Improved electrodes for High Temperature PEMFC using carbon nanospheres

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Abstract: This work evaluates the use of Carbon Nanospheres (CNS) in microporous layers (MPL) of HT-PEMFC electrodes and compares the characteristics and performance with those obtained using conventional MPL based on Vulcan XC72. XRD, hydrophobicity degree, BET and gas permeability of MPL prepared with CNS were the parameters evaluated. In addition, a short life test in a fuel cell was carried out to evaluate performance in accelerated stress conditions. Results demonstrate that CNS is a promising alternative to traditional carbonaceous materials because of its higher electrochemical stability, and it presents good electrical conductivity, suitable to be used in this technology.

Introduction

Nowadays, there is an increasing interest in the study of different energy sources and alternative technologies for transformation of energy. The final aim is to substitute the traditional fossil fuels, because of their negative environmental effects associated with the production, transportation and use of energy this type of these non-renewable energy sources. Specially, Fuel Cells (FC) have received extensive research, due its numerous advantages: adaptability of the operating temperature, depending to the specific type of fuel cell, high efficiency and power density, nearly zero emission, and silent working conditions [1, 2]. Particularly, Proton Exchange Membrane Fuel Cell (PEMFC) has received much attention over the past decade, for its application in transportation and portable devices. High cost of the platinum catalyst used in this technology, the easiness of its poisoning and the complex water management are the main problems to be solved in this technology.

Perhaps, the most promising solution has been carried out by High Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFC), a variety of PEMFC that operates with vapour water (at temperatures over 100°C). This technology may exhibit numerous

5]. However, these different operational conditions require new materials for membranes, different to the traditional polymers typically used in LT-PEMFC (such as Nafion). The most common material applied for this purpose is Polybenzimidazol (PBI). PBI-based membranes are typically doped with phosphoric acid, and they seem to be the most suitable for both, automobile and stationary applications [6,7].

Membrane-Electrode Assembly (MEA) is the key component of PEMFCs. The electrodes are made up with a Gas Diffusion Layer (GDL), which provides a good distribution of the reactants across the surface of the Fuel Cell, and a Catalyst Layer (CL), which contains the platinum catalyst supported on another material, usually carbon blacks. GDL is also divided into the Macroporous (MaPL) and the MicroPorous Layer (MPL). The MPL improves the diffusion of the reactants and products and minimizes the electric contact resistance between the catalyst layer and bipolar plates. Also, it prevents the catalyst migration to the GDL [1, 3, 6].

Commonly, carbon blacks are used to manufacture the MPL in HT-PEMFC [7]. The high surface area (250 m² g⁻¹ for Vulcan XC-72), low cost and its easy availability reduce the manufacturing cost of fuel cell. However, carbon black also shows important limitations related to its thermochemical instability and its corrosion in acidic conditions (produced by the phosphoric acid used to dope PBI based HT-PEMFC). It is also well-characterized the reduction in the catalyst activity associated to the sulphur impurities and the deep micro pores distribution (which suitable size to trap catalyst nanoparticles) [9, 10]. Finally, the high voltage values during the start-up and shut-down procedures of the lifetime of the fuel cell have an important role in the degradation of the fuel cell, especially the carbonaceous materials. Potentials over 0.207V vs RHE can produce carbon corrosion in moderate amount, but over 1.2V or in high lifetime services, this potential corrosion achieves high importance [11-12]. Thus, it is crucial the development of new materials that can address the entire positive features that those carbon materials exhibit and, at the same time, which may minimize their negative characteristics.

Over the last four decades, various carbon nanostructures formed by rolled-graphene sheets have been proposed and evaluated in order to overcome these limitations. Typically, these nanostructures are classified into: carbon nanotubes (CNT), carbon nanofibers (CNF) and carbon nanospheres (CNS). All of these nanostructured materials have revealed improved electrochemical and thermochemical resistance. Furthermore, higher power densities, improved ECSA of the catalyst and greater catalyst efficiency have been found when testing them as catalyst supports for PEMFCs [13-15].

This work is going to be focused on the latter nanostructures: the CNS. There are different production techniques (including a wide

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advantages as compared to conventional Low Temperature PEMFC (LT-PEMFC), overcoming several of their limitations [3-

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range of operation conditions) for CNS manufacturing, which produce nanostructures with a great deal of sizes and textural properties. The graphite sheets that form these structures are normally unclosed shells with waving flakes that give the nanospheres their well-known high chemical activity, and help to postulate them as potential (and perhaps promising) candidates for catalyst supports, energy storage and/or other electrochemical applications [14].

This work aims to evaluate the use of CNS in the electrodes for HT-PEMFCs. To meet this objective, it was carried out a physical, chemical and electrochemical characterization of electrodes prepared with this advanced nanocarbonaceous material. Fuel cell tests were also carried out in order to check the viability and main features in single cell operation, including a short preliminary lifetest.

Results and Discussion

Physical characterization of the carbonaceous powder used to prepare the microporous inks

CNS were manufactured according to the procedure described in the experimental section of this document [14], and its characterization is going to be described in this Section, looking for properties which can be of interest for the performance of HTPEMFC. Figure 1 shows a SEM micrograph in which the size of some of the CNS is marked for comparison purposes. As it can be observed, CNSs manufactured with this methodology have not uniform sizes, presenting particle size ranging between 300-1500 nm. The spherical shape is clearly observed, which means that CNS have been successfully synthesized.

Figure 1. SEM of the CNS manufactured for the MPL

Particle size was also tried to be measured using a Mastersizer particle sizer and results are summarized in Table 1.

Table 1. Particle size distribution for carbonaceous powders used in the MPL

Sample	CNS	Vulcan
Particle size (10% of particles) (μm)	21.92	6.13
Particle size (50% of particles) (μm)	113.97	13.28

Particle size (90% of particles) (μm)	303.55	44.03
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In this case, the results obtained applying this technique were not satisfactory, because they indicate a much higher size of the particles than that measured using the SEM technique. These unrealistic values can be easily explained in terms of the agglomeration of the CNS, because of its hydrophobicity. However, this information is valuable in the characterization of the nanoparticles, because the CNS is sprayed in a microporous ink in order to form the MPL, where they can also agglomerate. Hence expected agglomerated particles in the MPL could achieve the values measured in Mastersizer.

In order to get more information about the crystallinity of the carbonaceous materials and MPLs prepared with them, the XRD technique was used to obtain information about the crystallite size and distance between planes of CNSs and Vulcan carbon. Diffractograms are shown in Figure 2, for both, the bulk powder and also for the MPL prepared with it.

Figure 2. XRD analysis for both carbonaceous powders (a) and MPLs (b)

In Part a, it can be observed that CNS and Vulcan Carbon XC72 present characteristics carbon peaks at 2θ of 26° and 42° approximately, being the first one the main peak. It may be attributed to the face (0 0 2) [16]. In Part b, the XRD patterns of the electrodes prepared with MPLs of both materials are compared. As it can be shown, both patterns are closely similar, due to both MPLs are prepared with carbonaceous materials and no changes is expected in the material during the MPL manufacturing. Crystal size (L_c) and distance between planes (d_{002}) were calculated for each sample using equations (1) and (2), respectively, where L_c is the crystal size (nm), λ corresponds to

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the $K\alpha$ radiation of copper ($\lambda = 0.15418$ nm), B is the peak width of $I_{\max} / 2$ and θ the angle corresponding to $I_{\max}$. Table 2 shows the L_c and d_{002} values obtained for different powders and MPLs.

$$L_c = \frac{0.89 \cdot \lambda}{B \cdot \cos(\theta)} \quad [1]$$

$$d_{002} = \frac{\lambda}{2 \cdot \sin(\theta)} \quad [2]$$

Table 2. Particle size and distance between planes of different materials studied

Material	LC (nm)	d002 (nm)
Vulcan XC72 (Powder)	2.3	0.348
CNS (Powder)	2.5	0.341
Vulcan XC72 (MPL)	18.5	0.335
CNS (MPL)	21.4	0.336

Respect to d_{002} , it can be observed that values are comparable for the powder and the MPL samples. As expected, CNSs are more crystalline as compared to the Vulcan carbon, with a lower d_{002} value, which suggests a more organized distribution of crystal planes. In the case of MPLs, the much higher values observed for the L_c values should be considered as apparent, and can be explained in terms of the strong influence of the GDL carbonaceous paper substrate, which also presents a main peak at $2\theta = 26^\circ$ which affects to the measurements, and of the agglomeration of the carbonaceous materials as it has been previously pointed out in the discussion of the results obtained with the Master sizer.

Porosity, BET surface area and permeability are critical parameters in the materials to be used as MPL, because they may affect to the diffusion coefficient of porous substrates [17], that it is directly related to the gas permeability of the electrode. Table 3 shows BET values and pore volume for both carbonaceous materials. The main important information that can be drawn is that CNSs present lower BET and pore volume as compared with Vulcan carbon. This can be explained taking into account that CNS presents lesser microporous character than carbon black, which could explain the low values of BET and porosity obtained in the analysis.

Table 3. BET and pore volume properties of carbonaceous materials

Sample	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
CNS	14.3	0.05
Vulcan XC72	250.0	1.74

Permeability of the different reactive gases was evaluated in both MPLs. Figure 3 shows the pressure drop vs. volumetric flow plot in the MPL manufactured with both studied materials, for the three gases with interest in the study of HTPEMFC. As expected, lowest pressure drop is presented by hydrogen and highest by oxygen

and this is observed for Vulcan carbon and also for CNS made MPL. In comparing both carbonaceous MPL, the greater differences between gases flow were observed for the MPL made with CNS, for which oxygen and air shows a completely different behaviour in the whole range of volumetric flow tested. Comparing this behaviour with the observed in the MPL made with Vulcan carbon, it is important to point out that this difference becomes almost negligible in the case of the Vulcan carbon operating at low volumetric flows, in which even the performance with the hydrogen is comparable to the observed with oxygen and air. This clearly indicates a lower permeability and a greater potential selectivity of the MPL made with CNS towards gas flow, which is an important observation to be accounted in the explanation of the performance of HT-PEMFC.

Figure 3. Permeability curves of different MPLs to reactive gases. A) Air; B) Oxygen ; C) Hydrogen

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HT-PEMFC performance

In order to evaluate the performance of the CNS made MPL, a short lifetest of approximately 300 hours in a single cell was carried out. Figure 4 shows the changes in the cell potential. Throughout the life test, six characterization tests were carried out as detailed in the Section 2.3 and they are clearly observed in the plot with the discontinuities in the value of the cell voltage, that rapidly settle down to the expected cell voltage value.

Figure 4. Evolution of cell voltage vs time for MEA prepared with CNS based electrodes.

The initial voltage was 0.48 V and it increases continuously during the break-in period until a value close to 0.59 V. After this initial stage, the performance improves during the first 45 hours with an activation of 113 $\mu\text{V/h}$ but then, after this first stage, degradation becomes more significant and at the end of experiment, the total degradation rate of the fuel cell was around 100 $\mu\text{V/h}$. In comparing this value with other results previously shown in the literature, it can be noticed that the CNS MPL is improving the stability of the HTPEMFC with values much better than other reported in similar tests with Vulcan carbon MPL. Thus, for PBI-based membranes, degradation rates measured in previous studies were 250 $\mu\text{V/h}$ [18] and 194.2 $\mu\text{V/h}$ [19]. The low degradation rate noticed for the CNSs based MEA could be explained with the high electrochemical and thermal stability exhibited by carbon nanospheres [8], which could be related to the low BET surface area and high graphitic character shown by our CNS, which makes harder the physicochemical deterioration of this material.

In order to know more about the electrochemical characteristics of the CNS MEAs, several polarization curves were obtained in the HT-PEMFC fed with air and pure oxygen. Results obtained are shown in Figure 5.

Figure 5. Evolution of polarization curves and power density performed with air (A) and Oxygen (B) for CNS short life test.

The maximum power density reached is about 180 mW/cm^2 with air and 380 mW/cm^2 with oxygen as comburent, respectively. These values are slightly lower than values obtained by our research group (219 and 400 mW/cm^2) [19] using a standard Vulcan carbon support. However, this power density values are higher than others reported recently in the literature in which new materials have been tested. Thus, Kurdakova [20] reported power densities around 75 mW/cm^2 operating with air, at 150 $^{\circ}\text{C}$ and 0.5 mg Pt/cm^2 with commercial carbon cloth (HT140EW, E-TEK) in both electrodes, using a composite PBI-SiO₂ membrane and testing the MEA in a 5 cm^2 single cell. Osslander [21] reported only values around 33 mW/cm^2 operating at 160 $^{\circ}\text{C}$ and testing new Si-based composite PBI membranes in a 50 cm^2 single cell. No information about the catalyst loading was reported. Performance values obtained in recent studies carried out by our research group using SiC-based MPL for electrodes in HT-PEMFCs are also lower as compared with CNS-based electrodes results [21]. During the lifetest the power density decreased slightly, 13% with air and 8% with oxygen being the degradation higher with air. Moreover, during the lifetest the MEA showed very good open-circuit voltage values at 0.0 A/cm^2 , indicating that no short circuits, electrical losses or damages in the membrane occurred.

In order to characterize performance of the fuel cell in the region of mass transfer limitations, Figure 6 shows polarization curves obtained using a constant flow rate of air calculated for a current production of 0.4 A/cm^2 . Under those conditions it is expected that the mass transfer limitation region can be well studied. Opposite

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to what it was observed in Figure 5, the mass transfer limitation region is clearly shown in this polarization curves indicating that experimental conditions were properly selected. In comparing both MEAs, it can be seen that limitations are greater in the case of Vulcan support than using CNS support.

Figure 6. Polarization curves and power density at constant flow corresponding to a current density of 200 mA cm^{-2} with CNS (A) and standard carbon (B) at different times.

The slight increase of the performance of the fuel cell in the case of the CNS MEA as compared to this conventional Vulcan MEA is expected according to the permeability results commented in above.

As it was pointed out above, during the lifetest, impedance analyses were carried out at different operation times. Figure 7 shows the Nyquist plots of the MEA with CNS based electrodes. For comparison purposes, the Nyquist plots of a MEA with standard carbon based electrodes (Vulcan XC-72) are also shown, measured under the same operation conditions. As shown, the values and the shape of the graph are very similar to each other.

Figure 7. Nyquist plots of the MEA with Carbon Nanospheres (A) and standard carbon (B) at different times.

In order to know the resistance values originate in the fuel cell, an equivalent circuit $R(RQ)$ (RQ) was used to simulate the impedance data in this work [22, 23, 24]. The parameters obtained are shown in Table 4. This table also shows the values of ECSA calculated by cyclic voltammetry for comparison purposes.

Table 4. Fitting parameters of the two MPL to a $R(RQ)$ (RQ) model and ECSA

Parameter	Time	Air			Oxygen		ECSA
		Rohm	Rct	Rmt	Rohm	Rct	
Unit	hours	mΩ cm ²	mΩ cm ²	mΩ cm ²	mΩ cm ²	mΩ cm ²	m ² /g
CNS	0	173.8	800.0	561.3	175.5	575.5	17.22
	46	185.0	632.8	620.5	174.8	653.8	15.96
	100	182.0	735.5	606.3	177.0	722.8	15.18
Vulcan XC-72	0	184.0	402.3	867.5	182.0	446.5	27.88
	46	194.0	488.3	707.0	198.3	465.0	22.87
	100	203.5	514.8	576.0	199.8	458.5	22.58

No great changes are observed in the values of the parameters at the different times for which the impedance analysis were carried out, for any of the two MEA tested. In the case of the Vulcan carbon MEA at 100 hours, the experiment was switched off, because the voltage decay was over 10%. For this reason, comparison is only carried out up to this operation time. With respect to parameters obtained, the high frequency resistance is typically explained in terms of the sum of the ohmic resistances of the membrane electrolyte and the electric resistance of the electrode (GDL + MPL, mainly). It can be observed that this high

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frequency resistance is very similar between both types of electrodes, around $0.2 \Omega \text{ cm}^2$. Anyhow, the ohmic resistance of CNS is slightly lower than that of Vulcan XC-72.

Furthermore, the semicircle observed in the Nyquist plot is explained in terms of the charge transfer resistance (RCT) or of the oxygen reduction reaction (ORR) activation in the cathode catalyst layer. The electrodes prepared with the CNS based MPL show a higher RCT as compared to the carbonaceous supported MPL ($0.7 \Omega/\text{cm}^2$ vs $0.5 \Omega/\text{cm}^2$ for the standard one). These values are higher and they could explain the lower performance achieved by the MEA prepared with the CNS, although it has to be accounted that the novel CNS based electrodes are not optimized in terms of the overall composition, particle size, the ratio ionomer/CNS, the amount of phosphoric acid, etc.

On the other hand, at low frequency, another arc appears on the EIS that may be related to the mass transport limitations. From that arc it can be pointed out that the mass transfer resistances in the case of the CNS based electrodes are lower than Vulcan XC-72.

Table 4 also shows also the ECSA (ElectroChemical Surface Area) values obtained at different times of the essay. At the beginning, a value of $17.2 \text{ m}^2/\text{g}$ is obtained. In comparing this value with other shown in the literature, it can be observed that it is similar to the ECSA calculated by Modestov (above $19.4 \text{ m}^2/\text{g}$) [25]. However, there is a slightly decrease throughout the test obtaining a non-negligible percentage of degradation of 11.8 %, as it has been stated previously. This value, is lower than the one (19.0%) obtained by the electrode prepared with the standard MPL (Vulcan carbon) which means that the CNS based MPL contributed to a better stabilization of the catalyst layer. This observation is in agreement with the previous statement about the charge transfer resistance, where a better stability of the electrodes prepared with the CNS based MPL was observed.

As it has been pointed out in Table 1, the CNS particles are higher than Vulcan ones, then, some of the catalyst particles, (much lower than CNS) could be deposited between the space of the CNS during the deposition of the catalyst layer onto the MPL and they would not be available for the electrochemical reaction because those catalyst particles would not be in contact with the PBI membrane (electrolyte). This could contribute to achieve high values of RCT and low values of ECSA. Nevertheless, the fact that the CNSs have a bigger particle size than the Vulcan ones, could originate a less compact and a more porous structure and the access of the gases to the active sites of the catalyst layer would be favoured and hence, the mass transport resistance would be lower in the case of the MPL with CNSs. These effects are more noticeable when air is used as it can be observed in Table 4, because the oxygen concentration is lower. To clarify this explanation, Figure 8 shows a scheme of the structure of the MPL formed by the CNSs where some catalyst particles (Pt/C) are deposited between the CNS are observed. They would not be available for the electrochemical reaction which could explain the lower values of ECSA and higher values of RCT obtained by the electrodes prepared with the MPL with CNSs.

Figure 8. Schem of the structure of the MPL prepared with CNSs, where some Pt particles are deposited in the deep space between CNSs particles and do not participate in the electrochemical reaction.

Conclusions

For the first time, MPLs with CNS have been prepared and compared with a Vulcan carbon based MPL. Two important conclusions can be drawn from this work:

- 1) The electrical conductivity of CNS is slightly lower than Vulcan conductivity, but this fact seems not affect especially to the FC performance.
- 2) CNS showed much better electrochemical stability under the applied experimental conditions than Vulcan based MPLs.

Thus, it can be confirmed that CNS is a promising material that can be used in HT-PEMFCs technology and this work opens the door to further work to improve both, their fuel cell performance and their durability.

Experimental Section

Preparation of the MEA and Fuel cell tests

CNSs were synthesized in our lab according to a procedure described elsewhere [14]. Vulcan carbon was purchased from Cabot (Boston, USA). To manufacture the MPLs, CNS or Vulcan XC72 (depending on the tests) were deposited onto a gas diffusion media (Toray Carbon Paper -PTFE 10%, Fuel Cells Store, USA) by air-spraying a microporous ink consisting of the carbonaceous material and 10% PTFE (Teflon™ Emulsion Solution, Electrochem Inc.). After the deposition of the MPLs (2 mg cm^{-2}), sintering is attained by heating the electrodes at 360°C for 30 min. The catalyst layer was deposited by spraying the catalyst ink on the electrodes. The catalyst ink consisted of a 40% Pt/C catalyst on Vulcan XC-72R Carbon Black (Fuel Cell Store, USA), PBI ionomer (1.5 wt. % PBI in N, N-dimethylacetamide, DMAc), and DMAc as a dispersing solvent. In both cases, the Pt loading on each electrode was $0.6 \text{ mg Pt cm}^{-2}$. After the deposition of the catalyst layer, the electrodes were dried at 190°C for 2 h, with the purpose of removing traces of DMAc. The electrodes were then wetted with a solution of 10% phosphoric acid (PA). Electrodes were left to absorb the acid for one day. For the preparation of the MEA, a thermally treated PBI membrane was provided by Danish Power Systems®. This membrane was doped in 85 wt. % PA for 5 days, in order to achieve good proton conductivity. The doping level acquired

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by the membrane was 9 molecules of acid per polymer repeating unit. The corresponding thickness of the doped PBI membrane used was 83.2 μm . The superficial acid on the membrane was thoroughly wiped off with filter paper and the membrane was used to prepare the MEA. In order to fabricate the membrane-electrode assembly (MEA), the doped membrane was sandwiched between a couple of electrodes and the whole system was hot-pressed at 130 $^{\circ}\text{C}$ and 1 ton for 15 minutes. Vulcan carbon was always used for the MPL of the anodes whereas Vulcan or CNS were compared for the cathode, taking into account that cathodic reaction is the bottleneck in the overall process, in particular in terms of the dragging of catalyst components. The completed MEA was inserted into the cell between bipolar plates of graphite (with a five serpentine channels frame in each plate). The geometrical area of each electrode was 25 cm^2 .

Physicochemical characterization

XRD measurements were carried out by a Philips PW-1700 diffractometer with rotating anode, applying $\text{K}\alpha$ corresponding to the transition from copper radiation. CNS size was measured by SEM micrographs. Particle size of both carbonaceous materials evaluated was studied with particle analyser (MasterSizer Hydro 2000SM) using water as dispersant agent. Permeability of the reactive gases was also evaluated by studying the pressure drop at different hydrogen, oxygen and air flows. BET surface area of different samples and total pore volume were obtained using N_2 adsorption-desorption at 77 K (QUANTACHROME, model QUADRASORB 3SI).

Polarization curves and preliminary stability test

MEAs were mounted and characterized in a commercially-available Cell Compression Unit (CCU) provided by Baltic Fuel Cells GmbH (Germany). The break-in procedure consists of the operation at 0.1 A/cm^2 , and λ (H_2) 1.5 and λ (air) 2 for 48 hours. Then, a preliminary stability test was conducted by increasing the current density to 0.2 A/cm^2 (160 $^{\circ}\text{C}$). For further characterization, a protocol test was carried out every 48 h, since the end of the break-in procedure. This test consists of the following routine:

- Galvanostatic polarization curves. They were performed from the OCV to 0.4 V. First with air λ (H_2) 1.5 and λ (air) 2 and then with oxygen at λ (H_2) 1.2 and λ (air) 9.5.
- Electrochemical impedance spectroscopy (EIS) tests. The tests were performed at different current densities (0.03, 0.10, and 0.20 A/cm^2) with 10 mV AC perturbation amplitude and frequency ranging from 100 kHz to 100 MHz. This sequence of EIS tests was carried out first with air and then the same procedure was repeated with oxygen.
- Cyclic voltammetries (CV). The cathode side was purged with nitrogen and hydrogen flowed through anode side with flows of 0.1/0.1 L

min $^{-1}$ N_2/H_2 . The CV was carried out from 0.05 V to 1.0 V (scan rate of 100 mV s $^{-1}$). Results obtained were used to estimate the electrochemical surface area (ECSA) of the cathode.

- Linear sweep voltammetry (LSV). The same gases of the CV were fed with flows of 0.3/0.3 L min $^{-1}$ N_2/H_2 . This technique was performed to find out any crossover of gas flow through MEA.

Acknowledgements

The authors further thank the European Commission as this work was supported by the Seventh Framework Programme through the project CISTEM (FCH-JU Grant Agreement Number 325262). Danish Power System is also grateful for providing us the PBI based membranes.

Keywords: Carbon nanospheres • PEM fuel cells • microporous layer • electrode • PBI

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Excellent performance & stability!!