ELECTROCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES IN ALCOHOLIC ELECTROLYTES

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

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 Volta-Lab measuring system using voltamperometric 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 Voltamperometry) polarization curves of silver in various alcoholic solutions.

Anodic polarization curves of silver, in all alcohols (methanol, ethanol and n-propanol), 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...
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 electrolyte (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-propanol 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-propanol solutions (Table 1) is associated with a high affinity of alcohol to adsorption on a well-developed surface of nanoparticles.

### Table 1

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ag [%]</th>
<th>O [%]</th>
<th>Cl [%]</th>
<th>Zn [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001 M LiClO₄ – CH₃OH, E = 800mV, t = 2.5h, T = 298 K</td>
<td>83,60</td>
<td>10,59</td>
<td>3,09</td>
<td>1,75</td>
</tr>
<tr>
<td>0.001 M LiClO₄ – C₂H₅OH, E = 800mV, t = 2.5h, T = 298 K</td>
<td>37,78</td>
<td>17,54</td>
<td>0,08</td>
<td>43,88</td>
</tr>
<tr>
<td>0.001 M LiClO₄ – n-C₃H₇OH, E = 1000mV, t = 3h, T = 298 K</td>
<td>11,23</td>
<td>6,57</td>
<td>0,45</td>
<td>81,76</td>
</tr>
</tbody>
</table>
Fig. 2. SEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of LiClO₄ (0.001M): a) CH₃OH; b) C₂H₅OH; c) n-C₃H₇OH

Fig. 3. TEM analysis of silver nanoparticles acquired during chronoamperometric polarization in alcoholic solutions of 0.001M LiClO₄ (CH₃OH, E=1V, t=3h, T=298 K): a) morphology, b) electron diffraction, c) cubic silver match, d) Ag₂O 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$_2$O 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$_2$O match
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 ($E_B = 368.2$ eV). 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:

\[
\begin{align*}
\text{Ag} + \text{ROH} & \rightarrow \text{Ag(ROH)}^+ + e \\
\text{Ag} + \text{ROH} & \rightarrow \text{ROAg} + \text{H}^+ + e
\end{align*}
\]

Oxidation of alcohols:

\[
\text{ROH} \rightarrow \text{R'CHO} + 2\text{H}^+ + 2e
\]

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

\[
\begin{align*}
2\text{ROAg} & \rightarrow \text{Ag}_2\text{O} + \text{ROR} \\
\text{R'CHO} + \text{Ag}_2\text{O} & \rightarrow 2\text{Ag} + \text{R'COOH}
\end{align*}
\]

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:

\[
\text{Ag(ROH)}^+ + e \rightarrow \text{Ag} + \text{ROH}
\]

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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