Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1355–1358
www.elsevier.com/locate/jeurceramsoc

Electrochemical behaviour and degradation of (Ni,M)/YSZ cermet electrodes (M = Co,Cu,Fe) for high temperature applications of solid electrolytes

A. Ringuedé[a], D.P. Fagg[b], J.R. Frade[b,*]

[a]Laboratoire d'Electrochimie et de Chimie Analytique, UMR 7575, CNRS-ENSCP, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
[b]Ceramics and Glass Engineering Department (UIMC), University of Aveiro, 3810-193 Aveiro, Portugal

Abstract

Homogeneous powders of alternative (Ni,M)/YSZ cermets were prepared by combustion synthesis to obtain homogeneous mixtures of submicrocrystalline powders. These powders were used to prepare symmetrical cells cermet/YSZ/cermet, with porous cermet layers and a dense electrolyte. The cermets were reduced in H_2, and tested as potential fuel electrodes for high temperature electrochemical applications. The best performance was found for $Ni_{1-x}Co_x$/YSZ cermets but small fractions of Cu might also play a positive effect. Changes in capacitance suggest that this corresponds to cermets with enhanced microstructures. Lower firing conditions are probably needed to avoid the degradation of cermets containing Cu or Fe.

Keywords: Fuel cells; Impedance; Powders-solid state reactions; ZrO_2

1. Introduction

The performance of Ni/YSZ cermet anodes is mostly dependent on microstructural features[1–3] which might affect the phase connectivity and triple phase contacts. The triple boundary length plays a major role on the electrochemical oxidation of H_2,[3–7] and may also explain the minimum of polarisation resistance of Ni/YSZ cermets for about 40 vol.% of Ni.[5] However, a fraction of coarse YSZ particles may contribute to anchor the cermet microstructure yielding improved performance.[6]

One might also consider cermets with alternative compositions to modify the metal/YSZ contact angle, and thus enhance the triple contacts. For example, improved percolation was attained for Ni/YSZ-based cermets on adding small fractions of titania.[8] One may also seek other potential advantages such as changes in catalytic properties of the metallic phase, enhanced creep resistance, better oxidation resistance or better thermal expansion compatibility by changing the metallic components of the cermets.

Additions of Cu should improve the oxidation resistance of the cermets. However the relatively low melting temperatures of this metal and of the corresponding oxides do not allow high temperature processing and are also likely to cause faster microstructural ageing at typical cell working temperatures. Ni–Co and Ni–Fe alloys are less resistant to oxidation but should be less prone to difficulties of processing or fast ageing.

2. Experimental procedure

Cermet precursors were prepared by exothermic reaction of nitrates with urea.[9] These reactions are fast and yield very homogeneous mixtures of sub-microcrystalline powders, usually in the form of irregular agglomerates.[9] This contributes to prevent excessive shrinkage on firing at temperatures up to 1450 °C, except possibly for cermets containing Cu (Fig. 1).

Symmetrical cermet/electrolyte/cermet cells were prepared from those powders by co-pressing and co-firing at 1450 °C, and reducing in H_2 at 800 °C, yielding porous cermet layers bonded to a dense YSZ electrolyte

* Corresponding author. Tel.: +351-234-370-254; fax: +351-234-425-300.
E-mail address: jfrade@cv.ua.pt (J.R. Frade).

0955-2219/$ - see front matter
doi:10.1016/S0955-2219(03)00564-8

layer. Cu-containing cermets were prepared both as single layer $Ni_{1-x}Cu_x$ + YSZ cermets, and bilayered cermets (Ni + YSZ)/($Ni_{1-x}Cu_x$ + YSZ) to hinder diffusion of Cu into the electrolyte.

An Autolab spectrometer (ECO Chimie B.V.) was used to characterise the symmetrical cermet/YSZ/cermet cells in wet H_2 or wet $N_2 + H_2$ atmospheres, obtained by bubbling through water at temperatures in the range 20–56 °C. The oxygen partial pressure was monitored by a YSZ sensor, and these readings were used to evaluate the water vapour partial pressure in the atmosphere, on assuming equilibrium in the gas phase. The impedance spectra obtained under these conditions are suitable to separate the main contributions of the polarisation resistance.

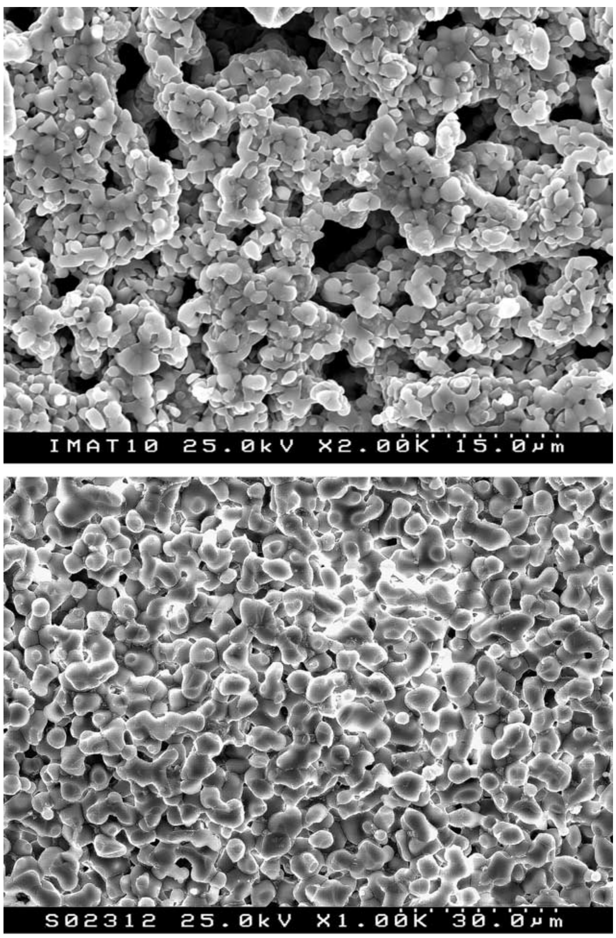

Fig. 1. SEM microstructures of $Ni_{0.5}Co_{0.5}$ + YSZ and $Ni_{0.96}Cu_{0.04}$ + YSZ cermets fired at 1450 °C.

3. Results and discussion

Fig. 2 shows typical impedance spectra obtained for cermet/YSZ/cermet cells. The polarisation resistance comprises a contribution in the low frequency range (1–6 Hz), and a contribution at higher frequencies. This contribution (R_{Hf}) is temperature dependent (Fig. 3), and is almost independent of the fraction of H_2 in the atmosphere (Figs. 4 and 5). On the contrary, the low frequency contribution is strongly dependent on the gas composition (Fig. 6) and is almost insensitive to changes in temperature. These trends thus resemble the main contributions reported for optimised Ni + YSZ cermets.[1] One might thus assume that the contribution R_{Hf} is mainly dependent on the cermet microstructure, as reported by those authors.

Partial substitution of Ni with Co lowers the contribution R_{Hf} (Fig. 3) whereas other (Ni,M) + YSZ cermets with M = Fe or Cu tend to yield poorer results, except for the bilayered (Ni + YSZ)/($Ni_{0.96}Cu_{0.04}$ + YSZ) cermet. The results in Figs. 4 and 5 show that improved behaviour usually correspond to higher capacitance C_{Hf} and vice-versa, thus suggesting that this is related to changes in triple phase boundary, as reported for Ni patterns onto YSZ substrates.[4,6] However, doping with Cu is likely to cause some degradation of the electrolyte (Fig. 2) possibly due to diffusion of Cu. This may also be the case for cermets containing Fe. Further work is thus needed to understand the effects of these additives

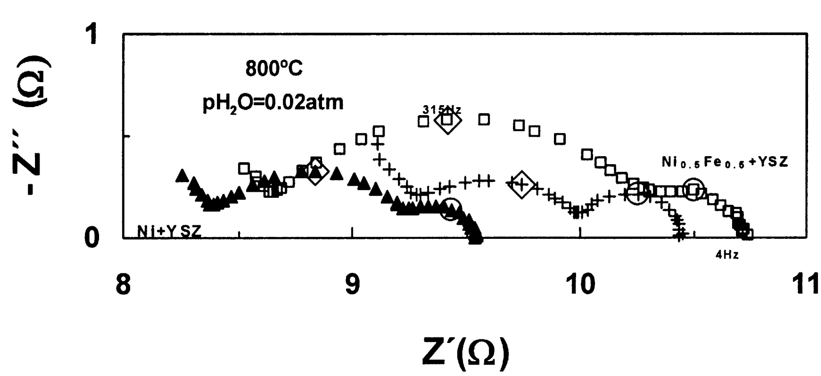

Fig. 2. Impedance spectra obtained for symmetrical cermet/YSZ/cermet cells with single layers cermets Ni + YSZ (▲) and $Ni_{0.5}Fe_{0.5}$ + YSZ (□), and double layer cermet (Ni + YSZ)/($Ni_{0.96}Cu_{0.04}$ + YSZ) (+) at 800 °C, in H_2 with $pH_2O \approx 0.02$ atm.

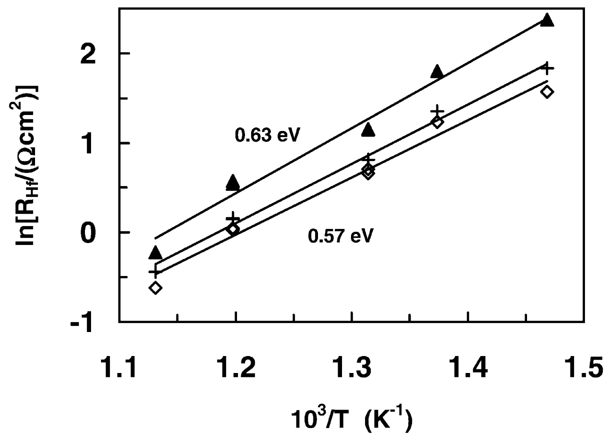

Fig. 3. Temperature dependence of the polarisation resistance in H_2 with $pH_2O = 0.04–0.05$ atm obtained for cermets Ni + YSZ (▲); $Ni_{0.7}Co_{0.3}$ + YSZ (+); and $Ni_{0.5}Co_{0.5}$ + YSZ (◇).

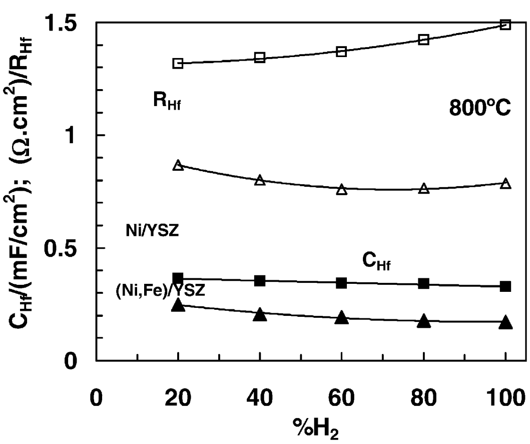

Fig. 4. Effects of H_2 content on R_{Hf} (open symbols) and C_{Hf} (closed symbols) for single layer cermets Ni + YSZ (■□) and $Ni_{0.5}Fe_{0.5}$ + YSZ (▲,△), at 800 °C, and under relatively dry atmospheres ($pH_2O \approx 0.02$ atm).

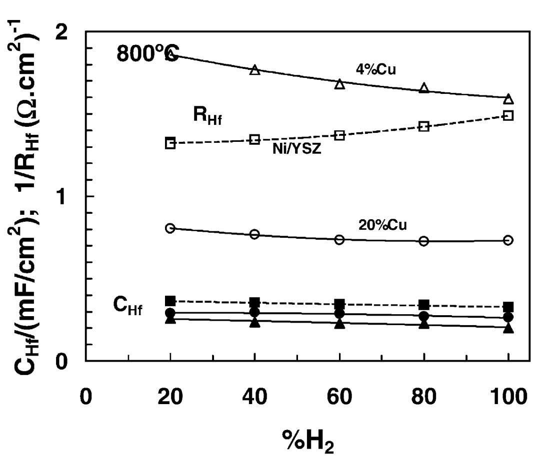

Fig. 5. Effects of H_2 content on R_{Hf} (open symbols) and C_{Hf} (closed symbols) for Ni + YSZ (■,□) and double layer cermets (Ni + YSZ)/($Ni_{1-x}Cu_x$ + YSZ), $x = 0.04$ (▲,△) and 0.2 (●,○), at 800 °C, and under relatively dry atmospheres ($pH_2O \approx 0.02$ atm).

and to attempt to optimise the composition and firing conditions of the cermets.

The dependence of the low frequency contribution of the polarisation resistance on the gas composition has been reported by many authors for Ni electrodes or Ni-based cermets.[1,10–13] Mizusaki and co-authors[4] proposed a Buttler–Volmer equation to explain the decrease in polarisation resistance with increasing partial pressures of H_2 and water vapour. A mechanism based on dissociative adsorption or diffusion on the surface of Ni should yield linear relations $1/R_{Lf} \propto pH_2O$, and $1/R_{Lf} \propto (pH_2)^{1/2}$. Jiang and Badwal[11] proposed a similar mechanism by taking into account that the temperature dependence of R_{Lf} is weak. On the contrary, Primdhal and Mogensen[14] proposed a model based on the assumption that gas flow limitations prevail. In this case, the resistance R_{Lf} should vary as $(1/pH_2O + 1/pH_2)$, the capacitance shows the opposite trend, $C_g \propto (1/pH_2O + 1/pH_2)^{-1}$, and the relaxation frequency should be independent of the gas composition. The actual results show that R_{Lf} drops almost linearly with temperature, whereas C_g usually shows a weaker dependence. The dependence of relaxation frequency on gas composition (Table 1) is also a

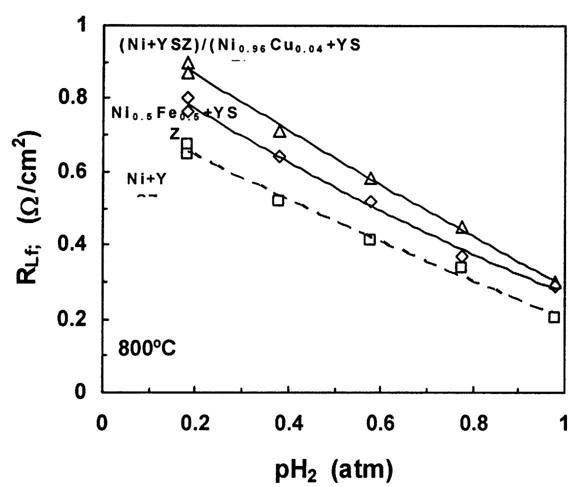

Fig. 6. Effects of H_2 content on the values of R_{Lf} obtained for cermets Ni + YSZ (□), $Ni_{0.5}Fe_{0.5}$ + YSZ (◇), and (Ni + YSZ)/($Ni_{0.96}Cu_{0.04}$ + YSZ) (△), at 800 °C and under relatively dry atmospheres ($pH_2O \approx 0.02$ atm).

Table 1
Relevant parameters of the low frequency contribution obtained for a cermet electrode (Ni + YSZ)/($Ni_{0.96}Cu_{0.04}$ + YSZ) with area 1.46 cm^2, at 700 °C and under $pH_2O = 0.02$ atm

pH_2	R_{Lf}	C_{Lf}	f_{Lf} (Hz)
0.18	1.14	0.109	1.3
0.38	0.952	0.103	1.6
0.58	0.777	0.107	1.9
0.78	0.577	0.11	2.5
0.98	0.364	0.118	3.7

confirmation that gas transport is unlikely to control the overall process.

4. Conclusions

Alternative (Ni,M) + YSZ cermets with M=Co, Fe, or Cu can be prepared from powders obtained by a combustion synthesis method, which yields uniform distributions of the cermet components. Cermet/YSZ/cermet cells were also prepared from those powders. The main features of the electrode behaviour obtained with such symmetrical cells in atmospheres containing H_2 and H_2O are close to results reported for optimised Ni/YSZ cermets in identical conditions, except possibly for the magnitude of the polarisation resistance. One of its contributions is still mainly dependent on temperature and probably also on microstructural features, and the low frequency contribution is mainly dependent on the gas composition. Changes in cermet composition effect the microstructural contribution, and may yield a decrease in polarisation resistance, especially for partial substitution of Ni by Co, or doping with copper.

Acknowledgements

This work was supported by the EC (project TMRX-CT93-0130), and FCT (Portugal); this includes a grant SFRH/BPD/3529/2000.

References

1. Primdhal, S. and Mogensen, M., Oxidation of hydrogen on Ni/yttria-stabilized zirconia cermet anodes. *J. Electrochem. Soc.*, 1997, **144**, 3409.
2. Simwonis, D., Tietz, F. and Stover, D., Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells. *Solid State Ionics*, 2000, **132**, 241.
3. Mizusaki, J., Tagawa, H., Saito, T., Kamitani, K., Yamamura, T., Hirano, K., Ehara, S., Takagi, T., Hikita, T., Ippommatsu, M., Nakagawa, S. and Hashimoto, K., Preparation of nickel pattern electrodes on YSZ and their electrochemical properties in H_2–H_2O atmospheres. *J. Electrochem. Soc.*, 1994, **141**, 2129.
4. Mizusaki, J., Tagawa, H., Saito, T., Yamamura, T., Ehara, S., Takagi, T., Hikita, T., Ippommatsu, M., Nakagawa, S. and Hashimoto, K., Kinetic studies of the reaction at the nickel pattern electrode on YSZ in H_2–H_2O atmospheres. *Solid State Ionics*, 1994, **70/71**, 52.
5. Bieberle, A. and Gauckler, L. J., Reaction mechanism of Ni pattern anodes for solid oxide fuel cells. *Solid State Ionics*, 2000, **135**, 337.
6. Itoh, H., Yamamoto, T., Mori, M., Horita, T., Sakai, N., Yokokawa, H. and Dokiya, M., Configurational and electrical behaviour of Ni-YSZ cermet with novel microstructure for solid oxide fuel cell anodes. *J. Electrochem. Soc.*, 1997, **144**, 641.
7. Koide, H., Someya, Y., Yoshida, T. and Maruyama, T., Properties of Ni/YSZ cermet as anode for SOFC. *Solid State Ionics*, 2000, **132**, 253.
8. Skarmoutsos, D., Nikolopoulos, P. and Tsoga, A., Titania doped YSZ for SOFC anode Ni-Cermet. *Ionics*, 1999, **5**, 455.
9. Ringuedé, A., Labrincha, J. A. and Frade, J. R., A combustion synthesis method to obtain alternative cermet materials for SOFC anodes. *Solid State Ionics*, 2001, **141–142**, 549.
10. Jiang, S. P. and Ramprakash, Y., H_2 oxidation on Ni/Y–TZP cermet electrodes—a comparison of electrode behaviour by GCI and EIS techniques. *Solid State Ionics*, 1999, **116**, 211.
11. Jiang, S. P. and Badwal, S. P. S., An electrode kinetics study of H_2 oxidation on Ni/Y_2O_3–ZrO_2 cermet electrode of the solid oxide fuel cell. *Solid State Ionics*, 1999, **123**, 209.
12. Jiang, S. P. and Badwal, S. P. S., Hydrogen oxidation at the nickel and platinum electrodes on yttria-tetragonal zirconia electrolyte. *J. Electrochem. Soc.*, 1997, **144**, 3777–3784.
13. Jiang, S. P. and Ramprakash, Y., H_2 oxidation on Ni/Y–TZP cermet electrodes—polarisation behaviour. *Solid State Ionics*, 1999, **116**, 145.
14. Primdhal, S. and Mogensen, M., Gas conversion impedance: SOFC anodes in H_2/H_2O atmospheres. In *Electrochemical Proceedings* (pp. 530–539, Vol. 97-18). The Electrochemical Society.