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Author: Mirosława Pawlyta, Bartłomiej Sobel, Barbara Liszka

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Estimation of the chemical specific surface area of catalytic nanoparticles by TEM images analysis

M. Pawlyta [a,*], B. Sobel [a], B. Liszka [b]

[a] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

[b] Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland

* Corresponding e-mail address: miroslawa.pawlyta@polsl.pl

ABSTRACT

Purpose: The purpose of this article is the development of quantitative methods for assessing the quality of nanocomposite materials used in fuel cells.

Design/methodology/approach: latinum is the most commonly used catalyst in fuel cells, commonly in the form of nanoparticles deposited on the surface of carbon black. Due to the nanometric size of platinum particles, transmission electron microscopy can be applied to evaluate the produced catalysts. TEM image also allow to determinate the approximate value of the chemical specific surface area) of platinum nanoparticles, but only in case of spherical particles.

Findings: In present work, taking into account additional assumptions resulting directly from the analysis of microscopic images, the method of estimation of the particle diameter and the chemical specific surface area for nonsymmetrical (elongated) nanoparticles is present.

Research limitations/implications: The presented work presents a method for determining the specific surface of platinum, when their shape is elongated. It is worth noting that the modified formulas for determining the particle diameter and the value of the chemically active specific surface of the platinum nanoparticles of the elongated shape are equivalent to the formulas previously given for spherical particles, if the particle length and its diameter are equal. In this case, patterns for symmetric particles and more general (modified) patterns can be used interchangeably.

Practical implications: Development of new and more effective catalysts for fuel cells.

Originality/value: The significance of the presented work results from the possibility of using the described method in the catalyst studies during real catalytic processes. It allows comparing catalytic activity after the process, also in unusual conditions and in an aggressive environment, using minimal amounts of material.

Keywords: TEM, Nanocomposite, Fuel cells, Carbon black, Platinum

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MATERIALS

1. Introduction

Carbon black (CB) is the oldest human-made nanomaterial [1]. Simple methods of producing soot used to make ink were already known in ancient China and Egypt. The CB was then obtained by burning oil or resin under suspended porcelain dishes. The importance of CB (soot obtained for industrial applications) has been systematically growing since the printing became popular, whereas the fundamental breakthrough came after the discovery that the addition of CB to rubber significantly improves its mechanical properties. This fact contributed to the development of the automotive industry, enabling the production of tires with tens of thousands of kilometres. Currently, CB is an industrial raw material primarily used as a filler in the production of tires and other rubber materials and as a pigment in the production of paints, varnishes and plastics [2]. On the other hand, as a nanomaterial, CB (soot) remains unappreciated. One of the few applications of carbon black, effectively using the possibilities resulting from the nano size, is the role of the support for catalytic nanoparticles, which can be evenly dispersed on its highly developed surface, which significantly increases the efficiency of the applied catalyst, while reducing its consumption and cost. The catalytic nanoparticles are defined as catalyst particles with a size ranging from 1 to 20 nm [3]. The importance of catalyst-based processes is growing dynamically, especially in the areas related to storage, receipt and conversion of energy, that is critical issues for the quality of human life and further development of civilization, therefore efforts to increase the efficiency of their use are justified, especially due to their high price and limited resources. This can be achieved by using a catalyst in the form of nanoparticles of appropriate size and shape, their more even and stable distribution on the surface of the support and the modification of the support itself.

Fuel cells are devices that convert the chemical energy of fuel and oxidant directly into electricity. Compared to conventional methods of generating electricity and heat, fuel cells have two basic advantages - higher efficiency and very low emission of harmful compounds, such as nitrogen oxides, sulfur, hydrocarbons and carbon monoxide. An intensively developed type of fuel cell is the PEMFC (Proton Exchange Membrane Fuel Cell). Its principle of operation is based on an electrochemical process that corresponds to reverse electrolysis of water and allows for a controlled reaction of combining hydrogen (coming from fuel) with oxygen (coming from the air) [4]. The power density provided by this type of cell is an order of magnitude higher than that of other fuel cells. The exceptions are very advanced, used in the space technology, Alkaline Fuel Cells.

The most commonly used catalyst in PEM cells is platinum, commonly used in the form of nanoparticles deposited on the surface of CB [5,6]. Considering the availability and significant diversity of carbon blacks, it is surprising to use both in the basic research and commercial applications just a few of its grades, presented in Table 1. The most common is the Vulcan XC-72 stove from Cabot (after this referred to as Vulcan) [7].

Table 1.
Characteristics of carbon black grades used in fuel cells as support of platinum nanoparticles [7,8]. S_{BET} – specific surface area, d_p – primary particles diameter

CB grade	Manufacturer	S_{BET}, m^2/g	d_p, nm
Vulcan XC-72	Cabot	254	38
Black Pearls 2000	Cabot	1475	15
Denka Black	Denka	58	40
Shavinigan	Gulf Oil	70-90	40-50
Ketjen EC300J	Ketjen Black International	800	40
Ketjen EC600JD	Ketjen Black International	1270	34

Due to the nanometric size of platinum particles, transmission electron microscopy is used to evaluate the produced catalysts. In the transmission electron microscope, a beam of high-energy electrons is used for imaging samples. The electron energy is usually in the range between 60 and 300 keV, which corresponds to a wavelength of several picometers (1 pm = 10^{-12} m) and provides the required spatial resolution. Modern transmission microscopes enable operation in TEM and STEM mode. The difference between them concerns the way an electron beam interacts with the sample. In the TEM transmission mode, a wide stationary electron beam is used to obtain the image. A parallel beam illuminates the sample, then the objective lens creates a flat (two-dimensional) image that is further magnified several times and projected onto the screen. For characterisation of nanostructured carbon materials decorated with metal nanoparticles, scanning electron microscopy (STEM) is particularly useful, especially the imaging technique using the HAADF detector (High Angle Annular Dark Field) [9,10]. STEM images are obtained as a result of recording the intensity of the scattered beam depending on the position of the beam falling on the surface of the sample. The electrons scattered at a high angle are recorded by the

HAADF detector. The large diffusion angle is the result of the interaction of electrons with the atomic nuclei of the analysed material (the predominant component is Rutherford scattering). To increase the efficiency of recording weak signal ring detectors are used. Differential cross-section on scattering is proportional to the square of the electric charge of the nucleus (I (χ) ~ Z^2). Thanks to this, scattered electrons are a source of information about the atomic nucleus charge, and HAADF images represent a qualitative chemical contrast. Heavy atoms or columns of such atoms in high resolution images are visible as bright points, while light ones are darker. If the detector is close enough to the sample (the scattering angle is sufficiently large), electrons dispersed coherently on crystals are not recorded (no diffraction contrast) and the interpretation of the obtained image is intuitive. It is not necessary to compare the images obtained with the results of computer simulations, as is the HRTEM images case, where the resulting intensity depends on many factors, including the excitation of the objective lens and the thickness of the sample.

Based on the recorded images of CB aggregates with platinum nanoparticles, the shape and size of the Pt particles can be characterised by measuring their area A_p and perimeter P. From each pair of measurements, $d_p(TEM)$ can be determined (the value corresponding to the diameter of the circle equal to the area occupied by particle on a microscopic image):

$$d_p(TEM) = 2 \cdot \sqrt{\frac{A_p}{\pi}} \tag{1}$$

and aspect ratio F:

$$F = \frac{4\pi A_p}{P^2} \tag{2}$$

and their mean values and histograms of Pt particle diameter distribution. TEM images also allow to determinate the approximate value of the *Chemical Specific Surface Area* (CSA) of platinum nanoparticles [cm^2/mg Pt] [11], based on the formula:

$$CSA = \frac{60000}{\rho_{Pt} d_p} \tag{3}$$

where ρ_{Pt} is the platinum density (21.4 g/cm^3).

The above formulas are correct only for particles of spherical shape (aspect ratio F approximately equal to 1). The aim of the presented work is to present the method of determining the particle diameter and the chemical specific surface area for nonsymmetrical (elongated) nanoparticles, taking into account additional assumptions resulting directly from the analysis of microscopic images.

2. Materials

The tested material was commercial carbon black Color Black FW200. The manufacturer of this carbon black grade (after this abbreviated as FW200) is Orion Engineered Carbons LLC (formerly Degussa). It is a gas, oxidised carbon black. The specific surface area of FW200 is S_{BET} = 550 m^2/g (value given by the manufacturer, determined in accordance with DIN 66131/2, ISO 4652). The diameter of the primary particles is d_p = 13 nm (value given by the manufacturer, determined by the TEM method). The manufacturer recommends this type of CB for dyeing high quality metallic and plastic coatings.

FW200 samples were heated in an Acheson furnace under argon (SGL CARBON Polska SA, Racibórz). The maximum temperature was 2700°C. At maximum temperatures, samples were kept for 30 minutes. In order to modify the surface of the graphitised FW200 by introducing additional defects of the structure and formation of functional groups, the material was placed in concentrated nitric acid (V) and then dispersed using ultrasonic waves and heated under reflux. The obtained material was filtered and repeatedly washed with deionised water until the reaction was neutral. The deposition of Pt nanoparticles was carried out according to the procedure described in [12], with minor modifications. The graphitised CB (after the functionalization process) was dispersed in ethylene glycol using ultrasound for 15 minutes. While stirring vigorously, acetone was added to the suspension, followed by the appropriate amount of hexachloroplatinic acid (IV) and sodium citrate. Then a 5% sodium hydroxide solution was added dropwise until the pH was 10. The mixture was stirred for half an hour and then heated under reflux for 5 hours. Then it was cooled to room temperature and maintained under stirring for 8 night. The product obtained was washed with water until the impurities were completely washed and the pH was neutral and dried at 105° C. Two samples were obtained for further tests: with a small (about 2%, FW200/Pt/A) and a large (20%, FW200/Pt/A) concentration of platinum embedded (Table 2).

For comparison, commercial material from Fuel Cells Etc (www.fuelcellsetc.com), designated as Vulcan/Pt, was used. These are platinum nanoparticles with a diameter of 2 nm deposited on the surface of the amorphous Vulcan carbon black. The specific surface area of platinum is

148 m^2/g, and the average size of platinum crystallites determined by XRD technique is 2.5 nm (values given by the manufacturer).

Table 2.
List of samples used for testing

Sample name	Description
FW200/Pt/A	Platinum nanoparticles (low concentration) deposited on the surface of FW200; own material
FW200/Pt/B	Platinum nanoparticles (high concentration) deposited on the surface of FW200; own material
Vulcan/Pt	Platinum nanoparticles deposited on the surface of Vulcan; commercial product

3. Methodology

Transmission electron microscopy was carried out using the S/TEM TITAN 80-300 microscope from FEI (Institute of Engineering and Biomedical Materials, Silesian University of Technology). Samples were prepared by dispersing in ethyl alcohol using ultrasound. The drop of the resulting suspension was then applied to the microscope grid covered with a carbon film.

During the experiments, the intensity of the beam and the exposure time were reduced and/or the lower (80 kV) accelerated voltage was used. CB structure decorated with platinum nanoparticles were performed in STEM using the HAADF and BF detector. Based on the recorded images, the areas A_p and the perimeter P of the platinum nanoparticles, as well as aspect ratio F were measured (using the ImageJ program [13]).

4. Results

4.1. Morphology of platinum nanoparticles deposited on the surface of graphitised FW200 at low concentration

When the platinum concentration was about 2%, the platinum particles were at a considerable distance from each other and had a spherical shape. Their size can be estimated at around 1-2 nm (Fig. 1). Such morphology and distribution are very beneficial for catalytic processes, but the concentration is insufficient to obtain a satisfactory effect. Therefore, it was necessary to increase the concentration of catalytic particles.

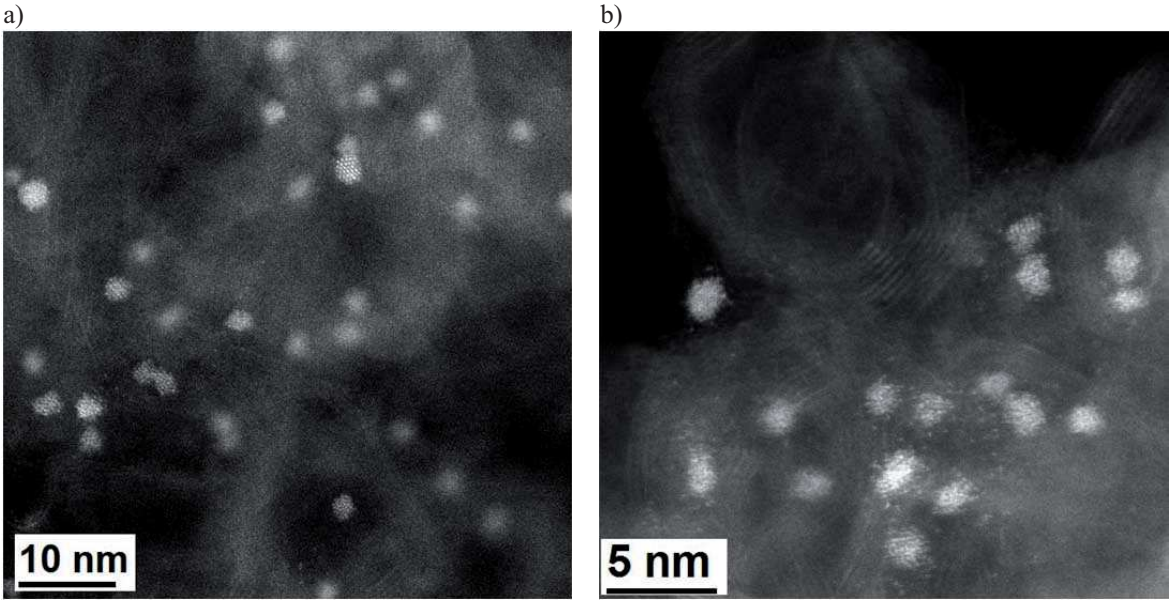

Fig. 1. STEM-HAADF images of spherical platinum nanoparticles (low concentration) on the surface of graphitised carbon black (FW 200/Pt/A)

4.2. Morphology of platinum nanoparticles deposited on the surface of graphitised FW200 at high concentration

Platinum nanoparticles at high concentration (20%) are also evenly distributed on the surface of the CB support (Fig. 2). The distance between the particles is significant and approximately constant. The characteristic feature of these particles, which is distinctive from the previous sample, is their elongated shape. Taking into account the results presented in the previous paragraph, it can be concluded that they arose as a result of combining several spherical particles, the number of particles being limited by the shape of the support. The edges of the prime particles of graphitised carbon black prevent the platinum nanoparticles from different walls to connect. The shape of these edges also determines the shape of the platinum nanoparticles be formed. It can be assumed that they are elongated, although they sometimes branch out. Their cross-section is approximately circular (diameter 1-2 nm). The ends are halves of spheres.

4.3. Morphology of platinum nanoparticles deposited on the surface of Vulcan

Platinum nanoparticles deposited on the Vulcan soot are spherical. They are uniform in size (1-2 nm) and distribution (Fig. 3). In this respect, they are similar to the FW 200/Pt/A sample. The concentration of platinum is much higher in the case of Vulcan.

4.4. Determination of the diameter and specific surface area of platinum nanoparticles with an elongated shape

At high concentration, the majority of platinum nanoparticles deposited on graphitised soot are of elongated shape (Fig. 2). Because particles can be tilted, so their length can be even larger than seen in the TEM images. The assessment of the shape of asymmetrical particles on the basis of microscopic images is difficult due to the fact that they present a two-dimensional projection of three-dimensional objects. In the case of the analysed particles, the evaluation of their shape is possible provided that additional assumptions are made. Based on the analysis of microscopic images, it is reasonable to consider that the platinum nanoparticles in the FW200/Pt/B sample were formed as a result of connection (linkage) particles of a spherical shape and the same size as was seen in the FW200/Pt/A sample. The shape of the platinum nanoparticles in the FW200/Pt/B sample can thus be approximated by cylinder, terminated with spherical halves (Fig. 4).

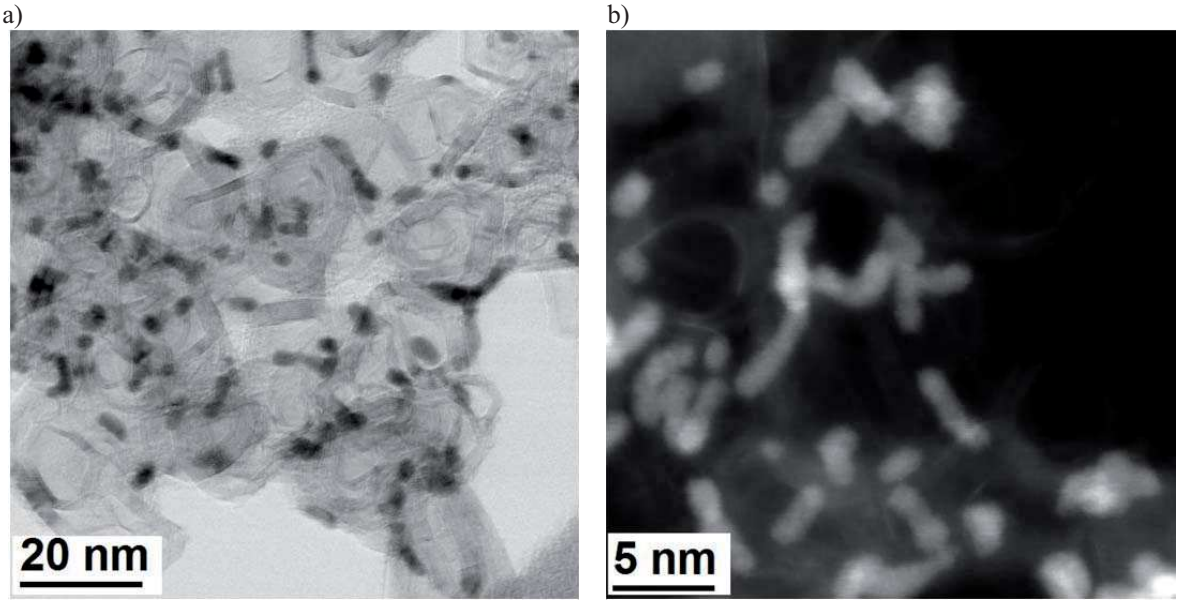

Fig. 2. STEM BF (a) and HAADF (b) images of elongated platinum nanoparticles (high concentration) on the surface of graphitised carbon black (FW 200/Pt/B)

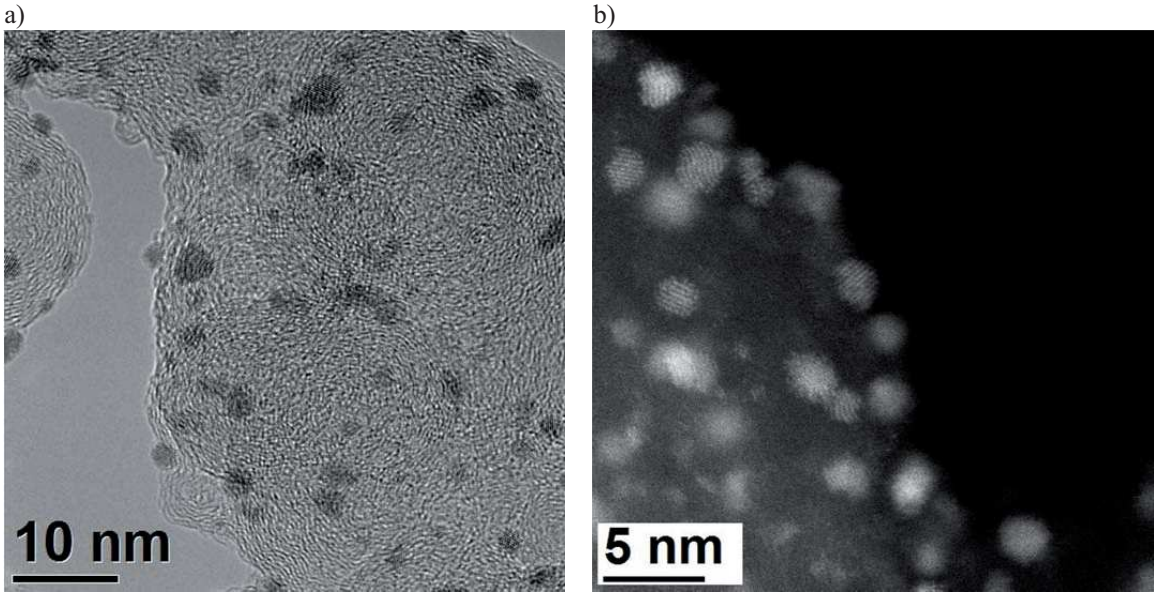

Fig. 3. STEM BF (a) and HAADF (b) images of spherical platinum nanoparticles on the surface of Vulcan

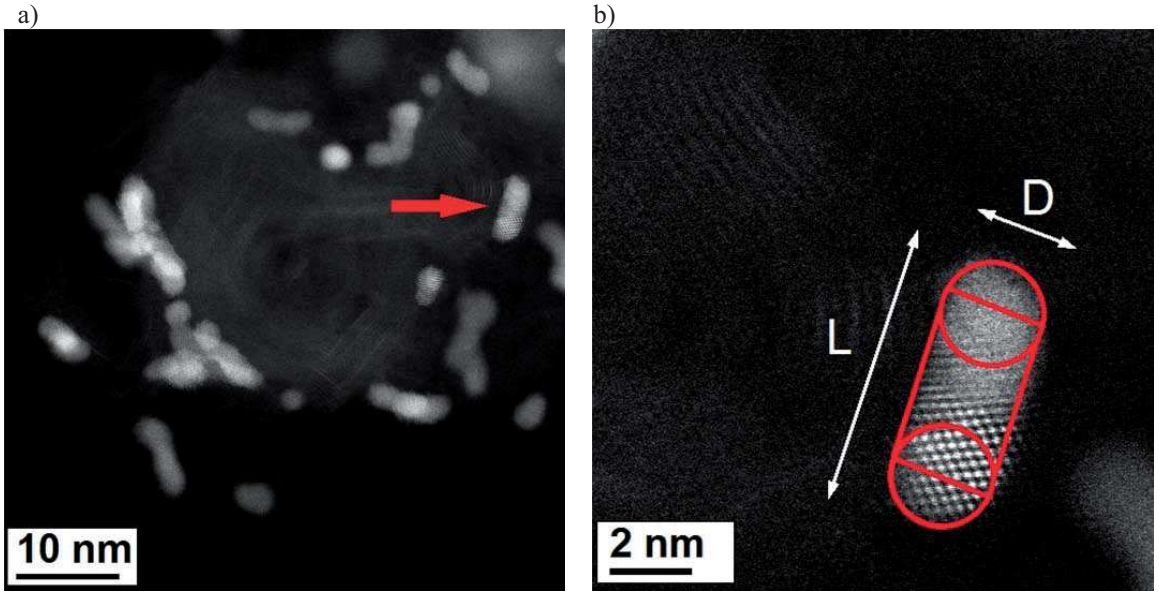

Fig. 4. HR STEM-HAADF image of graphitised FW200 decorated with platinum nanoparticles (FW 200/Pt/B) (a), enlargement of the platinum nanoparticle indicated by the arrow on the previous image (b)

Analysis of TEM images presenting platinum nanoparticles were based on measuring for each of them the value of the particle surface on the image A_p and its perimeter P. Next, on the basis of the obtained values, the length L and the particle diameter D were determined, assuming that its shape is similar to the cylinder ended with halves spheres:

$$D = \frac{P - 2\sqrt{\frac{P^2}{4} - \pi A_P}}{\pi} \tag{4}$$

$$L = \frac{P - D_{Pt}(\pi - 2)}{2} \tag{5}$$

The diameter of cylinder D is approximately constant over the entire length of the particle and does not depend

on the orientation of the particle (does not change depending on the angle of observation). The length of the particle L visible on the TEM image is a projection of the real length L_{Pt} (to obtain the actual value it is necessary to divide it by the value of the sine of the angle between the axis of the particle and the optical axis of the microscope). Assuming that the particles are arranged in a completely random manner, one can determine the relationship between the real and observed particle length as L_{Pt} = L+(L-D)/K, where the average reduction factor K = 0.635 (determined based on Monte Carlo computer simulations). Then one can determine the actual outer surface of the platinum particle P_{Pt} and its volume V_{Pt}:

$$P_{Pt} = (L_{Pt} - D)\pi D + \pi D^2 \quad (6)$$

$$V_{Pt} = (L_{Pt} - D)\frac{\pi}{4}D^d + \frac{\pi}{6}D^3 \quad (7)$$

and an equivalent particle diameter of platinum (equal to the diameter of the sphere with a V_{Pt} volume):

$$d_{Pt} = 2\sqrt[3]{\frac{6\,V_{Pt}}{\pi}} \quad (8)$$

The value of the specific surface area of CAS_{Pt} of platinum nanoparticles with elongated shape (similar to a cylinder) can then be calculated as:

$$CAS_{Pt} = \frac{P_{Pt}}{m} = \frac{P_{Pt}}{\rho V_{Pt}} \quad (9)$$

4.5. Comparison of the size and specific surface area of platinum nanoparticles deposited on Vulcan and graphitised carbon black FW200

The average value of the (equivalent) diameter of platinum particles deposited on Vulcan (amorphous black) is about 1.8 ± 0.3 nm. The particles are of a spherical shape (F = 0.99 ± 0.04). The surface area of CAS platinum (170 ± 80 m^2/g) calculated on the basis of microscopic images has a value similar to the one given by the manufacturer (148 m^2/g), which confirms the correctness of the proposed method.

The average value of the (equivalent) diameter of platinum particles deposited on graphitised carbon black, when the platinum concentration is low (FW200/Pt/A), is approx. 1.4 ± 0.3 nm (based on the measurement of 217 particles). The particles are symmetrical (F = 0.96 ± 0.04). The surface area of platinum calculated from microscopic images is 189 ± 68 m^2/g. For the material with high concentration of platinum particles deposited on graphitised carbon black (FW200/Pt/B), the average value of the platinum particle diameter is about 4.2 ± 0.3 nm (determined on the basis of 327 particles). The particles are asymmetrical (F = 0.64 ± 0.22). The surface area of platinum calculated from microscopic images is 98±18 m^2/g. A summary of the obtained results is presented in Table 3.

Table 3.
Parameters characterizing the shape of platinum nanoparticles deposited on the support, received from the TEM images (n_c – number of analysed particles; F – the aspect ratio (average value); A_p – size of the particle, P – perimeter of the particle; $d_p(TEM)$ – diameter of the platinum particles (average value); CSA_{Pt} – specific surface area of platinum nanoparticles

Sample name	n_c	$F=4\pi A_p/P^2$	d_{Pt} (TEM), nm	CSA_{Pt}, m^2/g Pt
Vulcan/Pt	348	0.99 ± 0.04	1.82 ± 0.32	170 ± 80
FW200/Pt/A	217	0.96 ± 0.04	1.360.29	189 ± 68
FW200/Pt/B	327	0.64 ± 0.22	4.24 ± 0.28	98± 18

5. Conclusions

Decorating CB (soot) and other nanostructured carbon materials with catalyst nanoparticles so that they are adequately small and uniform in size, uniformly distributed on the surface of the support and stable over a wide range of thermal and electrochemical conditions is a major research challenge. Differences in the shape and size of platinum nanoparticles requires quantitative information. For spherical particles, the diameter can be determined, based on the analysis of TEM images followed by the volume, mass and proportion of atoms found on the surface of the CAS platinum particles. The presented work presents a method for determining the specific surface of platinum, when their shape is elongated. It is worth noting that the modified formulas for determining the particle diameter d_{Pt} and the value of the chemically active specific surface CSA_{Pt} of the platinum nanoparticles of the elongated shape are equivalent to the formulas previously given for spherical particles, if the particle length and its diameter are equal (F≈1). In this case, patterns for symmetric particles and more general (modified) patterns can be used interchangeably.

The significance of the presented work results from the possibility of using the described method in the catalyst studies during real catalytic processes. It allows to compare catalytic activity after the process, also in unusual conditions and in an aggressive environment, using minimal amounts of material.

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