

Radiation–Grafted Alkaline Anion–Exchange Membranes Prepared with Reduced Monomer Quantities

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Abstract

Alkaline anion–exchange membranes (AAEM) for alkaline polymer electrolyte fuel cells (APEFC) were successfully prepared using electron beam irradiated poly(ethylene–co–tetrafluoroethylene) precursor films grafted with vinylbenzyl chloride (VBC) monomer. The resulting chloromethyl groups were subsequently reacted with trimethylamine to form quaternary ammonium anion–exchange functional head–groups. The concentration of toxic and expensive VBC, that is required to achieve an optimal level of grafting, was reduced from 100%v/v (undiluted) to 20%v/v by dilution with propan–2–ol and the inclusion of a surfactant. Fuel cell tests using hydrogen and oxygen gave the same peak power densities ($164 \pm 3 \text{ mW cm}^{-2}$) for the AAEMs prepared with both 100%v/v VBC and 20%v/v VBC. This highlights the (desirable) lack of any detrimental effect on performance of the resulting APEFC with the reduction in grafting monomer concentration used for the synthesis of the component AAEM.

Keywords: Poly(Ethylene–co–Tetrafluoroethylene); Vinylbenzyl Chloride; Radiation–Grafting; Alkaline Polymer Electrolyte Fuel Cell (APEFC), Alkaline Anion–Exchange Membrane (AAEM).

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have received a large amount of interest as power sources for both stationary and mobile applications. However, they commonly involve the incorporation of expensive commercial perfluorinated proton-exchange membranes (such as Nafion[®] by Du Pont) as the solid electrolyte and platinum-based electrocatalysts [1]. More recently, Alkaline Anion-Exchange Membranes (AAEMs) have been developed as an alternative electrolyte for use in low temperature fuel cells: such Alkaline Polymer Electrolyte Fuel Cells (APEFCs) have been shown to exhibit lower fuel permeability, across the AAEM (compared to proton exchange membranes) when used in direct alcohol mode [2], and the ability to utilise cheaper and more abundant non-precious-metal electrocatalysts (especially at the cathode due to a more facile oxygen reduction reaction at high pH) [3-5]. AAEMs consist of covalently bound positive functional head-groups, typically quaternary-ammonium-type ($-N^+R_3$), and mobile anions (*i.e.* cationic polymers with anion conduction). Having polymer-bound cationic groups, instead of the mobile metal cations found in traditional liquid electrolyte alkaline fuel cells, gives the APEFCs an enhanced resistance to the undesirable accumulation of metal carbonate precipitates [6].

AAEMs produced from the radiation-induced grafting of monomers onto preformed fluorinated, partially fluorinated, and non-fluorinated polymer films have been extensively studied and reported [7-10]. Generally, precursor polymer films are modified using either a simultaneous grafting method [11] or a pre-irradiation method [8,12] with either gamma-ray or electron-beam irradiation. Simultaneous radiation-grafting is where the precursor polymers are irradiated whilst submerged in the grafting monomer solution of choice and pre-irradiation-grafting is where the polymer precursors are initially irradiated (commonly in air) and then subsequently treated with the grafting monomer solution. The AAEMs produced at the University of Surrey are based on the electron-beam pre-irradiation-grafting of poly(ethylene-co-tetrafluoroethylene) (ETFE) with vinylbenzyl chloride (VBC) monomer (previously used in large quantities and undiluted) before subsequent quaternization with a tertiary amine of choice [12-14]. VBC is both expensive and hazardous when used in large quantities (potential mutagen, acutely

toxic on skin adsorption and ingestion, and very toxic to aquatic life): it is therefore vital to significantly reduce the quantity required during the grafting step. This has widely been reported for other monomers, such as styrene (used to synthesise radiation-grafted proton-exchange membranes), by dilution with appropriate solvents [15-17].

The reaction between monomer and the radiation induced reaction sites (peroxides and radicals) of the polymer is governed by the diffusion properties of the monomer and lifetimes of the reaction sites. Without solvents, grafting typically follows the grafting front mechanism [18,19]: this is where the grafting initially occurs at the surfaces of the polymer films, and more monomer molecules can then penetrate deeper, when the grafted layers subsequently swell. The introduction of a suitable additional solvent leads to enhanced swelling within the polymer substrate and increased monomer accessibility to the internal substrate layers, resulting in a higher (more uniform) level of grafting [20]. This is especially important for ion-exchange membranes, as homogeneous grafting throughout the entire membrane thickness is vital for effective ion conductivity. Nasef *et al.* measured the effect of several pure solvents on pristine ETFE films at ambient temperature and observed that the polymer film decreasingly swelled in the order; toluene > dimethylformamide >> propan-2-ol > ethanol > methanol. However, for the alcohol systems, the degree of swelling was substantially increased when ETFE was submerged in an alcohol-monomer mixture (*ca.* 50:50 v/v) compared to when submerged in only alcohol [16]. The dilution of the monomer can also affect the overall grafting as a result of concentration, and thus viscosity, effects. Elmidaoui *et al.* proposed that by decreasing the monomer concentration, the viscosity is lowered, and this leads to a higher diffusivity of monomer into the membrane thickness and allows facilitated access to the deeper grafting sites; however, this will also lead to a simultaneous decrease in local monomer concentration and a reduction in the diffusion via the graft front mechanism [21]. This situation becomes further complicated when the solubility of the monomer in the solvent is taken into account. It is well known that solvents with similar solubility parameters to the monomer improve the overall degree of grafting, whereas large differences in solubility parameters hinder the reaction [22]. The

differences between the monomer–solvent solubility parameters are, however, reduced by the inclusion of an appropriate surfactant [23]. Thus a balance needs to be struck regarding the influence the solvent has over both the membrane and monomer; making the correct choice of solvent to use essential. The most commonly encountered solvents are methanol [16,17], toluene [8,16,17,24], propan–2–ol [16,25,26] or combinations of these with water [27,28].

The ultimate aim is to use water as a VBC dispersion: Waring *et al*, described a post-irradiation emulsion technique where VBC was diluted with water along with an emulsifier and chain transfer agent [29]. However, ETFE based AAEMs (with quaternary amine (TMA) functionality produced using this method) evaluated in collaboration with Mamlouk *et al*, exhibited extremely low through-plane conductivity with high anisotropy, resulting in them being labelled “*unsuitable for fuel cell tests*”. This was attributed to the poor distribution of the VBC monomer through the profile of the membrane, due to the lack of polymer swelling in water and the low solubility of the VBC in water (the emulsion technique used a only 3%v/v VBC) [30]. The severe immiscibility of VBC in water (even within an emulsion based system) is proving difficult for the production of highly ionic conductive AAEMs with the pre-irradiation grafting method (that is more useful when the radiation source is not on site). Instead, this paper details the successful production of *m*²-*batch-sizes* of radiation-grafted trimethylammonium–type AAEMs using electron–beam pre-irradiated ETFE film where a significant reduction in VBC concentration was achieved by dilution in propan–2–ol. The solubility of VBC in propan–2–ol was further enhanced on addition of a non-ionic surfactant. This formulation promoted successful grafting with monomer concentrations as low as 20%v/v; the resultant AAEM had comparable properties to the benchmark produced using 100%v/v (*i.e.* undiluted) VBC.

2. Experimental Procedures

2.1. Chemicals and Materials

Poly(ethylene-co-tetrafluoroethylene) film, (ETFE, 50 μm thick, Nowoflon ET-film) was supplied by Nowofol Kunststoffprodukte GmbH (Germany). Vinylbenzyl chloride monomer (VBC, mixture of 3- and 4- isomers; used without removal of inhibitor) was purchased from Dow Chemicals (Germany). Surfadone LP-100 (*N*-Octyl-2-pyrrolidone) was obtained from ISPcorp (USA). Propan-2-ol, toluene, poly(vinylbenzyl chloride) were of reagent grade and supplied from Sigma-Aldrich (UK) while *N,N,N',N'*-tetramethylhexane-1,6-diamine (TMHDA) and trimethylamine (TMA, 50%wt in water) were supplied from Acros Organics (UK). Pt/C electrocatalyst (Johnson Matthey Hispec 3000, 20%mass Pt on Vulcan carbon) was purchased from Alfa Aesar (UK). The carbon cloth electrodes used for conductivity determination contained a micro-porous layer (MPL) on one side consisting of carbon powder (1 mg cm^{-2}) and 20%wt PTFE as a binder and were supplied by CeTech (Taiwan). The carbon paper electrodes used for fuel cell testing contained a MPL on one side of a wet proofed (20%wt PTFE) carbon paper gas diffusion layer [GDL] and was purchased from Hesen (China): the MPL consisting of 1 mg cm^{-2} of carbon powder with 20%wt PTFE as binder. All chemicals were used as received and the water used has a resistivity of $18.2 \text{ M}\Omega \text{ cm}$.

2.2. Membrane Preparation

The AAEMs were prepared from pre-formed ETFE films using the method previously reported [9] with modifications to the grafting step as detailed below and as summarised in scheme 1. The ETFE films were subjected to electron-beam irradiation in air to a total dose of 70 kGy (using a 4.5 MeV Dynamatron Continuous d.c. Electron-Beam Unit at Synergy Health, South Marston, UK). After irradiation, the films were transported back to the laboratory (University of Surrey) in dry ice, then stored at $-36 \pm 2 \text{ }^\circ\text{C}$ and used within 12 months of irradiation. The effect of extensive cold storage of the e-beamed ETFE (up to 16 months) has been shown to produce no statistically significant reduction in the ion-exchange capacities (IEC) of the resulting AEMs [31]. This is useful for large lab-scale production

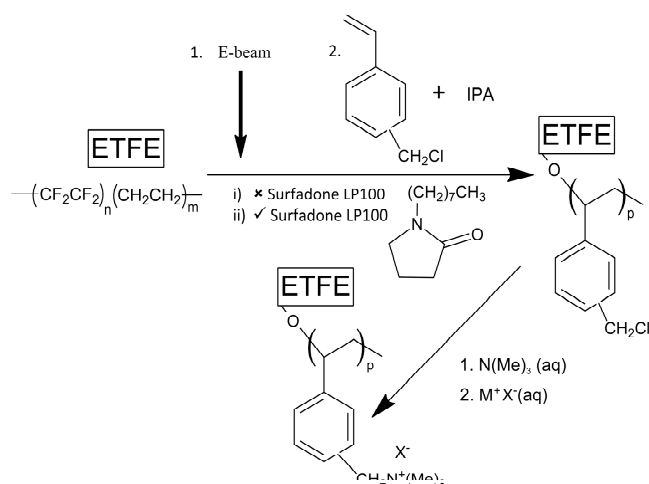
by allowing the flexibility to produce multiple grafted batches of different types of radiation-grafted AEMs from a single electron-beam treatment.

For the grafting step, the irradiated ETFE films were loosely wound in single ply tissue paper (in a *Swiss-roll* formation with the aim of separating the ETFE films from each other and facilitating monomer access to all of the ETFE surface areas) and immersed in propan-2-ol solutions of VBC at various concentrations (5 to 100%v/v VBC) in sealed vessels both with and without addition of surfactant (1%v/v Surfadone LP-100 [*N*-octyl-2-pyrrolidone]). Undiluted VBC was used to manufacture the benchmark membranes. Full details of the VBC dilutions used for each membrane are summarized in Table 1. The solutions were then purged with N₂ for 1 h (to deactivate the inhibitor present within the VBC) before the vessels were sealed and heated at 60°C for 72 h. After the reaction period, the films were removed from the solutions, washed in toluene and then heated in toluene at 70°C for 5 h; this process is employed to remove excess unreacted VBC and any VBC homopolymer (polymerized VBC that is not grafted to the ETFE) that may be present. The resulting intermediate ETFE-g-poly(VBC) films were subsequently dried at 70°C for 5 h in a vacuum oven to remove all traces of solvent.

In this study (and in-line with our other studies), the gravimetric degree of grafting (d.o.g.) was not recorded for any of the membrane samples. This was to minimise the time period between the irradiated ETFE films being removed from the freezer and subsequent submersion in the grafting solutions under study (i.e. the e-beamed ETFE films are not left at room temperature for longer periods than required). Previous studies have shown this can (due to lengthy time periods for weighing the membranes due to static issues) lead to larger errors in the IECs of the resulting AEMs. Our laboratory protocol is to use the IEC data as the primary indicator of the level of grafting.

The intermediate ETFE-g-poly(VBC) films were then submerged in the aqueous TMA at ambient temperature for 5 h, washed in water, and subsequently heated in fresh water at 60°C for 18 h; this procedure was adopted to remove any excess TMA. The resulting transparent (orange), chloride-anion form ETFE-g-poly(VBTMA⁺Cl⁻) anion-exchange membranes (AEM) were stored in water until

required. Where necessary, the AEMs were converted to the hydroxide-form AAEMs immediately before use and testing by submerging in aqueous KOH (1 mol dm⁻³) for 1 h (changing the solution twice during this period to ensure complete ion-exchange) followed by thorough washing with N₂-purged water; N₂-purged water was used to *minimise* the formation of carbonate/bicarbonate species through contamination with atmospheric carbon dioxide.



Scheme 1. The synthesis of the trimethylammonium AEMs via the radiation-grafting of VBC onto ETFE both (i) without surfactant and (ii) with surfactant. IPA = propan-2-ol.

Table 1. A summary of the composition of grafting solution for each AAEM synthesised.

Membrane	VBC (%v/v)	Propan-2-ol (%v/v)	Surfactant (%v/v)
M-1	10	90	0
M-2	20	80	0
M-3	30	70	0
M-4	40	60	0
M-5	50	50	0
M-6	100	0	0
M-7	5	94	1
M-8	10	89	1
M-9	15	84	1

M-10	20	79	1
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2.3. Membrane Characterization

2.3.1. FT–Raman Spectroscopy

FT–Raman spectra were recorded using a Perkin Elmer System 2000 NIR/FT–Raman spectrometer at a power of 1400 mW with a resolution of 4 cm⁻¹ and 128 scans. Due to the nature of Raman spectroscopy, no sample preparation was required and the spectra of M-6 and M-10 were recorded with the AEMs (chloride form) in fully hydrated conditions.

2.3.2. Ion Exchange Capacity (IEC)

The ion exchange capacities (IEC) of the functionalized AAEMs were measured using the back titration method previously reported [32].

2.3.3. Water Uptake (WU) and Through–Plane Dimensional Swelling (TPS)

The hydroxide exchanged AAEMs were soaked in N₂–purged water for 24 h at ambient temperature. Excess surface water was removed by dabbing with tissue and the hydrated masses (M_{hyd}) and thicknesses (T_{hyd}) were recorded. The AAEMs were subsequently dried by storage at relative humidity RH = 0 % (over anhydrous calcium chloride in a sealed desiccator) for 7 d before the dry masses (M_{dry}) and thicknesses (T_{dry}) were recorded. All measurements were conducted on three different samples of each membrane (with four thickness measurements performed on each individual sample [*i.e.* 4 thickness measurements on 3 samples of each AAEM]). The gravimetric water uptakes (WU) were calculated using Eq (1) and through–plane swellings using Eq (2):

$$\text{WU} = \frac{M_{\text{hyd}} - M_{\text{dry}}}{M_{\text{dry}}} \quad (1)$$

$$\text{TPS} = \frac{T_{\text{hyd}} - T_{\text{dry}}}{T_{\text{dry}}} \quad (2)$$

2.3.4. Ionic Conductivity

The through-plane ionic conductivities of the bicarbonate–anion–form AEMs were measured from 30 to 60°C, as previously reported, using a two–probe cell connected to a Solartron 1260 frequency response analyser / Solartron 1287 electrochemical interface combination controlled by ZPlot software (Scribner Associates) [33]. The AEMs were first cut to a circular diameter $\phi = 1.4$ cm and then hot–pressed between two $\phi = 1.3$ cm carbon cloth electrodes (CeTech) with 700 kg cm^{-2} force for 3 min at 60°C. The resulting mini–membrane electrode assemblies (mMEAs) were then soaked in deionised water for 18 h to fully rehydrate. They were then submerged in aqueous sodium bicarbonate (1 mol dm^{-3}) for 1 h (the solution was changed twice during this period to ensure complete ion–exchange) followed by thorough washing in N_2 –purged deionised water for 1 h (multiple changes of water during this period) to exchange the chloride counter ions to the bicarbonate anions.

This procedure follows the suggestion by Yan *et al.* where the ionic conductivities of AEMs that are measured in the bicarbonate form are multiplied by a “correction factor” of 3.8 to provide *routine and rapid* estimates of the conductivities of the AAEMs in the hydroxide form [34]; this has been extensively validated in our laboratory to give excellent estimates of the hydroxide conductivities for radiation–grafted ETFE–based AEMs [e.g. Fig. S5 in Reference [13]]. Converting the AEMs into the bicarbonate anion form, for conductivity determinations, avoids ambiguity in the counter ion present. Hydroxide counter–ions would risk exchange to carbonate and bicarbonate anions in the presence of even small amounts of CO_2 : the complete exclusion of CO_2 from the experimental set–up is highly time consuming and difficult to unequivocally achieve. The ionic conductivities ($\sigma / \text{S cm}^{-1}$) were calculated using Eqn. (3), where t is the thickness of the AEM (in cm), R is the resistance of the AEM (in Ω) [after correction for the series electronic resistance of the carbon electrodes and circuit] and A is the area (cm^2) of the parallel carbon cloth electrodes.

$$\sigma = \frac{t}{RA} \quad (3)$$

2.4 Fuel Cell Tests

The beginning-of-life performance of M-6 and M-10 (synthesised using 100%v/v VBC and 20%v/v VBC [diluted in 79% propan-2-ol and 1%v/v Surfadone] respectively) were evaluated in a H₂/O₂ fuel cell. To form both the anode and cathode, a catalyst ink consisting of Pt/C (20%wt Pt, HISPEC 3000, Alfa Aesar, UK), 15%wt poly(vinylbenzyl chloride) and ethyl acetate solvent was sprayed on top of the MPL of the Hensen electrodes (geometric area = 5.3 cm²) and allowed to dry in air: the total Pt loading of 0.40 ± 0.02 mg cm_{geo}⁻² was used for both electrodes. The dried electrodes were then submerged in undiluted TMHDA for 18 h to functionalize (and thus form Surrey's alkaline ionomer concept 1 – SION1 [12]). Both of the electrodes and AEMs were subsequently immersed in aqueous KOH (1 mol dm⁻³) for 1 h (with the solution refreshed twice more during this period to ensure complete ion-exchange) followed by thorough washing in deionised water. The anode/AAEM/cathode arrangement (no hot-pressing before assembly into the fuel cell) was then secured between two graphite plates with serpentine flow channels with a 5.5 N m torque. An 850e fuel cell test station (Scribner Associates, USA) was used for the testing: The fuel cell temperature was controlled at 50°C; H₂ and O₂ were supplied to the anode and cathode respectively at flow rates of 600 cm³ min⁻¹, at temperatures of 50°C (*i.e.* indirect determination of RH = 100%), and no back-pressurisation of the gas streams. Fuel cell data was collected under galvanostatic control.

3. Results and Discussion

The preparation of AAEMs from ETFE preformed films has been achieved via post irradiation grafting using VBC with subsequent functionalisation with TMA. The effect of a reduction in monomer concentration, with dilution in a suitable solvent (iso-propanol), is reported with the subsequent addition

of a surfactant. Surfadone LP-100 (1-Octyl-2-pyrrolidone) was chosen as a non-ionic surfactant for this procedure. The properties of the resulting ion exchange membranes are summarised in Table 2.

Table 2. A summary of the principal properties of AAEMs synthesised according to Table 1. ($n = 3$)

Membrane	Hydrated Thickness (μm)	IEC (mmol g^{-1})	Water Uptake (%)	Thickness Increase (%)	σ (S cm^{-1}) ^a
M-1	60 \pm 0	0.54 \pm 0.06	4.2 \pm 1.1	8.5 \pm 2.3	0.002 \pm 0.001
M-2	66 \pm 3	0.86 \pm 0.01	15.0 \pm 2.0	11.3 \pm 2.6	0.008 \pm 0.005
M-3	71 \pm 1	1.16 \pm 0.10	23.1 \pm 5.1	16.3 \pm 0.3	0.026 \pm 0.008
M-4	78 \pm 3	1.38 \pm 0.05	32.9 \pm 1.6	20.7 \pm 3.8	0.041 \pm 0.012
M-5	88 \pm 2	1.32 \pm 0.04	41.7 \pm 2.9	16.5 \pm 0.5	0.048 \pm 0.004
M-6	93 \pm 1	1.34 \pm 0.19	43.5 \pm 2.5	18.2 \pm 1.1	0.056 \pm 0.009
M-7	59 \pm 1	0.61 \pm 0.01	7.7 \pm 1.8	7.2 \pm 0.2	0.007 \pm 0.002
M-8	67 \pm 3	0.76 \pm 0.14	16.0 \pm 3.9	12.3 \pm 5.3	0.026 \pm 0.010
M-9	85 \pm 1	1.33 \pm 0.02	43.2 \pm 2.8	16.4 \pm 0.3	0.059 \pm 0.006
M-10	83 \pm 1	1.49 \pm 0.02	42.2 \pm 3.7	19.1 \pm 4.9	0.079 \pm 0.004

^a The calculated through plane hydroxide ion conductivities at 50°C for the fully hydrated membranes that were calculated from the experimentally determined bicarbonate ion conductivities.

3.1. Membrane Characterisation

FT-Raman spectroscopy was used to characterise the virgin ETFE precursor film (before e-beaming), the intermediate ETFE-poly(VBC) membrane used to produce AEM **M-10** (20%v/v VBC + 1%v/v Surfadone LP-100 in propan-2-ol solvent), select target radiation-grafted AEMs (produced both without and with inclusion of Surfadone LP-100 during the grafting step: **M-6** and **M-10** respectively), and the solid Surfadone LP-100 itself (all FT-Raman spectra presented in Fig. 1).

The spectrum of the ETFE precursor film contained CF_2 bands at 1329 and 1315 cm^{-1} and a CH_2 scissoring band at 1446 cm^{-1} as expected. The reaction of VBC with the irradiated ETFE film led to new

bands including aromatic ring breathing modes at 1001 and 1611 cm^{-1} and the highly diagnostic $-\text{CH}_2\text{Cl}$ deformation band at 1266 cm^{-1} [9]. The absence of the peaks at 932 cm^{-1} and 1699 cm^{-1} , corresponding to the (five-member) ring and the C=O [35] stretches of the Surfadone LP-100, suggests the complete removal of the surfactant from the grafted film (Fig.1(b)). Quaternization with trimethylamine, leads to the disappearance of the CH_2Cl band at 1266 cm^{-1} , indicating complete reaction of the CH_2Cl groups: concomitantly, a new band at 760 cm^{-1} was observed that is indicative of the quaternary ammonium $-\text{N}^+(\text{CH}_3)_3$ groups [36]. The use of Surfadone LP-100 in the synthesis of **M-10** yielded no additional Raman bands compared to the spectrum of **M-6** (synthesised without the use of surfactant). This is strong evidence that the final AEMs were surfactant free and that the quaternary ammonium peak at 760 cm^{-1} was a result of the reaction between the CH_2Cl groups and the trimethylamine (not the surfactant). FT-Raman data confirms that the chemical composition of the radiation-grafted AAEMs (of similar IEC) that were prepared both using undiluted VBC and with dilution to (20%v/v in propan-2-ol with addition of surfactant) were the same. The data was also consistent with the ETFE-based benzyltrimethylammonium-type radiation-grafted AAEMs (synthesised using undiluted VBC) that have been reported previously [9].

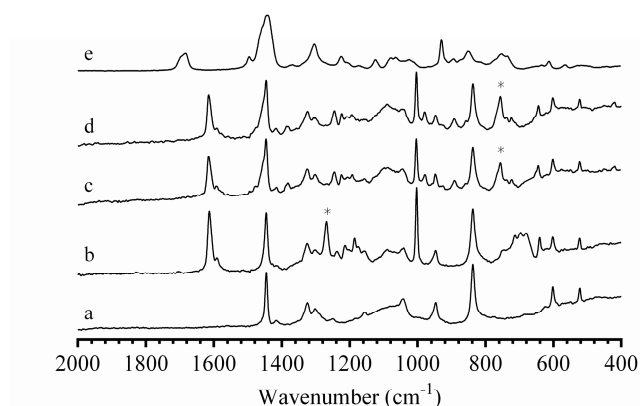


Figure 1. The FT-Raman spectra of (a) the precursor (non-e-beamed) ETFE film, (b) the ETFE-g-VBC grafted intermediate film, (c) M-6 (synthesised with 100%v/v VBC without surfactant), (d) M-10 (20%v/v VBC + 1%v/v Surfadone LP-100 in propan-2-ol solvent), and (e) the Surfadone LP-100 itself. The spectra were normalized using the height of the 1446 cm^{-1} peak for presentational purposes.

3.2. Membrane Physical Properties

Direct comparisons between the physical properties of the AEMs were conducted to evaluate the effect of dilution of the grafting agent. The IEC provides a guide to the gravimetric concentration of cationic functional sites in the AEMs (Fig. 2). Initial investigations focused on the dilution of VBC monomer using propan-2-ol without the addition of a surfactant. The IECs for AEMs produced with VBC monomer diluted in propan-2-ol increased from 0.54 mmol g⁻¹ with 10%v/v VBC (**M-1**) to 1.34 mmol g⁻¹ with 40%v/v VBC (**M-4**). A plateau in IEC was observed above 40%v/v VBC (**M-4** to **M-6**), indicating that the maximum number of grafted functional groups had been achieved with these experimental conditions and without the use of surfactant. The addition of 1%v/v Surfadone LP-100 (**M-7** to **M-10**) yielded an increase in IEC compared to the AAEMs produced with an equivalent VBC dilution and no surfactant (IEC = 1.33 ± 0.02 mmol g⁻¹ with a VBC concentration of 15%v/v and an improved IEC of 1.49 ± 0.02 mmol g⁻¹ with 20%v/v VBC). The higher IEC at lower monomer concentration results from a decrease in monomer-solvent solubility parameters (SUCH AS?) on addition of the surfactant. The lowering of this parameter is well known to improve the degree of grafting throughout the polymer [22].

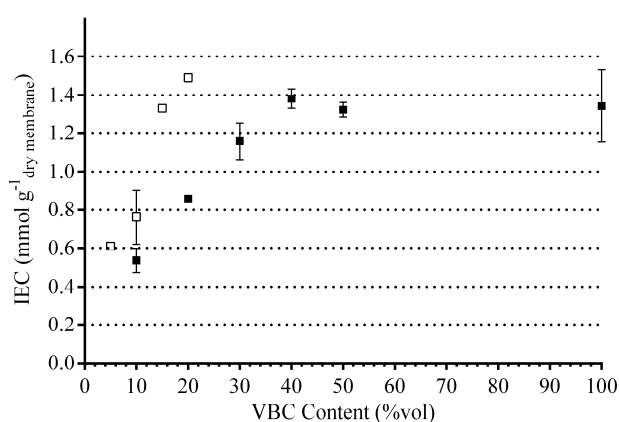


Figure 2. The IECs for the AAEMs produced with increasing VBC concentrations (using propan-2-ol as a solvent) and both without surfactant (■) and with 1%v/v Surfadone LP-100 (□).

The gravimetric WU and the TPS of an AAEM are two essential indicators of suitability for use in fuel cells (high conductivity at low swelling / water uptake is desired). The presence of water is important for anion mobility, whereas insufficient water content is detrimental to ionic conductivity. However, if the WU and dimensional swellings are too great, substantial mechanical instabilities will result and there will be an increased risk of membrane electrode assembly (MEA) delamination. As anticipated, the WUs of M-1 to M-6 showed a positive correlation with IECs up to a maximum WU of 43% (Fig. 3). This is due to the higher degree of hydrophilicity imparted by the increased ionic contents (IEC). A similar correlation was observed for the AAEMs produced using the surfactant, but the maximum WU (42%) was now achieved at a VBC concentration of 15%v/v (M-9). The TPS results (Fig. 4) followed a similar trend with an increase from 8.5% (M-1) up to *ca.* 18% for M-3 to M-6. The addition of surfactant again leads to increased TPS values compared to the values for the corresponding membranes synthesised using no surfactant: a maximum TPS = 19% was observed at a VBC concentration of 20%v/v (M-10). The IEC, WU and TPS values for **M-10** are comparable to those of **M-4** to **M-6**, highlighting that the addition of surfactant to the grafting solution reduced the quantity of monomer solution required to prepare equivalent AAEMs.

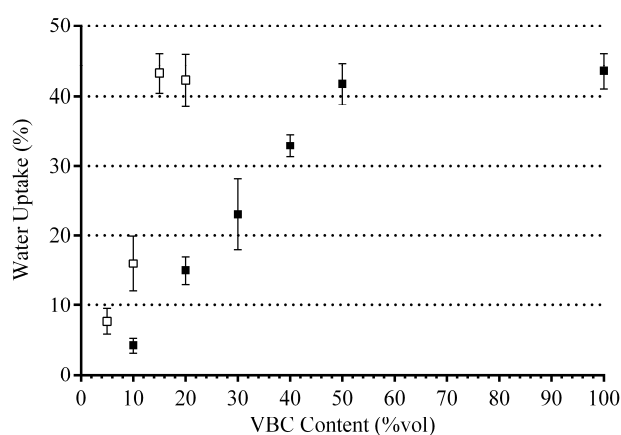


Figure 3. The gravimetric water uptakes (WU) for the AAEMs produced with increasing VBC concentrations (using propan-2-ol as a solvent) and both without surfactant (■) and with 1%v/v Surfadone LP-100 (□).

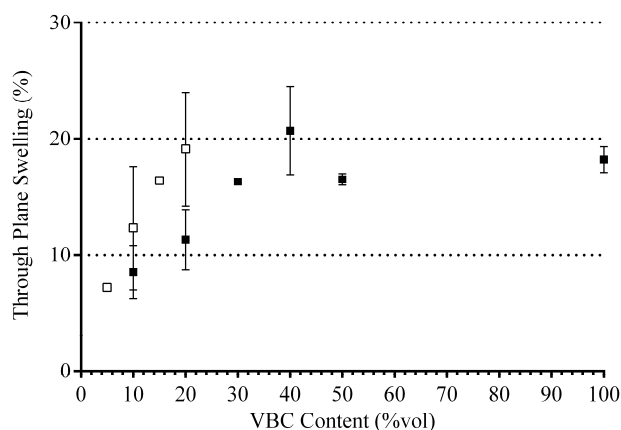


Figure 4. The through plane swelling (TPS) measurements for the AAEMs produced with increasing VBC concentrations (using propan-2-ol as a solvent) and both without surfactant (■) and with 1%v/v Surfadone LP-100 (□).

The hydroxide ion conductivity of an AAEM is crucial to its performance in a fuel cell. The experimental ionic conductivities measured in this study were measured on AEMs with bicarbonate counter anions (for stability in the nature of the counter-anion) as the routine through-plane test cells used cannot rigorously exclude CO₂ during the long experiment times that are required when varying the cell temperature. Carbonation is not a problem when the membranes are operated in a H₂/O₂ fuel cell, due to the continuous production of OH⁻ anions from the oxygen reduction reaction at the cathode [6]. The through-plane hydroxide conductivities, that were calculated from the experimental bicarbonate conductivities using the multiplication factor of 3.8 [34], are presented in Fig. 5 (as a function of temperature). The calculated hydroxide ion conductivities of **M-1** and **M-2** remained < 20 mS cm⁻¹ at all temperatures as a result of their low level of grafting (indicated by low IEC and WU values). The calculated hydroxide ion conductivities of **M-4**, **M-6** and **M-10** were 37, 45, and 55 mS cm⁻¹ at 30°C and 45, 65, and 89 mS cm⁻¹ at 60°C respectively; the increased water contents and faster ion mobilities led to the increase in conductivities at higher temperatures [37]. The high bicarbonate (and calculated hydroxide) ion conductivities in the through-plane direction of the AEMs provides evidence of an even distribution of the VBC monomer through the thickness of the AEMs, which is contrary to the

observations by Mamlouk *et al.* where an emulsion technique was used to prepare similar AEMs from ETFE preformed films but using water as the solvent [30].

Fig. 6 presents the calculated hydroxide ion conductivities for all AEMs at 50°C (values summarised in Table 2). A positive correlation between the observed ionic conductivities and the concentrations of VBC in grafting synthesis (and therefore AEM IEC) is clearly visible; this is a result of the higher concentration of cationic groups within the AEMs at higher IECs. The ionic conductivities of M-7 to M-10 (when surfactant was used for AEM synthesis) were again higher compared to the AEMs prepared with the same VBC concentrations and without any surfactant: the maximum (calculated) hydroxide ion conductivity at 50°C was for M-10 (79 mS cm⁻¹).

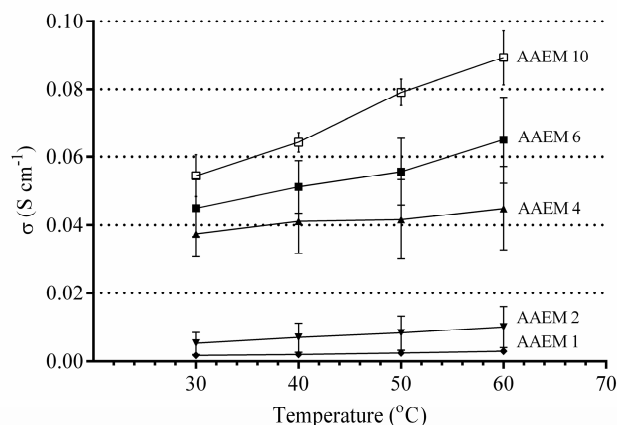


Figure 5. The hydroxide ion conductivities of selected AAEMs that were calculated (multiplication factor of 3.8) from the experimentally determined bicarbonate ion conductivities.

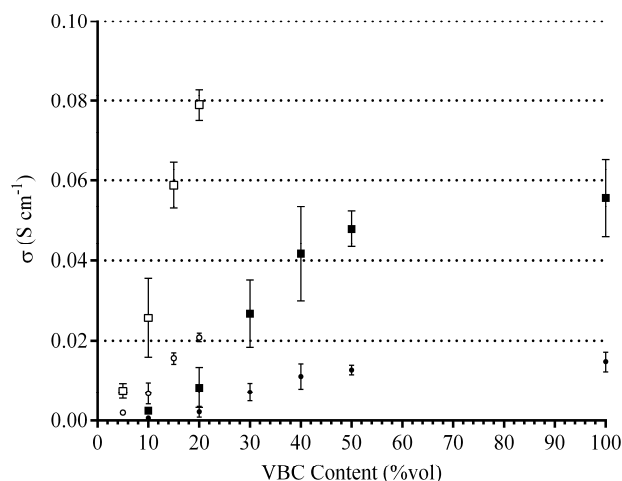


Figure 6. The hydroxide ion conductivities (■), calculated from the experimentally determined bicarbonate ion conductivities (●), at 50°C for the AAEMs produced with increasing VBC concentrations (using propan-2-ol as a solvent) and both without surfactant (filled) and with 1%v/v Surfadone LP-100 (hollow).

3.3. Fuel cell application

The beginning-of-life polarisation curves from the H₂/O₂ fuel cell tests of membrane electrode assemblies containing M-6 and M-10 are presented in Fig. 7. The open circuit voltages were high at 1050 and 1070 mV and the peak power densities were comparable at 166 and 161 mW cm_{geo}⁻² respectively. The similarity in fuel cell performance demonstrates that the reduction in concentration of VBC monomer in the grafting solution, using propan-2-ol and a surfactant, produced AAEMs that can still be used in alkaline polymer electrolyte fuel cells (fulfilling the aim of this study).

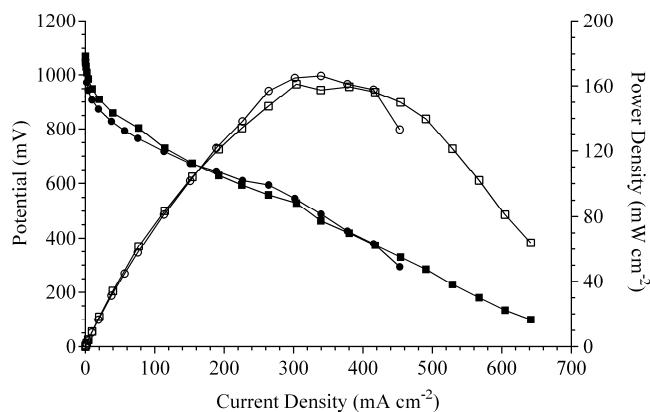


Figure 7. The beginning-of-life H₂/O₂ fuel cell performance curves for M-6 (● – synthesised with undiluted VBC as in prior reported studies on this system) and M-10 (■ – synthesised with reduced VBC concentrations) at 50°C. Hollow symbols = power density data and filled symbols = potential vs. current density data.

4. Conclusion

The preparation of radiation-grafted ETFE-based benzyltrimethylammonium-type alkaline anion-exchange membranes (AAEMs) was achieved with a significant reduction in vinylbenzyl chloride (VBC) monomer usage. The dilution of VBC monomer concentration to 50%v/v with propan-2-ol solvent led to AAEM with comparable *ex-situ* properties (e.g. ion-exchange capacities) compared to those prepared with undiluted (100%v/v) VBC. This initial reduction highlights the suitability of propan-2-ol as a solvent for VBC. The introduction of a surfactant (Surfadone LP-100) at only 1%v/v concentrations allowed the VBC monomer concentration to be further reduced to 20%v/v (for an equivalent AAEM [M-10] to that made using undiluted VBC [M-6]). However, the through-plane ionic conductivities for M-10 were improved compared to M-6; suggesting an enhanced level of grafting through the profile of the membrane was achieved with the use of diluted VBC along with surfactant.

The performance of both M-6 and M-10 were *in situ* evaluated in a fuel cell device under identical test parameters. Almost identical power curves (OCVs of 1.06 ± 0.01 V and peak power densities of 164 ± 3 mW cm⁻²) were obtained. These *ex-situ* and *in-situ* results highlight the ability to produce radiation-grafted AAEMs at substantially reduced cost (the cost of vinylbenzyl chloride monomer is not amenable for its undiluted use in the synthesis of large batches of AAEMs). The capability to tailor the properties of the final AAEMs (tailored ion-exchange capacities, gravimetric water uptakes, and ionic conductivities to suit a desired purpose is noteworthy).

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