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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 (O₂) 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 O₂ and CO₂-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(ethylene-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 the 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 H₂O), 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.⁶ Raman spectro-microscopy confirmed that the grafting and amination of VBC penetrated throughout the thickness of the ETFE-AEM (Figure S1 in the ESI); this explains

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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 data. See DOI: 10.1039/x0xx00000x
The high conductivities achieved. The ETFE-AEM produced had a tensile stress at break of 22 MPa (220% strain at break).

The ETFE-AEM was used to fabricate membrane electrodes assemblies (MEA) with electrodes (5 cm² geometric) containing the AEI powder (IEC = 1.26 ± 0.06 mmol g⁻¹) developed in a prior study, all the electrocatalyst inks in this study contained 20%wt AEI powder and 80% electrocatalyst and were sprayed directly onto PTFE-treated Toray TGP-H-60 carbon paper gas diffusion substrate (Alfa Aesar, UK) using propan-1-ol/H₂O mixed solvent. 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; all anodes contained 0.6 mg

| Thickness(dry) / μm | 21 ± 1 |
| Thickness(hydrated) / μm | 27 ± 1 |
| Degree of Grafting: DoG (%) | 70 |
| Ion-exchange capacity (IEC) / mmol g⁻¹ | 2.11 ± 0.04 |
| WU(%) | 59 ± 9 |
| λ | 16 ± 2 |
| TPS(%) | 28 ± 1 |
| α₂(25 °C) / mS cm⁻¹ | 23.8 ± 1.6 |
| α₂(70 °C) / mS cm⁻¹ | 57.8 ± 3.3 |

Calculated from eqn 1. in the ESI. Gravimetric water uptake calculated using eqn. 2 in ref 6. ‘Number of H₂O molecules per Cl⁻ anion calculated as: λ = WU(%) / (100 × 18.02 × IEC), where IEC is in mol g⁻¹. Through-plane swelling calculated using eqn. 3 in ref. 6. *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 Cl⁻ anion conductivities of the ETFE-AEM produced had a tensile stress at break of 22 MPa (220% strain at break). The ETFE-AEM was used to fabricate membrane electrodes assemblies (MEA) with electrodes (5 cm² geometric) containing the AEI powder (IEC = 1.26 ± 0.06 mmol g⁻¹) developed in a prior study, all the electrocatalyst inks in this study contained 20%wt AEI powder and 80% electrocatalyst and were sprayed directly onto PTFE-treated Toray TGP-H-60 carbon paper gas diffusion substrate (Alfa Aesar, UK) using propan-1-ol/H₂O mixed solvent. 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; all anodes contained 0.6 mg

**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 measurements on n = 3 samples.

The H₂/O₂ AEMFC performances at 70 °C of the ETFE-AEM with Pt/C (0.4 mgPt cm⁻²) and Ag/C (1.0 mgAg cm⁻²) cathodes. The anodes were PtRu/C (50%wt Pt and 25%wt Ru) with a Pt loading of 0.4 mgPt cm⁻². The 1.0 dm³ min⁻¹ (RH = 84%) gas supplies were not pressurised.

Figure 2 compares the performances of the MEA containing the Ag/C cathode supplied with either O₂ or CO₂-free air. The peak power density dropped to 699 mW cm⁻² (at 1700 mA cm⁻² and 44 mΩ cm²) when the cathode supply was switched to CO₂-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). Interestingly, the Ag/C cathode even outperformed the Pt/C cathode when supplied with CO₂-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 cm²) 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...

Conflicts of interest
There are no conflicts of interest to declare.

References


