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# Synthesis of $Ni_{0.9}Co_{2.1}O_4$ mixed oxides powders prepared by sol-gel method via propionic acid and characterization by X-ray, ICP, FTIR and XPS analysis

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**Abstract:** The bulk structural properties of the nickel cobaltite, $Ni_{0.9}Co_{2.1}O_4$ prepared by sol-gel via propionic acid method were examined by X-ray diffraction (XRD), inductively coupled plasma-optical emission spectrometry (ICP-OES), and Fourier Transform Infrared spectroscopy (FTIR). The XRD patterns show that oxides crystallize in a cubic spinel phase. The found data for metals determination by ICP-OES correspond well to the desired metallic stoichiometry. The proposed method, ICP-OES, indicated satisfactory measurement of trace metal in nickel cobaltites. Results of spectroscopy infrared show two absorption bands in regions of 657 $cm^{-1}$ and 570 $cm^{-1}$ corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltites. X-ray photoelectron spectroscopy (XPS) shows that the surface of $Ni_{0.9}Co_{2.1}O_4$ material have chemical composition containing $Co^{2+}$, $Co^{3+}$, $Ni^{2+}$ and $Ni^{3+}$ species.

**Key words:** ICP-OES, X-ray, FTIR, XPS, nickel cobaltite, sol-gel method, propionic acid

# Synthèse de poudres d'oxydes mixtes de $Ni_{0.9}Co_{2.1}O_4$ préparées par une méthode sol-gel avec l'acide propionique et analyse par DRX, ICP, IRTF et XPS

**Résumé:** Les propriétés structurales de la cobaltite de nickel, $Ni_{0.9}Co_{2.1}O_4$ préparée par le procédé sol-gel via la voie acide propionique ont été examinées par diffraction des rayons X (DRX) et par spectrométrie d'émission plasma (ICP-OES). Les diagrammes de diffraction des rayons X montrent que les oxydes cristallisent dans une phase spinelle cubique. Les valeurs trouvées pour la détermination des métaux par ICP-OES correspondent bien à la stœchiométrie métallique désirée. La méthode ICP-OES proposée a permis d'obtenir avec satisfaction les valeurs de traces de métaux dans les cobaltites de nickel. La spectrométrie infrarouge des échantillons montre deux bandes d'absorption à 657 $cm^{-1}$ et 570 $cm^{-1}$ correspondant respectivement à un étirement métal-oxygène des sites tétraédrique et octaédrique, qui sont caractéristiques des cobaltites. La spectroscopie de photoélectrons X montre que la surface du matériau $Ni_{0.9}Co_{2.1}O_4$ a une composition chimique contenant les espèces $Co^{2+}$, $Co^{3+}$, $Ni^{2+}$ et $Ni^{3+}$.

**Mots-clés:** ICP-OES, DRX, IRTF, XPS, cobaltite de nickel, sol-gel, acide propionique.

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## 1. Introduction

The oxygen reduction reaction (ORR) is one of the most important reactions in life process such as biological respiration, metal-air batteries, water electrolysis, energy conversion systems such as fuel cells, electrosynthesis and metal processing. In most processes the ORR rate is very low. But the oxygen electrode is known to be a highly irreversible system with a high activation overvoltage in aqueous solutions [1, 2]. In order to speed up the ORR kinetics to reach a practical usable level in fuel cells, nickel cobaltites ($Ni_xCo_{3-x}O_4$), are often studied as oxygen anode or cathode since they have promising activity and stability that have been demonstrated in alkaline solutions. The advantages of using these oxides as electrode materials are associated with their activity, availability, low cost, thermodynamic stability, low electrical resistance and their environmental friendship [3, 4]. Depending on the valences of metallic cations, nickel cobaltites have long been known to be active and stable catalysts not only for oxygen evolution, but also for organic electro-oxidation in alkaline media [5-7]. It is well known in the literature that Ni and Co mixed oxides present beneficial electrochemical and physical properties [8-10]. It has been demonstrated also that electrochemical activity depends on both the electronic and geometrical factors [11-13]. Powders are usually physically analyzed by means of classical X-ray diffraction and transmission spectroscopy, but the accuracy of results may be insufficient considering the small amount of metals in materials.

In this work, we report the preparation of $Ni_{0.9}Co_{2.1}O_4$ oxide using a sol-gel method via propionic acid and the characterization by X-ray powder diffraction (XRD), ICP-OES, Fourier Transform Infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The objective is to characterize the bulk and surface compositions of synthetized nickel cobaltites.

## 2. Experimental

### 2.1. Synthesis

$Ni_{0.9}Co_{2.1}O_4$ mixed valence oxide was synthesized by sol-gel technique via propionic acid as reported elsewhere. Stoichiometric amounts of precursors, namely $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich) were thoroughly mixed. The powder obtained was finally heat treated at 350 °C for 4 hours to attain a thermal equilibrium. This temperature treatment was chosen according to preliminary DTG analysis [14, 15].

The mixed stoichiometric amounts of nitrates were dissolved in excess propionic acid. The solution was heated at 120 °C to evaporate the propionic acid excess and to form a gel. Liquid nitrogen was added immediately to give a mixed nickel-cobalt propionate. It was subsequently heated at 140 °C to remove the excess of propionic acid and to obtain a mixed oxide under the form of a spinel phase.

### 2.2. Characterization

X-ray powder diffraction patterns were realized using a Siemens D-500 Diffractometer with a Guinier-Wolf chamber using an anode material of Cu Kα (λ = 1.54056 Å) and a quartz monochromator). The XRD patterns were recorded in the 5-95° range 2θ at a scanning rate of 0.0170 °/s.

The ratios of Ni and Co were calculated according to the stoichiometry. Beside, the ratios of Ni and Co were determined by inductively coupled plasma optical emission spectrometry ICP-OES. The ICP measurements were performed with a sequential ICP-OES spectrometer Varian 710ES (axial view), equipped with a sample preparation system Varian SPS3 (Agilent Technologies, USA). Instrumental parameters used for the analysis are listed in **table I**. The samples were digested in triplicate with $HNO_3$ 70%. The fused mixture was usually filtered through 0.45 µm pore size membrane filters before ICP analysis and it was noticed that some black particles were left in the filters.

The samples were very concentrated, so to stay in the calibration range they had been diluted 100 times, that would add some error to the results.

Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Spectrum Express Version 1.02.00 spectrophotometer in KBr pellets.

The XP spectra were recorded on a Thermo VG ESCALAB 250 spectrometer. Al K$\alpha$ radiation (1486,6 eV) operated at 200 W was used as a the X-ray excitation source. All the spectra were recorded at a take-off angle of 90°. The carbon 1s (C-C/C-H) binding energy (285 eV) was used to calibrate the binding energy. The operating pressure was $2.10^{-1}$mBar.

**Table I :**Instrumental operating conditions

| **Parameter** | **Value** |
|---|---|
| Power (kW) | 1.2 |
| Gaz flow | Argon |
| Plasma flow (L/min) | 15 |
| Auxiliary flow (L/min) | 1.5 |
| Nebulization pressure (kPa) | 240 |
| Pump rate (rpm) | 12 |
| Rinse time (s) | 30 |
| Replacateread time (s) | 5 |
| Instrumental stabilisation delay (s) | 15 |
| Sampleuptakedelay (s) | 30 |

## 3. Results and discussion

### 3.1. X-ray analysis

The XRD powder pattern of $Ni_{0.9}Co_{2.1}O_4$ prepared by sol-gel (propionic acid) route at 350 °C was recorded in a 2θ range from 5° to 95° (**Figure 1**). It indicates that a well crystallized phase with a spinel structure was obtained. The presence of X-ray picks corresponding to $Co_3O_4$ and CoO phases is not observed. As shown in **Figure 1**, nanoparticules lead to pronounced Bragg peaks corresponding to reflections of (111), (220), (311), (222), (400), (422), (511) and (440) planes. It clearly demonstrates the presence of a face-centered cubic (FCC) lattice (JCPDS No 73-1702). It agrees with research results by Wu et al [16] and Garg and co-workers [17]. The corresponding cubic cell parameter, *a*, were computed and found to be 8.102 Å. This value is very close to the standard value of 8.110 Å for $NiCo_2O_4$ (JCPDS No. 20-0781). In our previous works [15], we found for $NiCo_2O_4$ and using the same method of preparation a cell lattice of 8.095 Å. Nguyen-Cong. H. et al [18] found for both $Ni_xCo_{2-x}O_4$ compounds a cell parameter of 8.08 Å and 8.11 Å when x = 0.3 and 1, respectively. Chi et al [19] obtained values varying between 8.098 and 8.109 Å for $NiCo_2O_4$ prepared by an hydroxide co-precipitation method. Recently, Ding and co-workers [20] obtained a lattice parameter of 8.104 Å for a $NiCo_2O_4$ sample. The values of the cell parameter, *a*, calculated in the case of a cubic lattice, give interplanar distances $d_{hkl}$ in **table II**.

**Table II**: Cubic lattice parameters calculated from XRD data

| **Hkl** | **2θ (°)** | **$d_{hkl}$ (Å)** | **a (Å)** |
|---|---|---|---|
| 111 | 18.9821 | 4.67536 | 8.0979 |
| 220 | 31.2337 | 2.86377 | 8.0999 |
| 311 | 36.7963 | 2.44262 | 8.1012 |
| 222 | 38.5024 | 2.33823 | 8.0998 |
| 400 | 44.7274 | 2.02620 | 8.1048 |
| 422 | 55.5477 | 1.65443 | 8.1050 |
| 511 | 59.2417 | 1.55979 | 8.1049 |
| 440 | 65.1217 | 1.43245 | 8.1031 |

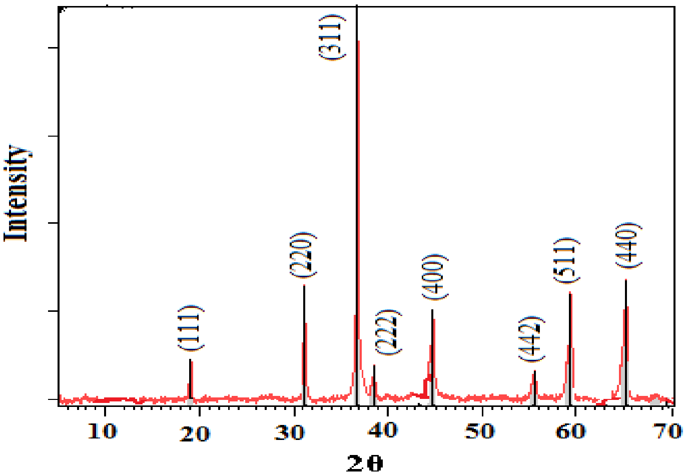

**Figure 1**. X-ray diffractogram of $Ni_{0.9}Co_{2.1}O_4$ prepared at 350° by sol-gel method (propionic acid)

### 3.2. ICP-OES analysis

The validation of methods is an important requirement in the practice of chemical analysis. It is the way of defining an analytical requirement, confirming that the method under consideration has performance capabilities that are consistent with application requirements. The estimation of the uncertainty associated with analytical methods is necessary in order to validate results. It is an important stage when reporting analytical results.

The contents of Ni and Co elements determined by calculation according to the stoichiometry and by ICP-OES are shown in **table III**. The obtained results show good agreement between calculated and experimental values, taking into account uncertainties. Li et al [21] obtained satisfactory result by calculated method and by ICP-OES for the determination of the ratios of Pt and $Mn_3O_4$ Pt-$Mn_3O_4$/C powder. Semenova and co-workers [22] also found contents of Li and Na in cobaltite $Li_xNa_yCoO_2$, by ICP-OES, that are 2.86 and 8.10 wt% respectively. Our characterization of $Ni_{1-x}Co_xSi_2$ shows that synthetized compositions (ICP) are similar to the stoichiometric compositions [23].

### 3.3. FTIR analysis

FTIR spectroscopy is a powerful tool to provide supplementary information on the type of metal oxides [24]. **Figure 2** shows the spectrum of $Ni_{0.9}Co_{2.1}O_4$ oxide. Two strong absorption bands at 570 $cm^{-1}$ and 657 $cm^{-1}$ are observed corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of pure spinel cobaltites [25, 26]. This observation is in good agreement with the XRD results (**Figure 1**). **Figure 2** also reveal the presence of an absorption band at 1384 $cm^{-1}$ attributed to the vibration mode of the carbonate ions [27, 28, 30]. This band is due to the fact that the calcined powders tend to physically absorb carbonate ions [30]. The observed absorption bands at about 1637 and 3469 $cm^{-1}$ are assigned to the H-O-H bending vibration and O-H stretching vibration of hydrated water, respectively [26, 28, 29].

**Table III**: Concentrations ($g.kg^{-1}$) of Ni and Co in oxide samples (n = 3) obtained by ICP-OES.

| **Elements** | **Concentration** | |
|---|---|---|
| | **(a)** | **(b)** |
| **Ni** | 231 ± 19 | 220 |
| **Co** | 483 ± 46 | 514 |

(a) Determined by ICP-OES. (b) Calculated from stoichiometry.

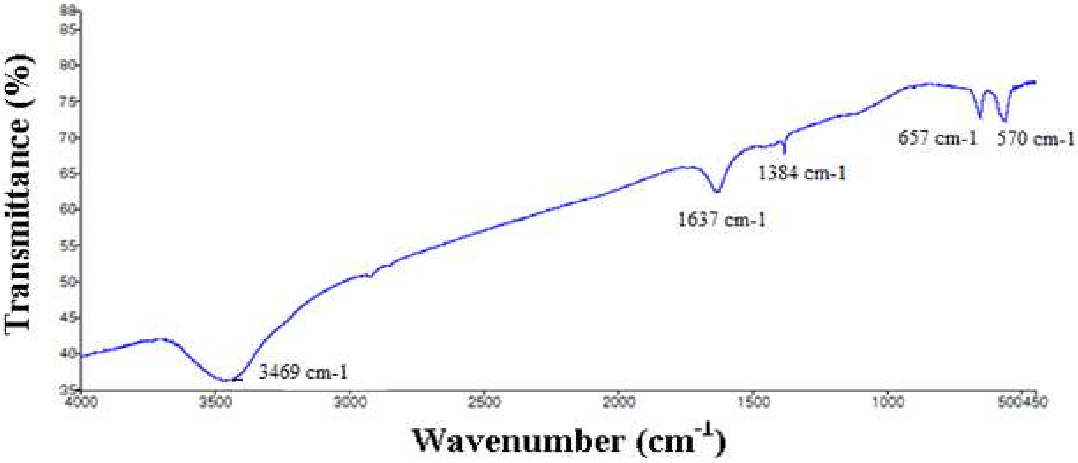

**Figure 2**: FTIR spectrum of $Ni_{0.9}Co_{2.1}O_4$ prepared at 350° by sol-gel method (propionic acid)

### 3.3. XPS analysis

The surface chemical properties (chemical bonding state and composition) of $Ni_{0.9}Co_{2.1}O_4$ material were obtained by XPS and are shown in Figure 3. Typical response of $Co_{2p}$, $Ni_{2p}$ and $O_{1s}$ core levels are obtained from the XPS. The $Co_{2p}$ binding energy and peak shape (**Figure 3a**) yield binding energies of 781 and 796.1 eV for the $2p_{3/2}$ and $2p_{1/2}$ transitions, respectively and two shakeup satellites (identified as “sat”). The relatively narrow peak width, the $2p_{3/2}$ to $2p_{1/2}$ separation of 15.1 eV and the very flat, weak satellite structure found to the high binding energy side of the $2p_{3/2}$ and $2p_{1/2}$ transitions indicate that few $Co^{2+}$cations occupy the octahedral sites of $Ni_{0.9}Co_{2.1}O_4$ spinel lattice and that the majority of cobalt found in the octahedral sites are $Co^{3+}$[17, 31].

$Ni_{2p}$ spectrum given in **Figure 3b** consist of two peaks at 856.2 eV for $2p_{3/2}$ and 873.8 eV for $2p_{1/2}$, attributed to $Ni^{2+}$ and $Ni^{3+}$ species with two shakeup satellite peaks (identified as “sat”) [20, 31, 32]. The $2p_{3/2}$ to $2p_{1/2}$ separation of 17.6 eV and the intense satellite structure indicate that the majority of nickel at the $Ni_{0.9}Co_{2.1}O_4$ surface is found as $Ni^{2+}$ in octahedral sites. It is in good agreement with the results reported by Kim et al [31].

$O_{1s}$ XPS spectrum (**Figure 3c**) shows three main contributions at 529.9, 531.2, and 533.1 eV. They are related to metal-oxygen bonds [32], to oxygen in hydroxyl groups or to defect sites with low oxygen coordination in the material with small particle size [20, 32], and to physi/chemisorbed water at surfaces and interfaces [20, 32, 33].

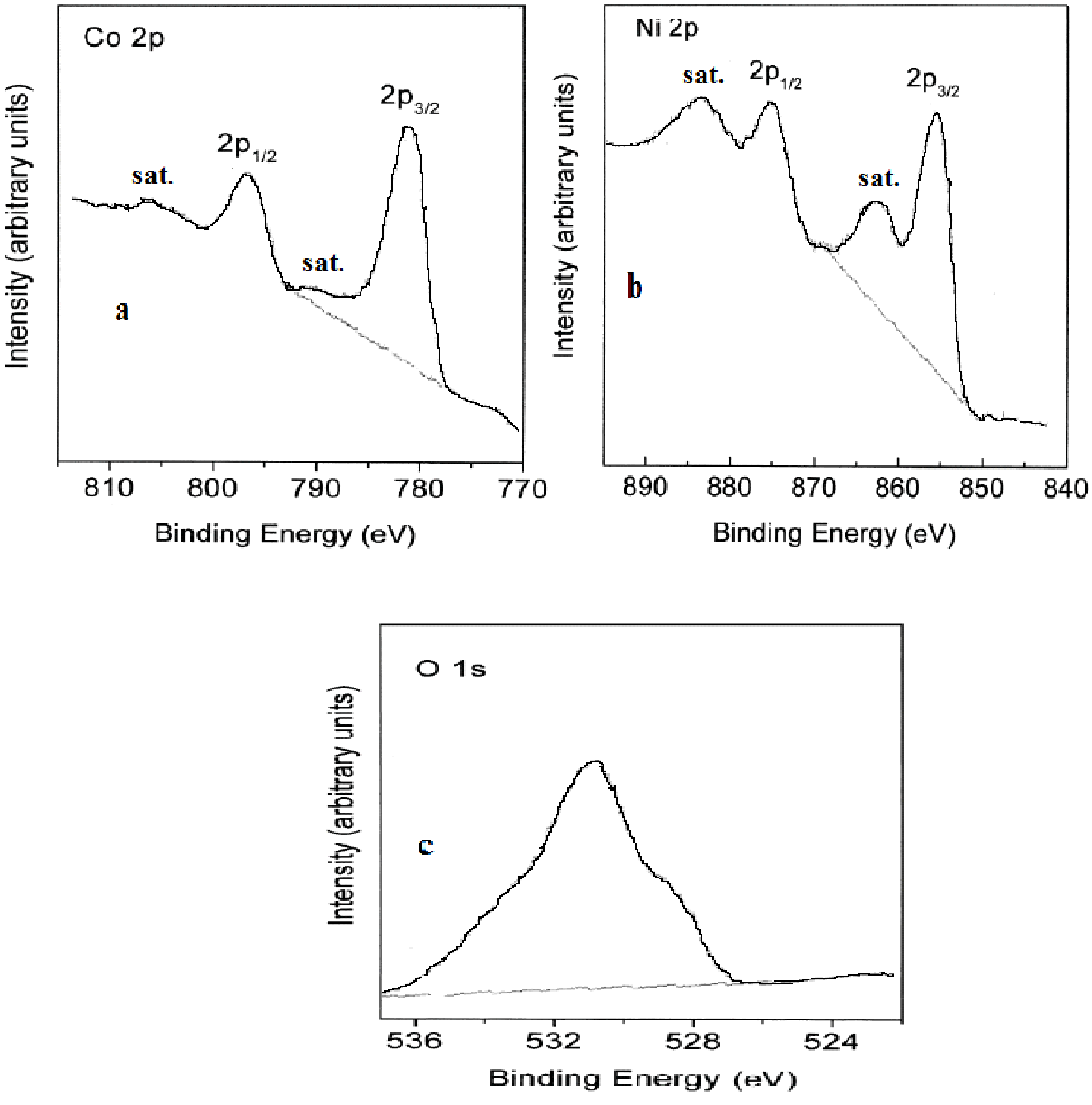

**Figure 3 :**XPS spectra of $Ni_{0.9}Co_{2.1}O_4$: (a). $Co_{2p}$, (b). $Ni_{2p}$ and (c). $O_{1s}$

## 4. Conclusion

The structural characterization of nickel cobalt oxide $Ni_{0.9}Co_{2.1}O_4$ prepared by sol-gel method via propionic acid by XRD diffraction, ICP-OES, FTIR and XPS analysis was performed.

$Ni_{0.9}Co_{2.1}O_4$ has a single phase spinel structure. X-ray diffraction shows typical Bragg peaks of spinel phase. FTIR spectrum evidences the occurence of Co-O and Ni-O vibrations in $Ni_{0.9}Co_{2.1}O_4$ samples. ICP-OES and XPS results confirmed the presence of Co, Ni and O elements in synthetized oxides. XPS results also indicate that nickel surface cations are predominantly present as octahedral coordinated $Ni^{2+}$ and that the type of the surface cobalt species is $Co^{3+}$.

## 5. Acknowledgements

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