

Thick films of YSZ electrolytes by dip-coating process

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Abstract.

Yttria stabilized zirconia (YSZ, 8% Y₂O₃) thick films were coated on porous Ni-YSZ substrates by dip-coating process using a new formulated suspension. The suspension was obtained by addition of a polymeric matrix in a stable suspension of a commercial YSZ (Tosoh) powders dispersed in an azeotropic MEK-EtOH mixture. The green layers are densified by an optimization of the suspension composition. YSZ Tosoh particles encapsulated by zirconium alkoxide sol and added with colloidal alkoxide precursor are used to load the suspension. The in-situ growth of these colloids increases significantly the layers density after an appropriated heat treatment. The obtained films are continuous, homogeneous and 20 micrometers thick. Different microstructures are obtained depending on the synthesis parameters of the suspension composition.

1 INTRODUCTION.

Due to good mechanical, excellent chemical stability and adequate level of oxygen-ion conductivity in both oxidizing and reducing environment, yttria stabilized zirconia (ZrO₂ – 8%Y₂O₃) is the most used electrolyte in SOFCs applications¹. In order to both increase the chemical stability of the SOFCs components and obtain a low cost working system, it is necessary to decrease the working temperature to around 700°C-800°C. The control of the microstructure and the thickness of the electrolyte may reduce the internal resistance of the YSZ electrolyte. An improvement of the performance of the cell could then be reached.

Tape casting is a conventional technique to synthesize YSZ electrolyte membrane or films^{2, 3, 4}. However the films thickness reached is typically in the range of 30-50 μm which is too important for electrolyte for SOFC working at low temperature.

The sol-gel based dip-coating method is also considered as effective and practical to produce YSZ films. But this method does not allow the synthesis of films thicker than few micrometers on porous Ni-YSZ substrates without several steps^{5, 6}.

Here, we report a novel method to synthesize thick films by using the advantages of both tape casting and dip-coating methods. The practical point of view of the dip-coating process is preserved and a dip-coating solution made of powders in suspensions allows the control of both the thickness and the density of the films. Based on previous works⁷, thick films of 10 to 20 μm were prepared on porous Ni-YSZ cermets substrates. In this case, the dip-coating solutions consist of a mixture of polymer matrix with a stable suspension of commercial YSZ powders in an azeotropic MEK-EtOH solvent. Nevertheless, the thick films were porous with micro-cracks.

The aim of this work is then to increase the green density of the films by adjusting the formulation of the dip-coating solutions. Colloidal zirconia precursors obtained by the alkoxide route are added to the YSZ suspensions. The YSZ commercial powder encapsulated in the alkoxide sol is also added to the previous mixture. Another route consists of the incorporation of pure metal nitrates in the polymer matrix.

The obtained microstructures are then been correlated to the main characteristics of the suspension composition. After heat treatment, films microstructure is investigated by Scanning Electron Microscopy.

2 EXPERIMENTAL.

YSZ commercial powder (Tosoh) is added, under mechanical stirring, in an azeotropic mixture as MEK-EtOH (Methylethylketone-Ethanol) with a polyester-phosphate (PE-312) type-additive used as dispersant. For the initial suspension, the mass ratio of YSZ powder / MEK-EtOH was kept to 1. A dispersant concentration of 2.5 wt% (in reference to the total YSZ mass) gave the best state of dispersion of the suspension (Part 1, figure 1). The solution was homogenized by ultrasonic stirring in a water bath⁸. A polymer matrix, derived from the Pecchini process⁹, was added to the previous YSZ suspension. This polymer matrix obtained by polymerization and polycondensation reactions between hexamethylenetetramin (HMTA)

and acetylacetone (acac) in acetic acid media upon heating. The viscosity was systematically adjusted at about 45 mPa.s at room temperature. R_m defined as the mass ratio of the polymer matrix on the YSZ suspension was kept to 0.2. This reference synthesis part is referred as the route 1 on the figure 1. This part is the starting formulation for all syntheses.

Colloidal YSZ nanoparticles were prepared using the sol-gel alkoxide route¹⁰. Zirconium n-propoxide, n-propanol, yttrium nitrate, acetylacetone and water were mixed to produce sols. The synthesis parameters used were the following: $C=0.5$ mol/L for the zirconium n-propoxide concentration, $R'=[acac]/\{[Zr(OC_3H_7)_4]+[Y_2O_3]\}=0.7$ for the complexing agent ratio and $W'=[H_2O]/\{[Zr(OC_3H_7)_4]+[Y_2O_3]\}=10$ for the hydrolysis ratio. The obtained sol is homogeneous, clear and transparent and consisted of very small colloidal primary particles about 2-3 nm^{11, 12} (Part2, figure 1). Different amounts of colloidal alkoxide sol are added to the initial YSZ suspension. The mass ratio of the colloidal sol on the YSZ suspension, is called R_a .

In route 3, some of the YSZ commercial particles were stabilized by encapsulation in the alkoxide sols. R_c was defined as the mass ratio of the pre-hydrated YSZ powder (Part 3, figure 1) to the alkoxide sol. This YSZ suspension was then added to the starting solution (route 3).

Moreover, it is possible to add pure metal nitrates in the polymer matrix. Precursors were zirconyl nitrate hydrate $Zr-O-(NO_3)_2-xH_2O$ and yttrium nitrate $Y(NO_3)_3-6H_2O$ previously dissolved in water. The initial metallic salts concentration was adjusted at $C_s=0.5$ mol/L compared to the polymer matrix volume.

The dip-coating solutions constituted of YSZ powders in suspensions were deposited on Ni-YSZ porous polycrystalline substrates. The withdrawal speed was about 30 cm/min. Several films were prepared from different final suspension compositions. Heat-treatment was optimized in order to both remove organics compounds and promote a good sintering process. In a typical experiment, the temperature was increased to 800°C with a heating rate of 20°C/h and then to 1400°C with a heating rate of 100°C/h. The time at the dwelling temperature was 2 hours.

PXRD analyses were achieved at room temperature using a Siemens D501 diffractometer with Cu-K α radiation. Scanning Electron Microscopy (JEOL JSM 6400) were performed to characterize both the morphology and the microstructure of YSZ thick films.

3 RESULTS.

First, it is necessary to identify the obtained powders from the initial amorphous zirconia precursors solution for both colloidal and polymeric routes. For the alkoxide sol, the obtained gel from a colloidal aggregation mechanism¹¹ is dried in air. After a heat treatment of 600°C during 2 hours, the obtained YSZ xerogels crystallize in the fluorine structure (figure 2). For the polymer sols, a pre-treatment was necessary at 500°C in order to remove the organic compounds. The as-formed amorphous powders were then heated at 1000°C in air during 2 hours in order to obtain the YSZ oxide.

Due to the refractory character of zirconia, a very high thermal treatment should be applied to assure a good densification. In order to maintain in some extent the open porosity of the cermet, different heat treatments were performed and the microstructure of the Ni-YSZ cermets was checked by Scanning Electron Microscopy. As it can be seen on the figure 3, heating the Ni-YSZ substrate at 1500°C leads to a decrease of the initial porosity while a heating at 1400°C does not affect it. A maximum temperature of 1400°C is then used for the synthesis of YSZ thick films.

Different suspension synthesis routes were used and compared in order to determine the best conditions for making dense thick films.

Figure 4 shows the microstructure of a layer obtained via the route 1 which is the starting suspension. The polymer matrix used in this case does not contain metal salts. The obtained layers are continuous, homogeneous with a thickness of about 15 micrometers. This thickness is suitable for electrolyte in SOFC working at 700°C. However, large microcracks are present at the surface of the films while some of them penetrate the films. Furthermore, films have through-connected open porosity. These results agree those obtained by Gaudon on YSZ dense substrates⁷. To improve the density of the layers with a maximal annealing temperature of 1400°C, one possibility is the increase of the green density of the layers. This is achieved by making suspensions with powders having multimodal nanometers particles size. An other

solution is to use in the suspensions, precursors of the YSZ particles, which after the sintering process give rise to the formation of YSZ nanopowders in such a way that the 'YSZ content' in the final layer increases. However, well-dispersed suspensions made multimodal nanometric particles remains a difficult problem then, precursors of YSZ particles in suspensions are used. An alkoxide colloidal sol is then added to the initial YSZ suspension as described on the route 2 figure 1. Figure 5 shows the SEM micrographs of the YSZ films heat treated obtained from suspensions with different Ra and $R_m = 0.2$. The higher the Ra ratio, the denser the layers microstructure. However, cracks penetrate the films for Ra superior to 0.17. Crack phenomenon is linked to the organics excess when the alkoxide sol proportion in the final suspension increases. Then, $R_a = 0.17$ seems to be the better compromise for improving the film density with a thickness ranging from 10 to 20 micrometers. The last possibility to improve once more the density, has been to develop a focused growth of YSZ colloids around the commercial powder particles by the encapsulating technique as described previously. Figure 6 shows SEM micrographs of thick films obtained from different synthesis parameters of the suspension. R_m was kept to 0.2, R_a was kept constant to 0.17 and R_c ranged from 0.11 to 1. The layers microstructure is improved with the incorporation of Tosoh particles in the alkoxide sol. The lower the R_c ratio, the lesser the microcracks in the films. For $R_c = 0.11$, only micropores are present at the surface layer. No cracks accros the films are observed. The layer is continuous and has a thickness of 25 micrometers. A better densification clearly appears. In this suspension, metallic salts were then added to the polymer matrix with a concentration C_s of 0.5 mol/L. This allows an increase of the concentration of YSZ powders in the films without solvent addition. In this case, the addition of metal salts in the polymer matrix does not modify the microstructure of the layer previously observed.

4 CONCLUSION.

An alternative experimental process which combines the advantages of both tape-casting and dip-coating methods was develop to prepare YSZ thick films on porous Ni-YSZ substrates. The dip-coating solution consist of YSZ commercial powders in suspensions in organics media, which contain a dispersive solvent and both polymeric and alkoxide sols. The obtained layers are continuous, homogeneous and adherent. The layers microstructure is significantly denser with the loss of the through-connected open porosity. The thickness of the films is in the range of 10 to 20 micrometers, which is fine for electrolyte in SOFC working at 700°C.

The originality of this work is the development of a low cost process to prepare dense YSZ layers. The films are obtained from both a single step dip-coating process and a non repetitive simple heat treatment. Permeation tests have to be done in order to confirm the gas-tight of layers particularly under hydrogen, i.e. in the real solid oxide fuel cell operating conditions.

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LIST OF CAPTIONS

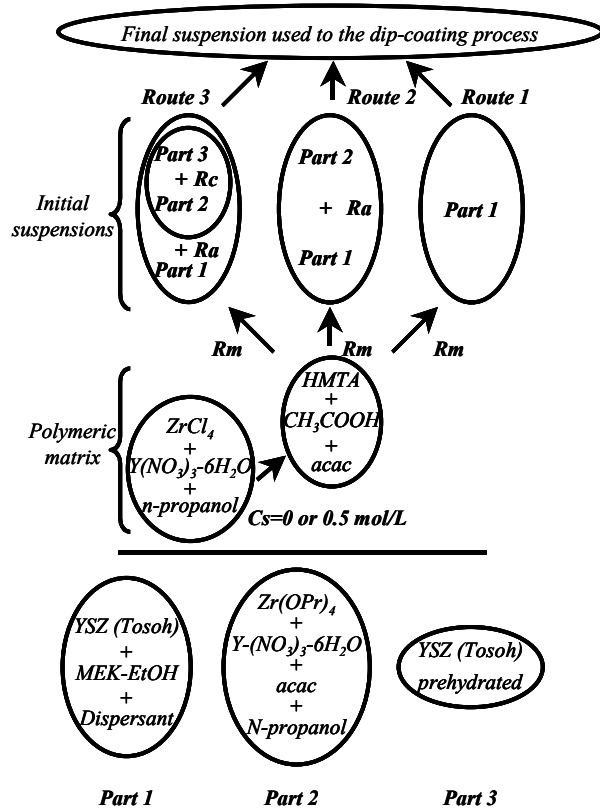


Figure 1. Flow chart illustrating processing route for final suspension composition preparation used to the dip-coating process.

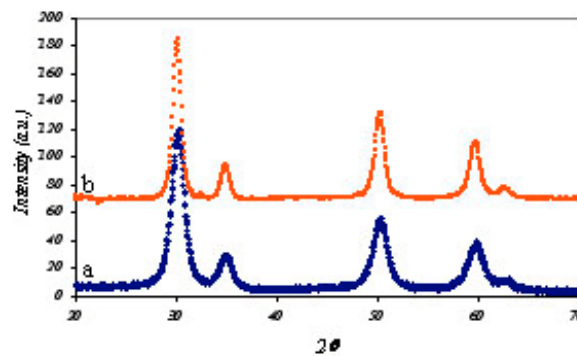


Figure 2. XRD pattern of YSZ powders obtained from the alkoxide route after calcination at 600°C during two hours and the polymeric route after calcination at 1000°C during 2 hours.

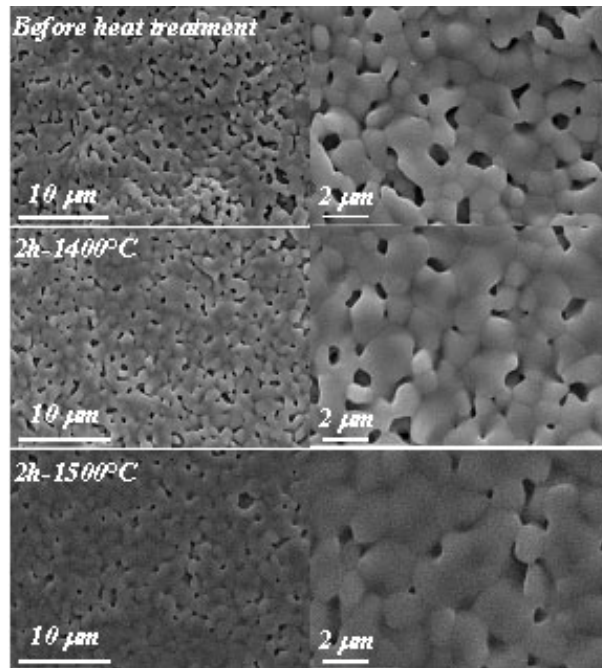


Figure 3. SEM micrographs of the Ni-YSZ porous cermet substrates before and after heat treatment at 1400°C and 1500°C during 2 hours.

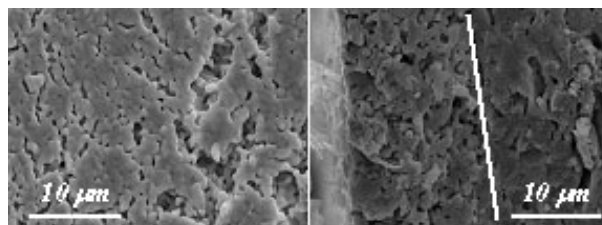


Figure 4. SEM micrographs of YSZ layers deposited on Ni-YSZ porous substrates after calcination at 1400°C during 2 hours. Synthesis parameters of the final suspension: $R_m = 0.2$; $R_a = 0$; $R_c = 0$ and $C_s = 0$ mol/L.

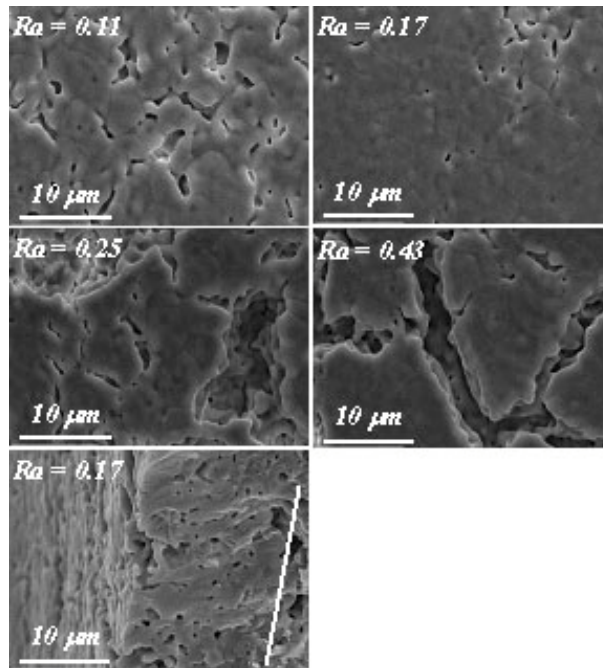


Figure 5. SEM micrographs of YSZ layers deposited on Ni-YSZ porous substrates after calcination at 1400°C during 2 hours. Synthesis parameters of the final suspension: $R_m = 0.2$; $R_a = 0.11, 0.17, 0.25, 0.43$; $R_c = 0$ and $C_s = 0$ mol/L.

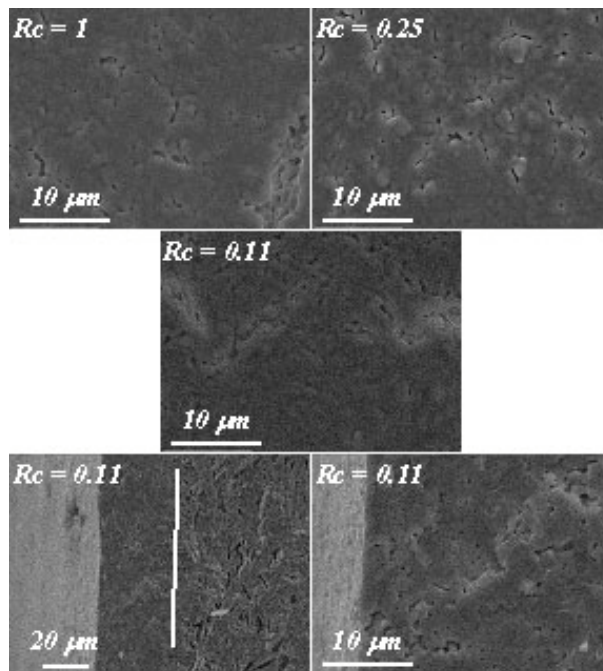


Figure 6. SEM micrographs of YSZ layers deposited on Ni-YSZ porous substrates after calcination at 1400°C during 2 hours. Synthesis parameters of the final suspension: $R_m = 0.2$; $R_a = 0.17$; $R_c = 1, 0.25, 0.11$ and $C_s = 0$ mol/L.