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A novel preparation method for $NiCo_2O_4$ electrodes stacked with hexagonal nanosheets for water electrolysis

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Abstract

In this paper, we describe the preparation of a porous nanosheet-stacked $NiCo_2O_4$ composite electrode using a novel electrophoretic deposition (EPD) calcination method. The effects of the deposition time and voltage, and of the calcination temperature have been investigated. The microstructure of the deposited films in the electrodes before and after calcination has also been investigated. The electrocatalytic properties of the electrodes have been investigated using cyclic voltammetry and polarization curves. The electrode films produced using this new technique have a porous structure composed of stacked hexagonal $NiCo_2O_4$ nanosheets. The resulting electrodes exhibit good electrocatalytic properties for water electrolysis.

1. Introduction

Composite transition metal oxides have been found to exhibit good catalytic activity in many redox reactions. Among these oxides nickel cobaltite, ($NiCo_2O_4$), has been studied intensively as a promising electrode material for alkaline water electrolysis, oxygen reduction and organic electrosynthesis [1–8]. With a spinel structure, $NiCo_2O_4$ is, however, a semi-conductive material and exhibits p-type conductivity [9, 10]. This material is therefore usually attached to an electrically conductive substrate (often metallic) through one of a number of methods to form a composite electrode [11].

Electrophoretic deposition (EPD) is a widely used technique for the rapid preparation of homogeneous thin or thick coatings on electrically conductive substrates. This technique also allows significant flexibility in the choice of electrode shape. As a result of these and other advantages, EPD has been widely investigated for potential applications in the areas of structural and functional coatings, laminar composites and fuel cells [11–15].

In this article, a novel method, called the EPD-calcination method, for preparing composite electrodes is described. In this method precursor powders prepared by co-precipitation are first deposited on a Ni substrate by EPD, and then calcined at an appropriate temperature. The effects of various key deposition process factors on the characteristics and electrocatalytic properties of $NiCo_2O_4$/Ni electrodes produced using this method have been studied.

2. Experiment

2.1. *Preparation of the composite electrodes*

The precursor powders were prepared by a co-precipitation method. First, 50 ml of 2.0 M sodium hydroxide aqueous solution was quickly added to 150 ml of an aqueous solution containing 0.02 mol of $Co(NO_3)_2$ and 0.01 mol of $Ni(NO_3)_2$, using magnetic stirring at room temperature. The mixed precipitate was filtered, washed thoroughly with distilled water, and then dried at 80 °C. The dried powders were ground and sieved using an 80-mesh sieve.

Next, 50 g of ethanol, 4.5 g of precursor powder and 0.0075 g $Ni(NO_3)_2$ were mixed together. The extra 0.0075 g $Ni(NO_3)_2$ was added as an electrolyte, in order to improve the conductivity of the resulting suspension. The mixture was sonicated for 15 min in order to form a well-dispersed and stable suspension in which no appreciable lamination was observed after 24 hours. Electrophoretic deposition was conducted using this suspension. A piece of Ni with an area of 1 cm^2 and a piece of stainless steel of area 2 cm^2 were used as the cathode and the counter electrode, respectively. During deposition the two electrodes were separated by 20 mm.

A DC power source was used to provide voltages of either 10 V or 20 V. The deposition times ranged from 2 to 10 min. After electrophoretic deposition, the as-deposited substrates were calcined at different conditions. Figure 1 shows a flow chart of the EPD-calcination method.

2.2. *Characterization*

Thermogravimetric analysis (TGA, Universal V2.3cTA) was conducted in air at a heating rate of 10 °C min^{-1}. The films deposited on the electrodes were characterized before and after calcination by scanning electron microscopy (SEM, JSM-6301, JEOL, Japan), transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan), and X-Ray diffraction (XRD, RIGAKU D/max-RB, Japan) with filtered Cu $K\alpha$ radiation at a wavelength of 0.15418 nm. The elemental ratios of the metals in the suspension before and after electrophoretic deposition and in the deposited films were analyzed using an atomic emission spectrometer (ICP-AES).

All investigations of the electrocatalytic properties of the electrodes were conducted in a conventional three-electrode glass cell at room temperature, using a CHI604A electrochemical analyzer (CH Instrument Corp. USA). 150 ml of 1 M KOH was used as the electrolyte. A bright Pt-foil of area 6 cm^2 was used as the auxiliary electrode. The potential of the working electrode was measured against a saturated calomel electrode (SCE) connected with a Lutin capillary.

3. Result and discussion

3.1. *EPD-calcination method*

The effects of deposition time and voltage are shown in Figure 2. The curves of deposition mass and deposition time were drawn using a curve fitting method according to Sarkar and Nicholson's work [16]. The deposition mass increases with increasing deposition time. For a fixed deposition time a higher voltage results in more deposition. The relation between the deposition time and deposition mass is nonlinear due to the changes in the suspension concentration and the deposition area as deposition takes place, and due to continuous stirring of the suspension during the electrophoretic deposition process.

Since the NaOH solution was more concentrated than required for complete precipitation of Ni^{2+} and Co^{2+}, and since the precipitating agent was added rapidly and the precipitate was subsequently filtered and washed as soon as possible, the precipitate was expected to be a brucite-like mixture of Co(OH)_2 and Ni(OH)_2 [14]. The X-ray diffraction patterns confirm this expectation (Figure 3): except for those peaks arising from the Ni substrate, all peaks can be assigned to precipitation of brucite-like hydroxides [14].

The ICP-AES results show that for each electrophoretically deposited film prepared in this study, the final mole ratio of metallic elements was very close to 2:1. This ratio is consistent with that in the suspension and with the stoichiometric proportion of NiCo_2O_4.

A TGA curve for heating of the precursor powder in air is shown in Figure 4. A weight loss of 14.33% occurs

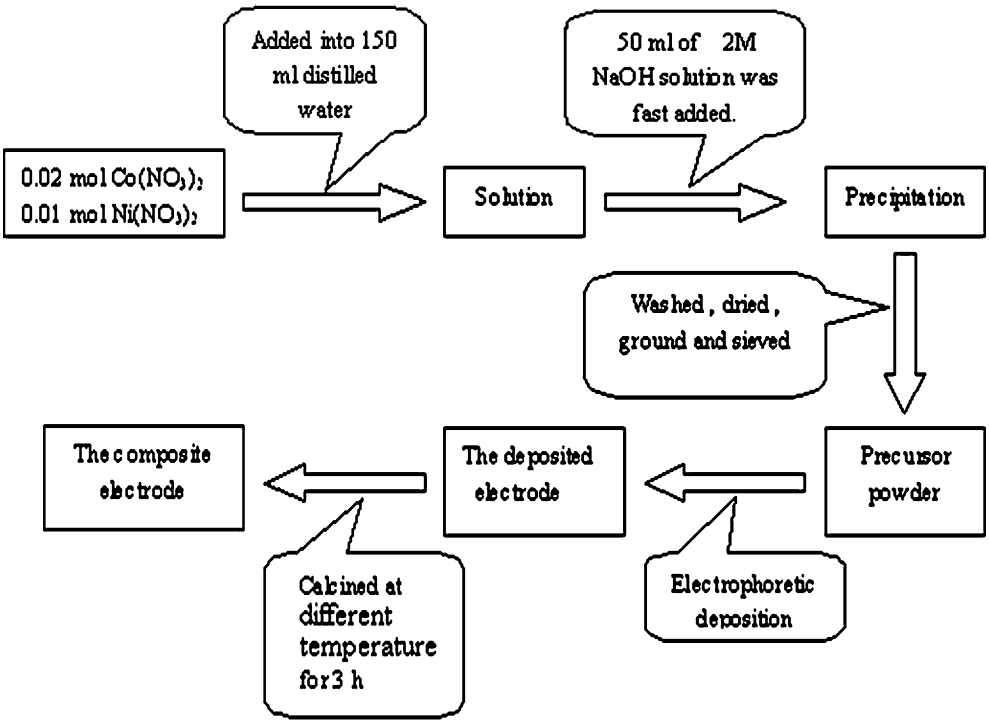

Fig. 1. The EPD-calcination method.

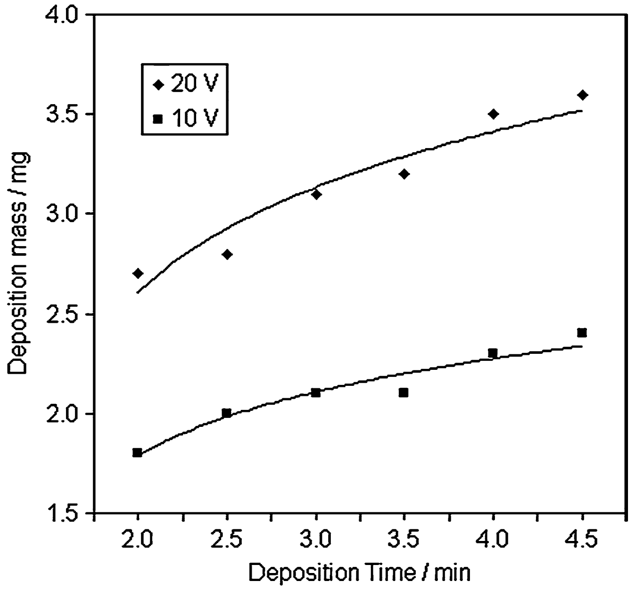

Fig. 2. Variation of deposition mass for different deposition times and different voltages.

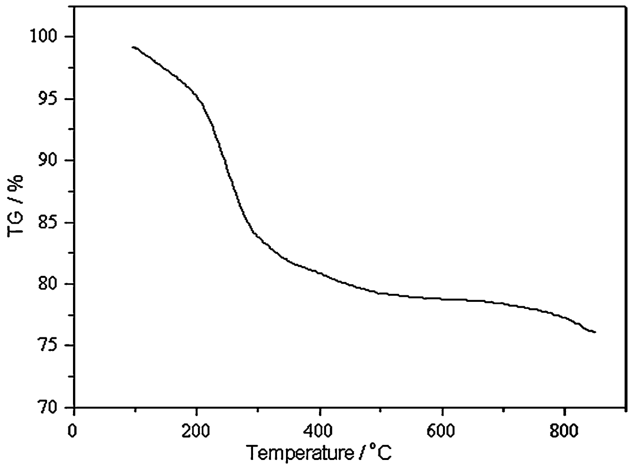

Fig. 4. TGA curve of the hydroxide precursor.

between 200 °C and 400 °C. This can be attributed to the decomposition of the hydroxide precursor powders and to the formation of spinel $NiCo_2O_4$. The overall reaction is as follows [1]:

$$2\ Co(OH)_2 + Ni(OH)_2 + 1/2\ O_2 \rightarrow NiCo_2O_4 + 3\ H_2O \qquad (1)$$

The as-deposited electrodes were calcined at either 250 °C, 300 °C, or 350 °C for 3 h. A nanosheet-stacked electrode was only obtained for a calcination temperature of 300 °C. When calcined at 250 °C, the films on the electrode consisted of particles of irregular form, presumably because of poor crystallinity. At a calcination temperature of 350 °C, the deposited film cracked so badly that some parts of the Ni substrate were exposed.

After calcination at 300 °C for 3 h, the hydroxide precursor decomposed and transformed into a $NiCo_2O_4$ spinel. The X-ray diffraction patterns of calcined deposited electrodes prepared at 10 V and 20 V for 2 min and 4 min are shown in Figure 5. Except for diffraction peaks arising from the Ni substrate, all peaks can be assigned to a $NiCo_2O_4$ spinel (JCPDS 20–781).

The surface morphology of an electrode prepared at 20 V for 3 min and then calcined at 300 °C for 3 h is shown in Figure 6. At low magnification the surface appears quite smooth (Figure 6(a)). After calcining the precursor film on the substrate is transformed into a porous and homogenous spinel film, consisting of quite regular hexagonal nanosheets, uniform in size, with an average diameter of about 200 nm, and a thickness of tens of nanometers (Figure 6(b, c)). In some places the nanosheets partially overlap one another (Figure 6), especially in the region nearest to the substrate. A TEM

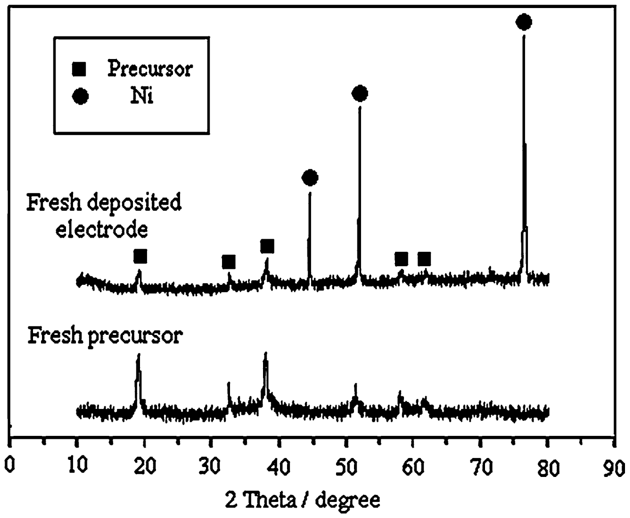

Fig. 3. XRD patterns of the as-deposited Ni substrate and fresh precursor.

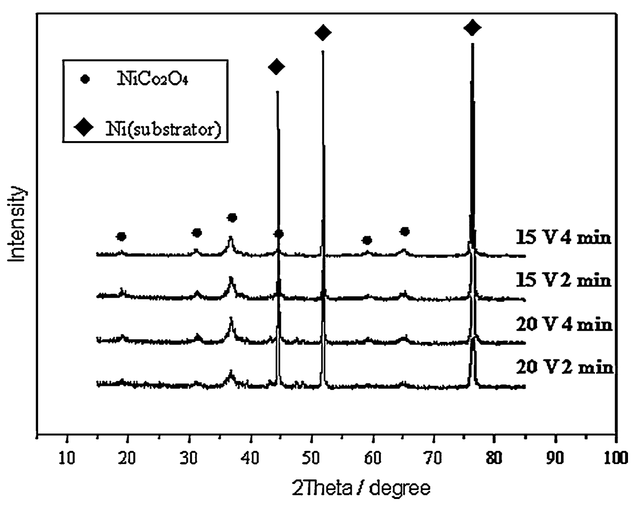

Fig. 5. XRD patterns of electrodes prepared under different conditions.

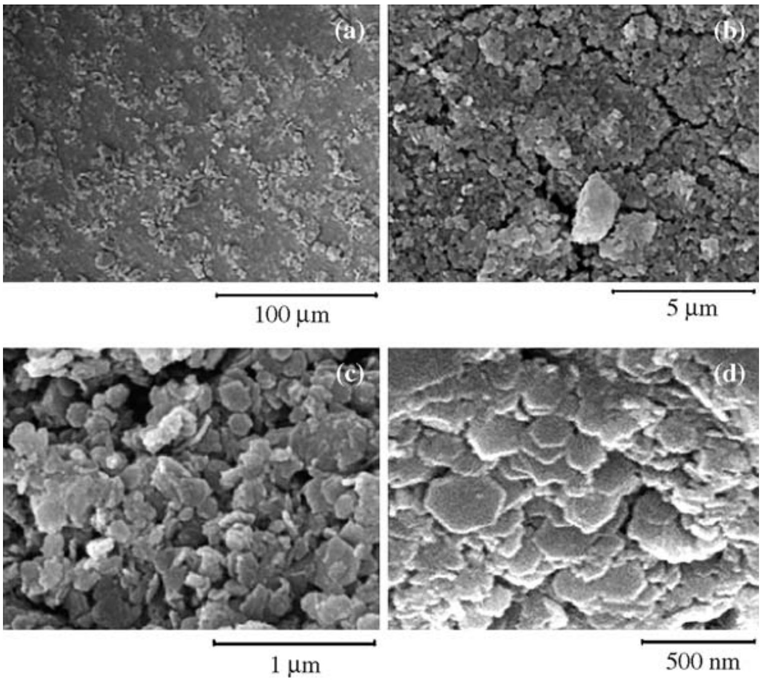

Fig. 6. SEM micrographs of an electrode surface at different magnifications. This electrode was deposited at 20 V for 3 min and then calcined at 300 °C for 3 h.

investigation confirmed that the nanosheets are crystalline and of a regular hexagonal shape (Figure 7).

The micrographs shown in Figure 6 illustrate that under the appropriate conditions an electrode consisting of a stack of nanosheets can be prepared using the EPD-calcination method. These results suggest that it may be possible to achieve an even better microstructure consisting of layers of closely aligned regularly arranged nanosheets by either modification of the current method, or development of new methods.

The surface area is an important parameter in characterizing the electrocatalytic properties of an electrode. A large surface area usually leads to better electrocatalytic properties. The surface roughness factor (Rf) can be used as a measure of the surface area of an electrode. This factor can be obtained using cyclic voltammetry [1]. The relation between Rf or Rf/mass (where the mass refers to the deposition mass) and the deposition mass for different electrodes is shown in Figure 8. Electrodes prepared by the EPD-calcination method all have large values of Rf. For a given voltage the values of Rf and Rf/mass both increase with increasing deposition mass. The values initially increase rapidly with deposition mass. Above a deposition mass of 2.8 mg the rate of increase in Rf and Rf/mass decreases significantly. At a deposition mass of 3.5 mg, the value of Rf reaches as high as 445 (Table 1).

3.2. *Electrocatalytic characterization*

Cyclic voltammograms for $NiCo_2O_4$ electrodes and a Ni electrode are shown in Figure 9. These were recorded between potentials of 0 V and 0.55 V at a scan rate of 10 mV s^{-1} in 1 M KOH at room temperature.

The electrode voltammogram changes with increasing deposition mass. When the deposit film is thin, a high

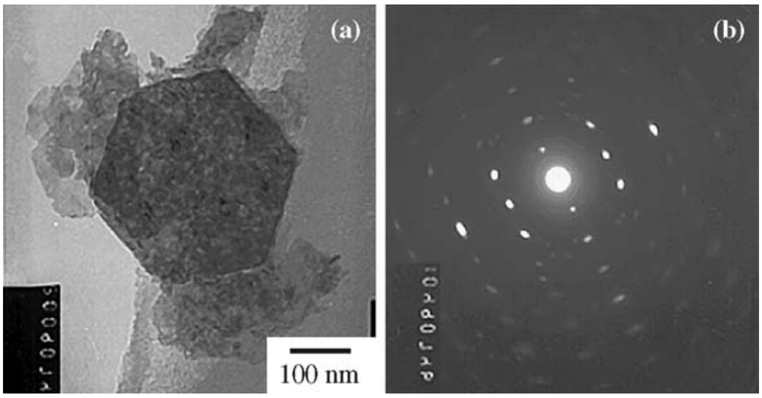

Fig. 7. (a) TEM micrograph; (b) Selected area electron diffraction pattern of a nanosheet.

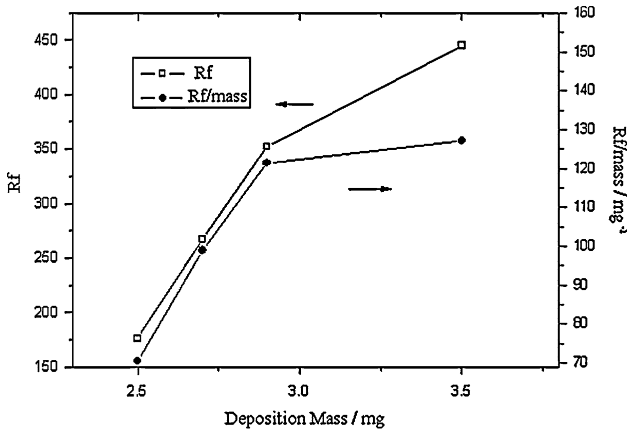

Fig. 8. The relationship between Rf or Rf/mass and the deposition mass.

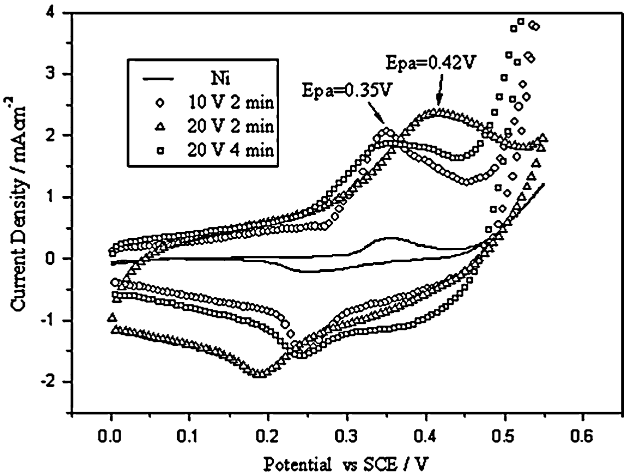

Fig. 9. Cyclic voltammograms for different $NiCo_2O_4$/Ni electrodes and for a Ni electrode in 1 M KOH.

single anodic peak (about Epa = 0.35 V) is observed, attributed to the Ni substrate. As the deposit film becomes thicker, the anodic peak (Epa = 0.35 V) becomes lower and finally disappears. At the same time a new anodic peak (Epa = 0.42 V) which can be attributed to the Co(II)/Co(III) redox couple, appears and broadens with increasing deposition mass. It has been shown that the occurrence of the transformation of Co(II)/Co(III) redox couple greatly lowers the overpotential of the $NiCo_2O_4$/Ni electrode [5].

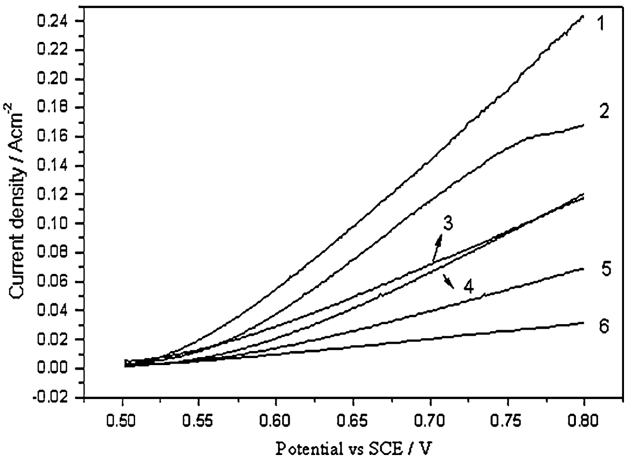

Fig. 10. Polarization curves of $NiCo_2O_4$/Ni electrodes prepared under different conditions: (1, 20 V 4 min, calcined at 300 °C; 2, 20 V 3 min, calcined at 300 °C; 3, 20 V 3 min, calcined at 250 °C; 4, 20 V 2 min, calcined at 300 °C, 5, 20 V 1 min, calcined at 300 °C). Also shown is a polarization curve for Ni electrode (6).

The anodic polarization curves of $NiCo_2O_4$/Ni electrodes prepared under different conditions measured at a scan rate of 0.1 mV s^{-1} in 1 M KOH at 25 °C, are shown in Figure 10. Values of roughness factors, the oxygen evolution overpotential at a current density of 100 mA cm^{-2}, the apparent current density and the apparent true current density at a constant potential (700 mV) are given in Table 1. The values of overpotential (η) can be obtained according to the equation:

$$\eta = E_{\text{real}} - (E_{\text{theory}} - 0.241\text{V}) \qquad (2)$$

Here E_{real} is the apparent potential measured at 100 mA cm^{-2} vs. SCE. E_{theory} is the standard electrode potential of O_2 evolution, which is 0.397 V in 1 M KOH. The value of 0.241 V is the potential of SCE electrode at 25 °C. For comparison results taken from the literature of a $NiCo_2O_4$ film electrode prepared by a sol–gel method [15] are also listed in Table 1.

As shown in Figure 10, the electrodes show better oxygen evolution reaction (OER) electrocatalytic properties compared to the Ni electrode. The electrode deposited at 20 V for 4 min has the best electrocatalytic properties of all the investigated electrodes in this study,

Table 1. Electrocatalytic parameters of electrodes deposited at different conditions

Preparation condition	Roughness factors	Overpotential V	i_{app} mA cm^{-2}	i_{real} mA cm^{-2}
Ni	–	–	20	–
20 V and 1 min	176	–	40	0.23
20 V and 2 min	267	0.512	66	0.25
20 V and 3 min	352	0.462	116	0.32
20 V and 4 min	445	0.438	144	0.32
$NiCo_2O_4$(propionic)[15]	130	–	10	0.08

Notes: (i) the apparent current density, i_{app}, was measured at a constant potential (700 mV) vs. SCE; (ii) the real current density, i_{real}, was taken as the apparent current density, i_{app}, divided by the roughness factor; (iii) the $NiCo_2O_4$ (propionic) film electrode was prepared by a sol–gel method, calcined at 300 °C [15].

with an apparent density current at a given potential of 700 mV of 144 mA cm^{-2}. After taking into account the roughness factors, at a potential of 700 mV the true current density of electrode deposited at 20 V for 4 min still shows the highest true current density values (0.32 mA cm^{-2}) of all electrodes.

The deposition mass increases with increasing deposition time. This leads to an increasing amount of $NiCo_2O_4$ spinel phase, which allows more and more transformations of the Co(II)/Co(III) redox couple, and consequently results in a reduction of the overpotential of the OER at the composite electrode. The electrode deposited at 20 V for 3 min and calcined at 300 °C has better electrocatalytic properties than that of the electrode deposited under 20 V for 3 min and calcined at 250 °C. The difference can be attributed to the better crystallinity of the $NiCo_2O_4$ calcined at the higher temperature [1]. Compared with $NiCo_2O_4$ film electrodes prepared by the sol–gel method [15], electrodes prepared by the EPD-calcination method exhibit higher roughness values and higher current densities (Table 1).

4. Conclusion

A porous nanosheet-stacked $NiCo_2O_4$/Ni composite electrode has been obtained for the first time. The electrode films exhibit a crystalline structure and are composed of regular hexagonal nanosheets, with an average diameter of about 200 nm and a thickness of several tens of nanometers. In many parts of the electrode, especially on the region nearest to the substrate, the nanosheets are quite planar and overlap one another. The deposition voltage and time significantly affect the deposition mass of the electrode. At a calcination temperature of 300 °C and a time of 3 h, more deposition mass leads to more $NiCo_2O_4$ spinel nanosheets and, consequently, better OER electrocatalytic properties. Electrodes deposited at 20 V for 4 min have the lowest overpotential (0.438 V at 100 mA cm^{-2}) and the highest current density (144 mA cm^{-2} at 700 mV).

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