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Preparation, Physical and Electrochemical Characterization of Nickel Cobaltites, $Ni_xCo_{3-x}O_4$ ($0 \leq x \leq 2.5$)

MAMADOU GUÈYE and 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

*Corresponding author: E-mail: maguene@gmail.com

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Mixed oxides of spinel type $Ni_xCo_{3-x}O_4$ with $0 \leq x \leq 2.5$ have been synthesized *via* several methods. We investigated their physico-chemical properties using X-ray diffraction, Brunauer-Emmett-Teller method and scanning electron microscopy. Their electrocatalytic performances have been investigated by cyclic voltammetry, steady state measurements and roughness factor. The X-ray diffraction patterns show that the oxides crystallize in a cubic spinel phase with a unit lattice parameter which increases with x and is function of the preparation method. The electrochemical surface area of the powders was estimated from the double layer capacitance, characterized through cyclic voltammograms. Oxides prepared by Pechini synthesis present larger surface area, higher electrical conductivity, roughness electrochemical activities. It seems that catalytical properties are essentially related to real surface area.

Keywords: Mixed oxides, Spinel, Pechini, XRD, SEM, Cyclic voltammetry, Roughness factor.

INTRODUCTION

Spinel type oxides from transition metals, particularly the nickel-cobalt oxide family, are interesting systems because of their potential for a variety of applications in the conversion of energy [1-3]. Different studies have already shown that mixed oxides of Co and Ni are very good electrocatalysts for the electrochemical reduction and evolution of oxygen in alkaline media [4-6]. It is well known that the preparation methods affect the texture properties, the specific area and consequently the electrocatalytic properties of oxides [7-10]. For example, it has been recently shown that the surface composition of $NiCo_2O_4$ prepared by thermal decomposition of nitrates in isopropanol solutions exhibits a strong enrichment in Ni [11]. The distribution of the cationic oxidation states appears to reflect the type of characterization technique and the method of synthesis of $Ni_xCo_{3-x}O_4$ [12]. In this paper we investigated four methods to prepare mixed oxides $Ni_xCo_{3-x}O_4$ [x = 0, 0.4, 0.6, 0.8, 1, 1.2, 2, 2.5] in order to examine the relations between their physico-chemical properties and electrochemical performances and the preparation methods and to underline the important parameters in this relation. For this determination, we use X-ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET) method, scanning electron microscopy (SEM), cyclic voltammetry (CV), steady state measurements (SSM) and roughness factor (RF).

EXPERIMENTAL

Synthesis of nickel cobaltites: The mixed oxides $Ni_xCo_{3-x}O_4$ [x = 0, 0.4, 0.6, 0.8, 1, 1.2, 2, 2.5] were prepared by four different methods: two sol-gel methods (Pechini and *via* propionic acid), thermal decomposition of nitrates and co-precipitation of hydroxides.

The general chemical reaction leading to the formation of mixed oxides from nitrates is:

$$xNi(NO_3)_2{\cdot}6H_2O + (3 - x)\ Co(NO_3)_2{\cdot}6H_2O \longrightarrow Ni_xCo_{3-x}O_4\ (s) + 3\ N_2O_2\ (g) + 18\ H_2O\ (liq)$$

Sol-gel method (Pechini process) [13]: 20 g of citric acid was dissolved in 20 mL of ethylene glycol and the solution was heated at 90 °C during 0.5 h. The stoichiometric amounts of nitrates of nickel and cobalt (Aldrich) were added and heated at 120 °C until the formation of a viscous liquid. To eliminate the excess of solvent, vacuum evaporation is carried out at 180 °C during 0.5 h under atmospheric pressure. The final product is thermally treated to obtain the spinel phase (see below for the different heat treatments used).

Sol-gel method (*via* propionic acid): A similar method was described elsewhere [8]. The stoichiometric amounts of nitrates of nickel and cobalt were dissolved in 20 mL of propionic acid. The mixture is gently heated at 120 °C to eliminate excess of propionic acid. A gel is formed which is afterwards broken

by the addition of liquid nitrogen. The fine powder obtained is heated at 140 °C to eliminate the excess of water and is thermally treated to get the spinel phase of the mixed oxides.

Thermal decomposition of nitrates: The stoichiometric amounts of nitrates of nickel and cobalt dissolved in their water of crystallization by soft heating were placed in an oven during 24 h at 90 °C to evaporate all the water. The mixture was then calcinated at 140 °C. The blackish solid obtained is thermally pre-treated during 4 h at 200 °C. A final heat treatment is realized to get the spinel phase [14].

Co-precipitation of hydroxides: The metallic salts were dissolved in distilled water. An excess of 3 M KOH solution 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 during 12 h and finally treated in an oven during 24 h [15].

All the products have been treated at two different temperatures: 300 and 350 °C. Only $Ni_{2.5}Co_{2.5}O_4$ was treated at 400 °C.

X-ray diffraction pattern and BET: All X-ray powder diffraction patterns were realized using a Siemens D 500 diffractometer with a CoK_α anti-cathode and a Ni filter at scanning rate of 0.05°/s, 2θ varying from 20 to 120°. The unit lattice parameter of the spinel structure α was determined using a least-square program on the basis of the observed interplanar *d*-spacing and Miller indexes hkl (in agreement with data in the ASTM Powder Diffraction File JCPDS-ICDD 37-878).

The determination of the specific surface area (BET) was realized using a Sorpty 1750 Erba instrument using nitrogen gas absorption at liquid nitrogen temperature.

Scanning electron microscopy (SEM): In order to estimate 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 details of surface morphology could be studied at magnifications of up to 300000X.

Electrochemical measurements: Cyclic voltammetries and steady state measurements were used to characterize the product. The experiments were carried out using a three-electrode cell. The electrolyte was a 1 M KOH solution prepared with twice-distilled water and Hg/HgO 1 M KOH reference was used. A Pt coil was used as auxiliary electrode and a potentio-galvanostat EG & G Princeton Model 263 interfaced with a computer was used. Nickel plates (1 × 2 cm^2) cut from a Ni foil (99 % Aldrich) were used to prepare the working electrode according to the following procedure: a suspension of mixed oxides powder 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 h in order to improve the active matter grip on the support. This operation was repeated 4 times for each sample.

RESULTS AND DISCUSSION

X-ray diffraction patterns: They were taken for all the mixed oxides and for the four methods of preparation [(Fig. 1a and 1b) for $Ni_{0.4}Co_{2.6}O_4$ and Co_3O_4].

A single phase with a spinel-related structure appears for all the prepared compounds ($0 \le x \le 1.2$) with the different

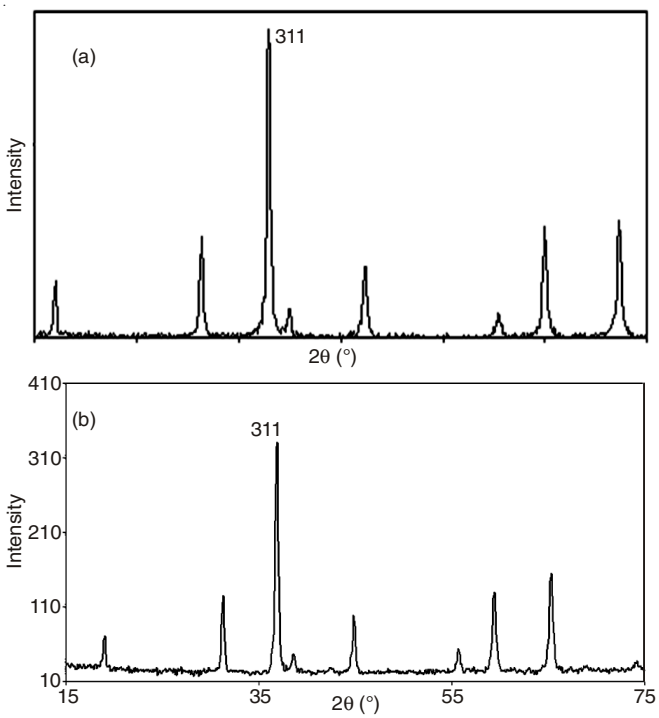

Fig. 1. X-ray diffractions of (a) $Ni_{0.4}Co_{2.6}O_4$ and (b) Co_3O_4

peaks belonging to this structure and in particular the characteristic 311 plane peak. For x = 2 and x = 2.5 some characteristic peaks of NiO appear but smaller than the spinel ones (Fig. 2). Comparing the samples prepared at 350 and 400 °C one can see that the amount of NiO phase increases with the temperature. This decomposition of NiO phase was also observed by Roginskaya *et al.* [16]. Hu *et al.* [17] 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. Depending to the preparation methods the compounds are more or less crystallized; the compounds from hydroxides co-precipitation being the poorly crystallized.

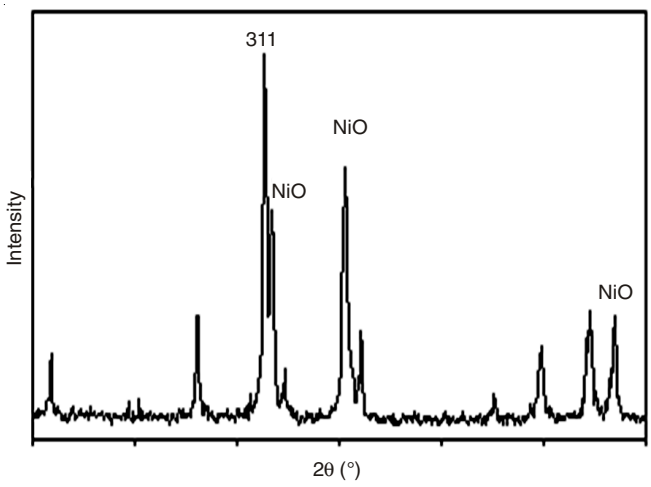

Fig. 2 XRD pattern of $Ni_xCo_{3-x}O_4$ [x = 2.5]

The crystallographic lattice parameter α, was determined as a function of the preparation method. Table-1 shows that the cells parameter increase with nickel x content which means that we have a progressive substitution of Co^{3+} in octahedral

sites by Ni^{2+}. The cubic lattice parameter α shows also slight variations with the synthesis method. The introduction of Ni leads to an expansion in the ionic radius of low spin Ni^{3+} which is slightly larger than the low spin Co^{3+} [11]. The values given in Table-1 compare well with the ones of the ASTM card ($a_{Co_3O_4}$ = 0.8084 nm and $a_{NiCo_2O_4}$ = 0.8128 nm) [JCPDS- ICDD 9-418 and 2-1O74)].

TABLE-1
EVOLUTION OF THE CELL PARAMETER (Å) WITH x AND THE PREPARATION METHOD

Methods compounds	Sol gel (Pechini)	T.D.N.	Sol-gel (propionic acid)	Co-precipitation of hydroxides
Co_3O_4	8.073	8.078	8.094	8.099
$Ni_{0.4}Co_{2.6}O_4$	8.078	8.088	8.094	8.103
$Ni_{0.6}Co_{2.4}O_4$	8.079	8.105	8.106	8.108
$Ni_{0.8}Co_{2.2}O_4$	8.087	8.108	8.107	8.110
$NiCo_2O_4$	8.089	8.109	8.110	8.161

BET surface area measurement: Table-2 and Fig. 3a and 3b show the evolution of the specific surface area, respectively as the function of the nickel content x and the method of preparation. This table shows an increase in specific surface area according to the degree of substitution x. In fact, the specific surface areas rapidly increase with the percentage of Ni. The results are in perfect correlation with those in the literature [18-20]. It is noted that the products prepared by sol-gel and particularly with sol gel Pechini present greater specific surface areas, which can be related to the nature of homogeneous crystals obtained with these methods.

Scanning electron microscopy: Fig. 4 shows the crystals of mixed oxides produced by different methods. It can be found the intrinsic dependence of the morphology of the oxide with the preparation method.

In case of oxides synthesized by Pechini (Fig. 4a), the crystals are spherical, of low dispersed sizes, average diameter of a few micrometers with a homogeneous and uniform texture.

The oxides prepared by sol-gel (*via* propionic acid) (Fig. 4b) have a planar structure with more or less discrete strata while those prepared by co-precipitation of hydroxides (Fig. 4c) of hydroxides and TDN (Fig. 4d) are a cottony appearance with more marked and significant in homogeneities porous appearance. In these cases, a greater impression of depth and contrast is observed.

Cyclic voltammetry: Fig. 5 shows cyclic voltammograms of mixed oxides. The voltamogramms were realized at varying scan rate (10 to 100 mV s^{-1}) with an Hg/HgO reference electrode in 1 M KOH at room temperature.

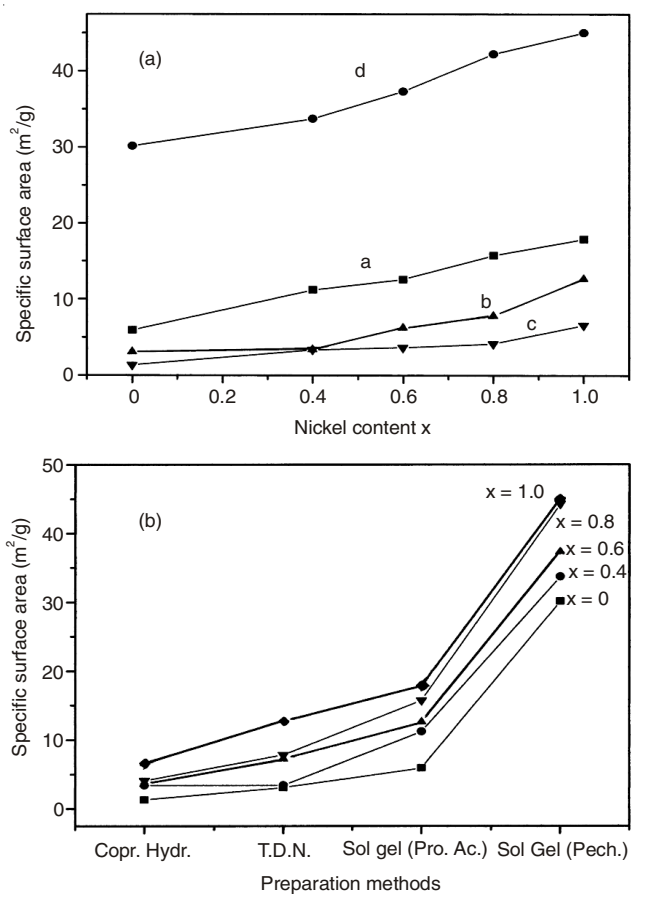

Fig. 3. Specific surface area of $Ni_xCo_{3-x}O_4$ (a) As a function of nickel content x (b) As a function of the preparation method

Each voltammogram has at least an anodic main peak at around 470 mV and its corresponding cathodic peak at about 360 mV, prior to the oxygen evolution. However, certain curves present a second shoulder oxidation peak at 370 mV. These phenomena have been previously studied [7,21-24] and can be attributed to the transition of the redox couple Co(II)/Co(III) in tetrahedral sites (for peak around 370 mV) and Co(III)/Co(IV) (for peak around 470 mV). The cathodic broad peak corresponds to the reduction of Co(IV) and Ni(III) species [24,25]. In the case of Co_3O_4, the anodic peaks potential correspond to the electrochemical oxidation reaction:

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^- \quad E° = 0.562\ V\ (HgO/Hg)$$

In the case of $Ni_xCo_{3-x}O_4$ ($x \neq 0$), the peaks observed have been assigned to the formation of a Ni^{3+}/Ni^{2+} couple following:

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

A small shift of the peaks potential towards more positive values is observed when the scan rate increases probably due

TABLE-2
SPECIFIC SURFACE AREA (BET) AND DOUBLE LAYER CAPACITANCE OF POWDERS SYNTHESIZED BY THE FOUR DIFFERENT METHODS AS A FUNCTION OF THE NICKEL CONTENT x

x	Sol-gel (propionic acid)		Sol-gel (Pechini)		T.D.N.		Co-precipitation of hydroxydes	
	S (m^2/g)	Cdl ($\mu F/cm^2$)	S (m^2/g)	Cdl ($\mu F/cm^2$)	S (m^2/g)	Cdl ($\mu F/cm^2$)	S (m^2/g)	Cdl ($\mu F/cm^2$)
0	6	340	30	560	3	360	1	350
0.4	11	480	34	780	3	420	3	420
0.6	13	410	37	960	7	660	4	540
0.8	16	720	44	1020	8	720	4	660
1.0	18	840	45	1260	13	780	7	660

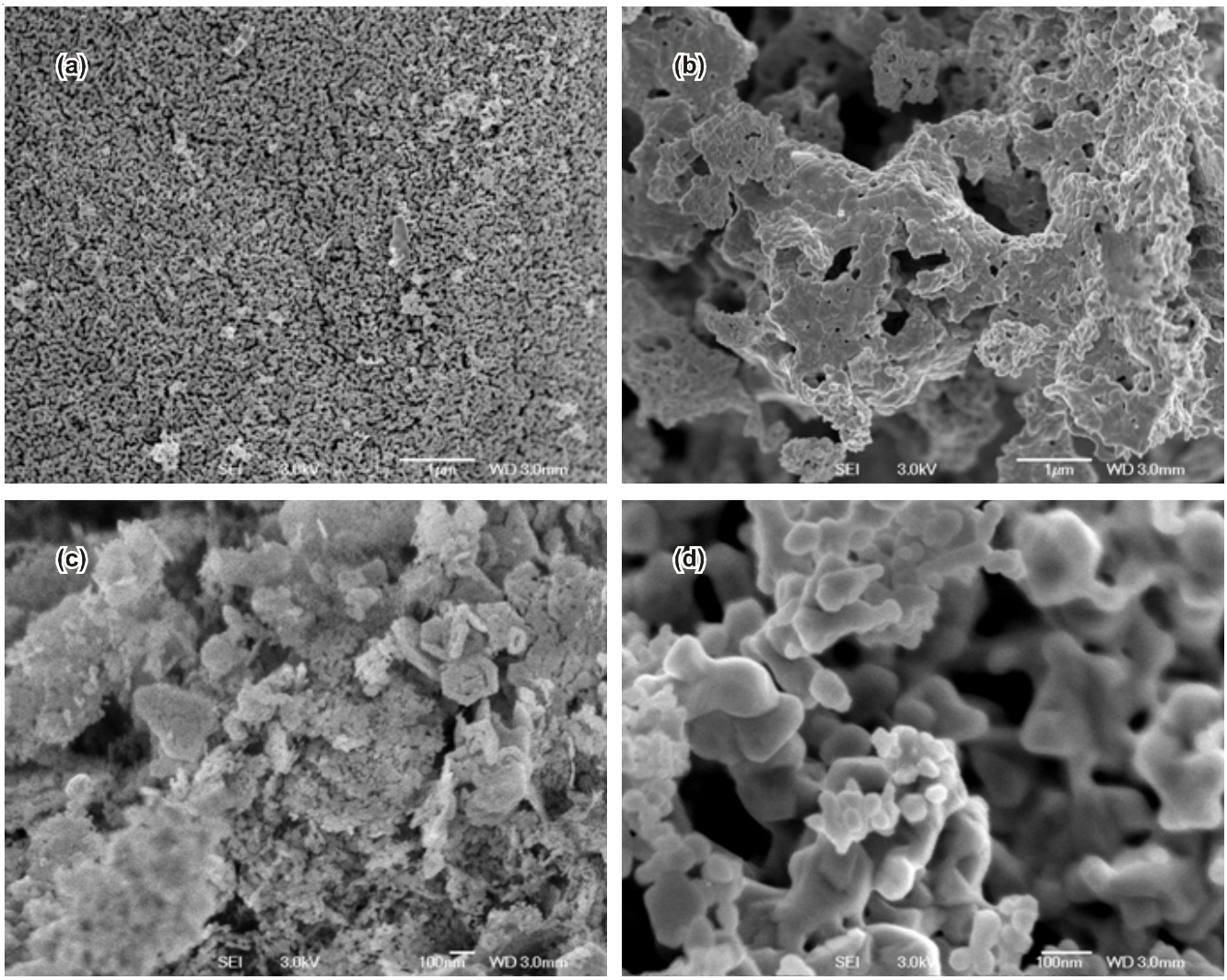

Fig. 4. SEM images of the synthesized mixed oxides $Ni_xCo_{3-x}O_4$ [x = 0, 0.4, 0.6, 0.8, 1, 1.2, 2, 2.5]

to the effect of the ohmic resistance of the oxide. However, the effects of scan rate were similar regardless of the mixed oxides or the method used.

Steady state measurements: The classical three-electrode layout was used. The electrode is submitted to a potential of 1 V during 0.5 h, then to an open-circuit, the potential stabilization happened after about 20 min. From the value obtained after stabilization, the potential is increased by step of 20 mV up to 1000 mV. The current is measured for each applied potential. Current densities are expressed in accordance of the geometric surface area of the electrode. The curves were not corrected for IR drops. Fig. 6 shows steady state current-potential data obtained from oxygen evolution on $Ni_xCo_{3-x}O_4$ electrodes synthesized using different methods. It can be seen that the catalytic activity increased in the order: co-precipitation of hydroxides < TDN < sol gel (propionic acid) < sol gel (Pechini). From the polarization curves it appears that mixed oxides prepared *via* Pechini route present better performances and the differences in the current densities between the distinct preparation methods are very clear. Fig. 6 shows that the Tafel lines show linear behavior in the lower current density region and that the slope becomes increasingly steep in the higher current density region. The increase of the Tafel slope in the higher current density region indicates a change in the rate-determining step in the oxygen evolution mechanism [26,27]. The oxygen evolution reaction over potential depends on the electrode manufacturing. And this variation is very sensitive to the mixed oxides roughness. So, it was necessary to characterize the roughness of electrode.

Roughness factor: Among the method which have been revised by Petrii and Trasatti [28] we choose the cyclic voltammetry method for its simplicity. The roughness factor, R_f, was calculated by dividing the electrode capacitance by the capacitance of smooth surface of $NiCo_2O_4$ (60 μF cm^{-2}) [24,29]. Although the validity of this procedure could be discussed [28], it is quite useful for comparative studies between the same types of oxides. The double layer capacities that we have obtained are good indicator of the comparative roughness of the electrodes. Table-2 gives the double layer capacities which were calculated from the capacitive currents measured by cycling the potential in a range between 0 and 0.05 V where the pseudo capacitive and faradic currents are supposed to be very low. Cyclic voltammograms of mixed oxides in Ar-saturated 1 M KOH were carried out at varying scan rates and can be seen in Fig. 7. These measurements allow us to see that the differences between the different current

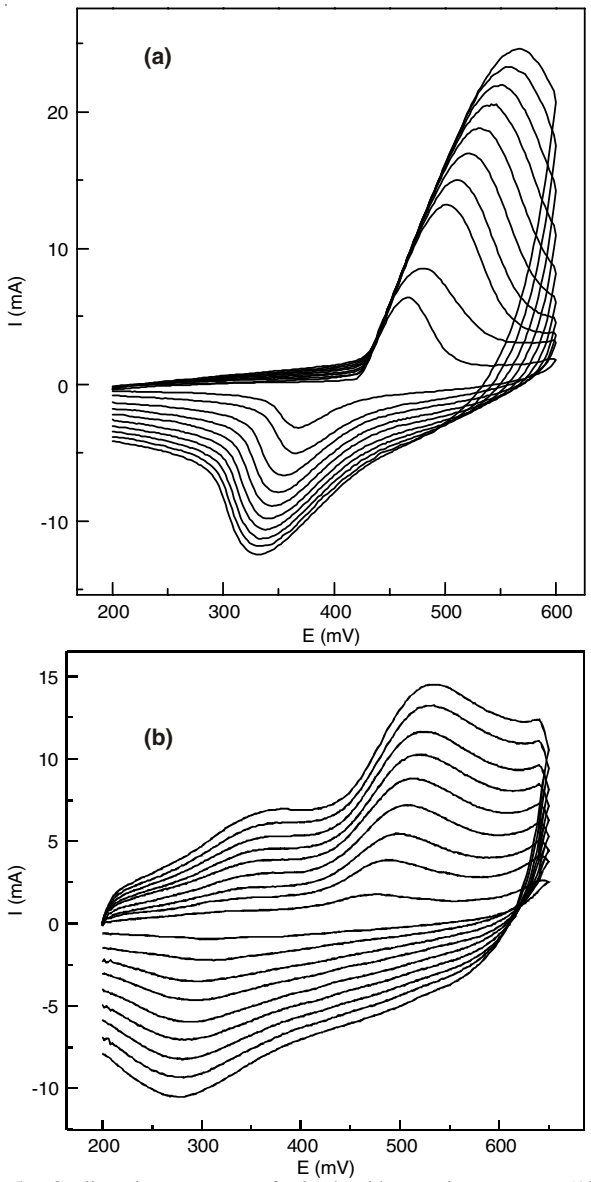

Fig. 5 Cyclic voltammograms of mixed oxides varying scan rate (10 to 100 mV s^{-1}) with an Hg/HgO reference electrode in 1 M KOH at room temperature

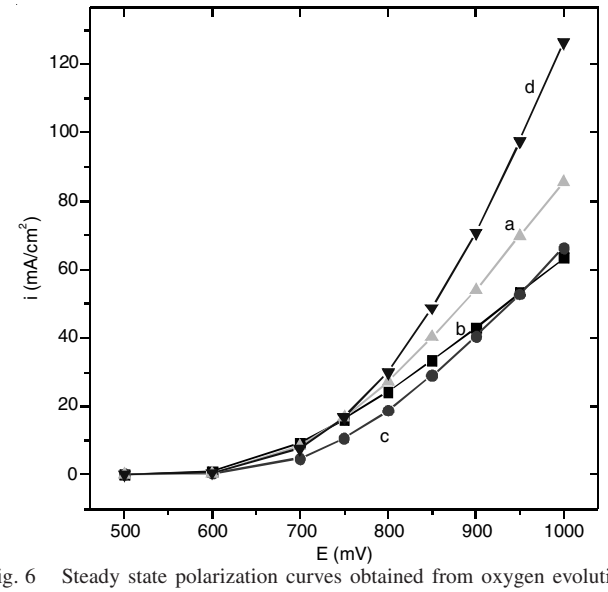

Fig. 6 Steady state polarization curves obtained from oxygen evolution on $Ni_xCo_{3-x}O_4$ electrodes synthesized using different methods

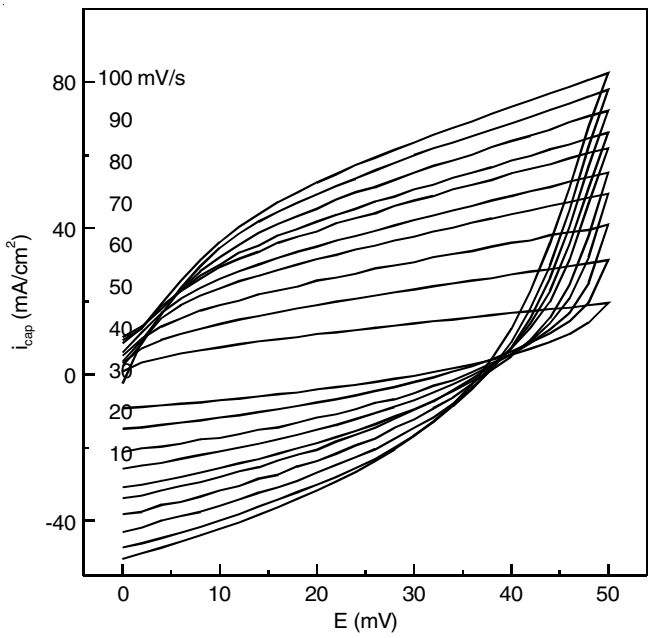

Fig. 7 Cyclic voltammograms of mixed oxides in Ar-saturated 1 M KOH at varying scan rates

densities could be attributed to different roughness of the electrodes more than different compositions.

Conclusion

This study has shown that the different synthesis methods yield $Ni_xCo_{3-x}O_4$ with simple spinel structure for x up to 1.2 and the possibility of a mixture of different spinels for $x > 1.2$ especially for sol-gel compounds. A dependence of specific surface area on the nickel content x and the synthesis method has been pointed out that can explain a difference in the electrocatalytical properties. This study shows the importance of the preparation method on these properties and that the Pechini process is an attractive method for synthesizing mixed oxides because of the enhancement of their specific active surface areas, principal characteristic of the texture properties.

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