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RESEARCH ARTICLE

SYNTHESIS AND STRUCTURAL, MORPHOLOGICAL AND ELECTROCHEMICAL CHARACTERIZATION OF NANOSTRUCTURED MIXED OXIDES OF NICKEL AND COBALT NI$_{0.5}$CO$_{2.5}$O$_4$ POWDER PREPARED BY CO-PRECIPITATION OF HYDROXIDES TECHNIQUE

***Makhtar Guène, Mamadou Guèye and Papa Charles Harris Mandiamy**

Laboratoire de Chimie Physique Organique et d'Analyse Environnementale, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal

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ABSTRACT

Nanostructured Nickel cobalt oxide $Ni_{0.5}Co_{2.5}O_4$ powders were prepared by co-precipitation of hydroxides technique from mixed stoichiometric amounts ofhexahydrated nickel nitrate $Ni(NO_3)_2.6H_2O$ and of hexahydrated cobalt nitrate $Co(NO_3)_2.6H_2O$ (Aldrich) as sources of nickel and cobalt, respectively. X-ray diffraction (XRD) patterns showed that the oxides crystallize in a cubic spinel phase. *I*nductively coupled plasma-optical emission spectrometry (ICP-OES) confirms the stoichiometric proportions of metals in the cobaltites of nickel. The scanning electron microscopy (SEM) images reveal a porous structure. Cyclic and steady state voltammetries (CV and CSV) indicated high electrochemical properties.

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INTRODUCTION

Nanomaterials compounds gained important consideration during last decade. This is the consequence of their multiple possibilities of application in different science fields as chemical (Peres *et al.*, 2012), physical (QuiYang *et al.*, 2014), pharmaceutical and biomedical technologies (Sangeeta *et al.*, 2012), superconductors (Xu Wang *et al.*, 2014). Among nanomaterials products spinel-type oxides, cobalt oxide, Co_3O_4, is considered as one of the most promising electro catalysts in alkaline solutions due to its low cost, good corrosion stability, large availability, and from an electro catalytic point of view, to its thermodynamic stability and electrocatalytic activity. However, to increase the physico-electrochemical properties of this cobaltite, the substitution of cobalt ions by nickel divalent metal is usually realized. So studies about characterization of the structural and electrochemical properties of metallic spinel-type mixed oxides have extensively been carried out (Makhtar Guene *et al.*, 2007; Manimekalai *et al.*, 2013) as binary metal oxide composite nanomaterials brings beneficial effects in the electrochemical and physical properties of mixed oxides (7). So mixed oxides of nickel and cobalt are used now in near all fields of research, supercapacitors (8), lithium batteries (9, 10), chemical sensors (11), electrocatalysts for oxygen reduction (12) etc.. On the other hand, recently it has been shown that the surface composition of $NiCo_2O_4$ prepared by thermal decomposition of nitrates shows a strong enrichment in Ni (13). In this paper we investigate the physico-electrochemical properties of nickel cobaltites synthesized by co-precipitation of hydroxides and characterized by *I*nductively coupled plasma-optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), scanning electronic microscope (SEM), cyclic and steady voltammetries (CV and CSV), Fourier transform infrared spectroscopy (FTIR). Its roughness factor and conductance were determined.

Experimental

Co-precipitation of hydroxides: The stoichiometric amounts of nitrates ($Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$) were dissolved in distilled water. An excess of 3*M* KOH solution

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****Corresponding author:*** **Makhtar Guène,**
Laboratoire de Chimie Physique Organique et d'Analyse Environnementale, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal.

was added, drop-wise, in order to co-precipitate the hydroxides. The solvent was evaporated and the precipitate washed with distilled water, and dried at 100 °C for 12 h and finally treated at 350 °C in an oven for 24h (Ponce *et al.*, 1999).

Characterization

All X-ray powder diffraction patterns were realized using a Siemens D 500 diffractometer using CoKα radiation (λ= 0.1789 nm) anti-cathode and a Ni filter at scanning rate of 0.05° s^{-1}, 2θ varying from 10° to 80°. Thermo gravimetric analyzer (TGA) measurement was carried out using TG 209 F3 Tarus (Netzsch). Field emission scanning electron microscopy (FESEM) images were taken with a JEOL apparatus (JSM 840). Infrared spectra were obtained using a Brucker Multipare CT 25000 spectrometer coupled with an Avatar 320 FTIR apparatus.

The ICP measurements were performed with a sequential ICP-OES spectrometer Varian 3710ES (axial view), equipped with a sample preparation system Varian SPS3 (Agilent Technologies, USA). Three samples, each containing $HNO_3$70% acid were prepared. The mixture is filtered through pore size membrane filters of 0.45 nm before ICP analysis. To avoid concentrated samples, in order to stay in the calibration range, we used 100 times diluted samples.That would explain the slight error measurements. Scanning electron microscopy (SEM) allows estimating the average aggregate size and crystallinity degree of the oxides, the microstructures of the powders were examined by scanning electron microscopy using a JEOL apparatus (JSM 840). The electrochemical measurements were performed at 25 °C in the classic three-electrodecell 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 acomputer 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

Thermogravimetric analyses TGA

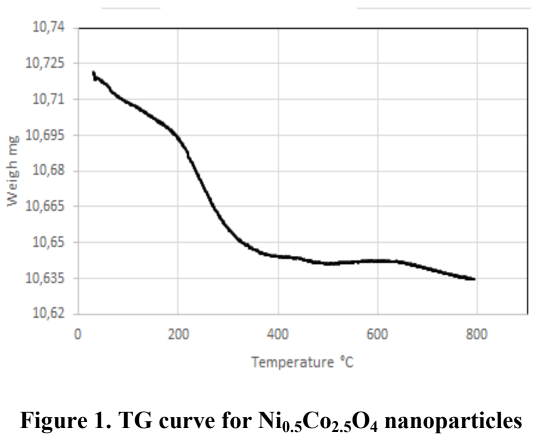

Figure 1. TG curve for $Ni_{0.5}Co_{2.5}O_4$ nanoparticles

The thermal properties of the binary nickelcobalt precurs or were characterized by the TG analyses in order to determine the suitable thermal decomposition temperature for preparing the mixed oxide. Figure 1 shows the thermal decomposition of the precursor from the ambient temperature to 800°C. It appears that the decomposition phenomenon occurs in three different steps (Chun-Chieh Tseng *et al.*, 2013; Chun-Tsung Hsu, 2013; Makhtar Guene *et al.*, 2005). The first step from room temperature to 225°C, corresponds to evaporation of the moisture and the dehydration of the nitrates. The second step, from 225 to 315°C, corresponding to the major weigh lost, can be attributed to the dehydration of the oxide hydrate and decomposition of nitrate anions. The last step, from 315°C to 700°C, suggests the formation of a well crystallized spinel structure.

X-ray analysis

The XRD powder pattern of $Ni_{0.5}Co_{2.5}O_4$ prepared by co-precipitation of hydroxides at 350 °C was recorded in a 2θ range from 10° to 80° (Figure 2).The diffraction peaks are observed at about 20.1, 37.3, 42.6, 43.5, 53.4, 66.9, 70.2 and 77.8°. They correspond to the (111), (220), (311), (400), (422), (511), and (440) planes of the $Ni_{0.5}Co_{2.5}O_4$ phase. All these peaks (in particular the characteristic one at 311) indicate clearly that the binary mixed oxide crystallized in cubic spinel phases spatial FD3m with a total absence of parasitic peaks such as NiO or CoO. This demonstrates the purity of the product and confirms the results obtained with ICP-OES.

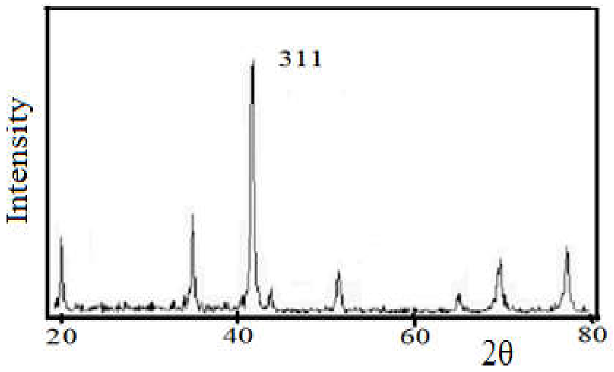

Figure 2: XRD patterns of $Ni_{0.5}Co_{2.5}O_4$

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:

$$a = d_{hkl}(h^2 + k^2 + l^2)\text{h, k and l are Miller indices}$$

hkl	111	220	311	222	400	422	511	440
d_{hkl} (nm)	4.671	2.852	2.435	2.335	1.648	1.688	1.558	1.430
a (Å)	8.089	8.066	8.073	8.084	8.073	8.084	8.086	8.080

The calculated average value is *a* = 8.079 ± 0.011 Å, result matching well the JCPDS ASTM files No. 9-418 and 2-1074 where $a_{NiCo_2O_4} = 8.128$ Å. This value is in good agreement with our previous works as we found 8.095 Å for $Ni_{0.6}Co_{2.6}O_4$ (Makhtar Guene, 2005) and 8.102 Å for $Ni_{0.9}Co_{2.1}O_4$ (Guèye *et al.*, 2016) prepared both by sol gel using propionic acid. Chi *et al* (Chi, 2004) obtained values from 8.098 to 8.109 Å for $NiCo_2O_4$ prepared by coprecipitation of hydroxides method. Ding and coworkers (20) obtained a lattice parameter of 8.104 Å for a $NiCo_2O_4$ sample

Inductively coupled plasma-optical emission spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a powerful and suitable technique for the determination of nickel amounts in a sample (Ferreira, 1999; Yunes *et al*., 2003). We show here that ICP-OES is also efficient to determine the quantity of cobalt contained in a sample. Table II gives the amounts of Ni and Co calculated according to the stoichiometry of $Ni_{0.5}Co_{2.5}O_4$ and determined from ICP-OES technique. Calculated and experimental values are in good agreement taking into account uncertainties. The ICP-OES procedure used here shown that it is easy besidesbeing simple and economical, to get the amount of cobalt contained in a sample. This technique has already been used by Li *et al.* (1999) to compare results obtained in calculated method and by ICP-OES in the determination of the ratios of Pt in Mn_3O_4 Pt-Mn_3O_4/C powder. Semenova and co-workers (22) used, also, ICP-OES to find contents of Li and Na in cobaltite $Li_xNa_yCoO_2$.

Table 2. Concentrations (g.kg^{-1}) of Ni and Co in oxide samples obtained by ICP-OES

Element	Ions concentrations (g/kg)	
	Determined from ICPOES	Calculated from stoichiometry
Ni	129 ± 11	122
Co	613 ± 20	588

Scanning electron microscopy SEM

The electrocatalytic performances of mixed oxides, when used as electrodes, depend on the electrolytes, the reactants, the transport of charges (electrons, ions). All these factors must be considered simultaneously as they are, mainly, function of the microstructure of the substances. Consequently, it is necessary to study the oxide morphology by SEM since microphotographs SEM give an idea of the compound surface morphology.

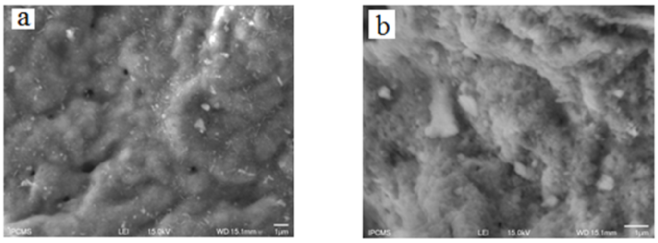

Figure 3: SEM migrographs of $Ni_{0.5}Co_{2.5}O_4$ a) X 6000 and b) X 10000

Themorphology of the oxide surface is displayed in Figure 3. It shows that $Ni_{0.5}Co_{2.5}O_4$ presents a very marked cottony appearance with porous homogeneity. This porous aspect of mixed oxides of Ni and Co has already been observed in the literature with both powders (Seung Ho Choi *et al*., 2015) and films (Zhi-Bin Zheng, 2016).This porous character of the oxide is of capital importance when used as electrode, in particular in the transport of electrical charges and ions diffusion. This fact gives it high electrocatalytic properties (Xuefei Gong *et al*., 2014).

Fourier transform infrared spectroscopy (FTIR)

We used FTIR spectroscopy in order to provide supplementary information on the type of metal oxides as it is known to be a powerful tool in the characterization of mixed oxides (Melendres, 1998). Figure 4 shows the spectrum of $Ni_{0.5}Co_{2.5}O_4$ oxide prepared by co-precipitation of hydroxides. The two strong absorption bands at 559 cm^{-1} and 656 cm^{-1} correspond to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of pure spinel cobaltites (Salvati-Niasari, 2009; Alizadeh-Gheshlaghi, 2012). No other peak has bee observed, confirming the purity of the synthetized oxide. This observation is in good agreement with the XRD and ICP-OESresults.

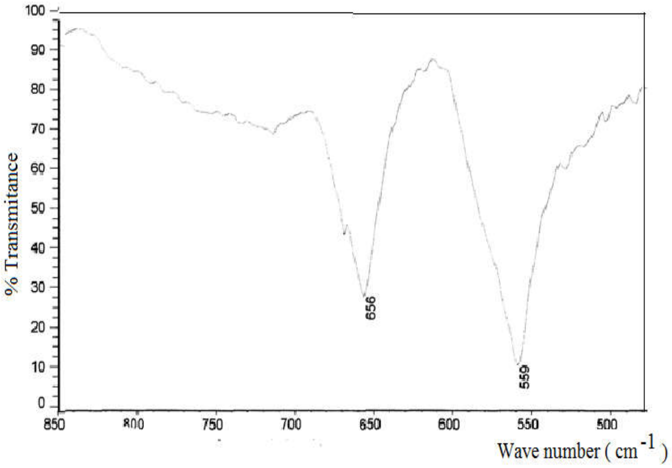

Figure 4: FFT-IR spectra of $Ni_{0.5}Co_{2.5}O_4$ catalysts prepared by co-precipitation and calcined at 350°C

Cyclic voltammetry

Figure 5 shows cyclic voltammetric behavior of $Ni_{0.5}Co_{2.5}O_4$ electrodes at scan rates from 10 mV/s to 100 mV/s in 1.0 mol/dm^{3}NaOH at room temperature. The current was normalized to the amount of activity materials in 1 cm^{2}electrode.

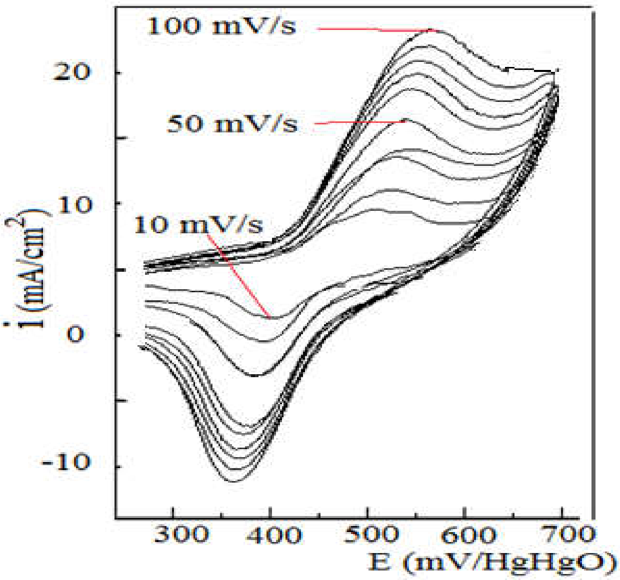

Figure 5: Cyclic voltammograms of $Ni_{0.5}Co_{2.5}O_4$ in 1.0 mol/L NaOH at scans rate varying from 10 mV/s to 100 mV/s.

Each cyclic voltammogram exhibits two sets of peak, an anodic peak at about 0.380V and its corresponding cathodic one at about 0.550 V/HgHgO prior to oxygen reduction. The intensity of the anodic and cathodic peaks increases with the scanning rates.

Anodic peaks shift towards positive potential and the cathodic peaks shift towards negative potential when scan rates increase. This phenomena has already been observed by Cuihua *et al.* (2012) and Guèye *et al.* (2016). The shapes of the well-defined peaks of the CV curves do not significantly changed with the increase of the scan rate, revealing the good electrochemical reversibility of the $Ni_{0.5}Co_{2.5}O_4$ electrode (Liu *et al.*, 2012). The redox peaks in cyclic volammetry are attributed to faradic reaction involving NiII/NiIII and NiII/NiIII with OH^- ions (Ediga Umeshbabu *et al.*, 2014). The redox peak of the electrode materials can be attributed to the following reactions.

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$$

And

$$2Ni_{0.5}Co_{2.5}O_4 + 2OH^- + 2H_2O \rightarrow NiOOH + 5CoOOH + 2e^-$$

And

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^-$$

The redox potentials of the NiII/NiIII and CoIII/CoIV transitionsare so close that the redox peaks observed are becoming anoverlapping ones (Wu, 2014). In both cases, the sudden increase of the current at high potentials (after the oxidation peak) corresponds to the oxygen evolution reaction according to:

$$4\,OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

Steady state cyclic voltammetry

Figure 6 gives typical voltamperometric curves of the capacitive currents as a function of the potential. The real surfaces are thus determined from the plot of the capacitive currents as a function of the scanning rate (36, 37) in a very low potential range (in this case between 0 and 50 mV) in which the faradaic current is assumed to be negligible compared to the capacitive currents. In fact, the capacitive current density i_{cap} and the scanning speed *v* are related by the relation

$$i_{cap} = C_{dc} \times v = C_{dc} \cdot \frac{dE}{dt}$$

Where C_{dc} is the double layer capacitance and corresponds to the slope of the line i = f (*v*). (Zhi-Bin *et al.*, 2016).

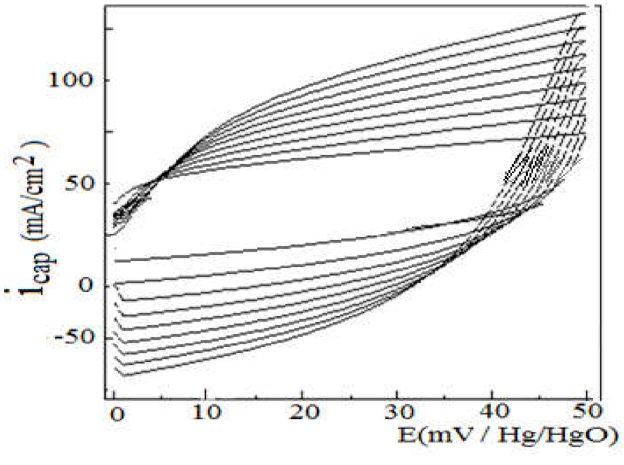

Figure 6: Cyclic voltammograms of $Ni_{0.5}Co_{2.5}O_4$ electrode in the potential range of 0 - 0.05V in 1.0 mol/L NaOH (scan rates in varying from 10 to 90 mV/s)

However, the presence of an intercept on the i_{cap} axis in Figure7 indicates a small occurrence of faradaic processes such as electrochemical adsorption of OH^- ions during the cyclic runs. To determine the roughness factor R_f, we choose the cyclic voltammetry method for its simplicity and its reproducibility. In this method, the determination of R_f is carried out assuming a double layer C_{dl} theoretical value of smooth surface of 60µF.cm^{-2} (Da Silva, 2001). The roughness factor, R_f, is obtained by dividing the electro decapacitance C_{dl} by the capacitance of smooth surface (Da Silva, 2001; Bangan Lu, 201138).The estimated C_{dl} and corresponding roughness factor R_f values in 1MKOH at 25◦C obtained from the slope of the curvei$_{cap}$ versus *v*, are respectively 0.490.10^{-3} F.cm^{-2} and 8. These values are similar to those already obtained for mixed oxides of Ni and Co (Bangan Lu, 2011) and of other types of mixed oxides (Singha, 2006)

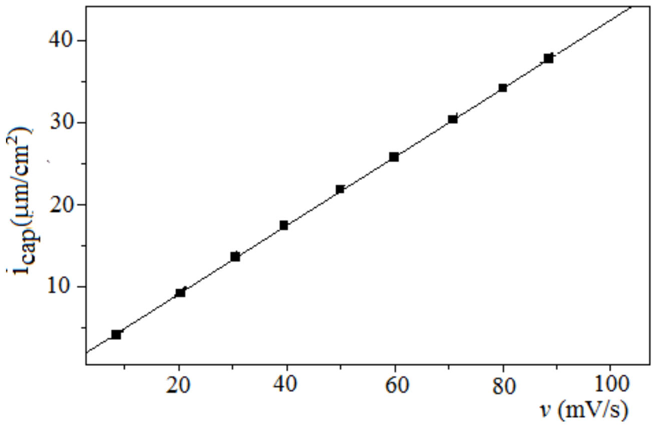

Figure 7: Double layer charging current density versus scan rates of $Ni_{0.5}Co_{2.5}O_4$ electrode in 1.0 mol/L NaOH (scan rates in varying from 10 to 100 mV/s)

Figure 7 gives the measurements in a potential range where oxygen evolution takes place according to the reaction: 4 OH^- → 2 H_2O + O_2 + 4e- which allows the release of molecular oxygen and occurs at from 0.6 V (Hg / HgO, 1M KOH)

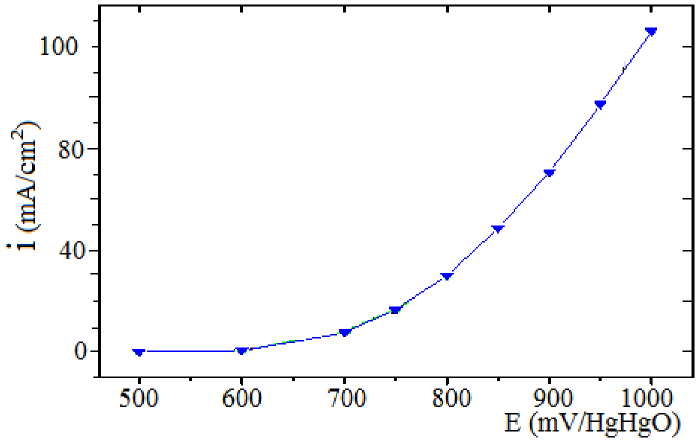

Figure 8 : Steady state polarization curve from oxygen evolution of $Ni_{0.5}Co_{2.5}O_4$ electrode

The curve (Fig. 8) shows two zones, the first one between 0.5 and 0.65 V and a second one over 0.65 V. This second zone, with a high slope, corresponds to the formation of oxygen bubbles (40). This overvoltage zone is a function of the method of preparation and the modification of the slope between the two zones can be associated with three distinct factors: a change in the mechanism of the reaction in the limiting step of the reaction rate (Bocca, 1999; Boon Siang

Yeo, 2011) and / or a modification of the surface area (Boon Siang Yeo, 2011).

Conclusion

$Ni_{0.5}Co_{2.5}O_4$ oxide was synthetized using the co-precipitation of hydroxides method which we used in this study as itis very simple, large-scale, inexpensive and is a traditional method to prepare powder samples. It allows to obtain easy reproducible results. We get pure mixed oxide capable to deliver excellent performance. The product have been characterized by techniques as such XRD, ICP-OES, SEM CV, and CSV. These techniques confirm stoichiometric compositions and purity of the mixed oxide, which means that the oxide crystallized in the spinel phase, space group Fd3m, with no parasitic phases. SEM microphptographs indicate porous aspect leading to good properties of the oxide in electrical charges and ions transport and diffusion. The CV and CSV point out high catalytic performance, good stability for the OER in NaOH solution. This work opens up the possibility for the fabrication of high-performance electrode.

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REFERENCES

Alizadeh-Gheshlaghi E., Shaabani B., Khodayari A., Azizian-Kalandaragh Y., Rahimi R. 2012. Powder Technology, 217, 330-339

Bahaa M. Abu-Zied, Soliman A. Soliman, Sarah E. Abdellah, 2014. "Pure and Ni-substituted Co_3O_4 spinel catalysts for direct N_2Odecomposition"*Chinese Journal of Catalysis 35 1105–1112*

Bangan Lu, Dianxue Cao*, Pan Wang, Guiling Wang, YinyiGao, 2011. "Oxygen evolution reaction on Ni-substituted Co_3O_4 nanowire array electrodes" international journal of hydrogen energy 3 6 72 -78

Bocca C. A. BarbucciM. Delucchi, G. Cerisola, 1999. "NICKEL–COBALT oxide-coated electrodes: influence of the preparation technique on oxygen evolution reaction (OER) in an alkaline solution"International Journal of Hydrogen Energy Vol. 24, Issue 1; 21-26

Boon Siang Yeo and Alexis T. Bell, 2011. "Enhanced Activity of Gold-Supported Cobalt Oxide for the Electrochemical Evolution of Oxygen"; |*J. Am. Chem. Soc., 133, 5587–5593*

Chi B, Li J, Han Y, Chen Y. 2004. "Effect of temperature on thepreparation and electrocatalytic properties of a spinel$NiCo_2O_4$/Ni electrode". *Int J Hydrogen Energy, 29:605-615.*

Chi. B., Li, J., Han, Y., Chen, Y. 2004. Int. J. Hydrogen Energy, 29, 605-616.

Chun-Chieh Tseng, Jeou-Long Lee, Yih-Ming Liu, Ming-Der Ger, Youn-Yuen Shu, 2013. « Microwave-assisted hydrothermal synthesis of spinel nickel cobaltite and application for supercapacitors »; *Journal of the Taiwan Institute of Chemical Engineers 44 415 - 419*

Chun-Tsung Hsu, Chi-Chang Hu. 2013. «Synthesis and characterization of mesoporous spinel $NiCo_2O_4$ using surfactant-assembled dispersion for asymmetric supercapacitors" *Journal of Power Sources 242 66 - 671*

Cuihua An, Yijing Wangn, YananHuang, Yanan Xu, Lifang Jiao, Huatang Yuan, 2014. "PorousNiCo2O4 nanostructuresforhigh performancesupercapacitorsvia a microemulsiontechnique", Nano Energy 10, 125–134

Da Silva LM, De Faria LA, Boodts JFC 2001. « Determination of themorphology factor of oxide layers"*Electrochim Acta 47: 395-403*.

Dinamani, M. and Vishnu Kamath, P. 2000. "Electrocatalysis of oxygen evolution at stainless steel anodes by electrosynthesized cobalt hydroxide coatings";*Journal of Applied Electrochemistry 30 1157-1161.*

Ding, R., Qi, L., Jia. M., Wang, H. 2014. *Journal of Power Sources,* 251, 287-295

EdigaUmeshbabu, G. Rajeshkhanna, G. Ranga Rao, 2014. "Urchin and sheaf-like $NiCo_2O_4$nanostructures: Synthesis and electrochemical energy storageapplication"; international journal of hydrogen energy 39 15627 - 15638

Ferreira, S.L.C., de Brito, C.F., Dantas, A.F., LopodeArau´ jo, N.M. Spinola Costa, A.C. 1999. Talanta 48 1173.

Guèyeet, J. M. M. Guène Synthesis of $Ni_{0.9}Co_{2.1}O_4$ mixed oxides powders prepared by sol-gel method viapropionic acid and characterization by X-ray, ICP, FTIR and XPS analysis" *Soc. Ouest-Afr. Chim. (2016) 041; 35- 40*

Larcher, D., Sudant, G., Leriche, J. B., Chabre, Y., Tarascon, J. M. 2002. The electrochemical reduction ofCo3O4 in a lithium cell. J. Electrochem. Soc., 149: A234.

Li Z., Shi S., Zhong Q., Zhang C., Xu C. 2014. ElectrochimicaActa 146, 119-124

Liu, Q., Zhang, X., Yang, B., Liu, Jingyuan, Li, R., Zhang, H., Liu, L., and Wang, J. 2012. "Construction of Three-Dimensional Homogeneous $NiCo_2O_4$ Core/Shell Nanostructure as High-Performance Electrodes forSupercapacitors". *J. Electrochem. Soc.,* 162 (12), E319-E324.

Makhtar Guene, Abdou Aziz Diagne, Modou Fall, MorMarème Dieng, and Gérard Poillerat, 2005. "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", *Chem. Soc. Ethiop. 19(2), 213-220.*

Makhtar Guene, Abdou Aziz Diagne, Modou Fall, MorMarèmeDieng, and Gérard Poillerat "Preparation of nickel - cobalt spinel oxides NixCO3-xO4. Comparison of two physical properties stemming from four different preparation methods and using carbon paste electrode", *Chem. Soc. Ethiop. 2007, 21(2), 255-262.*

Makhtar Guene, Abdou Aziz Diagne, Modou Fall, MorMarèmeDieng, and Gérard Poillerat, 2006. " Effects on the physicochemical properties of partial substitution of Ni for Co in $Ni_xCo_{3-x}O_4$ (x = 0, 0.4, 0.8) nickel – cobalt spinels using a new method of synthesis (Pechini Technique)"; *Ann. Chim. Sci. Mat., 31(1); 49-59*

MamadouGuèye, Makhtar Guène, 2016."Preparation, Physical and Electrochemical Characterization of Nickel Cobaltites, $Ni_xCo_{3-x}O_4$ (0 < x < 2.5)", *Asian Journal of Chemistry Vol.28 N°.5, 1133-1138.*

Manimekalai*, R., Kalpanadevi, K.and Sinduja, R. 2013. « Synthesis and Characterization of Cobaltite Spinels Using Infrared, Thermogravimetric Analyses and X-Ray Crystallography"; *Orbital: The Electronic Journal of ChemistryVol 5 No. 1 January-March.*

Melendres C. A., Bowmaker C. A., Leger J. M., Beden B. 1998. *Journal of Electroanalitical Chemistry* (1998) 449, 215-218

Meza, E., Ortiz, J., Ruíz-León, D., Marco, J.F., Gautier, J.L. 2012. “Lithium-nickel cobalt oxides with spinel structure prepared at low temperature. XRD, XPS, and EIS measurements »;*Materials Letters 70 189–192*

Peres, A.P.S., Limab,n, A.C., Barros, B.S., Melo, D.M.A. 2012. « Synthesis andcharacterizationof$NiCo_2O_4$ spinel usinggelatin as anorganicprecursor”; *Materials Letters 89 36–39*

Ponce, J., Rios, E., Rehspringer, J. L., Poillerat, G., Chartier, P., Gautier, J. L. 1999. “Preparation of NickelAluminum–Manganese Spinel Oxides Ni*x*Al1−*x*Mn2O4 for Oxygen Electrocatalysis in Alkaline Medium:Comparison of Properties Stemming from Different Preparation Methods”. J. Sol. State Chem., 145: 23.

QiuYang, Zhiyi Lu, Tian Li, Xiaoming Sunn, Junfeng Liun, 2014. “Hierarchicalconstructionofcore–shell metal oxidenanoarrayswithultrahigh areal capacitance”; *Nano Energy(2014) 7, 170–178*

Salvati-Niasari M., Mir N., Davar F. 2009. *Journal of Physics and Chemistry of Solids,* 70, 847-852

Sangeeta N. Kale, Anil D. Jadhav, Seema Verma, Soumya J. Koppikar, RuchikaKaul-Ghanekar,Sanjay D. Dhole, Satishchandra B. Ogale ; « Characterization of biocompatible$NiCo_2O_4$nanoparticles for applications in hyperthermia and drug delivery”; *Nanomedicine: Nanotechnology, Biology, and Medicine 8 (2012) 452–459*

Semenova E. V., Samigullina R. F., Shalaeva E. V.,Kourov N. Z., Kellerman D. G. 2011. International Journal of Inorganic Chemistry, volume Article ID 649183

Seung Ho Choi a, Sun Kyu Park b, Jung-Kul Lee b, *, Yun Chan Kang 2015. « Facile synthesis of multi-shell structured binary metal oxide powders with a Ni/Co mole ratio of 1:2 for Li-Ion batteries » *Journal of Power Sources 284 481-488*

Singha,∗ R.N., Singha, J.P., Nguyen Congb, H., Chartier, P. 2006. « Effect of partial substitution of Cr on electrocatalytic properties of $MnFe_2O_4$ towardsO_2-evolution in alkaline medium”; *International Journal of Hydrogen Energy 31 1372 – 1378*

Wu, Z., Zhu, Y., Ji, X. 2014. “NiCo2O4-based materials for electrochemical supercapacitors”, J. *Mater. Chem. A 2 14759–14772.*

Xu Wang, Chaoyi Yan, AfriyantiSumboja, 2014. Pooi See Leen “High performance porous nickel cobaltoxide nanowires for asymmetric supercapacitor » *Nano Energy, 3, 119–126*

Xu Wang, Chaoyi Yan, AfriyantiSumboja, Pooi See Lee; “High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor”;*Nano Energy(2014) 3, 119–126*

Xuefei Gong a, J.P. Cheng a, *, Fu Liu a, Li Zhang b, c, Xiaobin Zhang, 2014. “NickeleCobalt hydroxide microspheres electrodepositioned on nickel cobaltite nanowires grown on Ni foam for high-performance pseudo capacitors”, *Journal of Power Sources* 267 610-616

YaTanga,b , XinweiWanga , Qinghong Zhangb , Yaogang Lia, n, HongzhiWangb; 2012. « Solvothermal synthesis of Co1xNixFe2O4 nanoparticles and its application in ammonia vapors detection »; *Progress in Natural Science: Materials International, 22(1):53–58*

Yunes, N., Moyano, S., Cerutti, S., Ga´squez, J.A., Martinez, L.D. 2003. « On-line preconcentration and determination of nickel in natural water samples by flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES) » Talanta 59 943-949

Zhi-Bin Zheng a, Der-ShengChan b, Mao-Sung Wu 2016. « Highly porous nickel cobaltite film composedofnanosheetswith attached nanowires as an electrode material for electrochemical capacitors » *Materials Letters16946–49*

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