ELECTROCHEMICAL TRANSFORMATIONS ON THE SURFACE OF Al₂O₃ NANOPOWDERS

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ABSTRACT

The peculiarities of electrochemical transformations (hydrogen and oxygen reaction) on a carbon-paste electrode containing Al₂O₃ nanopowder were studied by cyclic voltammetry method. It was shown that δ-modification of Al₂O₃ has the highest reactivity in the hydrogen electrode reaction. Different behavior of Al₂O₃ nanopowders under electrochemical study of the anode (oxygen) reaction and isotopic oxygen exchange with the gas phase have been explained by the effect of amorphous phase.

INTRODUCTION

Cyclic voltammetry is a classic method for studying electrocatalytic reactions [1, 2]. Commonly electrocatalysts are prepared either in the form of small particles dispersed on a substrate or as a thin layer, again, on a support. The oxide γ-Al₂O₃ is used as a substratum for catalysts (for example, C₀ – MoO₃, Pd, Pt); while aluminum oxide may itself act as a catalyst [3]. There is a large number of studies on the electrocatalytic activity of different electrode materials (metals (review article [5]), alloys and compounds (reviewed in [6]) concerning the electrode reaction of hydrogen discharge / ionization.

In this paper, the cyclic voltammetry method was used to study the features of electrochemical transformations (hydrogen and oxygen reaction) on a carbon-paste electrode containing Al₂O₃ nano powder. The last was obtained by the explosion of aluminum wire.

EXPERIMENT

Preparation and characterization of Al₂O₃ nanopowders.
Four series of $\text{Al}_2\text{O}_3$ nanopowders were prepared by the explosion of aluminum wire at different values of superheat degree (K). The degree of superheating is defined as a ratio of the energy supplied to the wire to the sublimation energy of the wire material. All the powders were sedimentated in isopropyl alcohol in a mode that provided the extraction of particles with a diameter greater than 200nm.

The specific surface area of powders ($S$, $\text{m}^2/\text{g}$) was determined by adsorption-desorption of nitrogen from its mixture with helium using TriStar 3000 Analyzer (Micromeritics, USA). The phase composition was studied by X-ray diffraction on a Bruker D8 Discover diffractometer with GAADS (Bruker AXS, Germany). The extraction dynamics of water and gases absorbed by the powders (TG / DSC / MS data) was obtained using Demo-S TA 409 PC/4/H device (NETZSCH, Germany). The results of samples examination are presented in the table.

### Table

<table>
<thead>
<tr>
<th>Series №</th>
<th>Superheat degree, K</th>
<th>The phase composition, % mass</th>
<th>$S$, $\text{m}^2/\text{g}$</th>
<th>$D_{\text{CSR}}$*, nm</th>
<th>$d^{**}$, nm</th>
<th>$-\Delta m$, % mass (800°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,37</td>
<td>53 47</td>
<td>84</td>
<td>21±2</td>
<td>8,5</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>0,7</td>
<td>15 85</td>
<td>41,7</td>
<td>21±3</td>
<td>2,6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1,2</td>
<td>30 70</td>
<td>23,2</td>
<td>18,5±2</td>
<td>20,3</td>
<td>1,75</td>
</tr>
<tr>
<td>4</td>
<td>2,3</td>
<td>40 60</td>
<td>38,3</td>
<td>17±2</td>
<td>21,5</td>
<td>3,3</td>
</tr>
</tbody>
</table>

*D_{\text{CSR}}$ characterizes the size of the coherent scattering region for $\delta$-$\text{Al}_2\text{O}_3$ phase

**$d$ – the average particle size

The analysis of recorded diffraction patterns indicates the presence of an amorphous component in addition to the two crystalline phases in all the powders (Table). It has been impossible to define the amount of the amorphous component due to lack of information about the structure of $\delta$-$\text{Al}_2\text{O}_3$ phase.

### Electrochemical properties

Electrochemical studies were carried out by voltammetry method using carbon-paste electrode (CPE). The test substance was added to CPEs in the amount of 0.2g per 1g of the carbon powder made of the spectrally pure graphite “C-2”. The binder was dibutyl phthalate added in the amount of 0.3 ml per gram of the dry mixture. A glassy-carbon crucible acted simultaneously as the auxiliary electrode and the electrolyzer. The reference electrode was a saturated Ag/AgCl electrode of the EVL-1M1 type. All potentials in the text are reported relative to the Ag/AgCl electrode. The measurements were performed in air at room temperature over the potential range...
between −0.8 and +1.0 V, when the carbon paste was electrically inactive and did not produce signals.

RESULTS AND DISCUSSION

Figure 1 presents a cyclic voltammogram, which was recorded during polarization of CPE containing the sample from the first series (Al₂O₃-1) in 1M HCl at the potential scan rate of 20mVs⁻¹. One can discern two potential ranges which differ in character of the proceeding electrochemical processes:

1) an irreversible reduction process proceeds in the potential range from 0.00 to -0.75V;
2) the reversible redox reaction can be observed above 0.00V. It is seen more clearly from the inset in Fig. 1, where the cyclic polarization curve of the sample Al₂O₃-4 recorded in the potential range 0,0…+0,7V is shown.

Fig.1. Cyclic voltammogram of Al₂O₃-1 sample in 1 M HCl at the potential scan rate \( \nu=20\text{mVs}^{-1} \). The insert: cyclic voltammogram of Al₂O₃-4 sample recorded at the potential range 0,0…+0,7V.
From a thermodynamic viewpoint the proceeding of proper electrochemical transformation of \( \text{Al}_2\text{O}_3 \) oxide at the potential range under consideration is improbable. The following observations provide additional confirmation of that.

1. Chemical analysis reveals the almost complete absence of aluminum cations in the background solution throughout the potential scan range. This is consistent with [7], which affirms that \( \text{Al}_2\text{O}_3 \) is practically insoluble in dilute acid solutions.

2. In case of using CPE as a working electrode the substance consumption plays an important role; that manifests itself in a noticeable decrease in the intensity of electrochemical signals after each previous potential scan. For the objects under study in this work such an effect is absent. (Fig.1 shows the electrochemical behavior of \( \text{Al}_2\text{O}_3 \) during two cycles, Fig.2 presents a five-time cathodic polarization of \( \text{Al}_2\text{O}_3\)-3 electrode in 2M HCl at the potential scan rate of 5mVs\(^{-1}\) in the range +400...-1000mV).

The observed electrochemical responses during cathodic polarization of \( \text{Al}_2\text{O}_3 \) nanopowders can be explained by the reduction processes of oxygen [8] or hydrogen [8, 9], adsorbed on the electrode surface. According to Henze [8], dissolved in acid solution oxygen is reduced at the working electrode in two stages:

\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad \text{(from -0.1 to -0.3V)} \]
\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \quad \text{(from -0.7 to -1.3V)} \]

To verify this mechanism one can remove the dissolved oxygen by scavenging of background solution by pure nitrogen or argon for 5-10 min [8]. The use of this technique has not changed voltamperic curves, shown in Fig. 1 and 2.

Thus, the electrochemical response under cathodic polarization of \( \text{Al}_2\text{O}_3\)-electrodes should be associated with the reaction of hydrogen discharge:

\[ \text{H}_3\text{O}^+ + 2e^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O} \]

Figure 3 shows the cathodic voltammograms recorded at the polarization of CPE containing \( \text{Al}_2\text{O}_3 \) nanopowders with individual structural characteristics (Table). It can be seen the electrochemical activity of powders, except for sample \( \text{Al}_2\text{O}_3\)-1, decreases with increasing superheat degree of the metal.

According to X-ray data the phase composition of powders is represented by two modifications of the oxide: \( \gamma\)-\( \text{Al}_2\text{O}_3 \) and \( \delta\)-\( \text{Al}_2\text{O}_3 \) (Table); and the ratio of these phases \( \gamma/\delta \) correlates with a coefficient of superheat forming a sequence 2(0.176) – 3(0.429) – 4(0.67). With excluding the size factor from consideration, that allows estimating the extent of influence of phase composition on the electrochemical behavior of \( \text{Al}_2\text{O}_3 \) powders. Effective diameters of particles calculated by the formula:
\[ d_{BET} = 6(S\rho)^{-1}, \]

(S – the surface area, measured by BET method, \( \rho = \rho_{\gamma-Al_2O_3} + \rho_{\delta-Al_2O_3} \)) are arranged in a row 2(40нм)-4(45нм)-3(73нм).

Fig. 2. Five-time cathodic polarization of \( Al_2O_3-3 \) electrode in 2M HCl at the potential scan rate of 5mVs\(^{-1}\) in the range +400…-1000mV.

Fig. 3. Cathodic curves of \( Al_2O_3 \) nanopowder in 2M HCl at the scan rate of 10mVs\(^{-1}\). The numeral corresponds to the sample number in the table; 5 - background.

It can be seen; the powders 2 and 4 have almost the same size distribution. At the same time comparative analysis of the photographs of the particles and their size distribution obtained by an electron microscope JEM-200 (JEOL) reveals the actual particle size for powders of the third and the fourth series is almost identical (Fig. 4, Table).

Thus, it is fully justified to suppose the phase composition is the determining factor in the electrochemical activity of \( Al_2O_3 \) nanopowder.

Curve 5 in Fig. 3 corresponds to the hydrogen reaction proceeding on the surface of carbon electrode (background signal). Comparison of the last with voltampetric curves
recorded for the CPE-containing Al₂O₃ nanopowders leads to the conclusion the reduction potential of H⁺ ions is greatly shifted to the anode side. The decrease in overvoltage of hydrogen evolution was observed earlier in various compounds [5, 6, 8, 9]. This phenomenon has been attributed to the catalytic effect of the working electrode substance [1, 8, 9]. Taking into account the phase composition of samples and the results shown in Fig. 3 one can conclude that δ-Al₂O₃ modification is more effective catalyst to the reaction of electrochemical hydrogen evolution. Early [4] the catalytic effect of δ-Al₂O₃ on the formation of tioolibdate was demonstrated. Sample Al₂O₃-1 doesn’t obey the law. Such behavior can be attributed to its smaller particle size, on the one hand, and the possible influence of the amorphous phase - on the other. Comparing the amount of gas absorbed by samples (Δm in the Table) and taking into account the known property of amorphous Al₂O₃ to intensively absorb moisture, we can conclude that Al₂O₃-1 contains the amorphous phase approximately 2 times greater than other samples.

![Particle size distribution and their image JEM-200](image)

Fig.4. Particle size distribution and their image JEM-200 for Al₂O₃-4; N = 6114 (a) and Al₂O₃-3; N = 3506 (b).
Figure 5 presents the cyclic polarization curves for samples 1 and 4 registered in 1M HCl at the scan rate of 5mVs^{-1} in the potential range 0.00...0.95V. Fig. 5 shows the redox process is reversible in the electrochemical sense: the total anodic charge of $Q_A$ is equal to the total cathodic charge $Q_K$, within experimental error. Notice the following peculiarities of the electrochemical behavior of $\text{Al}_2\text{O}_3$ nanopowders at the potential range where the redox process proceeds:

1. The potentials of peaks do not depend on the scan rate, $\nu$.
2. The current value of the peaks is a linear function of $\nu$.
3. Multiple cycling of the potential does not affect the response; that is a steady-state voltammogram takes place.

![Cyclic voltammogram](image)

Fig.5. Cyclic voltammogram of $\text{Al}_2\text{O}_3$-1 (solid line) and $\text{Al}_2\text{O}_3$-4 (dotted line) in 1M HCl at the potential scan rate of 5mVc^{-1}.

These results are typical for fast reversible surface redox transitions [2, 10, 11]. Taking into account that in aqueous solutions the surface of $\gamma$-$\text{Al}_2\text{O}_3$ absorbs water and quickly hydroxylates [3, 12]:

$$\text{OH}^- \quad \text{OH}^-$$

$$\ldots \text{Al}^{3+} \quad \text{OH}^- \quad \text{Al}^{3+} \quad \text{OH}^- \ldots$$

$$\ldots \text{O}^{2-} \quad \text{Al}^{3+} \quad \text{O}^{2-} \quad \text{Al}^{3+} \ldots$$

one can represent the observed redox process in the form of electrode reaction:

$$2\text{OH}^- - 2\bar{e} \iff \text{H}_2\text{O} + \text{O}_{ads}$$  \hspace{1cm} (1)
Steady state of cyclic voltammograms testifies that the electrode surface is saturated with electro-active substance [11].

Comparison of the two cyclic voltammograms shown in Fig. 5 reveals a significant difference in the intensity of reaction (1). Electrochemical activity of Al₂O₃-4 electrode is much higher than that of Al₂O₃-1 electrode.

There is an opinion the ability of solid to absorb oxygen electrochemically correlates with the ability of oxides to exchange oxygen with the gas phase [9, 13]. In this respect, it is of interest to compare the obtained results with the data on isotopic exchange of Al₂O₃ nanopowders with gas-phase oxygen [14].

According to [14], isotopic oxygen exchange in the sample Al₂O₃-1 is in all respects much superior to that of the nanopowder Al₂O₃-4, while the electrochemical activity, on the contrary, is significantly higher in the latter (Fig. 5). Consequently, except for size [14] there is another factor affecting the behavior of Al₂O₃ nanopowder while in contact with oxygen-containing phase. By comparison with other samples Al₂O₃-1 nanopowder contains a much larger amount of amorphous phase, for which according to [15] the oxygen diffusion coefficient is 2-3 orders of magnitude greater than that of γ-Al₂O₃. This allows explaining the rapid kinetics of isotopic oxygen exchange between the gas phase and the sample Al₂O₃-1 [14]. On the other hand, the micrographs of the powder №1 obtained on JEM-200 show large particles (d>10 nm) are spherical in shape with clear boundaries, while smaller particles are merged into conglomerates with blurred (fractal) boundaries; it seems the crystallites in the associations are cemented by amorphous phase. Then, the electrochemical inactivity of the powder in the anode reaction can be explained by a decrease in the number of active sites on the electrode surface [13].

CONCLUSION

1. Nanosized powders of Al₂O₃ have been prepared by the explosion of aluminum wire. The degree of superheating (the ratio of supplied energy to the sublimation energy) influences on morphological characteristics and the phase composition of powder. For K>1 the particles have a regular spherical
shape, and form an ensemble as a branched cellular structure. This can present certain practical interest, e.g. in catalysis.

2. Electrocatalytic properties of nano Al$_2$O$_3$ have been investigated by chronoamperometry and cyclic voltammetry in 2M HCl aqueous solution.

3. It has been shown the $\delta$-modification of aluminum oxide exhibits a much higher catalytic activity in the range of the cathodic reaction (hydrogen reaction) compared to $\gamma$-Al$_2$O$_3$.

4. Different behavior of Al$_2$O$_3$ nanopowders under electrochemical study of the anode (oxygen) reaction and isotopic oxygen exchange with the gas phase have been explained by the effect of amorphous phase.

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REFERENCES


