

Development of nickel-cobalt bimetallic/conducting polymer composite used as a catalyst in the oxygen evolution reaction (OER)

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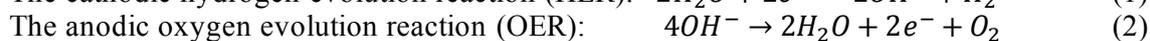
Abstract. This paper discusses results on the development of nickel-Cobalt Bimetallic/conducting polymer composite layer used as a catalyst in the Oxygen evolution reaction (OER). Based on cost, corrosion stability and over-potential, nickel is an advantageous material for the anode in alkaline water electrolysis. However, the use of this metal is associated with two main difficulties: the progressive deactivation of the anode occurs at higher potentials, presumably due to the modification of the active nickel species into inactive ones, and the potential becomes unavoidably increasingly positive over time, thus decreasing the efficiency of the electrode. Nickel-based bimetallic catalysts, such as Ni-Ir, Ni-Co, Ni-Mn, Ni-Fe, usually obtained by electrodeposition, have been widely studied in recent years in the search for catalysts that improve the activity of nickel towards the OER. However, polymeric films were used by several researchers to incorporate various metal complexes, with an aim of improving the activity and stability of electrodes surfaces. Modified electrodes obtained by these polymeric films are characterized by good ionic conductivity and permeability. These as well, we conducted a study of the oxygen evolution reaction in the basic medium on electrodes modified by polymerization of aniline and electrodeposition of (Nickel-Cobalt) bimetallic. In the present work, the electrodeposition technique has been adopted to introduce different amounts of cobalt into the nickel. Surface morphologies of the electrodeposits and their electrocatalytic properties have been studied for the oxygen evolution reaction in NaOH solutions. The Ni-Co bimetallic film is much more reactive than Ni for the OER. Co has a significant effect on the OER. The effect of Co deposited with NiO film depends on its content.

1. Introduction

The world of the scientific research was marked by a renewed interest carried on two types of materials: conducting organic polymers (COP) and inorganic semiconductors [1 -2]. The rise in prices of the energy resources, the search for an urban and rural environment durably healthy especially with the pressure of the ecology movements corroborate this orientation. The studies on polymers led to the development of new materials able to replace in certain cases metals, because of their lightness, of their corrosion resistance and their relative facility of manufacturing [3]. Research related to organic polymers became logical and convenient in electrochemistry for manufacturing electrodes [4]. Hydrogen is regarded as one of the most promising energy carriers in the future, among different possible methods; the electrochemical gas evolution during water electrolysis has attracted most of the attention as one of the



sustainable and renewable chemical technologies for producing hydrogen. Generally, Water electrolysis is carried out in alkaline medium because alkaline medium creates the possibility for cheap materials to be used as efficient electrodes [5-6]. In alkaline medium. Electrochemical water electrolysis consists of two parts:



However, the efficiency of water electrolysis in alkaline medium is severely limited by the large anodic overpotential of oxygen evolution reaction (OER). To address this problem, considerable efforts have been devoted to exploring the electrocatalyst with low OER over-potential, and great advances have been archived [7]. Over the past decade, noble metals have been investigated for the OER; Ruthenium (Ru) and iridium (Ir) are the best OER catalysts. However, the price of Ru and Ir is expensive. Therefore, the other noble metals such as Pt, Pd, and Au have been paid attention. It has been commonly accepted that Pt is the best catalyst for the Oxygen reduction reaction ORR, but Pt has an only moderate activity for the OER. Therefore, many researchers have devoted to looking for Pt-based catalysts based on the bifunctional mechanism for water electrolysis [8-9].

Oxidized species of cobalt (Co-O), nickel (Ni-O) and cobalt-nickel (CoNi-O) have been extensively investigated during many years because their interest as electrode materials to favor electrochemical reactions in alkaline media [10–11].

The oxidized species of Co, Ni, and CoNi Bimetallic have been proposed as sensors of biomolecules as glucose [12] or uric acid [13], catalysts for methanol electro-oxidation [14] and electro-synthesis of hydrogen or oxygen [15-16].

The electrodes are the seat of the electrochemical reactions. The choice of catalysts requires the taking into account of several factors:

1) Excellent intrinsic electrocatalytic properties; 2) high activate surface; 3) high electric conductivity; 4) mechanical, chemical and electrochemical stability in the long run; 5) Increased selectivity; 6) less problems caused by the gaseous emission of oxygen evolution reaction (OER); 7) availability and low costs of manufacturing; 8) deprived of harmful effect on health and the environment. All these requirements are met with difficulty in the same material.

2. Water electrolysis technologies

Water electrolyzers' are classified, depending on the kind of electrolyte and thus the type of ionic agent (OH^- , H^+ , O^{2-}), and the operation temperature, into three main categories: alkaline, solid oxide and polymer–electrolyte membrane (PEM). The operating principles of the three main types of electrolysis technologies are presented in table 1.

Table 1. Typical characteristics of the main electrolysis technologies [17-20].

	Alkaline electrolysis			Proton Exchange electrolysis	Oxygen ion electrolysis		
	Liquid	Polymer Electrolyte Membrane		Solid Oxide Electrolysis			
	Conventional	Solid alkaline	H ⁺ -PEM	H ⁺ -SOE	O ²⁻ -SOE	Co-electrolysis	
	Low temperature electrolysis			High temperature electrolysis			
▪ charge carrier	OH ⁻	OH ⁻	H ⁺	H ⁺	O ²⁻	O ²⁻	
▪ temperature	20-80°C	20-200°C	20-200°C	500-1000°C	500-1000°C	750-900°C	
▪ Electrolyte	Liquid	Solid(polymeric)	Solid(polymeric)	Solid(ceramic)	Solid(ceramic)	Solid(ceramic)	
▪ anodic reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$	
▪ Anodes	Ni/Co/Fe(Oxides)	Ni-based	IrO ₂ , RuO ₂ , Ir, Ru, O ₂ (Supports(TiO ₂ , TiC, ITO))	La, Sr, MnO ₃ + ZrO ₂		La, Sr, MnO ₃ + ZrO ₂ , CO ₂ + 2e ⁻ → CO + O ²⁻	
▪ Cathodic reaction (HER)	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	
▪ Cathodes	Ni-alloys	Ni-Ni-Fe-NiFe ₂ O ₄	Pt/C	Ni	Ni	Ni	
▪ Efficiency	59-70%		65-82%	Up to 100%	Up to 100%		
▪ applicability	Commercial	Laboratory Scale	near-term commercialization	Laboratory Scale	demonstration	Laboratory Scale	
▪ Advantages	Low capital cost, relatively stable, mature technology	combination of alkaline and H ⁺ PEM electrolysis	compact design, fast response/ start-up high-purity H ₂	enhanced kinetics thermodynamics lower energy demands, low capital cost	enhanced kinetics thermodynamics lower energy demands, low capital cost	direct production of syngas	
▪ Disadvantages	corrosive electrolyte, gas permeation, slow dynamics	Low OH ⁻ conductivity in polymeric membranes	High cost polymeric membranes; acidic: noble metals	mechanically unstable electrodes (cracking), safety issues: improper sealing			
▪ Challenges	Improve durability /reliability; and Oxygen Evolution	Improve electrolyte	Reduce noble-metal utilization				

The three types of electrolysis have its own advantages and disadvantages, but all three technologies are appealing and promising for sustainable energy application.

Main advantages of alkaline electrolysis are low cost owing to the use of no-noble electrodes and long-term stability. On the contrary, the acidic environment in PEM electrolyzers prevents the kinetics of the redox reactions and necessitates the use of expensive noble metal catalysts and materials for the bipolar plates. This, together with the high cost of polymeric membranes, is the main limitation for the commercialization of PEM electrolysis in the near term.

Alkaline electrolysis is well established as the most applied commercial technology. Water electrolysis in liquid alkaline media takes place at temperatures below 100 °C and is the simplest and most mature among the three electrolysis technologies [21].

Electrocatalysts exhibit deactivation after the long-term operation, improved electrocatalytic activity, mainly for the oxygen evolution reaction of which the kinetics are not favored in alkaline media. To meet these needs, research lines follow two main routes the Conductivity and catalysis [22]. The first is related to the conductive polymer (surface, porosity, conductivity) which also exhibit high efficiency and long-term stability. The second route one aims at the development of novel efficient and stable materials, either by doping Ni, Co, or Fe based electrocatalysts with other elements or by investigating alternative materials [23].

3. Experimental

3.1. Electrodes preparation

Before electrodeposition of a Ni-Co/PANI layer, the Glassy Carbon (GC) substrate was carefully prepared by mechanical wet-polishing using grit sandpaper (600 and 1500), followed by thorough rinsing with distilled water and cleaning in an ultrasonic bath for 6–7 min in order to remove polishing residues. Subsequently, the substrate was degreased with ethanol, rinsed with ultrapure water. The Nickel–Cobalt bimetallic hydroxide films were electrodeposited on the pretreated GC substrates in

nickel (II) nitrate hexahydrate and cobalt (II) nitrate hexahydrate aqueous solutions with composition ratios shown in Table 2. Potassium nitrate (0.1 M) was used as a support electrolyte and as a hydroxyl precursor. All prepared samples with increasing cobalt molar concentration deposition solutions. A three-electrode electrochemical cell, consisting of a pretreated GC, as a working electrode (diameter = 2 mm), a platinum foil counter electrode, and an Ag/AgCl (saturated KCl solution) as a reference electrode. The reference electrode was positioned as close to the surface of the working electrode as possible by means of a Luggin capillary. The electrodeposition experiments were carried out for 90 min. The deposition was carried out at a constant potential of -0.85 V vs. Ag/AgCl reference electrode. Table 1 present the experimental matrix for the synthesis of the Nickel–Cobalt and Nickel/Cobalt bimetallic.

Table 2. Experimental matrix for the synthesis of the nickel-cobalt and nickel/cobalt bimetallic.

Layer	Bath composition		Conditions of deposition
Polyaniline	Aniline, H ₂ SO ₄	0.01 M 0.5 M	Cycles of potential
Ni	Ni(NO ₃) ₃ •6H ₂ O, KNO ₃ , H ₂ SO ₄	0.01 M 0.1 M 0.5 M	Deposition potential: -0.85V Ag/AgCl Deposition time: 90 min
Ni-Co	Ni(NO ₃) ₃ •6H ₂ O Co(NO ₃) ₃ •6H ₂ O KNO ₃ H ₂ SO ₄	0.009 M 0.001 M 0.1 M 0.5 M	Deposition potential: -0.85V Ag/AgCl Deposition time: 90 min
Ni-Co	Ni(NO ₃) ₃ •6H ₂ O Co(NO ₃) ₃ •6H ₂ O KNO ₃ H ₂ SO ₄	0.005 M 0.005 M 0.1 M 0.5 M	Deposition potential: -0.85V Ag/AgCl Deposition time: 90 min
Ni-Co	Ni(NO ₃) ₃ •6H ₂ O Co(NO ₃) ₃ •6H ₂ O KNO ₃ H ₂ SO ₄	0.002 M 0.008 M 0.1 M 0.5 M	Deposition potential: -0.85V Ag/AgCl Deposition time: 90 min

3.2. Morphology of PANI, Ni/PANI, and Ni-Co/PAN

The morphological characteristics of the synthesized Ni–Co bimetallic films and the polyaniline were characterized by scanning electron microscopy (SEM) at the materials Platform of UATRS, CNRST of Rabat, Morocco.

Electrolytically deposited Ni-Co on polyaniline film covered glassy carbon electrode (Ni/PANI/CV)/ (Co/PANI/CV)/ (Ni-Co/PANI/CV) was used as the anode for the evolution oxygen reaction in alkaline medium. The electrochemical behavior and electrocatalytic activity of the electrode studied using cyclic voltammetry and chronoamperometry. The morphology and composition of the modified film were obtained using scanning electron microscope.

Morphology of conducting polymer layers deposited on a glassy carbon substrate was first characterized using a scanning electron microscopy technique.

Figure a-1 shows SEM morphology of PANI film obtained in a solution containing 0.1M aniline and 0.5M H₂SO₄ deposited onto GC. From this figure, the branched PANI fibrils as observed and the fibers are very regular and uniform. Besides, these fibers tend to agglomerate into interconnected networks, which exhibits many multiple pores.

The figure b-1 indicate the SEM morphology of the Ni-polyaniline. As seen there is a quite difference in structural surface morphology between PANI film and PANI film containing Nickel (PANI-NI). Ni

particles are clearly seen in PANI. It is to be noted that the incorporation of Ni into PANI does not significantly change the morphology of fiber. Indeed, this expresses the ability of particles to aggregate into larger structures.

Figure c-1 shows an SEM morphology of Nickel-Cobalt Bimetallic/polyaniline. Micrograph of the film containing 50% of Co is very similar to the pure NiOOH films or containing various Co contents Ni film. The Co has a negligible effect on the surface morphology. It can be deposited very homogeneously with Ni in the form of hydroxide.

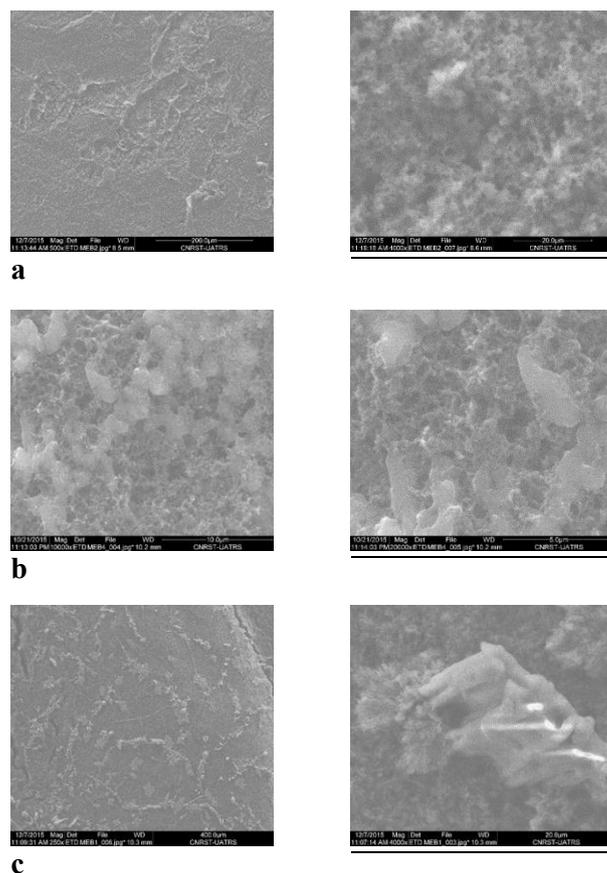


Figure 1. SME images showing a surface morphology of (a) polyaniline (PANI) electrodeposited on a GC substrate, (b) electrodes made by electrodeposition of Ni on a PANI layer on a GC substrate, and (c) electrodes made by electrodeposition of Ni-Co Bimetallic on a PANI layer on a GC substrate.

4. Results and discussion

The process of electrode preparation and modification consisted of two steps:

- Electrodes modified by polymerization of aniline;
- Electrodeposition of (Nickel-Cobalt) bimetallic.

4.1. Electropolymerization

Electropolymerization method such as potential cycling technique offers the possibility of controlling the thickness and homogeneity of the film on the electrode surface. The electrochemical synthesis of polyaniline in the form of emeraldine has been previously described by Park [2]. Electropolymerization method such as potential cycling technique offers the possibility of controlling the thickness and homogeneity of the film on the electrode surface. Figure 2 shows the cyclic voltammograms during the electropolymerization of aniline on the platinum electrode in a solution containing 0.1 M aniline and 0.5 M sulfuric acid for 15 cycles in the potential limits from -0.2 to 1, 2 V at a sweep rate of 50 mV/s. the

peak A obtained at 12 V / (Ag/AgCl) during the first cycle corresponds to the oxidation of aniline. The height of this peak decreases with the number of cycles until its disappearance.

Subsequent cycles (B-C and D) indicate a successive growth of the polyaniline film as evidenced by the increase in the redox current. Two redox couples are readily apparent with E values of 0.25 and 0.74 V in the CVs. Orata and Buttry have proposed that the wave at 0.13 V represents an initial oxidative process in which the polymer is converted from an insulator to a conductor [14]. Upon repeated potential cycling, the peak currents associated with the process around 0.13 and 0.72 V increase in magnitude, indicating the growth of polyaniline film.

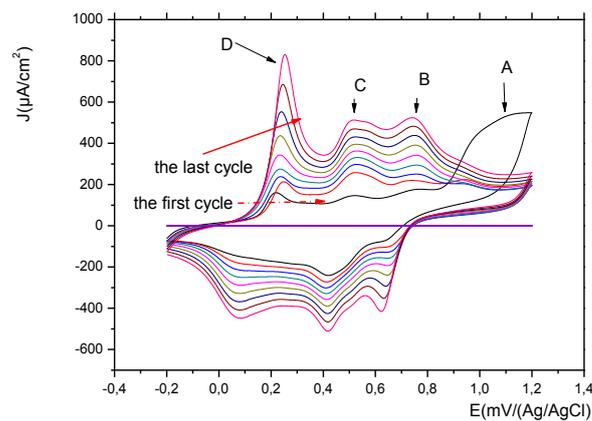
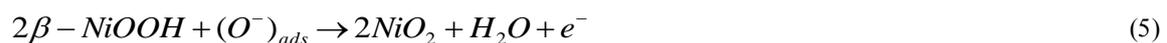


Figure 2. Cyclic voltammograms (9 cycles) showing the electropolymerization of aniline prepared from a 0.5 M sulphuric acid and 0.1 M aniline solution.

4.2. Electrodeposition

The generally accepted mechanism for the OER on nickel anode is written as:



The electrodes were cycled at 50 mV/s between -3.5 and 6 V/(Ag/AgCl). Figure 3, 4, and 5 show respectively, the voltammogram of Ni-Co/PANI/CV, Co/PANI/CV, and Ni/PANI/CV. The oxidation peak around 380 mV and the reduction peak around 200 mV are attributed to the OER.

The Ni-Co bimetallic film is much more reactive than Ni for the OER. Co has a significant effect on the OER. The effect of Co deposited with NiO film depends on its content. In addition, Co can reduce the peak potential of Ni-Co/PANI and the higher the Co content the more the potential is reduced.

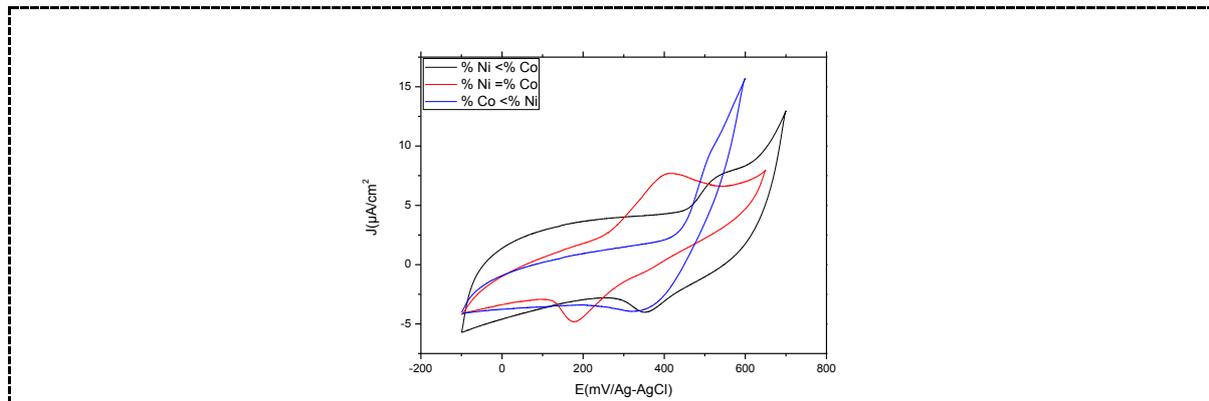


Figure 3. Voltammograms for Ni-Co deposited on the rotating disk electrode glassy carbon coated with a layer of polyaniline (PANI/CV).

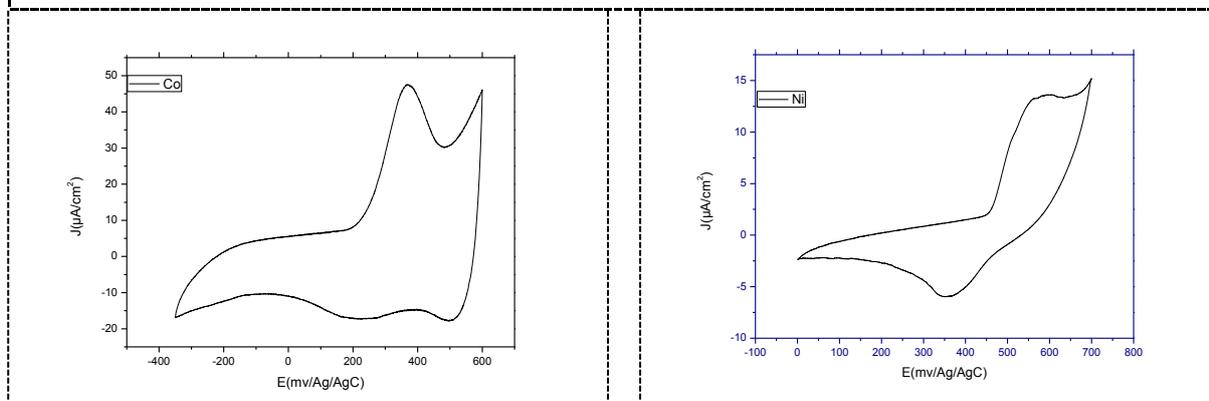


Figure 4. Voltammogram for Cobalt deposited on the rotating disk electrode glassy carbon coated with a layer of polyaniline (PANI/CV)

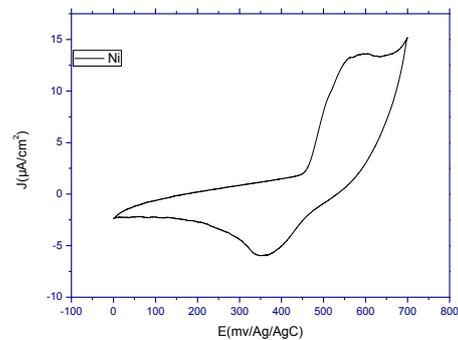


Figure 5. Voltammogram for Nickel deposited on the rotating disk electrode glassy carbon coated with a layer of polyaniline (PANI/CV)

4.3. Curve Koutecky-Levich

For a research on the electrode reaction mechanism and kinetics, particularly those of oxygen reduction reaction (OER), it is necessary to design some tools that could control and determine the reactant transportation near the electrode surface and its effect on the electron-transfer kinetics. The rotating disk electrode (RDE) technique has been widely used for this purpose, particularly for the OER. Limiting currents obey the Levich equation:

$$I_L = 0.62 \times nFSC \cdot D^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2} \quad \text{Eq. 1}$$

Or in short form:

$$I_L = B \cdot \omega^{1/2} \quad \text{Eq. 2}$$

Where n is the number of electrons transferred, F is Faraday's constant, S the electrode surface, C the concentration of the electroactive substance in the solution, D the diffusion coefficient, ν the kinematic viscosity of the solution, ω the rotation rate of RDE and B the Levich slope.

When cathodic limiting currents were plotted vs. ω a slightly curved line was obtained, but a plot of I_L^{-1} vs. $\omega^{-1/2}$ gave a straight line with nonzero intercept (Fig. 4). This plot is known as a Levich-Koutecky plot, based on the equation [24]:

$$\frac{1}{I_L} = \frac{1}{I_{Kin}} + \frac{1}{B \cdot \omega^{1/2}} \quad \text{Eq. 3}$$

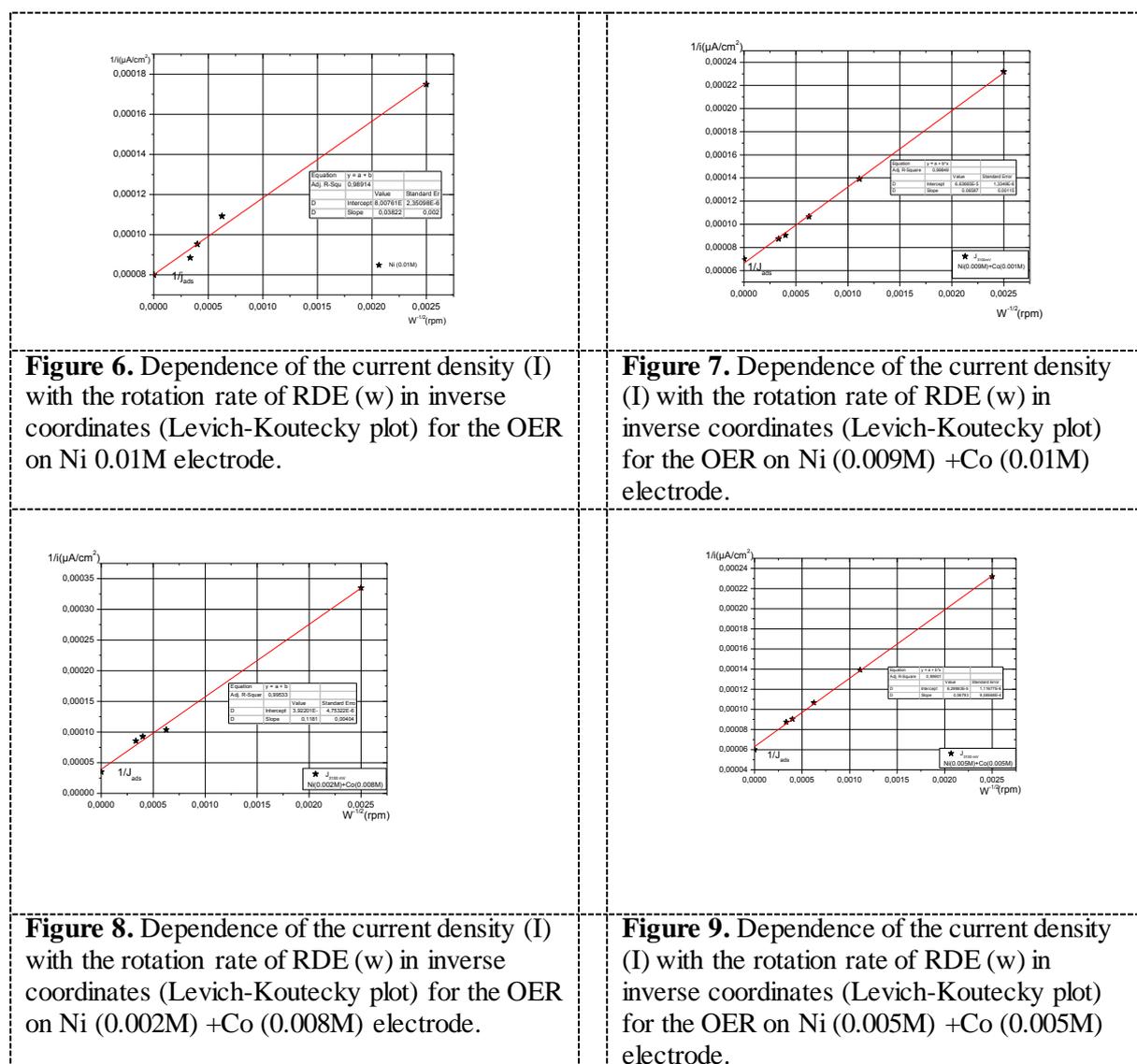
The nonzero intercept for limiting currents is explained by the presence of kinetic control of the reaction. The relationship between current and rotation rate for a film-covered electrode is the following:

$$\frac{1}{I_L} = \frac{1}{I_{Kin}} + \frac{1}{I_{dif}^{film}} + \frac{1}{B \cdot w^{1/2}} \quad \text{Eq. 4}$$

In accordance with Eq. 3, the dependence of the current density (I) has been plotted in inverse coordinates, as shown in Fig. 4, resulting in a linear interdependence. The extrapolation of this linear dependence to the zero value of $1/w^{1/2}$, to indefinitely high electrode rotation speed, enable to calculate the maximum kinetic current density I_{max} . The thickness of the polymer film is independent of the rate of rotation. The reaction of the evolution of oxygen in medium NaOH (0,1M) is governed by a mixed mode (diffusion and adsorption).

The OER overall current density (I) can be expressed in terms of the kinetic adsorption current density, I_{ads} , and the boundary-layer diffusion limited current density, I_{dif}^{film} by the equation:

$$\frac{1}{I} = \frac{1}{I_{dif}^{film}} + \frac{1}{I_{ads}} \quad \text{Eq. 5}$$



To calculate the number of electrons exchanged during the reaction of the evolution of oxygen on the two modified electrodes incorporated into the polyaniline, we used the law Koutecky-Levich equation, which gives the current in the region mixed control $\left(1/J_{ads-dif}\right)$.

5. Conclusions

In this work, we conducted a study of the oxygen evolution reaction in the basic medium on electrodes modified by polymerization of aniline and electrodeposition of (Nickel-Cobalt) bimetallic. The electrodeposition technique has been adopted to introduce different amounts of cobalt into the nickel. Surface morphologies of the electrodeposits and their electrocatalytic properties have been studied for the oxygen evolution reaction in NaOH solutions. Then, the data obtained have been treated according to Koutecky–Levich equation, and the values of a maximum kinetic current density. The present experimental study successfully demonstrates that the results of these tests have led to the conclusion that the catalyst Co in the film has an evident effect on the OER which varies with its content but does not change the mechanism.

Co has a significant effect on the OER. The effect of Co deposited with NiO film depends on its content. The electrocatalytic activity may be related, to the distribution and state of Ni-Co particles incorporated in polyaniline film matrix and the synergistic effects between the dispersed Ni-Co particle and the polyaniline film.

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