SOLID ELECTROLYTE ELEMENTS ON THE BASIS OF ZrO_2 FOR SMALL-SIZED FUEL CELLS AND OXYGEN SENSORS

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Introduction

The problem of electric power generating with the solid electrolyte ceramic fuel cells is among paramount problems of the modern materials science, which can more than twice increase efficiency of existing thermal power stations. Annual spending by the world-advanced countries on this problem exceed billion USA$. This problem is especially actual for Ukraine because of limitation of power resources. At the same time the zirconium ore reserves– the main raw material for manufacturing solid electrolyte zirconia based (ZrO_2) ceramics – are in Ukraine among the biggest in the world.

Practical use of various solid electrolyte devices based on ZrO_2 is growing constantly. It includes high temperature fuel cells, electrochemical oxygen sensors, devices for purification of melted salts and metals of oxygen, high temperature electrolyzers for decomposition of water vapor; devices for preparation of gas mixtures with specified oxygen activity etc. Due to different application there are a lot of different demands to reliability, service life, stability of the ceramics properties, as well as to its mechanical strength and thermal-shock resistance. For zirconia based materials the maximal electroconductivity and stability of properties are inherent to the fully stabilized ZrO_2 with dopant concentration which corresponds to low boundary of cubic solid solutions with fluorite structure (K- ZrO_2). For stabilization by yttria it corresponds to 8-10 mol. % Y_2O_3. But such ceramics has low mechanical strength and thermal-shock resistance.

The highest mechanical strength and thermal-shock resistance is inherent to tetragonal ZrO_2 based solid solutions (T-ZrO_2). The advance technologies allow to produce ceramics on the basis of tetragonal zirconia (T-ZrO_2), partially stabilized with 1,5-3,5 mol. % Y_2O_3, with high thermal-shock resistance and strength up to 2000-2500 MPa, and with addition of 20 % Al_2O_3 – up to 3000 MPa.

In this study we have investigated the possibility to use zirconia partially stabilized by yttria with the additions of scandia Sc_2O_3 and alumina Al_2O_3, and without them as solid electrolytes in small-sized fuel cells and oxygen sensors. For these purposes the samples ZrO_2 with additions of Y_2O_3 from 2 to 6 mol.% and the samples with composition ZrO_2 (8 mol. % Sc_2O_3) +Al_2O_3 have been synthesized and their electrophysical properties have been investigated.

Results and discussion

The samples' manufacturing techniques included synthesis of initial powders by chemical methods; molding of green compacts of samples in the form of disks with diameter 25 mm, height 4-5 mm by method of isostatic pressing in an elastic rubber cover at pressure 450-500 MPa; calcination during 2 h. at temperature 1250-1300 ^{0}C and sintering during 1 h. in vacuum at temperature 1750-1800 ^{0}C. Oxidizing calcination were made in air at temperature 1300-1350 ^{0}C during 2 h with simultaneous application of platinum electrodes by burning in the platinum paste.

Electroconductivity of these samples was measured in temperature range 500-1200 ^{O}C in air and in inert gas with oxygen partial pressure (P_{O2}) regulated in the range from 2.10^4 Pa up to 10^{-15} Pa by two electrode method with use of 1500 Hz alternating current in the conditions close to thermodynamic equilibrium of the sample with gas.

Uncertainty of electroconductivity measurements was about 10 %.

The phase composition and microstructure of samples have been investigated by X-ray diffraction and petrographic analyses using standard techniques. The sintered samples are homogeneous, high density, with fine-grained microstructure, average grain size of 5 ÷ 8 microns and porosity 3÷5 %. The phase composition is not single-phase: in ZrO_2 (Y_2O_3) samples along with tetragonal and cubic phases the monoclinic phase (M-ZrO_2) is also present their quantities being depended on dopants contents (tab. 1), and samples (8 mol.% Sc_2O_3) +Al_2O_3 consist of a mix of solid solutions on the basis of cubic K- ZrO_2 and α-Al_2O.

Table 1. Phase compositions of ZrO_2 (Y_2O_3) samples.

Y_2O_3, mol. %	Phase compositions of ZrO_2 (Y_2O_3) samples		
	T- ZrO_2	M-ZrO_2	K-ZrO_2
2,5	80	20	-
3,5	40	50	10
4,5	20	-	80
6,0	10	-	90

Table 2. Specific electrocoductivity (σ) vs. temperature for ZrO_2 based ceramics in air.

T, ^{0}C	σ of ZrO_2 based ceramics, $Ohm^{-1}.m^{-1}$				
	Content of Y_2O_3, mol.%:				Dopant -
	2	3	4,5	6	Sc_2O_3+Al_2O_3
550	0,05		0,14	0,2	0,02
600	0,09		0,25	0,4	0,04
780	0,5		1,27	1,7	0,25
840	0,76		2,0	2,5	0,4
900	1,1	2,5	2,89	3,6	
1060	2,4	4,6	6,25	7,7	
1150	3,6	5,8	9,08	10,5	

Table 3. Isotherms of specific electroconductivity (σ) vs. $P_{O2\ for}$ ceramics ZrO_2 (6 mol.%Y_2O_3).

T, ^{0}C	σ ZrO_2(6 mol.%Y_2O_3),$Ohm^{-1}.m^{-1}$, at P_{O2}(Pa)				
	4.10^4	1	10^{-5}	10^{-10}	10^{-15}
550	0,2	0,17	0,17	0,13	0,13
630	0,5	0,5	0,5	0,5	0,5
760	1,72	1,34	1,34	1,34	1,34
935	2,94	2,63	2,1	2,1	

The presented results of specific electroconductivity measurements vs. temperature testify that the electroconductivity increases when content of Y_2O_3 in ZrO_2 becomes bigger. The highest values of electroconductivity have been found in samples ZrO_2 (4,5 mol. % Y_2O_3) and ZrO_2 (6 mol. % Y_2O_3). Their electroconductivity is comparable with the most electroconductive compositions in solid solutions in systems ZrO_2+Y_2O_3, ZrO_2+CaO with big content of stabilizing oxide. The specified samples are characterized by the high content of cubic phase, and also by presence of the tetragonal phase (tab. 1), the last phase increases their mechanical characteristics.

The lowest electroconductivity has been found in samples with composition ZrO_2 (8 mol. % Sc_2O_3) +Al_2O_3

The temperature dependences of specific electroconductivity of the samples in co-ordinates lg *σ-1/T* can be approximated by one or two straight lines. Activation energy of the conductivity, calculated by inclination of these lines, make for ZrO_2 (2-6 mol. % Y_2O_3) 0,5-0,6 electroconductivity in high-temperature area and 0,8-1,0 eV in low-temperature area. For samples with composition ZrO_2 (8 mol. % Sc_2O_3) +Al_2O_3 these values are accordingly 0,7 eV and 1,5 eV.

Analysis of dependences of electroconductivity of P_{O2} at T_{const} for the same samples reveals that their electroconductivity in the specified interval of temperatures and oxygen partial pressure.

To study stability of electric characteristics of the samples their electroconductivity was measured before and after cyclic thermal processing: heating, endurance 4 h at 1350 ^{0}C, cooling. Quantity of such cycles - 25.

It has been found that for samples ZrO_2 (4,5-6 mol. % Y_2O_3) after storage totally 100 h at 1350 ^{0}C the electroconductivity practically do not change, thus testifies to high stability of electric properties. For samples ZrO_2 (2,5-4 mol. % Y_2O_3) after the specified heat treatment the electroconductivity increased approximately on 40-50 %.

The sensors based on solid electrolit made of ceramics ZrO_2 (4,5 mol. % Y_2O_3) have been used for measurements of melted steel deoxidizing, and sensors made of solid electrolit with composition ZrO_2 (8 mol. % Sc_2O_3) +Al_2O_3 have successfully passed preliminary technical tests in diagnostics systems of completeness of fuel combustion in water heating district boiler plant.

Conclusions

Thus, the received results testify the perspectivity of usage ceramics made of zirconia partially stabilised by yttria as solid electrolyte elements in a number of high-temperature electrochemical devices.