SYNTHESIS OF NANOPOWDERS IN THE SYSTEMS OF 
\( \text{Ce}_2\text{O}_3\)-ZrO\(_2\), \( \text{Y}_2\text{O}_3\)-ZrO\(_2\) AND \( \text{Y}_2\text{O}_3\)-\( \text{Ce}_2\text{O}_3\)-ZrO\(_2\) FOR 
FABRICATION OF OXYGEN SENSORS

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Abstract. In this investigation nano-sized powders in the systems of \( \text{Ce}_2\text{O}_3\)-ZrO\(_2\), \( \text{Y}_2\text{O}_3\)-ZrO\(_2\) and 
\( \text{Y}_2\text{O}_3\)-\( \text{Ce}_2\text{O}_3\)-ZrO\(_2\), were synthesized by a sol-gel method. On a basis of the \( \text{Y}_2\text{O}_3\)-ZrO\(_2\) nanopowder 
obtained, a sensor of the galvanic cell for measurements of oxygen properties at high tempera-
tures was fabricated. Characteristics of this sensor were determined.

1. INTRODUCTION

Development and serial production of high-temperature electrochemical sensors for measurement of 
ox oxygen partial pressure operating in gaseous media is the problem of great theoretical and practical 
importance. Theoretically this problem is closely connected with investigations of electrode pro-
cesses and functioning of solid electrolytes of different chemical nature. Practical importance of this 
problem is related to industrial needs of sensors for controlling of a completeness of a fuel burning-away 
and proceeding of high-temperature technological processes.

One of perspective constructions of solid-electrolyte sensors for oxygen analyzers is a construc-
tion with a sensitive element in the form of a tablet. Such constructions are simply in fabrication and 
possess enhanced reliability. Perspective material

for fabricating solid electrolytes is bulk nanoceramics 
made of precursors obtained by a sol-gel method. 
The purpose of the present work was to synthesize 
nano-sized precursor powders in the systems of 
\( \text{Ce}_2\text{O}_3\)-ZrO\(_2\), \( \text{Y}_2\text{O}_3\)-ZrO\(_2\) and \( \text{Y}_2\text{O}_3\)-\( \text{Ce}_2\text{O}_3\)-ZrO\(_2\), to fab-
ricate high-temperature sensors based on these 
powders and to determine their characteristics.

2. EXPERIMENTAL

The following compositions were chosen for investiga-
tion: 0.08Y\(_2\text{O}_3\)-0.92ZrO\(_2\), 0.05Ce\(_2\text{O}_3\)-0.95ZrO\(_2\), 
0.09Ce\(_2\text{O}_3\)-0.91ZrO\(_2\), 0.06Y\(_2\text{O}_3\)-0.06Ce\(_2\text{O}_3\)-0.88ZrO\(_2\) (mol.%). To synthesize nano-powders of such com-
positions a variation of sol-gel method was chosen, 
namely, the method of back-coprecipitation from 
solutions [1, 2]. As starting materials the following 
salt were taken: Y(NO\(_3\))\(_2\)-3H\(_2\)O (c.p.g.), 
Zr(NO\(_4\))\(_2\)-2H\(_2\)O (c.p.g.), and Ce(NO\(_3\))\(_3\)-6H\(_2\)O (p.p.a.).

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As a result of the coprecipitation, we obtained a gel mixture of hydroxides. An excess NH₄OH was removed from the gel with the help of a centrifuge. Then the gel was washed on a Buchner funnel with a filter of high density, dried at 400K and calcined at 900K. After these procedures a nanopowder with cubic structure was obtained.

X-ray powder diffraction analysis was performed on a DRON-3 diffractometer (CuKα radiation, Ni filter, 2θ = 15-65°) at room temperature on air. Differential thermal analysis (DTA) was carried out using a DSC calorimeter Netzch 404c on air in the range of 20-1000 °C. The grain size was measured by field-emission transmission electron microscopy (JEOL JEM 3000F) with an accelerating voltage of 300 kV.

From precursor bulk nanoceramics obtained in the system of Y₂O₃-ZrO₂ a potentiometer sensor of the following construction was made: a sensitive element is made in the form of a tablet (7.2 mm in diameter, 4 mm in thickness) to both surfaces of which gas-permeable electrodes are applied; the electrolytes were fabricated of the nanopowders obtained; working and reference electrodes are applied to the solid electrolyte surface as a paste of the composition [Pt+10%(ZrO₂+Y₂O₃)] on heating at 1720K during 2 hours. As-constructed galvanic cell was secured in the cover made of heat-strength steel. Hermetization was performed with the use of a high-temperature adhesive.

The salts were taken in amounts appropriate to obtain 0.1 mole of the resulting product. Aqueous solutions of these salts (of 1M concentration) were prepared. A 1.35M aqueous ammonium solution was used as a precipitant. The mixture of salt solutions was added dropwise at a rate of 20 ml/hr into the ten-fold excess NH₄OH upon continuous vigorous stirring and pH controlling. The coprecipitation was carried out on cooling: a glass with the reaction mixture was placed in a container with ice.
3. RESULTS AND DISCUSSION

Nanopowder precursors with a particle size of 70-80 nm (Fig. 1) and the temperature of amorphous-crystalline transition of 700-750K (Fig. 2) were synthesized in above-mentioned way.

In the temperature range of 750-1100K, the values of the following parameters were determined for the sensor fabricated from the nanopowder of the Y$_2$O$_3$-ZrO$_2$ system [3]:

- response time at a jump change in oxygen content in the (O$_2$+N$_2$) mixture;
- resistance of the cell on a frequency of 1 kHz;
- parasitic EMF;
- the time of achievement of the equilibrium potential.

Response time was determined at a jump change in oxygen pressure in the (O$_2$+N$_2$) mixture from 0.21 to 0.01 atm (Fig. 3). Resistance of the cell and parasitic EMF were determined when the values of oxygen pressure on working and reference electrodes were equal to each other (Figs. 4-7).

Response time in the temperature range of 873-1073K was less than 1 s. At temperatures below 820K a sharp increase in the values of response time was observed: 3 and 12 seconds at 810 and 770K, respectively (Fig. 3). The same tendency was noted for the values of the time of achievement of the equilibrium potential: 25, 90, and 1000 seconds at 900, 830, and 770K, respectively. The resistance values at these temperatures were 240, 620, and

Fig. 3. Temperature dependence of response time of oxygen sensor.

Fig. 4. Time dependence of parasitic EMF of oxygen sensor.

Fig. 5. Temperature dependence of parasitic EMF of oxygen sensor.

Fig. 6. Temperature dependence for deviations of the EMF values of oxygen sensor at $P_{O_2}=0.01$ atm from the EMF values calculated by Nernst equation.
3700 Ω, respectively. The most probable explanation of such a tendency is a decrease in diffusion rate and, in consequence of this, an increase in the time of achievement of equilibrium hole concentration in the electrolyte.

An increase in the temperature of the cell from 773 to 1073K resulted in an increase in the value of parasitic EMF from 3.6 to 5.8 mV; this fact can be explained by a change in the difference in temperatures of working and reference electrodes.

4. SUMMARY

Nano-sized powders in the systems of $\text{Ce}_2\text{O}_3$-$\text{ZrO}_2$, $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$-$\text{Ce}_2\text{O}_3$-$\text{ZrO}_2$ were synthesized by a sol-gel method. On a basis of the $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ nanopowder obtained, a sensor of the galvanic cell for measurements of oxygen properties at high temperatures was fabricated. Good characteristics of this sensor were obtained: response time at a jump change in oxygen content in the $\text{(O}_2$+$\text{N}_2$) mixture, resistance of the cell, parasitic EMF, the time of achievement of the equilibrium potential. Sensors based on nano-sized powders in the systems of $\text{Ce}_2\text{O}_3$-$\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$-$\text{Ce}_2\text{O}_3$-$\text{ZrO}_2$ will be studied in further works. It is expected that characteristics of these sensors will be even better than those of the sensor investigated in the present work.

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REFERENCES

