

Size and distribution of palladium nanoparticles electrodeposited on graphite

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Morphology and particle size distribution of palladium nanoparticles obtained by pulse electrodeposition on graphite surfaces in dimethylformamide solution containing 0.01 M PdCl₂ were examined by field emission scanning electron microscopy. Chemical composition of the deposits was determined by energy dispersive X-ray spectroscopy. It was found that the average size of palladium nanoparticles increased while their density decreased with the number of pulse cycles.

Keywords: palladium, pulse electrodeposition, DMF, SEM.

Методом електронної мікроскопії досліджено морфологію і розподіл наночастинок паладію, отриманих за імпульсного режиму електроосадження на поверхні графіту в диметилформамідних розчинах, що містять 0,01 М PdCl₂. Хімічний склад осадів визначено енерго-дисперсійною рентгеновською спектроскопією. Встановлено, що середні розміри наночастинок паладію збільшуються, тоді як їх густина зменшується з кількістю імпульсних циклів.

Розмір та розподіл наночастинок паладію електроосаджених на графіті. *І.Салдан, А.Джирелла, К.Міланезе, Е.Фратіні, О.Добровецька, І.Левчук, О.Кунтій.*

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1.Introduction

Activity of bulk palladium might be limited in comparison with nanodispersed and well distributed palladium nanoparticles (PdNPs), which show unexpectedly high catalytic activity in various chemical reac-

tions. Additionally, the PdNPs are preferred over platinum equivalents because of their higher resistance against poisoning by different reaction species [1, 2]. Detailed studies of the nanostructured palladium particles confirmed that their catalytic activity essentially depends on their size

wherever they are introduced — on solid support, an electrode surface or even colloidal solution [3]. For mono- or bimetallic PdNPs, together with the methods of physical [4, 5] and chemical [6–8] syntheses, electrochemical methods [9–14] are highly reproducible and handy in practice. Electrodeposition constitutes a suitable method since it is not expensive and enables to form the nanomaterials with a wide range of sizes and shapes. Electrochemical reduction of an appropriate precursor to zero valence metal in organic aprotic electrolyte (e.g. DMSO, DMF, PC, AN [15–22]) is a reasonable approach to avoid possible secondary reactions (hydroxide formation; oxygen/hydrogen evolution) in common aqueous electrolytes. Moreover, electrodeposition in a pulse mode was found to be an effective template-free electrochemical synthetic method for the monometallic [15, 16] PdNPs.

In the present work, pulse electrochemical deposition was used to prepare PdNPs from PdCl₂ salt dissolved in dimethylformamide. Morphology and chemical composition of the PdNPs were estimated by high resolution scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Based on the experimental results, a relationship between the mean value of the particles size and the number of pulse cycles was found.

2. Experimental

Organic aprotic solvent, i.e. N,N-dimethylformamide, (DMF, 99 %, AlfaAesar), together with tetrabutylammonium perchlorate (Bu₄NClO₄, ≥ 99.0 %, Sigma Aldrich) as supporting electrolyte and chloride salt as metal precursors (PdCl₂, 99.9 %, AlfaAesar) were used in the electrochemical experiments. The prepared electrolyte has concentration of 0.01 M in PdCl₂ and 0.05 M in Bu₄NClO₄, respectively, in the DMF solvent. Graphite rods (R8710, RINGSORFF, SGL Carbon, GmbH) encapsulated in fluoroplastic cartridge case and gold plate ($S = 2.2 \cdot 10^{-4} \text{ m}^2$) were used as working and counter electrodes, respectively. Silver chloride electrode manufactured as Ag/AgCl in saturated KCl solution was used as a reference electrode. Before each electrochemical experiment, the graphite rods surface was mechanically polished using ~ 3, ~ 1 and ~ 0.3 μm microfinishing SiC papers followed by polishing with alumina-based suspension (~ 0.3 μm, Metallchemie). After that, the surface of the working elec-

trode was washed with distilled water and isopropanol in an ultrasonic bath and then dried under argon flow. Subsequently the three electrodes were connected to IPC-Pro 200 potentiostat and immersed into a glass cell filled with ~ 50 cm³ of the electrolyte at 35°C. The electrodeposition process was carried out by pulse potentiostatic method at the potential (E) value of -1.2 V, pulse time (τ_{on}) of 6 ms and pause (τ_{off}) of 300 ms. These parameters were experimentally found in [15] as optimal to growth discrete nanoparticles uniformly distributed on the substrate and already used in practice for PdNPs [15, 16]. The number of the pulse-pause repetitions (N), so called "pulse cycles", varied from 3 to 50. The obtained nanoparticles were washed sequentially in DMF and isopropanol. After that, all the samples were dried under argon flow.

Morphology of the deposits was studied by field emission scanning electron microscopy (FE-SEM). Micrographs were obtained by SIGMA high-resolution scanning electron microscope (Carl Zeiss) based on the GEMINI(r) column which features is the high brightness Schottky field emission source, beam booster, and in-lens secondary electron detector. After the electrodeposition step, the graphite rods were mounted directly on standard aluminum stubs using a bi-adhesive conductive tape. The measurements were conducted at an acceleration potential of 20 kV and working distance of about 6–9 mm. The chemical composition of the deposits was determined by energy-dispersive X-ray (EDX) analysis, performed by a silicon-drift detector (Oxford Instruments), directly coupled to the FE-SEM, using the optimal working distance of 8.5 mm and at the same value of acceleration potential.

The particle size distribution for the obtained PdNPs was modeled using the Gaussian function:

$$f = a \cdot \exp\left[-\frac{1}{2}\left(\frac{x - x_0}{b}\right)^2\right], \quad (1)$$

where x_0 is the mean size; b is the dispersion associated to the mean value and a parameter is amplitude of the Gaussian function:

$$a = \frac{1}{b\sqrt{2 \cdot \pi}}. \quad (2)$$

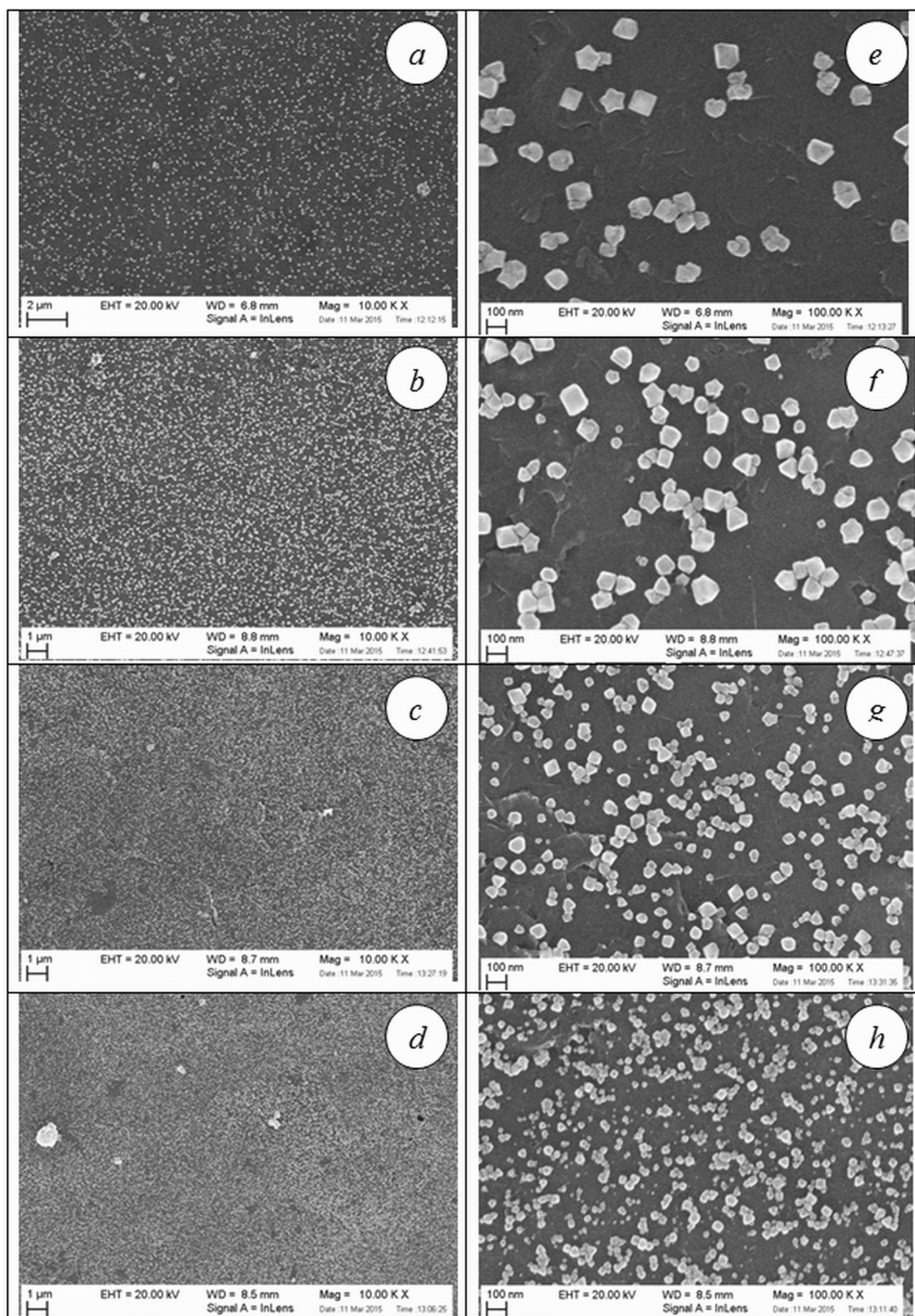


Fig. 1. SEM images for Pd deposition from 0.01 M PdCl₂ solutions in DMF after 50; 10; 5 and 3 pulse cycles at 10 000 magnification (a); (b); (c) and (d) as well at 100 000 magnification (e); (f); (g) and (h), correspondently.

3. Results and discussion

It is well-known that electrodeposition is a multi-stage process where diffusion in electrolyte is quite often the slowest stage, i.e. the limiting step in the whole electrochemical process. Recently, it was concluded that during the pulse mode of the gold-palladium electrodeposition in dimethylsulfoxide solutions the pause corresponds to the diffusion of precursor ions (from the bulk of electrolyte to pre-electrode area) while the pulse induces nucleation and particle growth [21]. It was afterwards confirmed that surface properties of the working electrode are mainly responsible for the nucleation of nanoclusters and their subsequent growth to nano- and microdeposits. These two stages take place on the electrode surface and very often supplement each other or stay in competition. In our case, the electrochemical reduction of Pd^{2+} ions to metallic palladium takes place at the base of the cylindrical graphite rods. EDX analysis on the graphite rods after the electrodeposition definitely showed the Pd L emission line confirming the presence of monometallic deposits of palladium on the graphite surface. SEM images for the palladium electrodeposition after 50; 10; 5 and 3 pulse cycles with magnification of 10 K and 100 K are shown in Fig. 1 to assess the surface morphology of the obtained PdNPs. In all cases, the uniformly distributed PdNPs were observed by SEM even though their size and density gradually changed depending on the number of pulse cycles.

The SEM images at 200 K magnification and the related calculated PdNPs average size distribution are shown in Fig. 2. Image analysis confirms that the PdNPs around 18 nm in diameter are obtained after 3 pulse cycles, that is comparable with 29 nm in diameter of AuNPs [22] while a higher number of pulse cycles leads to bigger particles. In particular, in our case, after 3, 5, 10 and 50 pulse cycles the mean diameter increased from ~18 to 46, 89 and 101 nm while the calculated coverage percentage of the deposited PdNPs were 27.9, 23.4, 22.0 and 12.8 %, respectively. Normalized autocorrelations (Fig. 3) were done on the SEM images from Fig. 2. The small maximum (Fig. 3) at distances higher than 100 nm gives the typical distance between PdNPs which is around ~200 nm in the case of 50 pulse cycles and ~400 nm for both the cases of 10 and 5 pulse cycles. Distance between the particles is not really defined in the case of 3 pulse cycles.

Additionally, it was observed that the density of particles decreased with the number of the applied pulse cycles (Figs. 1, 2). Experimental results confirm the hypothesis that after three pulse cycles the electrodeposition process is still dominated by nucleation while the growth is limited. The deposition process on a solid is thermodynamically favored at the surface defects and on the formed metallic nanoclusters. Thus, at the beginning of the electrodeposition, the palladium nanoclusters are formed at the surface defects, that is nucleation process. When all possible defects on the surface are occupied, subsequent portion of the metallic palladium covered the prepared nanoclusters, that is particle growth process. These two processes are in a permanent competition and the particle growth is preferred over nucleation at the higher number of pulse cycles.

Using the results from Fig. 2, the dependences of particle size and particle number per surface area on the number of pulse cycles are obtained (Fig. 4). The number of the PdNPs decreases while their sizes increase with the number of the pulse cycles. It is expected that the paraboloid dependence might be found experimentally using more detailed analysis beginning from the first pulse cycle. These relationships naturally confirmed a competition between the nucleation and growth stage during the pulse period.

4. Conclusions

The obtained experimental results confirmed the appearance of PdNPs on graphite during the beginning of palladium electrodeposition in the pulse mode. Well distributed PdNPs with size ≤ 100 nm in diameter were found by the SEM observation after 3–50 pulse cycles. The paraboloid dependence of the mean value of the particle size and particle number per surface area on the number of pulse cycles was experimentally found. Since the size of the PdNPs increased while their density decreased with the number of the pulse cycles a competition between the nucleation and the growth stage was proposed. In the next experimental works, attention will be focused on the geometrical shape of the PdNPs.

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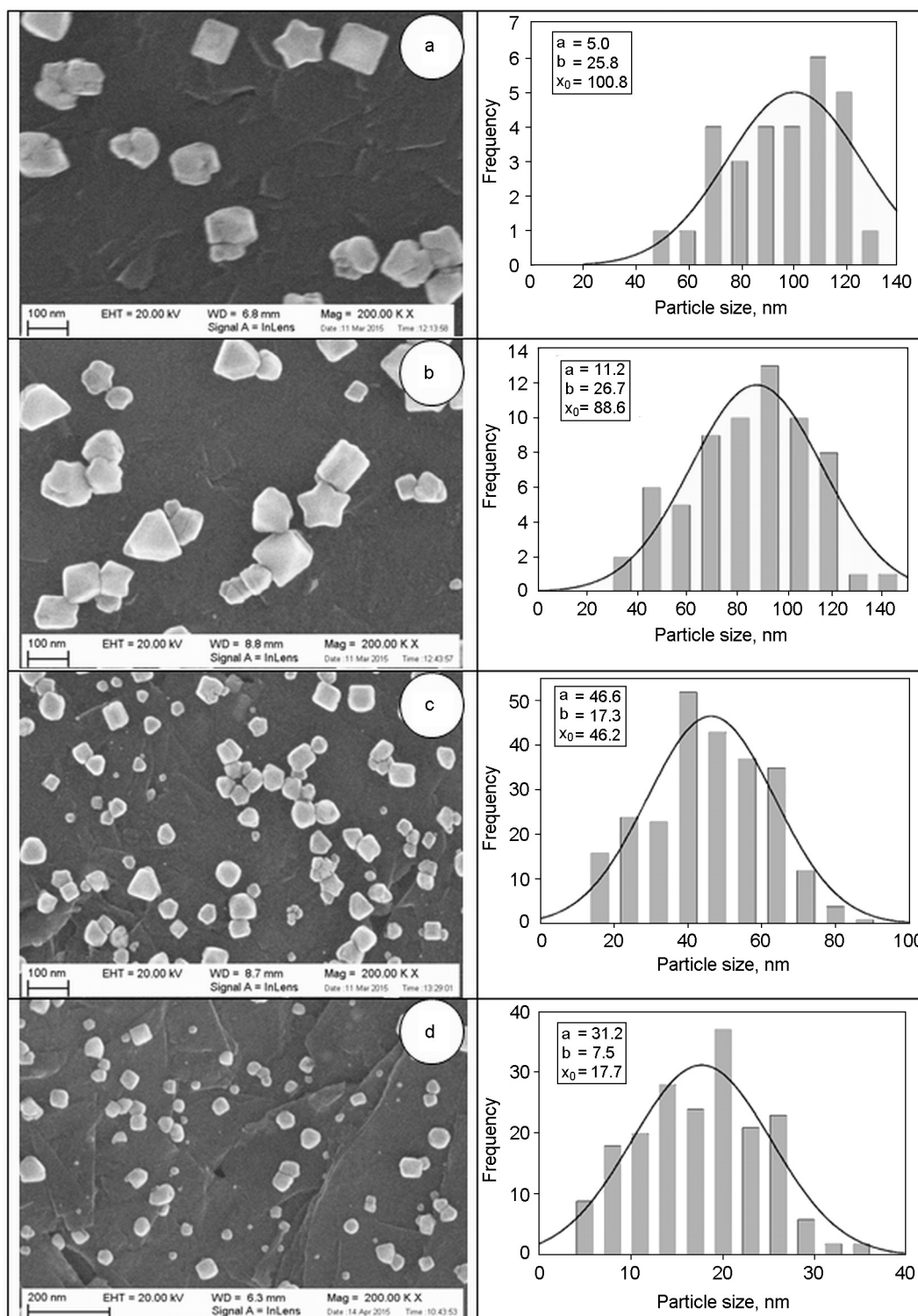


Fig. 2. SEM images for Pd deposition from 0.01 M PdCl₂ solutions in DMF after 50; 10; 5 and 3 pulse cycles at 200 000 magnification (a); (b); (c) and (d), correspondently. Calculated particles distribution is shown in (e); (f); (g) and (h), correspondently.

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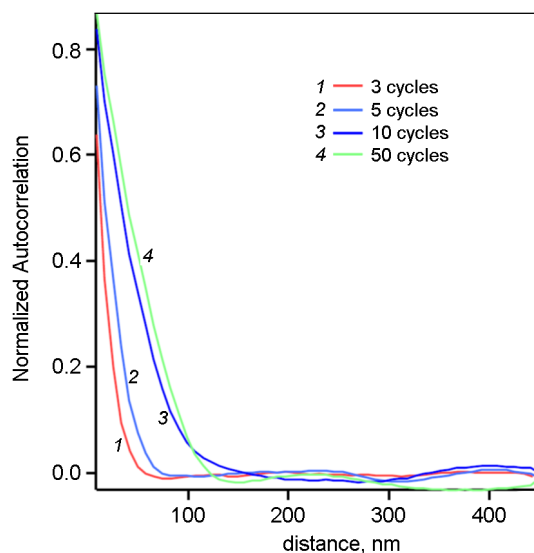


Fig. 3. Normalized autocorrelations done on the SEM images from Fig. 2. The average particle dimension can obtain via intercept on x -axis of tangent of the linear part at distances <100 nm.

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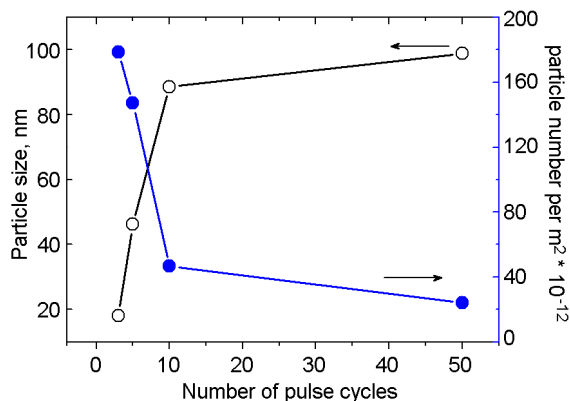


Fig. 4. Dependences of particle size and particle number per surface area on the number of pulse cycles for Pd deposition from 0.01 M PdCl₂ solutions in DMF.

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