# Effect of Co Addition on Sintering and Electrical Properties of Yttria-Stabilized Zirconia

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**Abstract**. Yttria-stabilized zirconia is the most developed solid electrolyte for use in high-temperature solid oxide fuel cell (SOFC). Commercial yttria-stabilized zirconia powders reach high densification at temperatures around 1400 ºC. The use of additives may increase the densification rate by means of a liquid phase formation during sintering. However, these additives should not cause any degradation on the ionic conductivity of the electrolyte. The main purpose of this work was to study the effect of Co addition on the densification and electrical conductivity of yttria-stabilized zirconia. Green compacts were prepared by pressureless sintering a mixture of commercial 8 mol% yttria-stabilized zirconia with cobalt carbonate. Linear shrinkage results show that the temperature at which the shrinkage starts decreases with increasing Co content. Impedance spectroscopy measurements reveal that Co additions to stabilized zirconia decrease the total electrolyte conductivity even for Co contents as low as 0.05 mol%.

## Introduction

Yttria-stabilized zirconia (YSZ) solid electrolyte is used in oxygen sensors, oxygen pumps and fuel cells. It has attracted wide attention for these applications because of its high ionic conductivity along with good mechanical properties [1,2].

The solid solution of $ZrO_2$ with 8 mol% $Y_2O_3$ (8YSZ) is the preferred solid electrolyte for use in solid oxide fuel cells. However, the presently available powders require

temperatures above 1400ºC for full densification. Reduction in the sintering temperature of 8YSZ is highly desirable in order to allow for a co-firing of the solid electrolyte and the anode materials, thereby reducing the cost for device fabrication.

One approach to attain high densification at a reduced temperature is the addition of a sintering aid. In this context, it is important that the sintering aid do not impart any change in the electrolyte properties.

Additions of $Bi_2O_3$ to yttria-stabilized zirconia proved to be effective in reducing the sintering temperature to 1077ºC. However, it may give rise to several spurious phases. The increased rate of densification was explained on the basis of a liquid phase mechanism [3]. It has been found that Cu and Mn also form a liquid phase during the sintering of YSZ providing a fast densification along with grain growth [4-6]. Addition of $Fe_2O_3$ increased the density of yttria-stabilized zirconia, but the grain and the grain boundary conductivities decreased accordingly [3]. $Nb_2O_5$ addition to zirconia-5 mol% yttria produced the stabilization of the cubic phase while decreasing the ionic conductivity [7]. The use of boron oxide as sintering aid to YSZ produced destabilization of the cubic structure [8]. In $ZrO_2$-12 mol% $Y_2O_3$ addition of $Co_2O_3$ up to 0.5 wt.% enhanced the conductivity with a maximum at 0.08 wt%. For higher contents of Co (from 0.5 to 4 at.%) substantial densification was obtained. However, reduction in the ionic conductivity was verified for all Co containing samples [9-11].

In this study, the effect of additions of Co to 8YSZ was investigated in detail. Densification study was carried out by dilatometry, and the electrical conductivity was determined by impedance spectroscopy.

## Experimental

Commercial zirconia-8 mol% yttria, 8YSZ (Tosoh Corp., Japan) and cobalt carbonate, $CoCO_3$ (99%, Alfa Aesar) were used as starting materials. Mixtures of 8YSZ-x mol% Co with $0 \leq x \leq 10$ were prepared in a mechanical mixer (Turbula, model T2C) with isopropyl alcohol and zirconia balls. Cylindrical specimens were obtained by uniaxial pressing followed by sintering.

The morphology of the mixed powders was evaluated by scanning electron microscopy, SEM (Philips, XL30) using secondary electrons. Dilatometry (Setaram, model Labsys) measurements were carried out in green compacts heating at a rate of $10ºC.min^{-1}$ from room temperature up to 1400ºC. Phase characterization was performed by X-ray diffraction, XRD (Bruker-AXS, D8 Advance) in the 20 to 80º 2θ range, and by Raman spectroscopy (Renishaw Raman microscope system 3000) using a He-Ne laser with 632.8 nm as excitation source. Electrical conductivity measurements were carried out by impedance spectroscopy (4192A Hewlett Packard) in the 200 to 500ºC and 5 Hz to 13 MHz temperature and frequency ranges, respectively. Silver was used as electrode material for electrical measurements.

## Results and Discussion

The morphology of powder mixtures examined in a scanning electron microscope reveals that they consist of very fine particles with spherical shape. An example is shown in Fig. 1.
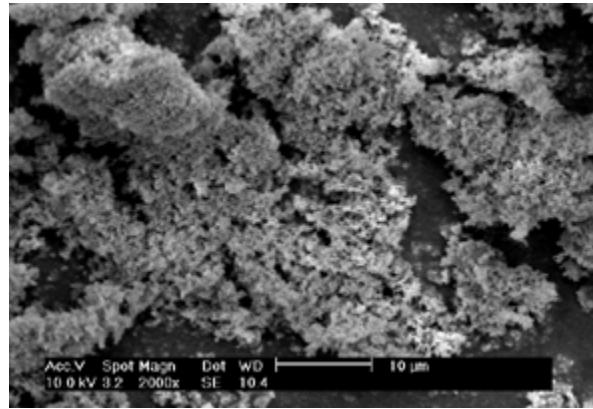
Fig. 1: SEM micrograph of 8YSZ+ 0.25 mol% Co powder mixture.

Cobalt carbonate as well as 8YSZ powders are very fine and loosely agglomerated. Then, their mixture should produce a chemically homogeneous material with good packing properties.

Fig. 2 shows linear shrinkage curves obtained for some of the investigated compositions. The 8YSZ green compact starts to shrink at ~ 1050ºC, and it does not finish up to 1400ºC. After a soaking time of 2 h at 1400 ºC, the linear shrinkage amounts ~ 23%.
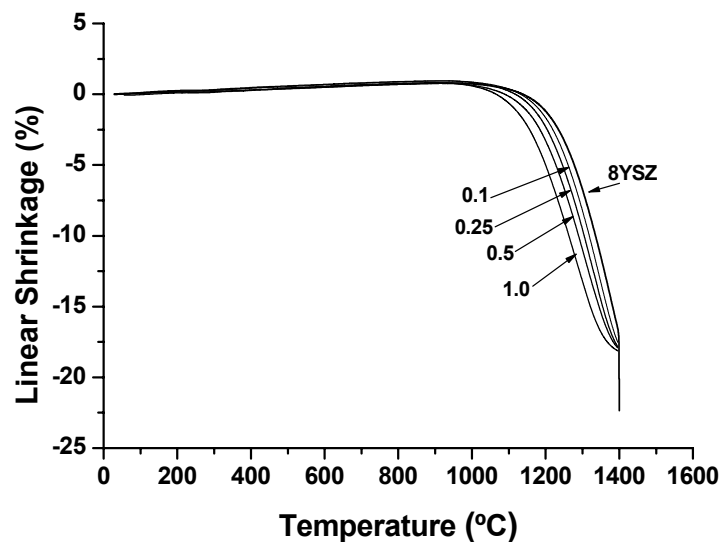


Fig. 2: Linear shrinkage of 8YSZ and 8YSZ + x mol% Co (x = 0.1, 0.25, 0.5 and 1) green compacts.

Addition of Co to YSZ shifts the onset temperature and the temperature of maximum densification rate to lower values. It is worth nothing that a relatively small amount of Co

(1 mol%) is sufficient to decrease the temperature of maximum densification rate by 100ºC. Thus, for higher Co contents it might be expected a considerable improvement in the densification of 8YSZ.

For crystallographic characterization, sintered pellets with high Co content were selected. Fig. 3 shows X-ray diffraction patterns for 8YSZ specimens containing 5 (a), 7.5 (b) and 10 (c) mol% Co.
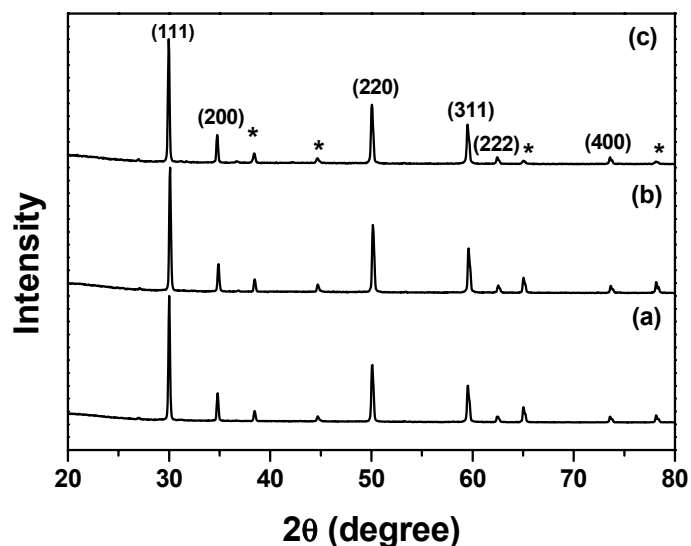


Fig. 3: XRD patterns of 8YSZ containing 5 (a), 7.5 (b) and 10 (c) mol% Co; *: $Co_3O_4$.

In these XRD patterns, most of the diffraction peaks could be indexed according to those of cubic fluorite-type zirconia (*Fm3m*, space group). Small intensity peaks marked with * in Fig. 3 are due to $Co_3O_4$ according to JCPDS 42-1467 file. These results indicate a solubility limit lower than 5 mol% for Co in 8YSZ. Previous results proposed a solubility limit of 7 mol% Co [9].

It is known [11] that the thermal decomposition of cobalt carbonate proceeds by formation of $Co_3O_4$, which is stable up to ~ 1000ºC, and for higher temperatures CoO is formed. However, cobaltous oxide (CoO) has a tendency to reoxidate by atmospheric oxygen to cobaltic oxide ($Co_3O_4$) on cooling down to room temperature. In addition, it should be taken into account that both the precursor materials and the method of preparation may give rise to different cobalt oxides in the product material, because the valence stability of transition metal oxides varies with minor impurities present in the precursors or introduced during processing steps [12].

In order to ascertain on the type of cobalt oxide present in the product material, additional structural characterization by Raman spectroscopy was undertaken. Fig. 4 shows Raman spectra obtained for 8YSZ and 8YSZ containing 10 mol% Co. The Raman spectrum of 8YSZ is characterized by only one sharp band centered at ~ 620 cm$^{-1}$ along with broad bands around 250 and 470 cm$^{-1}$. For the specimen containing cobalt, several bands in addition to the 620 cm$^{-1}$ were detected at 194, 482, 525 and 696 cm$^{-1}$. These bands correspond to those of $Co_3O_4$ [13] corroborating XRD results. Therefore, it may be concluded that most of cobalt exceeding the solubility limit is present in the product
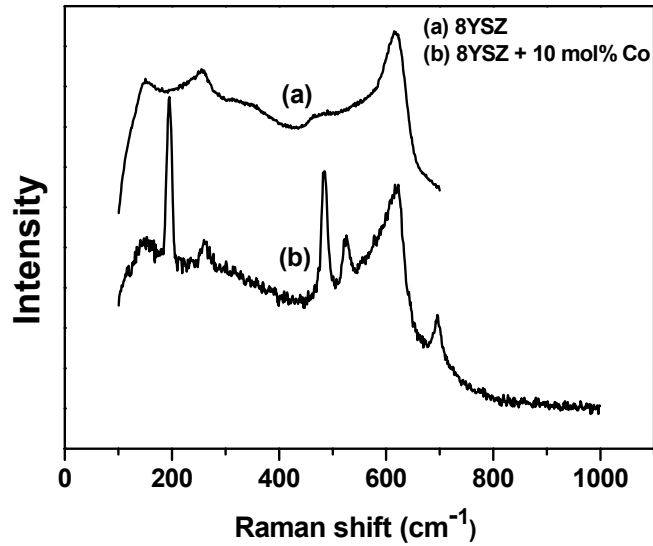
material as cobaltic oxide.



Fig. 4: Raman spectra of (a) 8YSZ, and (b) 8YSZ containing 10 mol% Co.

Impedance spectroscopy measurements were carried out in samples sintered at 1300ºC for 0.5 h. Arrhenius plots of the total electrical conductivity are shown in Fig. 5.
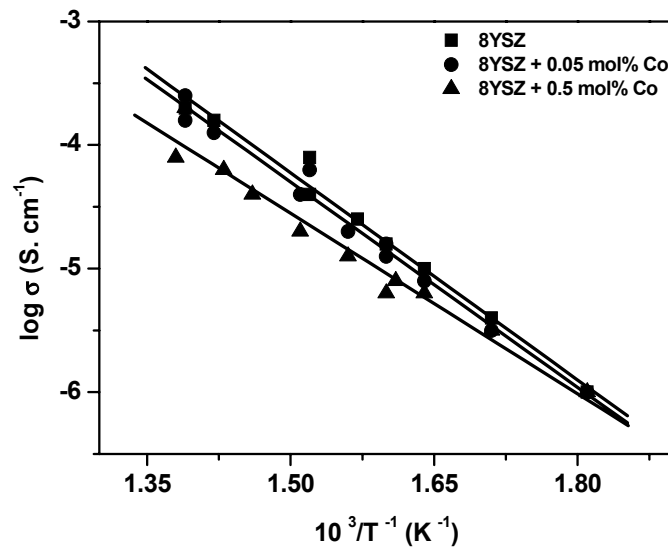


Fig. 5: Arrhenius plots of the total electrical conductivity of pure and Co containing 8YSZ.

The total electrical conductivity decreases with increasing the amount of additive. For low Co content (0.05 mol%) the activation energy for conduction is similar to that of pure 8YSZ. Increasing the additive content decreases the activation energy, which may be a consequence of an increase in the electronic component of the conductivity.

## Conclusions

Additions of Co increase the densification of 8YSZ even for contents as low as 0.05 mol%. The solubility limit for Co in 8YSZ is lower than 5 mol%. In specimens exceeding this limit, $Co_3O_4$ is the preferred formed phase, and no mixed oxide was formed up to 10 mol% Co.

The total electrical conductivity decreases with increasing Co content in 8YSZ, whereas the activation energy for conduction decreases, probably due to an increase in the electronic conductivity.

## Acknowledgements

## References

[1] E. C. Subbarao, in: *Science and Technology of Zirconia I*, *Advances in Ceramics vol, 3*, ed. A. H. Heuer and L. W. Hobbs, Am. Ceram. Soc., Columbus, Ohio (1981), pp. 1.

[2] R. Stevens: *Zirconia and Zirconia Ceramics* (Magnesium Electron Publication nº. 113, 1986).

[3] M. J. Verkerk, A. J. A. Winnubst and A. J. Burggraaf: J. Mater. Sci. Vol. 17 (1982), p. 3113.

[4] S. Machio, O. Sbaizero, S. Meriani and E. Bischoff: J. Mater. Sci. Vol. 27 (1992), p. 2734.

[5] J. L. Shi, T. S. Yen and H. Schubert: J. Mater. Sci. Vol. 32 (1997), p. 1341.

[6] C. Bowen, S. Ramesh, C. Gill and S. Lawson: J. Mater. Sci. Vol. 33 (1998), p. 5103.

[7] J. H. Lee and M. Yoshimura: Solid State Ionics Vol. 139 (2001), p. 197.

[8] D. Z. de Florio and R. Muccillo: Mater. Res. Bull. Vol. 39 (2004), p. 1539.

[9] G. Stochniol, A. Naoumidis, H. Nickel, K. Wippermann and U. Ruschewitz in: Proceed. of the 23rd International Conference on Microelectronics and 31st Symposium on Devices and Materials, 27-29 Sept, 1995, Ljubljana, Slovenia, ed. Midem-Soc Microelectron. Electron. Components & Mater., pp. 245.

[10] M. Hartmanová, F. Hanic, D. Tunega and K. Putyera: Chem. Papers Vo. 52 (1998) 12.

[11] G. A. El-Shobaky, A. S. Ahmad, A. N. Al-Noaimi and H. G. El-Shobaky, J. Thermal Anal. Calorim. Vol. 46 (1996), p. 1801.

[12] G. S. Lewis, A. Atkinson and B. C. H. Steele: J. Mater. Sci. Lett. Vol. 20 (2001), p. 1155.

[13] D. Gallant, M. Pézolet and S. Simard: J. Phys. Chem. Vol. B110 (2006), p. 6871.