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High Temperature Oxide Electrolytes for Electrochemical Devices Application

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Abstract

A coprecipitation–calcination method was used to synthesise powders of 25 mol% Y_2O_3 in ZrO_2 (25YSZ) or 12.5 mol% Y_2O_3 - 12.5 mol% Yb_2O_3 in ZrO_2 (12.5Yb12.5YSZ) solid solutions. The pellets were cold isostatically pressed and then sintered for 2 h at 1500°C. The corrosion resistance of 25YSZ, 12.5Yb12.5YSZ solid solutions, and $CaZrO_3$-based samples against molten metals, *i.e.*, copper, nickel or iron, were also examined. Based upon this investigation, it is evident that stability of both zirconia with 25 mol% Y_2O_3 in solid solution and the calcium zirconate containing 48 % CaO material is limited in molten iron. Electrical conductivity measurements were performed by dc four probe and ac impedance spectroscopy methods in the temperature range of 200-1000°C. The highest value of ionic conductivity was found for the sintered samples of 12.5 mol% Y_2O_3 - 12.5 mol% Yb_2O_3 in ZrO_2. These results indicate that partial substitution of Yb_2O_3 for Y_2O_3 in the 25YSZ solid solution leads to an increase of electrical conductivity compared to the solid solution of 25 mol%Y_2O_3 in ZrO_2. It was also found that ionic oxide transference numbers (t_{ion}) of 25YSZ and 12.5Yb12.5YSZ solid solutions were close to 1, what indicated on pure oxide ionic conduction in the materials prepared. Test results are also reported for 25YSZ and 12.5Yb12.5YSZ applied as electrolytes in electrochemical oxygen gas sensors as well as in solid oxide cells, involving $NiLa_2O_4$ or $NiAl_2O_4$. In this way, the Gibbs free energy of formation of $NiLa_2O_4$ or $NiAl_2O_4$ in the temperature range 800-1000ºC was determined. These materials seem to be promising solid oxide electrolytes for electrochemical oxygen probes, and solid oxide galvanic cells designed to study thermodynamic properties of materials important for SOFC technology and other areas of energy industry.

Keywords: Solid oxide electrolytes, Y_2O_3-Yb_2O_3-ZrO_2 solid solutions, Solid oxide galvanic cells

WYSOKOTEMPERATUROWE ELEKTROLITY TLENKOWE PRZEZNACZONE DO WYKORZYSTANIA W URZĄDZENIACH ELEKTROCHEMICZNYCH

Metodę współstrącania-kalcynacji wykorzystano do syntezy proszków roztworów stałych o składach 25 % mol. Y_2O_3 w ZrO_2 (25YSZ) i 12.5 % mol. Y_2O_3 - 12.5 % mol. Yb_2O_3 w ZrO_2 (12.5Yb12.5YSZ). Pastylki, które wcześniej sprasowano izostatycznie, spiekano w temperaturze 1500°C w czasie 2 h. Zbadano odporność korozyjną spieków roztworów stałych 25YSZ, 12.5Yb12.5YSZ, a także elektrolitów zawierających $CaZrO_3$ w środowisku ciekłych metali, takich jak miedź, nikiel i żelazo. Na podstawie tych badań stwierdzono, że stabilność spieków roztworów stałych 25 % mol. Y_2O_3 w ZrO_2 (25YSZ) oraz $CaZrO_3$ (48 % mol. CaO) jest ograniczona w ciekłym żelazie. Przewodnictwo elektryczne otrzymanych próbek zmierzono metodą 4-elektrodową stałoprądową oraz metodą spektroskopii impedancyjnej w temperaturach 200-1000ºC. Spiek roztworu stałego zawierającego 12.5 % mol. Y_2O_3 - 12.5 % mol. Yb_2O_3 w ZrO_2, charakteryzuje się najwyższymi wartościami przewodnictwa jonowego. Wyniki tych badań wskazują, że częściowe podstawienie tlenku itru(III) tlenkiem iterbu(III) w roztworze stałym 25 % mol. Y_2O_3 w ZrO_2 prowadzi do podwyższenia jego przewodności elektrycznej. Wyznaczone wartości liczby przenoszenia jonów tlenkowych (t_{ion}) dla spieków roztworów stałych 25YSZ i 12.5Yb12.5YSZ są bliskie jedności co wskazuje, że otrzymane materiały są praktycznie czystymi przewodnikami jonów tlenu. Materiały te przetestowano jako elektrolity tlenkowe do budowy elektrochemicznego sensora tlenu i ogniw galwanicznych przeznaczonych do badań właściwości termodynamicznych materiałów tlenkowych $NiLa_2O_4$ i $NiAl_2O_4$. W ten sposób wyznaczono wartości entalpii swobodnej ΔG dla tych materiałów w temperaturach 800-1000ºC. Badane roztwory stałe 25 % mol. Y_2O_3 w ZrO_2 oraz 12.5 % mol. Y_2O_3 - 12.5 % mol. Yb_2O_3 w ZrO_2 wydają się być obiecującymi elektrolitami tlenkowymi do budowy elektrochemicznego sensora tlenu oraz ogniw galwanicznych przeznaczonych do badania właściwości termodynamicznych materiałów tlenkowych ważnych dla technologii stałotlenkowych ogniw paliwowych i innych dziedzin energetyki.

Słowa kluczowe: elektrolity tlenkowe, roztwory stałeY_2O_3-Yb_2O_3-ZrO_2, ogniwa galwaniczne

1. Introduction

There is a growing interest in solid oxide electrolytes for high temperature applications. Beside their application in energy industry as components of solid oxide fuel cells, there is also a wide area of their prospective sensor applications for monitoring and control of the oxygen partial pressure in numerous industrial processes such as molten metal processing as well as in combustion processes (*e.g.*, in internal combustion engines) [1, 2]. Electrochemical oxygen sensors based on partially or fully stabilized zirconia (CaO, MgO, Y_2O_3) have been developed and are being used for

measuring oxygen activity in molten metals. Although ZrO_2-based sensors as single–reading probes have achieved a high chemical standard worldwide it is still necessary to improve their performance. Up to now there is no fully suitable oxygen probe for on–line measurements especially in steel production. Steels with very low oxygen content (< 50 ppm) can cause an oxygen partial pressure low enough for significant electronic conduction appearing in zirconia. Significant electronic conductivity in the electrolyte not only requires a more complicated computation of oxygen partial pressure or oxygen activity from measured electromotive force (EMF), but it also causes time-dependent polarization effects in long-term operation of oxygen probes, and as a consequence incorrect sensor output as well [3, 4].

Taking the above effects into account it is appropriate to search for other solid electrolytes with lower partial electronic conduction. Good mechanical properties, thermal shock resistance, and thermodynamic stability are also required for electrolytic materials in such applications. The ionic conduction limit for yttria-doped thoria (YDT) is lower than for stabilized zirconia. Thoria-based electrolytes perform better at low oxygen concentrations. Due to radioactivity of thorium, however it has been found rather limited application in steel industry [5, 6]. The previous author studies showed that $CaZrO_3$-based electrolytes could be applied as components of electrochemical probes to measure oxygen activity in molten metals as well as for thermodynamic studies of oxide systems with low equilibrium partial pressure [7, 8]. The main advantage of nonstoichiometric $CaZrO_3$ when compared to cubic calcia solid solution (CSZ) is lower electronic conduction which occurred in ceramic electrolytes in such applications at high temperatures above 1200ºC and under low oxygen partial pressure. The electrolytic domain of nonstoichiometric $CaZrO_3$ is close to thoria or hafnia-solid solution, considered to be more suitable oxide electrolytes than CSZ for high temperature application [9, 10]. Janke, *et al.* also found that 25 mol% M_2O_3 in ZrO_2, where M = Yb, Y, Gd or 12.5 mol% Y_2O_3-12.5 mol% M_2O_3 in ZrO_2, M = Gd, Yb, Sm solid solutions seem to be also adequate solid oxide electrolytes for high temperature (1200-1700°C) at low oxygen partial pressure application. The costs of producing the mentioned materials and $CaZrO_3$–based electrolytes are also lower than MO_2 solid solutions, where M = Th, Hf [11].

The present work is focused on comparison of electrical and electrochemical properties of both ZrO_2-Y_2O_3-Yb_2O_3 materials and $CaZrO_3$-based electrolytes, and the application of studied materials in electrochemical gas sensors and solid oxide galvanic cells; the latter are designed to study thermodynamic properties of oxide materials important for IT-SOFC technology.

2. Experimental

The 25 mol% Y_2O_3 in ZrO_2 (25YSZ) or 12.5 mol% Y_2O_3-12.5 mol% Yb_2O_3 in ZrO_2 (12.5Yb12.5YSZ) solid solutions were prepared by co-precipitation calcination method. The zirconyl nitrate solution (1.2 mol/dm^{-3}) was used as a starting reagent. The appropriate amount of Y_2O_3 and Yb_2O_3 were dissolved in zirconyl nitrate solution. The solutions were introduced dropwise into NH_3 solution. The dried gels were calcined at 1100°C for 1h and then rotary-vibratory milled. The grounded powders were compressed in pellets under 250 MPa. The samples were sintered at 1500°C for 2h. The phase composition of the powder and the sintered body was determined by X-ray diffraction analysis. Apparent density of samples was measured by the Archimedes method. To test the thermal resistance of $CaZrO_3$-based materials to molten metals involving copper, nickel, and iron, the selected samples were placed into corundum crucibles and dusted with an excess of copper, nickel, or iron, then annealed in molten metals in a resistance furnace. After a heat treatment in the liquid metals, the samples were subjected to rapid cooling. Scanning electron microscopy (JEOL JSM-5400) equipped with EDX analysis was used to observe the microstructures of 25YSZ and 12.5Yb12.5YSZ ceramic sinters. The electrical conductivity of sintered samples was measured as a function of temperature (200-1000°C) by the dc four probe method. Electrical properties of $CaZrO_3$-based materials were also investigated by means of impedance spectroscopy method. The impedance was measured in the automated setup assembled on Solartron 1260 Frequency Response Analyser in the frequency range from 1 Hz to 10^7 Hz and in the temperature range from 200 to 1000°C. Impedance spectra were analysed by using the program Firdravn [12]. Prior to electrical measurement of samples, Pt porous electrodes were applied at both sides of every pellet (Heraus Germany, Pt paste fired at 850°C/15 min). Ionic oxygen transference number (t_{ion}) was estimated from electromotive force (E_{obs}) measurements of oxide solid galvanic cells.

The 25YSZ and 12.5Yb12.5YSZ-based samples were tested as electrolytes in the solid galvanic cell (1), which may be shown schematically as follows:

$$\text{Pt} \mid \text{M, M}_x\text{O} \mid \text{25YSZ} \mid \text{NiO, Ni} \mid \text{Pt}, \qquad (1)$$

where M = Cu, Co, Cr, Fe, M_xO = Cu_2O, FeO, CoO, Cr_2O_3.

In the case of cell (1), two-phase mixtures (M, M_xO) and (Ni, NiO) with known equilibrium oxygen partial pressures were used as the half-cells. The procedure was practically the same as that presented in Ref. [13]. If an electrolyte separating the half cells in the cell (1) had a pure ionic conduction, only O^{2-} ions were transported, the electromotive force E_t, would be given by the Nernst equation:

$$E_t = \frac{p_{O_2(N,NiO)}}{p_{O_2(M,M_xO)}}, \qquad (2)$$

where p_{O_2} is the equilibrium oxygen partial pressure.

In the case of an electrolyte which contains another mobile charged species, the electromotive force observed, E_{obs}, can be expressed as:

$$E_{obs} = t_{ion} \cdot E_t. \qquad (3)$$

Knowing the transference number (t_{jon}), the 25YSZ or 12.5Yb12.5YSZ-sintered samples, were tested as solid oxide electrolytes in cells (4-6):

$$\text{Pt} \mid \text{O}_2\ [p\text{O}_2\ (\text{ref})] \mid \text{CaZrO}_3 \mid \text{O}_2\ [p\text{O}_2\ (\text{test})] \mid \text{Pt}, \qquad (4)$$

$$\text{Pt} \mid \text{Ni, NiO} \mid \text{25YSZ} \mid \text{NiLa}_2\text{O}_4, \text{La}_2\text{O}_3, \text{Ni} \mid \text{Pt}, \qquad (5)$$

$$\text{Pt} \mid \text{Ni, NiO} \mid \text{12.5Yb12.5YSZ} \mid \text{NiAl}_2\text{O}_4, \text{Al}_2\text{O}_3, \text{Ni} \mid \text{Pt}. \qquad (6)$$

The electromotive force of the cell (4) was measured as a function of temperature (600-1100ºC) and oxygen partial

pressure (from 10^{-7} atm to 1 atm). Pt/air was applied as a reference electrode. The gas mixtures with different composition were obtained by mixing argon and oxygen using mass flow controllers. The EMF and temperature were measured using Hewllet Packard HP-34401 multimeter, connected to multiplexer. The experimental setup was fully computer operated and allowed the continuous long-time measurements.

Based upon the investigation of cells (5-6) the thermodynamic properties of $LaNi_2O_4$ and $NiAl_2O_4$ were also investigated. The procedure of electromotive force measurements was similar to that described in papers [14, 15].

3. Results and discussion

The samples of 25 mol% Y_2O_3 in ZrO_2 (25YSZ) and 12.5 mol% Y_2O_3 plus 12.5 mol% Yb_2O_3 in ZrO_2 (12.5Yb12.5YSZ) were found to be single-phase cubic ZrO_2 materials. The typical microstructure of 25YSZ sintered samples is shown in Fig. 1. The material is composed of isometric grains of 1-4 μm size, and contains a small amount of closed porosity. The relative density of 25YSZ and 12.5Yb12.5YSZ sintered samples was above 98 % of theoretical density.

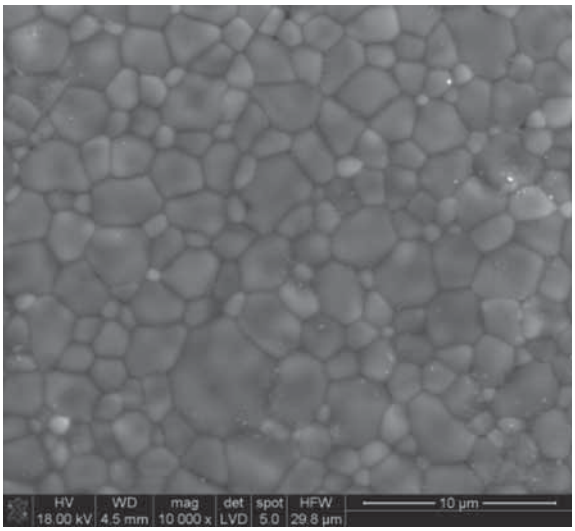


Fig. 1. Microstructure of 25YSZ samples sintered for 2 h at 1500ºC.

For engineering application of ceramic electrolytes as components of electrochemical probes for controlling oxygen dissolved in molten metal, it is important that 25YSZ and 12.5Yb12.5YSZ materials have a good tolerance against thermal shock and corrosion resistance in molten metals such as nickel, copper, or iron. The 25YSZ and 12.5Yb12.5YSZ samples did not show cracks after immersing them in molten nickel, or copper followed by rapid cooling. Similar results were observed for nonstoichiometric $CaZrO_3$ (51 mol% CaO) [9], and composite electrolytes, involving nonstoichiometric $CaZrO_3$ (48 mol% CaO). It was also found that contrary to $CaZrO_3$ with 51 mol% CaO content, stability of both 25YSZ and the electrolyte of $CaZrO_3$ with 48 mol% CaO content is limited in molten iron. In this case some cracks (Fig. 2) on the surface of these materials were observed.

One of the reasons for better chemical stability of nonstoichiometric $CaZrO_3$ (51 mol% CaO) in liquid iron contrary to zirconia-based solid solution, *e.g.*, CSZ, 25YSZ, is its lower thermal expansion.

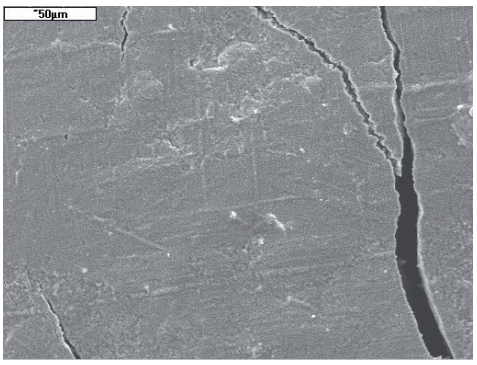
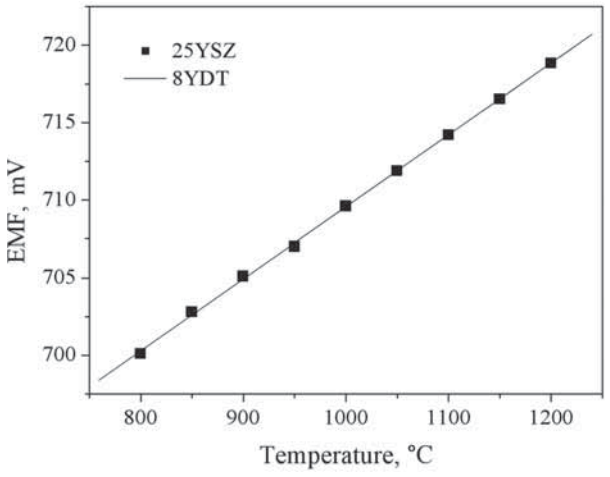


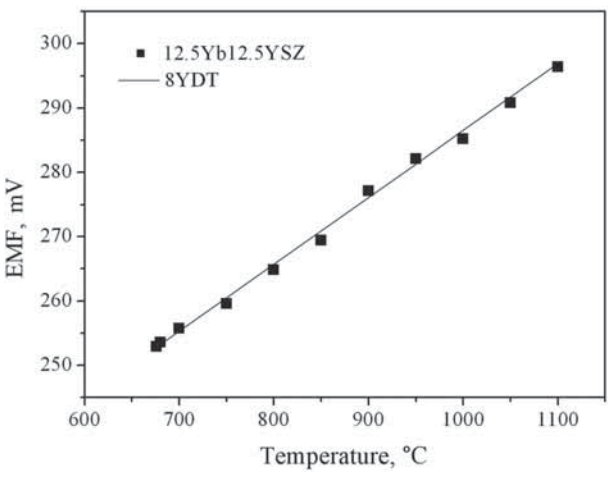
Fig. 2. Surface of 25YSZ sample sintered for 2 h at 1500ºC after immersion in molten iron.

The electrical and electrochemical properties of the 25YSZ and 12.5Yb12.5YSZ materials are crucial for their application as oxide electrolytes in electrochemical gas sensors. The EMF value of cell (1) with the 25YSZ or 12.5Yb12.5YSZ electrolyte measured at temperatures ranging from 600 to 1200°C (Figs. 3a and 3b) was compared to the respective EMFs measured with the same cell containing 8 mol% Y_2O_3 in ThO_2 (8YDT) as a reference solid electrolyte (E_t).

The calculated 25YSZ and 12.5Yb12.5YSZ oxygen transference numbers (t_{ion}) were found in the range of 0.99 to 1, which indicates practically pure oxygen ion conduction under low oxygen partial pressure.



a)



b)

Fig. 3. EMF as a function of temperature for solid galvanic cells: a) Ni, NiO | 25YSZ | Cr, Cr_2O_3, b) Ni, NiO | 12.5Yb12.5YSZ | Fe, FeO.

Temperature dependences of the total conductivity measured by dc four probe method in [S/cm] in dry air (Fig. 4) for the 25YSZ, 12.5Yb12.5YSZ and selected $CaZrO_3$-based samples are presented in Arrhenius graph. This plot shows that the 25YSZ and 12.5Yb12.5YSZ samples exhibited higher values of electrical conductivity than the $CaZrO_3$-based electrolytes, which are also considered solid oxide electrolytes for high temperature application.

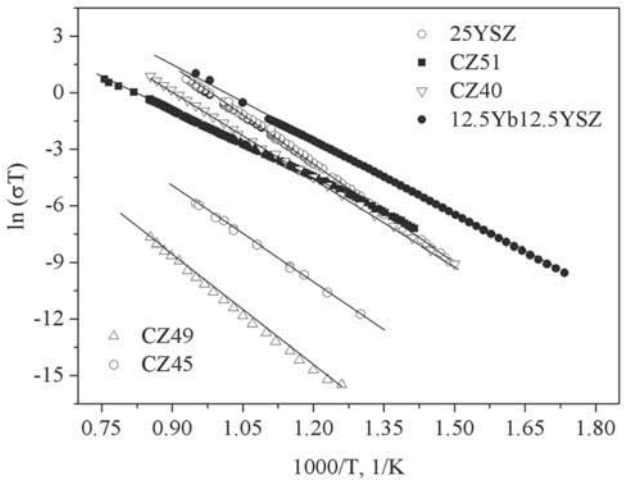


Fig. 4. Arrhenius plots for 25YSZ, 12.5Yb12.5YSZ and $CaZrO_3$-based samples; CZ45, CZ49, CZ51 denotes sintered samples of $CaZrO_3$ composed of 45, 49, or 51 mol% CaO.

The impedance spectroscopy method allowed bulk and grain boundary conductivity for the investigated samples to be determined. The temperature dependence of bulk and grain boundary conductivity for 12.5Yb12.5YSZ is shown in Fig. 5. The fully reproducible Arrhenius plots are observed for heating and cooling cycles.

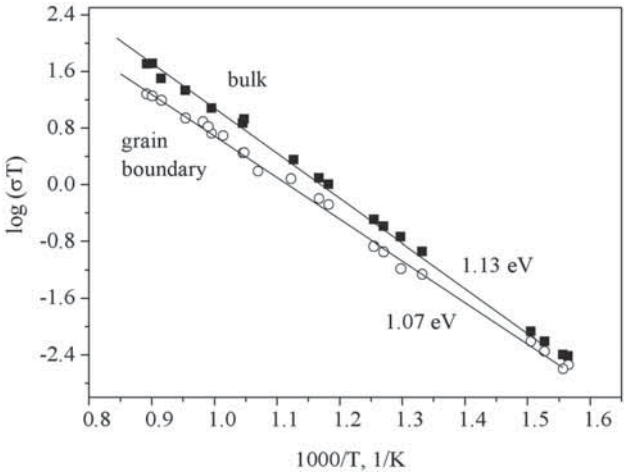


Fig. 5. Temperature dependence of bulk and grain boundary conductivity for 12.5Yb12.5YSZ samples.

The calculated values of total ionic conductivity at 800°C and 1000°C for the 25YSZ, 12.5Yb12.5YSZ samples sintered are shown in Table 1. For comparison the values of electrical conductivity σ_t are also presented for cubic zirconia containing 13 mol% CaO (13CSZ), 8 mol% Y_2O_3 in ZrO_2 (8YSZ), or 8 mol% Y_2O_3 in ThO_2 (8YDT).

The data regarding electrical properties clearly indicate that the 25YSZ and 12.5Yb12.5YSZ samples exhibited the values of electrical conductivity comparable to the 13CSZ and 8YDT electrolytes. The values of total electrical conductivity and oxygen transference number make the 25YSZ and 12.5Yb12.5YSZ materials suitable for the application as electrolytes at temperatures above 800ºC under low oxygen partial pressure. The electrical conductivity investigations also showed that the main advantage of the 25YSZ and 12.5Yb12.5YSZ solid electrolytes compared to $CaZrO_3$ modified by CaO excess (51 mol%) was a chemical stability under wet and hydrogen–containing atmospheres. Long lasting thermal treatment of the indicated $CaZrO_3$ material in such atmospheres led to decomposition of nonstoichiometric calcium zirconate accompanied by formation of CaO.

Table 1. Electrical conductivity of 25YSZ and 12.5Yb12.5YSZ sintered samples. For comparison, the data for selected $CaZrO_3$-based oxide electrolytes, 13CSZ and 8YDT are also listen.

Material	σ_t [S/cm]		References
	800°C	1000°C	
$CaZrO_3$ (51 mol% ZrO_2)	$4.8\cdot10^{-7}$	$6.8\cdot10^{-6}$	[16]
$CaZrO_3$ (55 mol% ZrO_2)	$3.9\cdot10^{-6}$	$4.60\cdot10^{-5}$	[16]
$CaZrO_3$ (51 mol% CaO)	$8.8\cdot10^{-4}$	$1.03\cdot10^{-2}$	[8]
13 mol% CaO in ZrO_2 (13CSZ)	$2.3\cdot10^{-3}$	$5.1\cdot10^{-2}$	[17]
8 mol% Y_2O_3 in ThO_2 (8YDT)	–	$1.1\cdot10^{-2}$ $6.7\cdot10^{-3}$	[18]
25 mol% Y_2O_3 in ZrO_2 (25YSZ)	$4.1\cdot10^{-3}$	$4.2\cdot10^{-2}$	this work
12.5 mol% Y_2O_3 and 12.5 mol% Yb_2O_3 in ZrO_2 (12.5Yb12.5YSZ)	$7.1\cdot10^{-3}$	$6.9\cdot10^{-2}$	this work

The 25YSZ and 12.5Yb12.5YSZ samples were applied as an electrolyte in electrochemical gas sensor operating above 600ºC. The temperature dependence of the EMF values measured for oxygen partial pressure p_x = 0.001 atm or 0.014 atm is shown in Fig. 6.

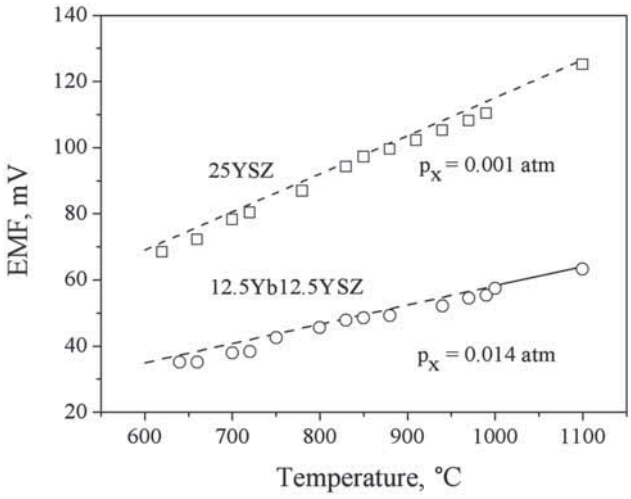


Fig. 6. EMF of cell (1) with 25YSZ or 12.5Yb12.5YSZ as a function of temperature.

Straight lines visible in Fig. 6 correspond to theoretical values calculated from the Nernst equation. The differences between the calculated and observed values did not exceed 2 mV, *i.e.*, they were only a few percent off the EMF values. The response time at applied temperature was not longer than 240 s.

The dependence of the EMF values on oxygen partial pressure determined at 660ºC is presented in Fig. 7. EMF of the investigated cell with 25YSZ or 12.5Yb12.5YSZ was found to be linear with the logarithm of oxygen partial pressure in the range 10^{-8}–1 atm and in the temperature range 600-1000ºC.

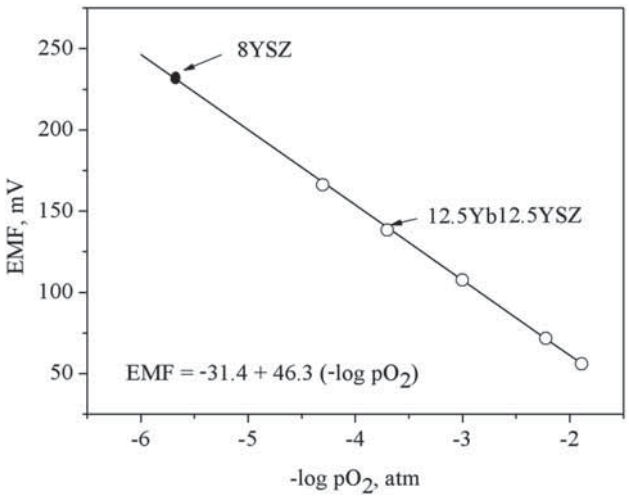


Fig. 7. EMF vs. oxygen partial pressure at 660ºC.

Another important area of possible application for the 25YSZ and 12.5Yb12.5YSZ materials could be solid oxide galvanic cells designed to study thermodynamic properties of oxide materials important for solid oxide fuel technology.

In this study the standard free energy ΔG_{ox} was determined for $LaNi_2O_4$ and $NiAl_2O_4$ by measurements of electromotive force with 25YSZ solid electrolyte. These materials are important as electrode materials, as cathode for SOFC, electrode materials for potentiometric NO_x gas sensor for exhaust gases [19, 20]. Fig. 9 shows the linear dependence of EMF measured for the cell (5) in the range 720-1220ºC (1000-1400 K) The EMF values were stable for more than 2 h.

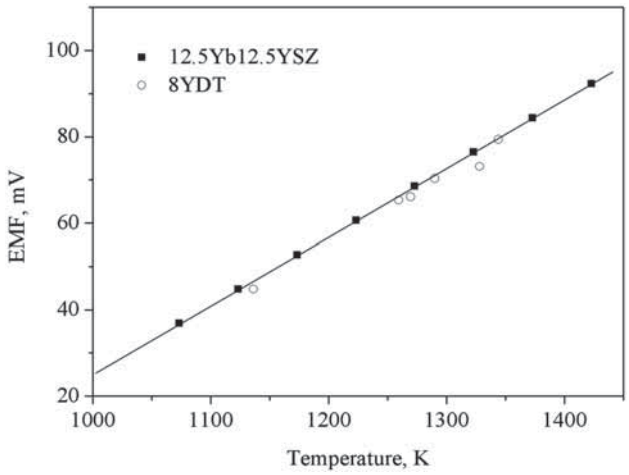


Fig. 8. Temperature dependence of EMF for cell (5) with 12.5Yb12.5YSZ.

The overall cell reaction for the galvanic cells (5) and (6) represents the formation of one mole respective lanthanite or aluminate from its constituent oxides. It may be written as follows:

$$NiO + La_2O_3 \rightarrow NiLa_2O_4, \quad (12)$$

Table 2. The standard molar Gibbs free energy, $\Delta_f G^o$, of formation of $NiLa_2O_4$ and $NiAl_2O_4$ from oxides at 1273º C.

Compound	D_fG^0, kJ·mol^{-1}	Ref.
$NiLa_2O_4$	12.85	[15]
	13.11	this work
$NiAl_2O_4$	18.44	[21]
	20.93	[22]
	23.74	this work

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4. \quad (13)$$

Taking into account that EMF of the cell (5) and (6) is connected with the standard Gibbs free energy of nickel lanthanite or nickel aluminate (from oxides) $\Delta_f G^0(NiLa_2O_4)$, can be calculated on the basis of the EMF values according to the equation:

$$\Delta_f G^0(NiLa_2O_4) = -2FE, \quad (14)$$

where E is the respective cell EMF value.

The determined $\Delta_f G^0(NiLa_2O_4)$ or $\Delta_f G^0(NiAl_2O_4)$ values at T = 1273ºC are presented in Table 2 together with data taking from the literature [15].

As it can be seen, the results are in good agreement with the data obtained by Sreedharan [15], who applied 8 mol% Y_2O_3 in ThO_2 (8YDT) as a solid electrolyte in the investigated cell.

4. Conclusions

The 25YSZ and 12.5Yb12.5YSZ sinterable powders were successfully synthesized by coprecipitation-calciantion method. The corrosion resistance of bulk bodies sintered for 2 h at 1500ºC was limited against molten iron, but the same materials were resistant to molten copper and nickel. The dense samples were applied as solid electrolytes in the electrochemical oxygen sensor operating above 600ºC and solid galvanic cells designed to study thermodynamic properties important to SOFC technology.The EMF value of oxygen concentrated galvanic cell found to be linear with the logarithm of oxygen partial pressure in the range of 10^{-7} atm to 1 atm and in the temperature range of 600-1100ºC and therefore can be applied as oxygen sensors in such conditions. The 25YSZ and 12.5Yb12.5YSZ solid electrolytes are also adequate solid oxide electrolytes for application of thermodynamic studies at low oxygen partial pressure.

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References

[1] Fray D.J.: Solid State Ionics, 86-88, (1996), 1045-1054.
[2] Chiang Y., Wagner C.C., Abkar S.A.: Sens. Act. B46, (1998), 208-212.
[3] Etsell T., Flengas T.: J. Electrochem. Soc., 119, (1972), 1-7.
[4] Pluschkell W.: Archiv. Eisenhuttenwesen, 46, (1975), 11-18.

[5] Jacob K.T., Mathews T.: in High Conductivity Solid Ionic Conductors – Recent Trends and Applications, Takahashi T. (Ed.), World Scientific, Singapore, 1989.
[6] Janke D.: Metall. Trans., 13B, (1982), 227-235.
[7] Róg G., Dudek M., Kozłowska–Róg A., Bućko M.: Electrochim. Acta, 47, (2002), 4523-4529.
[8] Dudek M., Drożdż-Cieśla E.: J. Alloys Compd., 475, (2009), 846-859.
[9] Janke D., Fischer W.A.: Archiv. Eisenhuttenwesen, 45, (1975), 477-482.
[10] Wang C., Xu X., Yu H., Wen Y., Zhao K.: Solid State Ionics, 28-30, (1988), 542-545.
[11] Weyl A., Janke D.: J. Am. Ceram. Soc., 80, (1997), 861-731.
[12] Dygas J.R., Breiter M.W.: Electrochim. Acta, 44, (1999), 4163-4174.
[13] Kiukola K., Wagner K.: J. Electrochem. Soc., 104, (1957), 366-375.
[14] Róg G., Kozłowska-Róg A., Dudek M.: J. Chem. Thermodynamics, 39, (2007), 275-278.
[15] Sreedharan O.M., Chandrasekharai S.M., Karakhanavala M.D.: High Temp. Sci., 8, (1976), 179-183.
[16] Dudek M.: Adv. Mater. Sci., 8, (2008), 15-30.
[17] Tien T.Y.: J. Am. Ceram. Soc., 11, (1964), 430-433.
[18] Subbarao E., Sutter P., Hrizo J.: J. Am. Ceram. Soc., 48, (1965), 443-446.
[19] Knibbe R., Drennan J., Dicks A., Love J.: J. Power Sour., 179, (2008), 511-519.
[20] Zhao H., Mauvy F., Lalanne C., Bassat J.M., Fourcade S., Grenier J.C.: Solid State Ionics, 179, (2008), 2000-2005.
[21] Schmalzried H.: Z. Pys. Chem., 25, (1960), 178.
[22] Tretjakov G.J., Schmalzried H.: Ber. Bunsenges. Phys. Chem., 69, (1965), 396.

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