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CERAMIC OXIDE ELECTROLYTES BASED ON $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ FOR SOLID GALVANIC CELLS APPLICATION

ABSTRACT

The $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ nanopowder was successfully synthesized by the citrate method. The XRD diffraction method evaluated that the orthorhombic CaZrO_3 phase was detected in powders or sintered samples. The sintered sample at 1450°C for 2 hours exhibits about 98 % of theoretical density. The electrical conductivity was measured by a.c impedance spectroscopy method in the temperature range of 200-800°C. The transference oxygen ion number of CaZrO_3 sample was estimated from electromotive force measurements (E_m) of galvanic cell in the temperature range of 550-1100°C. The $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ exhibits purely oxygen ion conductivity. It was successfully applied as a solid electrolyte in the electrochemical oxygen sensor operating at 660°C. The measured electromotive force of investigated cell was found to be linear with the logarithm of oxygen partial pressure in the range of 10^{-6} atm 1 atm and in the temperature range of 660-1000°C.

Key words: ceramic oxide electrolyte, electrochemical oxygen gas sensor, impedance spectroscopy, ionic transference number

INTRODUCTION

There has been a growing interest in solid oxide electrolytes for high temperature applications. Beside their utilization in energy industry, as a components of solid oxide fuel cells, there also exists a wide area of their prospective sensor applications in monitoring and control of the oxygen partial pressure, in numerous industrial processes – such as metallurgy (steel production) and in combustion processes (e.g. in internal combustion engines) [1-2]. The best known solid oxide electrolyte is the fully CaO - or Y_2O_3 -stabilized zirconia. This material is the one taken most frequently into account as a candidate for applications, even though it possesses some essential drawbacks. At high working temperatures CaO- ZrO_2 or Y_2O_3 - ZrO_2 solid solutions become highly reactive with the electrode and other components of solid galvanic cells.

The above features facilitate fast degradation, thus possibly becoming an unstable element of the electrochemical cell. Additionally, when oxygen pressure is lowered to less than 10^{-12} atm and temperature ranges from 1200 to 1500°C, zirconia-based electrolytes also exhibit electronic conduction which causes serious problems when designing sensor applications [3, 4]. Since the products of CaO- ZrO_2 degradation contain mainly calcium zirconate, CaZrO_3 , it is obvious that this compound must be much more chemically stable than stabilized zirconia

itself. Several investigators reported that materials based on calcium zirconate were also oxygen ion conductors at high temperatures [5,6]

Fischer *et al.* found that CaZrO_3 containing small amount of dispersed calcia or zirconia particles exhibited extremely high chemical stability, and practically pure ionic conduction, which furthermore might lead to using it as a sensor to measure oxygen activity in molten steel [7]. It was found that electrical properties of CaZrO_3 are strictly connected with its stoichiometry [8]. The introduction of excess CaO or ZrO_2 excess led to a significant improvement in ionic conductivity of CaZrO_3 -based materials, compared to stoichiometric CaZrO_3 . The analysis of electrical conductivity values for CaZrO_3 -doped excess CaO samples, with the formula $(\text{CaO})_x(\text{ZrO}_2)_{1-x}$ indicated that the total ionic conductivity reached a maximum value for composition $x = 51\text{--}52$ mol.%, which are close to solubility limit CaO in CaZrO_3 . Further increase in calcia content caused the occurrence of CaO as a second phase and led to a decrease of ionic conductivity for investigated materials. The improvement of electrical conductivity in the CaZrO_3 with excess ZrO_2 samples, where $30 < x < 49$ mol.%, was also noticed. In this case, an appearance as cubic calcia solid solution as better conductive phase than orthorhombic CaZrO_3 led to enhancement of ionic conductivity compared to monophasic CaZrO_3 [9]. The electrolytic domain of nonstoichiometric CaZrO_3 is close to thoria or hafania-solid solution, considered to be the most adequate oxide electrolytes for high temperature application. The costs of producing CaZrO_3 -based electrolytes are also lower than MO_2 , $M = \text{Th, Hf}$ -solid solutions [10]

Ch. Wang *et al.* also showed that CaZrO_3 doped with some oxides, as Y_2O_3 , Al_2O_3 or MgO samples, possessed extremely high chemical stability, and good tolerance against thermal shock. Experimental results indicated that these materials may be used as a solid electrolyte oxygen probe for deoxidised steel melts [11].

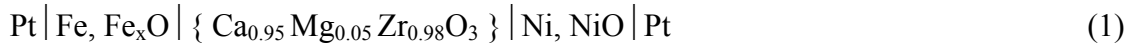
In applications such as electrochemical oxygen gas sensors or probes, it is important that the materials have good ionic conductivity ($> 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at the operating temperature). They also need to be pure ionic conductors (ion transport number $t_{\text{ion}} > 0.99$) over a wide range of oxygen partial pressures, and also impermeable to prevent direct molecular transport of oxygen through the samples (density $> 95\%$) [12].

The present study is focused on the preparation of fine, sinterable powder of $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ by citrate method, as well as on investigation of the properties crucial to application of the CaZrO_3 -based samples as an oxide electrolyte in solid oxide galvanic cells.

EXPERIMENTAL

$\text{Ca}_{0.95}\text{Mg}_{0.05}\text{Zr}_{0.98}\text{O}_3$ powder was prepared using a citrate route. Appropriate amounts of calcium, magnesium carbonate, and citric acid powders were dissolved in zirconyl nitrate aqueous solution. The solution was evaporated at 70°C to obtain hard gel. The gel was heated up to decompose citric precursor – the process was accompanied by several exothermic and endothermic effects. Finally, the powder was calcinated at 900°C for an hour, and then attrition-milled with zirconia grinding media in dry ethanol. The pellets were isothermally pressed under 300 MPa, and sintered at 1500°C for 2 hours in air. Transmission electron microscopy (TEM) was used to observe morphology of the powder. The phase composition of the powder, and sintered body was evaluated by x-ray diffraction analysis (XRD). Scanning electron microscopy (SEM) observations of the polished and thermally etched surface provided quantitative characteristic of the sample microstructure. Fracture toughness (K_{Ic}) was determined using the Vickers indentation method [13]

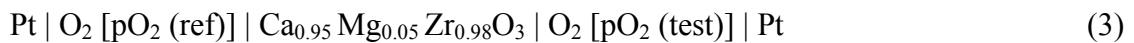
Electrical conductivity was measured by the a.c impedance spectroscopy method in the temperature range of 200-800°C. The reversible platinum electrodes were applied. Impedance was analysed by means of non-linear least-squares fitting of equivalent circuit using the Firdravn program. In order to estimate the oxygen ion transference number (t_{ion}) of the prepared calcium zirconate, the electromotive force measurements (E_m) of the following galvanic cell in the temperature range 550-1100°C were performed.



The two-phase mixtures (Fe, Fe_xO) and (Ni, NiO) with known equilibrium of oxygen partial pressures were used as half-cells. The procedure was practically identical to the one presented in the work of Kiukola and Wagner [14] concerning solid oxide galvanic cells, involving the cubic phase of the CaO-ZrO₂ solid solution. The ionic transference number (t_{ion}) in the sample was determined on the basis of the electromotive force values (E_m) measured for the cell (1), and on the electromotive force values (E_t) obtained for the cell (1) with a pure oxygen ion conductor:

$$t_{ion} = E_t / E_m \quad (2)$$

The obtained materials were tested as a solid electrolyte in the oxygen galvanic cell (3). The cell was investigated as the planar electrochemical oxygen gas sensor.



The electromotive force of the cell (4) was measured as a function of temperature (600-1100°C) and oxygen partial pressure (from 10⁻⁶ 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 electromotive force (E_m) and temperature were measured using Hewlett Packard HP-34401 multimeter, connected to multiplexer. The experimental setup was fully computer-operated, and allowed continuous long-time measurements. The details of experimental setup and procedure was previously described in papers [15,16].

RESULTS AND DISCUSSION

Orthorhombic CaZrO₃ was the only phase detected by XRD method in the powder and sintered samples. The morphology of calcined and ground powder is shown in Fig. 1.

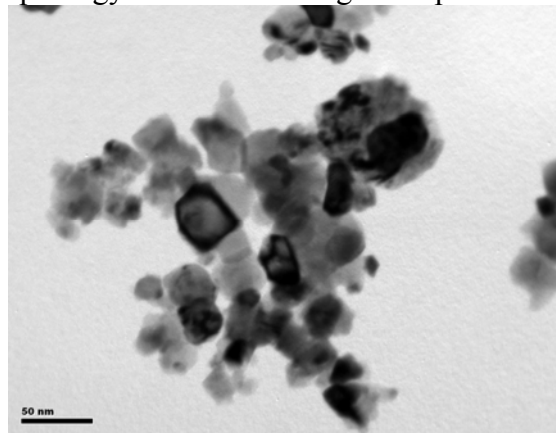


Fig. 1. The TEM microphotograph of the grounded Ca_{0.95}Mg_{0.05}ZrO₃ powder

The powders were mostly composed of nanoparticles (~ 35 nm) isometric in shape. The sintered $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ sample exhibits about 98 % of theoretical density. Fig. 2 presents a microstructure of the CaZrO_3 sintered body with isometric grains of $0.4\div 0.6$ μm in size.

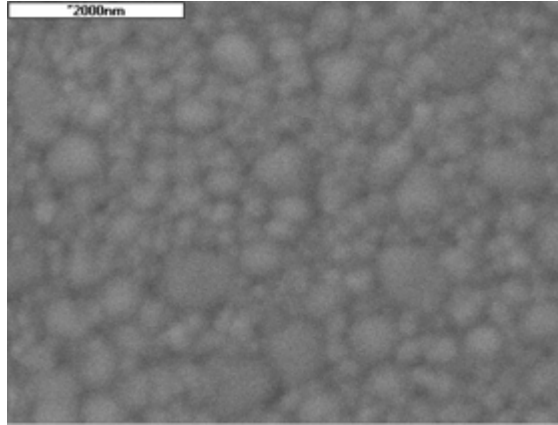


Fig. 2. The SEM microphotograph of the $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ sintered sample

The values of fracture toughness (3.34 ± 0.40 $\text{MPa}\cdot\text{m}^{0.5}$) of the materials were comparable to the zirconia solid solutions fully stabilized with calcia or yttria. Fig. 3 shows a typical impedance spectrum for the $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{Zr}_{0.98}\text{O}_3$ sample recorded at 600°C .

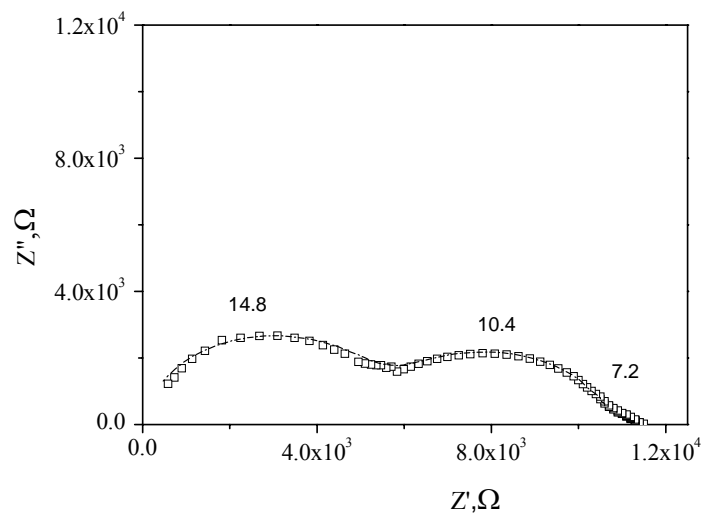


Fig. 3. Typical impedance plot for the $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{Zr}_{0.98}\text{O}_3$ sample recorded at 600°C

The spectrum was fitted by the impedance of equivalent circuit consisting on the series of 3 sub-circuits of parallel resistor-CPA elements. The sub-circuits were attributed to bulk, grain-boundary, and electrode dispersion. After successful fitting, the obtained values of the bulk and grain boundary resistor were recalculated respectively to the bulk and grain boundary conductivity. It was stated that the bulk conductivity amounted to $2.21\cdot 10^{-4}$, whereas the grain boundary conductivity to $2.14\cdot 10^{-4}$ $\text{S}\cdot\text{cm}^{-1}$ at the temperature 600°C . These values are comparable to the respective conductivities for other solid electrolytes applied as oxygen sensors e.g. cubic zirconia stabilised with 15 mol% of calcia

The temperature dependence of bulk and grain boundary conductivity for the $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{Zr}_{0.98}\text{O}_3$ sample is shown in Fig. 4.

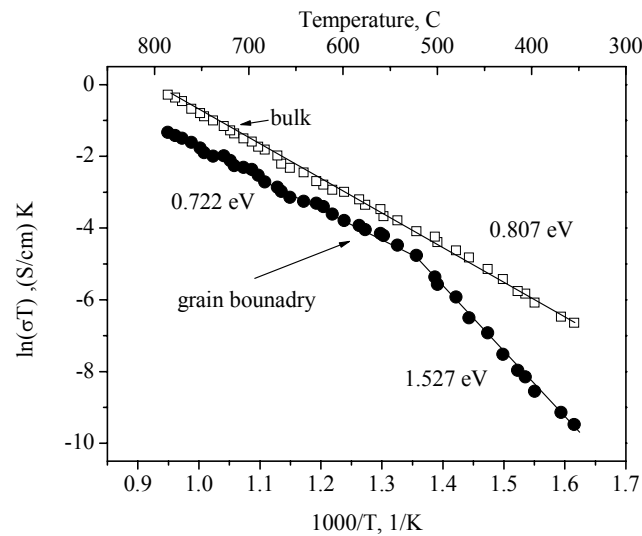


Fig. 4. Arrhenius plots for bulk and grain boundary conductivity for $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{ZrO}_3$ sample

The reproducible Arrhenius plots were observed for heating and cooling cycles. The values calculated by us, concerning energy activation of conduction process were also comparable to zirconia solid electrolytes.

The electromotive force (E_m) values of the cell (1) measured in the temperature range from 600 to 1000 $^{\circ}\text{C}$ (Fig. 5) were compared with the respective electromotive force (E_t) measured in the cell containing fully calcia-stabilized zirconia as a reference solid electrolyte.

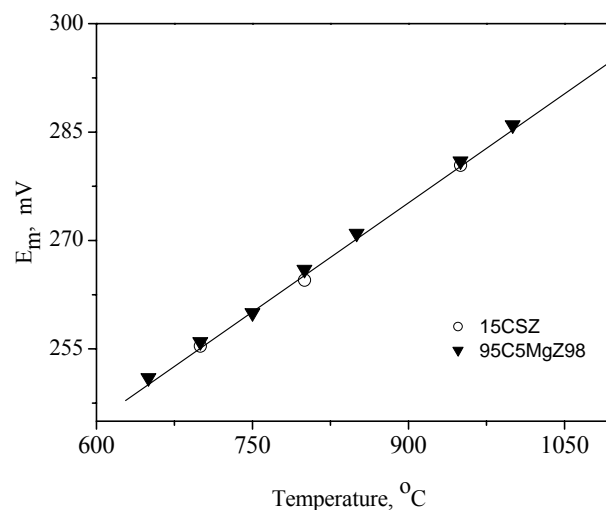


Fig. 5. The electromotive force measurements (E_m) of the cell

Pt | Fe, Fe_xO | { Ca_{0.95}Mg_{0.05}Zr_{0.98}O₃ } | Ni, NiO | Pt as a function of temperature.

The calculated values of the transference oxygen number (t_{ion}) of Ca_{0.95}Mg_{0.05}Zr_{0.98}O₃ were found to vary between 0.99 and 1, which indicates practically pure oxygen ion conduction in the sample. The Ca_{0.95}Mg_{0.05}Zr_{0.98}O₃ (95C5MgZ98) sintered sample was applied as an oxide electrolyte in oxygen gas sensor operating above 600°C. In this case the concentration cell (2) was investigated. The temperature dependence of the E_m values measured for oxygen partial pressure equal 0.014 atm and 0.01 atm is shown in Fig. 6.

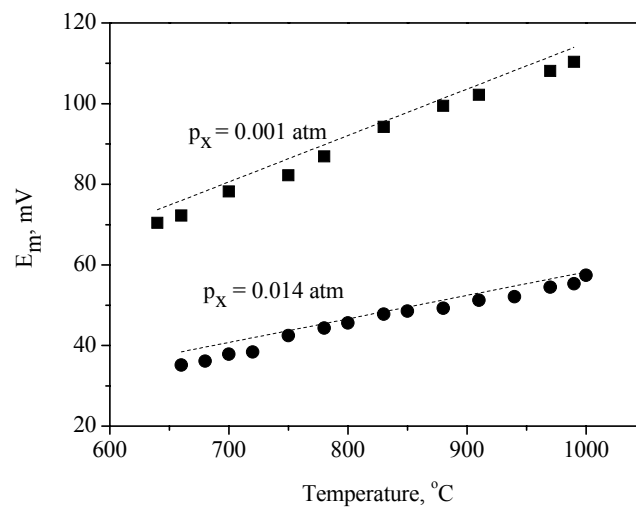


Fig. 6. The electromotive force (E_m) of the cell (3) as a function of temperature

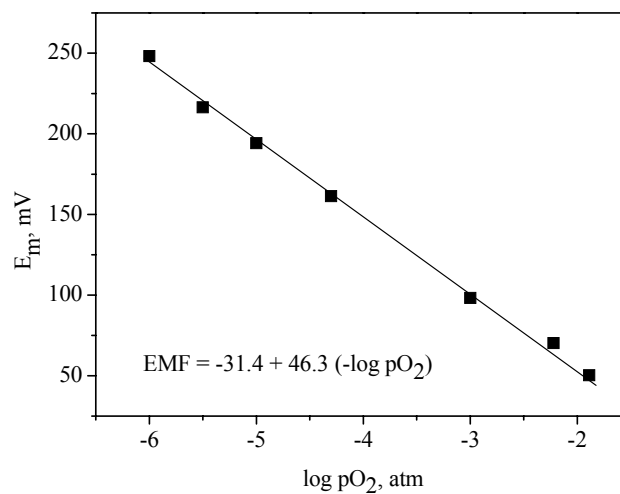


Fig. 7. The electromotive force (E_m) of the cell (3) as a function of oxygen partial pressure at 660°C

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

The dependence of the EMF values on oxygen partial pressure determined at 660°C is presented in Fig. 7. The EMF of the investigated cell was found to be linear with the logarithm of oxygen partial pressure in the range between 10^{-8} atm and 1 atm, and in the temperature range 600-1100°C.

CONCLUSIONS

The $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{Zr}_{0.98}\text{O}_3$ nanopowder (~35nm) was successfully synthesized by the citrate method. The dense sample, sintered at 1450°C for 2 hours, was applied as solid electrolyte in the electrochemical oxygen sensor operating above 600°C. The electromotive force (E_m) value of such galvanic cell was found to be linear with the logarithm of oxygen partial pressure in the 10^{-6} atm - 1 atm range, and in the temperature range of 600-1000°C and therefore can be applied as an oxygen sensor in such conditions.

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