Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Fabrication of microporous layer – free hierarchy gas diffusion electrode as a low Pt-loading PEMFC cathode by direct growth of helical carbon nanofibers

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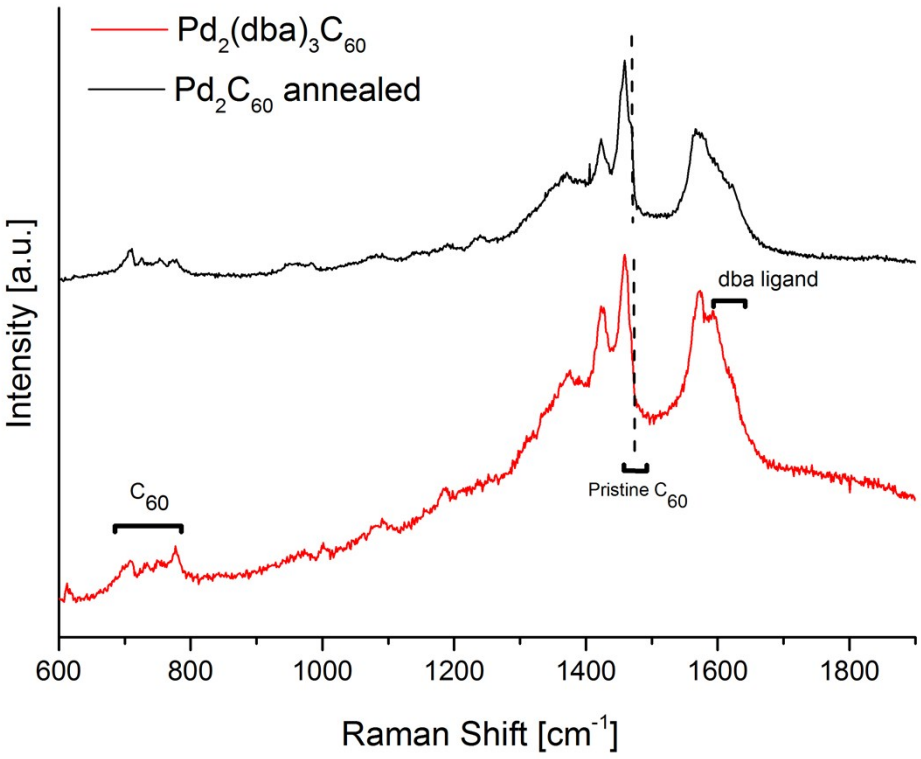

Fig. S1. *Raman spectra of the Pd_2C_{60} decorated carbon paper. A downshift in the C_{60} breathing mode evidences formation of Pd_2C_{60} phase already in the sonicated $Pd_2(dba)_3C_{60}$ mixture. In addition, a removal of dba ligands due to thermal annealing at 200°C is observed. The full mechanism of this process is detailed elsewhere[1].*

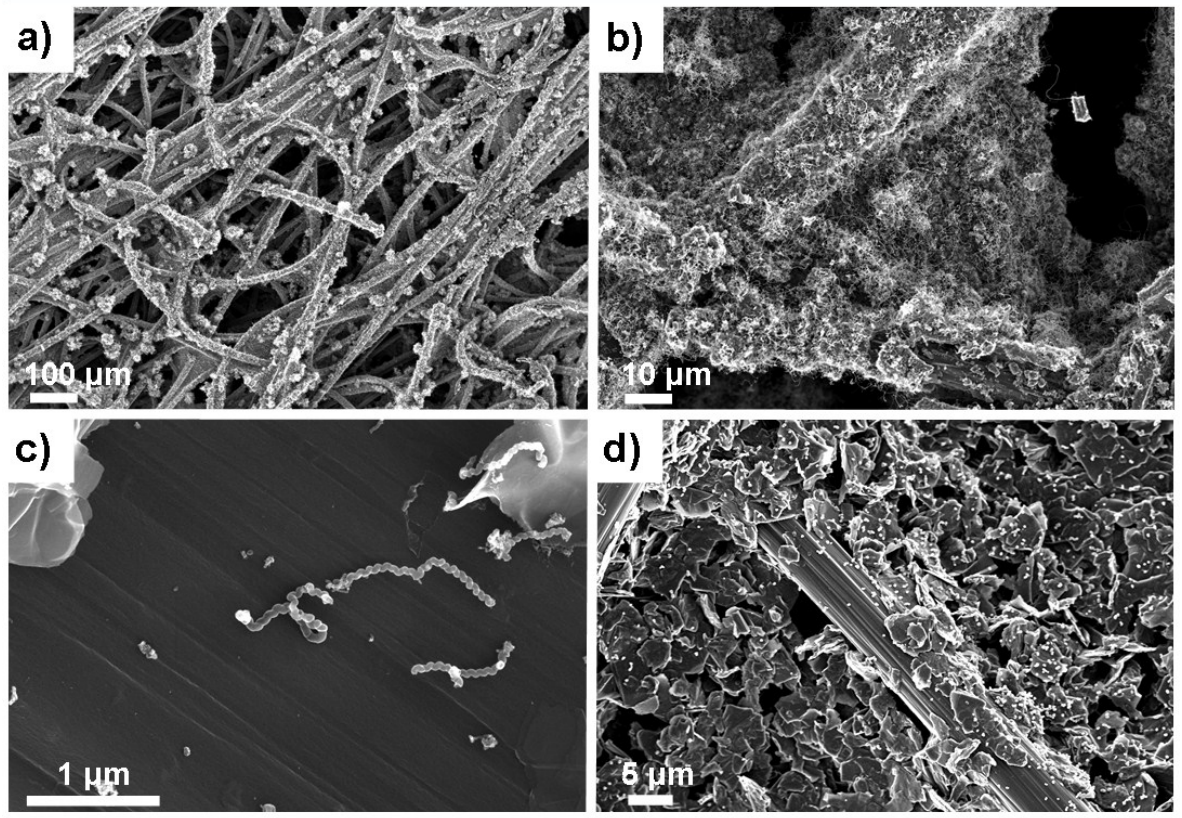

Fig. S2. *Additional SEMs displaying morphologies of CP-HCNFs in the case where a surplus of Pd catalyst was applied (a-b) and the initial stages of the growth is illustrated in (c). Pt traces could be observed on the other side of the CP (d) after Pt autoclave decoration.*

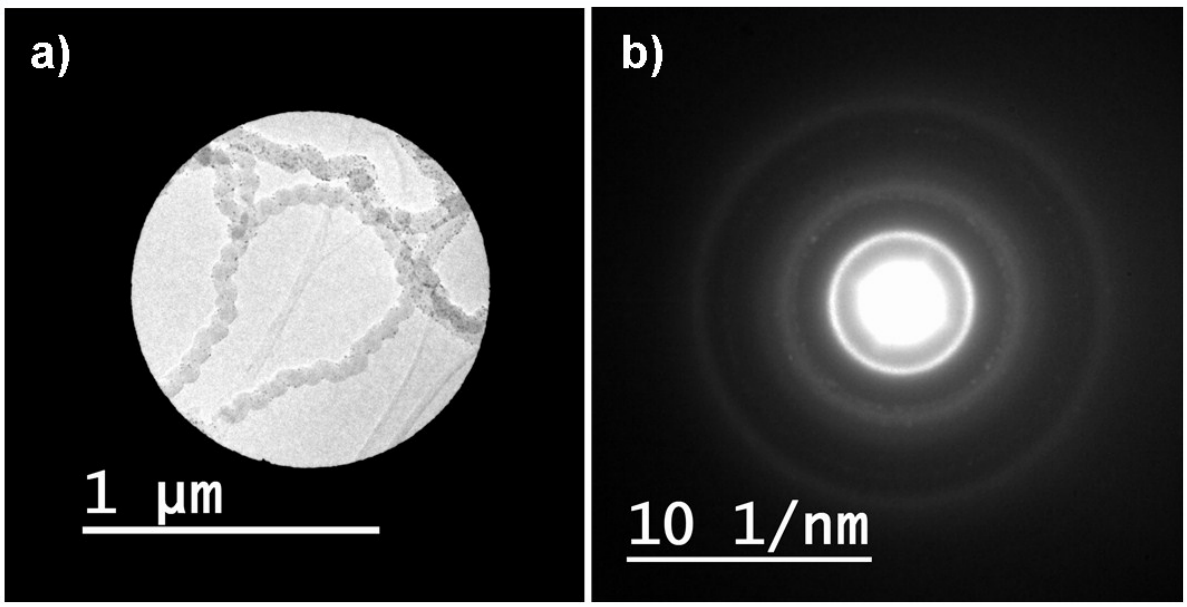

Fig. S3. *Intermediate lens aperture aimed at a selected Pt-HCNF cluster (a) and its corresponding Selected area electron diffraction (b) displaying crystalline Pt NPs .*

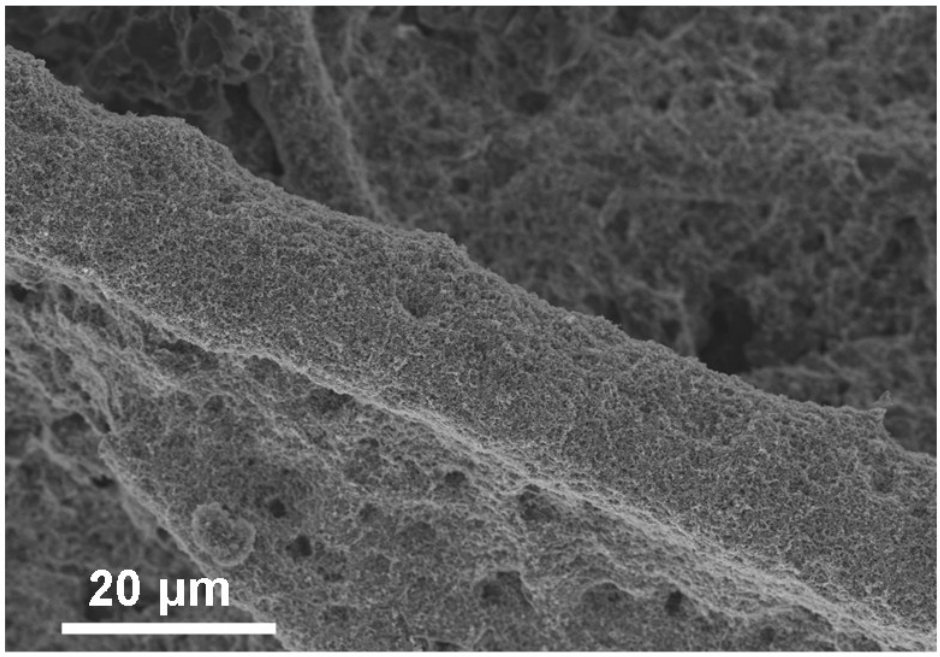

Fig. S4. *SEM of commercial Pt/C – Vulcan (20%) decorated on type 34 AA GDL by spraycoating. The Pt loading is similar to the fabricated Pt/HCNF GDL (0.05 mg_{Pt} cm^{-2}).*

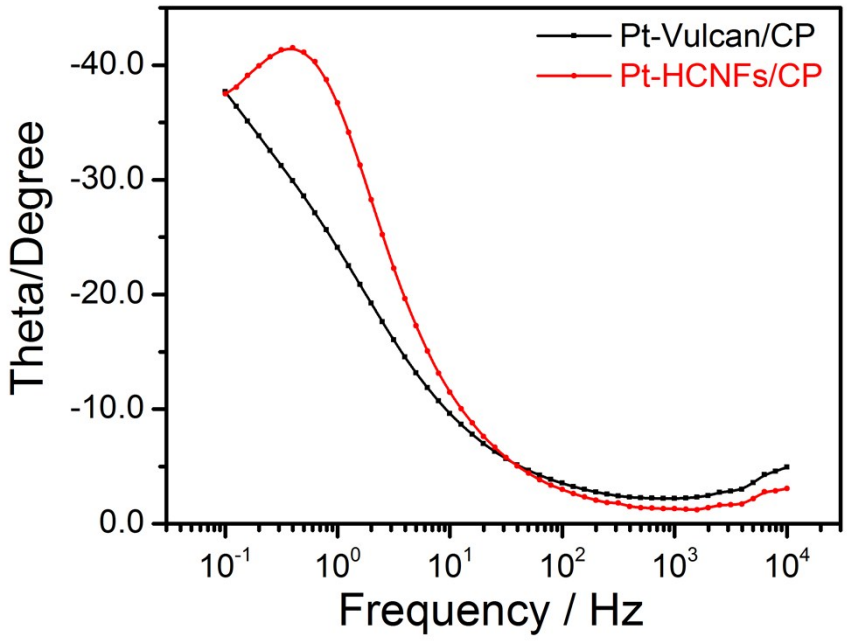

Fig. S5. *Bode phase plot corresponding to the EIS measurements performed (see Fig. 6 a).*

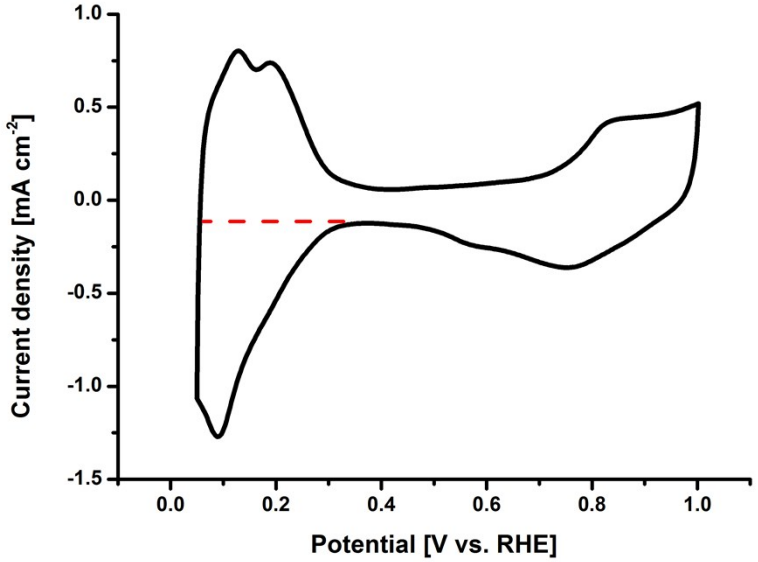

Fig. S6. *Hydrogen under potential deposition ECSA test of Pt/C – Vulcan (20%) performed on a conventional glassy carbon electrode on Ar saturated 0.1 M $HClO_4$ electrolyte. For comparison purposes, the Nafion® amount was set to 33 wt.%, yielding an ECSA of 68 m^2/g_{Pt}.*

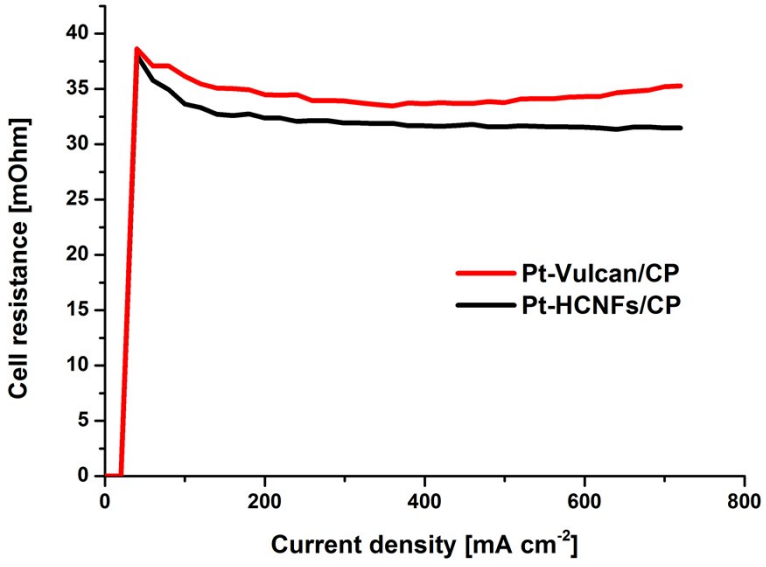

Fig. S7. *Cell resistance as measured by simultaneous I-interrupt during recording of polarization curves.*

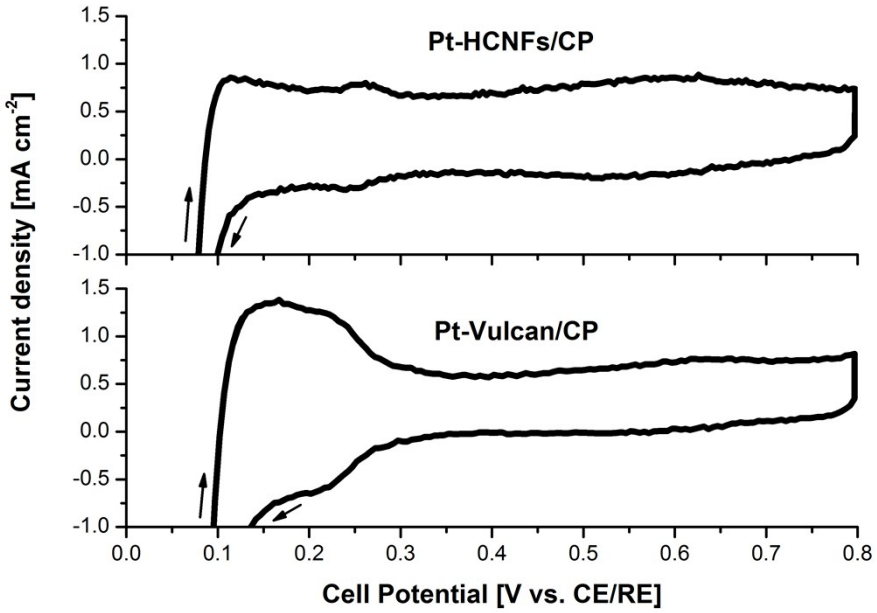

Fig. S8. *In situ ECSA measured under N_2 saturated cathode with the anode used as counter and reference electrode under H_2 flow. Several CV´s were recorded until reaching stable performance where cycling conditions were varied such that low fluctuations in current (noise) were reached. Presented curves are here recorded with 40 mV s^{-1} and 50 mV s^{-1} for Pt-HCNFs/CP and Pt-Vulcan/CP respectively. H_{UPD} Integration limited by the onset of H_2 evolution yields roughly 15.0 m^2/g_{Pt} and 7.5 m^2/g_{Pt} for Pt-Vulcan/CP and Pt-HCNFs/CP respectively.*

Table S1.*Summary of electrochemical data including EIS circuit fit, ECSA (in situ) and ECSA (ex situ). The ex situ ECSA could be measured in a conventional manner for the commercial catalyst for comparison purposes (shown in parenthesis). The real Pt utilization factors are calculated according to equation S1.*

Sample	*EIS fit (chi-square)*	*$R_S + R_{ele}$ [Ω]*	*R_{CT} [Ω]*	*CPE [mF]*	*ECSA (in situ), m^2 g^{-1}*	*ECSA (ex situ), m^2 g^{-1} (actual)*	*Utilization factor*	*Real utilization factor*
Pt-Vulcan/CP	*0.00030*	*346*	*40000*	*0.58*	*15.0*	*37.9 (68.0)*	*0.40*	*0.0032*
Pt-HCNFs/CP	*0.00029*	*209*	*25000*	*1.83*	*7.5*	*11.1*	*0.68*	*0.0013*

The real catalyst utilization (U_{Pt}) was calculated by

$$U_{Pt} = \frac{N_S}{N_t} * 100 \quad , \qquad \text{(S1)}$$

where N_S is the number of exposed surface atoms measured via the ex situ ECSA and N_t is the total number of Pt atoms within the electrode directly estimated through the Pt loading.

References

[1] F. Nitze, H.R. Barzegar, T. Wagberg, Phys. Status Solidi B-Basic Solid State Phys., 249 (2012) 2588-2591.