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Comparison of PVDF- and FEP-based radiation-grafted alkaline anion-exchange membranes for use in low temperature portable DMFCs

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Vinylbenzyl chloride has been radiation grafted onto both PVDF and FEP fluoropolymer films; subsequent amination and ion-exchange to give the hydroxide ion forms yield anion-exchange membranes suitable for use in low temperature direct methanol fuel cells for portable applications.

Two obstacles inhibiting application of direct methanol fuel cells (DMFCs) are (i) the relatively low activity and high costs of methanol electro-oxidation catalysts and (ii) methanol crossover through current generation proton-exchange membranes (PEMs).[1] Liquid alkaline fuel cells (AFCs) have been developed to a significant level; a principle reason for this is that the catalysts generally perform better in alkaline conditions and at lower loadings, and a wider range of catalysts may be used.[2] McLean *et al.* observed in a recent review on AFCs that there is great potential in the production of a polymer alkaline membrane fuel cell.[3] There has recently been growing interest in the literature in using anion-exchange membranes (AEMs) in fuel cells,[4] an example being recent work by Agel *et al.*[4a] on polyethylene oxide membranes containing dissolved potassium hydroxide. The stability of a commercially available AEM containing benzyltrimethylammonium groups radiation grafted onto PTFE membranes in aqueous sodium hydroxide solution (6 mol dm^{-3}) was good up to temperatures between 50–60 °C.[5] DMFCs operating at ambient conditions have been identified as ideal for replacing batteries for portable applications (laptops, cellular phones, human-portable power packs, *etc.*) due to the ever increasing power demands (especially with the imminent introduction of mobile broadband communications) that will surpass levels projected for secondary battery technology.[6] DMFCs are amenable to portable applications due to the good power density of the dense and easily replenished liquid fuel (methanol). Under alkaline conditions, the fuel cell reactions for the anode (eqn. 1) and the cathode (eqn. 2) are:

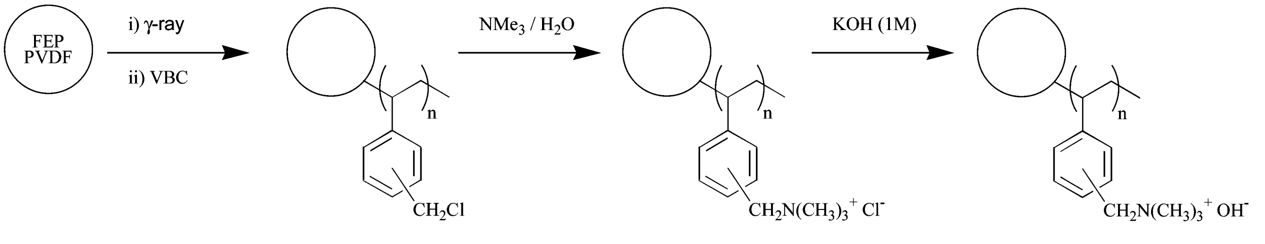
$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^- \tag{1}$$

$$3/2O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \tag{2}$$

Product water is formed at the anode, in contrast to a cell containing a PEM. The use of an alkaline AEM could resolve the problem of methanol crossover from the anode to the cathode as the electro-osmotic water transport occurs in the opposite direction; the use of cheaper catalysts would also be feasible. Polymer alkaline exchange membranes have been reported to function in the presence of carbonate species and could yield a solution to the problem of carbonate build-up in liquid-based AFCs.[3]

In fuel cell membrane research, much of the effort has been concentrated on PEMs,[7] with the focus being the development of cheaper alternatives to the industry standard Nafion®, produced by Dupont. A large proportion of this effort has examined styrene radiation grafting onto partially fluorinated films,[8,9] such as poly(vinylidene fluoride) (PVDF, $-[CH_2CF_2]_n-$), and fully fluorinated films,[9] such as poly(tetrafluoroethene-*co*-hexafluoropropylene) (FEP, $-[CF_2CF_2]_n[CF(CF_3)CF_2]_m-$), with subsequent sulfonation to form the cation-exchange sites. The attraction of this route is that the properties and compositions of the final materials can be easily controlled.[10] If vinylbenzyl chloride (VBC) is grafted onto PVDF and FEP, anion-exchange membranes, as opposed to proton-exchange membranes, are produced (Scheme 1).[11] Here, we report a comparison of AEMs produced using PVDF and FEP base polymers.

In a typical grafting procedure, PVDF (Solvay Chemicals, Solef® 1008 homopolymer film, 40 µm thickness) and FEP (Goodfellow, 50 µm thickness) were irradiated with γ-rays from a ^{60}Co source to a total dose of 6.3 Mrad in air. The



1 PVDF-*g*-PVBC
2 FEP-*g*-PVBC

3 PVDF-*g*-PVBTMACl
4 FEP-*g*-PVBTMACl

5 PVDF-*g*-PVBTMAOH
6 FEP-*g*-PVBTMAOH

Scheme 1 Radiation-grafting of VBC onto PVDF and FEP, and conversion to the anion-exchange membranes.

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irradiated films were then stored at -30 °C until used. Known masses of the films were loosely rolled and immersed in excess VBC (Dow Chemicals, 97% purity, *meta*:*para* ratio of 1.3, stabilised with 75 ppm 4-*tert*-butylcatechol and 733 ppm nitromethane, purged with nitrogen for 2 h before reaction) for around 1 week at 60 °C. Unattached VBC and poly (VBC) were removed by washing in toluene. A typical PVDF-*g*-PVBC membrane (**1**) was obtained with a degree of grafting (d.o.g.)† of 54% and an average thickness of 54 μm. FEP-*g*-PVBC membrane **2** was obtained with a d.o.g. of 27% and an average thickness of 66 μm. Membranes **1** and **2** were then aminated by immersion in trimethylamine (Acros Organics, 45% aqueous solution) at room temperature for 1 week, forming the chloride forms **3** and **4**, respectively. Immersion in excess aqueous potassium hydroxide (1 mol dm^{-3}) for 48 h yields the hydroxide ion forms **5** and **6**, respectively. The aminated PVDF materials were obtained as dark red–brown membranes, while the aminated FEP materials were obtained as clear, colourless membranes. The membrane **5** (60 μm) was brittle, showed a short-term temperature stability of 155 °C in flowing oxygen‡ and had an ion-exchange capacity (IEC)§ of 0.7 meq g^{-1}, compared with a calculated value of 2.0 meq g^{-1}; the hydroxide form of the FEP analogue **6** (95 μm) remained elastic and strong, showed a short term temperature stability of 160 °C in flowing oxygen and had an IEC of 1.0 meq g^{-1}, compared with a calculated value of 1.3 meq g^{-1}.

The brittleness and low IEC of **5** (considering the high d.o.g.) suggests structural collapse of the PVDF backbone on alkali treatment; dehydrofluorination of PVDF has been previously reported at elevated temperatures in the presence of concentrated hydroxide and surfactant,[12] so it is clear that the amination process has enabled this degradation process to occur at lower temperatures and with a lower concentration of hydroxide. Membrane **6** remained strong and exhibited a high IEC¶ suggesting the FEP-based material remained intact. The degradation of the PVDF-based membranes and the stability of the FEP-based membranes was clearly demonstrated when the $^{19}F\{^1H\}$ DP-MAS NMR spectra of PVDF‖, FEP** and membranes **1**–**6** were studied (Varian Unity 300 MHz spectrometer). Membrane **1** showed the same signals as PVDF, though a small amount of signal broadening indicated some morphological changes. However, on amination to **3**, the F^3 signal increased in intensity, while both the F^2 and F^3 signals broadened considerably. A small shoulder signal appeared at $\delta = -119$. This signal increased in intensity considerably on conversion to the hydroxide form **5**; the narrow linewidth suggests that this signal was due to a highly mobile species. These observations demonstrated that the backbone began to degrade with the amination step and that this degradation was exaggerated with immersion in alkali. In comparison, the ^{19}F signals for the FEP-based materials **2**, **4** and **6** did not change in any way, indicating structural stability.

The ^{15}N CP-MAS NMR spectrum of (vinylbenzyl)trimethylammonium chloride contains a single signal at $\delta = -329$. This single signal remains in the spectra of **3**–**6**, showing the only nitrogen species present in these AEMs is the benzyltrimethylammonium group. However, the signal to noise ratio is dramatically reduced for membrane **5**, indicating substantial removal of these ammonium groups; this correlates with the low IEC for this material and is further evidence of material degradation.

It can be concluded that AEMs produced using this synthetic methodology are promising only when fully fluorinated base films are used. PVDF-based membranes degrade on amination and hydroxide ion exchange. These results suggest the membranes synthesised by Svarfar *et al.*[11c] will be structurally unstable on contact with alkali.

Initial a.c. impedance spectroscopic measurements on membrane **6** gave conductivities of $\sigma = 0.02$ S cm^{-1} at ambient temperatures and atmospheric relative humidity RH = 100%. These initial results show that these AEMs are promising for the intended application as they are comparable with Nafion-117 under the same conditions (as measured in-house on the same equipment); increased levels of grafting should lead to increased conductivity. Further work will explore these results in detail, along with long-term temperature stabilities of the hydroxide form AEMs in water at various temperatures, and fuel cell test data with both hydrogen and methanol as fuels.

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Notes and references

†The d.o.g.(%) = $100 \times (m_f - m_i)/m_i$, where m_f is the grafted mass and m_i is the initial mass of the irradiated fluoropolymer.

‡Determined by thermogravimetric analysis from the onset temperature of the second observed mass loss (the first mass loss was due to loss of residual water and not polymer degradation).

§A sample of **5** or **6** was immersed in a known amount of aqueous HCl (0.1 mol dm^{-3}) for 48 h. The amount of unreacted H^+ was then determined by titration with aqueous KOH (0.1 mol dm^{-3}). The amount of H^+ reacted with the polymer divided by the mass of the dry membrane [converted back to the Cl^- form by immersion in aqueous HCl (1 mol dm^{-3}, 48 h) and dried in a desiccator over anhydrous $CaCl_2$ (RH = 0%, >1 week)] gives the IEC.

¶The value was lower than the theoretical maximum as the dried membrane still contains water associated with the quaternary ammonium groups (confirmed by infrared spectroscopy and thermogravimetry).

‖The ^{19}F NMR of PVDF has previously been assigned:[13] F^1 crystalline signal at $\delta = -82$, F^2 amorphous signal at $\delta = -91$, with the F^3 crystalline signal appearing as a shoulder, and the D^1 and D^2 defect signals at $\delta = -113$ and -115, respectively, corresponding to the head–head and tail–tail defect units.

**The ^{19}F NMR of FEP has previously been assigned:[14] intense signal at $\delta = -122$, (CF_2 backbone, also observed for PTFE) and weak signals at $\delta = -186$ [$CF(CF_3)$], -112 [CF_2 next to $CF(CF_3)$ groups] and -72 (CF_3)

1 J. Cruickshank, K. Scott and W. Taama, *J. Power Sources*, 1997, **65**, 159.
2 R. R. Adzic, M. C. Aramtor and A. V. Tripkovic, *Electrochim. Acta*, 1984, **29**, 907; J. Taraszewska and G. Roslonek, *J. Electroanal. Chem.*, 1994, **364**, 209.
3 G. F. McLean, T. Niet, S. Prince-Richard and N. Djilali, *Int. J. Hydrogen Energy*, 2002, **27**, 507.
4 (*a*) E. Agel, J. Bouet and J. F. Fauvarque, *J. Power Sources*, 2001, **101**, 267; (*b*) J. Divisek, *WO Pat.*, 01/61776/A1, 2001; (*c*) W. Yao, T. Tsai, Y.-M. Chang and M. Chen, *US Pat.*, 6,183,914, 2001.
5 T. Sata, M. Tsujimoto, T. Yamaguchi and K. Matsusaki, *J. Membr. Sci.*, 1996, **112**, 161.
6 X. Ren, P. Zelenay, S. Thomas, J. Davey and S. Gottesfeld, *J. Power Sources*, 2000, **86**, 111; J. W. Raadschelders and T. Jansen, *J. Power Sources*, 2001, **96**, 160; H. Chang, J. R. Kim, J. H. Cho, H. K. Kim and K. H. Choi, *Solid State Ionics*, 2002, **148**, 601; J. P. Meyers and H. L. Maynard, *J. Power Sources*, 2002, **109**, 76; C. Hebling and A. Heinzel, *Fuel Cell Bull.,*, 2002, July, 8; C. K. Dyer, *J. Power Sources*, 2002, **106**, 31; A. Heinzel, C. Hebling, M. Müller, M. Zedda and C. Müller, *J. Power Sources*, 2002, **105**, 250.
7 J. A. Kerres, *J. Membr. Sci.*, 2001, **185**, 3.
8 S. Hietala, S. L. Maunu, F. Sundholm, T. Lehtinen and G. Sundholm, *J. Polym. Sci., Part B: Polym. Phys.*, 1999, **37**, 2893; J. A. Horsfall and K. V. Lovell, *Fuel Cells*, 2002, **1**, 186; J. A. Horsfall and K. V. Lovell, *Polym. Adv. Technol.*, 2002, **13**,

381; K. Scott, W. M. Taama and P. Argyropoulos, *J. Membr. Sci.*, 2000, **171**, 119; C. Chuy, V. I. Basura, E. Simon, S. Holdcroft, J. Horsfall and K. V. Lovell, *J. Electrochem. Soc.*, 2000, **147**, 4453.

9 H.-P. Brack, H. G. Bührer, L. Bonorand and G. G. Scherer, *J. Mater. Chem.*, 2000, **10**, 1795.

10 K. V. Lovell and J. A. Horsfall, *Eur. Polym. J.*, 2002, **38**, 1671.

11 (*a*) T. Cohen, P. Dagard, J. Molénat, B. Brun and C. Gavach, *J. Electroanal. Chem.*, 1986, **210**, 329; (*b*) J. Sandeaux, R. Sandeaux, G. Pourcelly and J. Molénat, *J. Membr. Sci.*, 1993, **84**, 213; (*c*) B. L. Svarfar, K. B. Elkman, M. J. Sundell and J. H. Näsman, *Polym. Adv. Technol.*, 1996, **7**, 839.

12 G. J. Ross, J. F. Watts, M. P. Hill and P. Morrissey, *Polymer*, 2000, **41**, 1685; G. J. Ross, J. F. Watts, M. P. Hill and P. Morrissey, *Polymer*, 2001, **42**, 403; G. Moggi, P. Bonardelli, G. Chiodini, S. Conti and A. Fontana, *J. Fluorine Chem.*, 1985, **29**, 167.

13 P. Holstein, G. A. Monti and R. K. Harris, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3549; W. Su and D.-L. M. Tzou, *Polymer*, 2000, **41**, 7289; S. Ando, R. K. Harris and S. A. Reinsberg, *Magn. Reson. Chem.*, 2002, **40**, 97.

14 A. Oshima, S. Ikeda, E. Katoh and Y. Tabata, *Radiat. Phys. Chem.*, 2001, **62**, 39.