Direct spun aligned carbon nanotube web-reinforced proton exchange membranes for fuel cells

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A new method combining electrospinning of SPEEK and direct spinning of CNT forests has been used to prepare sulfonated poly(ether ether ketone) (SPEEK)/directly spinnable carbon nanotube (dsCNT) composite proton exchange membranes. The SPEEK/dsCNT membrane is more robust than SPEEK alone, and in a fuel cell significantly outperforms both SPEEK and the commercial Nafion 212 membranes.

Proton Exchange Membrane (PEM) fuel cells are clean and efficient electric power devices with a range of applications, and have been suggested as replacements for fossil fuelled engines.[1] A PEM requires high proton conductivity and selectivity, and hence must be thin to maximise efficiency. On the other hand, the membrane must also be gas-impermeable and mechanically, chemically and thermally robust. Maximising the proportion of proton-conductive groups, such as sulfonic acid (mmol SO^{3-} per g polymer), while minimising susceptibility to swelling and weakness is a key challenge for new PEM development. Inorganic additives such as silica,[2,3] titania[4,5] and heteropolyacids[6] can strengthen the membrane but decrease conductivity,[2] can be non-uniformly dispersed,[5] and have not improved cell performance.[6] The addition of carbon nanotubes (CNTs), either pristine[7] or functionalized with carboxylic[8] or sulfonic acid,[9–11] Nafion,[12] chitosan,[13] histadine[14] or poly(oxyalkylene)diamine[15] also did not significantly improve the performance of hydrogen–air PEM fuel cells mainly due to poor dispersion of the additive, but still showed potential in direct methanol fuel cells by lowering methanol crossover.

Unlike the randomly oriented commercial CNTs, our directly spinnable CNTs (dsCNTs) are drawn as a wide, thin web from special as-grown CNT forests.[16] In addition to the high thermal and electrical conductivity, and mechanical and chemical robustness of CNTs, the interconnectivity and excellent alignment in the direction of draw make the dsCNT webs attractive materials alone and as additives to other materials.[16] We herein introduce a novel method for producing a stable, thin and highly conductive composite PEM containing a model ionomer, sulfonated poly(ether ether ketone) (SPEEK), and dsCNT webs drawn from CNT forests. In this method, as the CNTs are drawn directly from CNT forests and each layer is placed in a controlled position in the membrane, the dsCNT webs do not undergo dispersion and wet-processing allowing alignment.

The CNTs in the dsCNT web are ∼10 nm in diameter (Fig. 1a) and SPEEK fibres (Fig. 1b) are 77 ± 7 nm in diameter, and sufficiently uniform to ensure intimate contact. The as-formed laminate (layers of electrospun SPEEK/dsCNT web) is very open so most of the porosity is removed by mechanical pressing and finally by solvent vapour fusion of the polymer. This approach preserves the SPEEK film structure and retains the excellent dsCNT alignment and central position within the membrane (Fig. 1c), which completely prevents possible short-circuiting during fuel cell operation as the conductive CNT web is inserted in the membrane matrix. The film is thin and translucent (Fig. 1d), with a uniform layer of about 270 nm containing the CNTs (*i.e.*, 6 dsCNT web layers of 45 nm each), being only ∼0.8% of the overall film thickness of 35 μm.

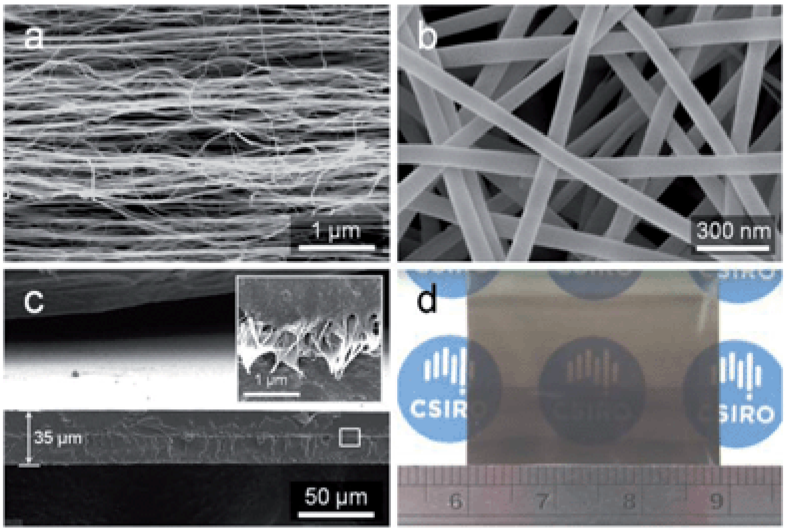

Fig. 1 SEM images of the (a) dsCNT web, (b) electrospun SPEEK (c) cross-section of SPEEK/dsCNT membrane, with inset image showing higher magnification and optical image (d) of the SPEEK/dsCNT membrane.

The SPEEK/dsCNT (35 µm thick), pristine SPEEK (37 µm) and standard commercial Nafion 212 (51 µm) membranes were evaluated for (i) swelling in water, (ii) proton conductivity in vapour and (iii) tensile strength in air (detailed test conditions shown in Experimental). The SPEEK/dsCNT and SPEEK swell similarly at 30–50 °C but the SPEEK/dsCNT swells substantially less at 60 °C (Fig. 2a,b), the dimensional stability of PEM at higher temperature being more important in fuel cell operation. Interconnected dsCNT webs could effectively reduce expansion pressure of SPEEK matrix when wet, which is more critical at higher temperature.

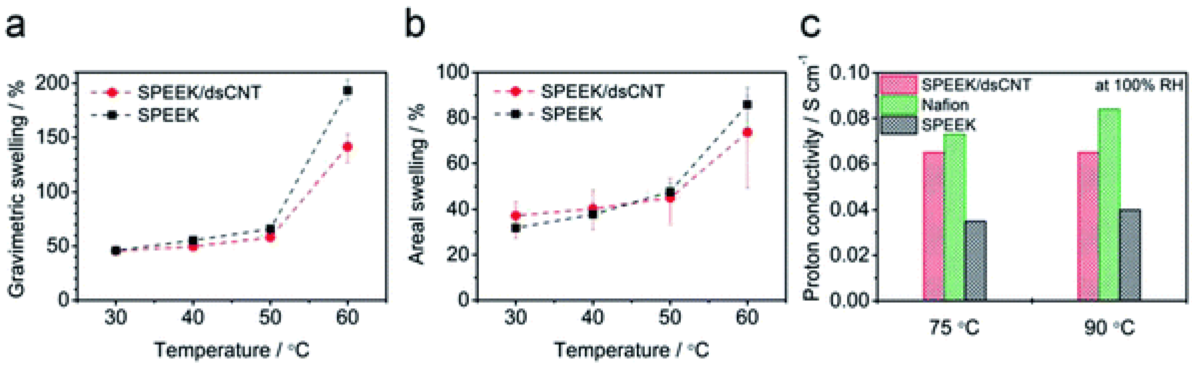

Fig. 2 (a) Gravimetric and (b) areal swelling of SPEEK/dsCNT and SPEEK, and the (c) proton conductivity and (d) stress–strain of SPEEK/dsCNT (parallel and perpendicular to the dsCNT web layer), SPEEK and Nafion membranes.

In general, the proton conductivity of all membranes was slightly higher at 90 °C than 75 °C (Fig. 2c), which is typical Arrhenius behaviour of proton conduction,[17,18] with Nafion 212 giving the highest and SPEEK the lowest result. Interestingly, SPEEK/dsCNT showed significantly higher proton conductivity than SPEEK alone (0.064 S cm^{-1} *vs.* 0.035 S cm^{-1} at 75 °C, 0.066 S cm^{-1} *vs.* 0.040 S cm^{-1} at 90 °C), which is attributed to the lower swelling of the SPEEK/dsCNT. In terms of proton conductivity SPEEK/dsCNT was slightly less than Nafion 212 (0.073 and 0.083 S cm^{-1} at 75 and 90 °C, respectively).

Mechanical strength and modulus are also of critical importance for fuel cell membranes as they must resist distortion or rupture under harsh and varying conditions. To investigate the effect of dsCNT inclusion and orientation, the tensile strength of SPEEK/dsCNT was measured parallel and perpendicular to the dsCNT web and compared to SPEEK alone and commercial Nafion 212 (Table 1). Note that unlike the SPEEK/dsCNT composite, single component films (SPEEK alone and Nafion 212 membranes) are considered to be isotropic. Parallel to the dsCNT alignment, the yield strength and proportional limit of the SPEEK/dsCNT are respectively 1.9 and 2.4 times higher than those of the SPEEK, and 2.8 and 3.2 times higher than for Nafion 212 (Fig. 2d). Perpendicular to the dsCNTs, strength and modulus are almost as high as in the parallel direction but elongation at break is much reduced, though still substantial. The strong CNT interaction in the direction of draw and the longitudinal CNT alignment resists transverse crack propagation and prolongs plastic deformation before failure. This is facilitated by close interaction of the SPEEK and dsCNT, as a pure dsCNT web is very strong and stiff but exhibits little strain to break.

Table 1 Tensile test results for the different membranes

	Young's modulus (MPa)	**Proportional limit (MPa)**	**Yield strength (MPa)**	**Ultimate strength (MPa)**	**Elongation at break (%)**
SPEEK/dsCNT (ǁ dsCNT)	665	41	51.0	58.5	81.2
SPEEK/dsCNT (⊥ dsCNT)	820	38	46.5	47.5	18.1
SPEEK	557	17	26.5	30.0	54.7
Nafion 212	388	13	18.5	22.0	39.2

Perpendicular to the web the membrane is similarly stiff and almost as strong, as the CNTs are not perfectly aligned to the draw direction, so provides significant reinforcement. However a small extension would separate these and they would then not resist crack propagation. The anisotropy clearly demonstrates that it is the dsCNT responsible for the improvement.

Although SPEEK/dsCNT has physical properties superior to the SPEEK and Nafion membranes, the critical test is to evaluate membrane performance in a single cell, which is represented as a cell voltage, V, *versus* the cell current, i. This was measured for the three membranes. The slope, $\Delta V/\Delta i$, in the cell voltage range of 0.30–0.83 V is the ohmic overpotential determined by membrane resistance to proton transport, which in turn dictates the power density. With all other factors controlled or accounted for, SPEEK/dsCNT significantly outperformed the SPEEK membrane at both 75 °C (Fig. 3a) and 90 °C (Fig. 3b). This is seen both in the voltage *vs.* current density graphs and in the power density plots, where the SPEEK/dsCNT exhibited 31% (1.24 *vs.* 0.95 W cm^{-2}) and 43% (1.14 *vs.* 0.80 W cm^{-2}), respectively, higher maximum power density. Most remarkably, the SPEEK/dsCNT composite membrane also outperformed Nafion 212 at both temperatures, and particularly at the more significant higher temperature. Note that in the single cell testing SPEEK/dsCNT outperformed Nafion 212 although the measured proton conductivity of SPEEK/dsCNT was lower than Nafion 212. To explain this we also examined the interfacial resistance of the membranes during operation. The interfacial resistance of the membrane was 44–58% lower for SPEEK/dsCNT than Nafion 212, and the difference in interfacial resistance between SPEEK/dsCNT and Nafion 212 increased as the temperature increased (see Table S1 in ESI†). We think this is a reflection of the superior physical properties of the SPEEK/dsCNT composite. To the best of our knowledge, this is the first SPEEK-type membrane to outperform Nafion at temperatures as high as 90 °C and under fully humidified conditions.

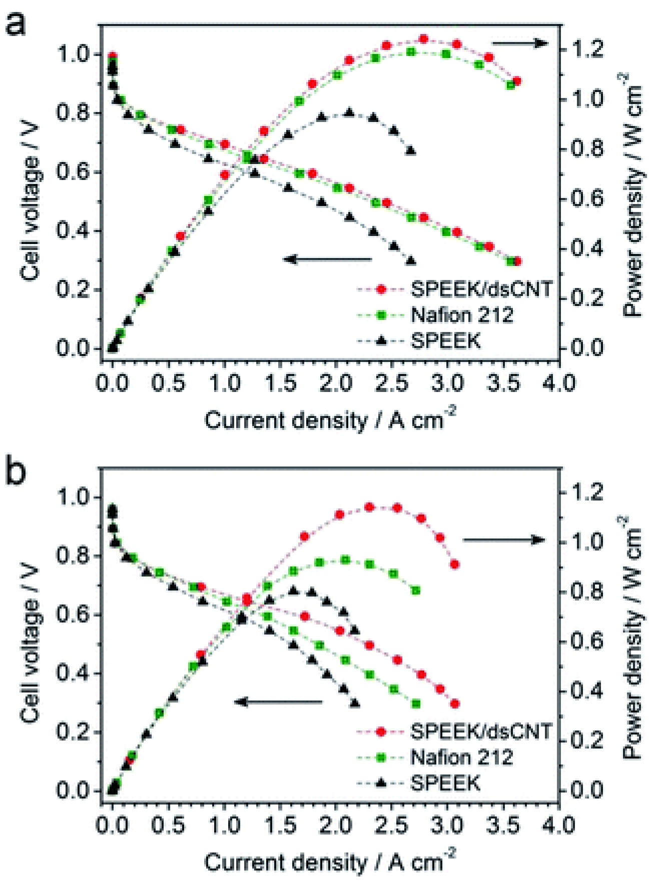

Fig. 3 Single cell performance of membrane-electrode-assembly (MEA) with SPEEK/dsCNT, SPEEK and Nafion 212 membranes at 100% RH and (a) 75 °C and (b) 90 °C.

It is particularly noteworthy that no short-circuit occurs during the testing as the dsCNTs are well controlled and isolated from the electrically conductive components. Short-circuiting is a major concern with dispersed-CNT-composite PEMs prepared by solution ting. Also, the dsCNT web layer gave no discernible interference to proton conduction through the membrane.

Conclusions

We have produced a SPEEK/dsCNT composite PEM that, in both physical and electrical performance at 75 or 90 °C and 100% RH, exceeds t SPEEK and, most notably, Nafion 212 membranes. No evidence of short circuiting or interference with proton conductivity was observed. This achievement was gained with just 0.8 vol% CNTs and six uniaxial dsCNT layers, leaving considerable scope for further improvement by, for example, varying the number of layers, their relative orientation and the distribution within the SPEEK structure. Finally, the novel method of dsCNT polymer composite membrane fabrication is not limited to fuel cell membranes but can be applied to other membrane areas such as water treatment and gas separation.

Experimental

dsCNT synthesis

dsCNTs were grown as forests of parallel-aligned fibres on silicon wafers bearing 50 nm thermal SiO_2 and 3.0 nm of iron by e-beam evaporation, annealed in a 90 mm id quartz tube reactor at 680 °C under helium (4000 sccm, 40 min) and then acetylene (100 sccm) and hydrogen (100 sccm) were added for 15 min to grow the ~300 µm long CNTs. Full details of this process are published.[19]

Membrane preparation

Electrospinning is a versatile technique used to prepare nanofibrous webs from a sufficiently entangled polymer solution or melt.[20] To prepare SPEEK/dsCNT PEMs, 20 wt% SPEEK in *N*,*N*-dimethylformamide (DMF) was electrospun (10 cm spinneret-to-collector distance, 16 kV applied potential, 0.080 mL h^{-1} solution feed rate) onto a drum collector surface (100 mm diameter, 60 mm lateral oscillation at 30 mm min^{-1} and 30 mm s^{-1} surface rotation (collecting face down)). After 2 mL of solution was electrospun, collection was paused and a 2.5 cm-wide dsCNT web (drawn from the CNT forest) was attached to the distal (up) face of the drum. Resumption of electrospinning and drum rotation results in the dsCNT web being drawn continuously over to the collecting face where it was coated with electrospun fibres. As the drum rotated the dsCNT layer was coated with the electrospun SPEEK until 6 layers of dsCNT web were deposited. This was followed by 2 mL of SPEEK solution applied as before. The laminate was compressed (~40 MPa) and exposed to DMF vapour to fuse the SPEEK fibres and eliminate porosity.[21] Without the dsCNT component, electrospun SPEEK is not stable to this preparation so, for comparison, a SPEEK film was t from 10 wt% SPEEK dissolved in DMF and dried (60 °C, 16 h). The membranes were immersed in 1 M H_2SO_4 (3 periods of 8 h), washed with deionised water (24 h) and dried (60 °C, overnight).

Membrane characterisation

Electrospun SPEEK, dsCNT webs and the SPEEK/dsCNT membrane were examined by SEM and measured with ImageJ software. Gravimetric and areal water-swelling for the SPEEK/dsCNT and SPEEK membranes were measured at 30, 40, 50, and 60 °C and calculated thus:

$$\text{Gravimetric swelling}\ (\%) = \frac{W_{\text{wet,T}} - W_{\text{dry,T}}}{W_{\text{dry,T}}} \times 100$$

$$\text{Areal swelling}\ (\%) = \frac{A_{\text{wet,T}} - A_{\text{dry,T}}}{A_{\text{dry,T}}} \times 100$$

The tensile strength of SPEEK/dsCNT (parallel and perpendicular to dsCNT web alignment), t SPEEK, and Nafion 212 membranes were measured at 17 °C and 25% RH by using a 200 gF (1.96 N) load cell (DACELL, South Korea).

Electrode preparation

A 'catalyst ink' comprising carbon-supported-Pt (40 wt% Pt on carbon black, Johnson Matthey), de-ionised water, Nafion® solution (5 wt% in short-chain alcohol/H_2O, EW = 1100, Aldrich) and isopropanol in a weight ratio of 5 : 20 : 2 : 60 was stirred for 5 min and ultrasonicated for 15 min (five times for 3 min each) in a cold bath. Membranes were airbrushed with the ink (0.4 mg cm^{-2} catalyst on each side), dried (100 °C, 1 h) and installed into a Membrane Electrode Assembly (MEA) with gas diffusion media (SGL 10BC) and Teflon gaskets without hot-pressing.

Single cell test

Single cell tests were performed at 100% RH and 75 °C or 90 °C (Bekktech PEMFC station, 1 cm^2 active area). Hydrogen (99.99%, 100 sccm) and oxygen (99.99%, 150 sccm), warmed to the test cell temperature and humidified, were supplied without back-pressure. Current and voltage were measured using an Agilent 6060B 300 W DC load, and membrane and interface resistances by *in situ* electrochemical impedance spectroscopy ((VSP®, BioLogic), 10 mV amplitude, 100 mHz to 10 kHz frequency). Data shown in Supplementary information.

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Supplementary Information

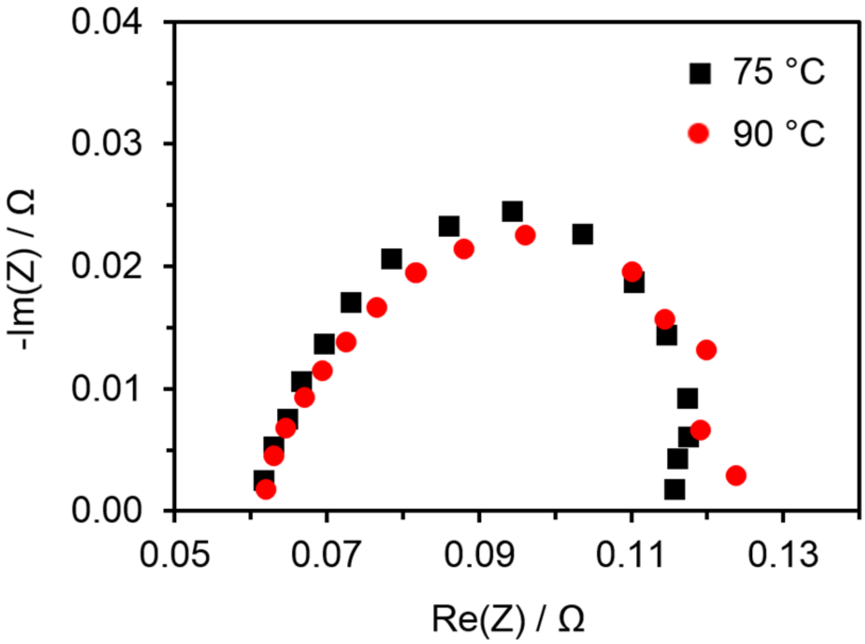

Figure S1. Nyquist plot of SPEEK/dsCNT membrane at 75 °C and 90 °C and 100% RH. The membrane resistance was 0.062 Ω (at 75 °C) and 0.062 Ω (at 90 °C), and interface resistance was 0.054 Ω (at 75 °C) and 0.062 Ω (at 90 °C).

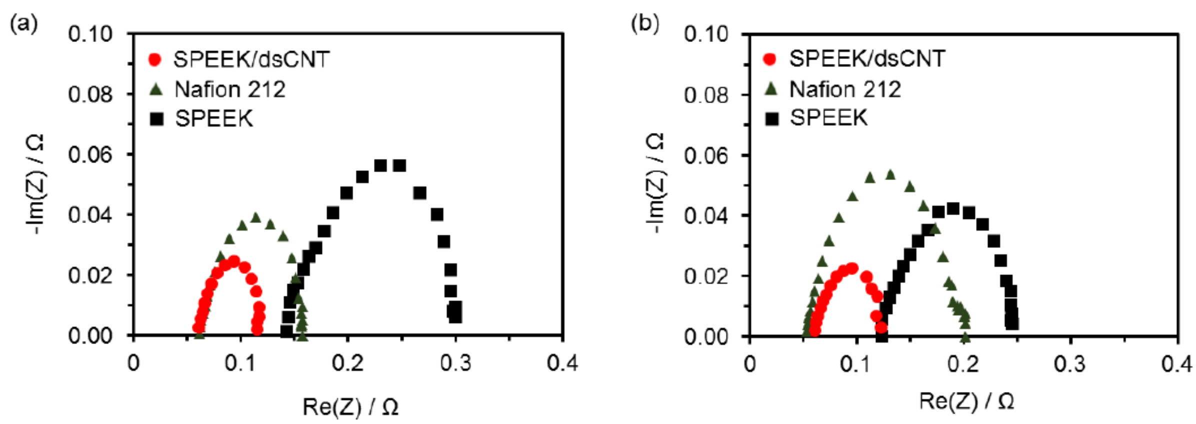

Figure S2. Nyquist plots of SPEEK/dsCNT, Nafion 212 and SPEEK membranes at 100% RH and (a) 75 °C or (b) 90 °C.

Table S1. Comparison of membrane resistance and interface resistance for SPEEK/dsCNT and Nafion 212 membranes.

Resistance	SPEEK/dsCNT	Nafion 212
Membrane resistance at 75 °C and 100% RH	0.062 Ω	0.061 Ω
Membrane resistance at 90 °C and 100% RH	0.062 Ω	0.053 Ω
Interface resistance at 75 °C and 100% RH	0.054 Ω	0.096 Ω
Interface resistance at 90 °C and 100% RH	0.062 Ω	0.148 Ω