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Electrochemical Properties of ZrO_2–Y_2O_3–TiO_2 Ceramics

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Abstract: The electrical conductivity of $(0{\cdot}98\text{–}x)ZrO_2{\cdot}0{\cdot}02Y_2O_3{\cdot}xTiO_2$ ceramic samples in the composition range $x = 0{\cdot}04$–$0{\cdot}60$ was measured in the temperature range 600–900°C and at 0·1 Pa oxygen partial pressure. Both the d.c. four-probe and the a.c. impedance spectroscopy method were applied. The electronic conductivity at 800°C was measured by the d.c. polarization technique. The ionic transport in the samples was determined using appropriate solid-state galvanic cells in the temperature range 800–1000°C. The samples consisting of monoclinic and tetragonal zirconia ($x = 0{\cdot}04$–$0{\cdot}13$) appeared to be practically pure ionic conductors. The samples containing zirconium titanate as a main phase exhibited a mixed ionic–electronic conduction.

1 INTRODUCTION

ZrO_2–Y_2O_3 solid solutions with fluorite structure are known to be pure oxygen ion conductors. They are used as solid electrolytes in solid-state galvanic cells, membranes in solid oxide fuel cells, and as separators in oxygen gas sensors. It was also found that tetragonal solid solutions formed in this system were pure oxygen ion conductors and below 700°C their conductivity was higher than that of cubic solutions.[1] The addition of TiO_2 dopant to the ZrO_2–Y_2O_3 solution is reported to enhance its electrical conductivity but the solubility limit is not known so far. Because of different valence states of Ti, electron conductivity will arise. As mixed conductors ZrO_2–Y_2O_3–TiO_2 materials can be potentially applied as electrodes in solid oxide fuel cells, in high-temperature steam electrolyzers and as membranes for gas separation. Further, ZrO_2–Y_2O_3–TiO_2 can be microstructurally designed to show rather high fracture toughness. Colomer *et al.*[2] prepared a series of materials with general formula $(0{\cdot}92ZrO_2{\cdot}0{\cdot}08Y_2O_3)_{1-x}(TiO_2)_x$ for $x < 30$ m/o and studied their transport properties in temperatures of 250–1000°C. They detected a second phase $ZrTiO_4$ in the samples with TiO_2 content higher than 10 m/o. They also observed that the ionic conductivity in air significantly decreased up to 5 m/o of TiO_2. However, the electronic conductivity increased markedly in a reducing atmosphere. In the next paper Colomer *et al.*[3] published a preliminary phase diagram. They confirmed the presence of $ZrTiO_4$ phase above 10 m/o TiO_2 in ZrO_2 containing 8 m/o Y_2O_3. Naito and Arashi[4] determined the electrical properties of samples with composition $(0{\cdot}9\text{–}x)ZrO_2{\cdot}0{\cdot}1Y_2O_3{\cdot}xTiO_2$, where x was 0·05, 0·075 and 0·1, in the temperature range 400–1200°C and in the oxygen pressure range 10^{-19}–10^{4} Pa. They found that the total electrical conductivity of the system decreased with increasing TiO_2 concentration and that the ionic conduction dominated in the high oxygen partial pressure range. The electronic conduction appeared in oxygen partial pressures lower than 10^{-12} Pa for samples with $x = 0{\cdot}1$. In the other paper Arashi and Naito[5] measured the oxygen permeability in yttria-stabilized zirconia containing 7·5 and 10 m/o TiO_2 up to 1500°C. They confirmed that the materials could be candidates for water electrolysis at high temperatures. Swieder and Worell measured mixed conduction in yttria-stabilized zirconia containing 5–15 m/o TiO_2 by impedance spectroscopy at temperatures of 570–860°C and proposed a conduction model.[6] Marques *et al.* studied yttria-stabilized zirconia with up to 5 m/o TiO_2 additions and found that increasing TiO_2 content slightly decreases conductivity at 800°C.[7] The samples were cycled between air and oxygen partial pressures in the order of 10^{-15} Pa.

In the present work the electrochemical properties of the $0{\cdot}98\ ZrO_2{\cdot}0{\cdot}02Y_2O_3$ solid solutions ceramic samples containing different amounts (up to 60 m/o) of TiO_2 were investigated. The purpose of the work was to observe how the properties changed with change in composition and microstructure. In this way the useful electrolytic range of the materials under study could be determined.

2 EXPERIMENTAL

2.1 Preparation of the materials

Nine $0{\cdot}98ZrO_2{\cdot}0{\cdot}02Y_2O_3$ powders with TiO_2 content ranging from 0 to 60 m/o were prepared by coprecipitation from an aqueous solution of the appropriate chlorides with ammonium hydroxide. The final pH of the suspension was held at 9 to obtain quantitative precipitation. The coprecipitated gels were thoroughly washed with distilled water to remove Cl^- ions and subsequently hydrothermally treated at 250°C for 4 h. The procedure was worked out by Haberko and described in Ref. 8. The powders were dried at 120°C and deagglomerated with 10 wt% water additive using an agate mortar. The pellets of 12 mm diameter and 3 mm thickness were uniaxially pressed at 50 MPa and subsequently cold isostatically pressed at 350 MPa. Sintering was performed in air at a heating rate of 6°C/min up to 1450°C and held for 2 h. The phase compositions of the samples were determined by X-ray diffraction. Density of the pellets was also controlled by an immersion method.

2.2 Electrical conductivity

The electrical conductivity was measured in the temperature range 600–900°C using a simple d.c. four-probe method. Four platinum wires were wrapped around the regular shape of $12 \times 5 \times 3$ mm^3 cut from the appropriate pellet. The sample was introduced in an electrical furnace. A small current was passed between the outer probes in both directions and the potential between the inner probes was measured. The electrical conductivity was calculated directly from the measured resistance and from dimensions of the sample.

Another method applied was a.c. complex impedance analysis. A Hewlett-Packard impedance analyser (model 3575A) over the frequency range of 5 Hz–5 MHz was used. Both faces of a pellet of 12 mm diameter and 2 mm thickness were polished on SiC papers, washed in acetone, dried and then sputtered with Pt in a vacuum chamber. Aluminium guard rings were used to prevent sputtering onto the edges of the sample. Electrical contacts were made via platinum wires connected with the platinized outer surfaces of a pellet. Each sample was held under slight spring tension in an alumina conductivity cell. The conductivity cell was electrically heated. All measurements were carried out in argon gas atmosphere with an oxygen partial pressure of about 0·1 Pa.

The electronic conductivity of the samples was determined using the Wagner asymmetric polarization technique.[9] As an ion blocking electrode platinum was used and as a reversible one a mixture of nickel and nickel oxide. The reversible electrode and ZrO_2–Y_2O_3–TiO_2 pellets were spring-loaded to form a cell according to the following scheme:

$$(-)\,Pt\,|\,Ni, NiO\,||\,ZrO_2-Y_2O_3-TiO_2\,||\,Pt\,(+) \quad (1)$$

On applying a voltage with the positive pole on the right-hand side O^{2-} ions migrate from the left to the right side. Under steady-state conditions migration of O^{2-} ions due to the electrical field is balanced by diffusion due to the O^{2-} concentration gradient, and the current is carried exclusively by electrons (excess electrons and electron holes). Then, the appropriate voltage was supplied by a constant-voltage regulator and the resulting current was measured using a high-ohmic (1000 MΩ) electrometer. The measurements were performed at 800°C in an argon atmosphere with 0·1 Pa oxygen partial pressure.

2.3 E.m.f. measurements

The ionic conductivity of ZrO_2–Y_2O_3–TiO_2 samples was also characterized by using the following electrochemical cell:

$$Pt\,|\,Fe, Fe_xO\,||\,ZrO_2-Y_2O_3-TiO_2\,||\,NiO, Ni\,|\,Pt \quad (2)$$

The two-phase mixtures (Fe, Fe_xO) and (Ni, NiO) having known oxygen equilibrium partial pressures at a given temperature, were used as electrodes in the cell. As long as the sample separating both electrodes exhibited a purely ionic conduction, the e.m.f. of the cell (2) under thermodynamic equilibrium conditions could be represented by Nernst's equation:

$$E_t = (RT/4F){\cdot}\ln[pO_2(Ni, NiO)/pO_2(Fe, Fe_xO)] \quad (3)$$

In the case of the sample, which shows electronic conduction, the e.m.f. of the cell (3) was less than

Table 1. Chemical and phase composition of ZrO_2–Y_2O_3–TiO_2

Sample no.	Mole fraction of			Primary phase[a]	Secondary phase[a]
	ZrO_2	Y_2O_3	TiO_2		
1	0·98	0·02	0	m-ZrO_2	—
2	0·94	0·02	0·04	m-ZrO_2	—
3	0·92	0·02	0·06	m-ZrO_2	t-ZrO_2
4	0·90	0·02	0·08	t-ZrO_2	m-ZrO_2
5	0·88	0·02	0·10	t-ZrO_2	—
6	0·85	0·02	0·13	t-ZrO_2	m-ZrO_2,$ZrTiO_4$
7	0·58	0·02	0·40	$ZrTiO_4$	t-ZrO_2
8	0·48	0·02	0·50	$ZrTiO_4$	—
9	0·38	0·02	0·60	$ZrTiO_4$	$ZrTi_2O_6$

[a] m = monoclinic ZrO_2; t = tetragonal ZrO_2.

of that containing a pure ionic conductor and could be expressed as:

$$E = t_i E_t \qquad (4)$$

where t denotes an effective ionic transference number of oxygen ions in the sample under study.[10]

E.m.f. measurements were performed in the following way: the half-cell and ZrO_2–Y_2O_3–TiO_2 pellets were assembled in a simple spring-loaded alumina holder according to the cell (2) arrangement. The cell was placed in an electrical resistance furnace and heated up to the measurement temperature. The e.m.f. values were monitored with a high-ohmic digital voltmeter. They were measured in the temperature range 800–1000°C, in an argon atmosphere with oxygen partial pressure 0·1 Pa. Prior to the measurements with ZrO_2–Y_2O_3–TiO_2 samples, the cell (3) was tested with calcia fully stabilized zirconia electrolyte.

3 RESULTS AND DISCUSSION

3.1 Phase composition

Phase compositions of the sintered samples are shown in Table 1. Pure and nearly pure monoclinic structures were exhibited by ZrO_2 samples containing 0·02 m/o of Y_2O_3 without TiO_2 and with TiO_2 (x = 0·04). Fully or nearly fully tetragonal bodies could be obtained within the x = 0·08–0·13 compositions. The samples containing more than x = 0·13 TiO_2 consisted of nearly pure $ZrTiO_4$ phase. Such compositions could be expected taking into account the phase diagram of the ZrO_2–Y_2O_3–TiO_2.[11]

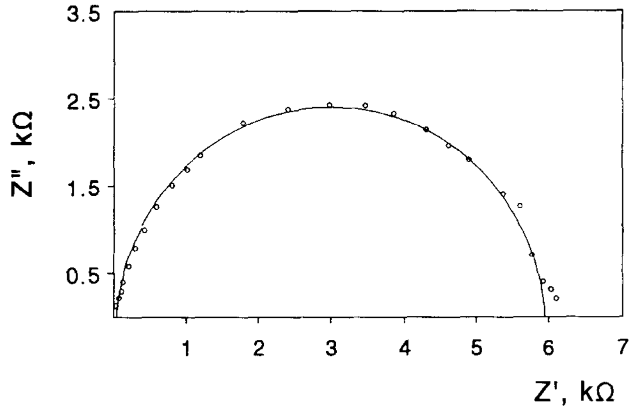

Fig. 1. Complex impedance plot for sample no. 2 (x = 0·04 TiO_2) at 800°C.

3.2 Electrical conductivity

The a.c. conductivity results were plotted in the complex impedance plane. The frequency data could be approximated to a characteristic shape of one semicircle having the high frequency intercept with the real axis passing through the origin, as it is shown in Fig. 1 for the sample of x = 0·04, measured at 800°C. The semicircular arc was centred below the real axis. Similar shapes were also obtained for this sample at other temperatures. For higher TiO_2 content the plots appeared to be more complicated; besides the first semicircle, a poorly developed second semicircle was also obtained. If the overall impedance of a polycrystalline sample is modelled by a series of bulk, grain boundary and electrode parallel resistance–capacitance elements three semicircles would be obtained and the first semicircle would pass through the origin of the coordinate system. Then the intersection of the first semicircle with the real axis would be attributed to the bulk resistance, that of the second one to the sum of bulk and grain boundary resistance of the sample and that of the third one to the sum of the bulk, grain boundary and electrode resistances.[12] The last two semicircles could be obtained at low and at very low frequencies. As we were limited in the frequency range we did not obtain the third semicircular arc, and the second arc was not well developed. Thus, the resistance calculated from the impedance plot was the bulk resistance only. However, the results of electrical conductivity obtained from d.c. four-probe method appeared to be more accurate than those from impedance spectroscopy. They gave the total conductivity values. The electrical conductivity, σ, was assumed to follow an Arrhenius equation of the form:

$$\sigma T = \sigma_0 \exp(-E_a/RT) \qquad (5)$$

where σ_0 is a constant, T is the absolute temperature, E_a is the activation energy for charge motion, and R is the gas constant.

In Table 2 the electrical conductivity at 800°C determined by both d.c. four-probe and a.c. impedance spectroscopy methods, as well the respective activation energy values calculated for

Table 2. Electrical conductivity of the samples at 800°C and activation energy of the conductivity in the temperature range 600 -900°C

Sample no.	Mole fraction of TiO_2	σ, $(\Omega\text{-cm})^{-1}$	E_a, kJ/mol
1	0	$4{\cdot}15{\cdot}10^{-5}$*	49·52
2	0·04	$2{\cdot}28{\cdot}10^{-5}$*	50·15
		$4{\cdot}41{\cdot}10^{-5}$**	48·13
3	0·06	$7{\cdot}56{\cdot}10^{-5}$*	43·20
4	0·08	$1{\cdot}26{\cdot}10^{-4}$*	42·75
5	0·10	$3{\cdot}25{\cdot}10^{-4}$*	41·15
6	0·13	$7{\cdot}30{\cdot}10^{-4}$*	40·75
		$1{\cdot}67{\cdot}10^{-3}$**	41·32
7	0·40	$4{\cdot}80{\cdot}10^{-5}$*	52·40
		$4{\cdot}60{\cdot}10^{-5}$**	55·80
8	0·50	$2{\cdot}67{\cdot}10^{-5}$*	52·15
		$2{\cdot}41{\cdot}10^{-5}$**	51·01
9	0·60	$4{\cdot}32{\cdot}10^{-5}$*	53·30
		$5{\cdot}46{\cdot}10^{-5}$**	50·59

*Values obtained by the a.c. four-probe method, ** values obtained by the a.c. spectroscopy impedance method.

the temperature range 600–900°C, are presented. The measurements by impedance spectroscopy gave higher conductivity values than those by the d.c. four-probe method for titania content in the range x = 0–0·13 and slightly lower ones in the range x = 0·13–0·60. This difference probably resulted from the different contribution of grain boundary conductivity in the measurements using direct and high frequency alternating current. However, the values obtained were of the same order of magnitude. Thus, they are considered to reflect bulk transport properties of the samples measured. To our knowledge this is the first investigation on tetragonal and monoclinic zirconia with a titania content as high as 60 m/o. Our results are in qualitative agreement with the findings of Kopp *et al.*[13] who studied tetragonal zirconia with titania additions up to 30 m/o. They however show a minimum around x = 10 m/o which was not observed by the aforementioned authors.

3.3 Electronic conductivity

According to Wagner[9] the current I in the cell (1) as a function of the applied voltage U is given by the equation:

$$I = (SRT/DF)\{\sigma_e[1 - \exp(-FU/RT)] + \sigma_h\,[\exp(FU/RT) - 1]\} \qquad (6)$$

where S is the cross-sectional area, D is the thickness of the sample, F is the Faraday constant, and σ_e and σ_h are the excess electron and electron holes conductivities of the sample, respectively.

Equation (6) can be transformed into a straight-line form:

$$Y = \sigma_h + \sigma_e X \qquad (7)$$

where

$$Y = (IDF)/\{SRT[\exp(FU/RT) - 1]\} \qquad (7a)$$

$$X = \exp(-FU/RT) \qquad (7b)$$

From the measurements of I at various values of U one can calculate Y as a function of X, and thus σ_e and σ_h using the least squares method. The values of σ_e (σ_h was practically equal to zero) at 800°C are given in Table 3 for all samples prepared except that one with the highest TiO_2 content. Furthermore, the electron transference number, t_e,

$$t_e = \sigma_e/\sigma \qquad (8)$$

(where $\sigma = \sigma_{ion} + \sigma_e$, and σ is the total conductivity of the sample determined by the d.c. four-probe method) were calculated and presented in Table 3. As seen from Table 3 the electronic conductivity values increased with titania content in the whole concentration range, though the electron transference number decreased in the range $x = 0 - 0{\cdot}10$. According to Refs 5 and 6 the electronic conductivity is due to the presence of Ti^{3+} ions besides Ti^{4+}, as well as to the presence of impurities in the sample. In the samples containing mainly $ZrTiO_4$ electrical conduction exhibited electronic character.

Table 3. Electronic conductivity of the samples at 800°C

Sample no.	Mole fraction of TiO_2	σ_e, $(\Omega\text{-cm})^{-1}$	t_e	t_{ion}
1	0	$2{\cdot}05{\cdot}10^{-6}$	0·05	0·95
2	0·04	$2{\cdot}51{\cdot}10^{-6}$	0·11	0·89
3	0·06	$5{\cdot}29{\cdot}10^{-6}$	0·07	0·93
4	0·08	$7{\cdot}56{\cdot}10^{-6}$	0·06	0·94
5	0·10	$9{\cdot}75{\cdot}10^{-6}$	0·03	0·97
6	0·13	$8{\cdot}03{\cdot}10^{-5}$	0·11	0·89
7	0·40	$3{\cdot}22{\cdot}10^{-5}$	0·67	0·33
8	0·50	$2{\cdot}46{\cdot}10^{-5}$	0·92	0·08

3.4 E.m.f. measurements

The results of e.m.f. measurement at temperatures of 800, 900 and 1000°C are presented in Table 4 and compared with the e.m.f. (E) measured with the cell (2) containing fully calcia-stabilized zirconia as a reference electrolyte, which corresponded to the e.m.f. values of the similar cell studied by Kiukkola and Wagner.[14] These values could be assumed as E_t in eqn (4). In Table 4 are also shown the values of coefficients $t = E/E_t$, related to the oxygen ion transference number in the samples. The samples with titania content in the range x = 0–0·13 mol fraction behaved as good solid elec-

Table 4. E.m.f. of the cell (2)

Sample no.	Mole fraction of TiO_2	E, mV			E/E_t		
		800°C	900°C	1000°C	800°C	900°C	1000°C
Reference		266·3	276·2	286·4	1·00	1·00	1·00
1	0	257·2	258·7	267·3	0·96	0·94	0·93
2	0·04	231·6	243·1	243·4	0·87	0·88	0·85
3	0·06	252·9	256·9	266·3	0·95	0·93	0·93
4	0·08	247·6	262·4	269·2	0·93	0·95	0·94
5	0·10	255·6	262·7	269·5	0·96	0·95	0·94
6	0·13	239·7	243·1	260·6	0·90	0·95	0·94
7	0·40	85·2	93·9	77·3	0·32	0·34	0·27
8	0·50	29·3	38·7	25·8	0·11	0·14	0·09
9	0·60	16·1	18·5	17·7	0·06	0·07	0·06

trolytes. However, the samples with high TiO_2 content showed mixed ionic–electronic conduction. The values of ion transference number (t_{ion}, see Table 3) determined by use of Wagner's polarization method at 800°C could be compared with t_i values presenting E/E_t ratio in Table 4, calculated for the same temperature. A quite reasonable accord between them is observed.

4 CONCLUSIONS

Ionic and electronic conductivity could be correlated with the phase composition of ZrO_2–Y_2O_3–TiO_2 samples. For the monoclinic and tetragonal zirconia solid solution electrical conductivity, measured in the temperature range 800–1000°C at oxygen partial pressure of 0·1 Pa, increased with Ti concentration. In this composition range the electronic conductivity was negligible with respect to the total conductivity, so the samples containing 0·04, 0·06, 0·08, 0·10, and 0·13 mole fraction of TiO_2 could be regarded as solid electrolytes. This conclusion was confirmed by e.m.f. measurements. However, the samples containing titanium zirconate as a main phase (0·40, 0·50 and 0·60 mole fraction of TiO_2) exhibited mixed electronic–ionic conduction.

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