

# **Thick films of YSZ electrolytes by dip-coating process**

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## **Abstract**

Yttria stabilized zirconia (YSZ, 8%  $Y_2O_3$ ) thick films were coated on porous Ni-YSZ substrates using the dip-coating process and a suspension with a new formulation. 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 were densified after an optimization of the suspension composition. YSZ Tosoh particles encapsulated by a 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  $\mu\text{m}$  thick. Different microstructures are obtained depending on the synthesis parameters of the suspension.

**Keywords:** Fuel cells;  $ZrO_2$ ; Sol-gel processes; Suspensions; Thick films

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## **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 ( $\text{ZrO}_2$ -8%  $\text{Y}_2\text{O}_3$ ) is the most used electrolyte in SOFCs applications.<sup>1</sup> In order to both increase the chemical stability of the SOFCs components and decrease the cell cost, it is necessary to decrease the working temperature to around 700–800 °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 membranes or films.<sup>2,3</sup> and <sup>4</sup> However the films thickness is typically in the range of 30–50  $\mu\text{m}$ , which is too high for SOFC electrolyte working at low temperature.

The sol–gel based on the dip-coating method is also considered as an effective and practical method to produce YSZ films. But this method does not allow the synthesis of films thicker than few micrometers on porous Ni-YSZ substrates in one step.<sup>5 and 6</sup>

Here, we report a method to synthesize thick films by using the dip-coating methods. A dip-coating solution similar with slurries composition used in tape casting techniques, made of powders in suspensions, has been optimized in order to control both thickness and density of the films. By dip-coating process, very commonly used in several industrial applications, films of 10–20  $\mu\text{m}$  thick were prepared on porous Ni-YSZ cermet substrates.<sup>7</sup> The originality of the method is in the formulation of the suspensions. The dip-coating solutions consist of a mixture of polymer matrix with a stable suspension of commercial YSZ powders in a MEK-EtOH azeotropic solvent.

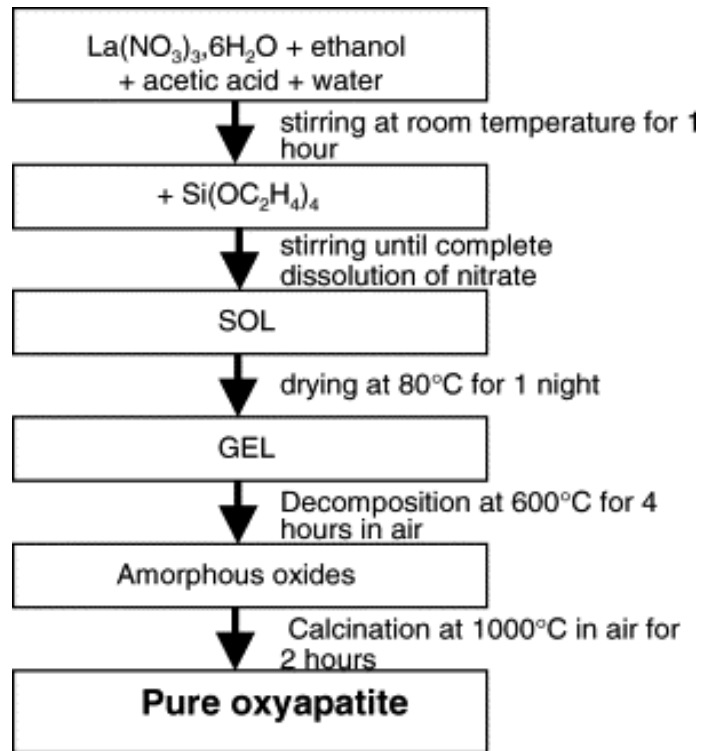
The aim of this work is then to increase the green density of the films by adjusting the formulation of the dip-coating solutions. Colloidal zirconia precursors obtained by the alkoxide route are added to the YSZ suspensions. The YSZ commercial powder encapsulated in the alkoxide sol is also added to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

The microstructures have then been correlated to the main characteristics of the suspension composition. After heat treatment, films microstructure is investigated by scanning electron microscopy.

## **2. Experimental**

ZrO<sub>2</sub>-8%Y<sub>2</sub>O<sub>3</sub> commercial powder (YSZ, Tosoh,  $d_{50} = 40 \mu\text{m}$ , crystallite size = 30 nm), is added, under mechanical stirring, in an azeotropic mixture MEK-EtOH (methyl ethyl ketone-ethanol) with a polyester-phosphate (PE-312) 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, [Fig. 1](#)). The solution was homogenized by ultrasonic disagglomeration of the powder and mechanical stirring in a water bath.<sup>8</sup> These slurries were very stable. After 72 h, no sediment volume was observed. A polymer matrix, derived from the Pecchini process,<sup>9</sup> was added to the previous YSZ suspension. This polymer matrix was obtained by polymerization and polycondensation reactions between hexamethylentetramin (HMTA, Acros Organics 99%) and acetylacetone (acac, Acros Organics +99%) in acetic acid (VWR) media. Rm defined as the mass ratio of the polymer matrix on the YSZ suspension was kept equal to 0.2. This reference synthesis part is referred as the route 1 in [Fig. 1](#). This part is the starting formulation for all syntheses.

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



Colloidal YSZ nanoparticles were prepared using the alkoxide route.<sup>10</sup> Zirconium *n*-propoxide (Aldrich, 70 wt.%), *n*-propanol (Acros organics +99%), yttrium nitrate (Acros Organics 99.9%), acetylaceton and water were mixed to synthesize sols. The synthesis parameters were the following:  $C = 0.5$  mol/L for the zirconium *n*-propoxide concentration,  $R' = [\text{acac}]/\{[\text{Zr}(\text{OC}_3\text{H}_7)_4] + [\text{Y}_2\text{O}_3]\} = 0.7$  for the complexing agent ratio and  $W' = [\text{H}_2\text{O}]/\{[\text{Zr}(\text{OC}_3\text{H}_7)_4] + [\text{Y}_2\text{O}_3]\} = 10$  for the hydrolysis ratio. The obtained sol is homogeneous, clear and transparent and consisted of very small colloidal primary particles about 2–3 nm<sup>11 and 12</sup> (Part 2, [Fig. 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 Ra.

In route 3, some of the YSZ commercial particles were added to alkoxide sols. The condensation reactions occur then at the surface of the oxide particles in the way that stable suspensions formed. Rc was defined as the mass ratio of the pre-hydrated YSZ powder (Part 3, [Fig. 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  $\text{Zr-O}-(\text{NO}_3)_2-x\text{H}_2\text{O}$  (Acros Organics 99.5%) and yttrium nitrate

$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  previously dissolved in water. The initial metallic salts concentration was adjusted at  $C_s = 0.5$  mol/L compared to the polymer matrix volume.

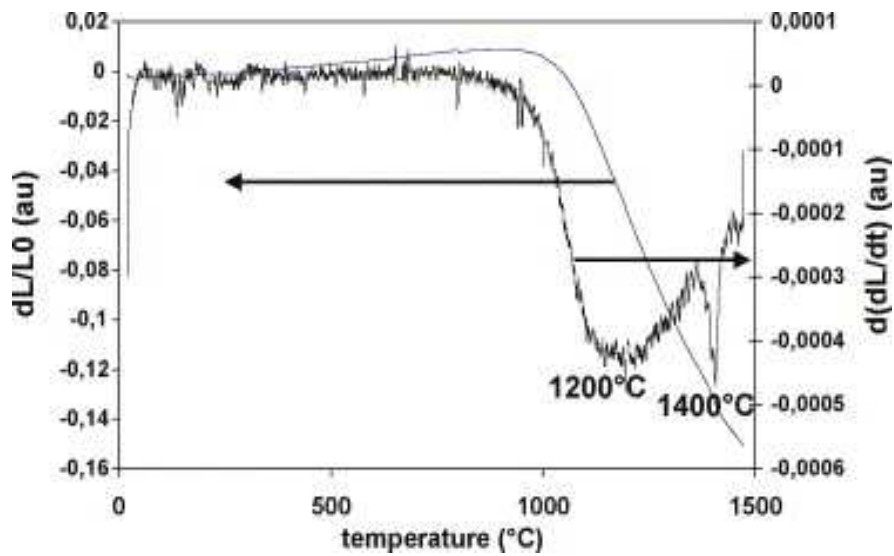
The dip-coating solutions constituted of YSZ powders in suspensions were deposited on Ni-YSZ (InDEC b.v. Netherland) porous polycrystalline substrates. The withdrawal speed was about 30 cm/min. Several films were prepared from different final suspension compositions. Heat-treatment was optimized in order to both remove organics compounds and promote a good sintering process. In a typical experiment, the thermal treatment was 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 h.

Powder analyses by X-ray diffraction were achieved at room temperature using a Siemens D501 diffractometer with Cu  $K\alpha$  radiation. Scanning electron microscopy (JEOL JSM 6400) was performed to characterize both morphology and microstructure of YSZ thick films.

### **3. Results**

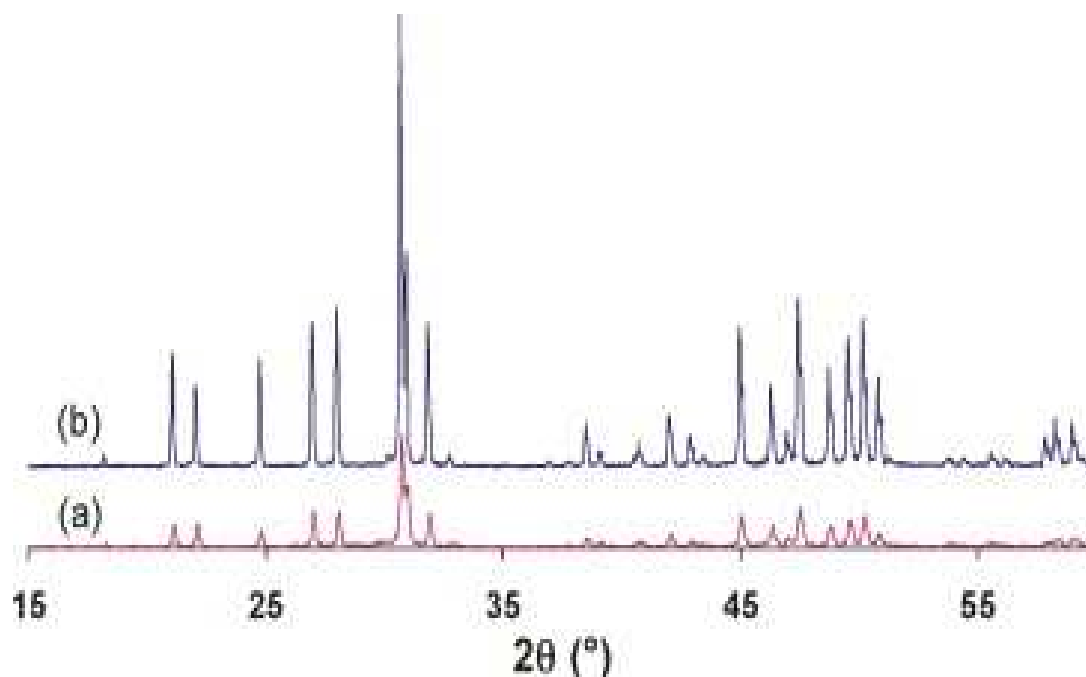
It is necessary to characterize the as-prepared powders from the initial amorphous zirconia precursors solution for both colloidal and polymeric routes. For the alkoxide sol, the obtained gel from a colloidal aggregation mechanism<sup>11</sup> is dried in air. After a heat treatment of 600 °C during 2 h, the obtained YSZ xerogels crystallize in the fluorine structure (Fig. 2). For the polymeric 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 h in order to obtain the oxide.

Fig. 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 h.



Due to the refractory character of zirconia, a very high thermal treatment should be applied to have a good densification. In order to keep 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 in [Fig. 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.

Fig. 3. SEM micrographs of the Ni-YSZ porous cermets substrates before and after heat treatment at 1400 °C and 1500 °C during 2 h.



Different routes were used and a comparison was established to determine the best conditions for making dense thick films.

Fig. 4 shows the microstructure of layer obtained via the route 1 which is the starting suspension. The polymer matrix used in this case is not constituted of metal salts. The as-prepared layers are continuous, homogeneous with a thickness of about 15  $\mu\text{m}$ . This thickness is suitable for SOFC electrolyte applications working at 700 °C. However, large microcracks appear at the surface of the films while some of them are present inside the films.

Furthermore, films have connected open porosity. These results agree with those obtained by Gaudon on YSZ dense substrates.<sup>7</sup> To improve the layers density with a maximal annealing temperature of 1400 °C, one possibility is the increase of the green density of the layers. This is achieved by the use of suspensions of powders with size multimodal distribution. Another solution is to incorporate, in the suspensions, precursors of the YSZ particles, which after the sintering process give rise to the formation of YSZ nanopowders. However, well-dispersed

suspensions made of nanometric particles are difficult to obtain. An alkoxide colloidal sol is then added to the initial YSZ suspension as described on the route 2, [Fig. 1](#). [Fig. 5](#) shows the SEM micrographs of the YSZ films obtained from suspensions with different Ra and  $R_m = 0.2$ . Higher the Ra ratio, the denser is 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  $\mu\text{m}$ . The last possibility to improve the film density has been to develop an in situ growth of YSZ colloids around the commercial powder particles by the encapsulating technique as described previously. [Fig. 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 commercial YSZ particles in the alkoxide sol. The lower the  $R_c$  ratio, the less the microcracks in the films. For  $R_c = 0.11$ , only micropores are present and no cracks across the films are observed. The layer is continuous and has a thickness of 25  $\mu\text{m}$ . A better densification clearly appears. In this suspension, metallic salts were then added to the polymeric 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.

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

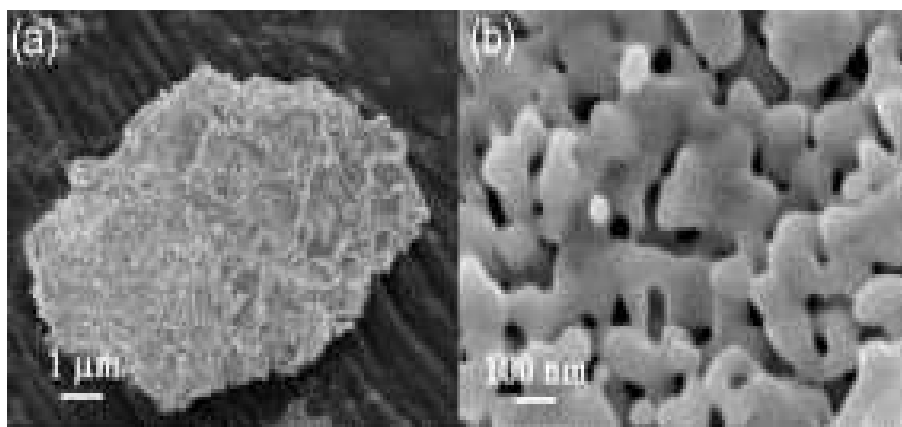




Fig. 5. SEM micrographs of YSZ layers deposited on Ni-YSZ porous substrates after calcination at 1400 °C during 2 h. Synthesis parameters of the final suspension:  $R_m = 0.2$ ;  $R_a = 0.11, 0.17, 0.25, 0.43$ ;  $R_c = 0$  and  $C_s = 0$  mol/L.

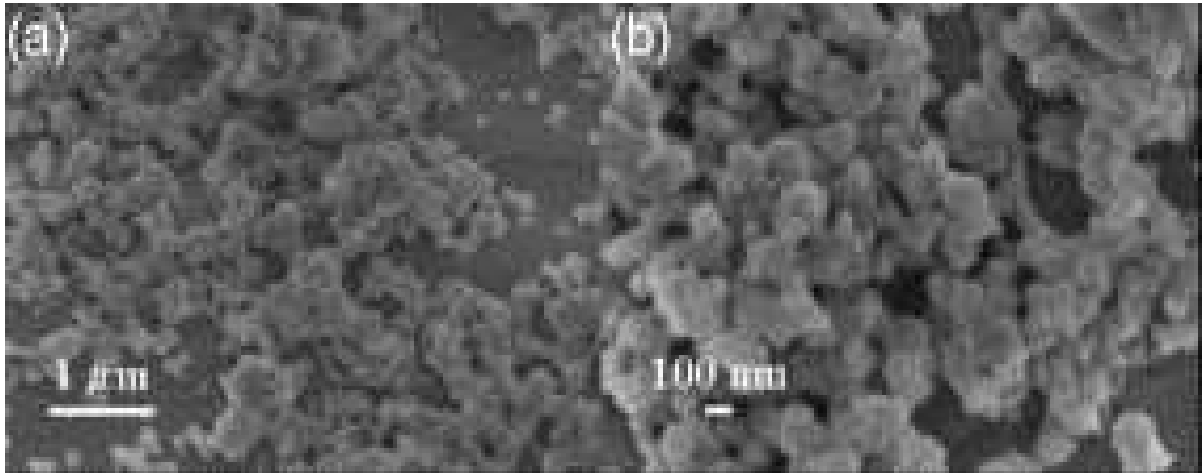
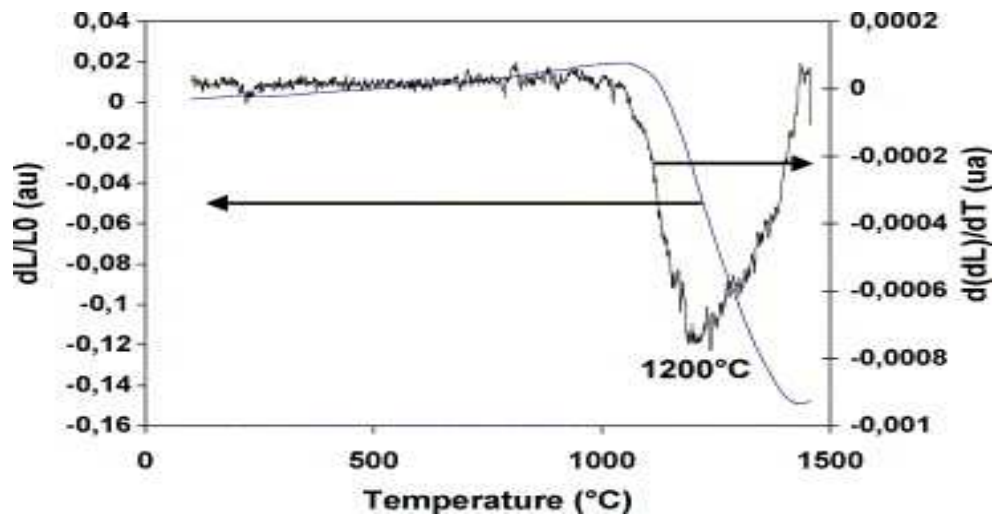


Fig. 6. SEM micrographs of YSZ layers deposited on Ni-YSZ porous substrates after calcination at 1400 °C during 2 h. Synthesis parameters of the final suspension:  $R_m = 0.2$ ;  $R_a = 0.17$ ;  $R_c = 1, 0.25, 0.11$  and  $C_s = 0$  mol/L.



#### 4. Conclusion

An alternative experimental process which combines the dip-coating method with optimized slurries was developed to prepare YSZ thick films on porous Ni-YSZ substrates. The dip-coating solution consists of YSZ commercial powders in suspensions in organic media, which contain a dispersion 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 connected open porosity. The films thickness is from 10 to 20  $\mu\text{m}$ , which is in good agreement with requirements for SOFC electrolyte 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 simple heat treatment.

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