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Potentialities of the sol–gel route to develop cathode and electrolyte thick layers Application to SOFC systems

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A B S T R A C T

In this work, we report the potential of sol–gel process to prepare cathode and electrolyte thin and thick layers on anodic NiO-YSZ supports which were also made from powders prepared by sol–gel route. YSZ and $\text{La}_{2-x}\text{NiO}_{4+\delta}$, $\text{La}_4\text{Ni}_3\text{O}_{10}$ were synthesized as electrolyte and cathode materials for SOFC applications. For electrolyte shaping, yttria stabilized zirconia (YSZ, 8% Y_2O_3) thick films were cast onto porous NiO-YSZ composite substrates by a dip-coating process using a new suspension formulation. Part of the YSZ precursor colloidal sol was added in the suspension to ensure both homogeneity and adhesion of the electrolyte on the anodic substrate after thermal treatment at 1400 °C for 2 h. By precisely controlling the synthesis parameters, dense and gas-tight layers with thicknesses in the range of 10–20 μm have been obtained. Gas-tightness was confirmed by He permeation measurements.

Concerning cathode processing, a duplex microstructured cathode consisting of both $\text{La}_{2-x}\text{NiO}_{4+\delta}$ ultra-thin films (few nanometers) and $\text{La}_{2-x}\text{NiO}_{4+\delta}$ and/or $\text{La}_4\text{Ni}_3\text{O}_{10}$ thick layers (few micrometers) was prepared on YSZ substrates by the dip-coating process, with the thickness being dependent on the nature of the dip-coated solution (polymeric sol or adequate suspension). The derived cathode microstructure, related to the number/thickness of layers and type of architecture, was correlated to the good cell electrochemical performances.

Keywords:

Sol–gel
Architectured cathode
Thick films electrolyte
Anode support
SOFC

1. Introduction

The development of SOFC technology with a planar configuration has been mainly driven by the objective to reduce both the working temperature (700–800 °C) and the cost of the elementary cell. A first step to reach these goals is to develop a single cell with an anode support which allows the reduction of both the electrolyte thickness and its internal resistance [1,2]. Thus, cell performances at lower temperature could be improved. In addition, the interfacial cathode/electrolyte resistances can be drastically decreased by having a better control of both composition and microstructure of the active materials.

A lot of work concerning nanomaterials synthesis by wet chemistry processes to SOFC application have been reported in the literature [3–5]. In this work, a low cost process as the sol–gel route derived from the Pechini process [6] has been developed to prepare active materials of the cell components as thin or thick films. Those layers are prepared by a dip-coating process from either polymeric sols or optimized slurries respectively [7,8]. Such process is of great interest because only a single deposition step is needed to deposit the whole layer before performing an adequate thermal treatment.

Due to its excellent chemical stability and sufficient oxygen-ion conductivity in both oxidizing and reducing environment at the targeted temperatures, yttria stabilized zirconia (ZrO_2 –8% Y_2O_3) is the most widely used electrolyte in SOFCs applications [9]. In this work, YSZ was selected as the main component of both the Ni-YSZ anode cermet and the electrolyte. On the basis of the attractive results recently published in the literature on lanthanum nickelates [10,11], these promising mixed ionic and electronic conductors were selected for the cathode.

2. Starting materials elaboration

2.1. Powders preparation

Prior to the shaping step of the elementary cell components, $\text{La}_{2-x}\text{NiO}_{4+\delta}$, $\text{La}_4\text{Ni}_3\text{O}_{10}$, YSZ (ZrO_2 –8% Y_2O_3) and NiO powders were prepared using a modified Pechini route [6,12]. This synthesis process has already been described for the preparation of oxides with various compositions [13–15]. Here, reagent-grade $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99%), $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (+98%), $\text{Y}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9%) and $\text{ZrO}(\text{CH}_3\text{COO})_2$ were used as starting cationic salts. Quantity of metallic salts, with respect to the molar compositions of the corresponding oxides, were dissolved in distilled water and added to a liquid polymeric matrix consisting of hexametylenetetramine (HMTA), acetylacetone (acac) – in equimolar

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ratio – and acetic acid (CH_3COOH). A thermal treatment at 90°C during 20 min was carried out to promote both polyesterification and polycondensation reactions and to adjust the starting sol viscosity to 40 mPa s at room temperature. A decomposition treatment at 400°C in air removes the main organic compounds and the crystallized oxides were obtained during the final thermal treatment above 800°C . The final annealing temperature was selected in order to control the morphology and the sintering degree of the different oxide powders.

2.2. Microstructural analysis

After a thermal treatment at 1100°C –2 h for YSZ and 800°C –2 h for NiO, the powders were crystallized in the cubic system (spatial group $F_{m\bar{3}m}$). The YSZ elementary particles were monocrystalline with spherical geometry and a monodisperse size of 50 nm, although the cubic faceted NiO particles were comprised between 50 and 300 nm and centered around 100 nm in size (Fig. 1). After a thermal treatment at 1000°C –2 h, the lanthanum nickelate powders were crystallized in the orthorhombic system (spatial group F_{mmm}), they were monocrystalline with spherical elementary particle diameter of 150 nm for $\text{La}_{2-x}\text{NiO}_{4+\delta}$ and acicular geometry of $200\text{ nm} \times 600\text{ nm}$ for $\text{La}_4\text{Ni}_3\text{O}_{10}$ (Fig. 2).

3. Results and discussion

3.1. Powders processing and characteristics of anodes

To ensure a good dispersion of both YSZ and NiO phases, the above synthesized powders were mechanically mixed. The quantity of NiO was adjusted in order to obtain, after a reduction treatment, a final composition of 50 vol.% Ni. The mixed powders were then pressed into pellets under 350 MPa and sintered in air at 1400°C for 2 h. The densification rate is about 96%. Pellets are then reduced in pure H_2 at 800°C for 1 h. As can be observed on the micrographs reported in

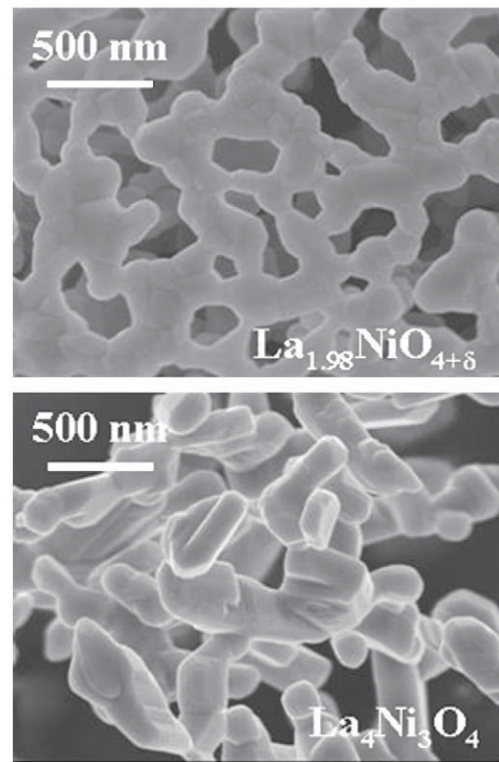


Fig. 2. S.E.M. micrographs of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ (a) and $\text{La}_4\text{Ni}_3\text{O}_{10}$ (b) powders synthesized by the polymeric route after thermal treatment at 1000°C –2 h.

Fig. 3, there is a homogenous distribution of the two phases (Ni and YSZ) and the densification rate is 72%. The electrical conductivity has been measured with the four-point technique. The measured

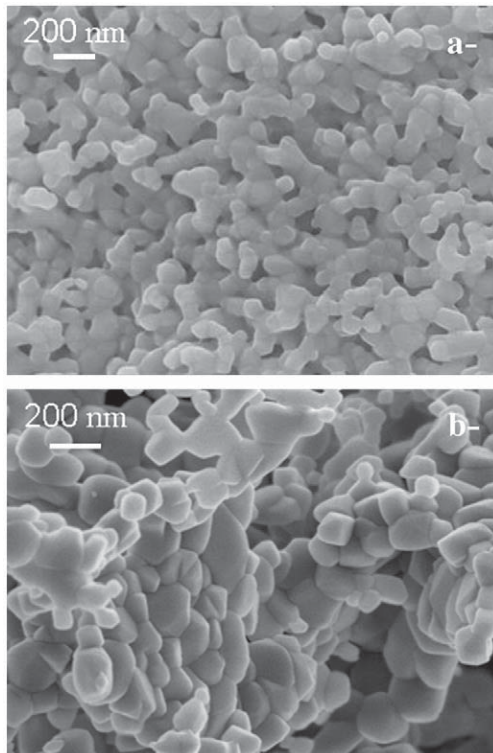


Fig. 1. S.E.M. micrographs of YSZ (a) and NiO (b) powders synthesized by the polymeric route after thermal treatment at 1100°C –2 h and 800°C –2 h respectively.

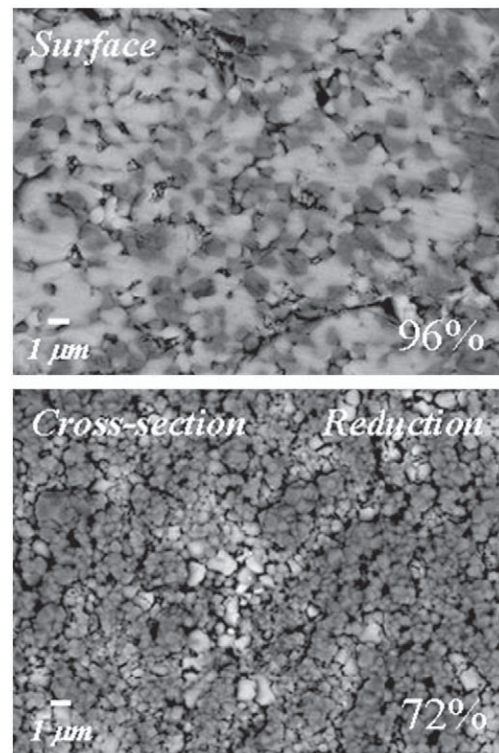


Fig. 3. S.E.M. micrographs NiO-YSZ composite after thermal treatment at 1400°C –2 h and after reduction at 800°C .

conductivity is around 500 S cm^{-1} at $800 \text{ }^\circ\text{C}$ [16] which is promising for IT-SOFC application since the required conductivity is only 200 S cm^{-1} at the working temperature [17,18].

3.2. Electrolyte processing and characterization of half cell electrolyte/anode

Thick electrolyte layers were deposited on NiO-YSZ composite substrates annealed at $1200 \text{ }^\circ\text{C}$ during 2 h. The final suspension used for the dip-coating process resulted from the mixture of an optimized suspension with a polymeric matrix. Optimized preparation conditions have been previously defined with YSZ commercial powders [19]. In this work, the process was adapted to the YSZ powders prepared by the polymeric route as described in the experimental part.

First, the YSZ sol-gel derived powder was incorporated, under mechanical stirring, in an azeotropic mixture as MEK-EtOH (Methyl-ethylketone-Ethanol) with a polyester-phosphate (PE-312) type-additive used as dispersant [20]. The massic ratio YSZ powder/MEK-EtOH was controlled and kept equal to 1. In order to break main aggregates and decrease mean particle size distribution, YSZ sol-gel derived powders have been mechanically ground during 4 h. The resulting suspensions were stable for several days. In parallel, YSZ precursor colloidal nanoparticles were synthesized using the alkoxide route as previously reported [21]. Aiming to improve the compaction degree of the thick films, the third step consists in a pre-hydration of the YSZ sol-gel powder before adding it to the alkoxide sol, so that the condensation reactions preferentially occur on the surface of the oxide particles. With this encapsulation technique, the cohesion between the YSZ particles was improved and the layer densification significantly increased after the thermal treatment. Ra was defined as the mass ratio of the pre-hydrated YSZ powder to the alkoxide sol. Finally, this last mixture was added to the previous YSZ suspension with a massic ratio Rb leading to an intermediary suspension. To obtain the final suspension, a polymeric matrix was added, similar to the one described in the experimental part for preparing the oxide powders. The role of the polymeric matrix was double: 1) Encapsulation of the YSZ particles in the polymeric chains and 2) improvement of adhesion between the final suspension and the substrate surface during the dip-coating process. Rm was defined as the massic ratio of the polymer matrix to the initial YSZ suspension previously described.

The experimental parameters of the final suspension leading to the best results were Ra=0.11, Rb=0.19 and Rm=0.2. Fig. 4 shows SEM micrographs of thick films obtained with these suspension synthesis parameters and after an adequate thermal treatment favouring both a slow removal of organics and an efficient sintering process. After thermal treatment at $1400 \text{ }^\circ\text{C}$ during 2 h, only micropores are present on the film surface and no cracks are observed across the films. The layer was continuous and about 20 micrometers thick. In the bulk

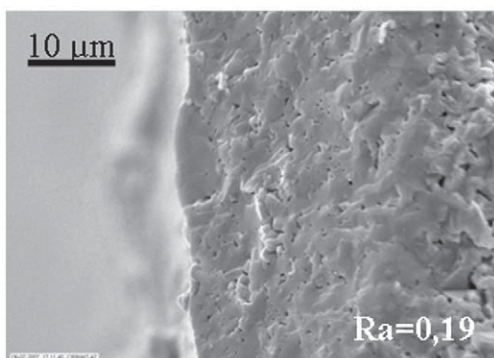


Fig. 4. S.E.M. micrograph of YSZ thick film cross-section deposited on NiO-YSZ substrate by the dip-coating process and annealed at $1400 \text{ }^\circ\text{C}$ -2 h.

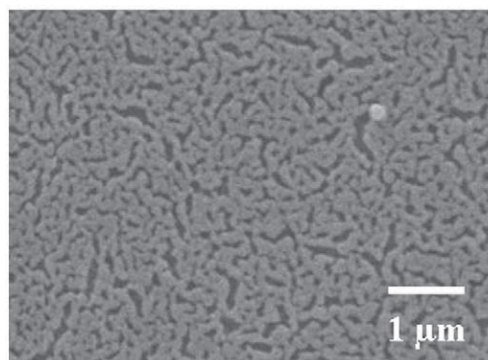


Fig. 5. S.E.M. micrograph of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ thin film deposited on YSZ substrate by the dip-coating process and annealed at $1000 \text{ }^\circ\text{C}$ -2 h.

electrolyte, several non connected closed pores were evidenced. Gas-tightness experimentations performed the half cell electrolyte/anode (home made system) demonstrated that He was not able to flow through the electrolyte when using a transmembrane pressure of 4 bars. When using an up-stream pressure of 4 bars helium, a diffusion coefficient in the range $20\text{--}30 \cdot 10^{-14} \text{ m}^2/\text{s}$ was measured for He through the electrolyte defects by using the time-lag method. The control of slurries preparation and co-sintering of both NiO-YSZ composite substrates and thick green YSZ layers lead to the formation of dense YSZ electrolyte films.

3.3. Cathode processing and characterization of half cell electrolyte/cathode

Based on recent numerical models pointing out the influence of the cell microstructure on its electrical, gas transport and catalytic properties, an architected cathode was prepared which consisted first of a thin mesoporous layer in order to increase the surface exchange at the cathode/electrolyte interface and second, of a porous thick film with an important specific surface area to increase the surface reactions.

Thin films were then prepared by dipping the YSZ ceramics substrate in a $\text{La}_{2-x}\text{NiO}_{4+\delta}$ polymeric sol and withdrawing at a constant speed of 3 cm/min . Before the coating step, YSZ substrates were polished (Ra ~ 15 nm) and cleaned. After annealing at $1000 \text{ }^\circ\text{C}$ in air during 2 h, the layer was continuous, homogeneous without cracks and around 80 nm thick. The microstructure was composed of randomly oriented nanocrystallized $\text{La}_{2-x}\text{NiO}_{4+\delta}$ particles of 40–50 nm in size. Their narrow size distribution favours self-stacking in a relatively dense close-packed microstructure which optimises the exchange surface at the interface (Fig. 5).

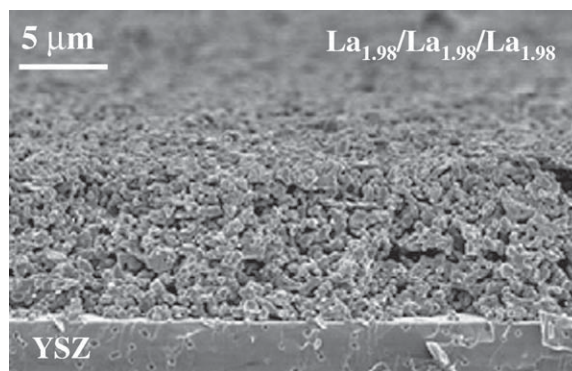


Fig. 6. S.E.M. micrograph of cathode thick film consisting of a stack of three $\text{La}_{2-x}\text{NiO}_{4+\delta}$ layers and annealed at $1150 \text{ }^\circ\text{C}$ -2 h.

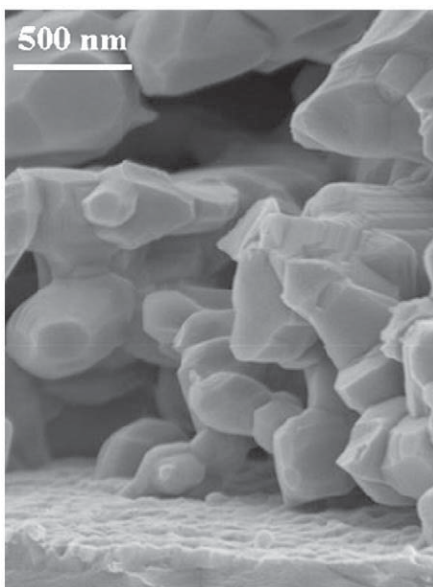


Fig. 7. S.E.M. micrograph of cathode thick film consisting of one interfacial $\text{La}_{2-x}\text{NiO}_{4+\delta}$ thin film, two $\text{La}_{2-x}\text{NiO}_{4+\delta}$ and one $\text{La}_4\text{Ni}_3\text{O}_{10}$ thick layers and annealed at $1150\text{ }^\circ\text{C}$ -2 h.

Thick layers with graded composition of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$ were prepared by a dip-coating process using stable slurries of lanthanum nickelates. The nanocrystallized powders are dispersed in an azeotropic mixture of methylethylketone (MEK) and ethanol (EtOH) in the presence of various additives such as a commercial dispersant C213, a PVB binder and a phthalate plasticizer. The experimental parameters leading to stable, homogeneous slurries with an adequate viscosity and cohesion were reported previously [22]. Different cathode architectures were then prepared by depositing several layers of $\text{La}_{2-x}\text{NiO}_{4+\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$ layers. An intermediate half an hour thermal treatment at $500\text{ }^\circ\text{C}$ was applied after each layer deposition in order to remove organic compounds. Finally, a 2 h thermal treatment at $1150\text{ }^\circ\text{C}$ ensures the cohesion and consolidates the whole cathode.

As an example, a SEM micrograph of a cathode made up of a stack of 3 $\text{La}_{2-x}\text{NiO}_{4+\delta}$ layers is shown in Fig. 6. After thermal treatment, the film were continuous, homogeneous, it were crack-free and seemed to adhere well to the electrolyte. The thickness was about $7\text{--}8\text{ }\mu\text{m}$ and an open connected porosity was observed.

The next part of the present work consists in preparing thick architected multilayers, with an interfacial thin layer on the electrolyte. The electrical conductivity of $\text{La}_4\text{Ni}_3\text{O}_{10}$ (about 95 S cm^{-1} at $700\text{ }^\circ\text{C}$) is higher than the $\text{La}_{2-x}\text{NiO}_{4+\delta}$ one which is only 60 S cm^{-1} . In addition, $\text{La}_{2-x}\text{NiO}_{4+\delta}$ is a mixed ionic and electronic conductor in which specific transport properties as the oxygen diffusion coefficient and surface exchange [23] are in favour of its application at the cathode/electrolyte interface. As a consequence, a sophisticated $8\text{ }\mu\text{m}$ thick cathode was deposited on the electrolyte by stacking one $\text{La}_{2-x}\text{NiO}_{4+\delta}$ thin layer, two $\text{La}_{2-x}\text{NiO}_{4+\delta}$ thick layers and finally one $\text{La}_4\text{Ni}_3\text{O}_{10}$ thick layer at the cathode/air interface. As shown in Fig. 7, a good coverage of the electrolyte was obtained after a 2 h thermal treatment at $1150\text{ }^\circ\text{C}$ and, considering the numerous anchorage points, the thick cathode seemed to adhere well to the electrolyte. The final thermal treatment ensured the formation of two interconnected networks, the porous one and the other one consisting of active materials.

Electrochemical tests of the above described architected cathodes have been performed to validate their performances and evidence the interest of such duplex structured cathodes. At $750\text{ }^\circ\text{C}$, the measured specific surface area resistance was only $9\text{ }\Omega\text{ cm}^2$ although the resistance measured for a more classical cathode consisting of 3 $\text{La}_{2-x}\text{NiO}_{4+\delta}$ layers was about $38\text{ }\Omega\text{ cm}^2$, i.e. 4 times higher.

4. Conclusion

In this work, the polymeric route has been developed in order to synthesize all the active materials of elementary SOFC cells. An alternative experimental process which combines the dip-coating method with optimized slurries was developed to prepare first YSZ thick films on porous NiO-YSZ composite substrates and second lanthanum nickelates on dense YSZ substrates.

By adjusting the slurry composition and controlling the co-firing step of both YSZ layer and porous substrate, continuous, homogeneous and gas-tight electrolyte thick films have been obtained from a single step dip-coating process and only one heat treatment.

For the cathode, a duplex microstructure consisting of a mesoporous $\text{La}_{2-x}\text{NiO}_{4+\delta}$ thin film and an assembly of $\text{La}_{2-x}\text{NiO}_{4+\delta}$, $\text{La}_4\text{Ni}_3\text{O}_{10}$ thick layers has been developed. For thick films, the composition of slurries containing active materials has been optimized before dip-coating. The number of deposits allows both controlling the final thickness of the active cathode and varying the materials composition. Such architected cathodes present improved electrochemistry performance

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