

Calcium zirconate as a solid electrolyte for electrochemical devices applied in metallurgy

M. DUDEK^{1*}, G. RÓG¹, W. BOGUSZ², A. KOZŁOWSKA-RÓG¹, M. BUĆKO¹, Ł. ZYCH¹

¹AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
al. Mickiewicza 30, 30-059 Cracow, Poland

²Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warsaw, Poland

Stoichiometric calcium zirconate and CaZrO₃ samples with an excess of calcia or zirconia were obtained from powders prepared by the citrate method. XRD measurements were used to determine the phase compositions of the sintered materials as well as their crystal structures. The compositional dependence of the calcium zirconate cell parameter indicates that an excess of calcia or zirconia form a solid solution. Stoichiometric CaZrO₃ appeared to be a rather poor oxygen ion conductor, whereas calcium zirconate samples with an excess of calcia or zirconia exhibit pure oxygen conductivity. The introduction of a respective excess of cations led in both cases to a significant enhancement of conductivity. The fracture toughness, hardness, and flexural strength of the samples were also investigated. The mechanical and electrical properties of CaZrO₃-based materials are comparable to those of zirconia solid electrolytes. The lower thermal expansion coefficient and better resistance to thermal shock make CaZrO₃ a more suitable solid electrolyte for metallurgical applications.

Key words: *perovskite; oxygen ion conductor; electrolyte; probe; metallic melt*

1. Introduction

Oxygen sensors based on partially or fully (CaO, MgO)-stabilized ZrO₂ have been developed and used for steel making and nickel and copper refining processes. It is known that the electronic conductivity of ZrO₂-based electrolytes should be taken into account when oxygen partial pressure falls below 10⁻⁷ Pa at temperatures close to 1300 °C [1, 2]. The electronic conductivity introduces time-dependent polarisation effects in the long-time operation of electrochemical oxygen probes. Additionally, at very low oxygen partial pressures, decomposition of zirconia occurs, which may cause serious errors in EMF measurements [3]. Taking the above effects into account,

*Corresponding author, e-mail: potoczek@uci.agh.edu.pl

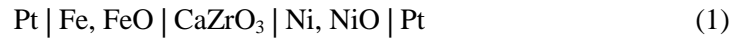
it is appropriate to search for other solid electrolytes with lower partial electronic conductivities. Good mechanical properties, thermal shock resistance, and thermodynamic stability are also required for electrolytic materials in such applications. The ionic conduction limit for yttria-doped thoria (YDT) is lower than that for stabilized zirconia. Hence, thoria-based electrolytes are superior at low oxygen concentrations. Due to the radioactivity of thorium, however, they have not found application in the steel industry [4]. Several investigators have reported CaZrO_3 with excess of zirconia or calcia being also an oxygen-ion conductor which might be applied as a solid electrolyte in electrochemical devices in the temperature range 1200–1600 °C and at partial oxygen pressures down to 10^{-13} Pa. Ceramic electrolytes based on CaZrO_3 have been successfully applied as probes in molten steel [5, 6]. One of the main disadvantages of such materials is EMF instability during long-time use. The CaZrO_3 -based samples with calcia inclusions applied by Janke et al. [6] as solid electrolytes showed significant porosity (15–20%) depending on chemical composition and sintering temperature. Chemical inhomogeneity could be an additional disadvantage for their application. Moreover, at temperatures higher than 1800 °C unfavourable microstructural changes can occur due to the phase transition of orthorhombic CaZrO_3 to its cubic form [7].

The present study is focused on the preparation of dense CaZrO_3 samples, as well as on investigations of the influence of an excess of zirconia or calcia on the structure and microstructure, and hence on the electrical and mechanical properties of CaZrO_3 . The practical purpose of this research was to obtain a CaZrO_3 -based material that could be applied as an electrolyte in electrochemical oxygen sensors with long-term stability.

2. Experimental

Calcium zirconate powders were prepared using the citrate method. Appropriate amounts of calcium carbonate and citric acid powders were dissolved in aqueous solution of zirconyl nitrate. The molar ratio of calcium to zirconium was fixed between 0.43 and 2.33. The solutions were evaporated at 70 °C to obtain hard gels. The gels were heated to decompose the citric precursor in a sequence of several exo- and endothermic effects. Finally, the powders were calcinated at 900 °C for 1 hour and then attrition-milled with a zirconia grinding media in dry ethanol. The pellets were isostatically pressed under 300 MPa and sintered at 1500 °C for 2 hours in air. The phase composition of the powders and sintered samples was evaluated by X-ray diffraction analysis. Scanning electron microscopy was used to observe the microstructure of the samples. The fracture toughness was determined using the Vickers indentation method. The specimens for three-point bending tests were cut from plates and their flat surfaces were polished. Thermal expansion coefficients were measured in the temperature range 20–1200 °C. The electrical conductivity was measured by ac impedance spectroscopy in the temperature range of 200–900 °C. For each sample,

impedance measurements were performed over two heating and cooling cycles. The transference oxygen number in all prepared samples was estimated from EMF measurements of a typical oxygen galvanic cell



in the temperature range of 550–1100 °C. The two-phase mixtures (Fe, Fe_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. [8]. If an electrolyte separating the half cells in cell (1) had a pure ionic conduction, and only O²⁻ ions were transported, the EMF, E_t would be given by the Nernst equation:

$$E_t = \frac{RT}{4F} \ln \frac{p_{\text{O}_2(\text{Ni, NiO})}}{p_{\text{O}_2(\text{Fe, Fe}_x\text{O})}} \quad (2)$$

where p_{O_2} is the equilibrium oxygen partial pressure. In the case of an electrolyte which contains another mobile charged species, the EMF of cell (1) can be expressed as

$$E = t_{\text{ion}} E_t \quad (3)$$

if only t_{ion} does not depend on the oxygen partial pressure in the galvanic cell. In such a case the term t_{ion} can be regarded as corresponding to the oxygen transference number in the CaZrO₃-based samples.

3. Results

Orthorhombic CaZrO₃ was the only phase detected by XRD in the samples containing from 0.50 to 0.515 mol fraction of calcia. Changes in the phase content of the samples strongly depended on the oxide, being in excess. Even in the sample with the smallest ZrO₂ excess, a significant amount of cubic zirconia solid solution was observed. In the case of samples with an excess of calcia, only very weak lines attributed to the CaO phase were detected for the material with the molar ratio CaO:ZrO₂ equal to 0.52:0.48. Figure 1 illustrates CaZrO₃ weight fraction changes, determined as a function of the initially assumed calcia to zirconia molar ratio. On the basis of X-ray investigations, the cell parameters and cell volume of CaZrO₃ with excess of calcia were calculated.

Figure 2 presents the compositional dependence of the CaZrO₃ cell volume. In both cases (excess of calcia and zirconia), an increase of volume cell was observed. In samples with excess of CaO, this increase is rather small and reaches a maximum for the material with 6 mol % of excess of calcia. The changes in cell parameters suggest that both excess of zirconia and calcia are in a solid solution form.

Figures 3a–c show typical microstructures of the samples. Generally, all samples achieved relative densities higher than 98%. Only the presence of CaO as a second

phase led to poorer densification and to the appearance of open porosity in samples. As shown in Figure 3, CaZrO_3 grain size decreases with the increasing excess of calcia or zirconia. The samples with an excess of zirconia exhibited an average grain size from 0.8 to 1.1 μm , whereas in those with excess of calcia the grain size ranged from 0.5 to 0.9 μm .

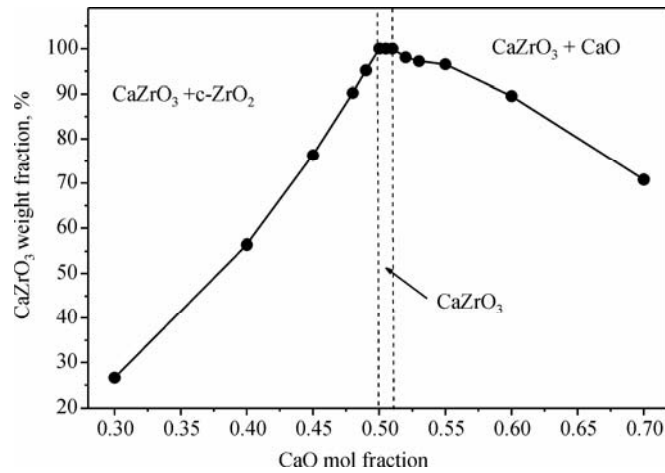


Fig. 1. Calcium zirconate weight fraction as a function of initially assumed calcia to zirconia molar ratio

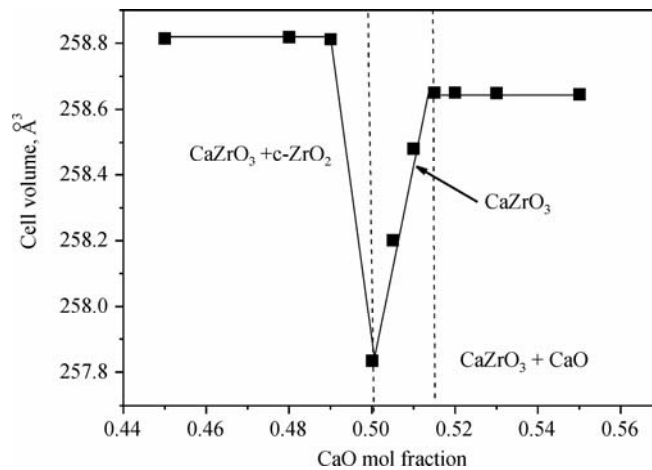


Fig. 2. Dependence of cell volume on molar fraction of calcia in all samples investigated

The K_{IC} measurements (Fig. 4) indicated relatively small increases in fracture toughness with increasing calcia concentration. On the other hand, in the case of samples with an excess of ZrO_2 K_{IC} remains unchanged within an experimental error.

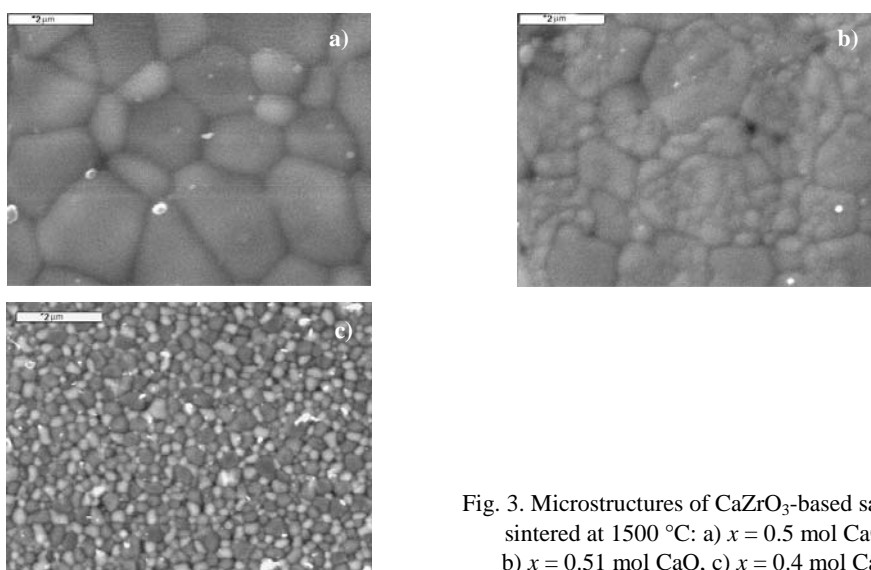


Fig. 3. Microstructures of CaZrO_3 -based samples sintered at 1500 °C: a) $x = 0.5$ mol CaO, b) $x = 0.51$ mol CaO, c) $x = 0.4$ mol CaO

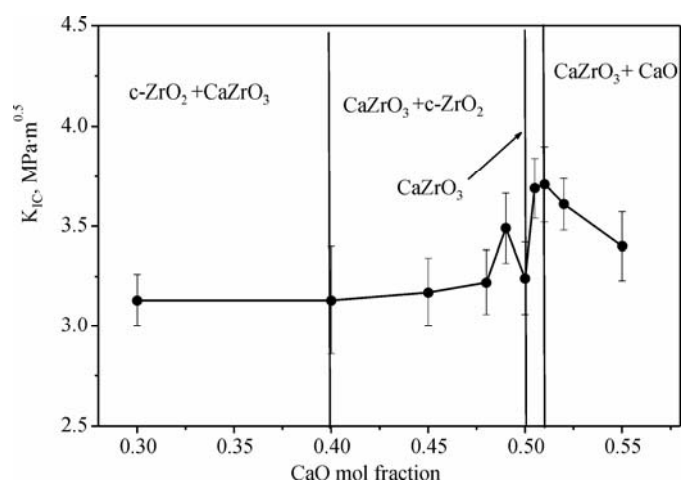


Fig. 4. Dependence of fracture toughness K_{IC} of calcium zirconate samples on calcia or zirconia excess

Mechanical properties of selected CaZrO_3 -based materials as well as of solid ZrO_2 -based electrolytes being potential electrolytes for oxygen-sensing applications are given in Table 1. These data clearly indicate that the mechanical properties of CaZrO_3 -based materials are comparable to those of zirconia-based solid solutions. Considering CaZrO_3 -based materials as potential solid electrolytes for applications in electrochemical oxygen probes used to determine oxygen activity in molten metals, it is required to have control over the expansion coefficient. Table 1 also compiles the determined values of the thermal expansion coefficient for selected CaZrO_3 samples

and for fully stabilized zirconia. The CaZrO_3 -based samples exhibited lower thermal expansion coefficients than that of zirconia solid electrolytes. This might indicate a better resistance to thermal shock in operating conditions involving temperature fluctuations.

Table 1. Selected properties of CaZrO_3 and calcia-, magnesia- or yttria- fully stabilised zirconia materials

Material	HV [GPa]	K_{IC} [MPa \times m ^{0.5}]	σ_f [MPa]	α [K ⁻¹]
CaZrO_3 0.51 CaO 0.49 ZrO_2	9.20 \pm 0.17	3.43 \pm 0.12	208 \pm 11	8.4 \times 10 ⁻⁶
CaZrO_3 0.45 CaO 0.55 ZrO_2	10.61 \pm 0.11	3.11 \pm 0.15	198 \pm 16	8.9 \times 10 ⁻⁶
15 mol % CaO in ZrO_2	12.20 \pm 0.13	2.30 \pm 0.15	220 \pm 13	2.1 \times 10 ⁻⁵
9 mol % MgO w ZrO_2	11.80 \pm 0.16	2.22 \pm 0.11	212 \pm 21	1.9 \times 10 ⁻⁵
8 mol % Y_2O_3 in ZrO_2	12.86 \pm 0.21	2.65 \pm 0.15	222 \pm 11	1.7 \times 10 ⁻⁵

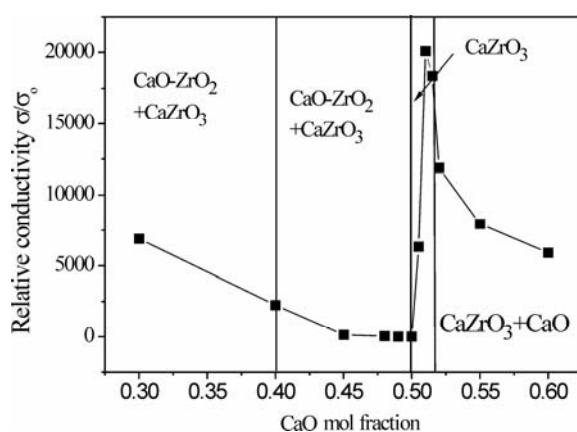


Fig. 5. Dependence of relative conductivity σ/σ_0 of calcium zirconate on calcia or zirconia excess

Impedance spectroscopy enabled determination of the bulk and grain boundary ionic conductivities of the sintered samples. Figure 5 illustrates the influence of the excess of zirconia or calcia on calcium zirconate electrical properties. In this figure, the relative total conductivity σ/σ_0 measured at 800 °C is plotted versus calcia mol fraction; σ_0 denotes the conductivity of stoichiometric calcium zirconate. An excess

of zirconia from 4 to 20 mol % leads to electrical conductivity enhancement by a factor from 3 to 48, respectively. A considerable increase in conductivity for samples

Table 2. Electrical properties of CaZrO_3 and calcia or magnesia fully-stabilised zirconia solid electrolytes in the temperature range of 200–1000 °C

Material	σ_c [S/cm] (at 1000 °C)	E_a [eV]
CaZrO_3	1.3×10^{-6}	2.20
CaZrO_3 (0.51 CaO, 0.49 ZrO_2)	1.4×10^{-2}	0.90
CaZrO_3 + c.s.s CaO– ZrO_2 (0.6 CaO; 0.4 ZrO_2)	2.6×10^{-3}	1.32
CaZrO_3 + c.s.s CaO– ZrO_2 (0.7 CaO, 0.3 ZrO_2)	6.2×10^{-3}	1.31
15 % mol CaO in ZrO_2	5.2×10^{-2}	1.15
9 % mol MgO in ZrO_2	4.5×10^{-2}	1.30

c.s.s – cubic solid solution CaO in ZrO_2 .

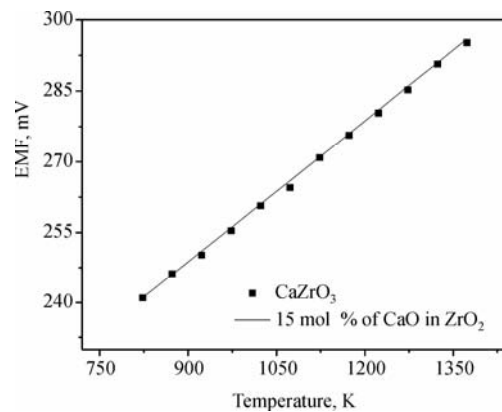


Fig. 6. The EMF of cell (1) as a function of temperature

with a larger excess of zirconia corresponds to the formation of cubic zirconia as a continuous phase, due to its better conduction properties as compared to CaZrO_3 electrolytes. On the other hand, introducing 4 mol % of calcia into calcium zirconate significantly increases conductivity by a factor of 2×10^4 . An increase of the excess of calcia by more than 6 mol % results in the formation of a larger CaO heterophase and leads to a decrease in electrical conductivity. The analysis of electrical conductivities of all samples investigated reveals that the bulk conductivity reaches a maximum value for the CaO: ZrO_2 ratio being 0.51:0.49. The calculated values of ionic conductivity at 1000 °C for the selected samples are shown in Table 2. For comparison, the values of electrical conductivity (σ_c) and activation energy (E_a) are also presented for calcia-, magnesia-, and yttria-stabilized zirconia. The data regarding electrical proper-

ties clearly indicate that the samples based on CaZrO_3 exhibit electrical conductivities and activation energies close to those of calcia and magnesia-stabilized zirconia.

The EMF value of cell (1) measured at temperatures from 823 to 1273 K (Fig. 6) was compared to the respective EMFs measured with the same cell containing fully calcia-stabilised zirconia as a reference solid electrolyte (E_r). The calculated CaZrO_3 oxygen transference numbers (t_{ion}) were found to vary from 0.99 to 1, which indicates practically pure oxygen ion conduction. The chemical stability of CaZrO_3 -based electrolytes in liquid metals such as nickel was also investigated.

Microstructural observations carried out with scanning microscopy and EDS analysis did not indicate any products of the reaction between CaZrO_3 -based samples and nickel or copper melts.

4. Conclusions

The introduction of excess of CaO or ZrO_2 into calcium zirconate leads to a significant enhancement of electrical conductivity and to the improvement of the fracture toughness (K_{IC}) of CaZrO_3 -based samples. The highest values of total electrical conductivity and fracture toughness were found in the calcium zirconate solid electrolyte containing 0.51 mol of CaO and 0.49 mol of ZrO_2 . Its electrical and mechanical properties are comparable to ZrO_2 -based solid electrolytes used commonly for oxygen probes in molten melts. The highest thermal shock resistance in cyclic temperature conditions and good corrosion resistance in molten metals make the prepared material a promising electrolyte for metallurgical applications.

Acknowledgement

This work was financially supported by the University of Science and Technology in Cracow under the contract No. 11.11. 160.110. One of authors, M. Dudek, acknowledges the financial support grant of the Foundation for Polish Science, awarded for young scientists in 2004.

References

- [1] JANKE D., [in:] *Science and Technology of Zirconia*, A. Heuer, W. Hobbs (Eds.), The American Ceramic Society, Inc., Columbus, OH, 1980, p. 419.
- [2] PLUSCHKELL W., *Archiv für Eisenhüttenwesen*, 46 (1975), 11.
- [3] JANKE D., *Metallurgical Trans.*, 13B (1982), 227.
- [4] JACOB K.T., MATHEWS T., [in:] *High Conductivity Solid Ionic Conductors – Recent Trends and Applications*, Takahashi T. (Ed.), World Scientific, Singapore, 1989.
- [5] FISCHER W., JANKE D., *Archiv für Eisenhüttenwesen*, 47 (1976), 51.
- [6] FISCHER W., JANKE D., *Archiv für Eisenhüttenwesen*, 47 (1976), 525.
- [7] KOOPMANS H.J., VAN DE VELDE G.M., GELLINGS M.P., *Acta Cryst. C*, 39 (1983), 1323.
- [8] CHARETTE G., FLENGAS S., *J. Electrochem. Sci.*, 115 (1968), 796.

Received 28 December 2004

Revised 17 January 2005

