here. A discussion of the thermodynamic considerations when using AAEMs in fuel cells has also been recently published [7].

The potential advantages when using AAEMs are summarised below:

- 1) Reduced methanol crossover because the conduction pathway of the OH^- ions proceeds from the cathode to the anode (opposite direction to proton migration in fuel cells involving PEMs); this and electro-osmotic drag oppose the direction of methanol flux through the membrane. Reduced methanol crossover will allow the use of thinner, less resistive membranes, improving fuel cell performances significantly.
- 2) Electrocatalysis of each of hydrogen oxidation, methanol oxidation, and oxygen reduction reactions in alkaline media (high *pH* regime) is more facile, enabling the

use of a wider range of catalysts (including cheaper non-noble metals *e.g.* nickel and silver [8,9]).

- 3) This larger repertoire of catalysts should allow the selection of a cathode catalyst that is inactive towards methanol oxidation, reducing crossover performance losses even further.
- 4) Reduction of flooding at the cathode in direct methanol fuel cells and better overall water management leading to simplified balance of plant (essential with passive DMFCs for portable devices).
- 5) At high in situ *pH*, the oxidative radical mechanism for polymer degradation is suppressed [10] and potentially enables the use of hydrocarbon only membranes (C-H backbone) with enhanced green credentials (manufacturing and disposal) when compared with inherently expensive fluorine-containing polymers.

An initial study on the operation of DMFC with a commercial anion-exchange membrane (Morgane® ADP membrane, Solvay S.A. Belgium) have been conducted by Scott *et al*; maximum power densities of around 11 mW cm⁻² and limiting current densities of around 70 mA cm⁻² were obtained when Pt/C electrodes when used at the anode and cathode of alkaline membrane DMFCs with air at the cathode [11]. The best performances were obtained when the gas diffusion layer was omitted from the anode and with non-teflonised carbon paper; humidification of the cathode air stream further improved performances (expected as water is essential at the cathode in order to form the OH⁻ conducting species). Similar performances were also obtained when platinised titanium mesh anodes were employed along with Pt/C-type cathodes [12]. The methanol solutions (1 to 4 mol dm⁻³) were all made from aqueous sodium hydroxide (1 mol dm⁻³); other fundamental electrochemical studies demonstrate that

electro-oxidation of methanol at the anode is improved at higher pH (higher NaOH concentrations) due to improved OH^- surface concentrations on the Pt catalyst particles [13,14]. The Morgane® ADP membrane exhibited a resistance across the membrane (termed the normal direction as opposed to the tangential surface resistance) that was 600% the value observed with Nafion®, which was a factor that was responsible for the limited fuel cell performances observed. The methanol diffusion coefficients in Nafion®, however, was about 280% that found for the Morgane® ADP membrane, indicating that lower methanol crossover is obtainable with this commercially developed AAEM [11.] However, the Morgane® ADP membrane discoloured when immersed in aqueous sodium hydroxide (1 mol dm^{-3}), symptomatic of the presence of some chemical instability under such conditions [11]. Similar performances were also found in DMFCs and direct ethylene glycol fuel cells containing another commercial anion-exchange membrane (Tokuyama AHA membrane, Tokuyama Co. Japan). Interestingly, the power densities obtained with ethylene glycol were superior to performances with methanol [15], which strongly indicates that the use of AAEMs in fuel cells can broaden the choice of the liquid fuels at the anode to include alcohols other than methanol in direct alcohol fuel cells.

A significant proportion of previous fuel cell membrane research has examined the radiation-grafting of styrene into non-fluorinated (*e.g.* LDPE), partially fluorinated (*e.g.* PVDF) and fully fluorinated films (*e.g.* FEP), with subsequent sulfonation to yield PEMs [16,17]. The properties and compositions of the final materials can easily controlled with this methodology [18,19]; radiation-grafted PEMs have been tested in DMFC mode and significantly exhibit lowered in situ methanol permeabilities [20,21]. Radiation-grafted PVDF-based cation- and anion-exchange membranes have

also been successfully applied to salt-splitting technologies [22-24]. Radiation grafting methodology produces ionomer membranes cheaply and has two major advantages: (1) preformed commercial polymer films are modified, alleviating the need for film formation steps; (2) the availability of a wealth of adjustable experimental parameters (*e.g.* radiation dose / type, temperature, film thickness) allowing a large degree of tailorability and customisation.

The radiation grafting of vinylbenzyl chloride (VBC) into FEP (forming intermediate FEP-*g*-PVBC) [25-27] with subsequent amination with trimethylamine and ion-exchange with aqueous potassium hydroxide yields alkaline, as opposed to acidic (proton-conducting), membranes (FEP-*g*-PVBTMAOH, Scheme 1). Preliminary investigations on such RG-AAEMs at Surrey have demonstrated that partially fluorinated films (such as PVDF, containing both C-F and C-H backbone components) are inappropriate starting films for the manufacture of such membranes in alkaline (OH⁻) form due to chemical degradation caused by dehydrofluorination. However, these preliminary studies demonstrated that fully fluorinated FEP-derived AAEMs retained structural and ion exchange (chemical) integrity even when heated at 60°C for over 2500 h in water while open to air (and therefore carbon dioxide) [26].

This article extends our previous work which detailed: (1) synthetic protocol optimisation for the fabrication of RG-AAEMs, and (2) their chemical, structural, and thermoanalytical characterisation [26,27]. The conductivities of such AAEMs are now reported and are related to the initial grafting yields, ion-exchange capacities, and water contents.

2. Experimental

2.1. Synthesis of alkaline anion-exchange membranes

The synthetic protocol for the anion-exchange membranes is described in detail in reference [27] and will only be summarised here. Reverse osmosis (RO) water was used throughout this study. Table 1 summarises the experimental conditions used to produce the FEP-g-PVBC intermediate membranes. The FEP films were irradiated with a ^{60}Co γ -ray source (Royal Military College of Science, Cranfield University, Shrivenham, Swindon, UK) at a temperature of $23 \pm 1^\circ\text{C}$ and with a dose rate of 0.04 MRad h^{-1} (0.4 kGy) and stored at $-37 \pm 3^\circ\text{C}$ until required. VBC (Dow Chemicals, 97%, m/p ratio = 1.30, stabilised with 75 ppm 4-*tert*-butylcatechol and 733 ppm nitromethane, 192 ppm residual water content) was stored in a refrigerator and used undiluted as the grafting monomer after being purged with nitrogen for 2 h. The degree of grafting (d.o.g., %) of the FEP-g-PVBC membranes were calculated as follows:

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

where m_g is the grafted mass and m_i is the initial mass of the irradiated FEP films. The FEP-g-PVBC intermediate membranes were subsequently submerged in aqueous trimethylamine (Acros, 50%wt) for 48 h. 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. 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 48 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 for two days with at least two changes of water to remove any lingering potassium hydroxide species. The final AAEMs (“as-synthesised”) were stored in water until required and were not allowed to dry out at any point before measurements were conducted.

2.2. Determination of ion-exchange capacities (IECs)

Standard aqueous solutions of potassium hydroxide (Riedel-de Haën, $0.1000 \pm 0.0001 \text{ mol dm}^{-3}$) and hydrochloric acid (Aldrich, $0.0990 \pm 0.0001 \text{ mol dm}^{-3}$) for IEC determination were used as received; all aqueous potassium hydroxide standards were replaced regularly to reduce the build of carbonate and prevent inaccuracies in the titrations.

The IECs (all IECs referred to in this paper are the strong anion-exchange capacities, *i.e.* OH^- ion content per g of polymer) were determined as follows. The AAEMs were immersed in $20.00 \pm 0.03 \text{ cm}^3$ (calibrated Class A pipette) of hydrochloric acid standard solution for 48 h. The solutions were then back titrated with potassium hydroxide standard solution using a Metrohm 716 DMS Titrino. The titrations were conducted dynamically with a minimum addition of potassium hydroxide titrant of 0.002 cm^3 ($\pm 0.002 \text{ cm}^3$ was taken as the volume error of the burette) and a maximum rate of addition of titrant of $0.5 \text{ cm}^3 \text{ min}^{-1}$. The endpoints were determined from largest maxima in the differential, $d(\text{pH})/dV_{\text{titrant}}$, titration curves (Figure 1 shows a

typical example). Three replicates were recorded for each membrane, and a blank run consisting of 20 cm³ of hydrochloric acid (aq, 0.1 mol dm⁻³) with no membrane was run alongside each batch to confirm the precision and accuracy of the titrations (a coefficient of variation of < 0.2% was found for all blank runs). The amount of hydroxide anions in the membrane was calculated from the difference between the initial amount of hydrochloric acid in which the membranes were soaked and the amount of hydrochloric acid titrand remaining after as determined from the titration. The membrane samples were then washed in water and soaked in excess potassium hydroxide (aq, 1 mol dm⁻³) for > 48 h with two changes of potassium hydroxide solution for complete ion-exchange to the alkaline forms. After being soaked in water for > 48 h (with at least two changes of water) the regenerated AAEMs were dried in a desiccator over anhydrous calcium chloride for > 1 week (relative humidity (RH) = 0%). It was determined experimentally that this drying protocol gave the same level of drying as treatment in a vacuum oven at 80°C for 4 h; this low temperature method was adopted for this characterization as it avoids elevated temperatures for elongated periods of time, which could potentially cause AAEM degradation. The ion-exchange capacities ($IEC / \text{eq g}^{-1}$) reported were calculated as below:

$$IEC = \frac{n_i(H^+) - n_f(H^+)}{m_{dry}(OH^-)} \quad (2)$$

where $n_i(H^+)$ is the amount of acid the membrane was soaked in, $n_f(H^+)$ is the amount of acid remaining as determined by the titration, and $m_{dry}(OH^-)$ is the mass of the dried regenerated AAEMs. [Note: the IECs in our previous synthetic studies [26,27] related to the IECs of the chloride-form anion-exchange membranes; the IECs in this study relate to the alkaline-form membranes to allow easier comparison with future fuel cell tests.]

2.3. Water uptake experiments

The AAEMs membranes “as-synthesised” were first weighed (surface water was removed by careful and quick blotting with tissue paper) to determine the hydrated mass. The samples were then dried at RH = 0% (as for IEC determination experiments) for > 1 week at ambient temperature. The dried masses were recorded and the water uptake (%) was calculated:

$$WU = \frac{m_{hyd} - m_{dry}}{m_{dry}} \times 100 \quad (3)$$

where m_{hyd} is the hydrated mass of the “as-synthesised” AAEMs and m_{dry} is the dry mass. The water uptakes were calculated as the average of three replicate membrane samples for each AAEM. The average number of water molecules per $\sim\text{NMe}_3^+$ anion-exchange site, λ , were then calculated as follows:

$$\lambda = \frac{WU}{IEC \times 100 \times 18.015} \quad (4)$$

where $18.015 \text{ g mol}^{-1}$ was taken as the molecular weight of water.

2.4. Membrane thicknesses (swelling)

During water uptake experiments, the thicknesses of the AAEMs were measured. Thicknesses (an average of four measurements for each of the three replicate membrane samples for each AAEM, twelve measurements in total) were measured for the hydrated membranes “as synthesised” and for the dried membranes (RH = 0%, 1 week). The thicknesses were recorded using an external micrometer (precision of $\pm 2 \text{ }\mu\text{m}$).

2.5. Conductivity measurements (via impedance spectroscopy)

The method for measuring the conductivities followed the impedance spectroscopy approach recently reported by Pozio *et al.* [28,29]. 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 (Z_{im} vs Z_{real} from the vector (in the complex plane), $Z(\omega) = R + j\chi$, where the resistance $R = Z_{real}$, the reactance $\chi = Z_{im}$, $\omega = 2\pi f$ (f is the frequency of the applied a.c. voltage), and $j = \sqrt{-1}$) was conducted using Zview v.2 software (Scribner Associates). This reported method is more suitable for thin and highly conductive membranes than the copper disk / silver dag method and cell design used previously at Surrey for thicker siloxane-based ionomer pellets [30].

The alkaline AAEM membranes to be tested (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 μm , circular diameter = 1.13 ± 0.02 cm, (area 1.00 ± 0.04 cm^2) with the powder side pressed to the membrane) at 500 ± 50 kg cm^{-2} at 100°C for 5 min. This temperature followed the AAEM MEA preparation methodology used by Scott *et al.* for fuel cell measurements [12]. After pressing, the resulting membrane electrode assemblies (MEAs) were stored in water for at least two days prior to conductivity measurements. The cell design, with circular graphite plates, was similar to that reported by Pozio [28], the only difference being that ELAT A-6 carbon cloth electrodes were used instead of Toray carbon paper. The cell assembly was placed in a beaker of RO water so that all of the MEA was submerged, while the gold jack plug

(for electrical connection) were kept outside of the water. Impedance measurements were conducted at increasing temperatures in the range 19 – 99°C (error of $\pm 1^\circ\text{C}$) by controlling the temperature of the water using a hotplate stirrer. Spectra were recorded at each temperature, after at least a 15 min delay to allow thermal equilibration, for $f = 100\text{ Hz} - 1\text{ MHz}$ and with 50 mV root mean squared (rms) voltage perturbation, 0.1 s integration time, and 0.1 s delay time (delay between signal application and commencement of measurements at each frequency). R_{tot} (the sum of the membrane, R_{mem} , and cell resistance, R_{cell}) was taken as the intercept with the x -axis.

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). Impedance measurements at each temperature were conducted for $f = 10\text{ Hz} - 1\text{ kHz}$ and with 50 mV rms voltage perturbation, 0.5 s integration time, and 0.5 s delay time. R_{cell} was taken as the intercept with the x -axis.

Commercial Nafion®-115 (N115) proton-exchange membrane (fully hydrated thickness determined to be $140 \pm 9\text{ }\mu\text{m}$) was used as a benchmark. N115 MEAs were prepared in a similar manner to that above, with the following slight modifications: the MEAs were pressed at 135°C for 5 min instead of 100°C and the MEAs were boiled in water for 2 h after preparation to ensure the expanded form of N115 was reformed after the hot pressing [28] (no delamination of the MEAs was observed in this boiling step). The N115 MEAs were then stored in water until required for impedance spectroscopy. Impedance measurements with N115 MEAs were conducted

for $f = 10 \text{ kHz} - 1 \text{ MHz}$ and with 50 mV rms voltage perturbation, 0.1 s integration time, and 0.1 s delay time. R_{tot} was taken as the intercept with the x -axis.

Figure 2 shows sample spectra obtained with a blank cell, a sample N115 MEA and a sample AAEM 1 MEA. The precision of the resistance readings (intercept on x -axis) for the N115 MEAs and the AAEM MEAs with this equipment and cell setup was estimated to be $\pm 0.005 \Omega$ (from multiple impedance scans on selected MEAs at room temperature). For the blank cell impedance measurements, the error was $\pm 0.001 \Omega$ (electronic conduction with no ion conduction lead to higher precision {see the scale on the inset in Figure 2} with this cell set up, again based on multiple scans on the blank cell at room temperature).

Conductivities, $\sigma / \text{S cm}^{-1}$, are calculated as below:

$$\sigma = \frac{l}{R_{mem} \times A} \quad (5)$$

where l is the membrane thickness in cm , A is the electrode area in cm^2 and R_{mem} is the membrane resistance in Ω calculated from $R_{tot} - R_{cell}$. The activation energies, $E_a / \text{kJ mol}^{-1}$, are calculated assuming Arrhenius behaviour (see results section for a comment on this) and the slope, b , of the linear regression of $\ln (\sigma / \text{S cm}^{-1})$ vs $(1000 / T) / \text{K}^{-1}$ plots:

$$E_a = -b \times R \quad (6)$$

where R is the gas constant $8.314472148 \text{ J K}^{-1} \text{ mol}^{-1}$ and the axes are plotted exactly as described above.

2.6. Statistical analysis

A consistent treatment of the precision of the measurements has been conducted. All errors are determined from sample standard deviations. Any confidence intervals mentioned in the text are at the 95% confidence level, based on the sample deviations and using the relevant student- t distribution ($N-1$ degrees of freedom, N is the number of samples tested for each membrane). The sample standard deviations over multiple samples for each membrane are compared to the expected calculated errors calculated from the standard deviations of the indeterminate errors of each physical measurement, *termed the calculated indeterminate error (CIE)* (see the Appendix for an example involving the calculation of the CIE for a conductivity). For the empirical activation energies of ion migration, E_a , the sample standard deviations over multiple samples of each membrane are compared to the errors calculated from the standard error of the slope of the linear regression (*abbreviated to ESLR*) calculated using SigmaPlot v8 graphing and statistical analysis software. If the standard deviation over multiple sample from each membrane is larger than the expected CIE or the ESLR, this suggests that there is variability in the measured results between the samples from each membrane (*i.e.* heterogeneity in the radiation-grafted AAEMs); full discussions of this can be found in the results and discussion section where it is required. The error bars presented on graphs are defined in the relevant figure captions.

3. Results and Discussion

3.1. The conductivity of fully hydrated Nafion®-115 (N115) as benchmark

Figure 3 shows the measured conductivities of 3 samples of N115 membrane as a function of temperature; Figure 4 shows the $\ln (\sigma / \text{S cm}^{-1})$ vs $(1000 / T) / \text{K}^{-1}$ representation of the same data. Table 2 gives the empirical values of σ at $50 \pm 1^\circ\text{C}$ and E_a for each sample of N115 membrane. The average conductivity at $50 \pm 1^\circ\text{C}$ over the three samples (arithmetic mean) is $0.104 \pm 0.008 \text{ S cm}^{-1}$ (Table 5). As the sample standard deviation over the three samples is the same magnitude as the CIEs, there is no significant variability between the MEAs of each sample of N115 when measuring the conductivities using this method and cell setup. The conductivity values obtained are much larger than those obtained by Pozio *et al.* for N115 ($\sigma = 0.045 \pm 0.004 \text{ S cm}^{-1}$ at 65°C) [28]. This can be explained by the fact that in this study the N115 MEAs were boiled for 2 h in water to reproduce the fully hydrated expanded form after hot-pressing and that the membrane thickness was taken as $140 \pm 9 \mu\text{m}$. In contrast, Pozio *et al.* took the membrane thickness to be the nominal value of $127 \mu\text{m}$ and only soaked the N115 MEAs in water after hot pressing ($\lambda = 10$), which, as stated by these authors, would not fully hydrate the N115 membrane to the expanded E-form with a restored hydrophilic cluster structure. However, the values of conductivities obtained in this study for N115 correlate well with values for fully hydrated ($\lambda = 22 - 23$) Nafion® membranes obtained from previous studies using different normal and tangential methods as reviewed in Tables 1 and 2 in Reference [28].

The mean value for E_a was $6.0 \pm 0.8 \text{ kJ mol}^{-1}$ (Table 5), which is smaller than the $7.9 \pm 0.1 \text{ kJ mol}^{-1}$ reported by Pozio *et al.*, suggesting that proton migrations in the N115 membranes used as benchmarks in this study were slightly less sensitive to temperature variations, possibly due to the higher level of hydration and restored ionic cluster structure.

In summary, this method for measuring the conductivities and activation energies of ion migration in thin conductive membranes gives only small deviations between samples of the same membrane. This method is a simple, quick, and accurate method for comparing the ion conductivities of different membranes. It will be especially suitable for AAEMs, as the initial studies by Scott *et al.* [11] suggest that area resistances of AAEMs are 600% than those of Nafion® membranes; the estimated largest indeterminate error is incurred when recording R_{mem} (a *constant error* of $\pm 0.005 \Omega$ due to inductance interferences when using the experimental setup described in the previous section), and higher resistance membranes will therefore produce a smaller *relative error* in the measured conductivities. The above was confirmed by an initial feasibility experiment on a single sample of AAEM **1** where a conductivity of $0.0192 \pm 0.0007 \text{ S cm}^{-1}$ (CIE) was recorded at $50 \pm 1^\circ\text{C}$ (Figure 3 and Table 4); this suggested further detailed investigations were justified.

3.2. Physical characterisation of the AAEMs

Table 3 summarised the non-electrochemical properties of the AAEMs used in this study. AAEMs synthesised from 50 μm FEP starting film showed no variation (within experimental precision) in the dry (RH = 0%, 1 week) and fully hydrated thicknesses,

which were found to be $65 \pm 2 \text{ }\mu\text{m}$ and $85 \pm 2 \text{ }\mu\text{m}$ respectively. These thicknesses reduced to $36 \pm 2 \text{ }\mu\text{m}$ and $45 \pm 2 \text{ }\mu\text{m}$ respectively for the AAEM derived from 25 μm FEP starting film. The hydration level, λ , was also constant across the AAEMS (within experimental precision) at 28 ± 2 . The number of water molecules per exchange-site in the AAEMs were higher than the values found for fully expanded Nafion® ($\lambda = 22 - 23$ [28]), which may indicate that more water molecules can be strongly bound (inner or outer sphere) to the larger OH⁻ anions compared with the smaller (but higher charge density) H⁺ cations in Nafion®. Another plausible explanation relates to the more open polymer structure expected for the AAEMs, compared with the ionic cluster model for Nafion®, allowing more water molecules to be accommodated; the shorter side chains in the AAEMs and the more homogeneous distribution (continuous graft penetration throughout the AAEMs [27]) and higher concentration (see IECs later) of the ionic exchange sites in the hydrophobic fluorinated medium cluster are not expected to yield such a constricted ionic cluster structure. As such, it is anticipated that the AAEMs can be fully hydrated when soaked in water at room temperature for a few days in contrast to the requirement for boiling for 2 h to obtain fully hydrated Nafion® [28]. This is important because AAEMs based on bound quaternary ammonium cation sites with OH⁻ anions show chemical instability when treated at temperatures above 60°C for extended periods of time (see Scheme 3 in Reference [6] for degradation mechanisms); this is why the AAEM MEAs for conductivity measurements were not boiled in water (the hot-pressing at 100°C was only for a very short period of time and was assumed to have a minimal impact on the polymer structure and IECs).

Figure 5 graphically compares the calculated and experimentally determined IECs (Table 3). The IECs are lower than expected from the synthetic methodology, even to the 95% confidence level (error bars). There are three potential reasons for this:

- (1) Displacement of the quaternary ammonium cation-exchange sites, especially on extended treatment in aqueous potassium hydroxide (1 mol dm^{-3}) for 48 h, to effect the ion-exchange to the alkaline forms.
- (2) Incomplete amination on treatment of the FEP-g-PVBC in aqueous trimethylamine (50% mass) for 48 h.
- (3) Trapped poly(VBC) homopolymer (oligomeric or polymeric) in the intermediate FEP-g-PVBC membranes, which contributes to the determination of the d.o.g. but is subsequently being released on amination and anion-exchange membrane swelling (boiling step with chloride ion forms).

Evidence for (1) above is the slight trimethylamine smell on drying the AAEMs (RH = 0%, 1 week) and after membrane treatment in potassium hydroxide (1 mol dm^{-3} , 48 h). Evidence for (3) above is that the experimentally determined IECs for the AAEM based on 25 μm FEP is 92% of expected IEC compared with 84 – 87 % for the AAEMs based on 50 μm FEP; this signifies that a smaller amount of trapped poly(VBC) homopolymer is present in, and easier to escape from, the thinner membranes. It has been previously observed that there is no increase in IEC when increasing the amination times above 24 h [27]; it is therefore accepted that the 48 h amination times used in this study will produce near 100% amination, and that reason (2) above is not a significant factor in the lower-than-expected experimentally determined IECs. The IEC of N115 was calculated to be $0.93 \pm 0.01 \text{ meq g}^{-1}$ from the reported equivalent weights = $1075 \pm 15 \text{ g mol}^{-1}$ [28].

3.3. Conductivities of AAEMs

Conductivities at $50 \pm 1^\circ\text{C}$ were chosen as benchmarks for comparing AAEM; temperatures above 60°C lead to AAEM degradation and 50°C was selected on the basis of a practical temperature for operation of fuel cells with AAEMs (high temperatures would be inadvisable in power supplies for portable devices such as laptop computers). Figure 6 shows the conductivities for the AAEMs as a function of temperature, with the values of σ at $50 \pm 1^\circ\text{C}$ summarized in Table 4 and 5. The spread of determined values for the conductivities, at all temperatures, between samples of the same AAEM are larger than the CIEs, indicating that the AAEMs exhibit a degree of grafting heterogeneity; this confirms IEC measurements in which the spread of experimentally determined IECs is larger than the CIEs (not reported). This demonstrates a possible requirement for more optimization work on the synthetic protocol to improve the homogeneity resulting from the radiation-grafting procedure and to yield AAEMs that exhibit homogeneous conductivities.

The values of σ at $50 \pm 1^\circ\text{C}$ do not increase with d.o.g in the range 21 – 26% (within the experimental uncertainties as indicated by the sample standard deviations about the mean values). Grafting levels below 21% clearly lead to undesirable decreases in conductivities for the final AAEMs. Grafting levels $> 26\%$ are not possible with this synthetic pre-irradiation grafting protocol as total doses > 7 Mrad (70 kGy) of γ -irradiation would be required and are known to lead to AAEM membrane brittleness (very undesirable for use as fuel cell fuel/oxidant gas separation and ion-conductive membranes); this limitation is mainly down to the choice FEP base polymer [19]. Viable solutions to overcome this limitation are summarized below:

- (1) A switch to the simultaneous irradiation methodology (where the FEP would be irradiated while soaked in the VBC monomer) as this requires lower radiation doses for enhanced grafting yields.
- (2) Substitution of FEP with a base polymer that exhibits superior radiation tolerance. This is the case with non-fluorinated LDPE and this is under active investigation, with results to be published in due course.
- (3) The use of a polymer system that does not involve irradiative techniques to produce AAEM functionality.

The maximum mean value of conductivity of $0.023 \pm 0.001 \text{ S cm}^{-1}$ (AAEM 2) at $50 \pm 1^\circ\text{C}$ is 20% of that found for fully hydrated N115 ($0.104 \pm 0.008 \text{ S cm}^{-1}$); however, absolute membrane resistances will be lower than this suggests as the AAEMs produced in this study are thinner than fully hydrated N115 (85 and 45 μm compared with 140 μm). Significantly, the conductivities for the AAEMs are only 50% of the value of $0.045 \pm 0.004 \text{ S cm}^{-1}$ at 65°C as determined by Pozio *et al.*, who used the nominal thickness of 127 μm for N115 in the calculation of the conductivity and did not boil the MEAs after hot pressing (boiling the MEAs in water is not always undertaken when preparing fuel cell MEAs), indicated by their determined $\lambda = 10$ (*c.f.* $\lambda = 23$ for fully hydrated Nafion®). This clearly indicates the suitability of the AAEMs produced for this study for application as alkaline fuel cell membranes. Due to the increased sensitivity towards increasing temperature (see discussions on activation energies below), conductivities around 90°C for the AAEMs are only 33% that found for fully hydrated N115; the AAEMs will not, however have long term thermal stability in this temperature regime.

The empirical activation energies for ion-migration, E_a , for the AAEMs are presented in Tables 4 and 5 and were determined from the linear regression of plots presented in Figure 7. There is some variation between the values for E_a found between samples of the same AAEM (the spread of values obtained between samples of the same AAEM is larger than the CIEs), corroborating conductivity and IEC trends. However, the mean values of E_a do not vary significantly between AAEMs (confidence limit of $12.6 \pm 0.6 \text{ kJ mol}^{-1}$ at the 95% confidence level over all twelve samples studies for AAEMs **2 – 5**). This value is twice that found with fully hydrated N115 in this study ($6.0 \pm 0.8 \text{ kJ mol}^{-1}$) and more than the value of $7.9 \pm 0.1 \text{ kJ mol}^{-1}$ determined by Pozio *et al.* for N115 [28]. This demonstrates that hydroxide ion mobility in these RG-AAEMs is significantly more sensitive to temperature than proton migration in N115, but interestingly only slightly more sensitive than proton-migration in thicker Nafion®-117 (nominal thickness of 183 μm , $E_a = 10.9 \pm 0.2 \text{ kJ mol}^{-1}$ [28])

A critical examination of the linear regressions in Figure 7 ($R^2 = 0.995 \pm 0.002$ over all twelve samples studied for AAEMs **2 – 5**) show a consistent and perceptible lowering of the conductivities at temperatures $> 65^\circ\text{C}$ when compared to the values expected if pure Arrhenius behaviour was observed (the gradient of decrease slopes lower slightly at higher temperatures). This is evidence of either (1) a limitation in the assumption of Arrhenius behaviour, (2) the presence of AAEM degradation (which is expected from the functional group chemistry as explained above), or (3) a change in hydration at elevated temperatures for the AAEMs. The behaviour is likely to result from a combination of all three. The E_a values given in this text should only be considered as an empirical indication of the temperature sensitivity of hydroxide ion mobility in the AAEMs.

4. Conclusions

A maximum conductivity of $0.023 \pm 0.001 \text{ S cm}^{-1}$ at $50 \pm 1^\circ\text{C}$ was demonstrated for the radiation-grafted AAEMs studied ($\lambda = 28 \pm 2$ water molecules per ion-exchange site) and was found to be between 20 – 50% of the values determined for Nafion®-115 ($\sigma = 0.045 \pm 0.004$ (65°C) – 0.104 ± 0.008 ($50 \pm 1^\circ\text{C}$) S cm^{-1} , depending on the level of hydration ($\lambda = 10$ and 23 respectively)). The AAEMs produced are, however, thinner ($45 - 85 \text{ }\mu\text{m}$) compared with N115 ($127 - 140 \text{ }\mu\text{m}$) and so the absolute resistances of the membranes are close to those found for N115. AAEMs with initial d.o.g. $> 21\%$ do not show a perceptible variation in conductivity at $50 \pm 1^\circ\text{C}$; however, conductivity does decrease on d.o.g. $< 21\%$. This significant result clearly indicates the suitability of these AAEMs for application in fuel cells below the accepted thermal stability limitation of 60°C for alkaline membranes based on a quaternary ammonium functionality. In-depth statistical analysis of the ion-exchange capacity and conductivity variations for the AAEMs indicate that there is some heterogeneity resulting from radiation-grafting synthetic procedure. The empirical activation energies (Arrhenius behaviour assumed) for hydroxide ion mobility in the AAEMs ($12.6 \pm 0.6 \text{ kJ mol}^{-1}$ at the 95% confidence level) is twice that for proton mobility in fully hydrated N115 ($6.0 \pm 0.8 \text{ kJ mol}^{-1}$), showing that hydroxide ion migration has a stronger temperature dependence.

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Appendix

The *calculated indeterminate errors* (CIEs) are calculated using standard rules from the indeterminate errors (precision) of each of the physical measurements. For example, the CIE for the conductivity, s_σ , is given by:

$$s_\sigma = \sigma \times \sqrt{\left(\frac{s_l}{l}\right)^2 + \left(\frac{s_A}{A}\right)^2 + \left(\frac{s_{R_{mem}}}{R_{mem}}\right)^2} \quad (7)$$

where s_l is the error in the membrane thickness, s_A is the error in the electrode area, and $s_{R_{mem}}$ is the error in the membrane resistance as measure using impedance spectroscopy. If $\sigma = 0.078 \text{ S cm}^{-1}$, $l = 0.0140 \pm 0.0009 \text{ cm}$, $A = 1.00 \pm 0.04 \text{ cm}^2$, $R_{tot} = 0.207 \pm 0.005 \text{ }\Omega$, $R_{cell} = 0.029 \pm 0.001 \text{ }\Omega$, then $R_{mem} = 0.207 - 0.029 = 0.178 \text{ }\Omega$, and $s_{R_{mem}} = \sqrt{0.001^2 + 0.005^2} = 0.005 \text{ }\Omega$, the CIE, s_σ , calculated to be $= 0.006 \text{ S cm}^{-1}$. The rules used in this study for calculating errors (logarithms, exponentials, additions *etc.* can be found in Table 2-5 of reference [31].

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Scheme 1: Preparation of FEP-g-PVBC radiation grafted membranes from FEP and vinylbenzyl chloride. Subsequent amination and ion-exchange yields FEP-grafted-poly(vinylbenzyltrimethylammonium hydroxide) alkaline anion-exchange membranes (FEP-g-PVBTMAOH RG-AAEMs).

Figure 1: Sample titration curves for a) a sample of AAEM **2** (0.3073 ± 0.0020 g) soaked in 20.00 ± 0.03 cm³ of aqueous hydrochloric acid titrand (0.0990 ± 0.0001 mol dm⁻³) for 48 h and b) 20.00 ± 0.03 cm³ of aqueous hydrochloric acid titrand (0.0990 ± 0.0001 mol dm⁻³) with no added AAEM (blank run). The concentration of the added aqueous potassium hydroxide titrant was 0.1000 ± 0.0001 mol dm⁻³. The solid lines with points are the pH vs. $V_{titrant}$ curves, while the dashed lines are the differential, $\frac{d(pH)}{dV_{titrant}}$, curves.

Figure 2: Sample impedance spectra (presented as Nyquist Plots) obtained with MEAs made with ELAT A-6 (E-Tek) electrode materials and (a) no membrane (blank cell for obtaining R_{cell}), (b) Nafion®-115 (in fully hydrated form), and (c) AAEM **1**. The inset is a close-up view of the Nyquist plot for the blank cell. Z_{im} axes have been flipped around the x -axis.

Figure 3: The conductivities at increasing temperatures for N115 sample 1, 2, and 3 and a sample of AAEM **1**. Error bars indicate the CIEs.

Figure 4: The $\ln(\sigma / S \text{ cm}^{-1})$ vs $(1000 / T) / K^{-1}$ plot for data in Figure 3; the lines indicate the linear regressions.

Figure 5: The theoretical (open circles, assuming 100% amination, no side reactions, and no trapped homopolymer in the intermediate FEP-*g*-PVBC membranes) and experimentally determined IECs (filled squares) for the AAEMs. The error bars represent the confidence intervals at the 95% confidence level over three replicate samples of each AAEM.

Figure 6: The conductivities at increasing temperatures of each of the samples tested for AAEMs **2 – 5**. Error bars indicate the CIEs.

Figure 7: The $\ln (\sigma / S \text{ cm}^{-1})$ vs $(1000 / T) / \text{K}^{-1}$ plot for data in Figure 6; the lines indicate the linear regressions

AAEM	Total dose / MRad	FEP thickness / μm	Grafting temperature / $^{\circ}\text{C}$	Grafting duration / h	d.o.g (%)
1	7.00	50	55	72	23.9
2	7.00	50	48	166	24.7
3	4.04	25	48	89	20.3
4	7.00	50	55	24	21.2
5	7.00	50	48	237	26.1

Table 1: The synthetic conditions used to produce the intermediate FEP-g-PVBC membranes for the AAEMs synthesised.

N115 Sample	σ / S cm^{-1}	E_a / kJ mol^{-1}
1	0.097 ± 0.008	6.8 ± 0.5
2	0.102 ± 0.008	5.3 ± 0.3
3	0.113 ± 0.009	5.8 ± 0.4

Table 2: The conductivities at $50 \pm 1^{\circ}\text{C}$ and activation energies of proton migration of three samples of N115 membrane. The errors given for σ are the calculated indeterminate errors (CIEs). The errors given for E_a are calculated from the standard error of the slope of each linear regression (ESLR).

AAEM	d.o.g. (%)	IEC / meq g^{-1}	IEC _{calc} / meq g^{-1}	t_{wet} / μm	t_{dry} / μm	WU / %	λ
1	23.9	1.02 ± 0.03	1.20	86 ± 2	65 ± 2	56 ± 5	30 ± 4
2	24.7	1.07 ± 0.04	1.23	84 ± 3	66 ± 2	50 ± 2	26 ± 1
3	20.3	0.98 ± 0.03	1.06	45 ± 3	36 ± 2	47 ± 3	27 ± 2
4	21.2	0.92 ± 0.05	1.10	83 ± 2	64 ± 2	48 ± 8	29 ± 5
5	26.1	1.10 ± 0.03	1.29	86 ± 2	63 ± 2	54 ± 3	27 ± 2

Table 3: The IECs, wet and dry thickness, water uptakes and number of water molecules per anion-exchange site (λ) in the AAEMs produced. The IEC_{calc} is the theoretical IEC based on the d.o.g. and assuming 100% amination, no side reactions (*e.g.* displacement of the anion-exchange sites), and no trapped poly(VBC) homopolymer in the intermediate FEP-g-PVBC membranes. The errors are the sample standard deviations over multiple samples of each AAEM.

AAEM [d.o.g. (%)]	Sample	$\sigma / \text{S cm}^{-1}$	$E_a / \text{kJ mol}^{-1}$
1 [23.9]	1	0.0192 ± 0.0007	15.1 ± 0.4
	1	0.0243 ± 0.0013	11.5 ± 0.3
	2	0.0229 ± 0.0012	12.7 ± 0.4
2 [24.7]	3	0.0223 ± 0.0012	13.6 ± 0.3
	1	0.0156 ± 0.0012	11.5 ± 0.2
	2	0.0167 ± 0.0013	12.6 ± 0.5
3 [20.3]	3	0.0182 ± 0.0014	12.9 ± 0.3
	1	0.0181 ± 0.0008	14.2 ± 0.3
	2	0.0208 ± 0.0009	13.3 ± 0.4
4 [21.2]	3	0.0247 ± 0.0011	11.1 ± 0.4
	1	0.0230 ± 0.0010	13.2 ± 0.5
	2	0.0204 ± 0.0009	12.3 ± 0.4
5 [26.1]	3	0.0231 ± 0.0010	12.8 ± 0.4

Table 4: The conductivities at $50 \pm 1^\circ\text{C}$ and activation energies of hydroxide migration of each of the AAEM samples. The errors given for σ are the CIEs. The errors given for E_a are calculated from the ESLR.

Membrane	$\sigma / \text{S cm}^{-1}$	$E_a / \text{kJ mol}^{-1}$
N115	0.104 ± 0.008	6.0 ± 0.8
AAEM 2	0.0232 ± 0.0010	12.6 ± 1.1
AAEM 3	0.0168 ± 0.0013	12.3 ± 0.7
AAEM 2	0.0212 ± 0.0033	12.9 ± 1.6
AAEM 3	0.0222 ± 0.0015	12.7 ± 0.5

Table 5: The mean values for the conductivities at $50 \pm 1^\circ\text{C}$ and empirical activation energies of hydroxide ion migration of each of the AAEMs (Arrhenius behavior was assumed). The errors are the sample standard deviations over three samples of each AAEM.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7