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# Synthesis of $\text{La}_2\text{NiO}_{4+\delta}$ oxides by sol–gel process: Structural and microstructural evolution from amorphous to nanocrystallized powders

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## Abstract

In this paper, the structural and microstructural transition from amorphous to  $\text{La}_2\text{NiO}_{4+\delta}$  nanocrystallized oxides synthesized by a polymeric route based on Pechini's work has been studied by several experimental techniques including infrared spectroscopy and wide angle X-ray scattering. The synthesis parameters which govern this transition have been identified in order to synthesize  $\text{La}_2\text{NiO}_{4+\delta}$  oxides with various mean crystallite sizes and non stoichiometry levels. Therefore, it has been demonstrated that the control of the nature and the content of organic compounds in the polymeric sols allows the preparation of  $\text{La}_2\text{NiO}_{4+\delta}$  metastable phases with a mean crystallite size ranging from 100 to 220 nm and a non stoichiometry level ranging from 0.15 to 0.22 at 25 °C. As the cathodic performance strongly depends on the physical characteristics of the oxides, this study shows that our versatile process may be suitable to elaborate electrodes with different electrochemical behaviours.

**Keywords:** A. Oxides; B. Sol–gel chemistry; C. Infrared spectroscopy; C. X-ray diffraction

## 1. Introduction

Currently, the development of the SOFC technology is limited by high cells working temperature. This necessitates the use of high-cost interconnector materials and reduces the cell life performance due to interdiffusion between its components, high electrode sintering and strong thermal stress. Therefore, lowering the operating temperature at 700 °C without decreasing the cell power density is the current challenge for this technology. This would allow the use of cheaper ancillary and an increase in the cell life [1,2]. However, preliminary results obtained on the regular manganite-based SOFCs cathodes showed that a reduced operating temperature leads to both high electrolyte resistivity and cathodic polarization resistance. To overcome these problems, various solutions have been proposed. Therefore, lot of works have been done to reduce the thickness of the electrolyte in order to decrease the ohmic drop. For the cathode materials, one approach is based on the optimisation of the electrode microstructure in order to

minimise the ohmic loss by increasing the triple boundary length [2,3]. Another solution is to use mixed conducting oxides as they provide a considerable decrease in the polarization resistance due to an enlargement of the electrochemical reaction zone [4].

Among the mixed conductors, the Ruddlesden–Popper phases  $\text{Ln}_2\text{NiO}_{4+\delta}$  have been receiving much attention in the last few years for their application as cathode material in solid oxide fuel cells working at intermediate temperature (ITSOFC) [5]. Much of this interest stemmed from the fact that these oxides present high oxygen ionic mobility due to their accommodation of high oxygen overstoichiometries. Moreover, they show strong electrocatalytic activity towards the oxygen reduction and have their thermal expansion coefficients close to those of the conventional electrolytes used in the SOFC device [5–8]. These promising properties have been shown to strongly enhance the cathodic electrochemical performance. Indeed, previous impedance spectroscopy studies have shown that  $\text{Ln}_2\text{NiO}_{4+\delta}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) exhibit lower polarization resistances than lanthanum strontium manganite (LSM) perovskite, the usual cathode material [8,9].

The present paper deals with the synthesis by a sol–gel route of  $\text{La}_2\text{NiO}_{4+\delta}$  nanomaterials and focuses on the study of the formation of the well-crystallized phase when two types of polymeric sols are used as precursors. The understanding of the structural transition from amorphous to crystallized powders and the determination of the relevant synthesis parameters will allow a better control of the physical characteristics of the powders. As cathodic electrochemical performance strongly depends on both grain size and non stoichiometry of the oxide, these parameters may be used as a way to prepare electrodes with different electrochemical behaviours.

## 2. Experimental

### 2.1. Preparation of $\text{La}_2\text{NiO}_{4+\delta}$ powders

$\text{La}_2\text{NiO}_{4+\delta}$  phases have been synthesized via a polymeric route using solutions similar to those outlined by Pechini [10]. Reagent grade  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  nitrates were used as starting salts. They were dissolved in deionised water in stoichiometric amounts, as described elsewhere [11].

In order to determine the effects of the resins nature on the  $\text{La}_2\text{NiO}_{4+\delta}$  formation, either hexamethylenetetramine, acetic acid and acetylacetone (referenced as P1 resin in this paper) or citric acid and ethylene glycol (referenced as P2 resin) were added to obtain an organic–polymeric complex containing the metal cations. In these resins, both acetylacetone and citric acid acted as chelating agents. According to our previous studies [12], the chelating agent to cations source ratio ( $R$ ) was ranging from 2 to 3 in order to obtain homogeneous sols.

The transition from polymeric sols to  $\text{La}_2\text{NiO}_{4+\delta}$  oxides has been studying using sols preliminary dehydrated in air at 80 °C. All green–brown powders were then divided into seven batches which were calcined in air at a temperature ranging from 200 to 700 °C for 2 h, with a heating rate of 100 °C/h. Dried sols were also calcined at 1000 °C in air for 2 h with a heating rate of 100 °C/h, in order to get a well-determined oxides structure.

### 2.2. Transition from polymeric sols to $\text{La}_2\text{NiO}_{4+\delta}$ oxides

#### 2.2.1. Infrared spectroscopy

Infrared spectroscopy was performed using a Perkin-Elmer 1760× Fourier Transformed Infrared spectrometer coupled with a TGS detector. Samples were incorporated in KBr pellets (2 mg of sample for 200 mg of KBr). One hundred and twenty-eight scans were recorded and the resolution of spectra was estimated to be 4  $\text{cm}^{-1}$ .

#### 2.2.2. Wide angle X-ray scattering

Powders were sealed in a Lindeman capillary. The X-ray diffraction profile for the sample irradiated with graphite monochromatized  $\text{Mo K}\alpha$  radiation, was obtained using a Philips PF 1380 diffractometer. 457 intensities corresponding to equidistant ‘ $s$ ’ points ( $s = 4\pi \sin \Theta/\lambda$ ;  $\delta s = 0.035 \text{ \AA}^{-1}$ ) were collected in the range of  $0 < \Theta < 65^\circ$ . In this paper, samples will be characterised by the reduced intensity representing the structural part of the scattering phenomenon after full corrections and the reduced radial distribution (RDF), which is the Fourier transform of this spectrum and corresponds to a histogram of ordered distances weighted by the distance multiplicity and the number of electrons engaged in these bonds.

### 2.2.3. Chemical analysis

The carbon, nitrogen and hydrogen residual content of each powder annealed from 200 to 700 °C was determined by ion-coupled plasma (I.C.P.) spectroscopic analysis performed at the L.C.C. laboratory.

### 2.2.4. XRD analysis

The determination of the crystallographic structure of powders annealed at 1000 °C was performed by X-ray diffraction using a Seifert XRD 3003 TT diffractometer with the Cu K $\alpha$  radiation ( $\alpha_{\text{Cu}} = 0.15418$  nm). The mean coherence length of the powders was calculated using the Sherrer's formula. Transmission electron microscopy (TEM) analyses have also been performed on these powders and showed that the grains have a spherical shape [15]. The mean grain sizes evaluated by TEM were in good agreement with the mean coherence lengths determined from XRD analyses, indicating that the mean coherence length corresponded to the crystallite size.

### 2.2.5. Non stoichiometry

The non stoichiometry  $\delta$  of  $\text{La}_2\text{NiO}_{4+\delta}$  oxides was determined through temperature programmed reduction (TPR) followed by thermogravimetric analysis under a mixture of 10%  $\text{H}_2/\text{Ar}$ . The experiments were carried out in a vertical lug flow reactor. The mass variation of the oxide (initially 80 mg) was followed with a Cahn D200 electrobalance. The sample was first depressed (1 Pa) at room temperature for 1 h and the reactor was then filled with the gas mixture, maintaining a flow of  $15 \text{ cm}^3 \text{ min}^{-1}$ . The temperature was then linearly increased with a heating rate of  $5 \text{ K min}^{-1}$  up to 900 °C. This process gives rise to the formation of  $\text{La}_2\text{O}_3$  oxide and Ni metal as shown by XRD analysis.

To confirm these non stoichiometry levels, iodometric titrations were done [13]. Both techniques lead to the determination of similar  $\delta$  values. Therefore, the non stoichiometry levels reported in this paper correspond to the average of both values determined by TPR and iodometric titration.

## 3. Results

The structural steps occurring during the sols thermal decomposition have been determined from the characterization by infrared spectroscopy of powders synthesized from both P1 and P2 resins, annealed in air from 200 to 700 °C. In the 3900–400  $\text{cm}^{-1}$  wave number range, the same evolution of the infrared spectra was observed whatever the nature of the resin, as shown in Fig. 1.

Three steps can be clearly distinguished as a function of the temperature. For the first one occurring below 300 °C, infrared spectra (a and b) exhibit five broad bands between 1900 and 900  $\text{cm}^{-1}$  that can be attributed to the formation of a stable polymeric precursor. In this range, the band pointing at 1380  $\text{cm}^{-1}$  is assigned to the  $\text{NO}_3^-$  anions coming from the metallic salts introduced in the initial solution. This indicates that nitrate species are still not completely decomposed below 300 °C.

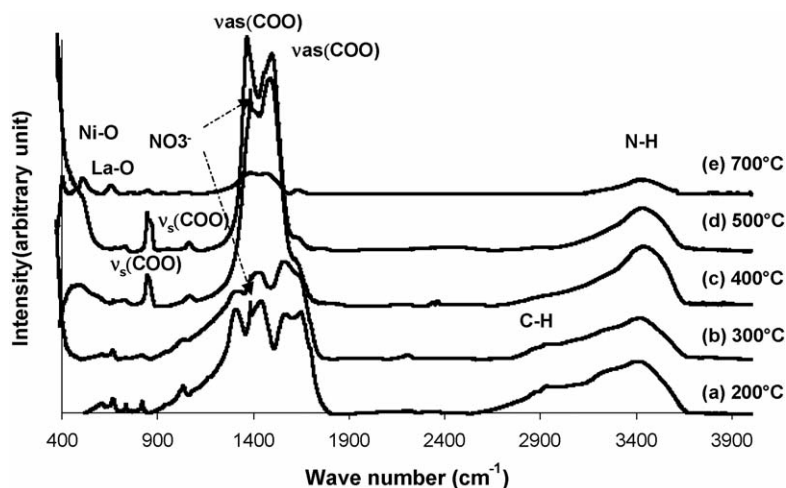


Fig. 1. Evolution of the infrared spectra of powders annealed in air at different temperatures with a dwelling time of 2 h, for P1 and P2 resins.

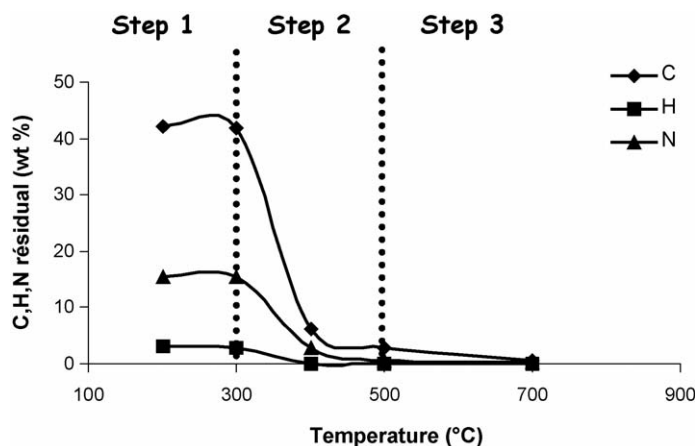


Fig. 2. Evolution of the nitrogen, carbon and hydrogen residual contents (weight ratio) in powders annealed in air at different temperatures, for 2 h.

The next step is characterized by the extinction of several adsorption bands between  $1900$  and  $900\text{ cm}^{-1}$  as the temperature increases up to  $500\text{ }^{\circ}\text{C}$ . On infrared spectra (c and d), four bands centred on  $1481$ ,  $1396$ ,  $850$  and  $1071\text{ cm}^{-1}$  appeared with high intensities that correspond to the  $\nu_s(\text{COO})$  and  $\nu_{as}(\text{COO})$  vibrations of  $\text{CO}_3^{2-}$  anions. One can also observe that the band pointing at  $1380\text{ cm}^{-1}$ , typical of  $\text{NO}_3^-$  anions, is still observed at these temperatures. Thus, spectra (c and d) point out the major contribution of carbonate species below  $500\text{ }^{\circ}\text{C}$ .

The last step occurs above  $600\text{ }^{\circ}\text{C}$ . The infrared spectrum (e) exhibit two fine bands at  $500$  and  $660\text{ cm}^{-1}$  typical of the M–O bonds in the  $\text{K}_2\text{NiF}_4$  structure [14]. A broad band with low intensity around  $2900\text{--}3400\text{ cm}^{-1}$  is also observed, due to the presence of N–H and C–H bonds. Therefore, it can be assumed that the increase in temperature up to  $700\text{ }^{\circ}\text{C}$  allows the formation of  $\text{La}_2\text{NiO}_{4+\delta}$  oxide while the most part of organic compounds has burned out.

These three steps have also been observed from the determination of the carbon, hydrogen and nitrogen residual contents in the annealed powders (Fig. 2). Below  $300\text{ }^{\circ}\text{C}$ , powders contain a large amount of organic species as shown by the high amounts of nitrogen and carbon (17 and 43 wt%, respectively). Then the increase in temperature up to  $500\text{ }^{\circ}\text{C}$  leads to a dramatic decrease in nitrogen and carbon contents (below 5 wt%). Finally, above  $600\text{ }^{\circ}\text{C}$ , a slow reduction of organic content occurs and at  $700\text{ }^{\circ}\text{C}$ , less than 1 wt% of nitrogen, carbon and hydrogen contents still remains in annealed powders.

In order to obtain structural data on the compounds formed during these three different steps, wide angle X-ray scattering analyses have been performed on powders synthesized from P1 and P2 resins. Comparable reduced intensity (Fig. 3) and radial distribution function (Fig. 4) were obtained whatever the nature of the resin. In agreement with

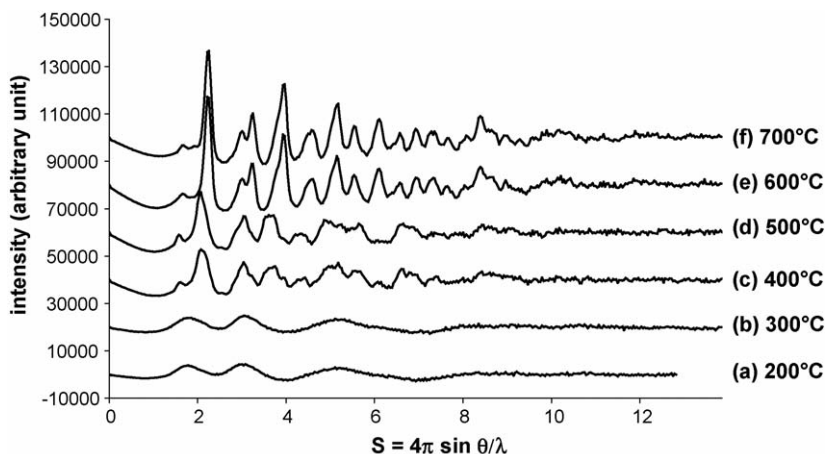


Fig. 3. Plots of the reduced intensity obtained for powders annealed in air for 2 h at different temperatures.

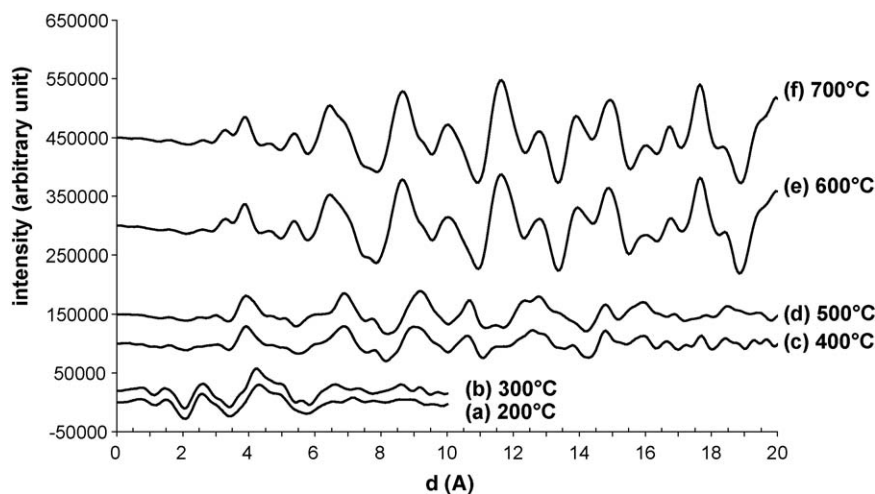


Fig. 4. Plots of the radial distribution obtained for powders annealed in air for 2 h at different temperatures.

infrared spectroscopy analyses, the reduced intensity and the reduced radial distribution point out three different structures as a function of the temperature.

Below 300 °C, the compound is amorphous according to the fact that there is no atomic order above 5 Å for the reduced radial distribution (Fig. 4). However, one can observe in plots (a and b) of the reduced radial distribution, several peaks correlated to the C–C, C–O and C–N bonds at 1.5 Å, to the metallic distances M–O at 2.6 Å and to the first M–M distances at 4.35 Å. It should be noted that both M–O and M–M distances are dominated by the contribution of La–O distances and La–La distances, respectively, as the lanthanum atom is heavier than the nickel one. The increase in the temperature to 400 °C leads to the formation of a nanocrystallized compound as shown by the extension of the atomic order up to 20 Å. Its structure is stable below 600 °C and is characterized by a shift of the M–M bonds towards shorter distances at 4 Å. One can also observe a shift of the M–O and M–C bonds, which are represented by a broad shoulder between 2.2 and 3.2 Å. At 600 °C, most part of the organic compounds is decomposed, whereas it still remains a peak at 1.5 Å with low intensity, attributed to the C–O bonds of carbonate groups.

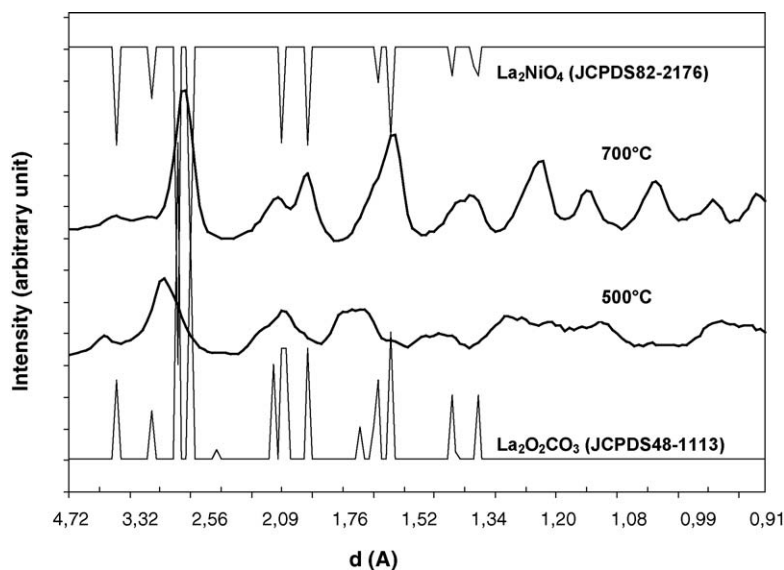


Fig. 5. Comparison of the scattered intensity of powders annealed in air at 500 and 700 °C for 2 h to the X-ray patterns obtained from I.C.C.D. files of  $\text{La}_2\text{O}_2\text{CO}_3$  and  $\text{La}_2\text{NiO}_{4+\delta}$ , respectively.



Table 1

Influence of the nature and the content of organic compounds on the mean crystallite size and the structure of powders annealed in air at 1000 °C for 2 h

Powders	XRD structure	Mean crystallite size (nm) at 1000 °C ( $\pm 10$ nm)	Non stoichiometry level at 25 °C ( $\pm 0.05$ )
P1 resin, $R = 2$	Fmmm	160	0.18
P1 resin, $R = 3$	Fmmm	220	0.22
P2 resin, $R = 2$	Fmmm	100	0.15
P2 resin, $R = 3$	Fmmm	130	0.16

The comparison of the experimental diffuse pattern to the diffracted pattern of  $\text{La}_2\text{O}_2\text{CO}_3$  oxycarbonate extracted from I.C.C.D. files (Fig. 5) shows strong similarities. This seems to indicate that the compound formed between below 600 °C may have a structure closed to that of an oxycarbonate, and may probably be a lanthanum-nickel mixed oxycarbonate. Nevertheless, from these experimental data, it was difficult to conclude about the exact nature of this intermediate compound, despite the fact that both infrared spectroscopy and wide angle X-ray scattering analyses show the formation of a well defined and stable nanocrystallized compound. Above 600 °C, the comparison of the diffuse/diffracted patterns with  $\text{La}_2\text{NiO}_{4+\delta}$  I.C.C.D. files shows that the Ruddlesden–Popper phase is formed (Fig. 5). The transition from the oxycarbonate to the  $\text{La}_2\text{NiO}_{4+\delta}$  oxide does not change the M–M bonds distances, still remaining at 4 Å, whereas the Ni–La distances are shifted to 4.6 Å.

In order to fully examine the influence of the nature and the content of organic compounds on the structure of  $\text{La}_2\text{NiO}_{4+\delta}$  oxides, the non stoichiometry levels and the mean crystallite sizes of  $\text{La}_2\text{NiO}_{4+\delta}$  powders annealed in air at 1000 °C were evaluated and are reported in Table 1. In all cases, pure  $\text{La}_2\text{NiO}_{4+\delta}$  phase is obtained and its structure determined by conventional XRD analysis is also reported in Table 1. From this table, it can be seen that high non stoichiometry levels are obtained in our processing conditions compared to the one usually reported in the literature (between 0.14 and 0.16), indicating that the obtained phases are metastable. Indeed, after two cycles at 1000 °C in air, all powders were finally characterized by a non stoichiometry level of 0.15 at 25 °C [15].

The higher mean crystallite sizes and non stoichiometry levels are obtained for powders synthesized from P1 resin. Moreover, the higher the  $R$  ratio, the higher the crystallite size and the non stoichiometry level, whatever the used resin.

#### 4. Discussion

According to infrared spectroscopy and wide angle X-ray scattering analyses, the transition from polymeric sols to  $\text{La}_2\text{NiO}_{4+\delta}$  oxides occurs in three structural steps corresponding firstly, to the formation of an amorphous polymeric precursor between 200 and 300 °C, followed by its transformation into a nanocrystallized oxycarbonate above 400 °C. Its structure is stable up to 500 °C. However, in between 400 and 500 °C, the  $\text{La}_2\text{NiO}_{4+\delta}$  oxides primary particles are already formed as shown by the first M–M distances of the Ruddlesden–Popper structure observed by wide angle X-ray scattering. Above 600 °C, the Ruddlesden–Popper phase has a well-defined structure, meaning that the last structural step corresponding to the transition from the oxycarbonate to the  $\text{La}_2\text{NiO}_{4+\delta}$  oxide starts below 600 °C and progressively occurred while the oxycarbonate structure decomposes. Indeed, in situ X-ray diffraction analyses showed that the step wise formation of oxide from the oxycarbonate starts around 540 °C and ends at 700 °C [16]. At 700 °C, the remaining carbonate groups observed by infrared spectroscopy and wide angle X-ray scattering (less than 1 wt%) are probably surface carbonates.

These structural investigations point out that the evolution from amorphous to  $\text{La}_2\text{NiO}_{4+\delta}$  crystallized powders seems to be independent on the sol synthesis parameters, as the same structural evolution is observed whatever the resins (P1 and P2) and the content of organic compounds ( $R = 2$  and 3) used as precursors. Indeed, we did not observe different intermediate structure while changing the nature of the resin as well as the content of organic compounds in the polymeric sols. However, after an annealing at 1000 °C for 2 h,  $\text{La}_2\text{NiO}_{4+\delta}$  oxides exhibit various mean crystallite sizes ranging from 100 to 220 nm and non stoichiometry levels ranging from 0.15 to 0.22 as a function of  $R$  and the nature of the resin.

The highest mean crystallite sizes were observed for powders synthesized from P1 resin with the highest  $R$  ratio. Moreover, it has been shown that the higher the mean crystallite size, the higher the non stoichiometry level. According to our previous studies, these variations are strongly correlated to the enthalpy of reaction and the local pressure developed during the decomposition of the polymeric sols [11].



Indeed, it has been shown that the nature and the content of organic compounds modify the heat released during their decomposition. A stronger heat is released from the decomposition of P1 resin compared to the P2 one. Moreover, the higher the organic content, the higher the heat released. Therefore, different reaction kinetics are attempted as a function of the  $R$  ratio and the nature of the resin. This is confirmed by the evolution of the mean crystallite size as a function of these parameters. Accordingly, the formation of  $\text{La}_2\text{NiO}_{4+\delta}$  oxide with highest mean crystallite size is obtained from P1 resin with  $R = 3$ .

Further, oxidizing atmospheres are obtained with the release of NO gas originates from the decomposition of nitrates salts and hexamethylenetetramine, leading to the stabilisation of high content of  $\text{Ni}^{3+}$  cations, and subsequently, to high oxygen non stoichiometry levels. Then, the higher  $R$ , the higher  $\delta$ . This also explains the difference in  $\delta$  between powders synthesized from P1 and P2 resins. Therefore, the formation of  $\text{La}_2\text{NiO}_{4+\delta}$  oxide with highest non stoichiometry level is obtained from P1 resin with  $R = 3$ .

Accordingly, these studies show that the relevant parameters controlling the physical characteristics of the oxides are the temperature and the local pressure developed during the polymeric sols decomposition. They can be indirectly adjusted by an appropriate choice of the organic compounds and their content in the polymeric sols. As a matter of fact, this allows the control of the mean crystallite size and the non stoichiometry levels of the oxides, leading to the formation of  $\text{La}_2\text{NiO}_{4+\delta}$  metastable phases with high values of  $\delta$ .

## 5. Conclusion

We synthesize  $\text{La}_2\text{NiO}_{4+\delta}$  oxides via a polymeric route. The crystallization of oxides proceeds from the formation of a polymeric precursor below 300 °C, which transformed into a nanocrystallized oxycarbonate above 400 °C. The transition from this compound to the oxides progressively occurs above 540 °C and ends at 700 °C. These structural steps are independent of the synthesis parameters, as the same evolution is observed whatever the content and the nature of the organic compounds.

However, these parameters have been shown to affect the structure and the microstructure of the as-formed oxides. Indeed, an appropriate choice of the resin and the content of organic compounds allows the preparation of  $\text{La}_2\text{NiO}_{4+\delta}$  oxides with a mean crystallite size ranging from 100 to 220 nm and a non stoichiometry level in the range of 0.15–0.22 at 25 °C. Therefore, this study shows that our versatile process is suitable to elaborate  $\text{La}_2\text{NiO}_{4+\delta}$  electrodes with different electrochemical behaviours.

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