PROCESSING OF NANOMATERIALS FOR SOLID OXIDE FUEL CELLS IN SUPERCRITICAL MEDIA

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Abstract

In this communication, we describe the synthesis of the SOFC cathode material $Nd_2NiO_{4+\delta}$ in a supercritical ethanol/water medium. Properties of the obtained nanopowders are studied as a function of the ethanol/water ratio, based on X-ray powder diffraction, electronic microscopy (SEM and TEM) and surface area measurements (BET). The synthesis of a new precursor via this route in a 90/10 ethanol/water mixture leads to the formation and crystallisation of the cathode material directly onto the electrolyte after a short thermal treatment. It could induce the formation of an original microstructure at the cathode/electrolyte interface and correspondingly improve the cathode performances. Indeed, using a nanostructured material could raise the kinetic of the electrochemical reactions occurring at the cathode and also lead to the optimisation of the electrode/electrolyte interface, thus allowing overcoming the principal limitations of such materials [1].

Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices able to convert the chemical energy of a fuel in a clean and efficient way. Their relatively high operating temperature (600-1000°C) allows the use of various fuels [2-4], thus overcoming the lack of a hydrogen infrastructure. Other advantages of this environmental friendly technology are its fairly high global efficiency [5,6] and its adjustable power delivery, from 10 W to the MW range (when combined with a gas turbine system) allowing various type of applications [7].

Currently, a major goal in this research field is to reduce the operating temperature down to 600°C, mainly to improve reliability and to reduce the cost of such devices, a reduced operating temperature allowing the use of cheaper materials, as metallic interconnectors for example. However, electrochemical reactions and transport properties are temperature-driven processes, consequently a major drawback in this approach is the decrease of the power density output and the cell efficiency upon decreasing temperature. Indeed, in this case the ohmic and polarization losses occurring respectively at the electrolyte, both electrodes and the electrode/electrolyte interface increase. Moreover, besides the intrinsic properties of the cathode materials, their performances really depend on shaping and microstructure. Optimisation of the interface between the cathode and the electrolyte as well as control of the micro-structural properties of the starting powder (particle size, morphology, cristallinity…) are crucial to optimize the electrochemical performances [8].

On the path to intermediate temperature SOFCs, the development of high performance cathode materials remains a challenge because few materials exhibit high electrocatalytic activity towards oxygen reduction, sufficient mixed (ionic and electronic) conductivity and good mechanical properties. The most commonly used cathode materials, doped lanthanum manganite perovskites are essentially electronic conductors and lead to poor performances at the target temperature. Many studies are focussed on the investigation of new cathode materials. Due to its structure able to stabilize an additional oxygen sub-lattice in the rock-salt layer, $Nd_2NiO_{4+\delta}$ exhibits high mixed ionic and electronic conductivity and emerges as a promising cathode material [9].

$Nd_2NiO_{4+\delta}$ is commonly prepared by solid state reaction of the corresponding oxides Nd_2O_3 and NiO at temperatures up to 1100°C during several hours. Alternatives synthesis such as co-precipitation,

nitrate-citrate or Pechini routes lead to finer particles and require lower synthesis temperature but a high temperature calcination step is still needed to obtain the required phase.

In the last 15 years, extensive work has been done on the synthesis in supercritical fluids of various oxides in nanopowder forms [10-18]. Hydrolysis of metal salts [11,12] or metal acetates [13-15] in supercritical water, followed by hydroxide dehydration are reported to be efficient routes to synthesize metal oxides. Recently, the synthesis of $La_4Ni_3O_{10}$ and $La_3Ni_2O_7$ in supercritical water using a continuous flow reactor was reported [19]. The synthesis of a mixture of lanthanum and nickel hydroxides, which then undergo a high temperature heat treatment during 12 hours, leads to the formation of the corresponding oxides. This result is significant because the formation of these materials generally requires lengthy heat treatment during several days.

Most papers are dedicated to the synthesis of oxides in supercritical water but only a few ones describe the synthesis of nanomaterials in a alcohol/water supercritical mixture [17,20]. Though, as shown especially in our team [17], this mixture could lead to interesting results, lowering the critical temperature and promoting the crystallization. Further efforts are still required to a fundamental comprehension of the role of alcohol in such mixtures.

In this communication, we describe the synthesis of the SOFC cathode material $Nd_2NiO_{4+\delta}$ in a supercritical ethanol/water medium. We will discuss the properties of the obtained nanopowders as a function of the ethanol/water ratio, based on X-ray powder diffraction, electronic microscopy (SEM and TEM) and surface area measurements (BET). Furthermore, deposition of the cathode onto the electrolyte was performed in order to characterize the electrochemical properties of this material.

Experimental section

The experiments were performed using a continuous flow reactor, allowing short reaction times and fine control of the operating parameters [16]. The setup consists of a high pressure pump, a tubular coiled reactor, external heating system, a cell for powder recovery and a back pressure regulator (see Figure 1).

First, neodymium and nickel acetates are easily dissolved into water. A few minutes before injection, a precise amount of ethanol is added to the solution. The precursor solution is injected via a high pressure pump through the tubular coiled reactor, where supersaturation in the supercritical fluid occurs, initiating the chemical reaction leading to the synthesis of nanopowders. The obtained powders are recovered at the end of the setup. Pressure inside the system is kept in the 20-25 MPa range, depending on the experiment. Temperature was varied from 200 to 500°C.

The influence of 1) the acetates concentration, 2) the initial Nd/Ni and $EtOH/H_2O$ ratios and 3) the reaction temperature were mainly studied.
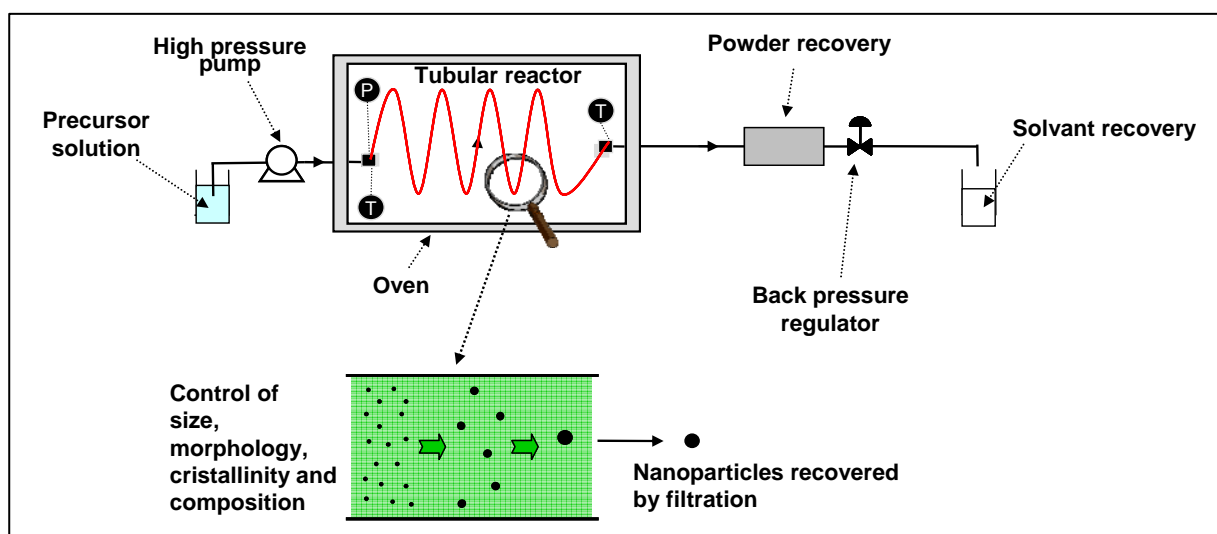

Figure 1: Scheme of the experimental setup (from [21])

Characterization of the synthesized phases was performed using X-ray powder diffraction (XRD, PANalytical X'pert MPD diffractometer in θ-θ configuration with a Cu Kα radiation (λ=1.5418 Å)). Particle size and morphology were determined by scanning electron microscopy (SEM, JEOL 840A, ZEISS Evo50, JEOL JSM6700F) and transmission electron microscopy (TEM JEOL 2000FX). BET surface of the powders was estimated with a Micromeritics ASAP 2010. Elementary analysis of the products was carried out using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 720-ES).

Results and discussion

Experiments with different ethanol/water molar ratios i.e. 90/10 (T_c=521 K, P_c=6.6 MPa), 75/25 (T_c=526 K, P_c=7.6 MPa), 50/50 (T_c=547 K, P_c=9.7 MPa), 25/75 (T_c=580 K, P_c=14.4 MPa), 0/100 (pure water, T_c=647 K, P_c=22.1 MPa) were conducted to evaluate the influence of the ethanol content in the supercritical mixture (see reference [22] for the critical coordinates of the ethanol/water mixtures). Analysis of the XRD patterns of the obtained powders (see Figure 2) shows that a reaction temperature below 300°C does not conduct directly to the formation of the $Nd_2NiO_{4+\delta}$ phase, this phase being usually formed after a heat treatment around 1100°C, either in the case of solid state reaction or wet chemical routes [23].

XRD pattern of the powders elaborated in a 90/10 mixture doesn't exhibit any identifiable peaks, neither those of the acetates precursors or those corresponding to the various expected decomposition products. We assume that this XRD pattern could correspond to a new crystalline "precursor" intimately composed of neodymium and nickel which composition and structure are currently under investigation.

In the case of the 75/25 mixture, the corresponding XRD pattern is quite similar to the previous one, exhibiting peaks attributed to the new "precursor" powder, except the addition of small diffraction peaks due to the hydroxide $Nd(OH)_3$ (JCPDS 83-2035).

For the experiments conducted with a molar ratio of 50/50, 25/75 and 0/100, XRD patterns are completely different from the previous ones and similar between them, the hydroxides $Nd(OH)_3$ and $Ni(OH)_2$ (JCPDS 14-0117) become the predominant phases. Note that some additional peaks due to $NdOHCO_3$ (JCPDS 70-1526) are also present to a small degree.
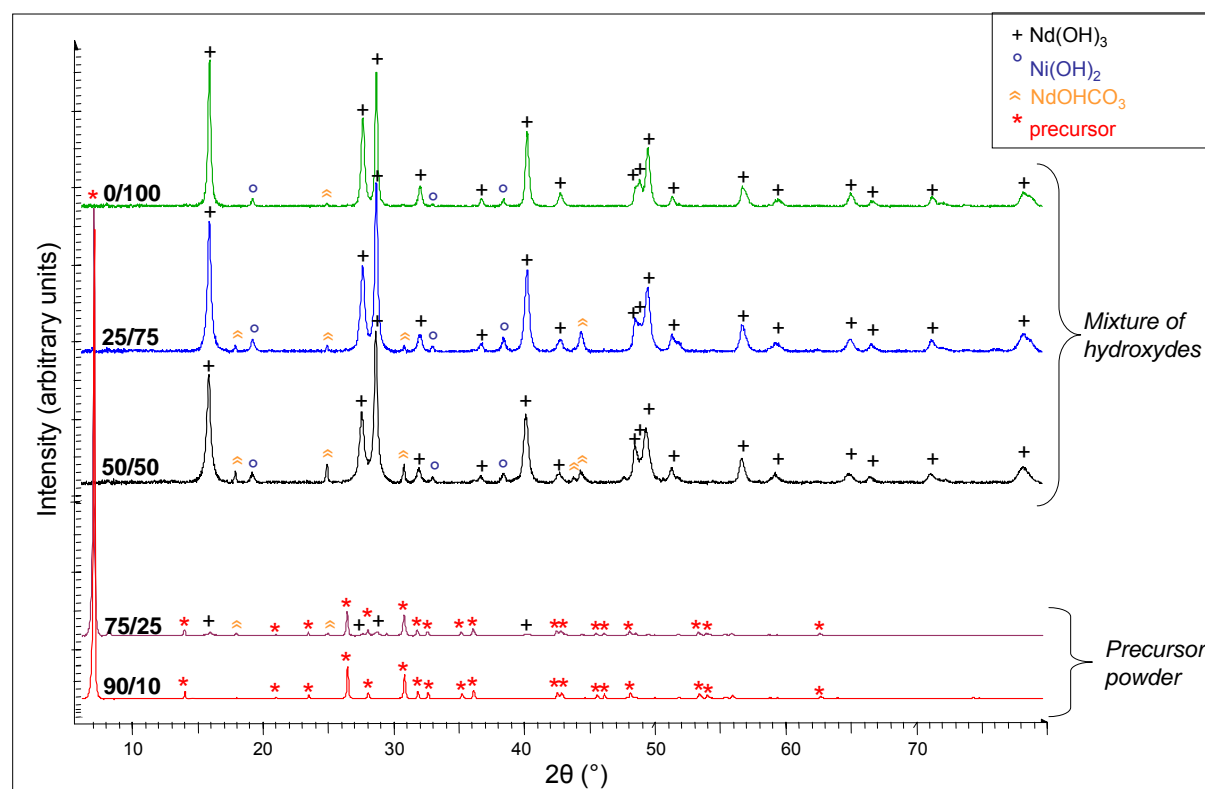

Figure 2: XRD patterns of powders elaborated at 290°C and 20 MPa with different ethanol/water ratios

Differences in the chemical composition of the obtained precursors underline the role of the ethanol ratio in the initial ethanol/water mixture. Controlling the ethanol content allows initiating one of the 2 different chemical reactions observed. The first reaction mechanism, still under investigation, leads to crystallisation of a new neodymium and nickel "precursor" and crystallisation of $Nd_2NiO_{4+\delta}$ as soon as 900°C. The second reaction mechanism is the first step of a more conventional hydrothermal reaction, hydrolysis of the metal acetates, leading to the formation of the corresponding hydroxides $Nd(OH)_3$ and $Ni(OH)_2$.

Further studies are still underway, investigation of the chemical composition and structure of the new "precursor" is crucial for the determination of the reaction mechanism involved during the elaboration of powders in an ethanol rich mixture.

In the case of a 90/10 ethanol/water ratio, no traces of the crystallisation of hydroxides appear. For a 75/25 ethanol/water mixture, the first reaction mechanism is still clearly predominant while the crystallisation of $Nd(OH)_3$ indicates that hydrolysis seems to occur simultaneously. As expected, hydrolysis becomes more predominant when increasing the water amount, it is clearly the predominant reaction from a 50/50 molar ratio to a 0/100 one (see Figure 2).

The ethanol/water ratio then controls the chemical reaction occurring during the synthesis. Consequently it has a great influence on the crystallographic structure of the material and morphology of the powders as checked by SEM and TEM analyses. Surface properties of the powders also depend on the ethanol content; BET surface varies from 10 m²/g (pure water) to 32 m²/g (90/10 ethanol/water ratio).

We focus now on the results obtained with the powders synthesized in the 90/10 ethanol/water mixture.

SEM and TEM analysis reveal a heterogeneous morphology of the "precursor" powders, consisting of needles and plates, partially agglomerated. One can note on the SEM pictures (see Figure 3) the diversity of the objects size, with aggregates in the range of the micrometer size and also finer objects.
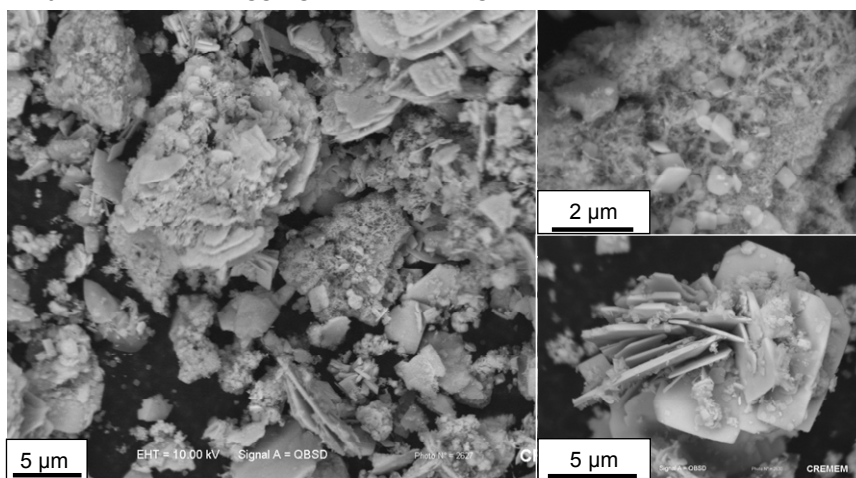
Figure 3: SEM pictures of "precursor" powders (T= 290°C, P=20 MPa, ethanol/water 90/10)

TEM analysis gives us more information on a smaller scale, plates are in the 100-500 nm range and very small needles seem to be located on the edge of them. Agglomerates are also present, presumably composed of the same plates and needles previously observed in SEM.

Given the heterogeneous morphology of these powders it is quite impossible to give a particle size; in order to evaluate the surface area of the powders, BET measurements were carried out under nitrogen, the BET surface of the "precursor" powders is evaluated at around 32m²/g which is a relatively high value.

To promote crystallisation of the required phase, heat treatments in static air of the "precursor" powders were conducted in the range 300-1100°C during 6 hours. Crystallisation of $Nd_2NiO_{4+\delta}$ (JCPDS 89-0131) is observed from 900°C, which is fairly low, however at this temperature additional

phases such as Nd_2O_3 (JCPDS 41-1089 and 65-3184) and NiO (JCPDS 44-1159) still remain important; annealing at 1100°C favours crystallisation of $Nd_2NiO_{4+\delta}$ over the single oxides. In order to optimize the purity of the final product, the influence of the initial Nd/Ni ratio is currently studied by elementary analysis (ICP-OES).

It is worth noticing that even if this process still requires a thermal treatment at high temperature, the calcination step is here shorter; XRD patterns corresponding to annealing at 1100°C for 1, 6 or 12 hours are almost identical. A calcination step of 1 hour is sufficient to obtain well crystallized $Nd_2NiO_{4+\delta}$. This relatively short annealing time enable the direct deposition of the "precursors" powders onto the electrolyte in order to form the cathode material directly onto this support, instead of cumulating steps of 1) calcination of powders until sufficient crystallization and 2) thermal treatment of the coating on the electrolyte. A short annealing time is also advantageous to minimize chemical reactivity and interdiffusion at the cathode/electrolyte interface.

As checked by XRD, $Nd_2NiO_{4+\delta}$ is well crystallized and rather pure after annealing of a "precursor" ink on the electrolyte (dense pellet of 8YSZ, 8 mol% Y_2O_3-doped ZrO_2) at 1100°C for 3 hours in air (see Figure 4).

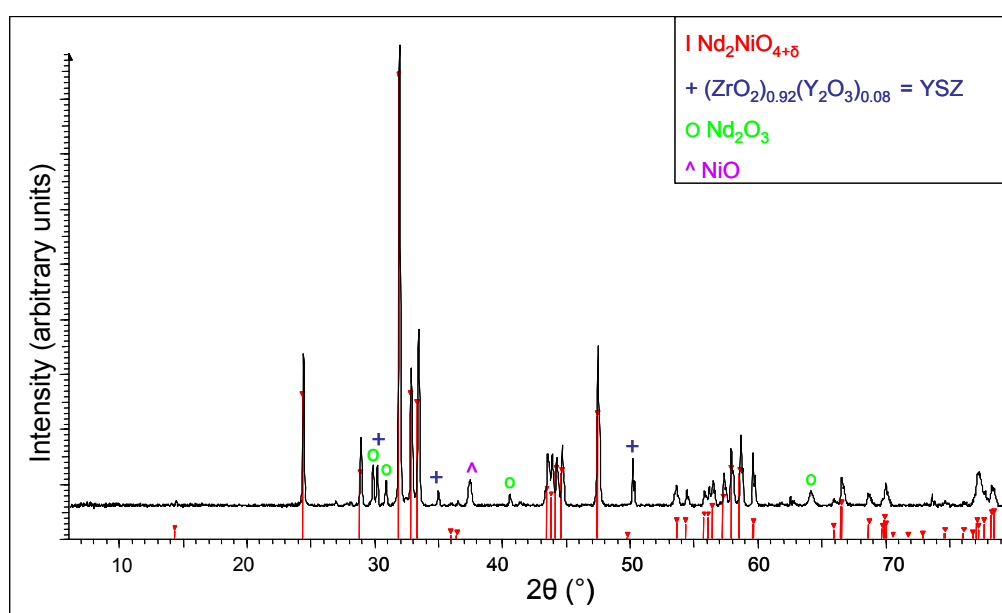Figure 4: XRD pattern of "precursor" ink coated on a YSZ pellet and treated 3 hours in air at 1100°C

After deposition on the electrolyte, the morphology of the cathode coating (20-30µm thin) consists of a porous network formed by percolated grains in the micrometer range (see Figure 5). The adhesion between the electrolyte and the cathode seems intimate, any delamination is observed.
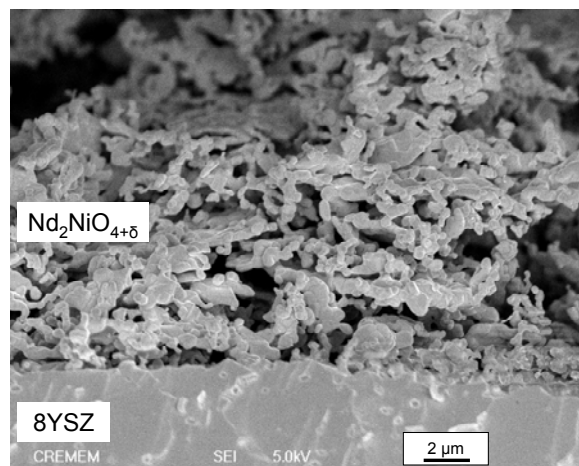

Figure 5: HR-SEM picture of the "precursor" ink coated on a YSZ pellet and treated 3 hours in air at 1100°C

Impedance spectroscopy measurements were carried out on a symmetrical half cell (consisting of an electrolyte (8YSZ, 8 mol% Y_2O_3-doped ZrO_2) pellet coated on both sides with the electrode material to characterize) to evaluate the electrochemical properties. For the deposition, a basic hand painting process was used, however the properties of the material largely depend on the deposition process; therefore the first results are encouraging, optimization of this step (i.e. optimisation of the deposition temperature, use of the screen printing method…) may lead to a significant decrease of the measured resistances.

Conclusion

A new neodymium-nickel crystalline precursor has been obtained in an ethanol/water supercritical mixture, leading to the direct formation of the cathode material $Nd_2NiO_{4+\delta}$ on the electrolyte during a short firing step (3 hours) at 1100°C. Electrochemical properties were evaluated via impedance spectroscopy; first results are encouraging and optimisation of the process is still underway.

Control of the nature of the chemical reaction is accessed via the initial ethanol/water ratio, allowing modifications of the powders properties, such as crystal structure, morphology and BET surface. Neodymium and nickel hydroxides in the nanometer range can be obtained from a 50/50 to a 0/100 ethanol/water ratio.

This work is now extended to the elaboration of numerous ceramics, one objective being the synthesis of composite ceramics in a one-step synthesis, in order to maximise the degree of intimacy of both ceramics with each other.

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