

**PREPARATION OF NICKEL - COBALT SPINEL OXIDES $Ni_xCo_{3-x}O_4$.
COMPARISON OF TWO PHYSICAL PROPERTIES STEMMING FROM
FOUR DIFFERENT PREPARATION METHODS AND USING
CARBON PASTE ELECTRODE**

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ABSTRACT. A comparative study of two electro-physical properties (porosity and electrical conductivity) of binary nickel cobalt oxides electrodes with spinels mixed oxides $Ni_xCo_{3-x}O_4$ as-active matter, was carried out. Four different routes were used to prepare spinel-type $Ni_xCo_{3-x}O_4$ ($0 \leq x \leq 2.5$) compounds in order to link these properties with the preparation method. The substitution of Ni for Co increases the conductivity and the porosity of the electrode till a certain ratio of nickel. X-ray diffraction patterns showed that the oxides crystallize in a cubic spinel phase. Electrical conductivity as well as porosity depends on the preparation route.

KEY WORDS: Nickel cobalt spinel oxides, Porosity, Electrical conductivity, Mixed oxides electrodes, Carbon paste electrode, Pechini sol-gel method

INTRODUCTION

During the last decade, the improvement of the alkaline water electrolysis cells has drained a lot of interest, especially due to an increase in consummation and prices of natural energetic resources. Oxides constitute a wide class of materials with good electrocatalytic activity for many electrode reactions from O_2 evolution to O_2 reduction. Nickel cobaltites, $Ni_xCo_{3-x}O_4$, are one of the most promising anode materials for oxygen evolution in alkaline electrolytes.

The use of carbon paste electrodes in electrochemical studies to characterize the properties of an electrode has already been described [1-3]. In this case the electrode behaves like a thin layer cell, the charge-transfer is released directly within the electroactive solid and the carbon particles bound with the electrolytic solution [4]. The carbon paste electrode has been used in order to understand the transformation mechanisms of several substances and to discriminate between the different allotropic forms of compounds such as metal oxides [5, 6].

Studies on the structural properties of metallic spinel-type mixed oxides have extensively been carried out [7, 8]. It is well known in the literature that mixing Ni and Co brings beneficial effects in the electrochemical and physical properties of mixed oxides [8-11]. It has been demonstrated also that electrochemical activity depends on both the electronic and geometric factors [12-14]. Despite these observations, we notice that very few studies focussed on the porosity and the electrical conductivity of mixed oxides electrodes. It has already been reported that many surface properties of mixed oxides depend on the surface sites and are intensive properties when one considers the surface acid-base properties in aqueous solution [15, 16].

The purpose of this work is to study the porosity and the electrical conductivity of mixed oxides electrodes made under the form of pastilles. The active matter in these electrodes is the

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spinel-type cobalt and nickel mixed oxides $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ ($x = 0; 0.4; 0.6; 0.8; 1; 1.2; 1.8; 2; 2.5$) prepared under four different routes.

EXPERIMENTAL

Synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ oxides

The chemical synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 2.5$) was realised by two sol-gel routes (Pechini and propionic acid), coprecipitation of hydroxides and thermal decomposition of nitrates (TDN). In the different procedures, stoichiometric amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) were intimately mixed. The amounts used to prepare the mixed oxide are given in Table 1. All the powders obtained were finally treated at 350 °C during 4 hours to get thermal equilibrium. These treatments temperatures are chosen according to DTG analysis.

Table 1. Amounts of nitrates used as precursors.

x	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (s)	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (s)	$\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ (s)
0	0	3.626	Co_3O_4 (s)
0.4	0.486	3.144	$\text{Ni}_{0.4}\text{Co}_{2.6}\text{O}_4$ (s)
0.6	0.725	2.900	$\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$ (s)
0.8	0.960	2.660	$\text{Ni}_{0.8}\text{Co}_{2.2}\text{O}_4$ (s)
1	1.209	2.420	NiCo_2O_4 (s)
1.2	1.450	2.178	$\text{Ni}_{1.2}\text{Co}_{1.8}\text{O}_4$ (s)
2	2.420	1.210	$\text{Ni}_2\text{Co}\text{O}_4$ (s)
2.5	3.027	0.605	$\text{Ni}_{2.5}\text{Co}_{0.5}\text{O}_4$ (s)

Pechini sol-gel method

The Pechini process [17, 18] is based on the ability of some weak acids to form polychelates with a certain number of cations. Fine and pure crystalline spinel phases can be obtained at low temperatures just after four hours of thermal treatment.

The stoichiometric amounts of the precursors $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added in 10 mL of glycol ethylene where were dissolved previously 10 g of citric acid. This mixture was then heated at 120 °C until the appearance of a viscous liquid. The excess of solvent was vacuum dried at 180 °C during an hour and the final thermal (350 °C) treatment was realised in an oven to get the spinel phase.

Sol gel method (propionic acid route)

This new process consists of hydrolysis of metal nitrates in propionic acid. It involves the formation of a viscous gel at 120 °C following the mixture in stoichiometric proportions of nitrates dissolved in 20 mL of pure liquid propionic acid (Aldrich 99 %). A gel is formed and quenched in liquid nitrogen to break it. The powder is heated at 140 °C to eliminate the excess of water and thermally (350 °C) treated to get the spinel phase [19].

Thermal decomposition of nitrates (TDN)

Stoichiometric amounts of salts were first mixed and heated at 90 °C in an oven to dryness and the blackish residue was pre-treated during four hours at 200 °C. The spinel phase was obtained after the final treatment (350 °C) [20].

Co-precipitation of hydroxides

The metal nitrates precursors were dissolved in distilled water and gently heated; an excess of 3 M KOH was dropwise added to co-precipitate the hydroxides. Pre-treatment was carried out in an oven after the solvent has been evaporated, the precipitate washed with distilled water and dried at 100 °C during 12 hours. The last treatment (350 °C) was then realised to obtain the spinel phase [21].

Techniques and apparatus

Carbon paste electrode was used. This technique has already been described elsewhere [22, 23]. Pellet electrodes were manufactured according to the Teflon-bonded method using carbon black (UCAR, Union Carbide) as a conductive additive [24]. The carbon paste electrode was prepared by mixing 100 mg of active matter ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$), 95 mg of carbon black and 5 mg of Teflon as binder. The mixture (200 mg) was finely homogenised in a mortar and compacted in a Beckman type hydraulic press during 5 minutes and under a pressure of 5 tons/cm² to form a pellet.

Conductivity

Conductivity measurements have been carried out using a cell in a U form, similar to that described by Yu *et al.* [25] (Figure 1).

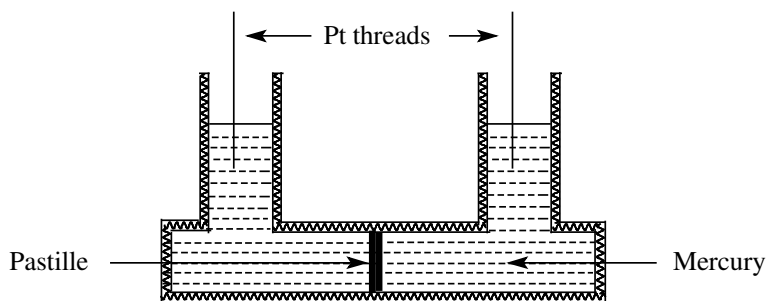


Figure 1. Transverse section of the U cell conductivity measurements.

The electrical conductivity value (λ_e) was determined by the relation: $\lambda_e = e/(Rs)$ where e is the sample thickness, R the measured resistance and s the area of cross section.

X-ray diffraction patterns

X-ray diffraction (XRD) studies of the oxide powders were carried out on a Siemens D-500 diffractometer with a Guinier-Wolf chamber using cobalt K_α radiation ($\lambda = 0.1789$ nm and a quartz monochromator). The XRD patterns were recorded in the 20-80° 2θ range at a scanning rate of 0.05 °/s

Porosity

The porosity is a very important characteristic of a carbon paste electrode. It measures the impregnation level of the electrode by the electrolyte and is defined as the quantity of electrolyte retained per gram of dry electrode. The mass M_0 of the dry paste was determined and it was immersed in a 1.5 M H_2SO_4 aqueous solution for 48 hours. It was then withdrawn and weighed

again (we took care to clean the layer of electrolyte deposited on its faces with filter paper). If M is the mass of the impregnated electrode, porosity value μ is obtained from the following expression:

$$\mu = \frac{(M - M_o) \cdot 1000}{M_o}$$

It is expressed thus in milligrams of electrolyte retained per gram of dry electrode (mg/g_{el}).

RESULTS AND DISCUSSION

Figures 2 show the X-ray diffraction patterns of some of the prepared oxide powders obtained at 350 °C. These spectra are representative for all the samples. They exhibit, all, the characteristic 311 spinel peak line. For the compositions up to $x = 1$ no other phases are pointed out. The substitution of Ni for Co does not modify the general aspect of the pattern, which remains the same for all substitution degrees lower than 1. No stray peaks due to lower cobalt oxides were observed. This is remarkable for a cobaltite prepared at a temperature of 350 °C. For $x > 1$ some characteristic peaks of NiO appear but smaller than the spinel ones. This demixion of NiO phase was also observed by Roginskaya *et al.* [26]. Hu *et al.* [27] have previously shown that the formation of NiO is linked to the percentage of Ni and that above a certain amount of Ni, anhydrous NiO is mainly formed.

Figure 3 shows the evolution of the porosity with the nickel content x . All the prepared spinel mixed oxides powder pellets present high porosity values. The influence of the preparation method is obvious in these results. Pastilles containing mixed oxides prepared by sol-gel methods give higher porosity values. This can be related to the fact that sol-gel compounds are known for their ultra fine and homogeneous spinel phases [17]. In all the series, porosity values increase with nickel content x from 0 to 1 and decrease when $x > 1$. This decreasing is explained by the demixion of NiO at high nickel content. Indeed, for x values higher than 1, NiO and Ni_{1-x}Co_{3-x}O₄ are simultaneously present in the samples [26].

Electrical conductivity measurements were carried out at room temperature on the pellet described above. Figure 4 displays the evolution of the electrical conductivity values with the nickel x content.

These results show that the conductivity increases with increasing Ni content when x varies from 0 to 1 and decreases for $x > 1$ and emphasize so the effectiveness of Ni incorporation into the spinel structure and the close correlation between porosity and conductivity factors. This behavior may suggest that the introduction of foreign ions results in a locally disordered crystallographic structure. It may be expected that modified compositions which lead to a lower degree of crystallinity give rise to reversible nickel incorporation. Pellets containing sol-gel prepared mixed oxides exhibit higher porosity and conductivity values (Figure 5).

The values obtained for the room temperature conductivities are higher than those obtained by Hamdani [28] with different methods of preparation. The order of magnitude of the electrical conductivities varies in the literature. For Co₃O₄, Tarasevich *et al.* [29] and Kononov *et al.* [30] found $0.01 \times 10^{-2} \text{ S.cm}^{-1}$ and for NiCo₃O₄ $2 \times 10^{-2} \text{ S.cm}^{-1}$ [29]. Shub *et al.* found $10^{-2} \text{ S.cm}^{-1}$ for Co₃O₄ films prepared by thermal decomposition of nitrates on titanium substrates at 350 °C [31].

As previously noted during the study of the porosity, the conductivity decreases when the nickel proportion becomes higher than 1, probably because of the demixion of NiO. The NiO phase, which is less conductive than the spinel phase dilutes the composition of the powders and the measured conductivity progressively decreases [32]. The highest values of conductivity were attained for Ni_{0.6}Co_{2.4}O₄, Ni_{0.8}Co_{2.2}O₄ and NiCo₂O₄. This is in agreement with the observations

of other workers [8]. Oxides prepared by sol-gel methods present higher conductivity values. This is due to the fact that these products are known to give homogenous and ultrafine crystalline spinel phases and can, also, be related on one hand, to the increase of the charge carriers concentration and, on the other hand, to an increase in their mobility by a decrease in Co-Co distance which may be inferred to the evolution of the cell parameter [33].

Ni-Co mixed oxides exhibit both good porosity and high electrical conductivity values and are of interest in solid oxide fuel cell and this is one of the features which make them attractive as electrocatalysts. The powders prepared by sol-gel methods have conductivities which predispose them to forming electrodes simply by pelletizing the pure phase.

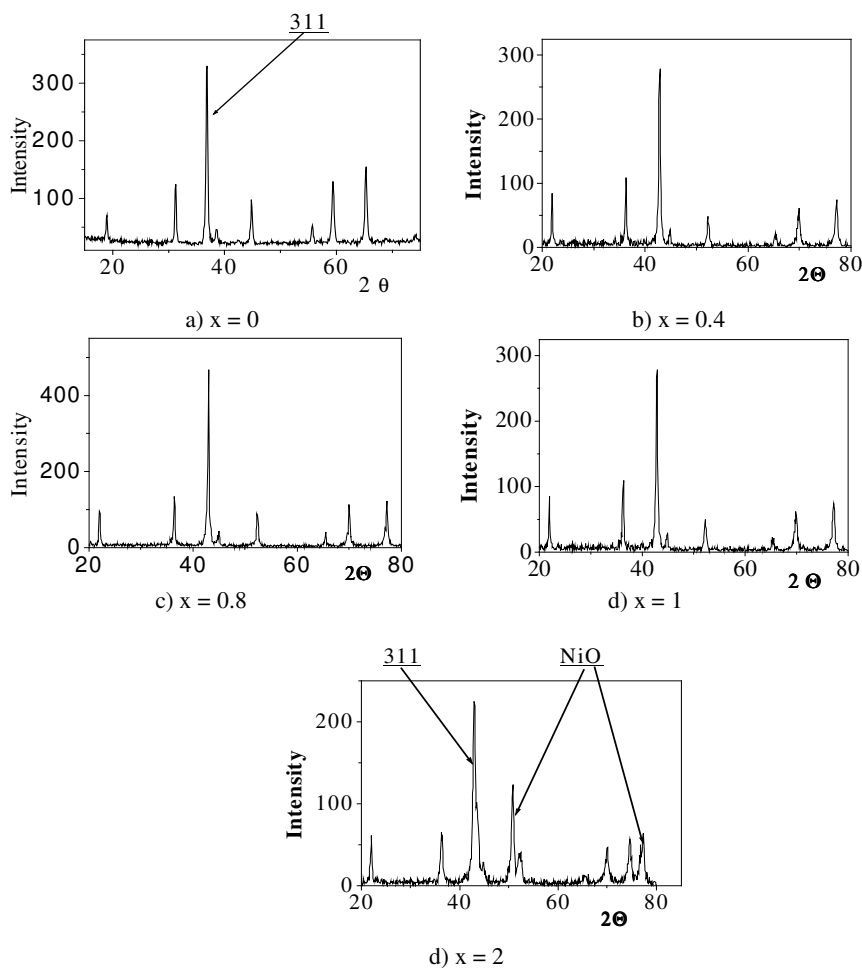


Figure 2. X-ray diffractogram of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ at 350°C prepared by: a) and e) sol gel (Pechini); b) sol gel via propionic acid; c) TDN; d) coprecipitation of hydroxides.

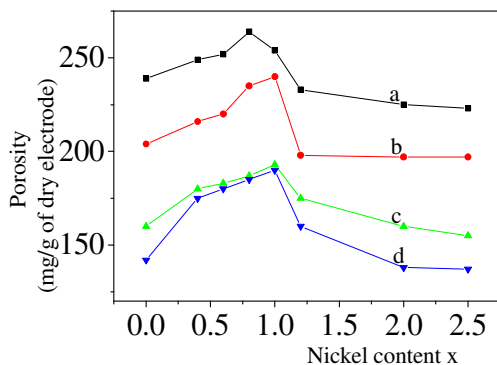


Figure 3. Variation of porosity with nickel content x: a) Sol-gel Pechini; b) Sol-gel (via propionic acid); c) TDN; d) Co-precipitation of hydroxides.

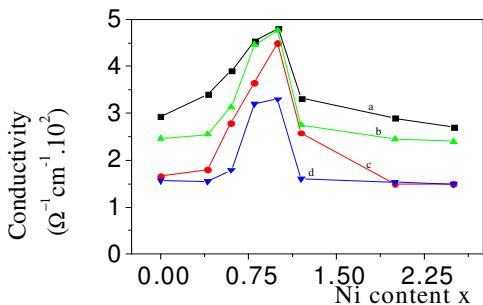


Figure 4. Variation of electrical conductivity with nickel content x: a) Pechini; b) Sol gel (via propionic acid); c) TDN; d) Co-precipitation of hydroxides.

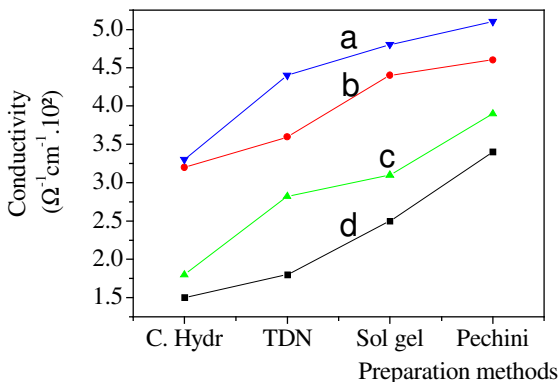


Figure 5. Evolution of the electrical conductivity of $Ni_xCo_{3-x}O_4$ as a function of the preparation method: a) $x=1$; b) $x=0.8$; c) $x=0.6$; d) $x=0.4$.

CONCLUSIONS

Conducting cobalt nickel oxide having the spinel crystal structure and the composition Ni_xCo_{3-x}O₄ were successfully prepared in this work at temperature as low as 350 °C via four different methods. The oxides crystallised in the spinel phase, space group Fd 3 m, with no parasitic phases detected by XRD for nickel ratio x smaller than 1. At high Ni concentration ($x > 1$), another phase appears, consecutive to NiO demixion and indicating that the Ni-Co oxide system can only be obtained in a limited composition extent.

Nickel cobalt spinel Ni_xCo_{3-x}O₄ ($0 \leq x \leq 1$) with high porosity and conductivity can be easily prepared. At high nickel content, the physical properties are more or less slightly depressed. Both conductivity and porosity are influenced by the nickel content. The conductivity of Co₃O₄ can be increased by incorporating nickel ions. The preparation method has important effects on the formation of Ni-Co mixed oxides. The study shows that the method of preparation affects the physical properties of the oxide system. It demonstrates also that mixed oxides prepared by sol-gel routes, and particularly by the Pechini method exhibits the best performances.

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