SYNTHESIS AND CHARACTERIZATION OF $Ni_{0.4}Co_{2.6}O_4$ SPINEL MIXED OXIDES POWDER: STUDY OF ITS SURFACE PROPERTIES BY VOLTAMMETRY, X-RAY, FTIR, UV-VIS-NIR SPECTROSCOPY AND SCANNING ELECTRON MICROSCOPY

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ABSTRACT. Electrochemical studies were carried out on $Ni_{0.4}Co_{2.6}O_4$ powders prepared by sol-gel via propionic acid method using cyclic and steady state voltammetries. The oxide surface was characterized by scanning electron microscopy (SEM), X-ray diffraction, UV-vis-NIR and FTIR spectroscopies. The results showed that the formation of homogeneous oxide with a single spinel phase occurred at 350°C. The surface redox couple $NiOOH/Ni(OH)_2$ is confined on the surface material l.

KEY WORDS: $Ni_{0.4}Co_{2.6}O_4$ spinel mixed oxides powder, Sol-gel process, Surface properties

INTRODUCTION

Spinel oxides have long been known to be active in electrochemical evolution and reduction of oxygen [1, 2]. It is known that in commercial alkaline water electrolysers, the oxygen evolving anode is not very stable under anodic conditions. Among spinel-type oxides, Co_3O_4 is considered as one of the most promising electrocatalysts in alkaline solutions due to its low cost, good corrosion stability, large availability on one hand, and from an electrocatalytic point of view, on the other hand, to its thermodynamic stability and electrocatalytic activity. Nevertheless, the weakness of its specific surface and its low activity and conductivity need improvement. Different strategies are used to improve these properties changes in the preparation method and/or metal ion doping.

In this paper we report on the electrochemical properties and the preparation of $Ni_{0.4}Co_{2.6}O_4$ oxide using a sol-gel method. We used X-ray diffraction, IR spectroscopy, UV-vis-NIR spectroscopy, BET surface area, roughness factors, cyclic and steady state voltammetries to characterize the surface and the electrochemical properties of the prepared mixed oxides.

EXPERIMENTAL

The chemical synthesis of $Ni_{0.4}Co_{2.6}O_4$ was realized by the sol-gel process via propionic acid. Stoichiometric amounts of $Ni(NO_3)_2 6H_2O$ and $Co(NO_3)_2.6H_2O$ (Aldrich) were intimately mixed. The amounts used to prepare the mixed oxides were respectively 0.486 g and 3.144 g. The powder obtained was finally treated at 350 °C for 4 hours to get thermal equilibrium. This temperature treatment was chosen according to DTG analysis [3].

Sol-gel (via propionic acid) method was described elsewhere [4]. The stoichiometric amounts of nitrates were dissolved in 20 mL of propionic acid. The mixture was gently heated at

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120 °C in an oven to eliminate the excess of propionic acid. A gel was formed which was, afterwards, broken by addition of liquid nitrogen. The powder was heated at 140 °C to eliminate the excess of water and was thermally treated to get the spinel phase of the mixed oxides.

X-ray powder diffraction patterns were realized using a Siemens D 500 Diffractometer with a Co anti-cathode and a Ni filter. Infrared spectra were obtained using a Brucker Multipare CT 25000 spectrometer coupled with an Avatar 320 FTIR apparatus. The UV-vis-NIR reflectance spectra were recorded using a Lambda 9 Perkin-Elmer spectrometer. An integration sphere of 60 mm diameter was used as standard detection system. Barium sulfate was the neutral material used inside the sphere due to its high diffusing power. The oxide morphology was determined by scanning electron microscopy (SEM), using a JEOL JSM 840 coupled to a computer.

The electrochemical measurements were performed at 25 °C in the classic three-electrode cell layout. The electrolyte was a 1 M KOH solution prepared with twice-distilled water. A Pt counter-electrode and a potentiostat-galvanostat EG & G PAR Model 263 coupled to a computer were used. Except where otherwise stated, an Hg/HgO 1 M KOH reference electrode (0.098 V/NHE) was used. Nickel plates (1 x 2 cm²) cut from a Ni foil (99%, Aldrich) were used to realize the working electrode according to the following procedure: a suspension of a powder of the mixed oxides in isopropylic acid was prepared. The paste of this suspension was brushed on the Ni plates and put in an oven between 200 and 250 °C for 4 hours in order to improve the active matter grip on the support. This operation was repeated 4 times for each sample.

RESULTS AND DISCUSSION

A XRD θ-2θ diffractogram of $Ni_{0.4}Co_{2.6}O_4$ prepared at 350 °C is displayed in Figure 1. It shows that a well crystallized phase with spinel structure is obtained. All the different peaks, belonging to this structure appeared, and particularly the characteristic 311-plane peak. Table 1 gives the values of the cell parameter (a) and of the interplanar distances d_{hkl}; the corresponding cubic cell parameter was calculated by means of the following formula for a cubic lattice:

$a = d_{hkl} (h^2 + k^2 + l^2)^{1/2}$, where h, k, and l are the Miller indices (Table 1).

Table 1. Characteristics of main planes peaks from the X-ray diffraction spinel pattern of $Ni_{0.4}Co_{2.6}O_4$.

hkl	2θ (°)	d_{hkl} (nm)	A (Å)
111	18.950	0.4679	8.104
220	31.199	0.2864	8.100
311	36.782	0.2441	8.095
222	38.470	0.2338	8.095
400	44.756	0.2023	8.092
422	55.554	0.1653	8.098
511	59.276	0.1558	8.095
440	65.126	0.1431	8.094
531	68.513	0.1368	8.093
620	73.993	0.1280	8.095

The calculated average value is a = 8.095 ± 0.005 Å, result matching well the JCPDS ASTM files No. 9-418 and 2-1074 where a_{Co3O4} = 0.8084 nm and $a_{NiCo2O4}$ = 0.8128 nm. El Baydi *et al*. [5] found for $NiCo_2O_4$ and for the same method of preparation at 350 °C a cell lattice equal to 8.119 Å. E. Rios. [6] found a = 8.091 Å and 8.099 Å for $Mn_{0.25}Co_{2.75}O_4$ and $Mn_{0.5}Co_{2.5}O_4$ respectively and Chi *et al*. [7] obtained values ranging between 0.8098 and 0.8109 nm for

$NiCo_2O_4$ prepared by the hydroxide co-precipitation method. However, the change of the cell parameter "a" with preparation methods indicates that the spinel is a solid solution and its composition and structure are intimately linked to these methods. The existence of other phases, as Co_3O_4 and CoO which often appeared in Ni-Co spinel preparations, was not detected by X-ray diffraction analysis.
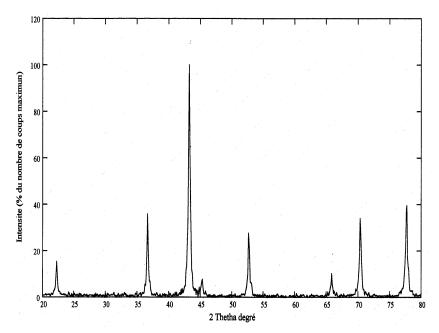

Figure 1. X-ray diffractogram of $Ni_{0.4}Co_{2.6}O_4$ at 350 °C (prepared by sol-gel via propionic acid).

An IR spectrum of the $Ni_{0.4}Co_{2.6}O_4$ mixed-oxide, taken in the mid domain (400 – 4000 cm^{-1}) is presented in Figure 2. It exhibits two high-frequency intense bands at 567 and 658 cm^{-1}. These two bands, characteristic of pure spinel crystals, are interpreted as metal-oxygen low spin vibrations in octahedral sites [8, 9]. They show that the formation of the spinel structure occurred already at 350 °C. The non-existence of impurities as CoO or NiO is confirmed by the absence of another absorption band in the spectrum.

Figure 3 shows the UV-vis-NIR reflectance spectrum of $Ni_{0.4}Co_{2.6}O_4$. It exhibits a broad bulk peak between 1200 and 1500 nm. This peak is related to non-stoichiometry and to charge transfer between Co^{2+} and Co^{3+} [10]. Nkeng *et al.* [11] have shown that in the same domain, $NiCo_2O_4$ presented continuous absorption. This is probably due to the total substitution of Ni^{2+} in octahedral sites for Co^{2+} while in our case we have a partial replacing of Co^{2+} in octahedral sites by Ni^{2+}. Belova *et al.* [12] reported that this transfer charges is due to the stabilization of Co^{3+} in high spin configuration in the octahedral sub-lattice of the spinel structure although Miedzinska *et al.* [10] considered that this is based upon the mechanisms of charge transfer between Co^{2+} and Co^{3+} and between oxygen and cobalt ions. So from our experimental value of the cell lattice and results already given in literature [13, 14] for metal oxygen distances in octahedral and tetrahedral sites, we propose an inverse spinel for $Ni_{0.4}Co_{2.6}O_4$ structure presenting the following ionic distribution: $Co_x^{2+}Co_{1-x}^{3+}$ $[Ni_{0.4}^{2+}Co_{0.6}^{2+}Co_{1+x}^{3+}]O_4$. This

distribution exhibits low spin Co^{2+}, Co^{3+} and Ni^{2+} ions in octahedral sites and high spin Co^{2+}, Co^{3+} in tetrahedral sites.
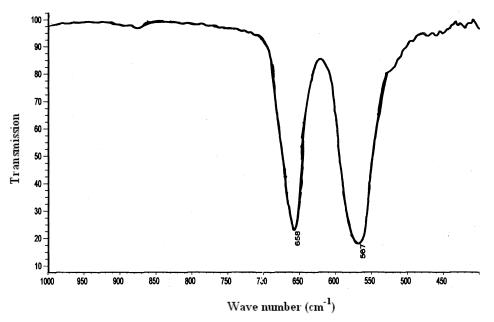

Figure 2. IR spectrum of $Ni_{0.4}Co_{2.6}O_4$ prepared by sol-gel via propionic acid.
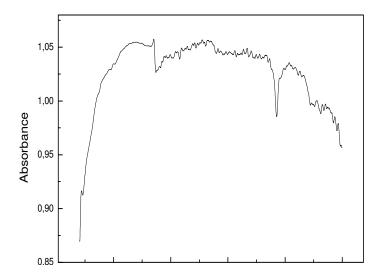

Figure 3. UV-vis-NIR reflectance spectrum of $Ni_{0.4}Co_{2.6}O_4$ prepared by sol-gel (propionic acid).

The SEM microphotograph gives an idea of the surface morphology of the compound. The morphology of the oxide surface is shown in Figure 4. It shows that $Ni_{0.4}Co_{2.6}O_4$ presents a regular repartition of nearly-spherical grains in a flat pattern and a rather highly porous homogeneous surface. Such morphology can be attributed to the nature of the solvent in the starting solution used, propionic acid seems to be very effective in producing an amorphous precursor yielding oxides with fine grains owing to the ability of certain weak acids to form polybasic acid chelates with various cations. This type of mixed oxides surface morphology has already been observed in the literature [15].
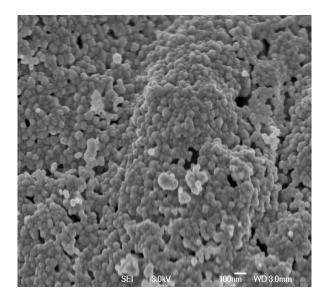

Figure 4. SEM microphotograph of $Ni_{0.4}Co_{2.6}O_4$ prepared by sol-gel (propionic acid).

Cyclic voltammograms of $Ni_{0.4}Co_{2.6}O_4$ were realized at varying scan rates (from 10 to 100 mV/s) with an Hg/HgO reference electrode in 1 M KOH (Figure 5). They were recorded between 200 mV and 650 mV in order to cover entirely the oxygen evolution domain potential. The voltammogram shows a set of two peaks corresponding to the anodic and cathodic reactions [16] prior to oxygen evolution. The mean peak potentials $E_p = \frac{1}{2} (E_{pa} + E_{pc})$ are 435 and 350 mV (Hg/HgO) for the highest scan rate (100 mV/s) and at the lowest one (10 mV/s), respectively. Singh [17] found in the case of mixed oxides films 525 mV and 420 mV for Co_3O_4 and $NiCo_2O_4$, respectively. These peaks have been assigned to the formation of the $NiOOH/Ni(OH)_2$ couple, following:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad [16, 18]$$

This means that OH^- ions are electroadsorbed in the Ni(III) active sites of the oxide surface prior to oxygen evolution.

A small shift of the peak potentials towards more positive values is observed when the scan rates increase, probably due to the effect of the ohmic resistance of the oxide. Indeed, this phenomenon could be related to a possible increase of the resistance in the interface when an increased roughness, owing to the pores, appears in the oxide.
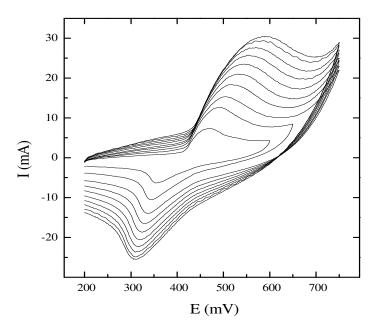
Figure 5. Cyclic voltammograms of $Ni_{0.4}Co_{2.6}O_4$ prepared by sol-gel (propionic acid) on Ni plates. Scan rates: from 10 to 100 mV/s.
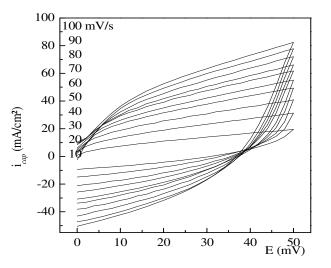

Figure 6. Cyclic voltammograms in the double-layer region of $Ni_{0.4}Co_{2.6}O_4$ (propionic acid sol-gel route).
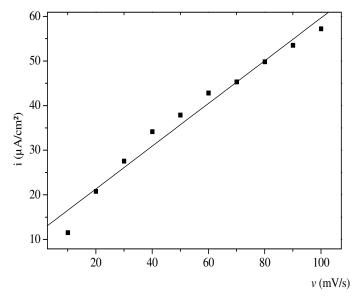
Figure 7. Capacitive current versus scan rate on $Ni_{0.4}Co_{2.6}O_4$ electrode.

To determine the electrochemical active surface area, cyclic voltammograms of the mixed oxide were recorded in a small potential region (between 0 and 0.05 V, near the open circuit potential). This region corresponds to the double layer capacitance domain, where the faradaic current is assumed to be negligible. The current is therefore, essentially, capacitive and varies linearly with the scan rate according to $i_{cap} = C_{dl}.v$ (where i_{cap} is the capacitive current and corresponds to the charging current measured at the middle of scan range, C_{dl} the double layer capacitance and v the scan rate). However, the presence of an intercept on the i_{cap} axis in Figure 6 indicates a small occurrence of faradaic processes such as electrochemical adsorption of OH^- ions during the cyclic runs [19]. From the slope of the curves i_{cap} versus v, the value of C_{dl} and the corresponding roughness factor are respectively $0.480.10^{-3}$ $F.cm^{-2}$ and 8 (Figure 6 and 7). Among the methods which have been revised by Petrii and Trasatti [20] we choose the cyclic voltammetry method for its simplicity and its reproducibility. In this method the determination of the roughness factor is carried out assuming a C_{dl} theoretical value of smooth surface of 60 $\mu F.cm^{-2}$ [20].

CONCLUSION

Oxygen evolution on Ni-Co mixed oxides has been studied by several workers. Depending on the preparation method, the experimental conditions and the nature of the support, various characteristics of this type of compound have been obtained. A new sol-gel process has been used to prepare mixed oxides powders for an electrochemical use in oxygen evolution. The process enables to get pure spinel phase with good electrochemical properties and high surface area electrocatalyts. The activity of Co_3O_4 can be increased by a partial substitution of nickel(II) ions for cobalt(II) ions.

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