Short Communication

An empirical study into the effect of long term storage (-36 ± 2 °C) of electron-beamed ETFE on the properties of radiation-grafted alkaline anion-exchange membranes[☆]

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H I G H L I G H T S

- EB-ETFE films can be used to synthesise viable AAEMs even after storage at -36 ± 2 °C for 16 months.
- The AAEMs exhibited ion-exchange capacities in the range 1.0–1.8 mmol g⁻¹ and ionic conductivities (through plane, fully hydrated) in the range 20–40 mS cm⁻¹ at room temperature.
- The ionic conductivities of the AAEMs are insensitive to the EB-ETFE storage time (up to the 16 months of this study).
- The previously reported bubble formation phenomenon (within the AAEMs) is a major interference in the determination of swelling and water uptake properties. This interference appears more prominent at longer EB-ETFE cold storage times.
- Water uptakes are too high for optimal utilisation in fuel cells and AAEMs with both improved ionic conductivities and lower swelling are required.

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The application of alkaline anion-exchange membranes (AAEM) in solid alkaline fuel cells is growing in prominence mainly due to enhanced tolerance to carbon dioxide, compared to alkaline fuel cells containing aqueous electrolytes, and the potential for using non precious metal catalysts. Radiation grafting is a common methodology for the production of functional polymers and membranes. This statistical study examines the synthesis of radiation grafted AAEMs that are formed from electron beam irradiated poly(ethylene-co-tetrafluoroethylene), EB-ETFE. It is shown that EB-ETFE can be cold stored for at least 16 months and still be used to produce ionically conductive AAEMs. The limitations of routine measurements of properties, such as dimensional increases, ion-exchange capacity, water uptakes and ionic conductivities, are also highlighted.

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1. Introduction

Among solutions for sustainable and clean energy generation, fuel cell technologies have gained increasing importance. In general, these devices use a chemical fuel, with prominence to hydrogen, to generate electrical energy. Although there are many types of fuel cell, the most dominant low temperature type is a proton exchange membrane fuel cell (PEMFC) particularly for automotive and small stationary applications (Kundu et al., 2007). However, PEMFCs require expensive perfluorinated polyelectrolytes (such as Nafion[®] from Du Pont) and

Pt-based catalysts. Pt-alloy nanoparticles have been developed to reduce cost and improve performance; however, the choices of catalyst becomes broader when adopting an alkaline electrolyte fuel cell system (Poynton et al., 2010). Within an alkaline anion-exchange membrane fuel cell (AAEMFC) the oxidation reduction reaction (ORR) kinetics are greatly improved.

This advantage, along with enhanced tolerance to CO₂ (Adams et al., 2008), compared to traditional alkaline fuel cells (that contain aqueous electrolyte) has led to interest in the application of alkaline anion-exchange membranes (AAEMs). Older commercially available anion-exchange membranes (AEMs) that were originally designed for water treatment etc. perform poorly in fuel cells. Fuel cell grade AAEMs, such as A201 and A901 (Tokuyama, Japan) have improved performances.

Radiation-grafting synthetic methodology offers control of membrane properties, excellent barrier properties, controllable thicknesses and tailorable chemistry; the use of pre-formed and cheap base films is also a major advantage (Nasef et al., 2003;

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Dargaville et al., 2003). A commonly used polymer substrate is the partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE). The irradiation process (gamma rays or electron beams) is known to generate at least two types of radicals when using ETFE: alkyl radicals (R, e.g. $-\text{CH}_2\text{C}\cdot\text{HCF}_2\text{CF}_2^-$) and peroxy radicals ($\text{ROO}\cdot$), depending on the atmosphere present during beaming (nitrogen and air respectively) (Mitov et al., 2006). Information on the stability of the peroxy radicals during long term storage for the synthesis of AAEMs is urgently required (it is known that both types of radicals within ETFE decay under increased temperatures over time (Mitov et al., 2006; Guilmeau et al., 1997)). The decay of radicals during storage will consequently affect the subsequent grafting reaction and the properties of the final AAEMs.

The objective of this investigation is to study the effect of cold storage of electron beamed ETFE on the resultant pre-irradiation grafted AAEM properties. The ETFE (irradiated in an air atmosphere) is stored at $-36 \pm 2^\circ\text{C}$ before reaction with vinylbenzyl chloride (VBC) monomer and then trimethylamine (TMA).

2. Experimental

2.1. Materials

The ETFE film used in this work was 50 μm in thickness (Nowofol Kunststoffprodukte, Germany). Electron irradiation was performed using either a 4.5 MeV Dynamatron Continuous DC Electron Beam Unit or a 5 MeV Tandem accelerator (Isotron's, South Marston UK and Harwell UK site, respectively) (www.isotron.com, 2013). The VBC was stored undiluted in a freezer (along with the pre-irradiated ETFE) at $-36 \pm 2^\circ\text{C}$ until required (Dow Chemicals: 96.2%, meta/para ratio=1.17, stabilised with 77 ppm 4-tert-butylcatechol and 795 ppm nitromethane, 125 ppm residual water content). Aqueous trimethylamine (TMA Acros Organics, 50% mass) was used, as supplied, for functionalizing the head-groups via reaction with the benzyl chloride groups of the polymerised VBC (Varcoe et al., 2007). The VBC was used without prior removal of inhibitors. Aqueous potassium hydroxide (KOH , 1 mol dm^{-3}) was used to anion exchange the AAEMs to the hydroxide form. KOH (Fluka, 0.1000 ± 0.0001 mol dm^{-3}) and hydrochloric acid (HCl , Fluka, 0.1041 ± 0.0004 mol dm^{-3}) aqueous standards were used for the acid–base back titrations.

2.2. Preparation of AAEMs (S80)

ETFE copolymer films were electron beam (EB) irradiated to 7 Mrad total dose (1–2 h irradiation time). The EB-ETFE films were then transported to Surrey stored in dry ice for either immediate reaction with VBC monomer or storage in the freezer at $-36 \pm 2^\circ\text{C}$ until required. Transportation takes 4 h, therefore the 0 day AAEMs were grafted 4 h after irradiation. The irradiated ETFE films were converted into AAEMs as previously reported by Varcoe et al. (2007) using VBC and TMA. The resulting quaternary ammonium functionalised AAEM (designated S80—approximately 80 mm thick when fully hydrated) in the chloride form were converted into the hydroxide form by submerging in aqueous KOH (1 mol dm^{-3}) for 1 h; the KOH solution was replaced twice during the hour to ensure complete ion exchange. Excess KOH was removed with copious amounts of washing with water (grade II deionised water was used in all experiments).

We do not weigh the electron-beamed ETFE (to calculate degree of grafting, D.O.G) as previous studies have shown this process increases the variability in the final properties of the AAEM. The typical performances of S80 AAEM in fuel cells have been previously reported by Poynton et al. (2010). Power densities of more than 100 mW cm^{-2} can be achieved. Detailed studies

indicate that water generated at the anode is a source of mass transport performance losses (Zeng et al., 2010a, 2010b).

2.3. Membrane characterisation

Thickness increases (TI) were determined by measuring both the hydrated and dehydrated AAEMs thickness using an external micrometre (precision $\pm 2 \mu\text{m}$), yielding the through-plane expansion properties. The results were calculated as a percentage using Eq. (1), where x_{hyd} is the measured hydrated membrane thickness and x_{dry} is the measured dehydrated (dry) membrane thickness. The gravimetric water uptakes (WU) were similarly calculated as a percentage using Eq. (1), where x is the corresponding hydrated or dehydrated mass measured using a calibrated 5 figure balance. In-plane expansion was determined using samples prepared with a circular 2.4 cm diameter die cutter. The area (calculated from the diameter) was then used to calculate the area increase (AI) using Eq. (1), where x is the corresponding hydrated or dehydrated measured area. The thickness increases, water uptakes and area increases were calculated from $n=5$ + samples taken from different areas of the hydrated AAEM.

$$\frac{x_{\text{hyd}} - x_{\text{dry}}}{x_{\text{hyd}}} \times 100 \quad (1)$$

The ion-exchange capacities (IEC) of the AAEMs were determined using the acid–base back titration method as previously described by Slade and Varcoe (2005). The hydroxide form AAEMs were submerged in hydrochloric acid standard for > 12 h. The solution was then titrated with standard potassium hydroxide using a Metrohm 716 DMS Titrino. The AAEMs were then converted back to the hydroxide form before dehydration in a desiccators $\text{RH}=0\%$ (over $\text{CaCl}_{2(s)}$) for 7 days. The dehydrated masses were then recorded so that the IECs could be calculated (2):

$$\text{IEC}(\text{mmol g}^{-1}) = \frac{n_i(\text{H}^+) - n_f(\text{H}^+)}{m_{\text{dry}}(\text{OH}^-)} \quad (2)$$

where $n_i(\text{H}^+)$ is the initial amount of acid in which the membrane was immersed, $n_f(\text{H}^+)$ is the amount of acid remaining (determined by titration) and $m_{\text{dry}}(\text{OH}^-)$ is mass of the dried membrane in the hydroxide form. The thickness increases, water uptakes, area increases and ion-exchange capacities were all measured at room temperature ($22 \pm 2^\circ\text{C}$).

The ionic through-plane conductivities of the AAEMs (submerged in water) were obtained via impedance spectra collected using a Solartron 1260/1287 frequency gain analyser/electrochemical interface with a maximum voltage amplitude of 100 mV and a frequency range (from high to low), of 1 MHz–1 kHz (Slade and Varcoe, 2005). The spectra were recorded at 20, 30, 40, 50 and 60°C using a controlled thermostated fan-assisted oven. Data analysis were conducted using ZView software (Scribner Associates). The spectrum of the blank short-circuited cell (containing electrodes but no AAEM) was also collected and this data was subtracted from each of the recorded spectra of the membranes and electrodes to eliminate the cell and wire ohmic (electronic) resistances. The spectra were viewed as complex impedance plots with the imaginary component of Z'' on the y-axis and the real component of Z' on the x-axis ($Z = Z' + iZ''$); the ionic resistances (R) were estimated from the linear intersection of the x-axis at high frequency ($\varphi=0^\circ$). The ionic resistance of the membrane was used to calculate the conductivity (3):

$$\sigma_{\text{membrane}}(\text{S cm}^{-1}) = \frac{t_{\text{membrane}}(\text{cm})}{R_{\text{membrane}}(\Omega) \times A_{\text{electrode}}(\text{cm}^2)} \quad (3)$$

where, A is the area of the carbon cloth electrodes, t is the membrane thickness (at the relevant temperature), and σ is the conductivity.

Fig. 1. Thickness increases (TI) at room temperature of AAEMs (S80) synthesised using ETFE that had been stored at -36 ± 2 °C for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations ($n=5$ for all samples). * is the use of electron beam facility 2 (Isotron, South Marston). All other membranes used facility 1 (Isotron, Harwell facility).

Fig. 2. Water uptakes at room temperature of AAEMs (S80) synthesised using ETFE that had been stored at -36 ± 2 °C for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations ($n=5$ for all samples except 0* where $n=6$). * is the use of electron beam facility 2 (Isotron, South Marston). All other membranes used facility 1 (Isotron, Harwell facility).

All statistical analyses (analysis of variables, ANOVA, analysis of means, ANOM and unpaired 2-tailed t -test) were conducted using GraphPad Prism software.

3. Results and discussion

3.1. Thickness increases

It is clear that the AAEM thickness increases do not vary between 0 and 100 days of cold storage after EB (Fig. 1). The null hypothesis (H_0) was accepted (95% confidence level, one-way ANOVA) for 0–100 days. Larger variations occur after 100 days of storage therefore (H_0) is rejected, however the means do not differ significantly up to 120 days storage (95% confidence level, analysis of means, ANOM).

After 100 days of storage, the TI parameter become increasingly erratic; bubble formation (Gupta et al., 1995) within the membrane matrix (particularly the surface) was interfering with accurate thickness determinations. This interference is clearly seen when comparing the AAEM (dehydrated) thicknesses of various areas of the membrane to the mean dehydrated thickness (shown as the error in Fig. 1); this is calculated $(t_i - t_{mean})/100\% = t_{mean}$, where t_i is a thickness measurement in area i . This erratic behaviour after 100 days of storage occurs in other measured membrane characteristics (e.g. Fig. 2).

Unfortunately, during the course of this study the Harwell EB facility closed and was replaced with the South Marston facility (2). It is clear that the TI values of the AAEMs produced with the new EB facility vary little from those produced with the original EB facility (Fig. 1).

This was proven as H_0 is accepted (95% confidence level, unpaired 2-tailed t -test) when comparing 0 day AAEMs from the different facilities, therefore there was no statistically significant difference in TI between the AAEMs produced at the two EB facilities.

3.2. Water uptakes

Gravimetric water uptakes (WU) after 100 days of EB-ETFE cold storage increase dramatically (Fig. 2). Unlike for TI (Fig. 1), the H_0 is accepted for the complete 16 months (480 days) storage (95% confidence level, one-way ANOVA). However, H_0 is rejected (95%

confidence level, ANOM) in almost all results, indicating large fluctuations in the means, hence no clear conclusion that can be drawn on the effect of storage time. The WU measurements are in the range of $65\% \pm 15\%$. Bubble formation is again an interference.

Unlike with TI, the WU of the AAEMs from the different EB facilities (0 vs. 0* in Fig. 2) differ significantly (H_0 is rejected at the 95% confidence level, unpaired 2-tailed t -test); however the difference in WU between the facilities is still $< 10\%$. Notably, the variation in all WU results is not serious over long EB-ETFE cold storage periods. A value of 65% is still too high for optimal application in fuel cells (keep in mind; the radiation-grafted AAEMs are less dense than perfluorinated membranes such as Nafion).

3.3. Area increases

The variations in AI between the AAEMs. H_0 is accepted at the 95% confidence level for both one-way ANOVA and ANOM for up to 16 months of cold storage of the EB ETFE (Fig. 3). These minimal variations are due to the tensile strength properties of the ETFE backbone (www.nowofol.de, 2013). Too high values for AI can lead to membrane electrode assembly delamination in the fuel cells on repeated swelling/contraction (humidity cycling).

The alternate EB facilities (0 vs. 0*) differ significantly with respect to AI (H_0 is rejected, 95% confidence level, unpaired 2-tailed t -test). In summary the variation in TI, WU and AI between EB-ETFE cold storage times is not major on a practical level.

3.4. Ion-exchange capacity

The ion-exchange capacity measurements reflect the degree of grafting (D.O.G) when assuming that all grafted VBC sites result in an anion-exchange site. Studies by Larsen et al. (2010), that determine the changes in the D.O.G depending on storage time and temperature, have shown a rapid decrease in radical concentration in the first 20 h of cold storage, (Larsen et al., 2010). After 100 h the radical concentration under both room temperature and cold storage begins to plateau. However, as there is no significant difference in the means of IEC between 0–20 days ETFE storage; H_0 for 0 and 20 days cold storage is accepted (95% confidence level, unpaired 2-tailed t -test) (Fig. 4).

Compared with the other AAEM properties, the IEC begins to deviate prior to 100 days of storage, as H_0 is accepted for 0 to 40

Fig. 3. Area increases at room temperature of AAEMs (S80) synthesised using ETFE that had been stored at $-36 \pm 2^\circ\text{C}$ for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations ($n=5$ for all samples but 0^* where $n=6$). * is the use of electron beam facility 2 (Isotron, South Marston). All other membranes used facility 1 (Isotron, Harwell facility).

Fig. 4. IECs at room temperature of AAEMs (S80) synthesised using ETFE that had been stored at $-36 \pm 2^\circ\text{C}$ for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations (n values given). * is the use of electron beam facility 2 (Isotron, South Marston). All other membranes used facility 1 (Isotron, Harwell facility).

days, but is rejected for 0 to 100 days of cold storage (95% confidence level, one-way ANOVA). After 100 days of storage the IEC measurements begin to fluctuate in a non-systematic way. Interestingly, H_0 for the 16 month (480 days) IEC is accepted when compared with 0 days cold storage (95% confidence level, unpaired 2-tailed t -test). These results show that EB-ETFE can be cold stored for over a year, as long as γ -ray irradiated ETFE films (Horsfall and Lovell, 2002) used to produce radiation-grafted proton-exchange membranes, and still produce viable AAEMs. However, electron beam facilities are commercially available (as they are used for sterilisation of medical equipment).

Previous research has shown that grafting of irradiated fluoropolymer films proceeds by the grafting front mechanism. The grafting is initiated first at the surface of the film; these regions become swollen by solvent and provide access to deeper reaction sites within the film for additional monomer polymerisation (Brack et al., 2000; Rager, 2003). However, crystallite regions of the film remain practically unaltered during the grafting process, meaning grafting predominately takes place in the amorphous

regions (Brack et al., 2004; Walsby et al., 2001). Therefore the fluctuations in IEC measurements may be disproportionately affected by the deterioration of the radical sites in the amorphous regions of the ETFE film.

A change in electron beam facility does not significantly affect IEC as H_0 is accepted (95% confidence level, unpaired 2-tailed t -test) for 0 vs. 0^* . With respect to AAEMFC performance, the IECs are adequate for AAEMFC application when the AAEMs are synthesised from EB-ETFE stored at $-36 \pm 2^\circ\text{C}$ for up to 16 months (480 days); the mean IEC remains above 1.25 mmol g^{-1} .

3.5. Conductivity

The ionic conductivity measurements appear erratic (Fig. 5); however H_0 is accepted for all results 0–480 days (95% confidence level, one-way ANOVA). AAEM conductivities when synthesised using the alternate EB sources show no significant difference, H_0 is accepted (95% confidence level, unpaired 2-tailed t -test) for 0 vs. 0^* . Hence, the conductivity of the AAEMs is insensitive to both the EB source and the cold storage duration, within the precision of the measurement technique used.

There is no clear correlation between ionic conductivity and IEC for the AAEMs (Fig. 6). It was expected that with increasing IEC the ionic conductivity would also increase (assuming no major increase in swelling and water uptake); the precision of the routine measurement technique used is insufficient to identify a clear trend.

The variations in conductivities with temperature shows the same general increase with temperature of ionic conductivity even between alternate EB sources and increasing EB-ETFE cold storage time (Fig. 7). The variation can occur between alternate conductivity cells, resulting in what appears to be outliers. It should be noted that rigorous CO_2 exclusion was not conducted with these routine conductivity measurements. Previous studies have shown that AAEMs in the OH^- form can change to AAEMs in mixed CO_3^{2-} and HCO_3^- forms on exposure to air (Kizewski et al., 2010; Yan and Hickner, 2010). Therefore, the ionic conductivities presented are representing AAEMs in mixed alkaline anion forms. The change in conductivity of a sample of S80 AAEM when submerged in nitrogen purged water (that is also exposed to air) (Fig. 8). This demonstrates that the presence of CO_2 lowers the conductivity values that are measured.

Fig. 5. Through-plane ionic conductivity at 60°C in deionised water of AAEMs (S80) synthesised using ETFE that had been stored at $-36 \pm 2^\circ\text{C}$ for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations ($n=3$ for all samples except 0^* where $n=5$). * is the use of electron beam facility 2 (Isotron, South Marston). All other membranes used facility 1 (Isotron, Harwell facility).

Fig. 6. Conductivity vs. IEC at room temperature of AAEMs (S80) synthesised using ETFE that had been stored at $-36 \pm 2^\circ\text{C}$ for an increasing number of days after electron-irradiation. The error bars represent sample standard deviations ($n=3$ for all samples except 0⁺ where $n=5$).

Fig. 7. Through-plane ionic conductivities (in water) of electron-beamed ETFE-based radiation-grafted AAEMs (S80). • is 0 days of cold storage at $-36 \pm 2^\circ\text{C}$ using EB facility 1 (Harwell). ◊ is 480 days of cold storage (EB facility 1). ◊ is 0 days of cold storage using the new EB facility 2 (South Marston).

4. Conclusion

This study investigates the effect of long term cold storage of electron-beamed poly(ethylene-co-tetrafluoroethylene), EB-ETFE, base films on the properties of the resulting radiation-grafted alkaline anion-exchange membranes (AAEM) that are targeted at application in alkaline polymer electrolyte fuel cells. The main conclusions are:

1. Most significantly, the EB-ETFE films can be used to synthesise viable AAEMs even after storage at $-36 \pm 2^\circ\text{C}$ for 16 months.
2. The AAEMs exhibited ion-exchange capacities in the range 1.0–1.8 mmol g^{-1} and ionic conductivities (through plane, fully hydrated) in the range 20–40 mS cm^{-1} at room temperature.
3. The ionic conductivities of the AAEMs are insensitive to the EB-ETFE storage time (up to the 16 months of this study).
4. The previously reported bubble formation phenomenon (within the AAEMs) is a major interference in the determination of swelling and water uptake properties. This interference appears more prominent at longer EB-ETFE cold storage times.
5. Water uptakes are too high for optimal utilisation in fuel cells and AAEMs with both improved ionic conductivities and lower swelling are required.

Fig. 8. Effect of water storage time on through-plane ionic conductivity with increasing temperature of electron-beamed ETFE-based radiation-grafted AAEM (S80). The water storage vessel was open to the air (hence CO_2 content). The 0 min measurement was conducted as in the data collected in Fig. 7 (i.e. CO_2 was not excluded from the sample preparation procedure). Error bars are standard deviations ($n=3$).

The techniques used in this study (to measure thickness increases, area increases, ion-exchange capacity and ionic conductivity) are useful for rapid routine measurements when relative standard deviations of less than ca. 20% are acceptable. A more rigorous methodology is essential in order to determine the ionic conductivity of AAEMs that are purely in the hydroxide (OH^-) anion forms; this will involve the scrupulous exclusion of carbon dioxide in every step of the method. Future method development work is underway to improve on these experimental techniques, whilst ensuring they can still be conducted routinely; this includes the development of a method for ensuring the AAEMs are in the OH^- form during measurements of ionic conductivity.

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