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A new route to prepare anodic coatings on dense and porous metallic supports for SOFC application

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A B S T R A C T

Metallic cell supports have been developed for the new generation of fuel cells. Sol–gel process has been used to prepare anodic coatings on these supports at moderate thermal treatment temperature, in order to keep a good support mechanical behavior and limit metallic corrosion. Indeed, we take advantage of the numerous reaction routes that sol–gel method can offer to first synthesize NiO–YSZ (yttria-stabilized zirconia) homogeneous composites, and then to process films of different thicknesses on metallic supports by dip-coating. In this work, the metallic supports could be either dense or porous. To begin with, duplex microstructured anodes were prepared from both thin and thick layers, directly deposited on dense metallic supports. The interfacial anodic layer, around 100 nm thick, improves adhesion and accommodates stresses between metallic interconnect and active thick anode. Moreover, by dipping the substrate into an optimized slurry containing sol–gel composite powders, films of a few microns thick have been obtained and constituted the active anodic part. A heat treatment at only 800 °C leads to a coherent anodic duplex stacking which is continuous, homogeneous and adherent. Subsequently, thick anodic films have also been deposited on two different porous supports, with both dip-coating process and slurries routes. These thick anodic coatings were characterized after thermal treatment at 800 °C.

1. Introduction

The development of SOFC (Solid Oxide Fuel Cell) technology has been made in several steps, in order to reduce the cost of a SOFC stack in light of future commercialization. A planar configuration has been considered first with an electrolyte support (SOFC of 1st generation) working at 1000 °C at least, then secondly with anode support (2nd generation) which helped to reduce electrolyte thickness and thus allowing good performances at lower temperature (700–800 °C). Moreover, this decrease in working temperature enables the use of metallic interconnects [1,2], that are less expensive than ceramic interconnects (like $LaCrO_3$) previously used in first generation SOFC. More recently, it was proven that only a third generation SOFC cell, which uses metal as mechanical support with deposited thin ceramic active materials (anode, electrolyte, cathode), could possibly reach acceptable cost ranges [3]. Indeed, the quantities of the ceramic material, which constitutes most of the cost, are reduced to the minimum, while maintaining excellent performances due to the electrolyte thickness being only a few tens of microns. The working temperature is in the range 600–700 °C. Furthermore, with a correct mechanical behaviour, the metallic interconnect support is not only a good electrical conductor to collect current, but also a good thermal conductor allowing a favourable temperature distribution [4]. Moreover, when assembling single cells in stack, it is easier to weld or connect metallic materials than ceramic ones.

In this prospect, this paper deals with the preparation of anodic layers, 10 μm thick, by a sol–gel process using dip-coating technique on metallic substrates which could be either dense or porous, knowing that porous ones are particularly interesting to control gas inlets.

Anodic material is Ni–YSZ because this well-known cermet is still the most commonly in use currently [5,6]. Nevertheless, improvement of Ni–YSZ performances requires the optimization electrochemical properties for such applications. Here, we propose to optimize microstructure and the distribution both phases (Ni and YSZ) by using original elaboration method (sol–gel synthesis and slurries) so that SOFC systems can be made economically competitive. By using the developed sol–gel route, a composite oxide powder is synthesized and has presented a good distribution of the two phases before the shaping step [8]. The advantage is that, by dip-coating process, this skeleton is preserved on the composite anodic coating. However, the use of metallic material as cell support induces thermal limitations such as the decrease in anodic material sintering temperature. Indeed, a heat thermal treatment above 800 °C would damage metal support, either mechanically or by corrosion. That is why it is necessary to consolidate and sinter anodic coating on the metallic support at relatively low temperatures. In this aim, sol–gel process is a convenient route to prepare duplex microstructured anode. Interestingly, this soft chemistry process, allowing an accurate stoechiometry control and ensuring composition

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homogeneity, is suitable for low cost preparation of complex formulation oxide compounds. Sol–gel route allows the preparation of various oxides at low temperature with controlled morphology, as well as to synthesize and to shape materials [7], without directional oxides growth. Film microstructure will depend on several parameters corresponding to the nature of the suspension (solvent, concentration, rheology), substrate (surface, topography), dip-coating technique (withdrawal speed) and thermal treatment. Homogeneous and adherent micronic layers with controlled porosity and thickness would result from a control of these experimental parameters.

In this work, we first consider duplex anodic coatings improvement on dense substrates. An anodic interfacial thin layer was directly deposited onto the dense support and the thicker layer was optimized by adjusting the composition and parameters of slurries. Then, thick anodic films on two different porous supports were prepared. Thick deposits were coated by dip-coating the substrates into the suspension. Anodic coatings were then characterized after thermal treatment at 800 °C.

2. Experimental

In this paper, we propose to prepare a Ni–YSZ duplex anode coating on three different types of metallic substrates, two of which are made of stainless steel with the same composition, one dense and the other porous, and the third type of support, composed of nickel and is porous.

The two types of steel were ferritic stainless steels with a chromium content of 17% wt that ensured a fairly good corrosion resistance provided by the formation of protective oxides (Cr_2O_3) and good mechanical properties at high temperature. The first type of substrate, which were dense, were manufactured by ArcelorMittal Company (ref: K41X). Surface roughness of these substrates is measured by optical interferometry device ("New View 100" ZYGO Corp). These steels present some surface roughnesses with an average value of 0.4 µm. The second ones are porous compacts, manufactured by ArcelorMittal Company and CEA (DTNM/LCE) (ref: porous K41X). Surface micrograph is reported in Fig. 1a: this porous support consists of steel spheres (diameter in the range 20–100 µm). These supports are 30% porous with pore size in the range 10–20 µm. The third kind of supports used in this work were nickel porous compacts prepared by powder metallurgy [8,9]. Metallic powders were prepared by a low cost process using soft chemistry (metallic oxalate precipitation) and shaped to compact metallic substrates with controlled porosity after compaction and sintering. The prepared Ni compacts were 40% porous with a monodispersed pore size distribution in the range of 2–5 µm. A micrograph of these porous substrates is reported in Fig. 1b.

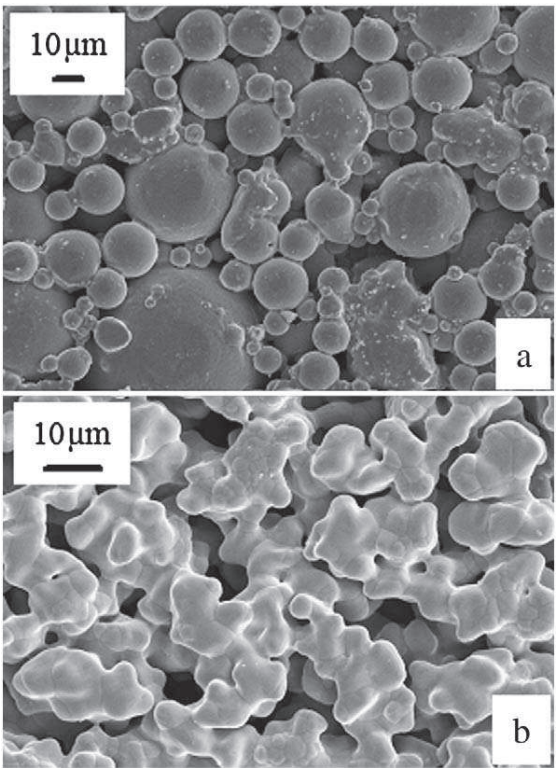

Fig. 1. S.E.M. micrographs of porous metallic supports: (a) steel, (b) Ni.

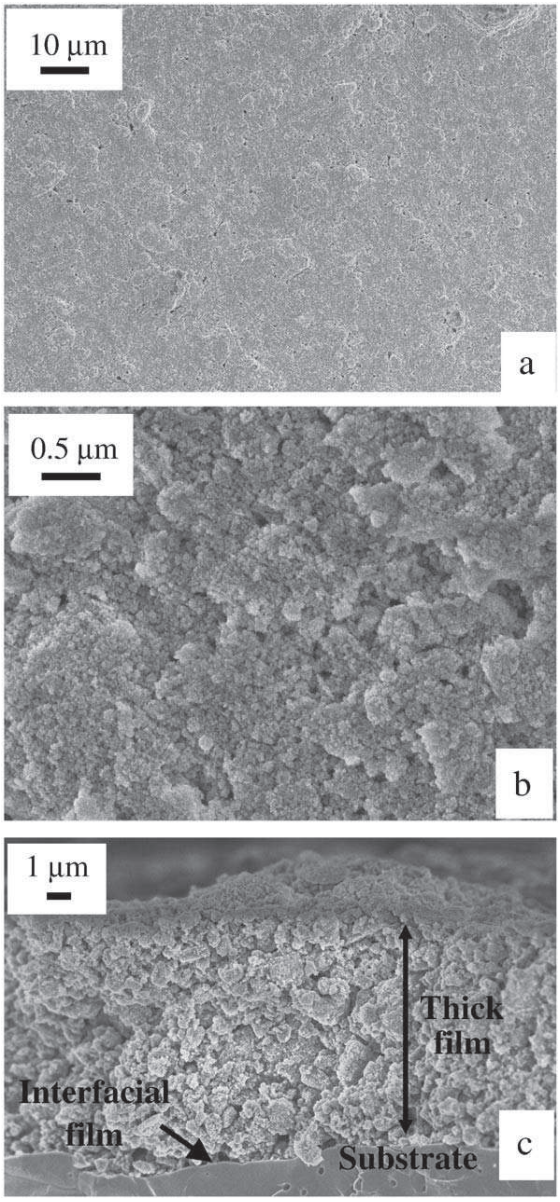

Fig. 2. S.E.M. micrographs of duplex NiO–YSZ composite films deposited on dense steel after annealing at 800 °C in air during 2 h: (a, b) surface, (c) cross-section.

Structural and microstructural analyses of supports and films were achieved, at room temperature, by X-ray diffraction using a D4 ENDEAVOR (BRUKER) diffractometer with the Cu Kα radiation, and Scanning Electron Microscopy (JEOL JSM 6700F).

In order to elaborate anodic interfacial films, an alkoxide composite sol has been synthesized [10]. Thick films were obtained by dip-coating

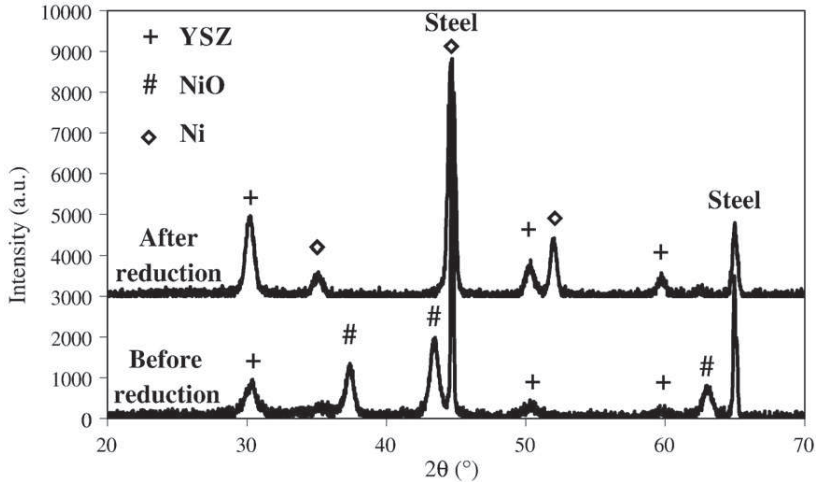

Fig. 3. X.R.D. patterns of thick composite film annealed 800 °C–2 h in air and of thick cermet film reduced at 800 °C–1 h under hydrogen.

process in a slurry composed of YSZ–NiO composite powders which were previously synthesized by a sol–gel polymeric route [10], derived from Pechini process [11]. Slurries were then prepared by the addition of these NiO–YSZ powders, under mechanical stirring, in an azeotropic mixture MEK–EtOH (methylethylketone–ethanol) with a polyester-phosphate (MELIORAN P312, CECA) additive used as a dispersant. In order to prepare stable slurries, the dispersant quantity has already been optimized [8] and adjusted to 2.5% with respect to mass powder. Alkoxide sol was also added in the suspensions in order to consolidate thick coatings. Nickel ratio in this anodic composite corresponded to 50% vol Ni obtained after reduction treatment in the final material.

A normalized adhesive (NF-A91-102 and NFT30-038) has been used to permit a qualitative evaluation of coatings adhesion onto the substrates.

3. Results and discussion

3.1. Improvement of thick anodic films coated on dense steels as supports

This part is based on previous work concerning preparation of duplex microstructured anodes (with both a thin and a thick layer) on metallic substrates [8]. Firstly, the interfacial anodic film was directly deposited on dense metallic supports by sol–gel process. Secondly, thick films of a few microns were prepared by dipping the substrate into a slurry (containing sol–gel composite powders, dispersive media and alkoxide sol). A coherent anodic duplex stacking (Fig. 2) was obtained after a heat treatment at only 800 °C. After reduction under H_2 at 800 °C during 1 h in order to obtain the cermet (Ni–YSZ) coating, the thick film was still adherent and homogeneous, even though some cracks were present. These ones can be reduced by adjusting the alkoxide sol content. To do this, alkoxide sol proportion had been changed in the slurry and the effect on anodic coatings before and after reduction could be seen. Mass ratio between powder and dispersive media (R_{pm}) was kept constant at 2. Then, the ratio called R_a and defined by R_a = alkoxide sol mass / R_{pm}, had been modified from 0 to 3. After preparation of these various slurries, dense supports are dip-coated into the slurry and withdrawn at 20 cm min^{-1} before sintering at 800 °C during 2 h.

In case of slurries with $R_a \leq 0.125$, coatings are neither homogeneous nor adherent.

When $0.25 \leq R_a \leq 0.75$, films, after sintering at only 800 °C, were continuous, adherent, porous, homogeneous and about 10 μm thick. For example, NiO–YSZ coatings micrographs from slurry with $R_a = 0.25$ are reported on Fig. 2. Small particles coated on bigger ones could be seen; particles from alkoxide sol act as composite powders cement. Alkoxide sol allows an "in situ" growth of NiO and YSZ, which consolidated the layer. We have then controlled phases purity by XRD (Fig. 3). After reduction under pure H_2 at 800 °C during 1 h to obtain the cermet (Ni–YSZ), thick films were still adherent and homogeneous (Fig. 4, with a $R_a = 0.25$). Coatings were more porous than those before reduction and they were still 10 μm thick. Some cracks were still present, but they have been limited (with a $R_a = 0.25$) in comparison to previous works [8]. Furthermore, XRD pattern, reported in Fig. 3, shows that NiO was reduced into Ni, and YSZ remained stable under reducing atmosphere and no secondary phase has been detected.

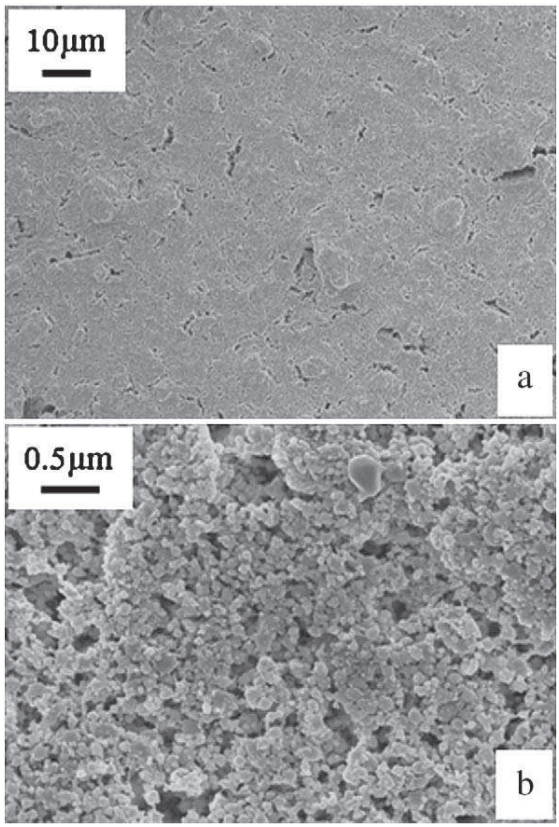

Fig. 4. S.E.M. micrographs of thick Ni–YSZ cermet film after reduction at 800 °C–1 h under hydrogen: (a, b) surface.

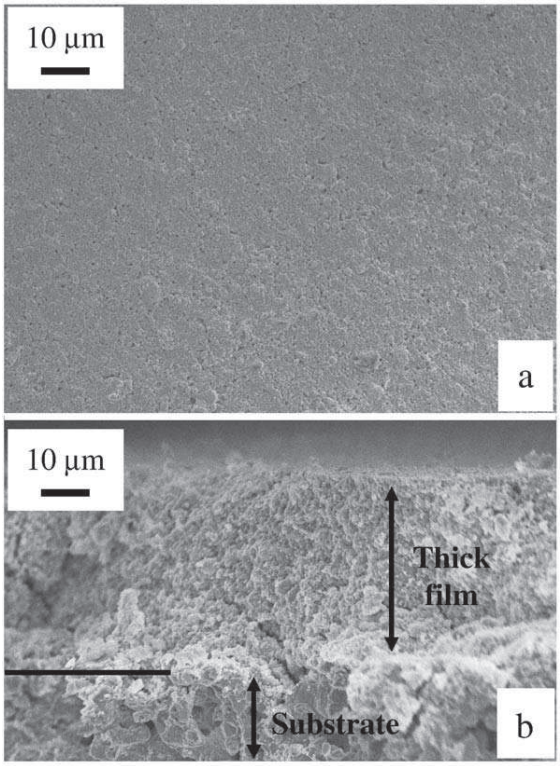

Fig. 5. S.E.M. micrographs of thick NiO–YSZ composite film deposited on porous Ni after annealing at 800 °C in air during 2 h: (a) surface, (b) cross-section.

In case of $R_a \geq 1$, coatings are not homogeneous because there was not enough powder in the slurry compared to liquid phase. The cover ratio of anodic film was not good and a decrease of anodic coatings thickness was observed. For example when $R_a = 2$, thickness is only 1 µm which is not sufficient for SOFC anodic applications.

In this part, we have prepared a series of slurry composition to shape thick active anodic layers on dense steel. With only one deposit and after thermal treatment at only 800 °C, anodic coatings of 10 µm thick were adherent and homogeneous. To our knowledge, very few works directly relate deposited anodes on metallic support. A german team (Jülich) has prepared anodic coatings on metallic support by a physical process: atmospheric plasma spraying (APS) [12,13], but not from chemical route.

3.2. Preparation of thick anodic films coated on porous metallic supports

Porous supports are particularly interesting for SOFC interconnect application to control gas inlets and moreover, an internal hydrocarbon fuel pre-reforming can also be considered.

The aim of this part is to transfer the knowledge of anodic coating developed on dense supports onto porous ones. Considering sol–gel or slurries routes, infiltration problems of anodic precursors can occur. So, two porous metallic supports have been tested with quite different pores size ranges: steel presented pores size up to 20 µm whereas Ni porous compacts pores size were in the range 2–5 µm. Nevertheless both porous metals present a similar total porosity of 30–40%, which is suitable for SOFC application.

With regards to the interfacial anodic film, during the dip-coating process, sol infiltrates in the whole metallic substrates due to their porosity. The thin film prepared in the case of dense substrates is not so useful in the case of porous ones, so it has not been prepared.

For thick films, the first tests were performed with the previous optimized slurry used on dense steels ($R_{pm} = 2$ and $R_a = 0.25$). Porous supports were dip-coated into the slurry and withdrawn at 20 cm min^{-1} before sintering at only 800 °C during 2 h in air. We report here works on Ni porous support but the results were similar with the porous steel, in spite of their pore size difference. Micrograph of anodic coating surface (Fig. 5a) shows that obtained NiO–YSZ films are continuous and homogeneous. Here, we notice the same phenomenon as for coatings on dense supports, where particles from alkoxide sol are a cement for composite powders which consolidate the layer. The film is about 20 µm thick as it can be seen on the cross-section micrograph (Fig. 5). In this case, thickness was double the thickness of film coated on dense support. This is due to a better mechanical anchorage of powder contained in the slurry during the withdrawal of porous support. In addition, there is an infiltration of anodic film in the porous support which, after thermal treatment at 800 °C, has led to an interface of few microns thick. In order to limit infiltration of anodic material during dip-coating, a polymer matrix with long carbonaceous chains was also added into the slurry (PEG: polyethylen glycol). Length of carbonaceous chain has been varied by control of the molar mass from 2000 to 20,000, but the infiltration was not significantly reduced. This is not a major problem for the application considering that the porous support is usually at least 1 mm thick.

The main problem for all these coatings is that they have a too weak adhesion on the porous supports (either nickel or steel). Further works will be devoted to improve this interfacial property.

4. Conclusions

NiO–YSZ anodic films were deposited onto both dense and porous metallic substrates by a low cost process which combines the dip-coating technique and the optimized slurries technology. In order to prepare thick coatings, dip-coating media is consisted of NiO–YSZ powders which were synthesized by sol–gel in organic suspensions, which contains a suitable content of alkoxide sol. After calcination at only 800 °C, the obtained layers, on both dense and porous metallic supports, were continuous and homogeneous. The 2 slurry key parameters to obtain such films, which are R_{pm} (mass ratio between powder and dispersive media) and R_a (ratio between alkoxide sol mass and R_{pm}), have been optimized to $R_{pm} = 2$ and $R_a = 0.25$. Some problems of adhesion have to be solved for anodic coatings directly on porous substrates. In all cases, the layer microstructure is significantly porous and thickness of films ranges from 10 to 20 µm depending on the type of support.

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