This item is the archived peer-reviewed author-version of:

Electrodeposition of highly porous Pt nanoparticles studied by quantitative 3D electron tomography : influence of growth mechanisms and potential cycling on the active surface area

Reference:

Ustarroz Jon, Geboes Bart, Vanrompay Hans, Şentosun Kadir, Bals Sara, Breugelmans Tom, Hubin Annick.- Electrodeposition of highly porous Pt nanoparticles studied by quantitative 3D electron tomography : influence of growth mechanisms and potential cycling on the active surface area

ACS applied materials and interfaces - ISSN 1944-8244 - 9:19(2017), p. 16168-16177

Full text (Publisher's DOI): <https://doi.org/10.1021/ACSAMI.7B01619>

To cite this reference: <http://hdl.handle.net/10067/1423450151162165141>

Electrodeposition of Highly Porous Pt Nanoparticles Studied by Quantitative 3D Electron Tomography: Influence of Growth Mechanisms and Potential Cycling on the Active Surface area

Jon Ustarroz,^{*,†} Bart Geboes,[‡] Hans Vanrompay,[¶] Kadir Sentosun,[¶] Sara Bals,[¶]
Tom Breugelmans,[‡] and Annick Hubin[†]

[†]*Vrije Universiteit Brussel (VUB), Research Group Electrochemical and Surface Engineering (SURF), Pleinlaan 2, 1050 Brussels, Belgium*

[‡]*Research Group Advanced Reactor Technology (ART), University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium*

[¶]*Electron Microscopy for Materials Research (EMAT), University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

E-mail: justarro@vub.ac.be

Abstract

Nanoporous Pt nanoparticles (NPs) are promising fuel cell catalysts due to their large surface area and increased electrocatalytic activity towards the oxygen reduction reaction (ORR). Herein, we report on the influence of the growth mechanisms on the surface properties of electrodeposited Pt dendritic NPs with large surface areas. The electrochemically active surface was studied by hydrogen underpotential deposition (H

UPD) and compared for the first time to high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) quantitative 3D electron tomography of individual nanoparticles. Large nucleation overpotential leads to a large surface coverage of Pt roughened spheroids, which provide large roughness factor (R_f) but low mass-specific electrochemically active surface area (EASA). Lowering the nucleation overpotential leads to highly porous Pt NPs with pores protruding to the center of the structure. At the expense of smaller R_f , the obtained EASA values of these structures are in the range of these of large surface area supported fuel cell catalysts. The active surface area of the Pt dendritic NPs was measured by electron tomography and it was found that the potential cycling in the H adsorption/desorption and Pt oxidation/reduction region, which is generally performed to determine the EASA, leads to a significant reduction of that surface area due to a partial collapse of their dendritic and porous morphology. Interestingly, the extrapolation of the microscopic tomography results to macroscopic electrochemical parameters indicated that the surface properties measured by H UPD are comparable to the values measured on individual NPs by electron tomography after the degradation caused by the H UPD measurement. These results highlight that the combination of electrochemical and quantitative 3D surface analysis techniques is essential to provide insights into the surface properties, the electrochemical stability and, hence, the applicability of these materials. Moreover, it indicates that care must be taken with widely used electrochemical methods of surface area determination, especially in the case of large surface area and possibly unstable nanostructures, since the measured surface can be strongly affected by the measurement itself.

Keywords

platinum, nanoparticle, electrodeposition, nanoporous, stability, hydrogen UPD, electron tomography

1 Introduction

It is widely known that nanostructured materials are one of the key elements in the recent advances of various technological fields. More precisely, energy conversion devices (fuel cells, batteries, solar cells, etc) have seen their efficiency boosted thanks to the engineering of materials in the nanoscale.¹ In addition to improving physico-chemical properties, bringing the characteristic dimensions of the materials to the nanoscale allows a dramatic increase of the surface area for the same amount of material. This is especially relevant for many energy conversion processes, since they are based on phenomena occurring at the interface between a solid surface and a given medium. The efficiency of these processes depends on many factors. Among them, increasing the surface to volume ratio (SVR) of the active materials is sought after in most energy conversion technologies. Moreover, large active surface areas are also targeted for highly sensitive (bio)sensors.^{2,3} Hence, optimizing the surface properties of nanostructured materials is of great interest.

More specifically, the performance/cost ratio of proton-exchange membrane fuel cells is mostly limited by the efficiency of the cathodic oxygen reduction reaction (ORR).^{4,5} In this context, platinum is known to be the most effective mono metallic catalyst to facilitate the reaction. Hence, current fuel cell cathode catalyst standards consist of platinum nanoparticles (NPs) supported on large surface area carbon materials.^{4,6,7} Nonetheless, efforts are being made to improve their catalytic performance by keeping the cost to the minimum.

The approach is normally twofold. On the one hand, the intrinsic properties of the surface need to be improved. In the case of the ORR process, this means that the specific activity of the electrochemically active surface needs to be increased. The use of alloys,⁸⁻¹⁰ core-shell NPs,¹¹⁻¹³ high-index crystallographic planes¹⁴ or localized defects in specific positions within the crystal structure¹⁵⁻¹⁷ has been proven to enhance the specific electrochemical activity towards the ORR. On the other hand, provided the intrinsic properties of the active surface have been optimized, the amount of surface available for a given amount of material, i.e., the mass-specific surface area (MSSA), also known as electrochemically active surface area

(EASA), also needs to be maximized. Besides, due to miniaturization needs, it becomes necessary to make the best use of the active surface within a given volume. Extensive literature and review articles are available about the enhancement of the intrinsic specific activity of Pt based materials.¹¹ This will not be addressed in this article. Contrarily, this work is focused on investigating possibilities to enhance the available catalytic surface for a given amount of material and within a given volume. In this context, a special emphasis is given to the methodology used to evaluate this surface.

Current Pt-based fuel cell cathode catalyst standards consist of platinum NPs supported on large surface area carbon materials and feature a MSSA between 30 and 90 m²/g_{Pt}.^{4,7,9} In this case, a large surface area support is decorated with small nanoparticles (few nm in diameter) of the active material. Recently, several approaches have been proposed to improve these values. On the one hand, different large surface area supports with improved properties are being investigated.¹⁸ Some examples are carbon nanotubes,^{19–23} TiO₂ nanofibres,²⁴ mesoporous carbon²⁵ or graphene sheets.^{23,26,27} Another possibility is to increase the MSSA and the ratio between real and geometric area (RRGA) of the Pt nanostructured material. This can be achieved by using nanoparticle agglomerates,²⁸ dendritic or highly-porous nanostructures^{23,29–31} and meso-structured platinum thin films.^{32,33} They conserve size-specific properties (MSSA and specific activity), while they form three-dimensional structures with a large surface area and a high concentration of surface defects.²⁸ Because of their three-dimensional nature, higher RRGA values are obtained.^{23,31} Therefore, large surface area carbon supports, which can degrade quickly under operating conditions,³² are no longer needed. In addition, these structures do not suffer from active area loss due to agglomeration under operating conditions, as it is the case for supported NPs.³⁴

The synthesis of this kind of material by a chemical approach has been widely reported and a strong mechanistic understanding of their formation exists.^{30,31,35,36} However, when Pt NPs are loaded on large surface area carbon supports, only a fraction of them participates in the electrochemical reaction of interest. Alternatively, electrochemical deposition ensures

that the catalyst material is only deposited on the regions of the substrate which are later accessible for the ORR or any other reaction. Therefore, by effectively using all the catalyst material, the performance/cost ratio of the fuel cell devices can be increased. Furthermore, electrochemical deposition allows the growth of the nanostructures directly on the final support improving electron transfer between the substrate, nanostructure and electrolyte. Therefore, electrochemical deposition has been proven effective to synthesize highly active nanostructures.^{14,23,28,32,33} However, a lack of understanding of the electrochemical nucleation and growth mechanisms of porous Pt NPs, has considerably shifted the research efforts to other synthesis methods.

It was recently shown that dendritic NPs with $\text{RRGA} \approx 7$ and $\text{MSSA} \approx 68 \text{ m}^2/\text{g}_{\text{Pt}}$ could be obtained by a simple potentiostatic single pulse deposition procedure.²⁹ These magnitudes have been recently reported to reach higher values ($\text{RRGA} \approx 10$) by electrodepositing Pt porous NPs by cyclic voltammetry.²³ In addition, it was also reported that highly porous Pt NPs prepared by a potentiostatic double pulse featured initial mass corrected activities of $0.1 \text{ A}/\text{mg}_{\text{Pt}}$ at 0.85 V vs RHE. In the latter case, two electrodeposition procedures were examined and their inner porosity, electrochemical activity towards the ORR and degradation after harsh fuel cell start-up conditions (2000 oxidation/reduction cycles) were evaluated citeGeboes2016.

Alternatively, in this work, we explore different electrochemical deposition procedures and experimental conditions to obtain distributions of Pt nanostructures with large surface areas. Furthermore, to evaluate the available Pt surface, in addition to conventional hydrogen underpotential deposition (H UPD), we use high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and quantitative 3D electron tomography. In this way, we can directly evaluate, with a high precision, the surface area of single NPs. The comparison between microscopically obtained values and electrochemical surface area measurements proves to be crucial for a correct evaluation of the active surface. As a consequence, it provides insights into the applicability of H UPD methods and the electro-

chemical stability of large surface area Pt nanostructures.

2 Experimental

2.1 Electrochemical measurements

An Autolab PGSTAT 302N potentiostat was used for the electrodeposition experiments and for the electrochemical characterization by cyclic voltammetry. A jacketed glass cell with a three-electrode setup was used in all electrochemical measurements. The temperature was kept constant at 25°C by using a thermostat. The working electrode consisted of a glassy carbon rotating disc (6 mm diameter), whereas Ag/AgCl was used as reference electrode and a Pt mesh as counter electrode. All potentials are reported against the Ag/AgCl reference electrode.

The glassy carbon substrate was pretreated by successive polishing using 1 μm , 0.3 μm and 0.05 μm alumina powder (Struers) suspended in ultra pure water (18.2 M Ω cm, Merck MilliPore). The electrodes were then subsequently sonicated in isopropanol (Acros, HPLC grade) and ultra pure water for 5 minutes. All electrochemical deposition experiments were carried out using a solution of 1 mM H_2PtCl_6 (Alfa Aesar, ACS grade) + 0.1 M KCl (Alfa Aesar, ACS grade). The pH of the solutions was modified by adding either KOH or HCl and was measured prior to all depositions. After adjusting the pH, the solutions were deaerated with N_2 for 2h. A nitrogen blanket was maintained on top of the solution during the electrochemical deposition experiments. When needed, the working electrodes were rotated using a Radiometer EDI-101 rotating disc electrode (RDE).

The EASA was evaluated through H UPD measurements. The three electrode configuration was adapted to fit a Luggin capillary, whereas other parameters were kept constant compared to the deposition setup. The electrolyte solution (0.1 M HClO_4 , Merck Emsure) was saturated with N_2 (99.999 %) during 15 minutes before the electrochemical measurements and a nitrogen blanket was maintained over the aqueous electrolyte during the mea-

surements.

2.2 Morphological and structural characterization

Ex-situ morphological characterization of the electrodeposited NPs was performed using a JEOL JSM-7000F field emission scanning electron microscope (FESEM) operated at 20kV. The particle distribution descriptors (average diameter, particle density and surface coverage) were calculated by analyzing 5 to 10 FESEM images per electrode with Image J. Three electrodes were imaged for each set of deposition parameters.

To perform transmission electron microscopy (TEM) analysis on as-electrodeposited NPs, carbon coated TEM grids (EMS, 300mesh, CF 300Au) were used as electrochemical working electrodes as described elsewhere.^{38,39} HAADF-STEM images were acquired using a FEI Tecnai G2 and Tecnai Osiris microscope operated at 200 kV. For electron tomography, the samples were mounted on a Fischione tomography holder (model 2020) and were tilted over an angular range of $\pm 74^\circ$ with a 3° increment. During the acquisition, a convergence semi-angle of 8 mrad was used in combination with inner and outer convergence angles of 66 mrad and 180 mrad, respectively, to ensure that the projection requirement was fulfilled.

These tilt series were used as input for the total variation minimization (TVM) reconstruction algorithm,⁴⁰ giving rise to three dimensional reconstructions of individual NPs. The obtained reconstructions were segmented and quantified using a tailor-made quantification procedure, implemented in MATLAB. During the segmentation step, voxels were classified as either platinum or void space. Afterwards the segmented reconstruction was analyzed in a three dimensional manner to further classify the voxels corresponding to the void space, based on the presence of a connection to the exterior or the lack thereof.³⁷

3 Notes on surface properties and electrochemically active surface measurement methods

When describing the surface properties of supported nanostructures, several magnitudes are used throughout the literature. Sometimes, different acronyms are employed to represent the same magnitude. To avoid confusion and for the sake of clarity, we present here a brief description of these magnitudes, their practical meaning, the ways to characterize them and the relation between them. Figure 1 is a schematic diagram that shows the surfaces that are considered to calculate some of the most employed surface area descriptors.

Figure 1: Schematic representation of some of the magnitudes used for the description of the electrochemically active surface area: (a) ratio between real and geometric area (RRGA), (b) surface coverage (SC) and (c) roughness factor (R_f). The marked region in green represents the area used in the calculations. The area used in the nominator is shown at the top of the figure, while the denominator is shown at the bottom.

Firstly, the ratio between real and geometric area (RRGA) [$\text{cm}^2 \text{ Pt} / \text{cm}^2 \text{ projected}$] describes how much active surface area is three-dimensionally available relative to the two-dimensional projection of the given NPs on the electrode. In most of the cases, this adimensional parameter depends only on the particle morphology. For spherical and hemispherical particles, the RRGA is 4 and 2, respectively, independently of the particle size. The RRGA of nanorods and nanotubes is almost proportional to the double and quadruple of their respective aspect ratio. However, for porous or dendritic NPs, the RRGA depends on more parameters, such as porosity, branch dimensions, etc. It was recently shown that, provided that dendritic particles of different sizes have similar morphological features, their porosity and SVR are independent of their size. As a result, the RRGA increases linearly with the

particle radius, being the constant of proportionality dependent on the porosity and SVR.²⁹ From a technological point of view, increasing this parameter is essential to hold as much active area as possible on a small electrode surface.

Secondly, the mass-specific surface area (MSSA), more commonly reported as electrochemically active surface area (EASA) [$\text{cm}^2 \text{ Pt} / \text{g Pt}$], describes the ratio between the active catalyst surface area and the mass of material. Similar to the previous magnitude, it depends only on the particle morphology and on the particle size. From a technological point of view, increasing this parameter is essential to reduce material costs. For simplicity, only the acronym EASA will be used hereafter to refer to this magnitude.

Thirdly, the surface coverage (SC), normally given as a percentage, describes the amount of electrode surface that is covered by active material. This magnitude does not depend on the particle morphology but only on the particle size and particle number density. Similar to the RRGa, increasing this parameter is beneficial to hold enough active area on a given electrode surface.

Fourthly, the surface to volume ratio (SVR) [nm^{-1}], which can be computed by electron tomography reconstructions, is used to describe the shape of individual NPs and as a measure of porosity. This value is related to the EASA by equation 1.

$$SVR = EASA \times \rho \times 10^{-7} \quad (1)$$

with ρ being the density of the material in g/cm^3 . For Pt, a density of $21.45 \text{ g}/\text{cm}^3$ is assumed.

Eventually, another magnitude is derived from the combination of the mentioned factors. The roughness factor (R_f) [$\text{cm}^2 \text{ Pt} / \text{cm}^2 \text{ geometric}$], which describes the available active surface with respect to the geometric electrode area, depends on the particle number density, size and morphology. The Pt loading [$\text{g Pt} / \text{cm}^2 \text{ geometric}$] is another measure of the amount of catalyst available for a given electrode area. These magnitudes are related by equations

2 and 3.

$$R_f = \text{RRGA} \times \text{SC} \quad (2)$$

$$\text{EASA} = R_f / \text{Pt loading} \quad (3)$$

To effectively use the catalytic material, the particle density, size and morphology need to be optimized to reach EASA, RRGA and SC values as high as possible. The standard approach is to obtain high RRGA values through the use of porous carbon supports and high EASA values through the use of small ($d \approx 2 - 3$ nm) Pt nanoparticles (NPs). The SC and consequently R_f are then determined by the Pt NP loading on the porous carbon support.

It must be pointed out that these magnitudes are measured experimentally using a multitude of methods. Indirect approaches are the most common, H UPD⁴¹ and CO stripping⁴² being the most frequently used. However, it has been shown that these methods may show a large deviation from the real surface area.⁴¹ Alternatively, measuring surface areas in a direct manner by high resolution microscopy is desirable. Electron tomography allows determining the surface properties of particles for virtually any shape.^{43,44} Therefore, the technique is of great interest for obtaining quantitative information of irregular and dendritic nanostructures and, more generally, to assess the correctness of indirect methods. An important point to consider here is that both H UPD and CO stripping methods provide the total available surface area, which is then related to the average morphology of the Pt NPs. On the other hand, electron tomography provides values for single NPs and, hence allows individual properties of different NPs within the distribution to be distinguished. In the following sections, the comparison between these two methodologies for electrodeposited Pt dendritic NPs is discussed.

4 Results and discussion

4.1 Electrochemical deposition of Pt dendritic NPs: towards high particle density conserving a highly porous morphology

It has been recently shown that highly porous Pt NPs featuring a large RRGa could be electrodeposited from a 1 mM hexachloroplatinic acid solution (pH 2.7) by a simple potentiostatic single pulse approach.²⁹ To obtain high porosity, it was suggested that Pt deposition should occur at potentials at which H is adsorbed on the Pt surface, but positive enough so that the adsorbed hydrogen would not evolve into H₂, as this would reduce the porosity of the NPs. Besides, up to a given diameter, the open porosity of these type of particles is assumed to be size independent, so their RRGa increases linearly with their radii.²⁹ Therefore, large particles (up to 100-200 nm) are sought after. One problem is that at potentials that maximize the porosity (and hence the RRGa), the overpotential for Pt reduction is relatively small, so the obtained particle densities are very small ($\approx 10^8$ particles/cm²).^{29,45} Therefore, although a large RRGa is obtained, SC and R_f values are very low.

As the hydrogen reduction reactions play an important role on the morphology of the Pt NPs, it seems reasonable to foresee that pH would have an important effect in the relation between deposition potential and particle morphology. For higher pH values, the regions of H adsorption and reduction into H₂ are shifted to more negative potentials. This allows keeping a highly porous particle morphology while applying larger overpotentials for Pt reduction and hence obtaining larger particle densities. It was previously shown that using a hexachloroplatinic acid solution with a natural pH of 2.7 led to less porous particles when applying potentials more negative than -0.2 V vs Ag/AgCl. However, increasing the pH to 6 allows highly porous particles to be obtained at potentials as negative as -0.4 V vs Ag/AgCl.³⁷ Consequently, in the experiments described in this manuscript, the pH of the solution is kept at 6.

Another common approach to increase particle density is to apply a short pulse of very

large overpotential to nucleate a large population of NPs, followed by a long pulse of small overpotential.^{46,47} This approach is generally referred to as potentiostatic double pulse. In this specific case, the idea behind this approach is to obtain a high number density of small NPs, which, even if they are not highly porous, will serve as seeds that will develop into larger dendritic structures during the growth pulse at small overpotential.

Figure 2: Representative FESEM images of Pt NPs electrodeposited under (a) stagnant conditions and a double pulse ($E_n = -0.6 \text{ V} / t_n = 20 \text{ s}$ and $E_g = -0.1 \text{ V} / t_g = 200 \text{ s}$), (b) forced convection and a double pulse ($\omega = 700 \text{ rpm}$ and $E_n = -0.6 \text{ V} / t_n = 20 \text{ s}$ and $E_g = -0.1 \text{ V} / t_g = 200 \text{ s}$) and (c) forced convection and a single pulse ($\omega = 700 \text{ rpm}$ and $E_n = -0.4 \text{ V} / t_n = 200 \text{ s}$).

Besides, provided the electrodeposition process is diffusion controlled, particle density can be increased by forcing the convection of Pt ions towards the surface. A controlled flow towards the electrode surface can be accomplished by using an RDE. Representative FESEM images of NPs electrodeposited by single and double pulses, with and without rotation, are shown in Figure 2. It can be seen that applying forced convection using an RDE together with a potentiostatic double pulse (Figure 2b) yields a larger SC. This procedure is then selected for further study.

4.2 Influence of potentiostatic double pulse deposition parameters on the surface properties of electrodeposited Pt NPs

In the current section, we describe the influence of the deposition parameters on the surface properties of the electrodeposited nanostructures. Nucleation potentials (E_n) of -0.6 V, -0.5 V and -0.4 V were chosen, whereas growth potentials (E_g) were either -0.1 V or -0.2 V. Different particle sizes, particle densities and surface coverages were obtained by varying nucleation and growth times (see Figure S1 of the Supporting Information).

Figure 3: (a) Evolution of average particle diameter in function of surface coverage for different nucleation and growth potentials and deposition times, using an RDE rotating at $\omega = 700$ rpm. The arrows indicate the trend when increasing deposition time. Representative FESEM images after electrodeposition with (b) $E_n = -0.6$ V, $t_n = 50$ s, $E_g = -0.1$ V, $t_g = 100$ s; (c) $E_n = -0.6$ V, $t_n = 50$ s, $E_g = -0.2$ V, $t_g = 200$ s; (d) $E_n = -0.5$ V, $t_n = 20$ s, $E_g = -0.1$ V, $t_g = 100$ s; (e) $E_n = -0.5$ V, $t_n = 20$ s, $E_g = -0.2$ V, $t_g = 200$ s.

The evolution of the average particle diameter versus the SC for different nucleation and growth potentials is summarized in Figure 3a. This representation is chosen over displaying these magnitudes versus deposition time, since both the RGA, which depends on the particle diameter, and the SC need to be maximized to efficiently use the catalytic material. Error bars indicate the standard deviation of the particle size distribution in each respective set of deposition parameters. Figures 3b to 3e are representative FESEM images of some of the deposition procedures represented in Figure 3a. It can be seen that, in order to obtain a

large SC, more negative nucleation potentials are needed. The effect of the growth potential is stronger when the nucleation potential is less negative. For $E_n = -0.6$ V, both $E_g = -0.1$ V and $E_g = -0.2$ V result in similar coverages of particles of comparable size (Figures 3b and 3c). This is due to the fact that a high nucleation density leads to a SC between 60% and 70%. This results into particle coalescence after a given growth time, regardless of the growth potential. However, when the nucleation potential is less negative (-0.4 V or -0.5 V), a smaller SC is obtained for particles of similar size, $d = 100$ - 150 nm (Figures 3d and 3e). As a consequence, a more negative growth potential, $E_g = -0.2$ V (Figure 3e), leads to larger particles and larger coverages than for $E_g = -0.1$ V (Figure 3d).

Figures 4a and 4b show representative HAADF-STEM images of Pt NPs electrodeposited with $E_n = -0.4$ V and $E_n = -0.6$ V, respectively. In both cases a porous dendritic morphology is depicted, albeit more pronounced in the particle obtained with a less negative potential. In this case, a less compact structure is formed with higher porosity and thinner Pt branches. This morphology is very similar to the one reported for Pt grown under a single potentiostatic pulse at $E_n \geq -0.2$ V with pH 2.7.²⁹ This confirms the hypothesis that the growth mechanism of Pt electrodeposited from a hexachloroplatinic bath is strongly affected by the H adsorption and reduction reactions. In the present study, the pH is sufficiently high so that the proton reduction reactions are shifted to more negative potentials and the Pt growth, at $E_n = -0.4$ V, is still limited by adsorbed hydrogen. This results into highly dendritic structures such as the one depicted in Figure 4a.

The fact that the NPs resulting from a more negative nucleation potential ($E_n = -0.6$ V) are more compact and have thicker branches is confirmed in Figure 4b. Still, the morphology is more dendritic than the one previously reported for single pulse electrodeposition with $E_n = -0.6$ V.²⁹ This can be explained as follows. When $E_n = -0.6$ V is applied, Pt nanostructures are expected to initially grow by the aggregation of small nanoclusters, whose growth is only partially limited by hydrogen adsorption.^{29,48} Since proton reduction occurs also at this potential, coalescence of Pt nanoclusters and growth by direct attachment is favored. This

Figure 4: Representative HAADF-STEM images of Pt dendritic NPs obtained at (a) $E_n = -0.4$ V, $t_n = 50$ s, $E_g = -0.1$ V, $t_g = 50$ s and (b) $E_n = -0.6$ V, $t_n = 50$ s, $E_g = -0.2$ V, $t_g = 100$ s; using a carbon coated TEM grid supported on an RDE rotating at $\omega = 700$ rpm.

results in irregular structures with a low level of porosity. However, when the growth proceeds at smaller overpotential, proton reduction does not occur, limiting coalescence and growth by direct attachment. Therefore, these particles exhibit an intermediate degree of porosity.

Figure 5 shows R_f (a), RRGa (b) and EASA (c) as a function of particle size for different nucleation and growth potentials. R_f was calculated by the H UPD method (see experimental section). The SC and particle size were inferred from FESEM analysis. Hence, the RRGa was then obtained through equation 2. R_f increases as the particle size (and thus SC) increases. Therefore, in order to attain a large R_f , more negative nucleation potentials are needed. To evaluate specific surface properties, independent of the SC, one has to look at the evolution of the RRGa with diameter. The RRGa increases linearly with particle diameter. This is an indication of the dendritic morphology of the particles. For non dendritic structures, the RRGa would remain constant, independent of the particle diameter. It is also interesting to note that, contrarily to the trend followed by R_f , the increase of the RRGa with diameter is stronger for less negative nucleation potentials. This is an indication of the influence of the nucleation potential on the dendritic morphology of the Pt NPs. The dashed blue lines represent the range of benchmark values for commercial fuel cell catalysts containing Pt NPs loaded on porous carbon.^{4,7} R_f values of the depositions with large overpotential, $E_n = -0.6$ V, are well in the range of the reference values. For the deposition with $E_n = -0.4$ V, the obtained values are approximately five times lower. This is

Figure 5: Evolution of (a) R_f , (b) $RRGA$ and (c) $EASA$ with particle diameter for different nucleation and growth potentials and deposition times, using an RDE rotating at $\omega = 700$ rpm. Green and blue dashed lines represent values obtained from mesoporous films³² and commercial Pt NP catalysts over large surface area supports,^{4,7} respectively.

due to the low SC obtained with these deposition procedures and it could be improved for practical applications by means of a multiple pulse⁴⁹ deposition procedure using an identical nucleation potential. For $E_n \leq -0.5$ V, the ratio at which the RRGAs increase with diameter, and hence the SVR of the deposited nanostructures, is smaller than previously predicted.²⁹ This is not the case for $E_n = -0.4$ V. This confirms that the application of a more negative nucleation potential favors the formation of more compact structures (see Figure 4).

In fact, this is also reflected when computing the EASA. Figure 5c shows the evolution of the EASA with average particle diameter for different electrodeposition parameters. The dashed lines represent benchmark values for two different cases: Pt small NPs loaded on porous carbon^{4,7} and Pt mesoporous films.³² The Pt loading and the EASA have been computed by analysis of FESEM images, assuming that the particles have an oblate ellipsoid geometry where the length of the z axis is 60% of the length of the x and y axes. A porosity of 25% has been used for the calculations. This approach was previously validated and the Pt mass calculated showed to be accurate (less than 15% error) when compared with ICP-MS analysis of stripping experiments.³⁷

From Figure 5c it can be inferred that higher EASA values are obtained for less negative nucleation potentials, independent of the applied growth potential. A less negative nucleation potential implies less compact Pt nuclei, which develop into particles with a more emphasized dendritic morphology. This, in turn, favors both the EASA and the RRGAs. It can be seen that the porous Pt NPs grown at a nucleation potential of -0.4 V, with an average diameter of approximately 90 nm, offer an EASA value which is in the range of carbon supported fuel cell electrocatalysts.^{4,7} This is especially relevant because this Pt morphology allows avoiding the use of a large surface area support and provides similar or even larger Pt active surface. Although the application of larger overpotentials has been found beneficial for R_f , applying smaller nucleation overpotentials is more beneficial in terms of the RRGAs and EASA, since the resulting nanostructures feature a larger SVR and, hence, a larger active surface area per mass. A possibility to enhance R_f without compromising RRGAs and EASA could be to

apply multiple nucleation pulses⁴⁹ at $E_n = -0.4$ V.

An important aspect that must be taken into account is the experimental procedure employed for the determination of the Pt surface and the consequent surface properties of the Pt NP distribution. The values shown in Figure 5 were obtained by H UPD. Alternatively, electron microscopy analysis (in particular TEM) was also used on a reduced number of particles. In principle, the H UPD method should be more representative because the whole electrode is measured. However, if a sufficient number of particles is evaluated by microscopy, the inferred surface area properties should be representative for the whole electrode area. Both methods are compared in the following section.

4.3 Surface area properties by electron tomography

Two electrodeposition procedures were selected to evaluate the Pt surface properties by microscopical techniques. The selected nucleation potentials were -0.6 V and -0.4 V, whereas the growth potentials were -0.2 V and -0.1 V, respectively. Figure 6 shows representative visualizations of 3D reconstructions of Pt NPs electrodeposited with nucleation potentials of $E_n = -0.4$ V (a-d) and $E_n = -0.6$ V (e-h). Electron tomography was carried on the same samples before and after electrochemical cycling. Figures on the left hand side show the morphology of the NPs before electrochemical cycling and figures on the right hand side show the morphology of the NPs after 600 potential cycles in the H adsorption/desorption and Pt oxidation/reduction region (0 V to 1.4 V vs. RHE).

The first striking result is that, for both electrodeposition procedures, the morphology of the Pt nanostructures changes drastically after successive oxidation/reduction cycles. In both cases, the nanostructures become more compact, their branches get thicker and the amount of open pores decreases significantly. It is important to emphasize that these results indicate that *the available Pt surface changes as a consequence of using an electrochemical method to measure it*, i.e., measuring the H UPD during electrochemical cycling in an acidic solution. This information, which could not have been obtained if an alternative method

Figure 6: Representative visualization of a 3D reconstruction of a Pt NP electrodeposited with $E_n = -0.4$ V (a) before and (b) after electrochemical cycling. Representative orthoslice of a Pt NP electrodeposited with $E_n = -0.4$ V (c) before and (d) after electrochemical cycling. Representative visualization of a 3D reconstruction of a Pt NP electrodeposited with a $E_n = -0.6$ V (e) before and (f) after electrochemical cycling. Representative orthoslice of a Pt NP electrodeposited with $E_n = -0.6$ V (g) before and (h) after electrochemical cycling. For both electrodeposition procedures, a carbon coated TEM grid was supported on an RDE rotating at $\omega = 700$ rpm.

(electron tomography) had not been employed, is extremely relevant to assess the correctness of the H UPD method to evaluate the electrochemically active surface area, especially in the case of large surface area and possibly unstable nanostructures. Electrochemically driven nanocluster aggregation,^{45,50,51} and coalescence^{29,52} at the nanoscale have been reported many times for Pt and other metals. This is a common problem that is mostly reported in studies about catalyst degradation upon electrochemical processes.⁵³ Therefore, it is not that surprising that the morphology of highly active Pt nanostructures would be modified by hydrogen adsorption/desorption processes and the formation and reduction of platinum oxides during the electrochemical cycling. Similar degradation processes have been recently reported by identical location transmission electron microscopy.^{52,54}

Figure 7 shows the calculated SVR (a) and RRGa (b) as a function of the NP diameter, as calculated from the electron tomography reconstructions. Each data point corresponds to the SVR and RRGa obtained from the 3D reconstruction of a single NP. Several particles have been analyzed either as-electrodeposited, or after H UPD measurements were carried out.

Before electrochemical cycling, particles electrodeposited with $E_n = -0.4$ V have higher SVR and RRGa than these obtained with $E_n = -0.6$ V. In the former case, the RRGa increases linearly with particle diameter. Besides, although the data has a large scatter, the SVR remains more or less constant around $2-3 \text{ nm}^{-1}$. The evolution of both these parameters with particle size confirms the hypothesis that the porous dendritic morphology of the NPs is maintained, even after long deposition times²⁹ (see HAADF-STEM image in Figure 4a and the 3D reconstruction in Figure 6a). In fact, a SVR value of 3 is expected for a spherical NP of 1 nm of radius ($\text{SVR} = 3/r$ for a sphere). The fact that we obtain a SVR of around 2-3 for particles of a much larger diameter is an indication of their dendritic morphology, with branches only several nm thick. This proves that with the appropriate conditions, Pt nanostructures can be grown to large sizes while conserving an open dendritic morphology. For the particles electrodeposited with more negative nucleation potentials ($E_n = -0.6$ V),

the RRGAs remain almost constant around 10 (it increases linearly with a very small slope). Accordingly, the SVR decreases exponentially when the diameter increases. For a solid spheroid, the RRGAs would be constant regardless of the diameter (2 for a hemisphere, 4 for a sphere) and the SVR will be inversely proportional to its size ($SVR = 3/r$ for a sphere). Therefore, the evolution of these parameters for nanostructures electrodeposited with $E_n = -0.6$ V indicates that the dendritic structure is not maintained when the particles grow to a certain size and that their surface properties would more resemble those of a roughened solid spheroid than those of a dendritic structure. However, it must be noted that, even for these roughened spheroids, obtained at $E_n = -0.6$ V, the SVR is about one order of magnitude larger than that of a solid hemisphere (Figure 7a, dashed line). This indicates the ability of these dendritic nanostructures to offer very large surface areas for their size.

Very importantly, as visualized in Figure 6, the calculated surface properties of the Pt dendritic NPs change during the H UPD measurements. The extent to which their surface is modified depends on the electrodeposition procedure. The change in surface properties upon electrochemical cycling is much more severe for the more dendritic particles with larger surface areas. This is due to the fact that the porous dendritic NPs are thermodynamically much less stable than the more compact ones. Hence, the driving force for surface minimization is much higher. In this case, the SVR decreases from 2-3 to 0.5-1. It can be noted that the SVR slightly decreases with particle size, but not inversely proportionally to its diameter. This means that, although the surface area has diminished by 4 to 6 times, the dendritic structure has not completely collapsed and still provides a decent active area ($RRGA \approx 20-30$). This can be visually depicted in Figure 6b.

Figure 7: Evolution of the (a) SVR and (b) RRGGA with particle diameter, calculated from electron tomography reconstructions before and after H UPD measurements (square markers) and calculated from the H UPD measurements themselves (starred markers). The dashed line in (a) is the calculated SVR for a solid hemisphere. ET: electron tomography.

Accordingly, the RRGGA values also diminish and this effect is more pronounced for larger particles. This can be interpreted in the following way. Even after electrochemical cycling, the RRGGA also increases with diameter, being a proof of the dendritic structure of these NPs. However, the slope of the RRGGA vs d plot decreases and this implies that their open porosity and, hence, their SVR have decreased. Alternatively, for the less porous Pt nanostructures grown at $E_n = -0.6 \text{ V}$, it can be seen that the decrease in both the SVR and RRGGA is less drastic. This is expected and can be seen as roughened spheroids that have been smoothed.

Moreover, Figures 7a and 7b also show the SVR and RRGa measured by the H UPD method for the selected deposition procedures. The RRGa is taken from Figure 5b and the SVR is calculated from the EASA value of Figure 5c by using equation 1. It is interesting to point out that both the RRGa and SVR values measured by H UPD, which are the average of the whole particle distribution over the electrode, are well in line with the values measured on individual NPs by electron tomography *after electrochemical cycling*. Therefore, although the H UPD method is well established for the determination of the Pt surface area, care has to be taken since successive potential cycling in the H adsorption/desorption and Pt oxidation/reduction region leads to a significant reduction of the active surface area due to a partial collapse of the nanoporous morphology.

5 Conclusions

Pt dendritic NPs with large surface area were successfully electrodeposited using a potentiostatic double pulse procedure under forced convection. The electrochemically active surface was studied by H UPD and compared for the first time with HAADF-STEM quantitative 3D electron tomography of individual nanoparticles.

The influence of the nucleation and growth potential on surface related properties relevant for electrocatalysis was studied. It was found that increased surface coverage could be attained under hydrodynamic conditions without losing the control on nanostructure morphology. Hence, a wide range of particle diameters, electrochemically active surface areas and roughness factors were within reach of the proposed potentiostatic deposition procedure. Whereas large roughness factors are attainable for large nucleation overpotentials, the morphologies obtained under these conditions resemble roughened spheroids and, therefore, the surface to volume ratios and mass-specific surface areas are smaller than these of Pt NPs supported on large surface area carbon. By lowering the nucleation overpotential, highly porous Pt nanostructures could be obtained with pores protruding to the center of the

structure. The obtained EASA values of these structures are in the range of these of large surface area supported fuel cell catalysts. However, the low surface coverage of these porous nanostructures needs to be augmented to increase the roughness factor to values comparable to commercial catalysts.

More importantly, studying the surface area of the Pt nanostructured catalysts by electron tomography has led to highly valuable information. Successive potential cycling in the H adsorption/desorption and Pt oxidation/reduction region leads to a significant reduction of the active surface area due to a partial collapse of the open nanopores, which results into more compact and smooth nanostructures. Interestingly, the extrapolation of the microscopic tomography results to macroscopic electrochemical parameters indicates that the surface properties measured by H UPD are comparable to the values measured on individual nanoparticles by electron tomography after the degradation caused by the H UPD measurement. Quantitative 3D surface analysis (HAADF-STEM electron tomography) techniques proved essential not only in correctly evaluating the surface properties and the electrochemical stability of these materials, but also in indicating that care must be taken with widely used electrochemical methods of surface area determination, especially in the case of large surface area and possibly unstable nanostructures, since *the measured surface can be strongly affected by the measurement itself*.

Acknowledgements

Jon Ustarroz acknowledges funding from the Fonds Wetenschappelijk Onderzoek in Flanders (FWO, postdoctoral grant 12I7816N). S. Bals acknowledges funding from the European Research Council (Starting Grant No. COLOURATOMS 335078). S.B. and T.B. acknowledge the University of Antwerp for financial support in the frame of a GOA project. H.V. gratefully acknowledges financial support by the Flemish Fund for Scientific Research (FWO Vlaanderen). All the authors acknowledge Laurens Stevaert for his contribution to the work

presented in this manuscript.

Supporting Information Available

Supporting Information Available: evolution of particle distribution descriptors with deposition parameters.

References

- (1) Aricò, A.; Bruce, P.; Scrosati, B. Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat. Mater.* **2005**, *4*, 366–377.
- (2) Carrara, S.; Ghoreishizadeh, S.; Olivo, J.; Taurino, I.; Baj-Rossi, C.; Cavallini, A.; de Beeck, M. O.; Dehollain, C.; Burleson, W.; Moussy, F. G.; Guiseppi-Elie, A.; de Micheli, G. Fully Integrated Biochip Platforms for Advanced Healthcare. *Sensors* **2012**, *12*, 11013–60.
- (3) Campbell, F. W.; Compton, R. G. The Use of Nanoparticles in Electroanalysis: an updated review. *Anal. Bioanal. Chem.* **2010**, *396*, 241–259.
- (4) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. Activity Benchmarks and Requirements for Pt, Pt-alloy, and non-Pt Oxygen Reduction Catalysts for PEMFCs. *Appl. Catal. B Environ.* **2005**, *56*, 9–35.
- (5) Vielstich, W.; Gasteiger, H. A.; Lamm, A.; Yokokawa, H. In *Handbook of Fuel Cells: Fundamentals, Technology, and Applications*; Vielstich, W., Gasteiger, H. A., Lamm, A., Eds.; John Wiley & Sons Ltd: New York, 2009.
- (6) Mayrhofer, K. J. J.; Strmcnik, D.; Blizanac, B.; Stamenkovic, V. R.; Arenz, M.; Markovic, N. M. Measurement of Oxygen Reduction Activities via the Rotating Disc

Electrode Method: from Pt Model Surfaces to Carbon-Supported High Surface Area Catalysts. *Electrochim. Acta* **2008**, *53*, 3181–3188.

- (7) Shinozaki, K.; Zack, J. W.; Richards, R. M.; Pivovar, B. S.; Kocha, S. S. Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique: I. Impact of Impurities, Measurement Protocols and Applied Corrections. *J. Electrochem. Soc.* **2015**, *162*, F1144–F1158.
- (8) Guo, S.; Zhang, S.; Sun, S. Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction. *Angew. Chemie - Int. Ed.* **2013**, *52*, 8526–8544.
- (9) Guterman, V. E.; Lastovina, T. A.; Belenov, S. V.; Tabachkova, N. Y.; Vlasenko, V. G.; Khodos, I. I.; Balakshina, E. N. PtM/C (M=Ni, Cu, or Ag) Electrocatalysts: Effects of Alloying Components on Morphology and Electrochemically Active Surface Areas. *J. Solid State Electrochem.* **2013**, *18*, 1307–1317.
- (10) Zheng, J. N.; He, L. L.; Chen, C.; Wang, A. J.; Ma, K. F.; Feng, J. J. One-Pot Synthesis of Platinum 3 Cobalt Nanoflowers with Enhanced Oxygen Reduction and Methanol Oxidation. *J. Power Sources* **2014**, *268*, 744–751.
- (11) Guo, S.; Li, D.; Zhu, H.; Zhang, S.; Markovic, N. M.; Stamenkovic, V. R.; Sun, S. FePt and CoPt Nanowires as Efficient Catalysts for the Oxygen Reduction Reaction. *Angew. Chemie - Int. Ed.* **2013**, *52*, 3465–3468.
- (12) Geboes, B.; Vanrenterghem, B.; Ustarroz, J.; Pauwels, D.; Sotiropoulos, S.; Hubin, A.; Breugelmans, T. Influence of the Morphology of Electrodeposited Nanoparticles on the Activity of Organic Halide Reduction. *Chem. Eng. Trans.* **2014**, *41*, 73–78.
- (13) Alia, S. M.; Larsen, B. a.; Pylypenko, S.; Cullen, D. a.; Diercks, D. R.; Neyerlin, K. C.; Kocha, S. S.; Pivovar, B. S. Platinum-Coated Nickel Nanowires as Oxygen-Reducing Electrocatalysts. *ACS Catal.* **2014**, *4*, 1114–1119.

- (14) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* (80-.). **2007**, *316*, 732–5.
- (15) Maciá, M. D.; Campiña, J. M.; Herrero, E.; Feliu, J. M. On the Kinetics of Oxygen Reduction on Platinum Stepped Surfaces in Acidic Media. *J. Electroanal. Chem.* **2004**, *564*, 141–150.
- (16) Kuzume, A.; Herrero, E.; Feliu, J. M. Oxygen Reduction on Stepped Platinum Surfaces in Acidic Media. *J. Electroanal. Chem.* **2007**, *599*, 333–343.
- (17) Chen, S.; Sheng, W.; Yabuuchi, N.; Ferreira, P. J.; Allard, L. F.; Shao-Horn, Y. Origin of Oxygen Reduction Reaction Activity on "Pt₃Co" Nanoparticles: Atomically Resolved Chemical Compositions and Structures. *J. Phys. Chem. C* **2009**, *113*, 1109–1125.
- (18) Shao, Y.; Liu, J.; Wang, Y.; Lin, Y. Novel Catalyst Support Materials for PEM Fuel Cells: Current Status and Future Prospects. *J. Mater. Chem.* **2009**, *19*, 46–59.
- (19) Wang, C.; Waje, M.; Wang, X.; Tang, J.; Haddon, R.; Yan, Y. Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes. *Nano Lett.* **2004**, *4*, 345–348.
- (20) Zhao, Y.; Fan, L.; Zhong, H.; Li, Y.; Yang, S. Platinum Nanoparticle Clusters Immobilized on Multiwalled Carbon Nanotubes: Electrodeposition and Enhanced Electrocatalytic Activity for Methanol Oxidation. *Adv. Funct. Mater.* **2007**, *17*, 1537–1541.
- (21) Sieben, J. M.; Duarte, M. M. E. Nanostructured Pt and PtSn Catalysts Supported on Oxidized Carbon Nanotubes for Ethanol and Ethylene Glycol Electro-Oxidation. *Int. J. Hydrogen Energy* **2011**, *36*, 3313–3321.
- (22) Kim, J.; Lee, S.; Carlton, C.; Shao-Horn, Y. Pt-Covered Multiwall Carbon Nanotubes

- for Oxygen Reduction in Fuel Cell Applications. *J. Phys. Chem. Lett.* **2011**, *2*, 1332–1336.
- (23) Fortunato, G. V.; De Lima, F.; Maia, G. Oxygen-Reduction Reaction Strongly Electrocatalyzed by Pt Electrodeposited onto Graphene or Graphene Nanoribbons. *J. Power Sources* **2016**, *302*, 247–258.
- (24) Savych, I.; Bernard d'Arbigny, J.; Subianto, S.; Cavaliere, S.; Jones, D.; Rozière, J. On the Effect of Non-Carbon Nanostructured Supports on the Stability of Pt Nanoparticles During Voltage Cycling: A Study of TiO₂ Nanofibres. *J. Power Sources* **2014**, *257*, 147–155.
- (25) Su, F. B.; Zeng, J. H.; Bao, X. Y.; Yu, Y. S.; Lee, J. Y.; Zhao, X. S. Preparation and Characterization of Highly Ordered Graphitic Mesoporous Carbon as a Pt Catalyst Support for Direct Methanol Fuel Cells. *Chem. Mater.* **2005**, *17*, 3960–3967.
- (26) Hsieh, C.-T.; Wei, J.-M.; Lin, J.-S.; Chen, W.-Y. Pulse Electrodeposition of Pt Nanocatalysts on Graphene-Based Electrodes for Proton Exchange Membrane Fuel Cells. *Catal. Commun.* **2011**, *16*, 220–224.
- (27) Kou, R.; Shao, Y.; Wang, D.; Engelhard, M. H.; Kwak, J. H.; Wang, J.; Viswanathan, V. V.; Wang, C.; Lin, Y.; Wang, Y.; Aksay, I. a.; Liu, J. Enhanced Activity and Stability of Pt Catalysts on Functionalized Graphene Sheets for Electrocatalytic Oxygen Reduction. *Electrochem. commun.* **2009**, *11*, 954–957.
- (28) Maillard, F.; Schreier, S.; Hanzlik, M. Influence of Particle Agglomeration on the Catalytic Activity of Carbon-Supported Pt nanoparticles in CO Monolayer Oxidation. *Phys. Chem. Chem. Phys.* **2005**, *7*, 385–393.
- (29) Ustarroz, J.; Altantzis, T.; Hammons, J. a.; Hubin, A.; Bals, S.; Terryn, H. The Role of Nanocluster Aggregation, Coalescence, and Recrystallization in the Electrochemical Deposition of Platinum Nanostructures. *Chem. Mater.* **2014**, *26*, 2396–2406.

- (30) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Science* (80-.). **2009**, *324*, 1302–5.
- (31) Fu, S.; Zhu, C.; Shi, Q.; Xia, H.; Du, D.; Lin, Y. Highly Branched PtCu Bimetallic Alloy Nanodendrites with Superior Electrocatalytic Activities for Oxygen Reduction Reactions. *Nanoscale* **2016**, *8*, 5076–5081.
- (32) Kibsgaard, J.; Gorlin, Y.; Chen, Z.; Jaramillo, T. F. Meso-Structured Platinum Thin Films: Active and Stable Electrocatalysts for the Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2012**, *134*, 7758–65.
- (33) Kim, J.; Kim, D.; Choi, S. Y.; Kim, S.-D.; Song, J. Y.; Kim, J. Electrochemical Deposition of Flat Nanoporous Pt Layers with Small Pore Dimensions. *Electrochim. Acta* **2016**, *189*, 196–204.
- (34) Hartl, K.; Nesselberger, M.; Mayrhofer, K. J. J.; Kunz, S.; Schweinberger, F. F.; Kwon, G.; Hanzlik, M.; Heiz, U.; Arenz, M. Electrochemically Induced Nanocluster Migration. *Electrochim. Acta* **2010**, *56*, 810–816.
- (35) Mohanty, A.; Garg, N.; Jin, R. A Universal Approach to the Synthesis of Noble Metal Nanodendrites and their Catalytic Properties. *Angew. Chemie - Int. Ed.* **2010**, *49*, 4962–6.
- (36) Xu, J.; Wilson, A. R.; Rathmell, A. R.; Howe, J.; Chi, M.; Wiley, B. J. Synthesis and Catalytic Properties of Au-Pd Nanoflowers. *ACS Nano* **2011**, *5*, 6119–27.
- (37) Geboes, B.; Ustarroz, J.; Sentosun, K.; Vanrompay, H.; Hubin, A.; Bals, S.; Breugelmans, T. Electrochemical Behavior of Electrodeposited Nanoporous Pt Catalysts for the Oxygen Reduction Reaction. *ACS Catal.* **2016**, *17*, 5856–5864.

- (38) Ustarroz, J.; Gupta, U.; Hubin, A.; Bals, S.; Terryn, H. Electrodeposition of Ag Nanoparticles onto Carbon Coated TEM Grids: A Direct Approach to Study Early Stages of Nucleation. *Electrochem. commun.* **2010**, *12*, 1706–1709.
- (39) Ustarroz, J.; Ke, X.; Hubin, A.; Bals, S.; Terryn, H. New Insights into the Early Stages of Nanoparticle Electrodeposition. *J. Phys. Chem. C* **2012**, *116*, 2322–2329.
- (40) Goris, B.; Van den Broek, W.; Batenburg, K. J.; Heidari Mezerji, H.; Bals, S. Electron Tomography Based on a Total Variation Minimization Reconstruction Technique. *Ultramicroscopy* **2012**, *113*, 120–130.
- (41) Søgaard, M.; Odgaard, M.; Skou, E. An Improved Method for the Determination of the Electrochemical Active Area of Porous Composite Platinum Electrodes. *Solid State Ionics* **2001**, *145*, 31–35.
- (42) Ochal, P.; Gomez De La Fuente, J. L.; Tsyppkin, M.; Seland, F.; Sunde, S.; Muthuswamy, N.; Rønning, M.; Chen, D.; Garcia, S.; Alayoglu, S.; Eichhorn, B. CO Stripping as an Electrochemical Tool for Characterization of Ru@Pt Core-Shell Catalysts. *J. Electroanal. Chem.* **2011**, *655*, 140–146.
- (43) Van Tendeloo, G.; Bals, S.; Van Aert, S.; Verbeeck, J.; Van Dyck, D. Advanced Electron Microscopy for Advanced Materials. *Adv. Mater.* **2012**, *24*, 5655–75.
- (44) Bals, S.; Goris, B.; Liz-Marzán, L. M.; Van Tendeloo, G. Three-Dimensional Characterization of Noble-Metal Nanoparticles and their Assemblies by Electron Tomography. *Angew. Chemie - Int. Ed.* **2014**, *53*, 10600–10610.
- (45) Ustarroz, J.; Hammons, J. A.; Altantzis, T.; Hubin, A.; Bals, S.; Terryn, H. A Generalized Electrochemical Aggregative Growth Mechanism. *J. Am. Chem. Soc.* **2013**, *135*, 11550–11561.

- (46) Liu, H.; Penner, R. M. Size-Selective Electrodeposition of Mesoscale Metal Particles in the Uncoupled Limit. *J. Phys. Chem. B* **2000**, *104*, 9131–9139.
- (47) Ueda, M.; Dietz, H.; Anders, A.; Knepppe, H.; Meixner, A. J.; Plieth, W. Double-Pulse Technique as an Electrochemical Tool for Controlling the Preparation of Metallic Nanoparticles. *Electrochim. Acta* **2002**, *48*, 377–386.
- (48) Liu, Y.; Gokcen, D.; Bertocci, U.; Moffat, T. P. Self-Terminating Growth of Platinum Films by Electrochemical Deposition. *Science (80-.)*. **2012**, *338*, 1327–30.
- (49) Wei, Z.; Chen, S.; Liu, Y.; Sun, C.; Shao, Z.; Shen, P. Electrodepositing Pt by Modulated Pulse Current on a Nafion-Bonded Carbon Substrate as an Electrode for PEMFC. *J. Phys. Chem. C* **2007**, *111*, 15456–15463.
- (50) Hartl, K.; Mayrhofer, K. J. J.; Lopez, M.; Goia, D.; Arenz, M. AuPt Core-Shell Nanocatalysts with Bulk Pt Activity. *Electrochem. commun.* **2010**, *12*, 1487–1489.
- (51) Zhao, Z.; Dubau, L.; Maillard, F. Evidences of the Migration of Pt Crystallites on High Surface Area Carbon Supports in the Presence of Reducing Molecules. *J. Power Sources* **2012**, *217*, 449–458.
- (52) Arán-Ais, R. M.; Yu, Y.; Hovden, R.; Solla-Gullón, J.; Herrero, E.; Feliu, J. M.; Abruña, H. D. Identical Location Transmission Electron Microscopy Imaging of Site-Selective Pt Nanocatalysts: Electrochemical Activation and Surface Disorder. *J. Am. Chem. Soc.* **2015**, *137*, 14992–14998.
- (53) Katsounaros, I.; Cherevko, S.; Zeradjanin, A. R.; Mayrhofer, K. J. J. Oxygen Electrochemistry as a Cornerstone for Sustainable Energy Conversion. *Angew. Chemie - Int. Ed.* **2014**, *53*, 102–121.
- (54) Castanheira, L.; Dubau, L.; Maillard, F. Accelerated Stress Tests of Pt/HSAC Elec-

trocatalysts: an Identical-Location Transmission Electron Microscopy Study on the Influence of Intermediate Characterizations. *Electrocatalysis* **2014**, *5*, 125–135.

Table Of Contents