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ELECTROCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES IN ALCOHOLIC ELECTROLYTES

ELEKTROCHEMICZNA SYNTEZA NANOCZĄSTEK SREBRA W ALKOHOLOWYCH ELEKTROLITACH

The results of study of anodic dissolution process of silver in alcoholic solutions of salts applied to the synthesis of nanoparticles of silver are presented. Silver electrode in alcoholic solutions of $LiClO_4$ dissolves at anodic potentials, higher than 0.6 V. Silver passes to the solution in the form of soluble complexes. As a result of further processes (oxidation-reduction) in electrolyte metallic silver nanoparticles are acquired. The silver nanoparticles were indentified using spectroscopic techniques; SEM, TEM, XPS. The mechanism of the process is proposed.

Keywords: silver nanoparticles, organic solvents, anodic dissolution

Przedstawiono wyniki badań anodowego roztwarzania srebra w alkoholowych roztworach soli oraz możliwość wykorzystania tego procesu do syntezy nanoczastek metalicznego srebra. Elektroda srebrna roztwarza się w alkoholowych roztworach LiClO4 przy potencjałach anodowych wyższych od 0.6 V. Srebro przechodzi do roztworu w postaci rozpuszczalnych kompleksów. W wyniku wtórnych procesów (oksydacyjno redukcyjnych) w elektrolicie tworzą się nanocząstki metalicznego srebra. Nanocząstki srebra były analizowane przy pomocy technik SEM, TEM, XPS. W pracy zaproponowano mechanizm procesu syntezy

1. Introduction

The study of the anodic dissolution of metals in organic solvents, in the area of high potentials [1] show that these processes may be a simple way to obtain nanoparticles of some metals, salts and oxides.

In the past decade, much attention has been paid to nanomaterials (metals, metal oxides as well as salts), due to their unique properties; magnetic, electrical, optical, catalytic and antibacterial [2-6]. Metallic powders (nanopowders) are frequently derived by reduction processes; chemical, thermochemical [7-9], photochemical [10], electrochemical [1, 3] and the radiochemical [11].

Our investigation focuses on the influence of solvent (alcohol type) on the synthesis of metallic silver nanoparticles.

2. Analysis methods and materials for research

Polarization studies were performed on the VoltaLab measuring system using voltamperommetric and chronoamperometric techniques. Anodic dissolution products were analyzed using spectroscopic techniques, scanning electron microscopy with X-ray analysis (SEM / EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). Spectral analysis were carried out on the powder, (obtained after evaporation of the solvent) after placing them on the pad (zinc, platinum, steel or graphite).

3. Results and discussion

In order to obtain silver nanoparticles, process of anodic dissolution of silver in the alcoholic solutions of lithium perchlorate ($LiClO_4$) was used. Figure 1a shows the LSV (Linear Sweep Voltamperommetry) polarization curves of silver in various alcoholic solutions.

Anodic polarization curves of silver, in all alcohols (methanol, ethanol and n-prophanol), are typical for the anodic behavior of metals in electrolytes with organic solvents [1]. There are clearly visible two areas on anodic curves; the plateau – at the potential range from

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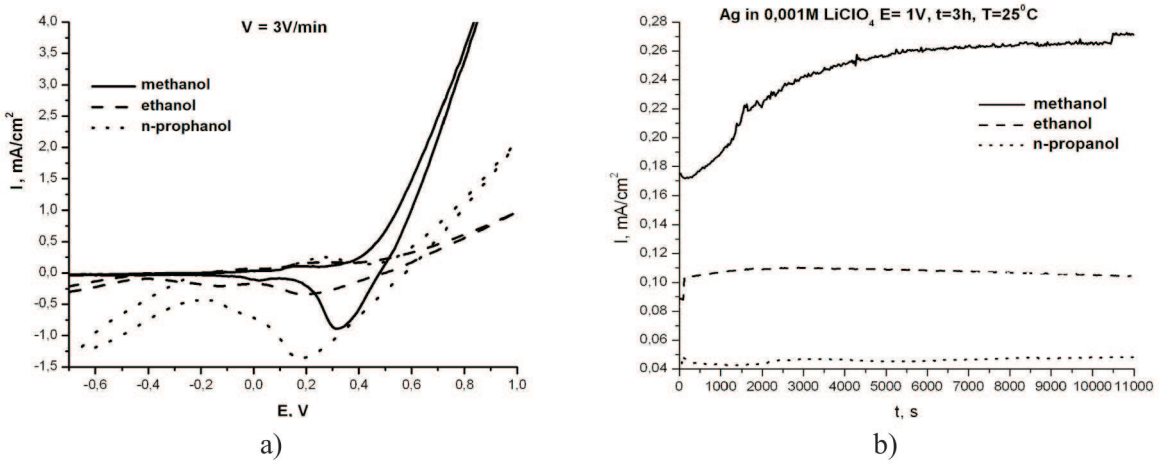

Fig. 1. Polarization curves for silver in various solvents, a) LSV curves, b) chronoamperometric curves

0.0 V to approximately 0.4 V and the second area, a sharp increase of the anodic current with growing potential values. The plateau area is mainly related to chemisorption of solvent. Potential at which the sharp increase of anodic current occurs is connected with the solvent desorption and is called the desorption potential.

In the last area, the metallic silver electrode is dissolving and forming colloidal solution of metallic silver in all studied alcoholic electrolytes. Anodic current density on the chronoamperometric curves (E=1V), monotonically decreases along with increasing carbon chain length of alcohol (Fig. 1b).

It indicates the increase of chemisorption energy of alcohols on the metal surface with the increase of alcohol chain length and thereby decrease the desorption rate and the formation of silver nanoparticles. The formation of nanoparticles proceeds at the potential above 0.6 V [1].

The presence of metallic silver nanoparticles in elecrtolyte (anolyte) is confirmed by the results of spectroscopic analysis (SEM / EDS, TEM and XPS). The results of these studies: chemical composition (SEM / EDS) are presented on Figures 2a, b, c, and Table 1. TEM analysis together with the diffraction images – Figures 3, 4, 5, clearly show the formation of nanocrystalline silver in anolyte. The nanoparticles formation process is the fastest and the most efficient in methanol solvent, as confirmed by the parameters of the anodic process (Fig. 1a, b). Silver nanoparticles formed in methanol solution are diverse in shape and diameter from approximately a few to 850 nm (Fig. 2). With increasing of alcohol chain length, size of nanoparticles decreases. Smaller and more uniform nanoparticles (diameter < 20 nm) were obtained in solutions with ethanol and n-prophanol as solvents (Fig. 4a and 5a).

The presence of significant quantities of oxygen (high molar ratio of oxygen to silver) on the surface of nanoparticles, especially in n-prophanol solutions (Table 1) is associated with a high affinity of alcohol to adsorption on a well-developed surface of nanoparticles.

TABLE 1

EDS analysis of silver nanoparticles acquired in alcoholic solutions of $LiClO_4$

Solution	Ag [%]	O [%]	Cl [%]	Zn [%]
0.001 M $LiClO_4$ – CH_3OH, E = 800mV, t = 2,5h, T = 298 K	83,60	10,59	3,09	1,75
0.001 M $LiClO_4$ – C_2H_5OH, E = 800mV, t = 2,5h, T = 298 K	37,78	17,54	0,08	43,88
0.001 M $LiClO_4$ – n-C_3H_7OH, E = 1000mV, t = 3h, T = 298 K	11,23	6,57	0,45	81,76

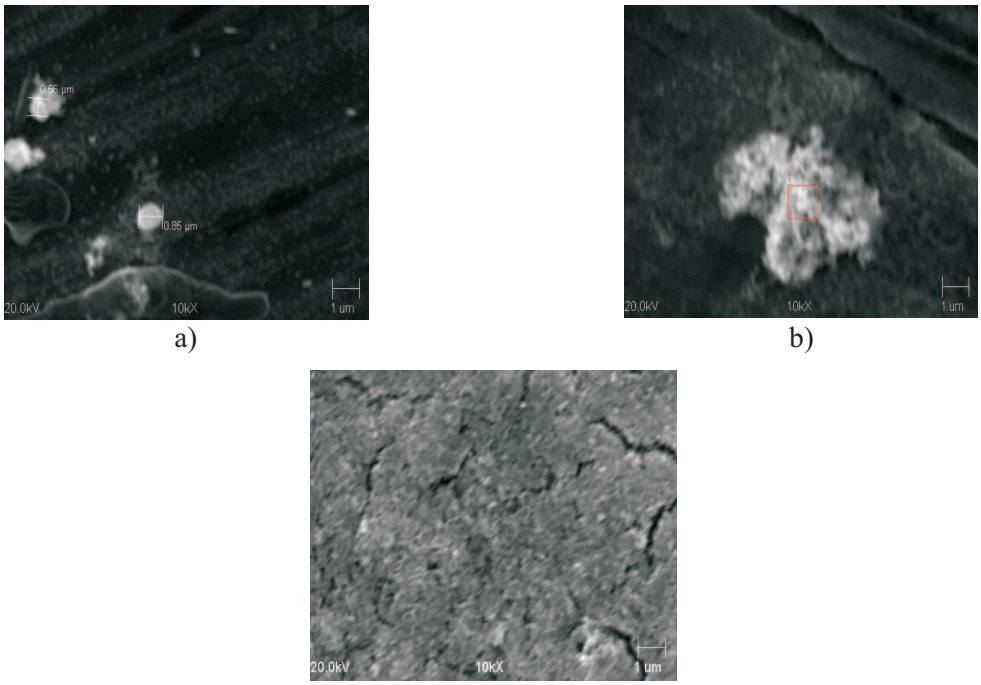

Fig. 2. SEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of $LiClO_4$ (0,001M): a) CH_3OH; b) C_2H_5OH; c) n-C_3H_7OH

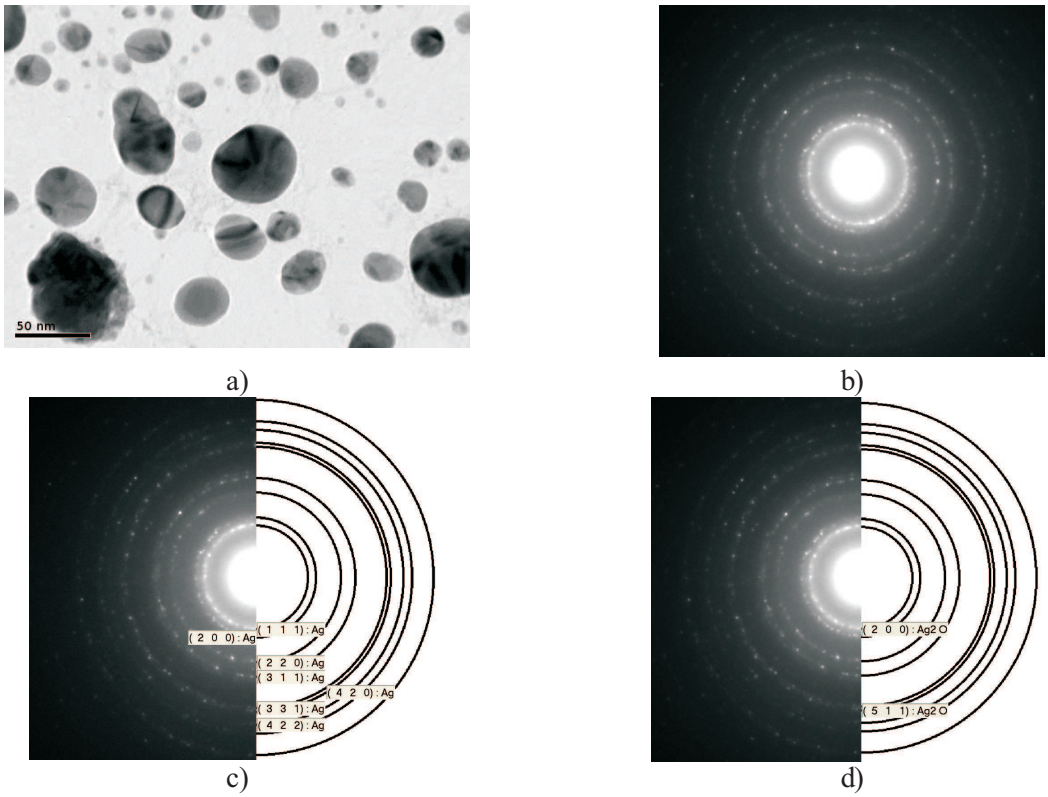

Fig. 3. TEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of 0,001M $LiClO_4$ (CH_3OH, E=1V, t=3h, T=298 K): a) morphology, b) electron diffraction, c) cubic silver match, d) Ag_2O match

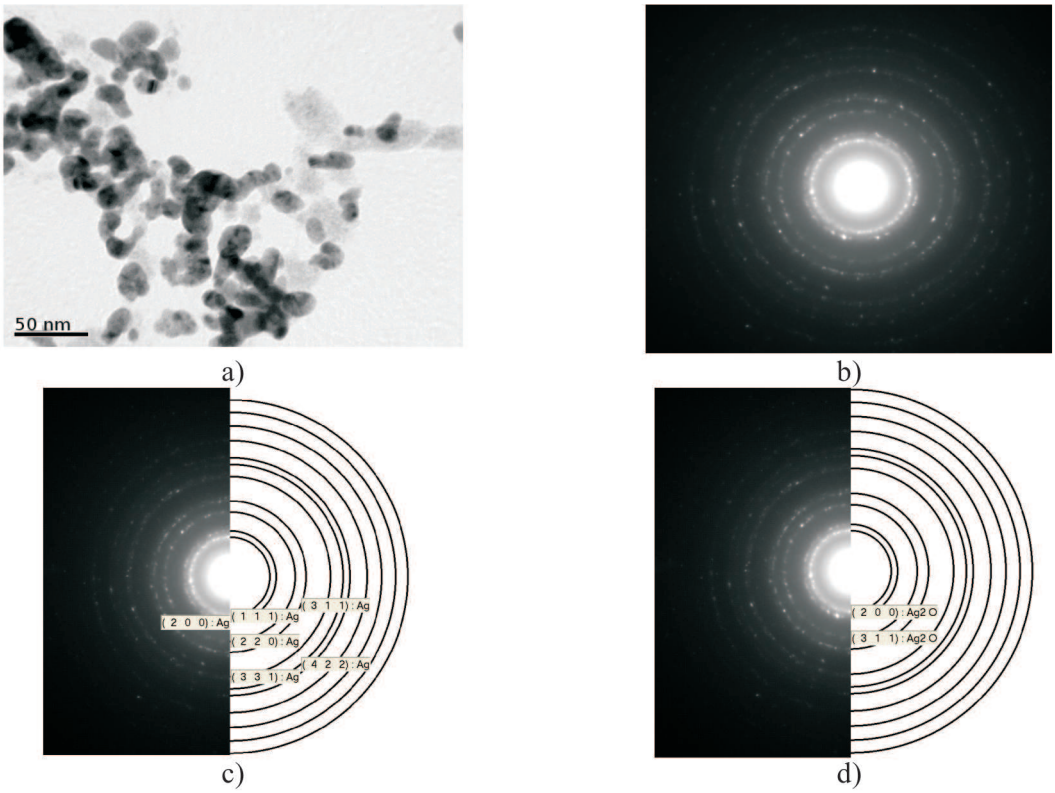

Fig. 4. TEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of 0,001M $LiClO_4$ (C_2H_5OH, E=1V, t=3h, T=298 K): a) morphology, b) electron diffraction, c) cubic silver match, d) Ag_2O match

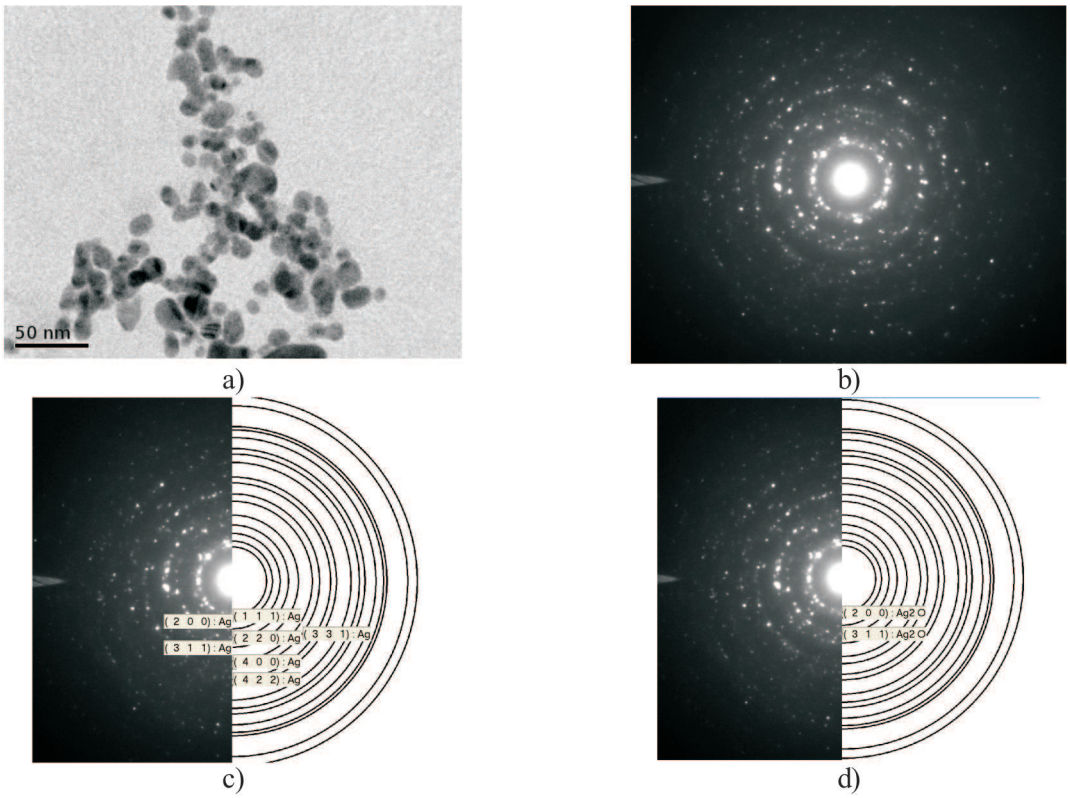

Fig. 5. TEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of 0,001M $LiClO_4$ (n-C_3H_7OH, E=1V, t=3h, T=298 K): a) morphology, b) electron diffraction, c) cubic silver match, d) Ag_2O match

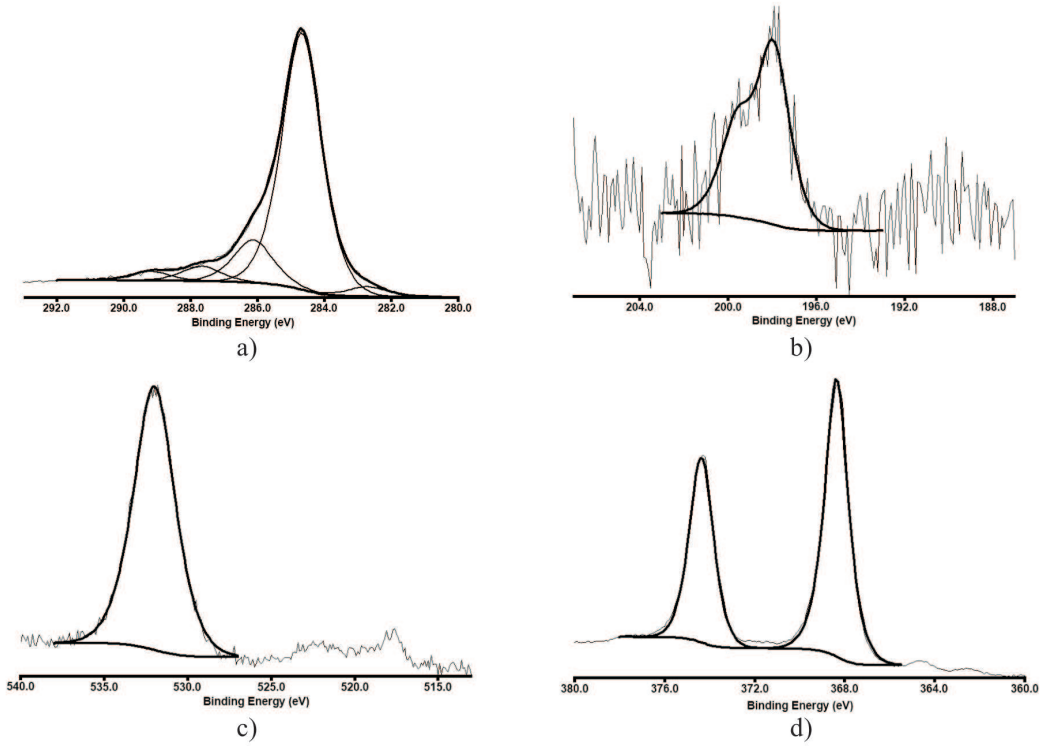

Fig. 6. XPS spectra of silver nanoparticles acquired in 0.001M $LiClO_4$ – C_2H_5OH solution, (E=1V), t=3h, T = 298 K in the bands: a) C 1s, b) Cl 2p, c) O 1s, d) Ag 3d

TABLE 2

XPS analysis of silver nanoparticles and concentration of elements

0,001M $LiClO_4$ –C_2H_5OH	Total concentration of element [%]	E_B [eV]	Formula	Part [%]	literature
Ag $3d_{5/2}$	7.41	368.29	Ag^0	100.00	368,2 eV – Ag^0[12] 368,3 Ag^0 [13]
Cl 2p	0.55	197.85	LiCl	100.00	198,1 LiCl [12]
O 1s	14.19	531.93	OH or CO,	99.96	530.7-532,5 $[OH]_{ads}$ on Ag [14] 532,2 C=O , -O- [15]
		533.43	-O-	0.04	533,6 -O- (esters) [15]

In order to determine the surface structure of silver nanoparticles the XPS studies were performed. Figure 6 shows the XPS spectra of C 1s, Ag 3d, O 1s and Cl 2p bands.

Photoelectron energy (E_B) values, in relation to literature data, and the percentage composition are shown in Table 2.

The value of E_B for band $Ag3d_{5/2}$ (368.29 ± 0.1 eV) corresponds to the energy values for metallic silver (E_B = 368.2eV). The values of E_B in the band O 1s and C 1s show the presence of carbon and oxygen atoms in organic compounds (alcohols and products of oxidation of alcohols). The results confirm the strong adsorption of alcohol on the surface of silver nanoparticles, significantly higher compared to anions.

The SEM, TEM and XPS analysis of anodic dissolution products, show that the final product of the process are the metallic silver nanoparticles.

Parallel to the process of anodic silver dissolution, there is a process of oxidation of alcohols running. It is indicated by the equilibrium potentials of the oxidation of alcohols (methanol 0.5 V, ethanol approximately 0.8V) and the polarization curves of platinum electrode [1]. The process of oxidation of alcohols initiated on silver electrode, is also present in the volume of the electrolyte with use of the intermediate products of oxidation of silver (soluble complexes or colloidal silver oxide)

as oxidants. The steps of this process are identical for all studied alcoholic solutions and as the same for the ethanol [1].

Reactions on the silver electrode (anode) run as follows:

$$Ag + ROH \rightarrow Ag(ROH)^+ + e \quad (1)$$

$$Ag + ROH \rightarrow ROAg + H^+ + e \quad (2)$$

Oxidation of alcohols:

$$ROH \rightarrow R`CHO + 2H^+ + 2e \quad (3)$$

Secondary reactions (on electrode and electrolyte) are the alcoholates decomposition and reducing of silver oxide:

$$2ROAg \rightarrow Ag_2O + ROR \quad (4)$$

$$R`CHO + Ag_2O \rightarrow 2Ag + R`COOH \quad (5)$$

The presence of silver oxide on the surface of the electrode was confirmed by XPS studies, Fig. 6, Table 2. Additionally complex ion $Ag(ROH)^+$ can be reduced on the cathode:

$$Ag(ROH)^+ + e \rightarrow Ag + ROH \quad (6)$$

4. Conclusions

Metallic silver is dissolving in all studied alcoholic solutions of lithium chlorate (VII), in the area of high anodic potentials (above the potential of desorption and oxidation of alcohols). As a result of secondary processes on the electrode and in the electrolyte volume, colloidal solutions of metallic silver nanoparticles are formed. The rate of the process and the size of nanoparticles decreases with increasing carbon chain length of alcohol particle.

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