Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1177–1180

www.elsevier.com/locate/jeurceramsoc

Conductivity of Mn and Ni-doped stabilized zirconia electrolyte

Jan Van Herle*, Ruben Vasquez

Laboratory for Industrial Energy Systems (LENI), Faculty of Engineering (STI), Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

Abstract

We develop SOFC based on a NiO–YSZ anode support, a thin YSZ layer (5–10 μm) and a $LaSrMnO_3$ cathode. Mn and Ni can dissolve into thin zirconia during high temperature fabrication. On cells, we consistently measured higher ohmic losses than expected from the YSZ resistivity. To investigate whether ionic conductivity of YSZ is affected, dense tape cast YSZ doped with 1 at.% Mn or 2 mol% NiO was fabricated and the conductivities in O_2 and H_2 measured between 300 and 850 °C. Both dopants acted as sintering agents. No abnormal grain boundary resistivity was noted with either dopant. Ni-doped YSZ underwent an irreversible bulk conductivity loss (−60%) when switching from oxidizing (O_2) to reducing atmosphere (H_2), at 850 °C. This effect can therefore contribute to the higher ohmic loss measured on thin zirconia SOFC.

Keywords: Applications; Compositions: ZrO_2; Fuel cells; Grain boundaries; Ionic conductivity; Impedance; Properties; Structure

1. Introduction

Eight molecular percent Yttria-stabilized zirconia (8YSZ) is the common oxygen ion conductor in solid oxide fuel cells (SOFC). An employed planar SOFC concept is to support thin 8YSZ (5–10 μm) on the anode, typically NiO–YSZ (50–50 wt.%) cermet acting as supporting structure.[1,2] Support and thin electrolyte are cosintered at high temperature (1300–1400 °C). A cathode containing $LaSrMnO_3$ is then deposited, by spraying or screenprinting, and sintered onto the electrolyte (1100–1300 °C). An advantage of the concept is the reduction in ohmic resistance due to the low electrolyte thickness.

In our work on tape cocast cells,[3] we consistently observed larger ohmic loss than the expected value, by a factor between 3 and 9. This intrinsic cell ohmic loss is too high and requires investigation.

Other developers have reported similar results.[1,2] They strongly depend upon the cathode nature (Table 1). The lower the cathode porosity and the larger its oxygen permeability, the lower the measured resistance. Part of the explanation for the large resistance thus lies in a current constriction effect.

Another factor could be a change in ionic conductivity of YSZ itself, due to elements originating from the electrodes. At sintering temperature, Mn and Ni diffuse and dissolve into the zirconia matrix.[4,5] To study this effect, separate doping into 8YSZ electrolyte tapes of small quantities of Mn and Ni was investigated, emphasizing the measurement of bulk and grain boundary ionic conductivity.

Similar work conducted in parallel by Risø Laboratory (Danmark) was recently published.[6,7] For the case of Mn,[6] doping was achieved by mixing $MnCO_3$ into a slurry for tape casting and firing at 1350 °C/8 h. Conductivity measurements and ageing in air were carried out at 850 and 1000 °C. Mn doping was always found to reduce bulk conductivity. On the other hand, Mn stabilizes the cubic zirconia phase and therefore delays the cubic to tetragonal ($c->t$) phase transformation, responsible for slow conductivity decay (>1000 h) at high temperature (850–1000 °C).

For the case of Ni,[7] doping was achieved by powder mixing, pelletizing and sintering at 1500 °C/2 h. Four-point conductivity measurement was carried out at 1000 °C in air, followed by a switch to reducing atmosphere ($H_2/N_2/H_2O$) after 20 h. A drop in conductivity was observed over 20–80 h to stabilize at a value that

---

* Corresponding author. Tel.: +41-21-693-35-10; fax: +41-21-693-3502.

E-mail address: jan.vanherle@epfl.ch (J. Van Herle).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00471-0

was not reversed by a reoxidation step. Upon reduction, dissolved bulk NiO was exsolved as Ni particles, believed to act as nucleation sites for accelerated $c->t$ phase transformation, as evidenced by TEM observation of 10–40 nm tetragonal ZrO_2 precipitates.[7] However, only 10% of t-phase was estimated to be present, whereas only >60 vol.% of t-phase could explain this large drop in ionic conductivity. Other explanations were therefore suggested, for example the presence of the large amount of grain boundaries due to precipitated nanosized t-ZrO_2.[7]

The aim of this study is to provide complementary data to that work.[6,7] Differences in employed conditions between this study and the other studies[6,7] are described in the experimental section.

2. Experimental

Mn (1 at.%) and Ni (2 mol% NiO) were doped into 8YSZ tapes (final thickness 0.33 mm) by dissolving nitrate salts into casting slurries and firing at 1300 °C (2 h). The samples appeared homogeneous, transparent and of blackish-violet (Mn-doped) and olive-green colour (Ni-doped). Electrochemical impedance spectroscopy (EIS) was used to resolve grain and grain boundary responses of the ionic conductivity measured in a small tubular oven between 270 and 850 °C in atmospheres of pure O_2, an inert gas (N_2 or He) and pure H_2. Sintered tape pieces were contacted on both faces with Ag paint electrodes (0.5–1 cm^2).

All EIS spectra (ca. 130) were fitted to equivalent electrical circuits using software from Zahner Elektrik (Germany). The measurement sequence was : 850–270 °C in O_2, 270–850 °C in inert gas, 850–270 °C in H_2, each time allowing temperature and changed atmosphere to stabilize. The Mn sample was kept for 80 h in O_2, 170 h in He and 120 h in H_2, the Ni sample for 30 h in O_2, 90 h in N_2 and 170 h in H_2. At the end gas was switched back to O_2 for 50 h to reoxidize the sample. Over such periods (350 h total) and temperature ranges, "natural" decay of 8YSZ conductivity due to $c->t$ transformation should be minimal (<1%) so as not to superimpose effects due to the dopants. SEM and TEM of as sintered samples was performed. Preliminary TEM results will be briefly mentioned here, but reported in more detail in a later communication.

Table 1
Measured ohmic resistance (R_m) on fuel cells with thin YSZ electrolyte, compared to the expected theoretical resistance for YSZ alone

Cathode	$R_{measured}$ (Ωcm^2)	R_m/R_{theor}	Ref.
$LaSrMnO_3$ (LSM)	0.23	8.5	[3]
LSM–YSZ	0.224	6.8	[2]
LSM–YSZ	0.074	5.7	[1]
LSM–YSZ	0.14	5.2	[3]
$LaSrCoO_3$ (LSC), porous	0.124	4.6	[3]
LSM–Ag	0.09	4.5	[3]
Ag dense	0.08	4.0	[3]
LSC, dense	0.106	3.9	[3]

3. Results and discussion

3.1. Microstructure

Fig. 1 shows a SEM fracture view of the Mn-doped sample, Fig. 2 of the Ni-doped sample and Fig. 3 of an undoped sample, all fired at 1300 °C/2 h. The Mn-doped sample is particularly dense, with virtually no pores remaining. Grain growth is pronounced, with sizes up to 10 µm. The Ni-doped sample is slightly less densified, with remaining evenly distributed small pores and a distinctly smaller grain size (2 µm). In stark contrast,

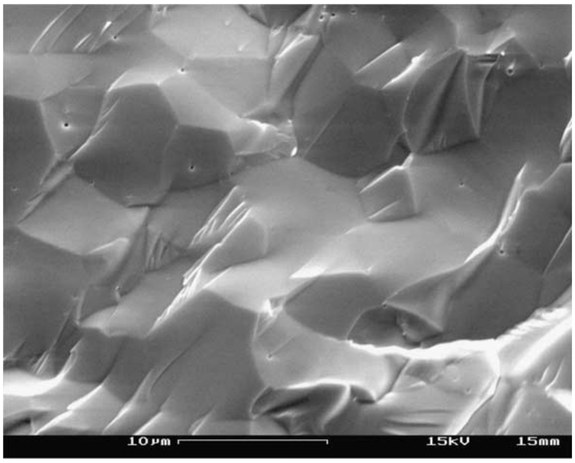

Fig. 1. Fracture surface view (SEM) of 1% Mn-doped 8YSZ sintered at 1300 °C (2 h).

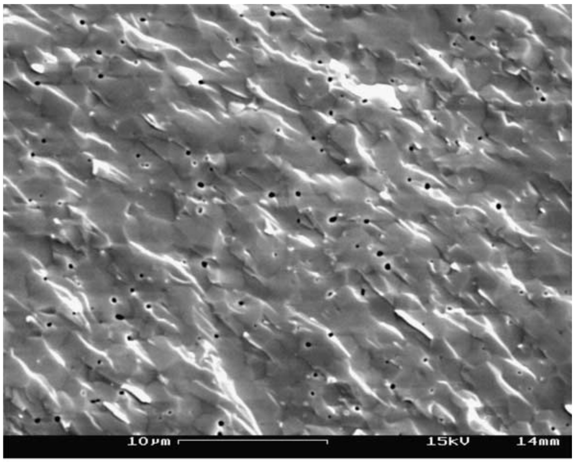

Fig. 2. Fracture surface view (SEM) of 2% Ni-doped 8YSZ sintered at 1300 °C (2 h).

the undoped sample has started particle necking but was unable to densify in the employed conditions.

3.2. Conductivity

Fig. 4 displays EIS reponses (at 300 °C) for the Mn-doped sample, Fig. 5 for the Ni-doped sample (at 400 °C). We reported before[8] the EIS response of well-densified, undoped 8YSZ (sintered at 1400 °C). Upon the measurement scan in O_2, both doped samples show standard conductivity behaviour with no anomalous grain boundary effect. The high frequency grain and intermediate frequency grain boundary semicircles are well resolved and both in magnitude and frequency regime entirely similar to undoped 8YSZ.[8]

The resemblance to undoped 8YSZ is further exemplified in the Arrhenius plots of Fig. 6. Conductivity behaviours in air (oxygen) for doped and undoped samples are seen to differ insignificantly. The grain boundary resistance as %fraction of the total resistance was typically, both for doped and undoped[8] samples, 20–30% at low temperature (300–500 °C) to vanish at 600–700 °C.

In the case of Mn-doping, no difference in conductivity response was detectable (Fig. 4) between O_2 and H_2 atmospheres, with these measurements separated by >260 h and a stabilisation time of 25 h in H_2 at 850 °C.

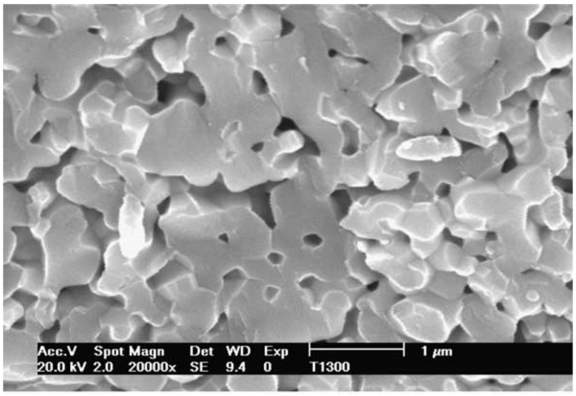

Fig. 3. Fracture surface view (SEM) of undoped 8YSZ sintered at 1300 °C (2 h).

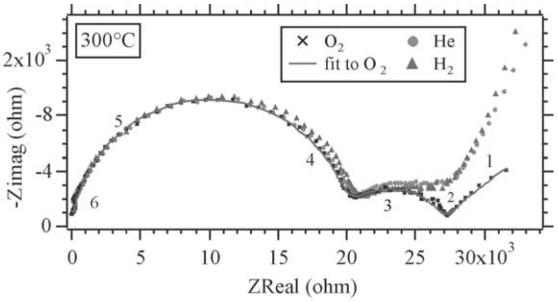

Fig. 4. EIS response of 1%Mn-doped 8SYZ at 300 °C in O_2 (t =75 h), He (t=95 h) and H_2 (t=363 h). Numbers indicate frequencies in powers of 10 Hz.

In the case of Ni-doping, a clear difference was observed (Fig. 5), partly corroborating the result obtained before[7] at 1000 °C. Unlike that result,[7] switching to H_2 gas at 850 °C did not lead to an immediate change in conductivity during the first 50 h, afterwards however conductivity did gradually drop over the next 100 h where it stabilized. The shown spectra for 400 °C (to illustrate grain and grain boundary responses) were then taken after this stabilisation. Bulk conductivity is seen to drop by as much as 60%, whereas grain boundary conductivity changed markedly less. When switching back to O_2, no further changes

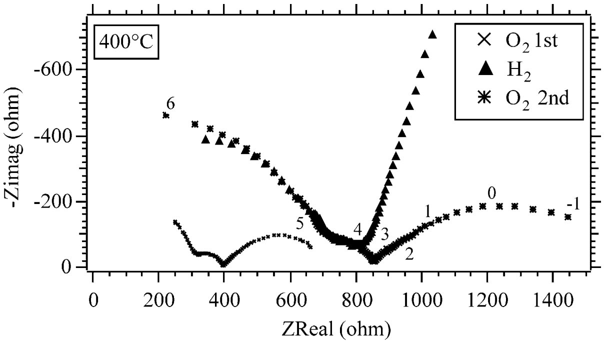

Fig. 5. EIS response of 2%Ni-doped 8SYZ at 400 °C in O_2 (t =30 h), H_2 (t=273 h) and again O_2 (t=298 h).

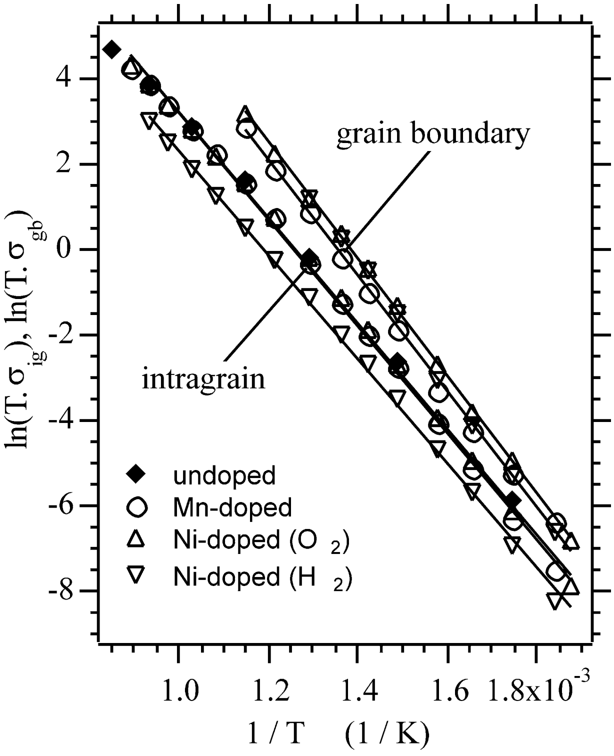

Fig. 6. Arrhenius plots of doped and undoped 8YSZ. Only for the reduced Ni-doped sample is a clearly different behaviour evident.

occur. With the grain boundary response appearing slighty higher, it is still largely outweighted by the bulk response change.

Doping with 1% Mn did not decrease initial 8YSZ conductivity, unlike the result (−20%) reported by Appel.[6] The microstructure here differs from that work,[6] where grain growth was moderate (2–4 μm) and where the presence of the dopant led to more porosity than with the undoped sample. Here essentially pore-free highly dense 8YSZ was obtained, with Mn working as a powerful sintering aid. Tapes could be fully densified even at 1200 °C with 1% Mn. No anomalous bulk or grain boundary behaviour was observed. No change occurred when switching from oxygen to reducing atmosphere (850 °C, 25 h stabilisation). TEM-EDX results show very homogeneously distributed Mn in the grain bulk next to clean grain boundaries.

Doping with 2% NiO did not decrease initial 8YSZ conductivity, unlike the result reported (−20%) by Linderoth.[7] Reduction by H_2 led here to a final decrease (−60%), irreversible to reoxidation, similar (−50%) to that work,[7] albeit not immediately but after a delay of 50 h, which may be due to the difference in temperature at the moment of change in atmosphere (850 °C compared to 1000 °C). The effect is little related to grain boundaries but dominated by the bulk. TEM-EDX results show a constant distribution (concentration 1.5%) of dissolved Ni in the grain bulk next to clean grain boundaries, but also precipitated particles rich in Ni (excess NiO above the solubility limit in YSZ), especially at grain boundaries. This concentration value agrees with the reported NiO solubility data[4] of 1.1–1.7 mol% in YSZ between 1200 and 1600 °C. The effect observed and explained for Ni-doped YSZ after reduction (see Section 1 and Ref. 7) is confirmed here.

4. Conclusions

Mn (1 at.%) and Ni (2 mol% NiO) were doped into 8YSZ by a solution method and sintering at 1300 °C. Both act as strong sintering aids, where Mn is especially effective leading to important grain growth and very high density. 1% Mn dissolves entirely in the bulk, whereas Ni dissolves to only 1.5% (1300 °C), the excess amount (0.5%) precipitating as Ni-rich particles at the grain boundaries. However, no unusual conductivity behaviour is seen from EIS data over a wide temperature range with both samples in O_2 as compared to undoped 8YSZ.[8]

The Mn-sample was unaffected by a reduction cycle (850 °C, 25 h), whereas the Ni-sample irreversibly decreased its bulk conductivity by −60% over an exposure of 150 h at 850 °C, in accordance with the recent observation.[7] This phenomenon can therefore partly explain the unusual high ohmic resistances (larger than expected by a factor 3–9) observed consistently with thin film YSZ SOFC (Table 1), where the thin electrolyte is likely doped with Mn and Ni due to the high temperature fabrication processes.

In future work, higher doping of Mn and longer exposure to reducing atmosphere will be conducted, as well as codoping of Mn and Ni into 8YSZ. Elemental depth profiling and TEM-EDX on real anode supported electrolyte SOFC cells will be performed, after fabrication and long term operation, in order to try and determine the actual Mn and Ni contents in the electrolyte.

Acknowledgements

Financial support by the New Energy Development Organisation (NEDO), Japan and the European COST Materials Action 525 is gratefully acknowledged.

References

1. Ouweltjes, J. P., van Berkel, F. P. F., Nammensma, P. and Christie, G. M., Development of 2nd generation, supported electrolyte, flat plate SOFC components at ECN. In *Solid Oxide Fuel Cells VI, The Electrochemical Society Proceedings Series*, ed. S. C. Singhal and M. Dokiya. , 1999, pp. 803–811.
2. Ghosh, D., Wang, G., Brule, R., Tang, E. and Huang, P., Performance of anode supported planar SOFC cells. In *Solid Oxide Fuel Cells VI*, ed. S. C. Singhal and M. Dokiya. The Electrochemical Society Proceedings Series, Pennington (NJ), 1999, pp. 822–829.
3. Ihringer, R., Electrolytes minces sur supports anode dans les piles à combustible SOFC. PhD thesis, Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland (2001).
4. Linderoth, S. and Kuzjukevics, A., NiO in ytrria-doped zirconia. In *Solid Oxide Fuel Cells V*, ed. U. Stimming, S. C. Singhal, H. Tagawa and W. Lehnert. The Electrochemical Society Proceedings Series Vol 97-40, Pennington (NJ), 1997, pp. 1076–1085.
5. Linderoth, S. and Mogensen, M., Improving durability of SOFC stacks. In *Proceedings of the 4th European Solid Oxide Fuel Cell Forum*, ed. A. McEvoy. European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000, pp. 141–150.
6. Appel, C. C., Bonanos, N., Horsewell, A. and Linderoth, S., Ageing behaviour of zirconia stabilised by yttria and manganese oxide. *J. Mat. Sci.*, 2001, **36**, 4493–4501.
7. Linderoth, S., Bonanos, N., Jensen, K. V. and Bilde-Sorensen, J. B., Effect of NiO-to-Ni transformation on conductivity and structure of yttria-stabilized ZrO_2. *J. Am. Ceram. Soc.*, 2001, **84**(1), 2652–2656.
8. Van Herle, J., Vasquez, R., Akyuz, D. and Barthel, K., Microstructure-conductivity correlation for hot-pressed 8YSZ powders. *J. Eur. Ceram. Soc.*, 2001, **21**, 1851–1854.