

OPTIMISATION OF SOLID OXIDE FUEL CELL MATERIALS VIA UNCONVENTIONAL ROUTES: SUPERCRITICAL FLUIDS AND SPRAY PYROLYSIS

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I. INTRODUCTION :

Nowadays it is crucial to find new ways to produce environmentally-friendly energy in a highly efficient way. In this respect, solid oxide fuel cells (SOFCs) are a promising technology, offering significant advantages such as a high global efficiency via cogeneration of heat and electricity or the possibility to use various fuels as a primary source of energy like hydrogen or natural gas or gasoline, for instance.

Materials with Mixed Ionic and Electronic Conductivity (MIEC) turn out particularly interesting as cathode materials for IT-SOFC (Intermediate Temperature SOFCs, operating temperature around 600 °C). Nickelates $\text{Ln}_2\text{NiO}_{4+\delta}$ (with Ln =La, Nd, Pr) with K_2NiF_4 -type structure exhibit a reasonable electronic conductivity associated with an important ionic conductivity due to their structural oxygen overstoichiometry [1,2]. The compound $\text{Nd}_2\text{NiO}_{4+\delta}$ was selected for its good electrocatalytic properties (surface exchange coefficient k) and oxygen transport properties (oxygen diffusion coefficient D^*) [3,4]. Its performances as a cathode material are promising since impedance spectroscopy measurements carried at the ICMCB lead to Area Specific Resistance (ASR) lower than $1 \text{ } \Omega\cdot\text{cm}^2$ at 700 °C [5]. Nevertheless the interfacial resistance between the cathode and the electrolyte was identified as the limiting step in the process of oxygen reduction [6]. Thus to improve this interface, the present work focuses on the synthesis of nanoparticles.

We carried out two original techniques to synthesize this material: chemistry in supercritical fluids [7,8] and ultrasonic spray pyrolysis [9]. Both processes involve reactions at moderate temperatures (respectively 300 and 700 °C compared to solid state reaction at 1100 °C) associated with very short residence times (around 10 seconds).

II. SUPERCRITICAL FLUID ROUTE :

In the last 15 years, extensive work has been done on the synthesis in supercritical fluids of various oxides in nanopowder forms [10-13]. 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 [12,14]. Though, as shown especially in our team [12], 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.

The experiments were performed using a continuous flow reactor, allowing short reaction times and fine control of the operating parameters [7,15]. 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.

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.

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 [16] for the critical coordinates of the ethanol/water mixtures). Analysis of the XRD patterns of the obtained powders shows that a reaction temperature below 500°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 [17].

XRD pattern of the powders elaborated in a 90/10 ethanol/water mixture doesn't exhibit any identifiable peaks, neither those of the acetates precursors or those corresponding to the various expected decomposition products. In the case of the 75/25 mixture, the corresponding XRD pattern is quite similar to the previous one, except the addition of small diffraction peaks due to the hydroxide $Nd(OH)_3$ (JCPDS 83-2035).

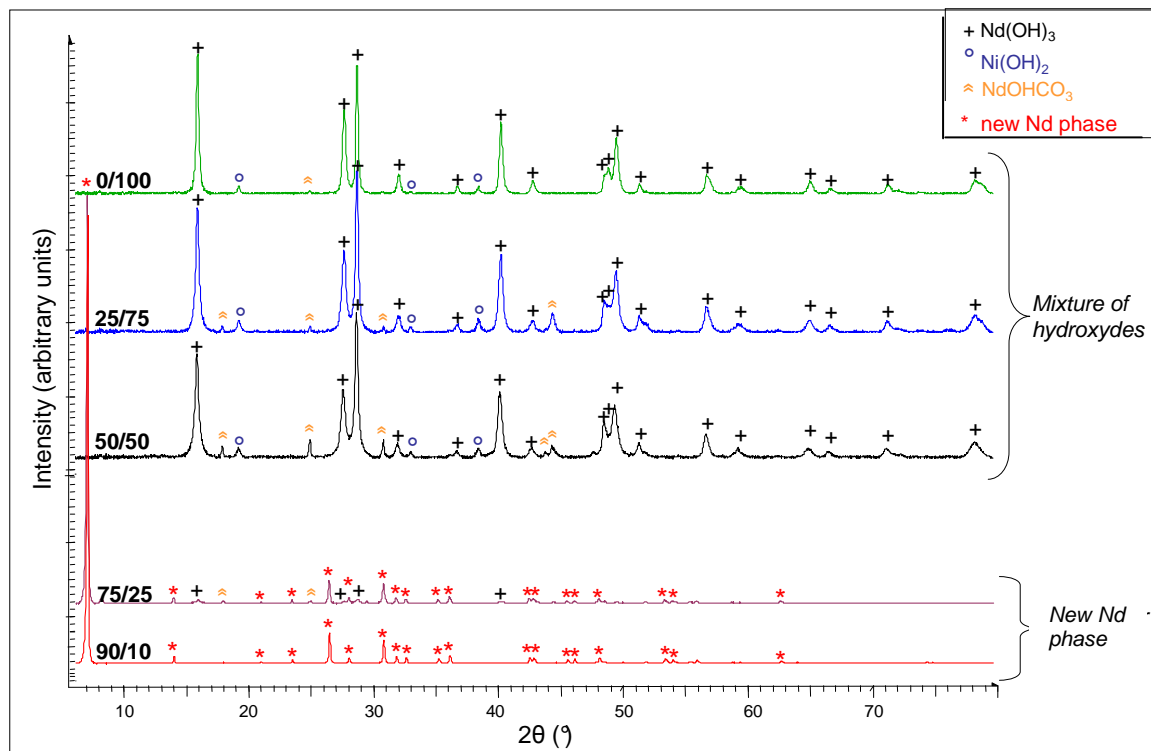


Figure 1: XRD patterns of powders elaborated at 290°C and 20 MPa with different ethanol/water ratios

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 $\text{Nd}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ (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 (see Figure 1). Differences in the chemical composition of the obtained powders 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 is still under investigation, the second one is the first step of a more conventional hydrothermal reaction, hydrolysis of the metal acetates, leading to the formation of the corresponding hydroxides $\text{Nd}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$.

Further investigations of the chemical composition and structure of the phase obtained in a 90/10 ethanol/water mixture is crucial for the determination of the reaction mechanism involved during the elaboration of powders in an ethanol rich mixture. First it appeared that this is only a Nd phase as synthesis carried without Ni acetate leads to the same XRD pattern (it is reasonable to think that Ni remained mainly amorphous in previous experiments). CHNS elementary analysis shows a non negligible carbon content (around 10 weight percent) indicating that hydrolysis of the acetate precursor is probably incomplete. Nevertheless TGA data show that this phase is quite thermally stable, exhibiting only a 5% weight loss at 380 °C. Profile matching of this XRD pattern using the Fullprof software shows very good agreement with a tetragonal structure (cell parameters $a=3,978 \text{ \AA}$, $c=12,744 \text{ \AA}$). The high c cell parameter tends to indicate this phase could have a lamellar structure; structural refinements are still currently under way.

The ethanol/water ratio 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 m^2/g (pure water) to 32 m^2/g (90/10 ethanol/water ratio). SEM and TEM analysis reveal a heterogeneous morphology of the powder obtained in a 90/10 mixture, consisting of needles and plates, partially agglomerated. One can note on the SEM pictures (see Figure 2) the diversity of the objects size, with aggregates in the range of the micrometer size and also finer objects.

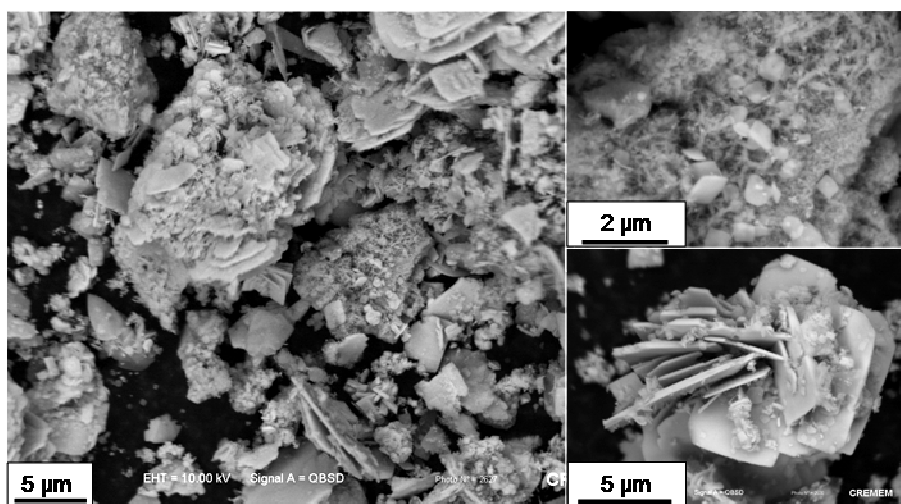


Figure 2: SEM micrographs of Nd-Ni powders synthesized in supercritical fluids ($T= 290^\circ\text{C}$, $P=20 \text{ MPa}$, ethanol/water 90/10)

Calcination in air of these powders at 1100 °C for 1h leads to crystallisation of the desired phase Nd₂NiO_{4+δ}.

III. ULTRASONIC SPRAY PYROLYSIS METHOD :

In an effort to obtain nanopowders of Nd₂NiO_{4+δ}, we also explored a second way of synthesis, namely ultrasonic spray pyrolysis. This technique has been developed since 1970 and is a convenient way to obtain nanopowders or thin films (in this work we only focused on the elaboration of nanopowders). Its principle is quite simple; the reaction mechanism can be described in 3 steps. First a precursor solution (generally aqueous) is sonicated, generating an aerosol. Then this aerosol is carried thanks to a gas through a high temperature furnace where pyrolysis of the droplets occurs, leading to solvent evaporation, precursor decomposition and powder formation. In the end gases are vented and dry powders are recovered via a filter. In our experiments we used an aqueous precursor solution of Nd and Ni nitrates, synthetic air as a gas carrier and an electrostatic filter was put in the end of the setup to recover dry powders.

The main parameters influencing the powder properties are the temperature, gas flow (controlling the residence time), precursor concentration and ultrasonic frequency. Reaction temperature doesn't greatly affect the particle morphology as for 700, 900 and 1100 °C the particles showed the same spherical shape and a broad particle size distribution; but it certainly affects the crystallisation of these particles. In fact, at 1100 °C the only phase observed by XRD is Nd₂NiO_{4+δ}, small width at half maximum of the diffraction peaks indicating high crystallinity whereas at 700 °C no phase is easily identified, the XRD pattern consisting mainly of 3 very broad peaks indicating the amorphous nature of the powder at this moderate temperature. Calcination at 900 °C during 1h leads to crystallisation of pure Nd₂NiO_{4+δ}; as expected, raising the temperature promotes crystallisation.

Precursor concentration also plays an important role on the reaction mechanism; low concentration (i.e. 10⁻⁴ M) allows to obtain pure Nd₂NiO_{4+δ} while high precursor concentration (i.e. 10⁻² M) facilitates the formation of Nd₂O₃ along with Nd₂NiO_{4+δ}. Anyway, calcination at 900 °C during 1h leads to enhanced crystallisation and Nd₂NiO_{4+δ} then remains the only crystallised phase. This suggests that high concentrations may be detrimental to the formation of the mixed oxide during the reaction, partly leading to crystallisation of Nd₂O₃ and decomposition of Ni precursor in a rather amorphous state, then requiring further annealing to complete Nd₂NiO_{4+δ} formation.

It is also important to take the effect of the ultrasonic frequency into account. It is well known that this frequency directly controls the droplet size in the aerosol and so the particle size in the end (theoretical particle size is proportional to frequency to the power -2/3). We performed experiments using 2 different frequencies, 1.7 and 2.5 MHz. According to Lang's equation [18], going from 1.7 to 2.5 MHz should correspond to a size reduction factor of about 1.3. Experimentally we effectively observed a great size reduction, even exceeding the theoretical one. In both cases the smaller particles have roughly the same size but with the highest frequency the larger particles are much smaller (about a factor of 2) which tends to suggest that higher frequency helps preventing aggregation during the reaction, thus narrowing the particle size distribution as illustrated in Figure 3. With an ultrasonic frequency of 2.5 MHz (reaction temperature of 700 or 1100 °C), particle size varies between 5 and 500 nm, BET surface area measurements exhibiting BET surface of 15 m².g⁻¹.

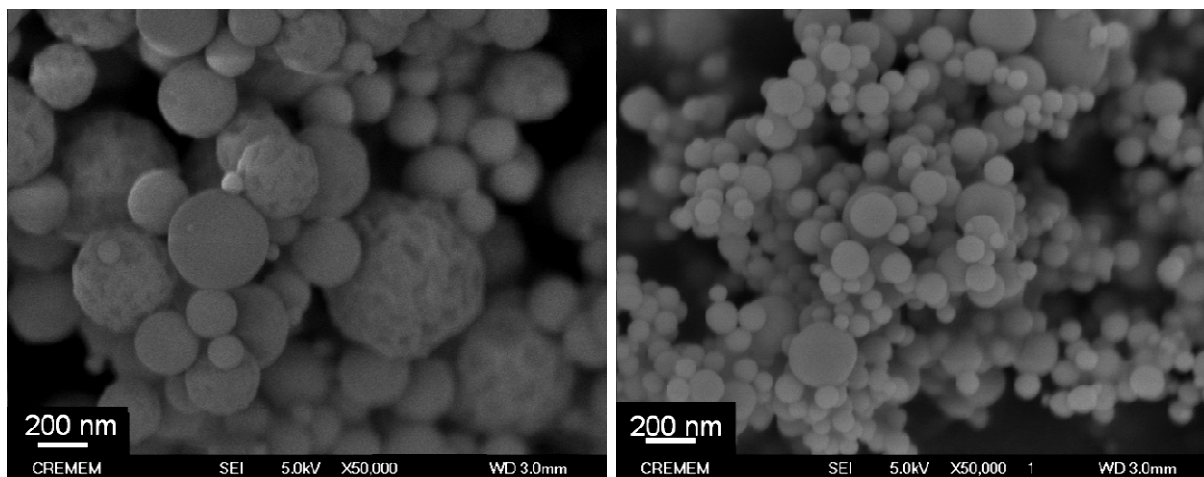


Figure 3: SEM-FEG pictures of Nd-Ni powders synthesized by spray pyrolysis ($T=700^{\circ}\text{C}$, $C=10^{-4}\text{ M}$)
 a. $f=1.7\text{ MHz}$, b. $f=2.5\text{ MHz}$

IV. CONCLUSION :

Supercritical fluids and ultrasonic spray pyrolysis have proved effective to synthesize $\text{Nd}_2\text{NiO}_{4+\delta}$ powders with a very short reaction time and moderate temperatures, powders exhibiting different morphologies and particle sizes, and requiring minimum heat treatments to obtain crystalline $\text{Nd}_2\text{NiO}_{4+\delta}$ (respectively 1100°C 1h and 900°C 1h, no heat treatment required for spray pyrolysis experiments at 1100°C).

Electrochemical properties of these powders were studied by electrochemical impedance spectroscopy. Measurements were carried on symmetrical half cells, consisting of an electrolyte coated on both sides with a cathode layer. Powders were mixed with different solvents to turn into inks then applied on both sides of a YSZ (Yttria Stabilized Zirconia, 8 mol% Y) electrolyte pellet. Influence of the synthesis parameters (reaction temperature, concentration...) as well as influence of the post-synthesis treatment (powder calcined or not prior to deposition, sintering temperature after deposition) have been studied.

REFERENCES :

- [1] E. Boehm et al. *Solid State Ionics*, 176, **2005**, 2717.
- [2] G. Amow and S. Skinner. *J. Solid State Electrochem.*, 10, **2006**, 538.
- [3] J. Wan, J.B. Goodenough, and J.H. Zhu. *Solid State Ionics*, 178, **2007**, 281.
- [4] C. Lalanne et al. *J. Eur. Ceram. Soc.*, 27, **2007**, 4195.
- [5] C. Lalanne et al., *Proc. 6th Europ. SOFC*, **2004**, (M. Mogensen, Ed.), ISBN 3-905592-15-0, p.1351.
- [6] F. Mauvy et al. *J. Eur. Ceram. Soc.*, 25, **2005**, 2669.
- [7] C. Aymonier et al. *J. Supercrit. Fluids*, 38, **2006**, 242.
- [8] C. Aymonier et al. *J. Supercrit. Fluids*, 48 (1), **2009**, 79.
- [9] E. Djurado, E. Meunier, *J. Solid State Chem.*, 141, **1998**, 191.
- [10] T. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.*, 75(4), **1992**, 1019.

- [11] A. Cabañas, J.A. Darr, E. Lester, M. Poliakoff, *J. Mater. Chem.*, 11, **2001**, 561.
- [12] C. Aymonier, C. Elissalde, H. Reveron, F. Weill, M. Maglione, F. Cansell, *J. Nanosci. Nanotech.*, 5, **2005**, 980.
- [13] X. Weng, P. Boldrin, I. Abrahams, S.J. Skinner, J.A. Darr, *Chem. Mater.*, 19, **2007**, 4382.
- [14] A. Cabañas, J. Li, P. Blood, T. Chudoba, W. Lojkowski, M. Poliakoff, E. Lester, *J. Supercrit. Fluids*, 40, **2007**, 284-292.
- [15] S. Moisan, J.D. Marty, F. Cansell, C. Aymonier, *Chem. Commun.*, **2008**, 1428.
- [16] A.R. Bazaev, I.M. Abdulagatov, E.A. Bazaev, A. Abdurashidova, *J. Chem. Thermodynamics*, 39, **2007**, 385-411.
- [17] J. Wan, J.B. Goodenough, J.H. Zhu, *Solid State Ionics*, 178, **2007**, 281.
- [18] R.J. Lang, *J. Acoust. Soc. Am.* 34, **1962**, 6.