

COLLOID CHEMISTRY  
AND ELECTROCHEMISTRY

Redox Potentials of Gold–Palladium Powders  
in Aqueous Solutions of  $H_2PdCl_4$

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**Abstract**—The redox potential of fine-dispersed and compact bimetallic powders of the palladium–gold system in hydrochloric acid solutions of  $H_2PdCl_4$  at a temperature of 60°C was studied. It was found that the redox potential increases with gold enrichment of the solid solution in accordance with the Nernst equation. The effect of gold–palladium particle size on this redox potential is shown. The morphology, sizes, and composition of bimetallic particles are determined via transmission electron microscopy and X-ray diffraction analysis.

**Keywords:** bimetallic powders, gold–palladium, redox potential.

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INTRODUCTION

The continuing interest of experts in physics, chemistry, and materials science in the study of fine-dispersed powders of platinum group metals is due to these powders exhibiting special properties that distinguish them from analogous macroscopic objects. Palladium nanoparticles are used advantageously in various domains of science and engineering. Synthesis techniques for palladium nanoparticles and studies of their structure and physicochemical properties have been described in, e.g., [1, 2]. Promising new spheres of application of palladium are of particular importance for Russia, since it is a major producer of this metal [3].

Bimetallic powders based on noble metals have recently attracted special interest, as they are used in such varied domains as heterogeneous catalysis, hydrogen power–engineering, electronics, electrical engineering, medicine, and biology [4–6]. Fine-dispersed gold–palladium objects are thus in some cases more efficient than their monometallic analogs.

A number of studies concern the problems of synthesizing bimetallic powders with desired characteristics and revealing the effect of structure and dispersion on their properties [7–9]. The catalytic properties of bimetallic materials are largely determined by their surface composition and structure. Many researchers agree that the structure of the resulting materials (mechanical mixture, solid solution, or shell–core structure) is determined by such experimental param-

eters as temperature, synthesis time, and reagent concentration [9, 10].

Present-day research methods (particularly electron microscopy and X-ray diffraction) make it possible to derive reproducible information on the structure and composition of nanopowders; in some cases, however, easily available and informative rapid methods are required for qualitative estimation of the properties of objects during synthesis. Using electrochemical methods to study their physicochemical properties (especially of size and surface) is very attractive in devising and developing efficient and handy methods for controlling and testing nanopowders.

It was shown in [11] that reproducible results in determining the characteristics of nanoparticles can be obtained through the integrated use of electron microscopic, probe, and electrochemical techniques; the latter are used to obtain certain reference points. In the same study, it was proposed that we quantitatively estimate the geometric parameters of the nanostructure of dispersed platinum group metals using coulometric and microscopic data.

The authors of [12] found the values of shifts of the redox potentials of nanocrystalline copper, palladium, and nickel in the negative direction relative to bulk materials. In [13, 14], Kravchenko et al. showed the contribution from the size factor to the electrode potential of copper-containing electron–ion exchangers. In addition to experimentally determining the impact of size effects on stationary potentials, a computational model allowing for the contribution from

size effects was proposed that was consistent with experimental data [13].

Using electrochemical measurements, the authors of [15] determined the shift of the potential of fine-dispersed palladium powders in the negative direction with respect to the potential of a compact material. It was found that the dependence of the equilibrium potential of  $\text{PdCl}_4^{2-}/\text{Pd}^0$  on the dispersion of metallic palladium is satisfactorily described through the Thomson equation. In [16], studying the  $\text{PdCl}_4^{2-}/\text{Pd}^0$  system via cyclic voltammetry revealed that the area of the cathode peak of the CVA curve depends linearly on the weight and degree of dispersion of metallic palladium in the working electrode, i.e., on the specific surface area of the material. The derived values of specific surface areas of palladium powders were consistent with data from gas adsorption measurements [16].

The electrochemical behavior of a palladium electrode and its electrochemical dissolution and oxidation processes were discussed in [17].

Electrochemical methods are promising for the study of both monometallic and bimetallic particles; [18] thus concerned investigating binary alloys of a gold–palladium system via cyclic voltammetry. Particular attention was given to the effect of the amount of hydrogen adsorbed by the alloy on voltammetric characteristics. Based on data derived from studies of the electrooxidation of palladium–gold electrolytic deposits via stripping voltammetry, it was shown in [19] that such deposits are solid solutions. The authors of [20] used cyclic voltammetry along with X-ray and electron microscopy techniques to study the surface composition of synthesized bimetallic gold–palladium particles. Electrochemical measurements served the basis for determining the surface distribution of palladium and gold atoms.

The search for physicochemical dependences on the structure and composition of bimetallic gold–palladium powders using electrochemical methods is therefore a problem of considerable interest. The aim of this work was to study the effect of synthesis conditions, size, and the composition of bimetallic powders of a gold–palladium system on the redox potential of  $\text{PdCl}_4^{2-}/(\text{Pd}, \text{Au})$ .

## EXPERIMENTAL

In this work, we used  $\text{PdCl}_2$ ,  $\text{AuCl}_3$ , and  $\text{KCl}$  of reagent grade and  $\text{HCl}$  of special purity grade 20-4. Palladium black was synthesized according to the technique developed in [21]. Bimetallic gold–palladium particles were prepared via the contact reduction of gold chlorocomplexes by fine-dispersed metallic palladium in autoclaves using both conventional and microwave heating techniques [22].

Compact solid solutions of the gold–palladium system were prepared by annealing powders of palladium and gold in an argon atmosphere in a tube furnace at  $600^\circ\text{C}$  for 20 h. The composition and structure of the solid phase were then determined via X-ray diffraction analysis.

X-ray diffraction patterns of the solid phase were obtained on a DRON-4M powder diffractometer using  $\text{CuK}_\alpha$  radiation with a graphite monochromator in the reflected beam. Scanning was done in a  $2\theta$  angle range of  $30^\circ$  to  $130^\circ$ . The fine crystalline structure parameters (e.g., the dispersion of blocks ( $D$ ) and lattice microstrain values ( $\Delta a/a$ )) produced a measurable physical broadening  $\Delta a/a$  of X-ray lines in the X-ray diffraction pattern. The line broadening was used to calculate the linear sizes of coherent scattering blocks  $D$  by means of Rietveld full-profile analysis [23]. The composition of the solid phase was determined according to the change in the lattice parameter.

The concentration and forms of palladium(II) chlorocomplexes in solution were determined via atomic absorption and spectrophotometric analysis. The absorption spectra were measured using a Shimadzu UV300 spectrophotometer in the wavelength range of 200–600 nm. We used quartz cells with a length of 0.1 to 1 cm; 1 M hydrochloric acid served a reference solution.

The structure of samples was studied using a JEOL JEM-2100 transmission electron microscope equipped with an Oxford Instruments INCA x-sight energy dispersive spectrometer. The studies were carried out at an accelerating voltage of 200 kV. The bimetallic gold–palladium powders under study were dispersed in isopropyl alcohol using an ultrasonic bath. A drop of the resulting suspension was then deposited on a thin carbon film on an electron microscopic object grid.

Electrochemical measurements were performed in a sealed thermostated cell that we developed; its design is described in [15]. The current-collecting elements were metal plates of platinum or gold, which are inert in hydrochloric acid solutions of divalent palladium chloride and do not yield a stable electrochemical couple. Argon was passed continuously through the cell during the experiment. Values of the potential were measured relative to a silver chloride reference electrode.

## RESULTS AND DISCUSSION

All electrochemical measurements were performed at a temperature of  $60^\circ\text{C}$ ; at this temperature, a state of equilibrium is rapidly achieved and there are no structural changes, as was confirmed by X-ray diffraction analysis, transmission electron microscopy, and gas adsorption methods.

In studying the redox potentials of complex compounds, special attention must be given to the forms in which the complex compounds in the solution occur.

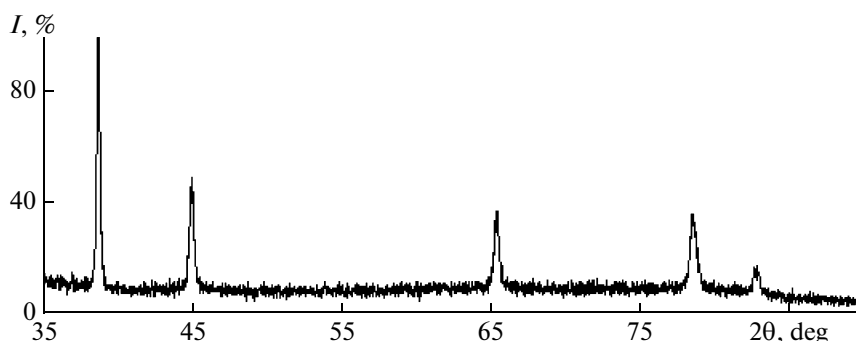


Fig. 1. X-ray diffraction pattern of a compact solid solution of  $\text{Pd}_{0.2}\text{Au}_{0.8}$  ( $a = 4.0406 \text{ \AA}$ ).

In this work, we determined spectrophotometrically that under the conditions described in [24], only the complex ion  $[\text{PdCl}_4]^{2-}$  is found in the solution. The criterion for the reliability of the electrochemical measurements served to fulfill the Nernst equation, which has the following form for low concentrations:

$$E = E^0 + \frac{RT}{2F} \ln c_{\text{PdCl}_4^{2-}}.$$

It was found that the potential of metallic gold in hydrochloric acid solutions of palladium(II) chloride is extremely unstable and varies over a wide range, which is indicative of the absence of a potential-determining couple in the system. After the addition of palladium(0) to gold (i.e., in the presence of a mechanical mixture of gold(0) and palladium(0)), the potential is established quite rapidly

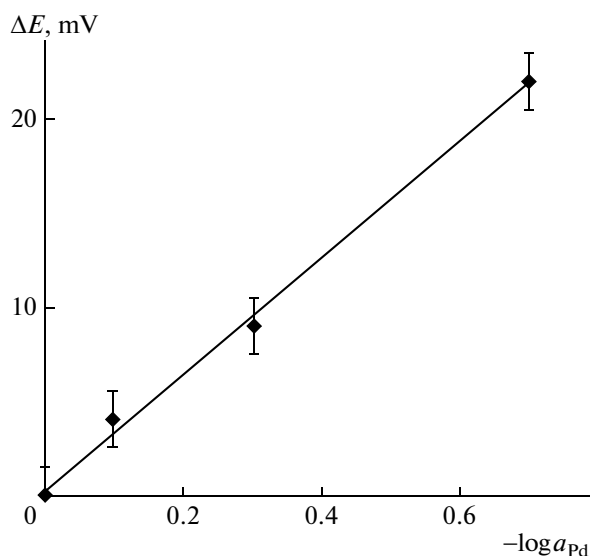


Fig. 2. Potential shift of the  $\text{PdCl}_4^{2-}/(\text{Pd}, \text{Au})$  couple with respect to the potential on compact palladium(0) versus the composition of the gold-palladium solid solution.

and corresponds to the  $\text{PdCl}_4^{2-}/\text{Pd}^0$  couple in terms of its dispersion.

It is known that the gold-palladium system is characterized by the formation of a continuous series of solid solutions. Via the high-temperature annealing of a mixture of gold and palladium, we obtained samples with a molar fraction of palladium of 0.2, 0.5, and 0.8; a single phase of substitution solid solution with lattice parameters of 4.0406, 3.9835, and 3.9269  $\text{\AA}$  respectively, was recorded in their X-ray diffraction patterns (Fig. 1); in addition, the line broadening is attributed only to the instrument component.

The redox potential of compact powders of Pd-Au substitution solid solutions corresponds to the  $\text{PdCl}_4^{2-}/(\text{Pd}, \text{Au})$  couple and obeys the Nernst equation with variation in the concentration of  $\text{H}_2\text{PdCl}_4$  over a range of  $1 \times 10^{-2}$  to  $3 \times 10^{-4}$  mol/l:

$$E = E^0 + \frac{RT}{2F} \ln a_{\text{PdCl}_4^{2-}} - \frac{RT}{2F} \ln a_{\text{Pd}}, \quad (1)$$

where  $a_{\text{Pd}}$  is the mole fraction of palladium in a solid solution.

The values of redox potentials with the participation of compact gold-palladium solid solutions shift in the positive direction relative to the values for compact palladium with gold enrichment of the Pd-Au solid solution (Fig. 2).

The fine-dispersed bimetallic samples under study and the methods for their synthesis are listed in the table. The laws of the effect of synthesis conditions on the structure and composition of bimetallic particles are discussed in detail in [22]. X-ray diffraction analysis revealed the presence of two phases, i.e., palladium and gold-palladium substitution solid solution. The pattern of formation of the latter can be explained through the previously proposed mechanism [25].

Electron microscopic studies showed (Fig. 3) that the average particle size is 20–40 nm. Studies of Pd-Au nanoparticles using high-resolution transmission electron microscopy revealed that the particles have a defect-free crystal structure. Figure 4 presents

a high-resolution electron microscopy image of a Pd–Au particle, in which the direct resolution of atomic planes is visible. The distance between the atomic planes is  $\approx 0.23$  nm. The result from a Fourier transform of the high-resolution image (see the inset in Fig. 4) indicates that the structure of the particle is a face-centered cubic lattice with  $\langle 111 \rangle$  orientation.

It was found that as the duration of the synthesis of fine-dispersed bimetallic powders increased, the solid phase was enriched in gold (similar to the palladium–platinum system discussed in [26]). No concentration changes in the system were observed after 4 h of synthesis at a temperature of  $130^\circ\text{C}$ , and the quantity of gold(III) was not reduced. This can be explained by the presence of a thin film of gold(0) insulating the palladium from the solution on the surface of the investigated powders. The insulation of particles by a gold film was also confirmed by the lack of solubility of these particles in nitric acid. Electrochemical studies of these objects showed that the measured electrochemical potential was unstable (samples A3 and A4, table); i.e., the powders behave like pure gold.

The redox potentials of the three sets of bimetallic samples prepared under different conditions (table) measured in solutions of palladium(II) chlorocomplexes in a concentration range of  $1 \times 10^{-2}$  to  $3 \times 10^{-4}$  mol/l are well described by the Nernst equation. It should be noted that after the electrochemical measurements of fine-dispersed bimetallic powders, the presence of gold ions was not recorded in the solution of  $\text{H}_2\text{PdCl}_4$ ; this eliminates the possibility of any other potential-determining couples except for the one under study occurring in the system. As the duration of the powders' synthesis becomes longer, the potential shift in the positive range increases; this could be due to both the consolidation of the powders and the gold enrichment of the surface layer.

Synthesis conditions and composition of the samples ( $\tau$  is the duration of synthesis)

Sample	$T, ^\circ\text{C}$	$\tau, \text{min}$	Solid phase composition	
			Pd, %	Au, %
Conventional heating				
A1	130	30	83.2	16.8
A2	130	60	65.0	35.0
A3	130	240	59.5	40.5
A4	130	480	58.0	42.0
B1	110	60	69.3	30.7
B2	110	240	68.6	31.4
Microwave heating				
C1	110	15	61.8	38.2
C2	110	60	41.5	58.5
C3	110	90	35.3	64.7

Electron microscopy revealed no significant coarsening of the particles prepared under exposure to microwave radiation (set C) and under conventional heating at  $110^\circ\text{C}$  (set B). In addition, the size of bimetallic particles in the case of powder synthesis under the action of microwave radiation is (within error) similar to the size of the parent palladium; i.e., there is no coarsening during synthesis, which is explained by the lower synthesis temperature. Fragments of a micrograph of samples B1 and C2 (table) are shown in Fig. 4. The increase in potential values is thus attributed to a change in the surface composition. Using the derived values of the potential of bimetallic particles and knowing the information on the effect of dispersion on the redox potential of the  $\text{PdCl}_4^{2-}/\text{Pd}^0$  system

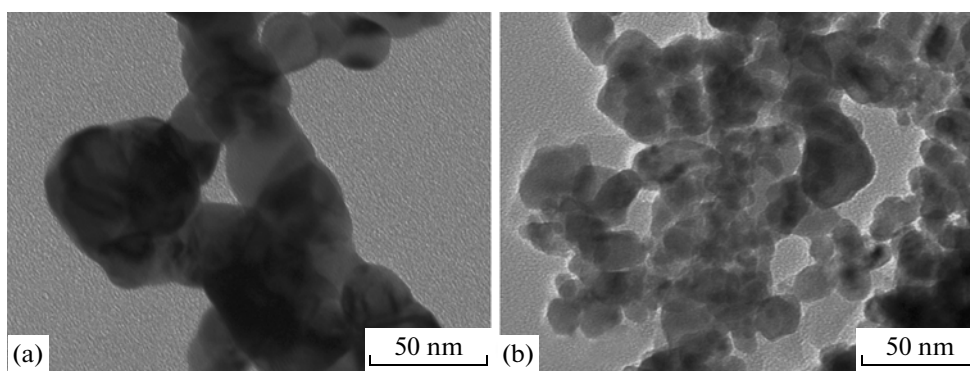
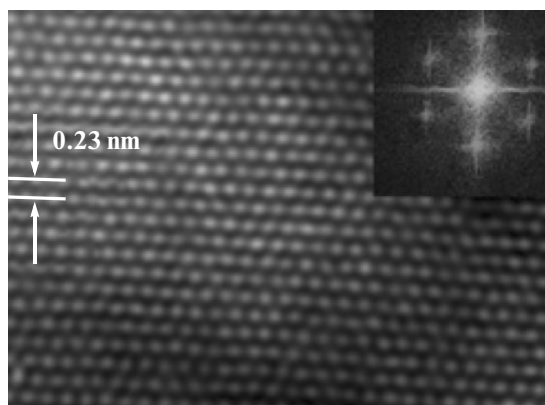


Fig. 3. Fragments of a micrograph of Pd–Au bimetallic particles: (a) sample B1 and (b) sample C2.



**Fig. 4.** High-resolution electron microscopy image of a Pd–Au nanoparticle. The inset shows the result from the Fourier transform of this image.

[15], we can estimate the surface composition of the samples.

### CONCLUSIONS

By studying the equilibrium potentials of electrodes of the first kind with the participation of metallic powders, including fine-dispersed, it is possible to estimate qualitatively the composition and size of bimetallic (Pd,Au) particles and to identify the shell–core structure of such particles (palladium insulated by a thin surface layer of gold).

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