

# Plasma based platinum nano-aggregates deposited on carbon nano-fibres improve fuel cell efficiency

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ABSTRACT.

Improved platinum catalytic utilisation has been achieved by creating an open support structure based on aligned carbon nano-fibres (CNF) attached to carbon loaded carbon cloth electrodes (GDLs). The nickel catalyst used to initiate the CNFs growth, the CNFs themselves and the 5 nm Pt nano-aggregates were deposited sequentially in the same low pressure plasma reactor. This oriented catalyst structure was incorporated into a Membrane Electrode Assembly (MEA) and tested with and without CNFs and on carbon paper or GDL. The performance of the fuel cells based on the new Pt/CNFs/GDL structure was better over the entire range of operating current.

KEYWORDS. platinum nano-aggregates, carbon nano-fibers, oriented catalyst layer, proton exchange membrane fuel cell

The Proton Exchange Membrane Fuel Cell (PEMFC) offers attractive mass market applications, primarily in personal transport aimed at reducing urban pollution. Its efficiency strongly depends on the membrane-electrode-assembly (MEA) and one of the challenges in its commercialization is the high cost of noble metals used as catalyst (e.g Pt) in the electrodes. Increasing the Pt utilisation efficiency in order to decrease the Pt amount in the catalytic layer has been one of the major concerns during the past decade <sup>1</sup>. However, even with the most advanced conventional electrodes where small 2-3 nm Pt nanoparticles are dispersed in a porous carbon particles skeleton flooded in a conduction proton solution (Nafion®), Pt utilisation remains low.

Carbon nanofibers or carbon nanotubes have already been proposed as a replacement for traditional carbon particle powders in PEMFC electrode because of their high electrical conductivity and chemical inertia. These nanocomposites have usually been used in powders mixed with Nafion® and spread on electronic conductive supports such as carbon cloth or carbon paper <sup>2-5</sup>. In this case, the results did not show many advantages over conventional carbon particle powders because this resulting configuration presented similar limitations to those of the conventional designs. The CNF/CNTs (CNT: Carbon Nanotube) were isolated from electron pathways due to the Nafion® coverage leading to a low electronic conductivity <sup>6</sup>; the convoluted electrode architecture resulted in poor gas diffusivity and access to the Pt catalyst.

The feasibility of a fuel cell using carbon nanotubes directly grown on electrodes has been recently demonstrated using silica gel to catalyse CNT growth <sup>7,8</sup> or using a process of electrodeposition of Pt on CNTs grown by CVD on carbon paper after an initial electrodeposition of Co catalyst <sup>6,9,10</sup>. Unfortunately, the subsequent MEA performance remained low, possibly as a result of the large diameter (25 nm) of the Pt particle size.

In earlier publications, we reported the role of sputter plasma deposited Pt on carbon electrodes as a technique for improving PEMFC efficiency <sup>11-13</sup>. For much lower Pt loadings, a similar MEA voltage

current curve was obtained but only for low fuel flow rates. Nevertheless, it was demonstrated that plasma sputtering of catalyst is a suitable method for obtaining efficient use of the catalyst.

The present experiments aim to combine the plasma growth of carbon aligned nano-fibres with plasma sputtering growth of platinum nano-aggregates to create an oriented catalyst layer<sup>14,15</sup> that is sufficiently porous to allow a free flow of fuel gas while exposing the fuel to an effective amount of catalyst. To achieve this aim a low pressure high density radio frequency plasma discharge system shown in FIG. 1 has been constructed that is based on the helicon plasma source which can operate at a variety of different gas pressures. In order to allow a comparison of different techniques, four different types of catalytic layer have been deposited: two on carbon loaded carbon cloth and two on carbon paper, of which one each had additional carbon nano-fibres deposited. Subsequently, all four were subjected to the same plasma deposition of the Pt catalyst.

A conventional fuel cell electrode consists of a carbon loaded carbon cloth called Gas Diffusion Layer (typically Vulcan XC72 and PTFE particles) and of an active layer (Pt/C catalyst and Nafion®). In the present procedure, three consecutive plasma deposition steps were carried out in the helicon reactor: the nickel catalyst used to initiate the growth of the 35 nm diameter 2 micrometre long CNFs, the CNFs themselves and the 5 nm nano-clusters of platinum. The electrode holder is placed in the centre of the plasma diffusion chamber which is contiguously attached to the low pressure high density radiofrequency (13.56 MHz) helicon plasma source, about 10 cm above the electrode holder. The Pt and Ni targets are positioned between the source and the 72 mm-diameter electrode holder on either side of the “bright dress shape” plasma.

The 25-35 nm Ni catalyst clusters are grown on two of the four electrodes by using a 500 W, 5 mTorr argon plasma, to sputter a -300 V biased Ni target. Subsequent to the Ni catalyst deposition, the thermal substrate temperature induced by a spiral heater is gradually increased to 400 °C over a period of 15 min in secondary vacuum (below  $5 \cdot 10^{-6}$  mbar). The well aligned 2 microns long CNFs are subsequently grown on -100 V biased substrate at 400 degrees for 45 min in a 5 mTorr CH<sub>4</sub>/H<sub>2</sub> plasma

(flow rate ratio of 1:4). For the final Pt catalyst deposition step on the four electrodes, an argon plasma of density about  $n = 10^{11} \text{ cm}^{-3}$  operating at a pressure of 5 mTorr is used to sputter a -300 V biased Pt target and deposit the 3-10 nm in size Pt nano-particles. A sputtering time of 4 min is used, resulting in a platinum loading of  $0.02 \text{ mg.cm}^{-2}$ . A schematic of the four electrode structures is shown in FIGs. 2(a,b,c,d): Pt/carbon paper (a), Pt/CNFs/carbon paper (b), Pt/GDL (c), Pt/CNFs/GDL (d).

The synthesis carbon nanofibers were characterized using scanning electron microscopy (Hitachi, S4500) and a transmission electron microscopy TEM (Hitachi, H7100FA).

The SEM photographs of two of these four synthesized electrodes [Pt/CNFs/carbon paper (b) and Pt/CNFs/GDL (d) electrodes], prior to the final coating with Nafion®, are shown on FIGs. 3(a,b), respectively. FIGs. 4 shows the TEM pictures of the upper end of a CNF before (a) and after (b) platinum deposition. The presence of the Ni catalyst at the tip of the CNF suggests a ‘tip’ growth model<sup>16, 17</sup>. The Ni particle usually adopts a characteristic faceted or biconical shape. A closer inspection of the CNF shows graphene layers oriented parallel to the growth direction, in a typical stacked structure<sup>18</sup>. Most of the CNFs have a narrow statistical distribution of diameters that peak at around 35 nm, corresponding to the mean Ni particle diameter. At the end of the process, each Ni particle is surrounded by a thin carbon layer on the face exposed to the  $\text{CH}_4/\text{H}_2$  plasma, an important advantage for fuel cell application. This carbon film prevents both nickel dissolution in the fuel cell’s corrosive environment and nickel conduction throughout the hydrated membrane, which would result in closing proton conduction channels. The surface area of the high aspect ratio CNFs of the two electrodes shown on FIGs. 2(a,b), (before platinum coating) is found to be in the range 15 – 20  $\text{m}^2/\text{g}$  range. FIG. 4(b) shows that the 2  $\mu\text{m}$ -long CNF is covered by well dispersed Pt nanoparticles all along its length, yielding efficient utilisation of the large surface area of the CNFs. The diameter distribution of these nanoparticles decreases near the base of the CNFs that is attached to the carbon support: 8 nm diameter at 100 nm from CNFs carpet surface, 5 nm at 250 nm and 3 nm at 600 nm. The Pt nanoparticles density is higher at the electrode–membrane interface where the Pt catalyst is the most active<sup>19</sup>. Previous studies

of the plasma sputter-deposition of Pt on the GDL without CNFs, e.g. electrode (c), have shown typical diffusion lengths of the Pt into the GDL between 400 nm and 1.5  $\mu\text{m}$  and an agglomeration of Pt clusters to form a dense clustering at the surface of the GDL for large Pt loading. In the electrodes constructed here, a large proportion of the platinum penetrates to the 2  $\mu\text{m}$  length of the CNF.

The four electrodes were successively tested on the cathode side of a MEA assembly in a fuel cell test station. Standard E-TEK electrodes with a Pt loading of 0.5  $\text{mg}/\text{cm}^2$  were used at the anode side and a commercial Nafion® 115 membrane was used between the two electrodes. A Nafion® 5 wt.% solution was spread onto the electrodes to assure proton access from the membrane to the Pt nanoparticles (1  $\text{mg}/\text{cm}^2$  on cathode and 1.5  $\text{mg}/\text{cm}^2$  on anode). The MEA was hot pressed at 150°C for 120 s under a pressure of 40  $\text{kg}/\text{cm}^2$  to ensure good contact between the cell components. The corresponding polarization curve is obtained in a single 5  $\text{cm}^2$  Fuel cell test station (Fuel Cell Store).

The polarization curves corresponding to the four electrodes (a,b,c,d) are shown on FIG. 5. These results clearly show that the presence of the CNFs as catalyst support significantly improves the cell performance as a result of an increased catalytic surface area. Although the relative increase of performance with CNFs on carbon paper is drastic over the whole range of investigated current, the voltage is consistently lower than that obtained for the electrodes on carbon cloth with a GDL. According to Wang<sup>8</sup>, the PTFE particles present in the GDL contribute to its hydrophobicity and water evacuation in operation, whereas carbon paper wets easily preventing oxygen fuel from accessing the catalytic sites.

Improvement of the cell with CNFs grown on GDL is more noticeable at higher current: at a current density of 650  $\text{mA}/\text{cm}^2$ , the achieved power densities is close to 250 and 360  $\text{mW}/\text{cm}^2$  without and with CNFs, respectively. This indicates a lower cell resistance, hence a higher electronic and protonic conductivity from the oriented catalyst layer based on aligned CNFs.

Plasma techniques have been used to grow vertically aligned CNFs and to deposit nano-aggregates platinum along their length of 2  $\mu\text{m}$  thereby significantly increasing the fuel catalysis and usage. Tests of MEAs show that the best results were obtained for CNFs grown on GDLs consisting of carbon black and PTFE particles to provide adequate hydrophobicity and water evacuation during operation.

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## FIGURE CAPTIONS.

FIG. 1: Schematic of the Helicon PECVD reactor “Southern Cross”

FIG. 2: Schematic of the four physically prepared electrodes: (a) Pt / carbon paper, (b) Pt / CNFs / carbon paper, (c) Pt / GDL, and (d) Pt / CNFs / GDL.

FIG. 3: SEM images of CNFs based electrodes on carbon paper (a) and on GDL (b), respectively corresponding to the schematics of electrode (b) and electrode (d) shown on FIG. 2.

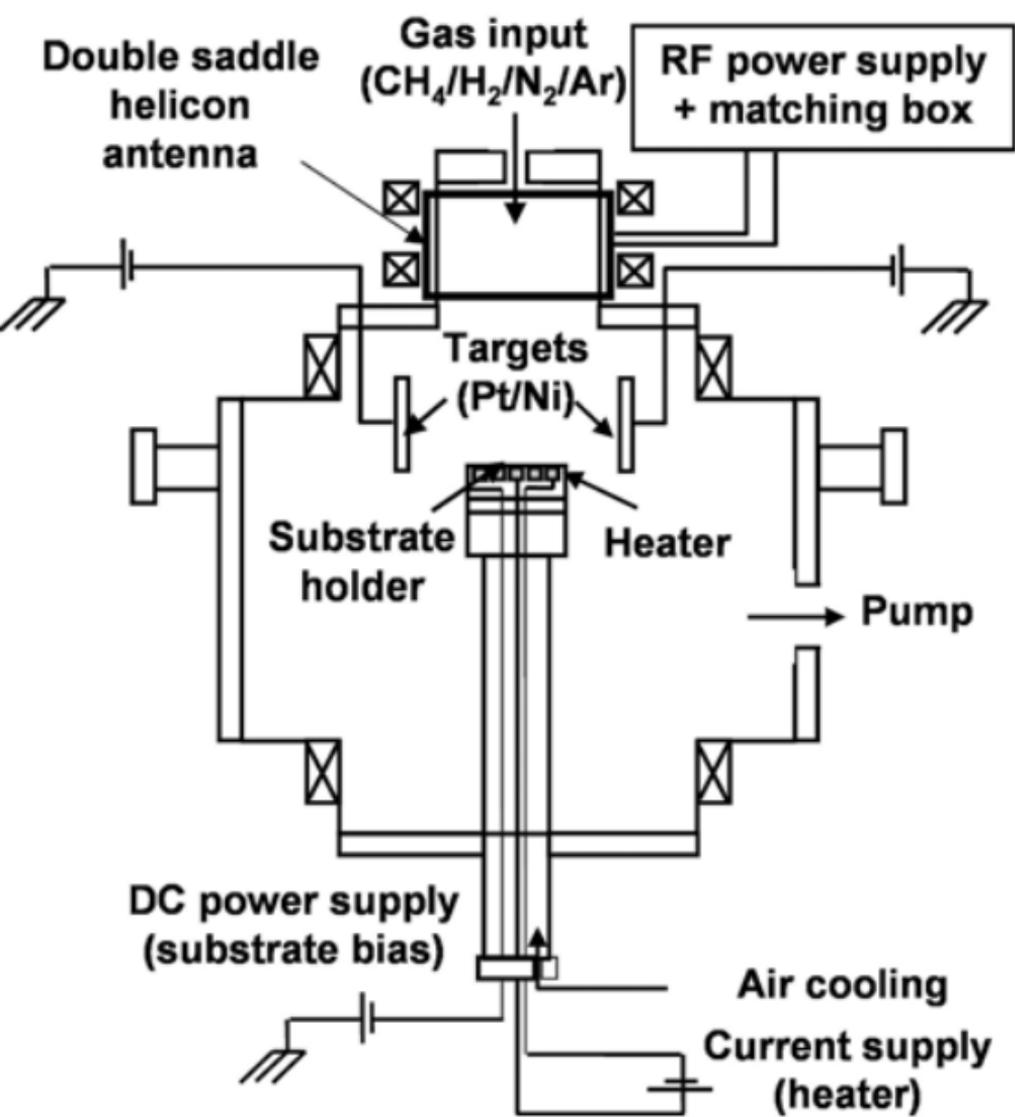
FIG. 4: TEM images of a CNF before (a) and after (b) Pt sputtering.

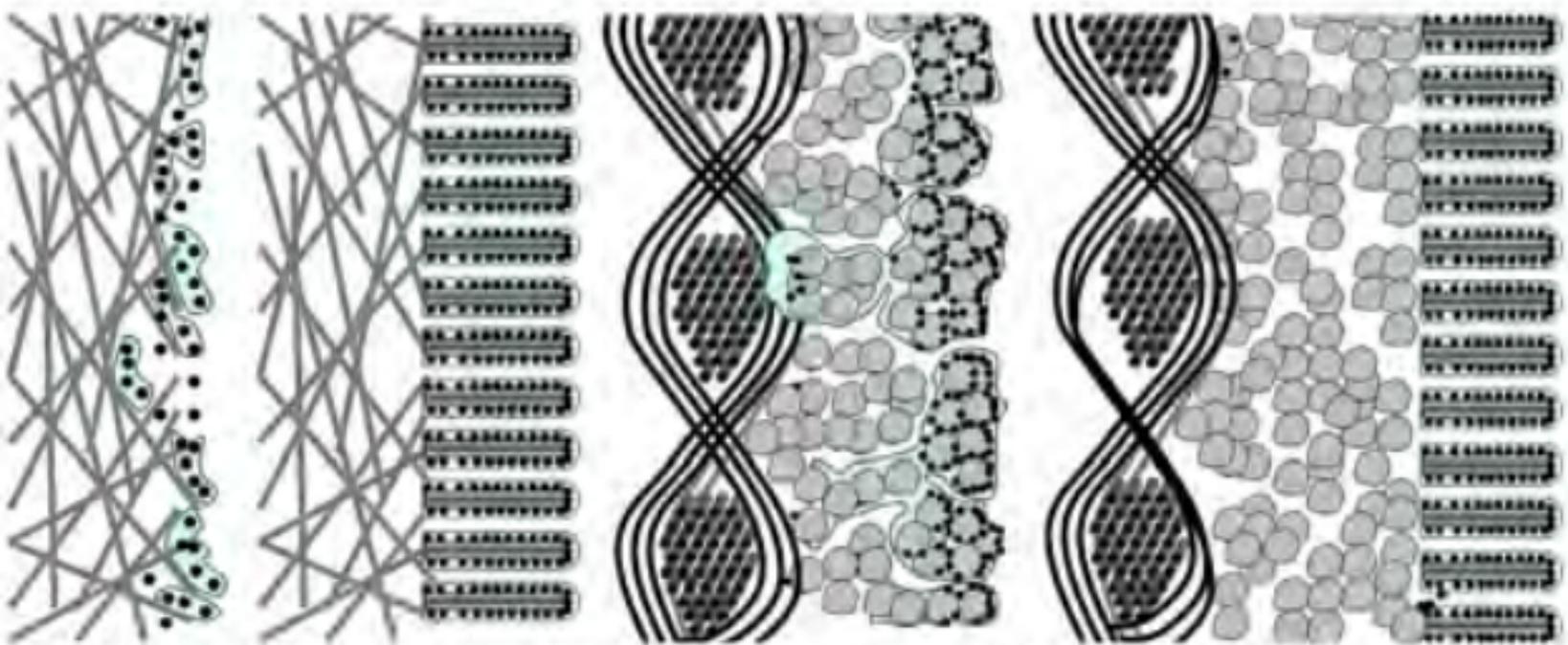
FIG. 5: Cell voltage  $E$  vs. current density  $j$  curves for the four prepared electrode schematized in Fig.2: (a) Pt / carbon paper, (b) Pt / CNFs / carbon paper, (c) Pt / GDL, and (d) Pt / CNFs / GDL. The PEMFC surface area is  $5 \text{ cm}^2$  and the Pt loading is  $0.02 \text{ mg cm}^{-2}$ .

( $P_{\text{H}_2} = 3 \text{ bars}$ ;  $\text{H}_2 \text{ flow} = 100 \text{ sccm}$ ;  $P_{\text{O}_2} = 3 \text{ bars}$ ;  $\text{O}_2 \text{ flow} = 100 \text{ sccm}$ ,  $T_{\text{cell}} = 80^\circ\text{C}$ , Membrane Nafion<sup>®</sup> 115)

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(a)

(b)

(c)

(d)

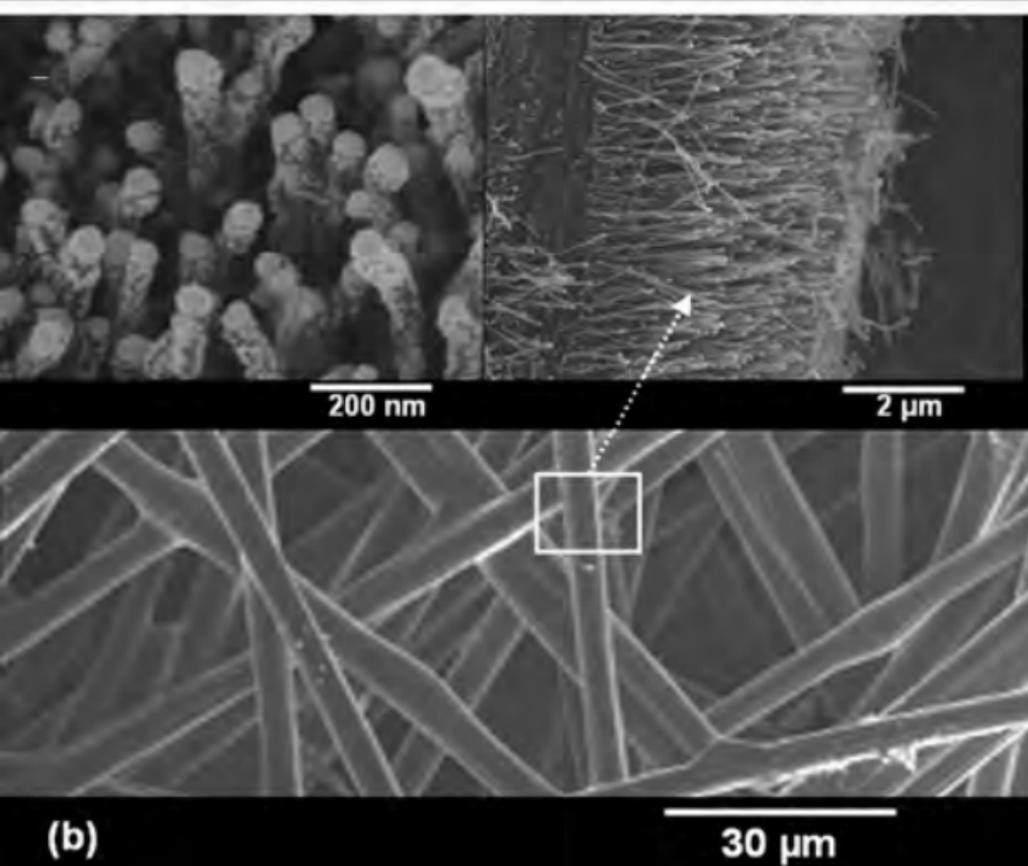
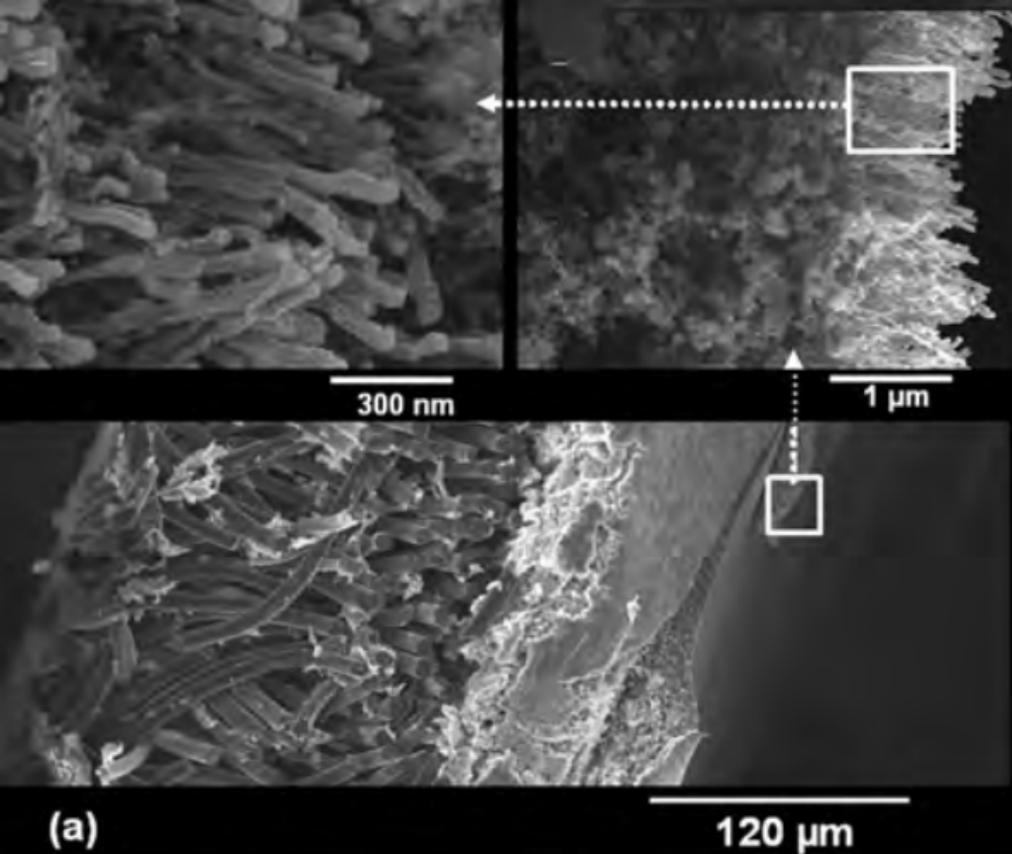
 Pt nanoparticles  
 Carbon particle





Carbon nanofiber surrounded by Pt nanoparticles and Nafion

Carbon particle surrounded by Pt nanoparticles and Nafion



(b)

200 nm

$\varnothing_{\text{Pt}} = 8 \text{ nm}$

$\varnothing_{\text{Pt}} = 5 \text{ nm}$

$\varnothing_{\text{Pt}} = 3 \text{ nm}$

(a)

40 m

