

Nitrogen-doped carbon nanofiber catalyst for ORR in PEM fuel cell stack: performance, durability and market application aspects

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Abstract

A noble metal-free catalyst based on N-doped carbon nanofibers supported on graphite (N-CNF¹) was employed for the oxygen reduction at the cathode of a Nafion PEMFC with a commercial Pt/C anode. Obtained performance in pure H₂ and O₂ indicated the presence of significant mass-transport limitations when utilizing catalyst loadings between 1 and 10 mg cm⁻². Strategies to reduce the limitations were explored by optimization of the cathode ionomer content, catalyst loading and application technique. Pore-formers (Li₂CO₃, (NH₄)₂CO₃ and polystyrene microspheres) were utilized to improve the mass-transport within the layer. A maximum of 72 mW cm⁻² and 1400 A g⁻¹ or 300 W g⁻¹ at peak power was demonstrated. The catalyst was then applied to the cathode of a 10-cell fuel cell stack, and a 400-hour durability test was conducted. The average cell voltage decay amounted to 162 μV h⁻¹. Finally, a market application analysis was conducted by comparing the capital and operating costs of FC systems based on Pt/C and on N-CNF cathodes. While the cheap (3,32 € g⁻¹) N-CNF catalyst reduces the single MEA cost by almost a third, the total cost of ownership of an N-CNF based PEMFC system is still higher due to lower cell performance.

Keywords

Noble metal-free catalysts
Nitrogen-doped carbon
Oxygen reduction reaction
PEM fuel cell
Cathode
Durability
Market application analysis

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have been in development for decades, but only recently started to penetrate the real markets in such areas as automotive transport, distributed power generation and auxiliary power units [1]. Between 20 and 40% of the total PEMFC cost is the cost of Pt/C catalyst for oxygen reduction reaction (ORR) at the cathode [[2,3]]. So far only Pt and

¹ *Abbreviations:* N-CNF: N-doped carbon nanofibers supported on graphite; FC, fuel cell; PEMFC, polymer electrolyte membrane fuel cell; MEA, membrane-electrode assembly; ORR, oxygen reduction reaction; PGM, platinum group metals; NCR, Nafion : catalyst ratio; GDL, gas diffusion layer; DMFC, direct methanol fuel cell; OCV, open circuit voltage; RRDE, rotating ring-disc electrode; ICO, integral cost of ownership; CAPEX, capital expenses; OPEX, operational expenses.

platinum group metal (PGM) catalysts were successfully utilized at commercial PEMFC cathodes, as no other material could demonstrate comparable ORR activity and durability in the acidic conditions of PEMFCs. However, platinum is listed by the European Commission as a critical raw material, and its resources are limited and expected to be depleted by the end of the 21st century regardless of the introduction of fuel cell vehicles [[4]]. Therefore, it is important to find alternative and also cheaper catalysts. While non-PGM catalysts of different types have been attempted for some decades [5–7], a new type of catalytic materials - nitrogen-doped carbons – has recently received a lot of attention [8–18]. These materials are highly conductive, corrosion resistant and can be produced in large quantities at only a fraction of the cost of Pt.

A novel non-PGM catalyst based on N-doped carbon nanofibers (N-CNF) was synthesized by decomposing ammonia and carbon monoxide over Fe nanoparticles supported on expanded graphite as described elsewhere [[19]]. In this article we report the performance and durability of the N-CNF catalyst for ORR in PEMFCs in both single cell and a 10-cell FC stack, applied to the cathodes of MEAs by a conventional method and at high loadings (1-10 mg cm⁻²). In addition, results of a market application analysis are reported.

2. Experimental:

2.1 N-CNF catalyst synthesis

The noble-metal free N-CNF catalyst was prepared by a catalytic chemical vapour deposition method. Briefly, the N-CNFs were grown at 650 °C from 20 wt% Fe nanoparticles supported on expanded graphite by using a gas mixture of CO : NH₃ : H₂ (150 : 6.5 : 20 ml min⁻¹). The physical properties of the N-CNFs were characterized by N₂ adsorption measurements (Micromeritics TriStar II 3020), SEM imaging (Hitachi S-5500 S(T)EM) and XPS analysis (Kratos Axis Ultra DLD spectrometer, Al K α radiation). Detailed synthesis procedures and characterization are reported elsewhere [19].

2.2 MEA preparation

MEAs for single cell tests

Three iterations of cathodes have been prepared. Initially, both anode and cathode electrodes were prepared by a roll-printing method using propanediol solvent. The catalysts (HiSPEC4000 catalyst from AlfaAesar (Pt⁴⁰/C) on anodes and N-CNF catalyst on cathodes) were mixed with 5% Nafion solution in isopropanol (IonPower) to achieve the desired Nafion : catalyst ratio (NCR). On the anodes a 0.32 : 1 Nafion : catalyst dry mass ratio (NCR ratio) was used in all tests, while for cathodes the NCR were 0.5 : 1, 1 : 1 and 2 : 1. Surfactant (polyvinylpyrrolidone, 18 % to the mass of the catalyst) was used only for the anode to improve the ink stability. The propanediol solvent was then added, and the mixtures were sonicated by ultrasonic tip for 15-30 minutes to achieve uniform stable dispersions (catalytic ink). Afterwards the catalytic ink was applied to the surface of a piece of gas diffusion layer (GDL) (SGL - Sigracet 24 BC) by hand using a mask and a Teflon roller to achieve the catalyst loading of approximately 1 mg cm⁻² on the anodes (0.4 mg cm⁻² Pt). The cathode catalyst loading varied between 0.3 and 10 mg cm⁻². GDLs with applied ink were subsequently dried in an oven at 100 °C for 5 minutes to remove the solvent.

The second batch of cathodes was prepared by spraying. Here, isopropanol was used as solvent instead of propanediol, and the amount of solvent relative to catalyst was higher to achieve thinner catalytic ink. An airbrush (Iwata HP-C, nozzle 0.3 mm) was connected to the source of compressed air (2-3 bar), and the catalytic ink was manually sprayed over the surface of the GDL. NCR of 1 : 1 was used exclusively for this batch, while the catalyst loading varied between 0.36 and 2.32 mg cm⁻². The same roll-printed hydrogen electrodes as in all other tests were used in these MEAs.

Finally, the sprayed cathodes preparation method was modified by adding pore-forming agents: (a) Polystyrene latex microspheres 1 μm in diameter, (b) ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ and (c) lithium carbonate Li_2CO_3 , all purchased from Sigma Aldrich. All three pore-forming agents were added to the catalyst and ionomer mixture prior to sonication at the mass ratio of 1 : 1 to the catalyst. The removal of the pore-forming agents from the layers to produce pores was done by (a) soaking in toluene at room temperature for 48 hours and subsequent drying in an oven at 130 $^\circ\text{C}$ for 1 hour, (b) heating in the oven at 130 $^\circ\text{C}$ for 1 hour and (c) soaking in 0.5 M sulphuric acid for 1.5 hours followed by thorough rinsing in deionised water and drying in the oven at 130 $^\circ\text{C}$ for 0.5 hours.

Squares of approximately 6 cm^2 area were cut from all prepared GDLs with applied catalyst to form gas diffusion electrodes for single cell tests. Nafion N-212 (52 μm thick) membrane with a thermoplast border on both sides was used in all MEAs. Electrodes were laminated onto both sides of the membrane at 10 bar and 135 $^\circ\text{C}$ for 10 min each.

2.2.2 MEAs for the fuel cell stack

A total of 11 large MEAs for the fuel cell stack (active area 75 cm^2) were produced utilizing the third iteration of cathodes with $(\text{NH}_4)_2\text{CO}_3$ pore former. First, the catalytic ink for both electrodes was prepared. For that, the catalyst was mixed in 50 mL vials with Nafion ionomer solution, ammonium carbonate (cathode only) and solvent (isopropanol for cathode and propanediol for anode, 1 vial per MEA) and stirred for 15 min at 50 $^\circ\text{C}$. The mixture in each vial was then sonicated with an ultrasonic tip for 60 min and poured into a large Erlenmeyer flask, where it was stored for at least 24 hours before further processing. Both inks were applied onto the pieces of Sigracet 24BC gas diffusion media with pre-applied carbon microporous layer (IonPower) to form gas-diffusion electrodes. The cathode ink was manually sprayed onto the GDL, while the anode ink was applied using a screen-printing machine (DEK 247). The electrodes were dried at 125 $^\circ\text{C}$ for 15 min and weighed to calculate the catalyst loading prior to hot-pressing onto Nafion N-212 membrane at 135 $^\circ\text{C}$ for 5 min. Thin polyolefin sub-gaskets were used on both sides of MEAs to protect the membrane from mechanical damage, applied at the edge of each electrode prior to the hot-pressing.

2.3 Single cell test setup

The test cell used in single cell experiments is shown in Figure 1a and features graphite monopolar plates with machined serpentine gas flow channels, electrical heating and an active area of 6 cm^2 . MEAs were placed in the cell, and it was heated up to 80 $^\circ\text{C}$ on the test bench. Pure hydrogen and pure oxygen were supplied to the anode and cathode sides of the cell, respectively, and the MEA was allowed to stabilize for 2 hours prior to recording polarization curves. Flow rates were in the range of 0 – 40 mL min^{-1} for H_2 and 0 – 20 mL min^{-1} for O_2 . All measurements were repeated also the next day and sometimes on the third day. Back pressure regulators were used to increase the operating pressure in the test cell up to 1,6 barg. Polarization curves were recorded using a Chroma DC Electronic load 63112.

2.4 Fuel cell stack and the test setup

A 10-cell PEM FC stack was assembled featuring the N-CNF cathodes, Figure 1c. The active area of the stack electrodes was 75 cm^2 . The stack consisted of carbon/graphite composite bipolar plates with machined serpentine flow channels, insulating manifold plates, coated copper current collectors and stainless steel end plates, tied together by six tie rods. The stack was heated by a water circulator (Julabo) and kept at a constant temperature of +75 $^\circ\text{C}$. Hydrogen and oxygen were supplied by mass-flow controllers (Bronkhorst) controlled via CompactRio and LabView (National Instruments). Two proton-exchange membrane – based gas humidifiers (Fumatech) were used to humidify the gas. During the durability testing, the stack was kept at constant current of 1.5 A using an electronic load

(Tti). Voltage of each cell was monitored separately using a cell voltage monitor (Lynntech) and LabView software.

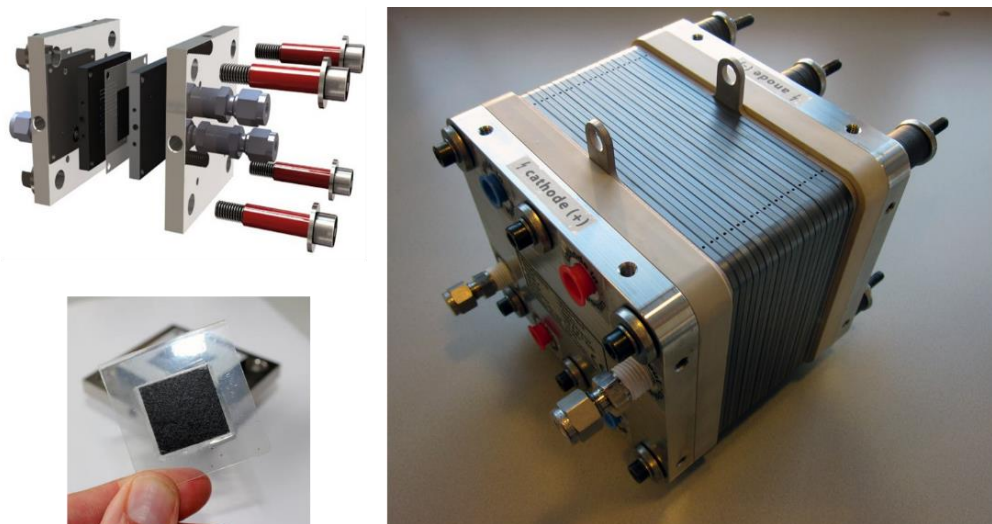


Fig. 1 – (a) Illustration of the test cell and (b) MEA used in the single cell experiments. (c) The 10-cell PEM FC stack.

The performance degradation was quantified by measuring the decline of voltage of each cell while maintaining a constant current through it. A current of 1.5 A was chosen for the 10-cell stack (translating to 20 mA cm⁻²), so that the voltage of each cell at that current was in the range 0.4 – 0.6 V. The performance of the cells is represented by polarization curves taken from OCV to low voltage, current increasing, with at least 30 seconds at each point to stabilize the voltage. Degradation rate of each cell ($\mu\text{V h}^{-1}$) was calculated separately, and then averaged over the 10 cells.

2.5 SEM imaging and samples preparation

The in-plane pore structure of N-CNF catalytic layers sprayed onto the surface of Sigracet 24 BC was analysed using a Hitachi S-5500 scanning electron microscope. Both pristine GDL (identical to batch 2) and pore formed GDL (batch 3) were used for this study. The samples were prepared by cutting the GDL into a thin section (around 7 mm × 7 mm) and attaching it to a conductive carbon tape in such a way that the catalyst coated layer was facing the electron beam.

3. Results and discussion

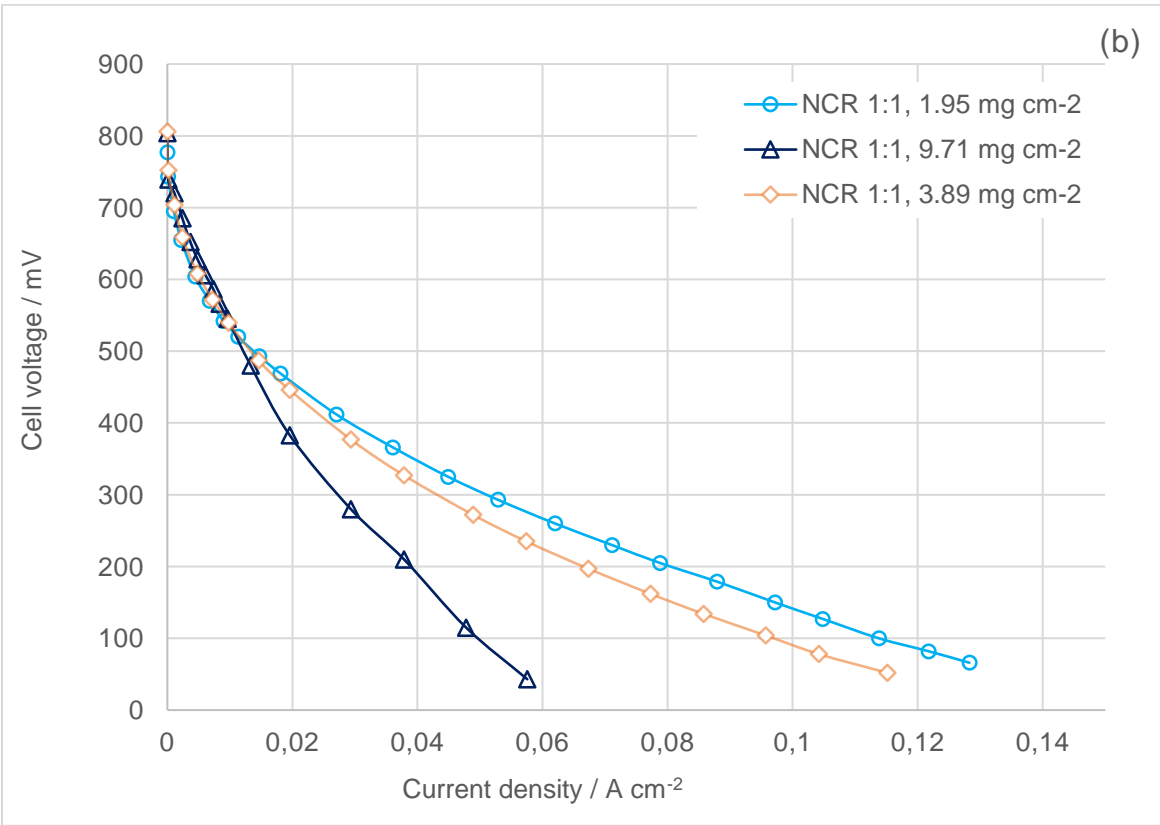
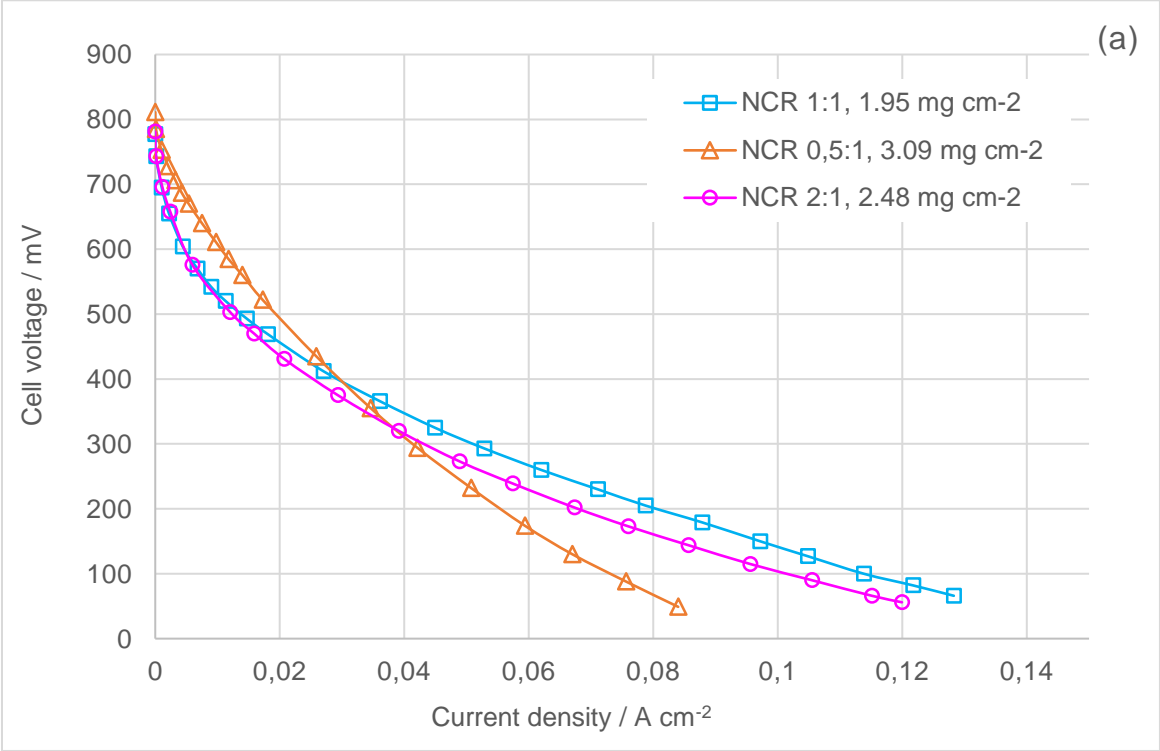
N-CNF catalyst

In short, the physical characterization of the N-CNF catalyst by N₂-adsorption measurements and XPS analysis revealed a BET surface area of 225 m² g⁻¹ and a nitrogen content of 3 at% in the surface of the N-CNFs. Deconvolution of the N 1s peak from XPS also showed that the N-CNFs had a high pyridinic nitrogen content (40%). Furthermore, the N-CNFs displayed a bamboo-like structure with encapsulated Fe particles in the tip of the fibres. More details about the properties of the N-CNFs are reported elsewhere [19].

3.2 Optimization of the cathode catalytic layer (ionomer and catalyst loading)

Over the decades of PEM fuel cell research, it has been shown that the NCR ratio in the catalytic layer of PEM fuel cells has a major impact on FC performance. While a value of 20 – 40% of Nafion ionomer to the commercially “standard” Pt²⁰/C catalyst weight was somewhat established, it is recognised that variations in the catalyst properties may greatly influence the optimal NCR for both

Pt-based [20,21] and non PGM-based [22,23] catalysts. Since the N-CNF system is different from widely used Pt on carbon, it is necessary to perform at least a rough screening to find a suitable NCR. We compared the performance of cells featuring three NCRs at the cathode: 0.5 : 1, 1 : 1 and 2 : 1, corresponding to 33, 50 and 75 % by mass, respectively. Unfortunately, it proved to be difficult to control the catalyst loading in these tests, hence the polarisation curves featured in Fig. 2 (a) correspond to slightly different loadings of N-CNF.



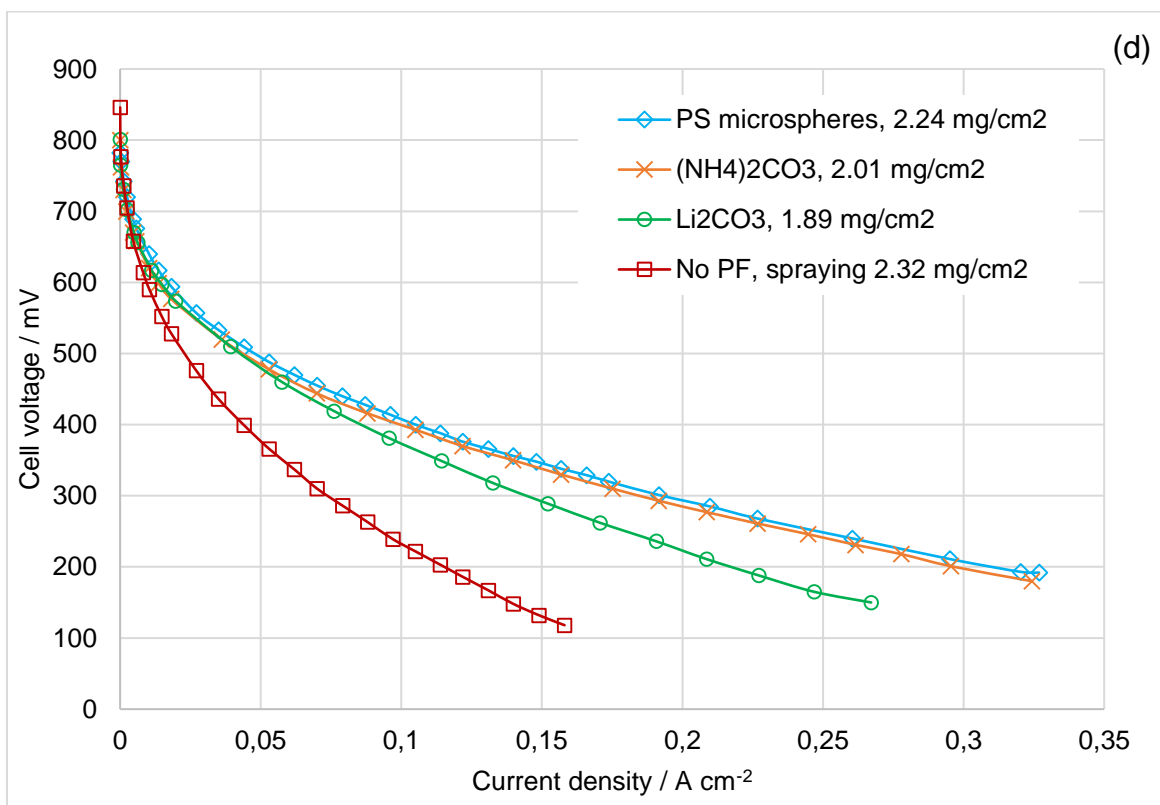
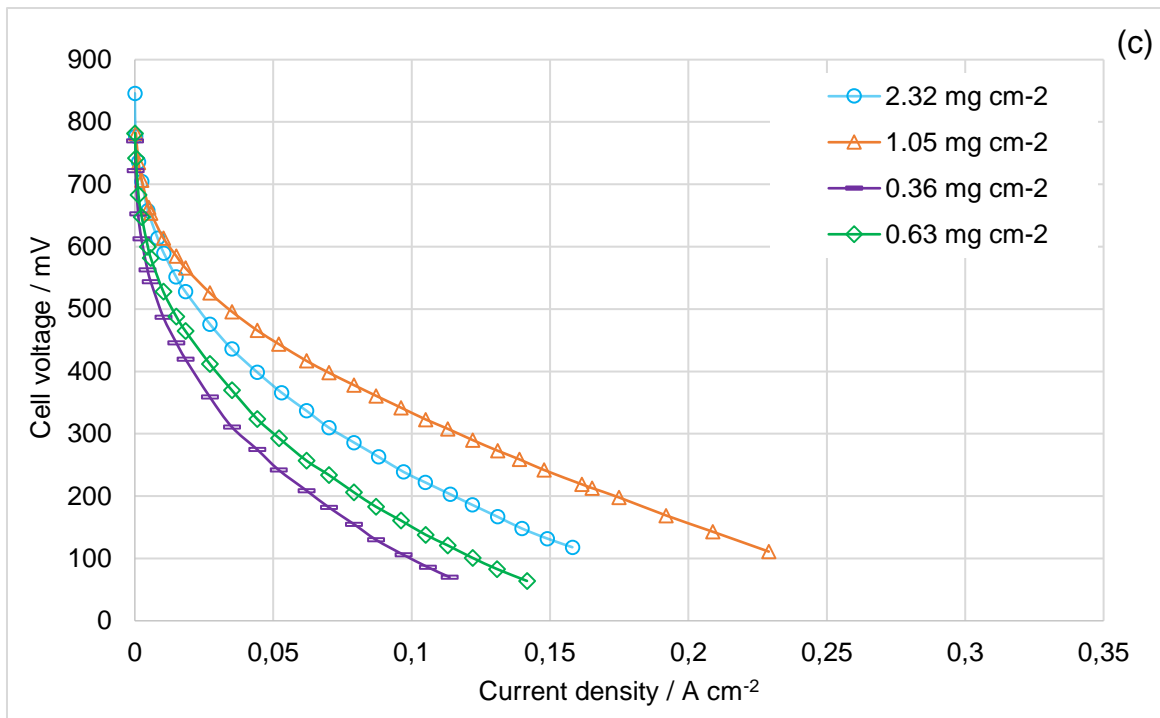


Fig. 2 - Polarisation curves obtained during performance optimisation of MEAs with N-CNF cathodes. (a) Roll-printed cathodes with different NCR; (b) Roll-printed cathodes with varied N-CNF loading; (c) Sprayed cathodes with varied N-CNF loading; (d) Sprayed cathodes with added pore-formers. 6 cm² single cell, 80 °C, Nafion N-212, H₂ / O₂ 40/20 cm³ min⁻¹, 0 barg.

The obtained data suggests that there is no dramatic difference in cell performance when the NCR is varied in the range 33 – 75% utilizing N-CNF loadings between 2 and 3 mg cm⁻². The MEAs with NCR 1

: 1 had slightly higher current densities at potentials below 0.4 V, and this ratio was used in all subsequent experiments.

The N-CNF catalyst is relatively cheap to produce and does not utilise any critical raw materials, so the loading on a FC electrode is not limited by cost. However, it is limited by layer thickness: the larger the loading, the higher are the mass-transport limitations and correspondingly lower catalyst utilization [24]. Attempts to find the loading providing the highest absolute power values of the fuel cell were therefore performed. However, increasing the N-CNF cathode loading from 2 to 10 mg cm⁻² did not improve the performance (see Figure 2 (b)). At a loading of 10 mg cm⁻² mass transport limitations are to be expected. In order to improve the mass-transport within the layers, the cathode formation technique was changed from roll-printing to spraying, as spraying is known to produce higher porosity. This led to an improved performance of the single cell (Figure 2 (c)).

However, a similar trend between loading / performance was observed again, where loadings higher than 1 mg cm⁻² only led to decreased current densities. This problem is often encountered in direct methanol fuel cells (DMFCs), where very high loading of catalyst is commonly used on the anode. In order to improve the single cell performance further, the cathode porosity was therefore augmented by utilizing pore-forming techniques as reported for DMFCs [25], [26].

By using N-CNF cathode catalyst loading of around 2 mg cm⁻² and a spraying technique, cathodes prepared with polystyrene microspheres, ammonium carbonate and lithium carbonate as pore forming agents were prepared. Removal of the pore-forming agents after spraying the ink onto the GDL produces extra pores. Polarization curves of the MEAs featuring these cathodes are shown in Figure 2 (d). The obtained cell performance was almost equal for MEAs prepared with the polystyrene microspheres and with ammonium carbonate, and slightly lower in case of Li₂CO₃. Since it is substantially easier to remove the ammonium carbonate than the other two compounds, (NH₄)₂CO₃ was chosen as the preferred method.

In-plane SEM images of the cathode layers with and without the pore-former (NH₄)₂CO₃ are shown in Figure 3. The in-plane microscopic images of catalyst coated GDL without pore former (Figure 3 (a)) reveal a surface densely packed with N-CNFs/graphite composite having almost no visible pores. However, the surface of the pore formed GDL has a loosely packed open porous structure (Figure 3 (b)). At higher magnifications, N-CNFs are observed deep inside the pores and also at the walls of each pore (Figure 3 (c) and (d), respectively). These large pores act as a passage for transport of oxygen and water in the thick N-CNF cathodes and thus lead to better performance.

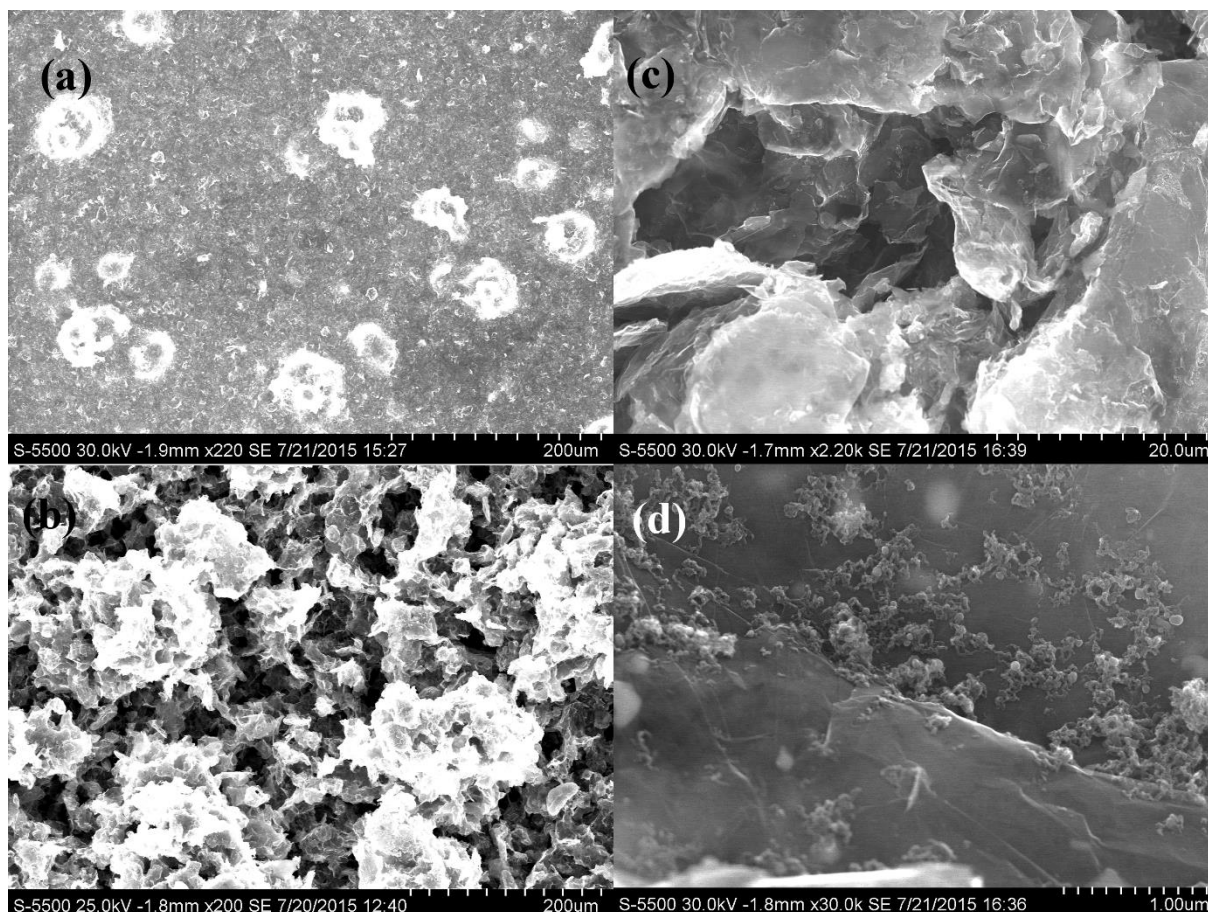


Fig. 3 - SEM images of the cathode catalytic layers. (a) In-plane, no pore-former; (b) In-plane, pore-former $(\text{NH}_4)_2\text{CO}_3$; (c) A single pore, $(\text{NH}_4)_2\text{CO}_3$; (d) Pore wall magnified, $(\text{NH}_4)_2\text{CO}_3$;

The mass transport issues limiting the maximum power of MEAs prepared by traditional techniques, even augmented by adding the pore-formers, can be further illustrated by plotting the specific current density per gram of N-CNF catalyst at different cathode loadings. While the N-CNF loading on the cathode reduces from 4.6 to 0.24 mg cm^{-2} , the specific current at 0.3 V improves from 42 to 309 A g^{-1} . When the cathode pressure is additionally raised to 1.6 bar, the specific current improves from 309 A g^{-1} to 860 A g^{-1} or 281 W g^{-1} (Figure 4 (b)).

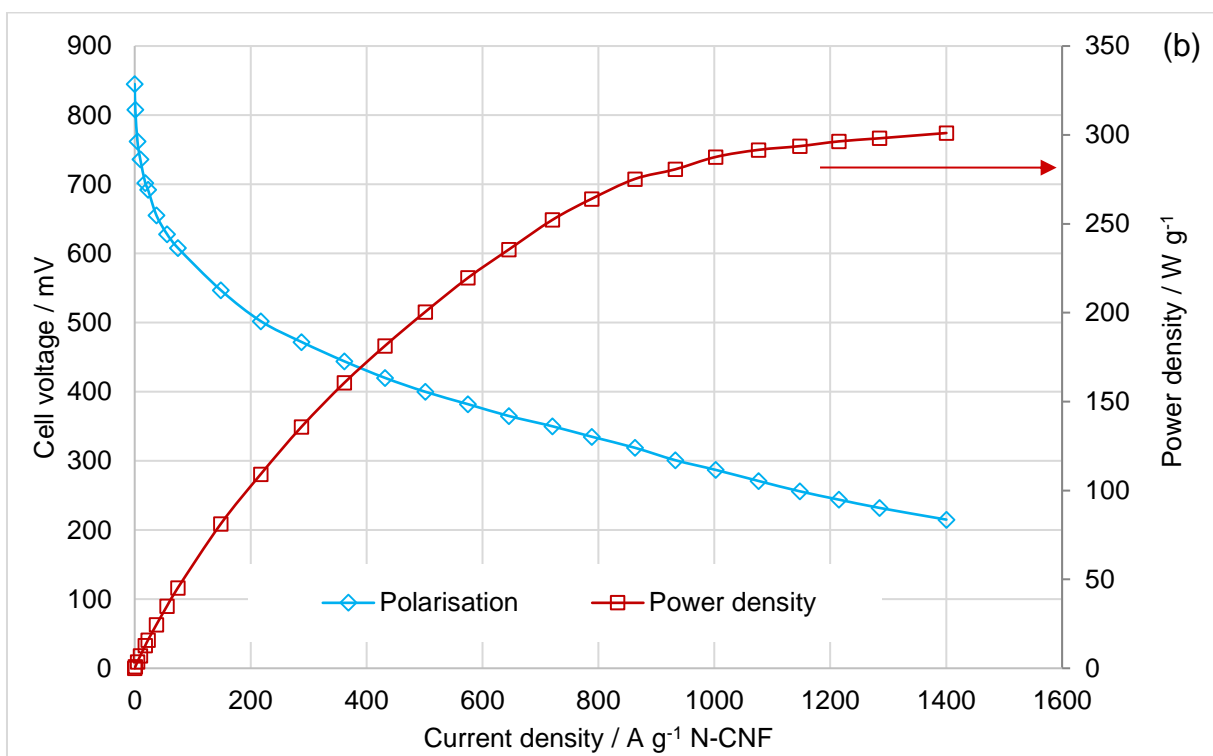
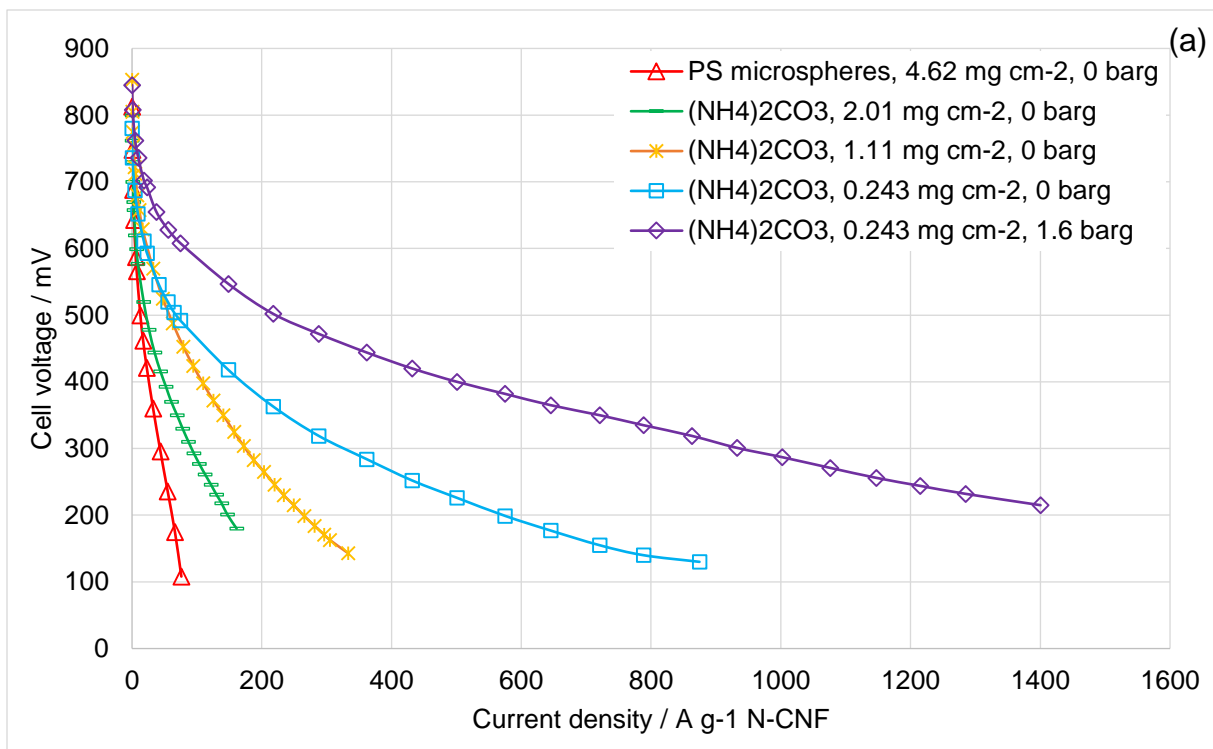


Fig. 4 - (a) Polarisation curves at decreasing N-CNF cathode loading expressed in gravimetric units (A g^{-1} N-CNF); (b) Cell polarisation and power density as a function of gravimetric current for N-CNF loading of 0.243 mg cm^{-2} at 1.6 barg H_2 / O_2 pressure. 6 cm^2 single cell, 80°C , Nafion N-212, H_2 / O_2 $40/20 \text{ cm}^3 \text{ min}^{-1}$.

The catalyst utilization in case of N-CNF catalytic layers could not be calculated because the number of active sites on the N-CNF type catalysts is not constant per unit of surface, as it is in the case of platinum. There is no well-established method to estimate the electrochemical active surface area

for N-doped carbon materials the way it is estimated by either CO stripping or H_{UPD} (hydrogen under potential desorption) method for Pt catalysts.

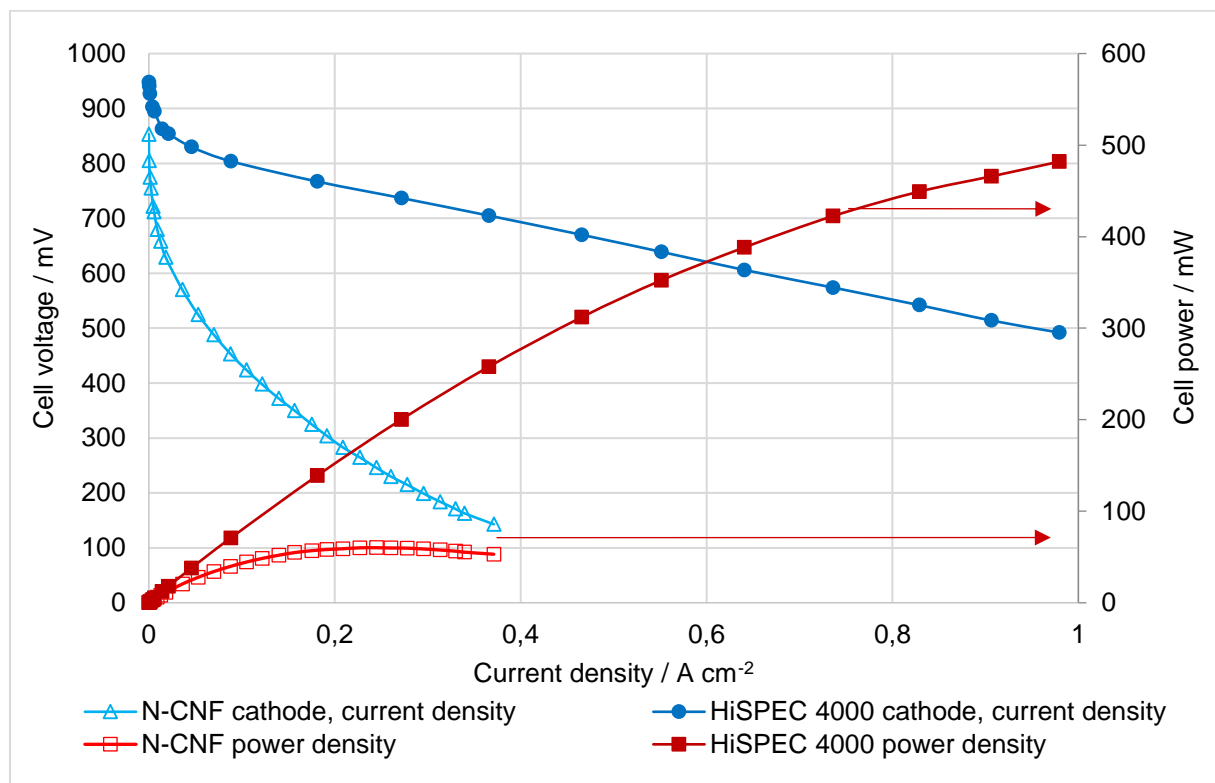


Fig. 5 - Cell polarisation and geometric power density as a function of geometric current for the MEA with the optimized cathode ($2 \text{ mg cm}^{-2} \text{ N-CNF} + (\text{NH}_4)_2\text{CO}_3$) compared to a Pt/Pt MEA ($0.184 \text{ mg Pt cm}^{-2}$). 6 cm^2 single cell, $80 \text{ }^\circ\text{C}$, Nafion N-212, H_2 / O_2 $40/20 \text{ cm}^3 \text{ min}^{-1}$, 90% relative humidity, 0 barg.

The highest geometric power density obtained in this work utilizing the N-CNF cathodes with ammonium carbonate as pore-former at 0 barg H_2 / O_2 was 60 mW cm^{-2} of the electrode area at 250-300 mV. A comparison between the best-performing MEA with N-CNF cathode and an in-house produced MEA with Pt/C cathode (HiSPEC 4000) is shown in Figure 5. It can also be noted that the open circuit voltage (OCV) of the cell with the N-CNF catalyst is about 0.1 – 0.15 V lower than that of the Pt/Pt MEA, similar to OCV for some other reported non-PGM ORR catalysts in PEM FC conditions [13,17,18,27,28]. Comparison of the results obtained in this report with data reported for other non-PGM ORR catalysts is presented in Table 1.

Table 1 - Performance and durability data reported for PGM-free ORR catalysts in PEM fuel cells

Catalyst type	Current at 0.7 V (A cm ⁻²)	Current at 0.3 V (A cm ⁻²)	Peak power	Durability data in fuel cell	Catalyst loading (cathode) (mg cm ⁻²)	H_2 / O_2 back pressure (barg)	Reference, year
N-G-CNT+KB (N-doped graphene + CNT + Ketjenblack carbon black)	0.075*	0.75*	300 W g^{-1}	30% current density loss in 100 hours at cell voltage of 0.5 V, N-G-CNT+KB loading 0.5 mg cm^{-2} , H_2/O_2	2	2	[10], 2015
3CoP1000 (N-doped)		0.86*	0.21 W cm^{-2}		3.8	3.5	[13], 2010

nanoshell carbon)							
UF-C (nitrogen-modified carbon-based catalyst)	-	0.52*	-	No performance loss in 200 hours at cell voltage of 0.4 V, H ₂ /O ₂	4	2.08/2.76	[17], 2009
NMCC-SiO ₂ -800-3 (nitrogen-modified carbon composite)	0.07*	1.54*	0.45 W cm ⁻²	40% current density loss in 90 hours at 0.4 V cell voltage, H ₂ /air	2	2.08	[18], 2010
N-CNF	0.0045	0.228	0.073 W cm⁻², 300 W g⁻¹	162 μVh⁻¹ or 17% power loss in 400 h at 20 mA cm⁻² current density, H₂/O₂ 0 barg, 75 °C, 5 start-stop cycles including cooling down	0.243	1.6	This work

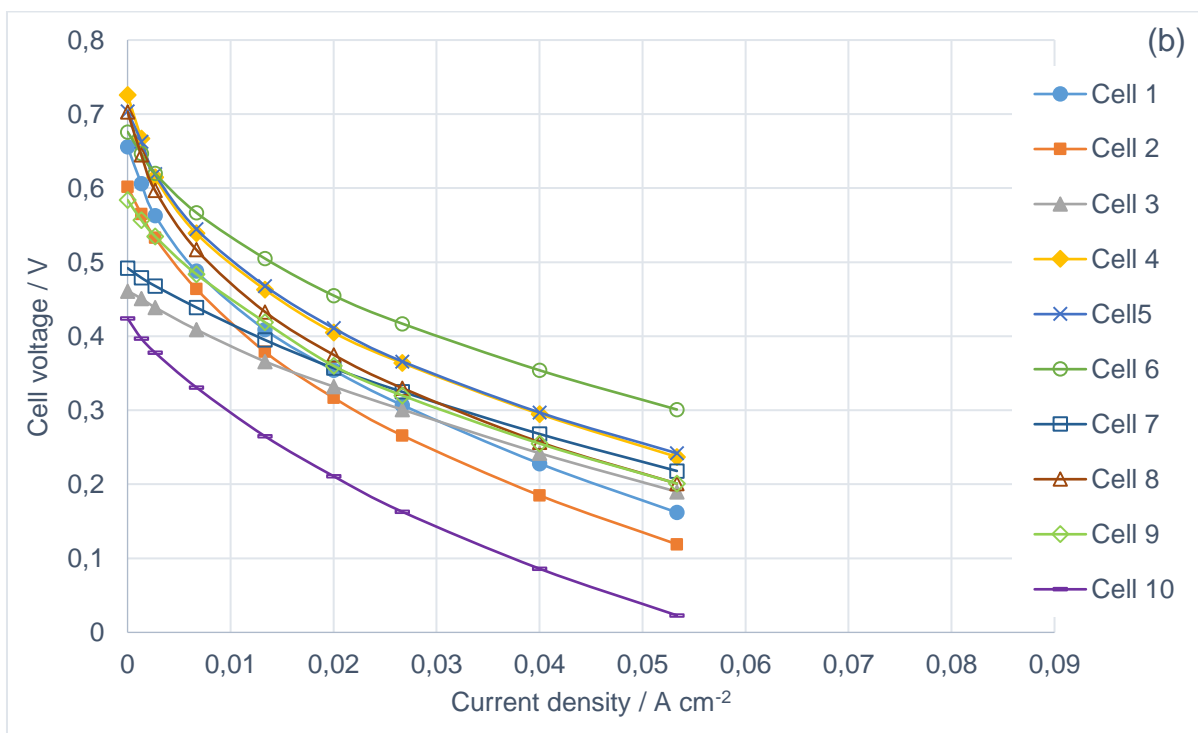
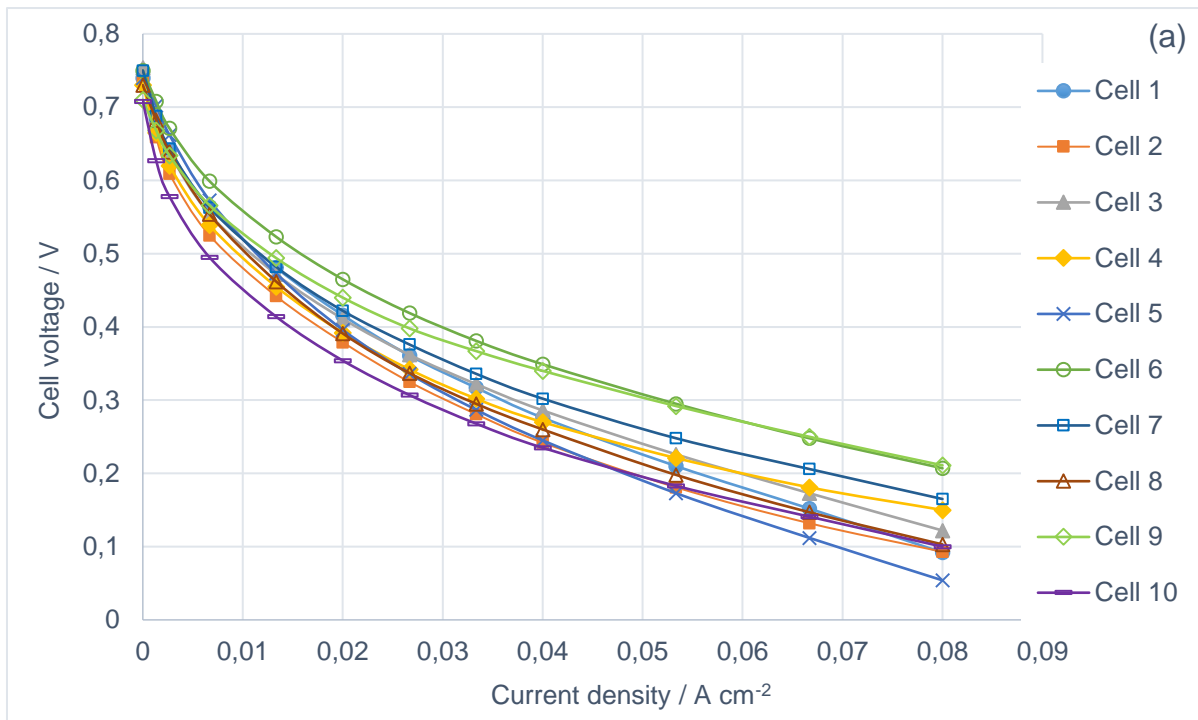
*Numbers are taken from polarisation curves

Measured performance values in this work are generally lower than the best values reported by other groups for doped carbon materials, but are in the same order of magnitude. Compared to the nitrogen-containing carbon materials, recently synthesised metal/N/C catalysts exhibit higher performances in fuel cells. While both types of non-PGM catalysts show great promise, their long-term performance needs to be improved further in order to substitute platinum in PEMFCs.

Geometric current and power density values obtained in this work are lower than the ones obtained by some other groups, although still in the same order of magnitude. We attribute this at least partly to the under-optimised catalytic layer. However, the gravimetric power density at low loadings is on par with results of [10], suggesting high intrinsic activity of N-CNF catalyst. At the same time the degradation rates obtained in this work are lower than most results reported in the literature for non-PGM catalysts in acidic environment of PEMFCs [29–31].

3.1 Performance and durability of the short FC stack with N-CNF cathodes

A PEM FC stack featuring 10 cells with N-CNF cathodes and an active area of 75 cm² was assembled and tested at 1.5 A total current (20 mA cm⁻²) for 400 hours. The test scale was increased in order to not only look at the degradation rate, but also assess possible scaling up issues. Polarization curves for each cell of the stack at the start of operation (20 hours) and at 400 hours of operation are shown in Figure 6 (a) and (b) respectively. Furthermore, the voltage degradation over 400 h for each cell and as an average for the 10-cell stack are shown in Figure 6 (c) and (d) respectively.



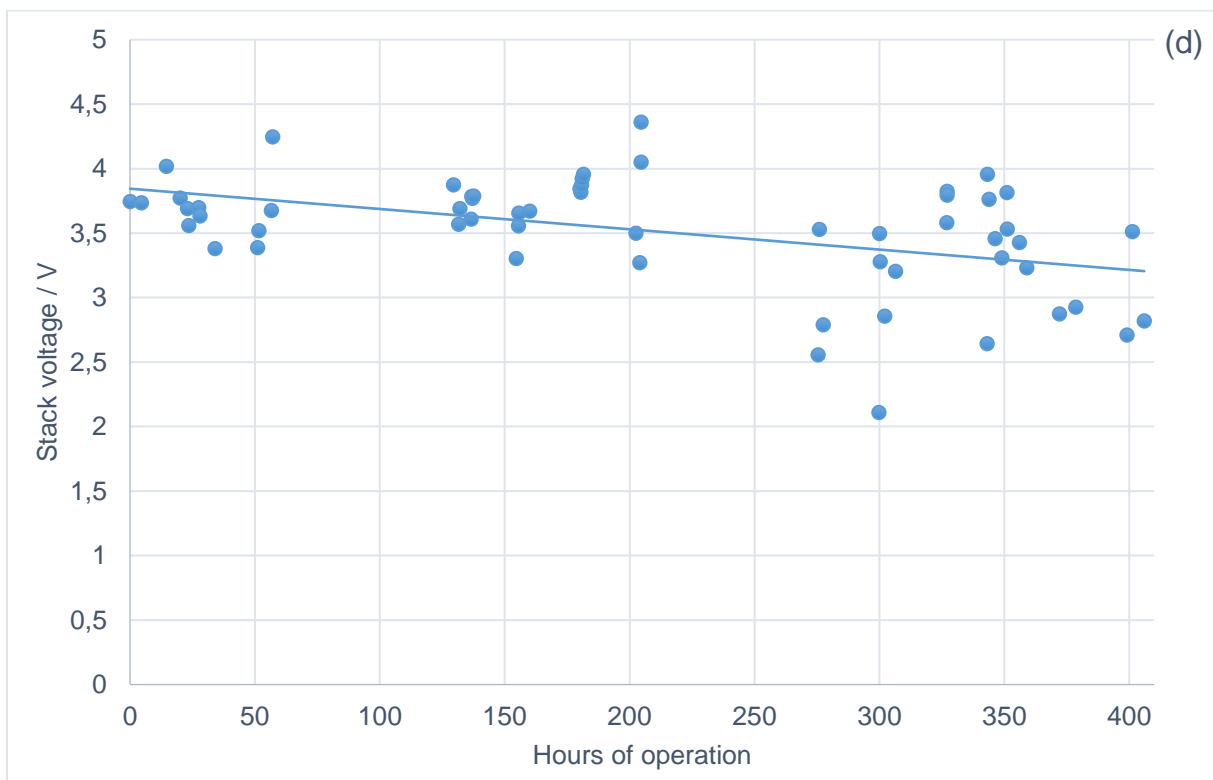
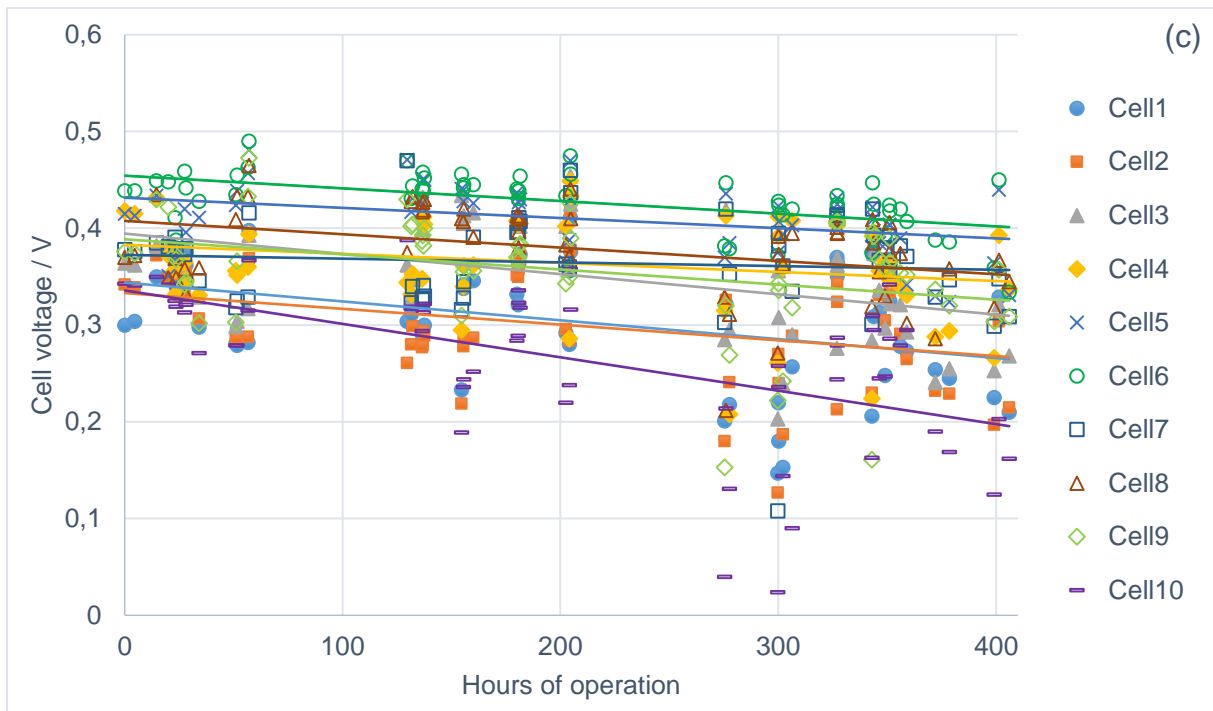


Fig. 6 - Performance and voltage degradation for the 10-cell PEM FC stack with 75cm² active area. (a) Cell polarisation curves at 20 h of operation, (b) Cell polarisation curves after 400 h of operation, (c) Cells voltage over time, (d) Stack voltage over time. Semi-continuous operation at 20 mA cm⁻² with a total of 5 shutdowns (cooling to room temperature under N₂ flow). 75 °C, H₂ / O₂ at 1.1 stoichiometric flow rate with periodic flushing. Membrane humidifiers (Fumatech) at 70 °C.

Cell performance in the 10-cell stack even at the start of operation was significantly lower than in the small single cell. It is always more difficult to obtain optimal operating conditions in larger cells of a fuel cell stack than it is in a small single cell. However, an almost 4 times decrease in current density relative to the single cell data indicates additional issues. We noticed a very strong dependence of stack performance on the gas humidity. During the test period we had to stop gases several times and re-humidify the MEAs in the stack by flooding with deionized water and then purging with nitrogen. Such re-humidification would sometimes double the performance of the least humidified cells. At the same time, a 2-3 °C difference between the end cells and the middle-stack cells brought significant cell performance differences due to slight changes in humidity levels. Having operated a similar PEM FC stack with all-Pt MEAs previously, we can attribute this behaviour to the new N-CNF cathodes. It is likely that the large amounts of ionomer in the thick cathode catalytic layers require more efficient humidification than what is sufficient for standard all-Pt MEAs. It is also possible that the morphology and water affinity of the catalyst itself also played a role. The humidity issue could at least partly be the reason for the observed spread in the polarisation curves for the cells in the stack already at the start of the operation, and might also be the reason for the increased spread in the polarisation curves towards the end of the testing.

Cell voltages at 20 mA cm⁻² current density, measured at various times during the 400-hour operation, are shown on Figure 6(c). The points are the measured voltages of all 10 cells, while the straight lines are the linear approximations of the data points. In our tests, the “worst” cell degraded at a rate of 375 μV h⁻¹, while the “best” at a rate of 132 μV h⁻¹, with an average for the stack being 162 μV h⁻¹. Table 1 lists some literature data found on the degradation of the non-PGM and doped carbon based ORR catalysts in PEM fuel cells. The N-CNF catalyst tested in this work has very good durability compared to the other doped carbon catalysts, even including the humidity issue described above. Its degradation rate is also superior to the Fe-N-C based catalysts [29–31]. For comparison, degradation data for state-of-the-art Pt-based PEMFCs [32,33] can be used. For the Pt-based systems it is common to express degradation rate in μVh⁻¹. For steady-state operation the average value in PEMFCs is about 5 μV h⁻¹, while accelerated testing protocols including potential cycling and start-stop operation typically result in the rates of 50-60 μVh⁻¹. The rate of 162 μV h⁻¹ is therefore comparable to the accelerated testing degradation rates of the Pt-based ORR catalysts.

The measured PEMFC stack performance degradation is an integral value, resulting from all the degradation processes inside the fuel cell. These processes, apart from degradation of the catalyst itself, include degradation of membrane, delamination of catalytic layers from the membrane, degradation of gas-diffusion layers and stack elements. It is known, for example, that sub-optimal humidity conditions lead to membrane cracking, delamination and accelerated oxidation of the carbon support [32]. Having the thick cathode catalytic layers with large amount of ionomer, it is therefore possible that the humidity conditions during our stack testing could play an important role in the performance degradation of the stack and could affect the membranes integrity by the end of testing. This is indirectly supported by the low OCV values of some cells by the end of testing.

Another factor that could cause degradation of the stack performance was the presence of encapsulated Fe particles in the tips of the N-CNF catalyst remaining from the synthesis procedure. It was shown in a previous work [[19]] that 20-30% of all the oxygen reacting on the N-CNF catalyst was reduced to hydrogen peroxide via a 2-electron mechanism during rotating ring-disc electrode (RRDE) testing in 0.5 M H₂SO₄. Free radicals such as ·OH and ·OOH readily form from H₂O₂ when oxidizable ions such as Fe²⁺ are present. Free radicals attacking the Nafion ionomer are a major factor causing the degradation of Nafion polymers [34], [35].

Therefore, despite being a valuable result, the obtained degradation rate in the fuel cell stack requires additional investigation to determine the contribution of the N-CNF catalyst to the integral degradation value and to find ways to alleviate the decline.

3.2 Market application analysis

Economic and market application assessment for the fuel cell system utilizing the new doped nanostructured carbon catalyst is based on calculating the integral cost of ownership (ICO). An ICO is the sum of all capital (CAPEX) and operational (OPEX) expenses needed when using a fuel cell system for its lifetime. These costs are calculated based on the current fuel cell market data [36], performance and degradation data obtained in this work and commercial data available for the state-of-the-art fuel cell systems and components. The analysis is based on comparison of the ICO for two PEMFC systems: one utilising the N-CNF cathodes and one utilising commercial Pt/C cathodes. The calculation takes into account the obtained cost values for the new N-CNF catalyst. N-CNF cost was calculated for the mass production scenario, where the prices tend to the raw goods value. The bulk costs of all precursors and chemicals involved in the laboratory synthesis (ammonia, iron nitrate, hydrogen, carbon monoxide, argon, ethanol, electricity for the oven) and catalyst characterisation (oxygen, sulphuric acid, deionised water) multiplied by their consumption per 1 kg of N-CNF were added. Equipment depreciation was not taken into account.

A fuel cell system consists of one or several fuel cell stacks and auxiliary components, usually referred to as balance-of-plant (BOP): pump(s), filters, tubing, humidifiers, control, sensors, electrical interface etc. The cost of the BOP components is estimated as a percentage of the FC stack cost based on a model 1 kW fuel cell backup power unit.

The ICO of a fuel cell system is based on the cost of its core, –the fuel cell stack, and is schematically shown on Figure 7. It consists of CAPEX and OPEX; CAPEX include the MEA cost (of which the new N-CNF catalyst is a part) and the other stack components cost (bipolar plates, end plates, manifolds, current collectors, fittings etc.). These costs were calculated for two scenarios: “As-built” (all components and chemicals procured as single orders) and “Mass production” (MEA production volume > 125 000 m²/year).

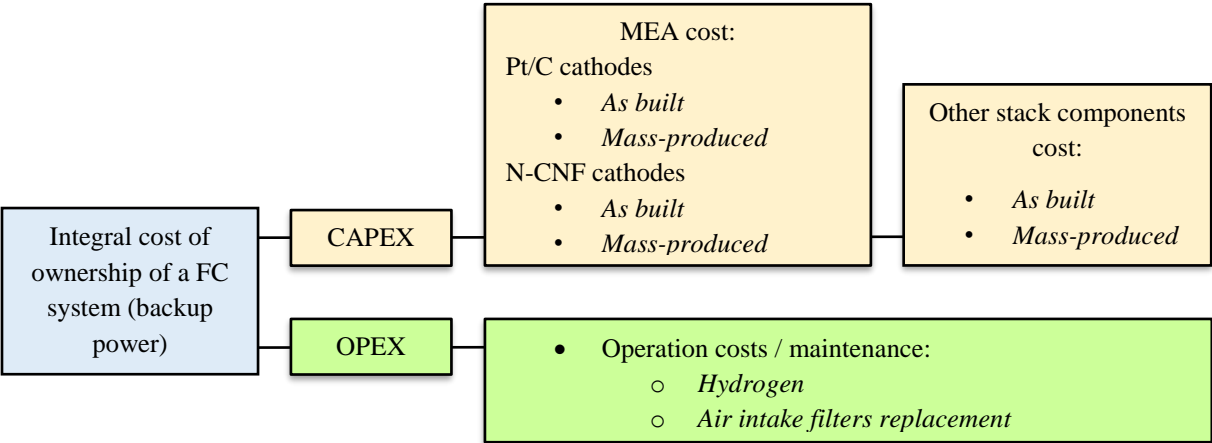


Fig. 7 - Schematic representation of the integral cost of ownership of a PEMFC system.

The OPEX of the fuel cell system consist of operation costs and maintenance costs, which are comprised of only two components: hydrogen fuel cost and replacement of air intake filters. However, in order to arrive at the designed 10-year lifetime of the FC stack using the N-CNF

cathodes, the MEAs in the model system need to be exchanged several times. This cost is also added as a maintenance cost.

3.2.1 Capital costs

The results of the MEA cost calculations are plotted on pie-charts on Figure 8. The calculation is based on prices and currency conversion rates on 03.03.2015.

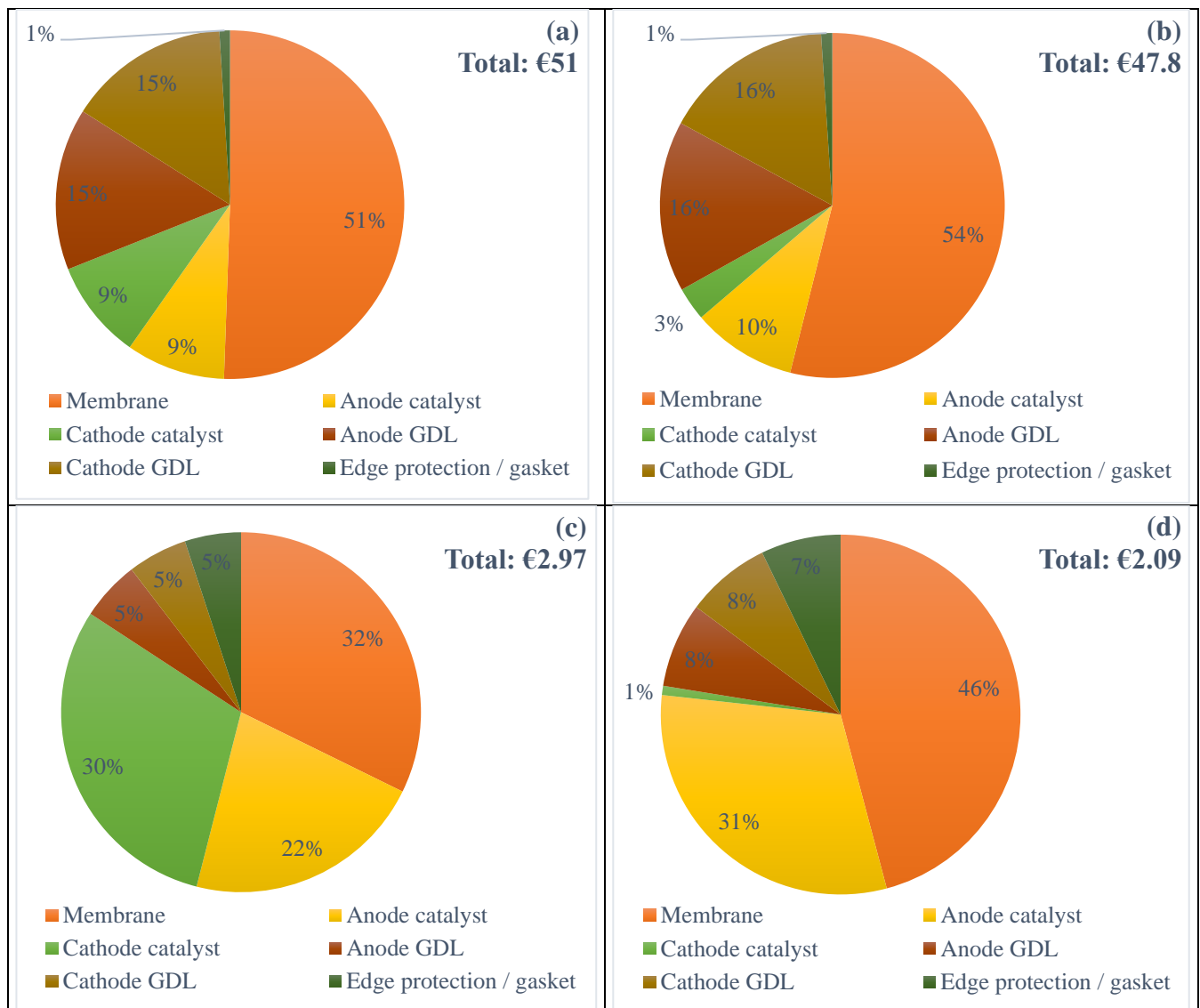


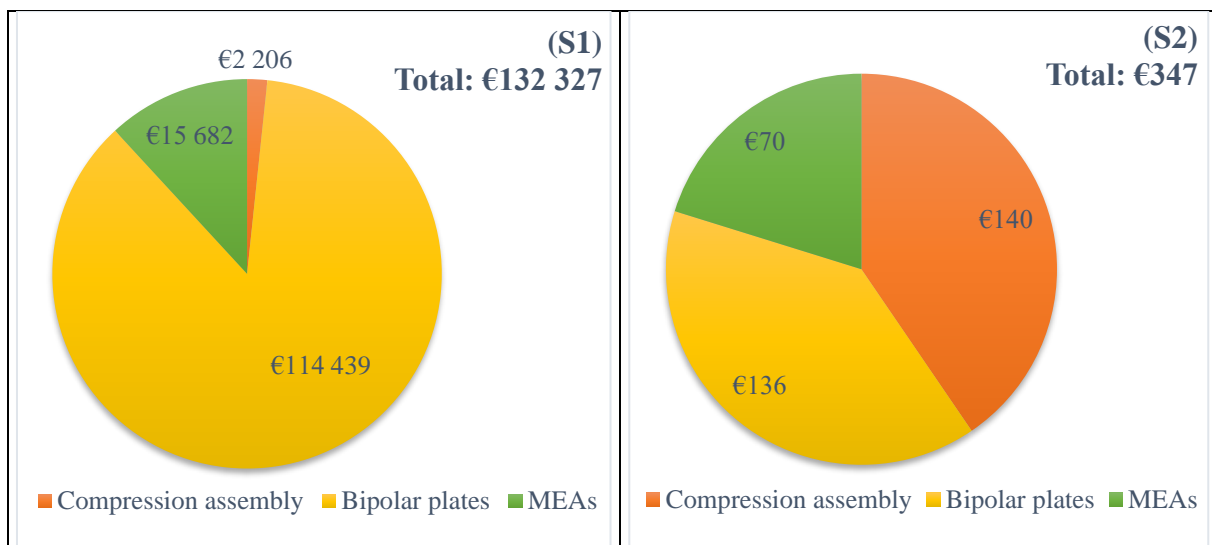
Fig. 8 - Calculated MEA cost distribution. (a) As-built, Pt/C cathode; (b) As-built, N-CNF cathodes; (c) Mass-produced, Pt/C cathodes; (d) Mass-produced, N-CNF cathodes.

In the as-built scenario the Nafion membrane accounts for over half of the total MEA cost, and the ORR catalyst based on Pt/C makes up a total of only 9%. When MEAs are mass-produced, however, the total cost of goods contained in the MEA tends to the raw materials cost, and the price of Pt contributes to a total of 30% of the MEA cost. Here the N-CNF catalyst really has potential for cost reduction, as it is priced at only a fraction of the Pt cost. It accounts for about 3% of the MEA cost in the as-built scenario and about 0.82% in the mass-produced scenario. The total MEA cost is therefore reduced as well, so MEAs featuring N-CNF cathodes can be almost 30% cheaper than an all-Pt MEA. However, the performance obtained from MEAs with N-CNF cathodes (Figure 5) is low, each MEA therefore provides less power than an all-Pt MEA, so more cells are needed to get the same power output from the FC stack.

Capital costs for a fuel cell stack consist of the costs of bipolar plates and other structural elements. Added to the cost of MEAs, they make up the total fuel cell stack capital cost. The calculation of total stack cost was done for three scenarios: (S1) N-CNF cathodes, a single 1 kW stack procured; (S2) Pt/C cathodes, mass produced and (S3) N-CNF cathodes, mass produced. To calculate the total amount of cells in the FC stack, we used the following performance figures:

- (S1): 0.12 A cm⁻² @ 400 mV (obtained in this work in single cell tests);
- (S2): 1 A cm⁻² @ 650 mV;
- (S3): 0.8 A cm⁻² @ 400 mV (projection, assuming performance improvement after optimisation).

The calculation data is shown in Figure 9. In the (S1) scenario the MEAs constitute only 13% of the total cost, but the stack would cost more than €130 000. In the mass-production scenarios (with the performance assumptions) the MEA contribution rises to 19-20%. This percentage is almost the same for the two scenarios, but the total stack cost is lower for the all-Pt stack (S2): around €350 vs. €530 in (S3) due to the larger number of cells needed with the N-CNF catalyst. The amount of cells, a parameter critical for the FC stack cost, obviously depends on the catalyst (MEA) performance. For the (S3) scenario an increase of about 6.5 times in comparison to the obtained test results was assumed (from 3.6 W/cell to 23.8 W/cell). It may be optimistic, but it shows the important point that the performance of the MEAs featuring the new catalyst needs to be close to the performance of the state-of-the-art MEAs, otherwise the capital expenses for stack components outweigh the gain in the price of a single MEA.



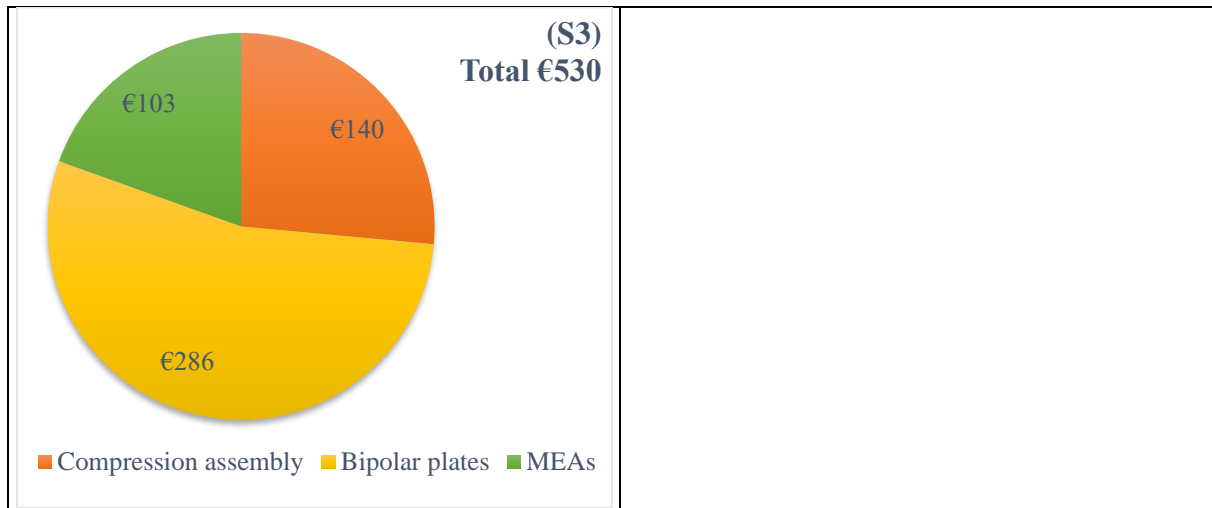


Fig. 9 - Cost distribution inside the fuel cell stack. (S1) N-CNF cathodes, a single 1 kW stack procured; (S2) Pt/C cathodes, mass produced and (S3) N-CNF cathodes, mass produced.

3.2.2 Total cost of ownership of a FC system

The total cost of ownership of a fuel cell system combines the capital and operating expenses over the lifetime of the system. The operating expenses in this model are the cost of hydrogen fuel only (set at 10 €/kg). There is also the maintenance cost, which consists of replacement of air intake filters (100 €/year). For the system using MEAs with N-CNF cathodes, MEA replacement is also needed, adding to the total capital cost. The cost of the balance of plant components for the fuel cell system in the model is set to 4 times the cost of the fuel cell stack. This is based on practical experience, comparison of costs of stacks and systems from producers such as Ballard and literature data [37] (no actual system engineering was done). The lifetime of the system is set to 15 000 hours, of which the system is available 90% of the time (a measure of reliability). The backup power system is set to provide power for 15% of its total lifetime (when main power is not available), this corresponds to 13 years of technical life. The hydrogen consumption takes into account the electrical efficiency of the fuel cell, which is lower for the N-CNF based system due to lower operating voltage of cells. The MEAs in the stack with N-CNF cathodes have to be changed 5 times during the expected lifetime of the system. This number is based on the projected voltage degradation rate of $40 \mu\text{Vh}^{-1}$, 4 times lower than the rate obtained in the tests in this work. The integral cost of ownership is only calculated for a mass-production scenario, comparing systems with the two different cathode catalysts. The results of the calculation are shown in Figure 10.

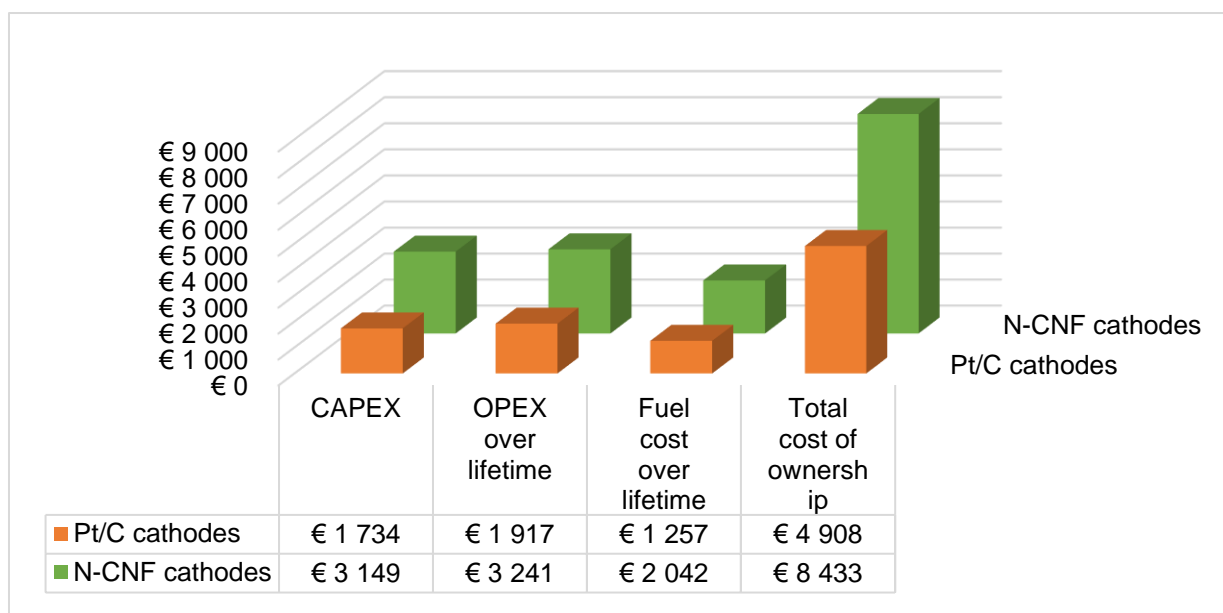


Fig. 10 - Total cost of ownership of a 1 kW backup energy system calculated for the mass-production scenario.

The assessment results in both capital costs and operation costs of the system with the novel N-CNF catalyst being higher than that of the Pt/C system, despite the N-CNF catalyst being more than 30 times less expensive. This result leads to an important conclusion: any fuel cell catalyst aimed as a platinum or platinum-group metal replacement has to yield a similar fuel cell performance (even with much higher loading) and have a similar degradation rate to be cost competitive on the market (at least while platinum is still available). Specific threshold numbers, however, depend on the application and will vary greatly with the power rating required (from a few watts to tens and hundreds of kilowatts), the cost of the elements of the FC stack (primarily the bipolar plates) and expected lifetime.

4. Conclusions

A novel N-doped carbon nanofiber catalyst was employed for the oxygen reduction at the cathode of a PEMFC. Significant mass-transport limitations were identified at the new cathodes for N-CNF catalyst loadings above 1 mg cm^{-2} . However, improving the fabrication procedure by utilizing a spraying technique and ammonium carbonate as pore-former improved the single cell performance significantly. The resulting maximum power density obtained was 73 mW cm^{-2} or 300 W g^{-1} at cell voltages between 250 and 300 mV with pure hydrogen and oxygen gas. Even after modification by pore-forming agents, agglomerates of ionomer and dense areas with low porosity could be observed in SEM images of the N-CNF catalytic layers, suggesting that the structure is still under-optimised.

A 10-cell stack with a cell active area of 75 cm^2 was produced and tested for 400 hours. The average cell voltage degradation rate obtained was $162 \text{ } \mu\text{Vh}^{-1}$. By using the test results, a simple market application model was prepared. It is based on calculation of the total cost of ownership of a 1 kW PEM FC backup power unit with N-CNF cathodes. In conclusion, even a near-complete elimination of the cathode catalyst cost by substitution of platinum with a carbon-based catalyst cannot produce a cost competitive product unless both the performance and the durability of the fuel cell with the new catalyst are close to that of the state-of-the-art system. Nevertheless, this new class of carbon-based catalysts is promising, and the reported results can help the research community to arrive at an adequate alternative to platinum catalyst for fuel cells.

Acknowledgements

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Figure captions

Fig. 1 – (a) Illustration of the test cell and (b) MEA used in the single cell experiments. (c) The 10-cell PEM FC stack.

Fig. 2 - Polarisation curves obtained during performance optimisation of MEAs with N-CNF cathodes. (a) Roll-printed cathodes with different NCR; (b) Roll-printed cathodes with varied N-CNF loading; (c) Sprayed cathodes with varied N-CNF loading; (d) Sprayed cathodes with added pore-formers. 6 cm² single cell, 80 °C, Nafion N-212, H₂ / O₂ 40/20 cm³ min⁻¹, 0 barg.

Fig. 3 - SEM images of the cathode catalytic layers. (a) In-plane, no pore-former; (b) In-plane, pore-former (NH₄)₂CO₃; (c) A single pore, (NH₄)₂CO₃; (d) Pore wall magnified, (NH₄)₂CO₃;

Fig. 4 - (a) Polarisation curves at decreasing N-CNF cathode loading expressed in gravimetric units (A g⁻¹ N-CNF); (b) Cell polarisation and power density as a function of gravimetric current for N-CNF loading of 0.243 mg cm⁻² at 1.6 barg H₂ / O₂ pressure. 6 cm² single cell, 80 °C, Nafion N-212, H₂ / O₂ 40/20 cm³ min⁻¹.

Fig. 5 - Cell polarisation and geometric power density as a function of geometric current for the MEA with the optimized cathode (2 mg cm⁻² N-CNF + (NH₄)₂CO₃) compared to a Pt/Pt MEA (0.184 mg Pt cm⁻²). 6 cm² single cell, 80 °C, Nafion N-212, H₂ / O₂ 40/20 cm³ min⁻¹, 0 barg.

Fig. 6 - Performance and voltage degradation for the 10-cell FC stack with 75cm² active area. (a) Cell polarisation curves at 20 h of operation, (b) Cell polarisation curves after 400 h of operation, (c) Cells voltage over time, (d) Stack voltage over time. Semi-continuous operation at 20 mA cm⁻² with a total of 5 shutdowns (cooling to room temperature under N₂ flow). 75 °C, H₂ / O₂ at 1.1 stoichiometric flow rate with periodic flushing. Membrane humidifiers (Fumatech) at 70 °C.

Fig. 7 - Schematic representation of the integral cost of ownership of a PEMFC system.

Fig. 8 - Calculated MEA cost distribution. (a) As-built, Pt/C cathode; (b) As-built, N-CNF cathodes; (c) Mass-produced, Pt/C cathodes; (d) Mass-produced, N-CNF cathodes.

Fig. 9 - Cost distribution inside the fuel cell stack. (S1) N-CNF cathodes, a single 1 kW stack procured; (S2) Pt/C cathodes, mass produced and (S3) N-CNF cathodes, mass produced.

Fig. 10 - Total cost of ownership of a 1 kW backup energy system calculated for the mass-production scenario.

Tables

Table 1. Performance data reported for PGM-free ORR catalysts in PEM fuel cells