SYNTHESIS OF Ag⁺ - CONDUCTING MEMBRANES BASED ON β–Al₂O₃ FOR THE DEVELOPMENT OF HIGH-TEMPERATURE SENSORS OF SULFUR-CONTAINING GASES

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ABSTRACT

The ecology of large industrial cities, regions with power plants, metallurgical, mining, oil and other enterprises suffers from the large amount of sulfur-containing gas (generally in SO₂ form) blowouts. The monitoring of SO₂ concentrations directly in the hot zone of the outcoming gases is necessary to control such blowouts, in turn, it needs the development of new sensors giving the opportunity to determine SO₂ at temperatures of 600-800 °C. The perspective material for such sensor is β–alumina with the structure in which Na⁺ ions are replaced by Ag⁺. β–alumina is also a promising material for the development of solid electrolytes with high conductivity due to its layered structure; in one of such layers the transit of Na⁺ (Ag⁺) ions occurs. The work describes the pyrolytic synthesis of β–alumina with different compositions performed to manufacture the precursor powder of maximal dispersity. The phase composition of the samples was determined and the replacement of Na⁺ ions by Ag⁺ was carried out. The temperature dependencies of β–alumina in sodium and silver forms are discussed.

INTRODUCTION

The ecology of large industrial cities, regions with power plants, metallurgical, mining, oil and other enterprises suffers from the large amount of sulfur-containing gas (generally in SO₂ form) blowouts. The monitoring of SO₂ concentrations directly in the hot zone of the outcoming gases is necessary to control such blowouts, in turn, it needs the development of new sensors giving the opportunity to determine SO₂ at temperatures of 600-800 °C. The perspective material for such sensor is β–alumina with the structure in which Na⁺ ions are replaced by Ag⁺. Two forms of β–alumina with similar structure exist in NaAlO₂-Al₂O₃ system: β- alumina and α β - alumina. Due to their high cation conductivity at temperatures over 500K, ceramics based on these compounds is believed to be very perspective solid electrolyte in various electrochemical systems including solid-phase batteries and accumulators with high storage capacity, gas analyzers, memory elements, etc. [1].

Stoichiometric β- alumina formula usually written as Na₂O-11Al₂O₃ is a tentative one. In fact, β- alumina is a typical non-stoichiometric phase which is stable in some concentration range with Na₂O excess with respect to Na₂O-11Al₂O₃. The tentative ideal stoichiometric composition of β-Al₂O₃ is Na₂O-5.33Al₂O₃; in fact, this metastable phase is also non-stoichiometric. The estimates of the temperature-concentration ranges of the homogeneity regions reported for these forms of β-alumina are contradictory, this fact manifests itself in numerous versions of NaAlO₂-Al₂O₃ phase diagrams [2-4]. In particular, one can note that β-Al₂O₃ was reported to form at following Na₂O to Al₂O₃ ratios: 1:9-1:11 [2], 1:7-1:9.5 [3], 1:8-1:11 [4]; for β-Al₂O₃ phase these ratios were determined as 1:6-1:7 [2], 1:5-1:6 [3], 1:5-1:7 [4].
\[ \beta\text{-alumina phase is a hexagonal one (P6}_3/mmc), and } \beta'\text{-alumina phase has rhombohedral (R3m) symmetry. The lattice parameters in the hexagonal conception are } a_0 = a_\beta = 5.59 \text{ Å and } 1.5 \epsilon_0 = c_\beta = 33.95 \text{ Å [4-6].} \]

Crystalline layered lattices of \( \beta \)- and \( \beta' \)-alumina consist of spinel blocks \([\text{Al}_{11}\text{O}_{16}]\) separated by conductive planes perpendicular to c-axis. The conductive plane contains non-compactly packed oxygen layer and Na\(^+\) cations. The spinel block is formed by four compactly packed oxygen layers and Al\(^{3+}\) cations localized in tetra- and octahedral positions. The elementary cells of \( \beta \)- alumina and \( \beta' \)-alumina contain two and three spinel blocks, respectively; for this reason, they are usually called two- and three-blocks \( \beta \)-alumina. Suggesting the formula for the ideal \( \beta \)-alumina as Na\(_3\)Al\(_{15}\)O\(_{31}\) and for \( \beta' \)-alumina – as Na\(_6\)Al\(_{32}\)O\(_{51}\), one can obviously consider that the latter one is formed from the \( \beta \)-phase via the replacement of one Al\(^{3+}\) ion in spinel blocks by three Na\(^+\) ions in the conductive plane; thus, the conductivity of \( \beta \)-alumina should be higher than that of \( \beta' \)-alumina. Indeed, paper [4] reports the conductivity of \( \beta \)- and \( \beta' \)-alumina phases at 573K as 0.08 \text{ and } 0.2 \text{ Ohm}^{-1}\text{cm}^{-1}, respectively.

The structure similarity and the close values of the horizontal lattice parameters of \( \beta \)- and \( \beta' \)-Al\(_2\)O\(_3\) phases do not contradict the possibility of epitaxial integration of their crystal lattices in the basal plane with the formation of some mixed-layered structure. Such mixed-layered structure can be formed in NaAlO\(_2\)-Al\(_2\)O\(_3\) system at temperatures below 1823K instead of the mechanical mixture of \( \beta \)- and \( \beta' \)-alumina phases; note that the layers with \( \beta \)- and \( \beta' \)-structures never form an array. The content of metastable \( \beta \)-alumina intercalations in the mixed-layered phase decreases with the increase in the temperature of the thermal treatment and its duration, while the content of stable \( \beta' \)-alumina phase intercalations increases [5, 7-11].

It is well known that physical-chemical properties of solid electrolytes depend on synthesis conditions; this fact is absolutely true for super-ionic conductors based on sodium polyaluminates. The synthesis of such ceramics is complicated by high temperatures necessary for the formation and baking of cation-conducting phase or phases resulting in the non-controlled Na\(_2\)O loss as well as by the absence of the valid phase diagram of the system. The latter is due to the problems with XRD identification of \( \beta \)-, \( \beta' \)-alumina, and mixed-layered structure; since the structure of these objects is quite similar, their XRD pattern are also very close, see [6,11]. As can be concluded from this work, the discussed XRD patterns have a lot of peaks; most of them are common for all phases. In addition, the identification problem is more complex due to the presence of defects in the structures, the absence of an arrayed order of \( \beta \)- and \( \beta' \)-alumina intercalations in the mixed-layered phase, sample texture, etc. Authors of [9] state that the problem of the quantitative determination of the phase ratio in the region of NaAlO\(_2\)-Al\(_2\)O\(_3\) system with low alkali content is possible only by coupling of experimental study with computer modeling.

The task of the present work was the study of sodium polyaluminates Na\(_2\)O-nAl\(_2\)O\(_3\) (5.5 \( \leq n \leq 9.5\) ) electroconductivity as a function of the synthesis approach and treatment parameters of the final ceramics.

**EXPERIMENTAL**

Solid-phase (s) and liquid-phase (l) synthesis in a version of joint salt decomposition from their water solution were used. It is generally accepted that, in contrast to solid-phase method, pyrolytic (liquid-phase) approach gives the opportunity to provide the reagent mixture at molecular level. The temperatures of the final ceramic calcination were chosen regarding to the phase diagram reported in [3] which is considered to be the most reliable one, see Fig. 1.
Figure 1. Phase diagrams of NaAlO$_2$-Al$_2$O$_3$ system according to [3]. 2Bβ –β- alumina phase, 3Bβ - β - alumina phase.

Solid-Phase Synthesis

Corundum and sodium carbonate were used as the initial reagents. To obtain 0.09 mole of the final ceramics, the reagent mixture taken in proper amount was ball milled with the rotation rate of 500 rpm during 40 reverse cycles, the duration of each cycle was 5 minutes. Ball milling was performed in agate bowl by agate balls with the diameter of 15-20 mm. The obtained powder was compacted in the press-form under the pressure of ~16 kg/cm$^2$, the resulting pellets were ~ 3 mm in width and ~ 15 mm in diameter. At the final step, the pellets were calcined at 1793-1803K for 4 hours.

Pyrolytic (Liquid-Phase) Synthesis

The initial reagents in this approach were Al(NO$_3$)$_3$·6H$_2$O and sodium formate. To obtain 0.12 mole of the final product, the proper amounts of the reagents were dissolved in 1400 mL of distilled water. To prevent the aluminum nitrate hydrolysis, the solution was aciditated by formic acid up to the pH value of 4. The reaction mixture was evaporated using the sand bath; the solidified solution was moved into the crystallization vessel which was placed in the drying box. Salt decomposition occurred at 393K at periodic stirring until the end of nitrogen oxides isolation, the duration of this step was about 12 hours. The obtained precursor was milled and mechanoactivated in a ball mill at 450 rpm during 20 reverse cycles, each of 5 minutes. Then the powder was compacted into the pellets which were calcined at 1253-1293K for two hours (initial calcination). At the next step, the pellets were broken in the Abbich mortar and ball milled (400 rpm, 15 reverse cycles, 5 min. each). The obtained powder was compacted into the pellets and calcined at 1793-1803K for two hours (final calcination), the pellet size and the compacting pressure were the same as in solid-phase synthesis.
Synthesis of Strengthened Electrolytes

It is well known that solid electrolytes should possess high mechanical strength. Ceramics strengthening can be performed by different technological approaches; one of them is an optimal combination of the compacting pressure, calcination temperatures, the number of calcination cycles and their duration. According to our preliminary experience on the chemical resistance of sodium polyaluminates, the samples with Na$_2$O-6Al$_2$O$_3$ composition could be considered as an optimal choice with respect to electroconductivity properties. For this reason, the strengthened samples of the ceramics with such composition were synthesized both by solid-phase (s) and liquid-phase (l) approaches using the following regimes.

Solid-phase synthesis – initial ball milling in a planetary mill (350 rpm, 12 reverse cycles, 5 min. each cycle); initial calcination at 1773 K for 2 hours, secondary milling for 30 minutes, compacting (binding agent less than 2 wt.% is acceptable) at 30 t/cm$^2$ with isostatic exposure for 3 min.; 72 hours drying at 393K; secondary calcination at 1923K for one hour, temperature lowering down to 1773K during 30 min., and calcination at this temperature for 1 hour.

Liquid-phase synthesis – the salt solution was kept at 363K for four hours and then evaporated during 14-hour drying at 383K. The initial calcination was performed at 433K (10 hours); the secondary calcination was done at 1173K (4 hours). The obtained precursor was milled (400 rpm, 12 reverse cycles, 5 min. each); compacted (binding agent less than 1.5 wt.% is acceptable) at 30 t/cm$^2$ with isostatic exposure for 3 min.; dried for 72 hours at 393K; calcined at 1923K for one hour. The calcination temperature was then lowered down to 1773K (30 minutes) and the sample was kept at this temperature for 2 hours. The solution of the synthetic rubber in white-spirit was used as the binding agent in both cases (solid- and liquid-phase synthesis).

The density of the strengthened samples (indicated as s.s. and s.l. for solid-phase and liquid phase synthesis, respectively) was measured by pyknometer, it was determined as being 93 and 98% of the theoretical value for s.s. and s.l., respectively.

The analysis of the synthesized ceramics was performed by atomic adsorption spectroscopy (AAS-100). At first, the samples were neutralized in water up to the constant pH value; neutralized solution was analyzed for Na$_2$O content. The decrease in Na$_2$O concentration by 8-10% from the specified one was observed in all measurements; but, for convenience, hereinafter, the compositions are listed with respect for synthesis.

According to XRD data obtained using Shimadzu XRD-6000, α-Al$_2$O$_3$ was detected only in the samples with Na$_2$O-9.5Al$_2$O$_3$ and Na$_2$O- 8.75Al$_2$O$_3$ compositions. XRD patterns prove the formation of α- and β'- alumina in all samples, however, the quantitative analysis was not possible due to the problems discussed above.

Electroconductivity measurements were carried out by two-electrode method at 1 kHz in air in the temperature range from 313 to 625K. The pellets were prepared to the tests according the following procedure: both sides of the pellet were ground and thoroughly cleaned; the width of the pellets was measured with the accuracy of ±0.01 mm. At last, graphite electrodes were deposited on both pellet sides. The prepared pellets were mounted in the measuring cell using the holders with platinum contacts; the cell was placed in a furnace with the controlled temperature; the accuracy of temperature control was ±2 K.

The replacement of Na$^+$ to Ag$^+$ ions was performed in the silver nitrate melts at the temperature 15 °C higher than its melting temperature (209.7 °C). The samples were cleaned from the silver nitrate in ethanol. The completeness of the ion exchange was controlled by weight method – the measured weight changes were compared with the calculated values. As a result, the samples with 99% replacement of Na$^+$ ions by Ag$^+$ ions were manufactured.
RESULTS AND DISCUSSION

The dependence of the specific resistance (ρ) on the reverse absolute temperature (T) for all samples can be well approximated by linear function; hence, the well-known relationship for the specific conductivity of crystals (σ) can be used:

\[ \sigma = \sigma_0 \exp(E_a/2RT), \]

Since \( \sigma = 1/\rho \), equation (1) can be rewritten as

\[ \lg \rho = \lg \rho_0 + E_a/4.606RT, \]

where \( \rho_0 \) is a pre-exponential factor which is equal to the specific resistivity at \( T \to \infty \), \( E_a \) is the activation energy of the conductivity, and \( R \) is the gas constant.

The specific resistance was calculated according the formula \( \rho = rS/L \), where \( r \) and \( L \) are the resistance and the width of the sample, respectively, and \( S \) is the area of the graphite electrode (1 cm²). The value of \( E_a \) was determined from the slope of the smoothed \( \lg \rho = f(1/T) \) plots.

Table 1 presents the compositions of the samples studied along with the synthesis method and the calculated values of the specific resistance at 373 and 573K. As an illustration, Fig. 2 demonstrates a typical \( \lg \rho = f(1/T) \) plot for one of the samples.

<table>
<thead>
<tr>
<th>N</th>
<th>Composition</th>
<th>Sintering method</th>
<th>( E_a ) eV</th>
<th>( \lg(\rho_{373}, \text{Ohm cm}) )</th>
<th>( \lg(\rho_{573}, \text{Ohm cm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na(_2)O-9.5Al(_2)O(_3)</td>
<td>1</td>
<td>1.01</td>
<td>6.11</td>
<td>3.73</td>
</tr>
<tr>
<td>2</td>
<td>Na(_2)O-8.75Al(_2)O(_3)</td>
<td>1</td>
<td>0.768</td>
<td>6.22</td>
<td>4.41</td>
</tr>
<tr>
<td>3</td>
<td>Na(_2)O-8Al(_2)O(_3)</td>
<td>1</td>
<td>0.525</td>
<td>5.58</td>
<td>4.34</td>
</tr>
<tr>
<td>4</td>
<td>Na(_2)O-6Al(_2)O(_3)</td>
<td>s</td>
<td>0.697</td>
<td>4.31</td>
<td>2.67</td>
</tr>
<tr>
<td>5</td>
<td>Na(_2)O-6-Al(_2)O(_3)</td>
<td>s.s.</td>
<td>0.427</td>
<td>4.98</td>
<td>3.97</td>
</tr>
<tr>
<td>6</td>
<td>Na(_2)O-6Al(_2)O(_3)</td>
<td>s.l.</td>
<td>0.397</td>
<td>4.69</td>
<td>3.87</td>
</tr>
<tr>
<td>7</td>
<td>Na(_2)O-5.5Al(_2)O(_3)</td>
<td>1</td>
<td>0.662</td>
<td>4.80</td>
<td>3.26</td>
</tr>
</tbody>
</table>

The resistance of the samples decreases with the increase in Na\(_2\)O content, see Fig. 3.
Figure 2. Temperature dependence of the specific resistance of the strengthened Na₂O-6Al₂O₃ sample synthesized by liquid-phase method (N6 in Table 1).

Figure 3. The dependence of the specific resistance of sodium polyaluminate (Na₂O-nAl₂O₃) samples synthesized by different methods on the sample composition at 373K (A) and 573K (A’); 1 – liquid-phase method; 2 – solid-phase method, 3 – strengthened ceramics produced by solid-phase synthesis, and 4 – strengthened ceramics produced by liquid-phase synthesis.

This behavior can be attributed to the increase in the content of β'-alumina phase which is more conductive or with the increase in the number of intercalations containing this phase; in addition, this can be due to the disappearance of isolating α-Al₂O₃ phase from all samples (the only exceptions are samples N1 and N2, see Table 1). An interesting effect is the drastic decrease of the Na₂O-9.5Al₂O₃ sample (N1 in Table 1, see also Fig. 3) resistance at 573K; this fact will be discussed later.
Fig. 3 demonstrates the dependence of the resistivity of Na$_2$O-6Al$_2$O$_3$ samples on their synthesis conditions. It is reasonable to suggest that this sample mainly contains β-alumina phase.

As it was shown in [3], polycrystalline β-alumina possesses higher conductivity than the monocystal of the same composition. The integral conductivity of the polycrystalline sample is the sum of the volume (σ$_V$) and the surface (σ$_{g,b}$) grain conductivities; at that, σ$_{g,b}$ is much lower than σ$_V$. The less is the grain size, the higher is the integral resistivity and the activation energy of the conductivity. So, the significant input of the resistance on the grain boundaries in the integral resistivity is a reason for higher resistivity of the polycrystalline sample as compared with monocrystalline one. According the data reported by different authors, E$_a$ values for polycrystalline β-alumina lay in the range from 0.2 to 0.606 eV [13]; these data are in good agreement with the values determined in the present work. Thus, the microstructure of the polycrystalline sample (the shape and the size of grains and crystallites in the grains, mutual orientation of grains and crystallites in the grains, inter-crystal and between-crystal porosity, etc.) which is determined by sintering conditions would affect the sample conductivity.

Sample N 4 (see Table 1) synthesized by solid-phase method possesses lower conductivity. Regarding E$_a$, ρ$_{373}$ and ρ$_{573}$ values determined for this sample, one can assume that it consists of larger grains than strengthened N5 and N6 samples (see Table 1 and Fig. 2). The high compacting pressures (30 t/cm$^2$) could possibly prevent the formation of the large grains resulting in higher ρ$_{373}$ and ρ$_{573}$ values for these samples as compared with those for N4 sample. In fact, the ratio of σ$_V$ and σ$_{g,b}$ inputs in the integral conductivity may depend not only on the grain size, but on temperature as well. Paper [13] reported this ratio for polycrystalline β-alumina determined by impedance spectroscopy. It was shown that σ$_{g,b}$ is ten times lower than σ$_V$ at T<300K. However, these values become close with temperature increase and, at last, σ$_{g,b}$ becomes higher than σ$_V$ at T>473K. At that, the activation energy for σ$_{g,b}$ reaches 0.9 eV (E$_a$=0.36 eV for σ$_V$). In other words, temperature increase promotes the activation of the larger number of the current carriers placed on the grain surfaces (current carriers in the grain volume are activated at lower temperatures (T<300K) due to the low E$_a$ values); that results in the integral conductivity increase. The same effect could be possibly observed for N1 sample (Na$_2$O-9.5Al$_2$O$_3$) synthesized by pyrolytic method, the evidence of this is rather high E$_a$ value (Table 1, Fig. 3).

The study of the sample electroconductivity at high temperatures was carried out in the sensor elements consisting of gas input manifold manufactured from stainless steel with the solid electrolyte pellet welded at the end of the tube using non-conducting high-temperature glass sealant MBB-0. The pellet diameter here was 10.55 mm, its width was 4.15 mm. Pellet surface was coated by silver with welded golden contact wires. This sensor was placed in the furnace and its conductivity was studied in the temperature range from 573 to 1073K. Measurements were carried out at frequencies of 100, 1000 and 10000 Hz with the current peak value of 0.5 V. Measurements were carried out both for sodium and silver β-Al$_2$O$_3$.

Analyzing the results, one can state that all samples studied show the similar frequency dependence for the specific conductivity. Figures 4 and 5 demonstrate the typical conductivity dependencies measured for Na$_2$O-9Al$_2$O$_3$, Ag$_2$O-9Al$_2$O$_3$, Na$_2$O-6.5Al$_2$O$_3$ and Ag$_2$O-6.5Al$_2$O$_3$ samples. Electrolytes with Na$_2$O-9Al$_2$O$_3$, Ag$_2$O-9Al$_2$O$_3$ compositions show the higher conductivity of sodium β-alumina as compared with silver one in the whole temperature range; this fact can be explained by lower Ag$^+$ ion mobility. In addition, this fact also supports the assumption about the complete sodium ions replacement by silver ions in the samples of given composition which was identified by XRD as β-alumina phase with less than 5% β$^+$-alumina addition.
Figure 4. Temperature dependencies of the conductivity for Na$_2$O-9Al$_2$O$_3$ and Ag$_2$O-9Al$_2$O$_3$ samples at 1000 Hz.

Another type of temperature dependencies of the conductivity is typical for Na$_2$O-6.5Al$_2$O$_3$ and Ag$_2$O-6.5Al$_2$O$_3$ samples, see Fig. 5. The measured conductivity values are close here, moreover, the plots intersect in the 800-900K region. This can be due to incomplete replacement of Na$^+$ ions by Ag$^+$; in turn, this possibly results from the sample structure with β- alumina to β$'^*$-alumina ratio determined as 3:1.
CONCLUSIONS

The study of the electroconductivity of polycrystalline Na$_2$O-nAl$_2$O$_3$ samples (5.5 ≤ n ≤ 9.5) at 313-625K has been performed. It was shown that the specific resistance decreases with the increase in Na$_2$O content due to the increase in the content of β-alumina phase. The study of the sample with Na$_2$O-6Al$_2$O$_3$ composition indicated that the increase in the compacting pressure results in the decrease in the final ceramics conductivity.

REFERENCES