Preparation of radiation-grafted powders for use as anion exchange ionomers in alkaline polymer electrolyte fuel cells†

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A novel alkaline exchange ionomer (AEI) was prepared from the radiation-grafting of vinylbenzyl chloride (VBC) onto poly(ethylene-co-tetrafluoroethylene) [ETFE] powders with powder particle sizes of less than 100 μm diameter. Quaternisation of the VBC grafted ETFE powders with trimethylamine resulted in AEIs that were chemically the same as the ETFE-based radiation-grafted alkaline anion exchange membranes (AAEM) that had been previously developed for use in low temperature alkaline polymer electrolyte fuel cells (APEFC). The integration of the AEI powders into the catalyst layers (CL) of both electrodes resulted in a H2/O2 fuel cell peak power density of 240 mW cm−2 at 50 °C (compared to 180 mW cm−2 with a benchmark membrane electrode assembly containing identical components apart from the use of a previous generation AEI). This result is promising considering the wholly un-optimised nature of the AEI inclusion into the catalyst layers.

Introduction

Alkaline polymer electrolyte fuel cells (APEFC) have received a considerable amount of attention in recent years as analogous alternatives to the more heavily investigated proton exchange membrane fuel cells (PEMFC).1–3 The higher pH of APEFCs facilitates the use of a range of non-precious metal catalysts (reducing the requirement for the expensive platinum catalysts that are typical in PEMFCs), especially at the cathode for the oxygen reduction reaction.4–6 Alkaline anion exchange membranes (AAEM) can also exhibit lower fuel permeabilities, compared to proton exchange membranes (PEM), when used in direct alcohol fuel cells.7 Additionally, the susceptibility to CO2-derived performance losses is perceived to be reduced with APEFCs compared to traditional aqueous electrolyte (KOH) alkaline fuel cells:8–11 this is thought to be especially the case when APEFCs are developed that can operate at 80 °C over long periods of time.

The synthesis of anion exchange polymer electrolyte materials via radiation-grafting (RG, using either an electron beam (EB), UV, or γ-ray radiation) of pre-formed precursor polymer materials (available in industrial bulk quantities) have been widely reported. Irradiation leads to the formation of radicals or peroxy groups (when irradiated under inert atmosphere or air, respectively) that can be distributed throughout the thickness of the base polymer material (UV grafting tends to bias towards surface only functionalisation).12 RG generally uses vinyl-based monomers (such as vinylbenzyl chloride, VBC) and can involve a subsequent post-grafting functionalisation step (such as reaction of the CH2Cl groups of the VBC grafts with tertiary amine to form quaternary ammonium head groups that are capable of conducting anions, see Scheme 1).13–19

Scheme 1 The preparation of AEIs and AAEMs via radiation-grafting of vinylbenzyl chloride onto precursor poly(ethylene-co-tetrafluoroethylene) [ETFE] and subsequent quaternisation with trimethylamine.
The process of RG is not limited to the modification of thin films (a common process reported in the prior literature). Polymer powders have also been subjected to RG and chemical functionalisation (including for fabrication of fuel cell materials). A common approach is subjection of poly(vinylidene fluoride) (PVDF) powders to $^{60}$Co $\gamma$-radiation followed by grafting using monomers such as: styrene, $^{20}N,N$-dimethylacrylamide, $^{21}$glycidyl methacrylate, $^{22}$a combination of acrylic acid and methacrylic acid, $^{23}$or a dimethylaminoethyl methacrylate-styrene mixture (to introduce amphoteric properties). $^{24}$Subsequently, these RG powders are typically manufactured into thin films either via a melt process or by dissolution in solvents (such as NMP) followed by a subsequent casting step. Thin film PEMs (for PEMFC application) have also been prepared from PTFE powders: the PTFE was initially subjected to EB radiation (up to 600 kGy under N$_2$) to induce cross-linking and was then followed by a further step involving a second exposure to EB, grafting with styrene, and functionalisation with chlorosulfonic acid (to introduce sulfonic acid groups). $^{25}$The irradiation of ultra-high molecular weight polyethylene powder using $^{60}$Co has also been reported with subsequent grafting of either styrene $^{26-28}$or vinylbenzyl chloride (VBC). $^{29}$These non-fluorinated graft powders were also manufactured into thin films (via a melt process) and post-graft functionalised with either chlorosulfonic acid or trimethylamine to yield PEMs and anion-exchange membranes (AEM) respectively.

In the known cases (detailed above) that involved RG of powders specifically for fuel cell application, the functionalised powders were all processed into thin films to be used as the ion exchange membranes. The use in fuel cells of the functionalised powders directly in the “particulate” form has not been reported: e.g. to formulate into a conductive ionomer coating within the electrocatalyst layer to extending the three phase boundary between reactant gases, electrocatalyst and electrolyte. Ionomers with an inherent functionality (e.g. DuPont Naflon® dispersions for PEMFCs or Tokuyama A3/A4-S™ anion-exchange ionomer (AEI) solutions for APEFCs), are typically supplied either dissolved or dispersed in a solvent. $^{30,31}$Additionally for APEFCs, a polymer such as poly(vinylbenzyl chloride) can be deposited in the catalyst layer (CL) and subsequently functionalised [e.g. by treatment with $N,N,N',N'$-tetramethylhexane-1,6-diamine $^{32}$or trimethylamine (TMA) $^{33}$] to form an AEI in situ.

Here we investigate the application of RG poly(ethylene-co-tetrafluoroethylene) [ETF, -(CH$_2$CH$_2$)$_n$(CF$_2$CF$_2$)$_m$] powders as an AEI concept for use in APEFCs. This process is amenable to bulk production of AEIs for supply to research collaborators and industrial concerns. As the incorporation of the AEI powders was far from optimised (see below), high power performances were not anticipated. However, surprisingly good performances were observed (verified in an independent laboratory), which highlights the future potential with the use of RG powders in the development of high performance AEIs (especially if an optimised dispersion or solution can be formulated).

### Experimental

#### Materials

ETF powders (Z8820X, particle size specification 20–30 µm) were supplied by AGC Chemicals Europe (UK). Vinylbenzyl chloride monomer (VBC, mixture of 3- and 4-isomers, used without removal of inhibitors) was purchased from Dow Chemical (Germany). Surfacdone LP-100 was obtained from ISPECorp (USA). Propan-2-ol and toluene were of reagent grade and supplied from Sigma-Aldrich (UK) while trimethylamine (TMA, 50%mass in water) was supplied from Acros Organics (UK). Pt/C electrocatalyst (Johnson Matthey HiSPEC 3000, 20% mass Pt on Vulcan carbon black) was purchased from Alfa Aesar (UK). The carbon paper electrodes used for fuel cell testing contained a micro-porous layer (MPL) on one side of a wet proofed (20%mass PTFE) carbon paper gas diffusion layer (GDL) and were purchased from Hesen (China): the MPL consisting of 1 mg cm$^{-2}$ carbon powder with 20%mass PTFE as binder. All chemicals were used as received and deionised water was used throughout (resistivity $= 18.2$ MΩ cm).

#### Synthesis of ETFE-g-poly(vinylbenzyl chloride) [ETF-g-poly(VBC)]

The ETFE powders were irradiated 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), submerged in a pre-mixed solution of VBC, propan-2-ol, and Surfacdone LP-100 (1.00 : 3.95 : 0.05 volume ratio), purged with N$_2$ for 2 h, and then sealed and heated for 72 h at 60 °C. The resultant ETFE-g-poly(VBC) grafted powder was then recovered by filtration, washed with toluene (to remove any excess VBC and homopolymer), and dried in a vacuum oven at 50 °C.

#### Synthesis of ETFE-g-poly(vinylbenzyltrimethylammonium chloride) [ETF-g-poly(VBTMAC)]

The ETFE-g-poly(VBC) powders were submerged in aqueous TMA solution for 5 h at ambient temperature. The product was washed five times with water before being heated in (fresh) water for 18 h at 50 °C. The resulting ETFE-g-poly(VBTMAC) powders were washed a further 5× with water, dried in a vacuum oven at 40 °C for 5 day, and stored for later use.

#### Characterisation

The Raman spectra of the powder samples were recorded on 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. Thermal analysis was carried out on a Universal Instruments Q500 Thermogravimetric Analyser (TGA). Samples were heated from ambient temperature to 600 °C at a heating rate of 5 °C min$^{-1}$ under an inert N$_2$ gas flow. The particle size of the dehydrated ETFE-g-poly(VBTMAC) powder was measured by lightly pressing a dry aluminium scanning electron microscope (SEM) stub (thoroughly cleaned with acetone before use) onto the powder. A gold coating of 9 nm (prepared using 6 $\times$ 1.5 nm layers) was applied to the stub to reduce charging...
of the non-electrically conductive particles. A Jeol JMS 7100F SEM
was used to image the AEI (analysed using ImageJ software).

The ETFE-g-poly(VBTMAC) powder samples were immersed in
aqueous KCl (1 mol dm$^{-3}$) for 1 h (the solution was
exchanged twice during this period to ensure all counter anions
were ion-exchanged); the samples were subsequently thor-
oughly washed with water (at least 10 times) to remove excess
KCl (to give metal-cation-free powders). The complete removal
of excess K$^+$ anions was verified by testing the post-wash
solutions with aqueous AgNO$_3$ as a visual indicator. Samples of
the ETFE-g-poly(VBTMAC) powder (now in the Cl$^-$ only form)
were then soaked in N$_2$ purged water for 24 h at ambient
temperature. After recovery by filtration, excess surface water
was then removed by dabbing with tissue and the hydrated
masses ($M_{\text{dry}}$) were then quickly recorded. The samples were
then dried in the vacuum oven at 40 °C for 5 days before the dry
masses ($M_{\text{dry}}$) were recorded. The gravimetric water uptakes
(WU) were calculated ($n = 4$ samples) using eqn (1):

$$\text{WU} = \frac{M_{\text{dry}} - M_{\text{hydr}}}{M_{\text{dry}}}$$

The ion exchange capacities (IEC) were determined using the
dried samples (in Cl$^-$ anion form) recovered from the WU
measurements (above). The samples (known dried mass) were
first immersed into 20 cm$^3$ of aqueous NaNO$_3$ (2 mol dm$^{-3}$)
solution for 24 h. The solutions were subsequently acidified with
aqueous HNO$_3$ (2 cm$^3$, 2 mol dm$^{-3}$) and titrated with standard-
ised aqueous AgNO$_3$ (0.0200 mol dm$^{-3}$) solution. A Meth-
rohm 848 Titroino Plus autotitrator equipped with a Ag Titrode
was used for the titrations. The IEC (mmol g$^{-1}$) was calculated
from the end point (Ep, cm$^3$, taken as the maxima in the first
differential plot of the potential vs. volume data) using eqn (2):

$$\text{IEC (Cl$^-$)} = \frac{E_p \times 0.0200}{M_{\text{dry}}}$$

**Fuel cell testing**

**Electrode preparation.** Prior to formulation of the electro-
catalyst ink, the ETFE-g-poly(VBTMAC) powder (as produced) was
ground with a pestle and mortar for 10 min to reduce the
number of aggregate particles: pleasingly, there were no issues
with handling (electrostatics). Pt/C (20%mass Pt) and ETFE-g-
poly(VBTMAC) AEI (either 15 or 20%mass of the total Pt/C catalyst
powder loading) were mixed in a pestle and mortar with 1 cm$^3$
water for 10 min until a visually even ink was produced. Propan-2-
ol (10 cm$^3$) was added to the catalyst ink, which was then blended
in the pestle and mortar for a further 5 min before being homo-
genised with ultrasound for 1 h. The ETFE-g-poly(VBTMAC)
powder showed no signs of any solubility. The catalyst ink was
sprayed onto the MPLs of the carbon paper gas di-

**Results and discussions**

**AEI characterisation**

AEIs were prepared from precursor ETFE powder using an
analogous RG method to that previously employed to fabricate
AAEMs from precursor ETFE films. The resultant ETFE-g-pol-
y(VBTMAC) powders were yellow in colour (the initial ETFE
powder was white and opaque). The FT-Raman spectra of the
base ETFE powder, ETFE-g-poly(VBC) and functional ETFE-g-
poly(VBTMAC) AEI powders are presented in Fig. 1. The spec-
trum of the precursor ETFE powder contained the widely
reported CF$_2$ bands at 1300 and 1324 cm$^{-1}$ and a CH$_2$ scissoring
band at 1446 cm$^{-1}$. The RG of VBC onto the ETFE powder
introduced new bands including aromatic derived modes at
1002 and 1614 cm$^{-1}$ and the highly diagnostic CH$_2$Cl deforma-
tion band at 1271 cm$^{-1}$. On quaternisation with TMA, the
CH$_2$Cl band at 1271 cm$^{-1}$ disappeared (as expected) with new
bands appearing at 760 and 1409 cm$^{-1}$ (indicative of the pres-
ence of –N+Me$_3$ groups).

The IEC of the AEI powder produced was $1.24 \pm 0.06$ meq g$^{-1}$
($n = 4$), which is only slightly lower to the IEC recorded when
preparing AAEM from a 50 μm thick ETFE film (not powder)
using an identical procedure \([1.49 \pm 0.02 \text{ meq g}^{-1} (n = 3)]\). The WU was simultaneously measured for the AEI(Cl\(^-\)) samples: the measured values of 155.4 \(\pm\) 1.8% were considerably larger compared to RG AAEMs prepared with similar IEC values (typical WUs in the range 30–65%). The higher experimental WU for the AEI powders was expected as a result of the increased surface area of the powder and, hence, the less rigorous and consistent removal of surface adsorbed water of the powder particles (compared to the thin film AAEMs). The high WU may not necessarily be detrimental to APEFC performance due to the pivotal importance of water for ion (including OH\(^-\)) conduction: water is also a cathode reactant \([2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-]\).

Thermogravimetric analyses (TGA) of the base ETFE powders, intermediate ETFE-g-poly(VBC) powders, and the final AEI powders (in both Cl\(^-\) and OH\(^-\) forms) are presented in Fig. 2. The precursor (non-irradiated) ETFE powder showed the expected simple thermal degradation curve, with a single decomposition step in the range 360–490 \(^\circ\)C. The intermediate ETFE-g-poly(VBC) powder underwent multiple weight losses. The first-step-like weight loss commenced at 280 \(^\circ\)C and has previously been attributed to the decomposition of the vinylbenzyl chloride grafts. The final weight loss between 380 and 520 \(^\circ\)C stems from the decomposition of the ETFE polymer backbone. The addition of the quaternary ammonium functionality in the AEI(Cl\(^^-\)) and AEI(OH\(^-\)) powders introduces a mass loss step below 100 \(^\circ\)C due to loss of residual water content (the powders were dried in the vacuum oven prior to measurement but were exposed to the atmosphere during TGA sample preparation). The decomposition of the quaternary ammonium group commenced at 150 \(^\circ\)C for the Cl\(^-\) form material (in good agreement with that observed previously), however, it was observed to initiate at a lower temperature (nearer 100 \(^\circ\)C) for the OH\(^-\) form. The next decomposition step now commences at the slightly higher temperature of 330 \(^\circ\)C (for both counter-ions), while the final degradation step occurs above 425 \(^\circ\)C: the degradation of the non-ETFE remnants and the ETFE component are starting to overlap.

The difference in quaternary ammonium decomposition temperature for the two anions highlights both the greater susceptibility towards thermal degradation with this functional group in the presence of OH\(^-\) ions (and the necessity to evaluate such functional groups in the counter-ion environment in which they will be used). The TGA results with the AEI powders give an indication of short-term thermal stabilities only (i.e. over the ca. 110 min of the experiment); this is not a comment on the long term in situ stabilities (more relevant to application in APEFCs).

The surface morphology of the AEI(Cl\(^-\)) particles was observed using SEM. As presented in Fig. 3a, the particles were non-uniform in respect to both size and shape. A mean particle size of 24.5 \(\pm\) 9.8 \(\mu\)m (sample population of \(n = 311\)) was measured for the dehydrated particles. A minimum and maximum particle size of 6 and 75 \(\mu\)m was observed in the sample of AEI studied using SEM. Visual inspection of the images of the surface of the particles reveal exteriors composed of irregular platelets with a small degree of internal porosity (Fig. 3b and c).

**AEI incorporation into fuel cell electrodes**

The application of the AEI(Cl\(^-\)) into the catalyst layers was via formation of a sprayable “ink” containing the electrocatalyst, AEI, and solvent. SEM images of the GDE (catalyst layer) prepared with 15%mass AEI(Cl\(^-\)) are presented in Fig. 4. Cracks on the surface of the GDE (that diverge in all directions) result from the drying of the solvent (propan-2-ol and water) under ambient conditions. Distinct, isolated AEI particles are randomly distributed across the surface of the GDE. A proportion of these particles are visibly lying below a layer of electrocatalyst. The size and shape of these AEI particles are similar to that seen in Fig. 3. Magnification \((\times2000)\) of one of these particles (Fig. 4b) reveals a rough morphology of small globular spheres covering the entire surface of the AEI particle. Surrounding the isolated AEI “islands” are smooth regions with no clear visual evidence of \(\mu\)m sized AEI particles. A “particle free” region is highlighted in Fig. 4d (magnified \(\times2000\) in...
of the globules that coat the entire electrode surface. Fig. 5a and b respectively show the elemental Pt and F contents for an exemplar particle and particle-free region (associated SEM at 10 000× magnification). F was only observed with the AEI particle sample zone and not for the particle-free region, while the Pt signal was strong for both sample regions. The F signal originates from the –CF₂⁻ groups within the ETFE base polymer of the AEI, while the Pt signal comes from the Pt/C electrocatalyst. Further confirmation as to the location of the F (and thus AEI) across the GDE is given by the elemental maps presented in Fig. 5c. It is clear that the F signals are only associated with the randomly distributed particles, while the Pt signal is more evenly spread across the electrode surface. Thus, the particle-free zones are generally devoid of AEI. This was not unexpected given the crude fabrication method used. The localised distribution of AEI particles across the GDE will result in a concentration of the ionic conductivity into isolated regions (within the electrocatalyst layer), while the majority of the “catalyst layer” will not exhibit significant ionic conduction. This obviously has major implications for the catalyst utilisation of the electrode, as it significantly reduces the electrochemically active surface area (of the catalyst) for both the oxygen reduction and hydrogen oxidation reactions. Therefore, in situ performances were expected to be poor.

To verify this expectation, single cell H₂/O₂ APEFCs were tested at 50 °C using MEAs with either 15 or 20%mass AEI in the electrodes (symmetrical AEI contents in both the anode and cathode in each MEA). The polarisation and power density curves are presented in Fig. 6. The OCVs for the 15 and 20% mass AEI loadings were high at 1.05 and 1.07 V, respectively (for H₂/O₂ APEFCs). Both electrodes, however, suffered from a significant initial drop in potential at low current density (indicating kinetic limitations due to an uneven distribution of the AEI across the electrode surface). The lower AEI loading of 15%mass yields a larger overpotential at low current densities relative to the electrode with 20%mass AEI.

Even with the considerable catalyst utilisation limitations, the maximum geometric power densities recorded for both AEI loading levels were high (considering the use of a relatively thick 80 μm AAEM and a low temperature of 50 °C): the 15%mass AEI showed a peak power density = 180 mW cm⁻² (at 475 mA cm⁻²), while 20%mass AEI showed a peak power density = 240 mW cm⁻² (at 630 mA cm⁻²). A typical value for a similar MEA (tested under similar conditions) but with Surrey’s previous generation ionomer (15%mass polymer loading) is 140 mW cm⁻². In addition to the uneven AEI distribution (evident in Fig. 4), the surface morphology of the electrodes were not flat. The contact resistances within both MEAs (without prior hot-pressing to laminate the electrodes to the AAEM) were 193 and 154 mΩ cm² (determined from current interrupt measurements recorded automatically by the Scribner fuel cell test station) for the 15% mass and 20%mass AEI, respectively.

Given that such promising performances were not anticipated, the AAEM and AEI materials were then sent for interlaboratory testing (at the University of Connecticut). Despite different MEA fabrication and test conditions being used, higher than expected performances were again observed (see
It appears that access to OH\(^{-}\) anions through the catalyst layers is less critical than any blocking of gas permeation by ionomer binder in the fabricated electrodes. The higher than expected fuel cell performances may also be due to the identical chemistry of the AEI and AAEM used (only the morphological form and IEC being different).

We acknowledge that these AEI powders cannot be realistically used in APEFCs in such a morphological (powder) form; however, the high performances obtained (in un-optimised MEAs and fuel cell conditions) indicates that this class of materials has a potential (for use as an AEI) that needs to be further developed. Efforts are now on-going that are focusing on developing a more suitable dispersion or solubilisation of the RG AEI particles (of smaller particle sizes) that would allow a more even distribution of AEI in the catalyst layers.

**Conclusions**

The use of novel radiation-grafted ETFE benzyltrimethylammonium powders as anion-exchange ionomers (AEI) within the electrocatalyst layer of an alkaline polymer electrolyte fuel cell is reported. The AEI powders were produced with comparable ion-exchange capacities to previously developed alkaline anion-exchange membranes (of identical
chemistry). An average AEI particle size of 25 ± 10 μm led to a poor, uneven, distribution of the AEIs particles across the surface of the electrode. This led to the expectation that the resulting H2/O2 performances would be poor. However, higher than expected power performances were achieved (verified in 2 different laboratories). Considering that a large proportion of the electrocatalyst surface was not in contact with an ionic conducting phase, the high performances were surprising. This AEI concept shows promise and further research is on-going to conduct further experiments to optimise dispersion/solubilisation for more realistic application.

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