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The first anion-exchange membrane fuel cell to exceed 1 W cm^{-2} at 70 °C with a non-Pt-group (O_2) cathode†

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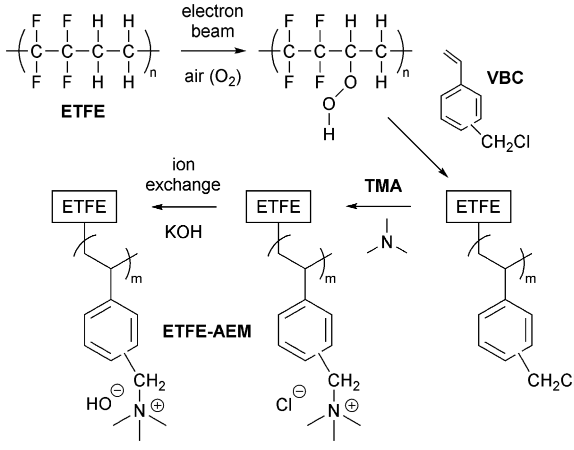
Anion-exchange membrane fuel cells face two challenges: performance and durability. Addressing the first, we demonstrate high performance with both O_2 and CO_2-free air supplies, even when using a Ag/C cathode. This was enabled by the development of a radiation-grafted anion-exchange membrane that was less than 30 μm thick when hydrated.

Anion-exchange membrane fuel cells (AEMFC) have attracted research interest since 2000,[1] which has mainly been justified by their potential for the utilisation of non-Pt electrocatalysts (an ultimate target is the use of non-precious-metal electrocatalysts).[2] The two critical *in situ* issues that need to be overcome are: (1) performance and (2) durability towards chemical attack of the anion-exchange membrane (AEM) and ionomer (AEI) components by hydroxide anions and peroxy radicals. Achieving AEM/AEI durability is especially challenging but there has been some notable progress in the last few years.[3] To move the technology forward, we feel that it is also important to establish if materials can be developed that allow high AEMFC performances to be demonstrated. In the last few years, improved performances have been reported and this has led to an increased level of interest in this class of low-temperature fuel cells.[4–6] With this aim, this communication presents the next break-through in AEMFC performance.

ETFE-[poly(ethyene-*co*-tetrafluoroethylene)]-based radiation-grafted (RG) AEM and AEI ionomers have previously been developed for use in AEMFCs.[6–9] Following the trend set by the application of proton-exchange membranes (PEM) in proton-exchange membrane fuel cells (PEMFCs), we have investigated the use of a thinner RG-AEM in AEMFCs. This proved more problematic than originally anticipated, but a suitable supplier and grade of ETFE was recently identified (12.7 μm thick ETFE00127/1550 from Polyflon Technology Ltd, Eccleshall UK): this enabled the (more repeatable) synthesis of a sub-30 μm RG-AEM, which both underwent radiation-grafting to a satisfactory degree and was robust enough to test in an AEMFC at a temperature above 60 °C. This 12.7 μm thick Polyflon ETFE exhibited 55 MPa tensile stress at break (180% strain at break), which compares to the values 55 MPa/320% and 55 MPa/880% obtained with 25 and 50 μm ETFE films, respectively (the grade of ETFE used in prior studies and supplied by Nowofol, Germany).[6,8]

The ETFE-based RG-AEM discussed in this communication (designated **ETFE-AEM** from now on) was synthesised by subjecting the ETFE film to 30 kGy absorbed dose (using a 4.5 MeV e$^-$-beam), grafting with vinylbenzyl chloride (VBC) monomer (dispersed in H_2O), and aminating with aqueous trimethylamine (see Scheme 1 and the Experimental section in the ESI†). Table 1 summarises the key properties of the **ETFE-AEM** produced. Raman spectro-microscopy confirmed that the grafting and amination of VBC penetrated throughout the thickness of the **ETFE-AEM** (Fig. S1 in the ESI†); this explains the high conductivities achieved. The **ETFE-AEM** produced had a tensile stress at break of 22 MPa (220% strain at break).



Scheme 1 An outline of the synthesis of the **ETFE-AEM** tested in this study.

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† Electronic supplementary information (ESI) available: Detailed descriptions of the anion-exchange membrane synthesis, membrane-electrode assembly preparation, and fuel cell test procedures. Additional Raman and SEM data. See DOI: 10.1039/c7cc06392j

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Table 1 A summary of the properties of the **ETFE-AEM** studied. All measurements were conducted on the Cl^- anion forms using the exact experimental methods described in detail in ref. 6. Errors are from measurements on $n = 3$ samples

Thickness(dry)/μm	21 ± 1
Thickness(hydrated)/μm	27 ± 1
Degree of grafting: DoG[a] (%)	70
Ion-exchange capacity (IEC)/mmol g^{-1}	2.11 ± 0.04
WU[b] (%)	59 ± 9
λ[c]	16 ± 2
TPS[d] (%)	28 ± 1
σ_{Cl}(25 °C)[e]/mS cm^{-1}	23.8 ± 1.6
σ_{Cl}(70 °C)[e]/mS cm^{-1}	57.8 ± 3.3

[a] Calculated from eqn (S1) in the ESI. [b] Gravimetric water uptake calculated using eqn (2) in ref. 6. [c] Number of H_2O molecules per Cl^- anion calculated as: λ = WU(%)/(100 × 18.02 × IEC), where IEC is in mol g^{-1}. [d] Through-plane swelling calculated using eqn (3) in ref. 6. [e] The Cl^- anion conductivities of the fully hydrated **ETFE-AEM** (4-probe, in-plane measurements with the RG-AEM submerged in water) calculated using eqn (5) in ref. 6.

The **ETFE-AEM** was used to fabricate membrane electrode assemblies (MEA) with electrodes (5 cm^2 geometric) containing the AEI powder (IEC = 1.26 ± 0.06 mmol g^{-1}) developed in a prior study:[9] all the electrocatalyst inks in this study contained 20%wt AEI powder and 80%wt electrocatalyst and were sprayed directly onto PTFE-treated Toray TGP-H-60 carbon paper gas diffusion substrate (Alfa Aesar, UK) using propan-1-ol/H_2O mixed solvent.[6] PtRu/C(Johnson Matthey UK, HiSpec 12100, 50%wt Pt and 25%wt Ru) was used as an anode electrocatalyst throughout this study as the hydrogen oxidation reaction on Pt is poorer in alkali than in acid:[5,10] all anodes contained 0.6 mg cm^{-2} total metal loadings (= 0.4 mg_{Pt} cm^{-2}). Pt/C(Johnson Matthey UK, HiSpec 4000, 40%wt) or Ag/C (BASF Fuel Cell Inc., 40%wt Ag) were used as the cathode electrocatalysts: 0.4 mg_{Pt} cm^{-2} and 1.0 mg_{Ag} cm^{-2} loadings were used, respectively. The MEAs were converted to the OH^- forms by ion-exchange with aqueous KOH (1 mol dm^{-3}) and then evaluated in both H_2/O_2 and H_2/air(CO_2 free) AEMFCs at 70 °C. Gas flow rates of 1 dm^3 min^{-1} were used with no back-pressurisation: gas dew points were set at 66 °C, which equates to 84% relative humidities (RH) with a cell temperature of 70 °C. The ESI† contains more details on the preparation and AEMFC testing of the MEAs, which were carefully aligned to prior published methods.[6] A cell temperature of 70 °C was selected for AMEFC testing as this was the highest temperature that could be consistently used without acute MEA failure occurring during testing.

Fig. 1 compares the H_2/O_2 AEMFC fuel cell performance of **ETFE-AEM**-based MEAs containing Pt/C and Ag/C cathodes. The Ag/C cathode yielded a peak power density of 1110 mW cm^{-2} (at 2400 mA cm^{-2}), which compared favourably to the Pt/C cathode that yielded 1570 mW cm^{-2} (at 2800 mA cm^{-2}): internal ohmic area resistances were 36 and 44 Ω cm^2, respectively (at peak power densities). However, the open circuit voltages (OCV) were <0.95 V, which are much lower than the >1.0 V OCVs obtained with AEMFCs containing thicker ETFE-based RG-AEMs.[6,8] This OCV data suggests that reasonably high gas crossover rates across the thin **ETFE-AEM** and that moving to even thinner ETFE-based RG-AEMs would be unwise.

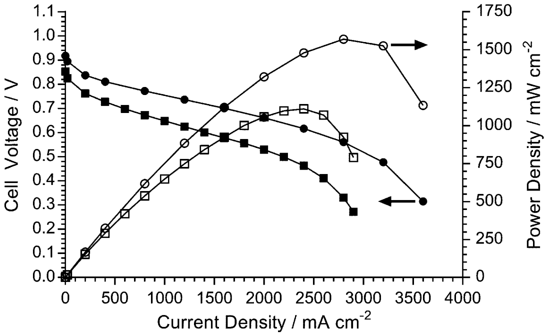

Fig. 1 The H_2/O_2 AEMFC performances at 70 °C of the **ETFE-AEM** with Pt/C (0.4 mg_{Pt} cm^{-2}) (●, ○) and Ag/C (1.0 mg_{Ag} cm^{-2}) (■, □) cathodes. The anodes were PtRu/C(50%wt Pt and 25%wt Ru) with a Pt loading of 0.4 mg_{Pt} cm^{-2}. The 1.0 dm^3 min^{-1} (RH = 84%) gas supplies were not pressurised.

Fig. 2 compares the performances of the MEA containing the Ag/C cathode supplied with either O_2 or CO_2-free air. The peak power density dropped to 699 mW cm^{-2} (at 1700 mA cm^{-2} and 44 mΩ cm^2) when the cathode supply was switched to CO_2-free air. This is still a respectable power density, especially considering the lower cost of Ag compared to Pt: Ag was only 1.7% of the price of Pt as of 11th August 2017 (US\$17 g^{-1} *vs.* US\$980 g^{-1}, respectively).[11] Interestingly, the Ag/C cathode even outperformed the Pt/C cathode when supplied with CO_2-free air at a cell temperature of 70 °C: the Pt/C cathode yielded only a peak power density of 650 mW cm^{-2} (at 1000 mA cm^{-2} and 39 mΩ cm^2) due to larger apparent mass transport losses. This is clearly a phenomenon that needs to be investigated further in an extended study.

In summary, we show that the use of a sub-30 μm ETFE-based radiation-grafted anion-exchange membrane leads to anion-exchange membrane fuel cell (AEMFC) performances higher than 1 W cm^{-2} even with the use of a Ag/C cathode electrocatalysts. This demonstrates that the performances of AEMFCs are reaching levels (especially on a cost *vs.* power basis) that could lead to heightened commercial interest. To move the technology further forward, we acknowledge that a harder challenge must be cracked: the search for a chemically-compatible anion-exchange membrane-ionomer combination that is both high performance and durable for >1000 h (mechanically robust, chemically stable) continues.

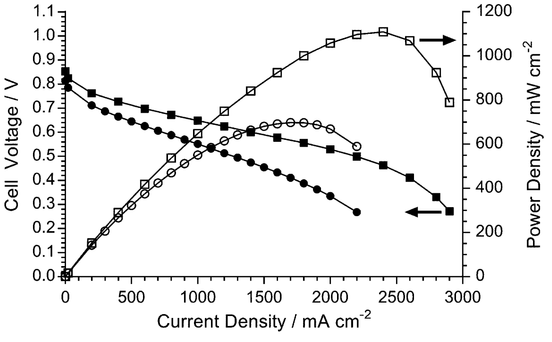

Fig. 2 The H_2 AEMFC performances at 70 °C of the **ETFE-AEM** with Ag/C (1.0 mg_{Ag} cm^{-2}) cathodes supplied with either O_2 (■, □) or CO_2-free air (●, ○).

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Conflicts of interest

There are no conflicts of interest to declare.

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