

Ni-TiO₂ nanocomposite coatings as cathode material for hydrogen evolution reaction

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The paper aims to investigate the Ni/TiO₂ nanocomposite layers with different concentrations of TiO₂ nanoparticles (mean diameter size of 10 nm) for electrocatalytic activity of hydrogen evolution reaction in 0.5 M NaOH solution by cathodic linear polarization measurements (LP) and electrochemical impedance spectroscopy (EIS) performed at cathodic potentials. Knowing that nickel and nickel alloys have good electrocatalytic activity for the hydrogen evolution reaction (HER) and good resistance to corrosion in alkaline environment, the research work compares the electrocatalytic activity of Ni/TiO₂ nanocomposite layers with pure nickel coating. The results show an improving of electrocatalytic activity by adding nano dispersed TiO₂ particles into nickel matrix.

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1. Introduction

In chloro-sodium industry, or application to obtain hydrogen by water electrolysis and industrial electrochemical processes, development of new materials with electrocatalytic activity is very important in saving energy consumption by decreasing the hydrogen reduction overvoltage (potential) [1, 2]. The hydrogen is still considered a clean fuel due to the development of fuel cell technologies [3-5]. Compared with fossil fuels, the combustion product of hydrogen is only water, which provides numerous environmental benefits. Hydrogen also has many other applications in petroleum refining, ammonia production, metals refining, heat treatment in inert atmosphere and the combustion cells [6-10]. Hydrogen can be produced by catalytic reforming of natural gas, coal and oil gasification methods causing major environmental problems [6]. Alternatively, the hydrogen production by water electrolysis is considered a sustainable method capable of using renewable energy sources [6, 11, 12]. In this process the materials electrodes play an important role to improve energy conversion and electrolysis process cost reduction. Thus there are many interests in the investigation of the hydrogen evolution reaction (HER) focused on the development of new materials for electrodes so as to increase electrocatalytic activity and reduce overpotential of hydrogen reduction [13, 14].

Basically electrode materials with low HER potential must have two characteristics, e.g. intrinsic catalytic activity and high active surface area [13-20]. It is well known that nickel and nickel alloys have good

electrocatalytic activity for the HER and good resistance to corrosion in alkaline environment [20]. Compared with nickel alloys, nickel-based composites with dispersed active phases are becoming increasingly studied internationally as new materials, suitable candidates for electrode materials with electrocatalytic activity such as: Ni/MoO₂, Ni/MoO₃ [21, 22], Ni/Mo powder [18], Ni/rare earth compounds [19, 20] and Ni/polyaniline [11]. The particles embedded in the nickel matrix can decrease nickel crystals size resulting electrodes with high active surface area. Thus these electrodes formed from nickel matrix composite materials provide higher electrocatalytic activity than that of pure nickel.

The Ni/TiO₂ as nanocomposite layers have not been sufficiently investigated for electrocatalytic activity and especially correlated with morphology, microtopography, roughness or specific active surface.

This paper investigates the Ni-TiO₂ nanocomposite coatings as cathode material for the hydrogen evolution reaction in 0.5 M NaOH solution. The nanocomposite coatings were obtained by electro-co-deposition of nano-TiO₂ dispersed phase (mean diameter size of 10 nm) with nickel at optimized parameters to obtain coating thicknesses of $21 \pm 01 \mu\text{m}$. Electrochemical methods as cathodic linear polarization measurements and electrochemical impedance spectroscopy performed at cathodic potentials were used in this study.

2. Experimental

2.1. Materials

TiO₂ nanoparticles incorporated in the nickel matrix by electro-co-deposition affect the morphology, topography and preferential orientation of nickel crystals in the Ni/TiO₂ nanocomposite coatings [23]. Four types of electrodes were considered to test their electrocatalytic activity for hydrogen evolution reaction, in order to trace the effect of nanoparticles inclusion into nickel matrix and the effect of their concentration. These electrodes are the followings:

- pure Ni (0 % nanoparticles included);
- Ni/TiO₂ (10 gL⁻¹ nanoparticles in electrolyte);
- Ni/TiO₂ (15 gL⁻¹ nanoparticles in electrolyte);
- Ni/TiO₂ (20 gL⁻¹ nanoparticles in electrolyte).

The electrodes were obtained by electrodeposition on stainless steel support [23].

The microtopography of the studied samples and values of average surface roughness (R_a) are presented in the Figs. 1 - 4.

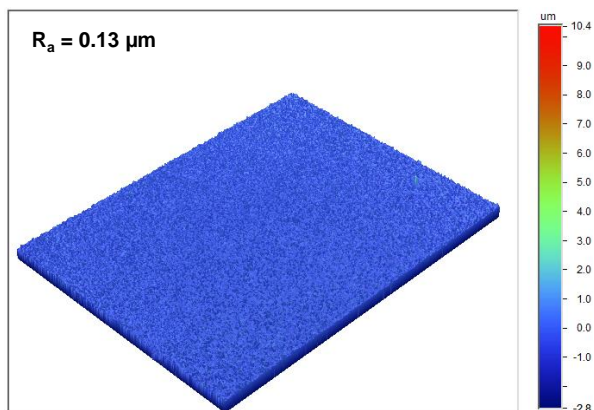


Fig. 1. Electrode surface microtopography of pure Ni coating (0 % nanoparticles included).

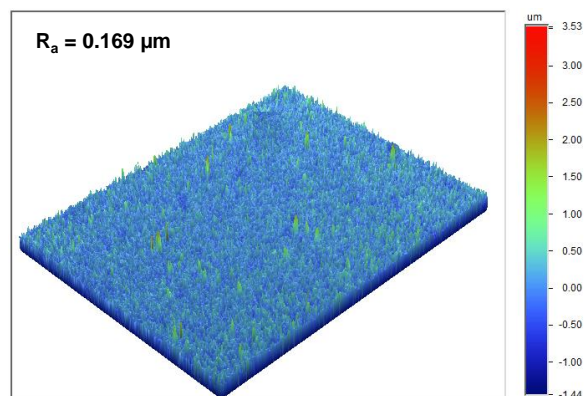


Fig. 2. Electrode surface microtopography of Ni/nano-TiO₂ (10 gL⁻¹) nanocomposite coating.

2.2. Methods

Cathodic linear polarization (LP) diagrams were performed in 0.5 M NaOH solution at a scan rate of 5 mV/min. and the curve of current density, j versus - potential, E were drawn.

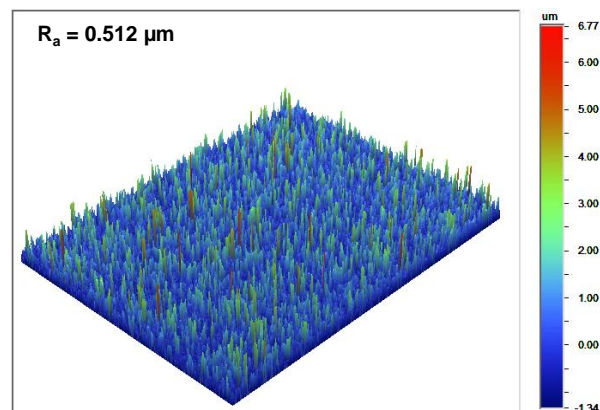


Fig. 3. Electrode surface microtopography of Ni/nano-TiO₂ (15 gL⁻¹) nanocomposite coating.

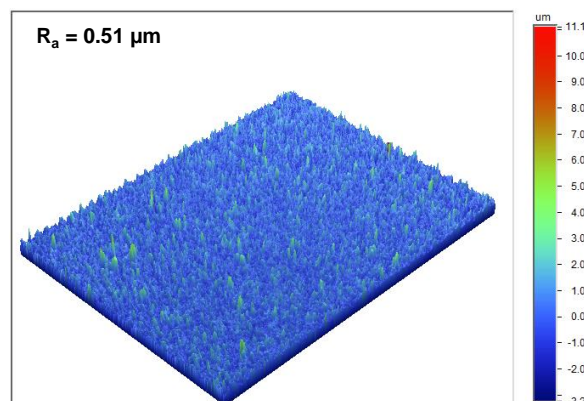


Fig. 4. Electrodes surface microtopography of Ni/nano-TiO₂ (20 gL⁻¹) nanocomposite coating.

2.2. Methods

The nanocomposites and pure nickel coatings were also comparatively studied for hydrogen discharge by electrochemical spectroscopy measurements (EIS) at cathodic potentials in 0.5 M NaOH solution in the frequency range from 100 kHz to 10 mHz with an amplitude of sinusoidal signal of 10 mV.

The electrocatalytic activity tests of the nanocomposite coatings in alkaline solution were performed using a potentiostat/galvanostat Voltalab PGZ 100 and an electrochemical cell with three electrodes: working electrode (WE) being the test sample on which surface measuring was made, counter - electrode (CE) as circular platinum grid and Ag/AgCl/saturated KCl + AgCl as reference electrode ($E = + 199$ mV/EHS).

An alkaline solution of 0.5 M NaOH with the pH of 11.90 was prepared, which was used in an electrolytic cell

with a constant volume of 350 mL.

3. Results and discussion

3.1. Linear polarization curves

Cathodic polarization diagrams are shown in Fig. 5 (current density curves, j versus potential, E) and Fig. 6 ($\log j - E$). The analysis of these diagrams shows the followings:

-Current-potential curves (overvoltage) for hydrogen reduction have different values depending on the two types of surfaces tested, respectively electrodeposited pure nickel, and Ni-TiO₂ nanocomposite coatings with different concentrations of nano TiO₂ dispersed phase included on the nickel matrix.

-Hydrogen reduction overvoltage is less on the composite surface Ni/nano-TiO₂, (Fig. 5, curves marked with the letter (a)), as compared with pure nickel surface (Fig. 5, curve marked with the letter (b)).

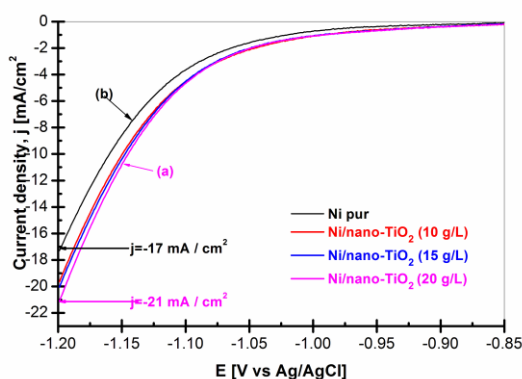


Fig. 5. Linear polarization curves for hydrogen evolution reaction in 0.5M NaOH solution for pure Ni and Ni/nano-TiO₂ composite coatings.

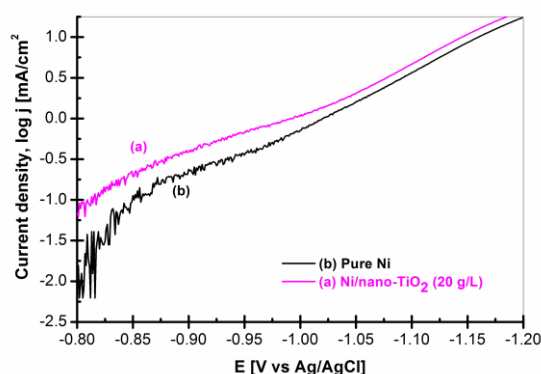


Fig. 6. Logarithmic representation of the linear polarization curves for the hydrogen evolution reaction in 0.5M NaOH solution for pure Ni and composite Ni/nano-TiO₂ composite coatings.

If we consider the same potential for hydrogen reduction on the cathode, respectively -1200 mV (vs. Ag/AgCl), on the pure nickel surface (Fig. 5 (a)) there is a current density of -17 mA/cm² and higher, respectively equal to -21 mA/cm², on the Ni/nano-TiO₂ composite surface. Between these three composite surfaces, the highest current density was observed at the concentration of 20 gL⁻¹ TiO₂ as dispersed phase (Fig. 5(b)).

Therefore the current efficiency increases on the nanocomposite surfaces as compared to pure nickel, which for an electrochemical industrial process means a significant reduction in energy consumption.

From polarization diagrams the typical Tafel region was analyzed, which can be described using the Tafel equation as following.

$$\eta_c = \frac{2,3RT}{\alpha nF} \log j_0 + \frac{2,3RT}{\alpha nF} \log j$$

$$\eta_c = a + b \log j$$

Where: η_c is the cathode overpotential, R is the ideal gas constant, and T is the absolute temperature, α , n and F are the charge-transfer coefficient, number of electrons exchanged and the Faraday constant, respectively. The j_0 is the apparent exchange current density, which can represent the HER catalytic activity of the electrodes [11, 18, 19].

Tafel slope b is an important parameter and can provide insight into the HER mechanism on the studied electrodes.

The measured slope values for these HER electrodes are as followings:

-The Ni electrode exhibits a slope around 100 mV/dec.

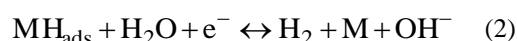
-The presence of the TiO₂ nanoparticles in the Ni matrix results in increasing the Tafel slope value from 174 mV/dec. for Ni/nano-TiO₂ (10 gL⁻¹) to 187 mV/dec. for Ni/nano-TiO₂ (20 gL⁻¹).

This phenomenon indicates that the electrode containing solid metal oxides shows a high Tafel slope value and it is in good agreement with other researchers [11, 18].

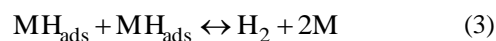
The electrochemical HER mechanism model in alkaline solution, as proposed, takes place through the following three reactions:



Volmer reaction



Heyrovsky reaction



Tafel reaction.

According to these models for HER mechanisms [2, 18], the Volmer, Heyrovsky and Tafel mechanism, reactions (1)-(3), may display three different slopes: 116.3,

38.8 or 29.1 mV/dec at 20°C. When Heyrovsky reaction is the rate determining step, r.d.s., the slope is 38.8 mV/dec. and when the Tafel reaction is the r.d.s. slope is 29.1 mV/dec., but when the slope of 116.3 mV/dec. is observed it is impossible to distinguish which step is the rate determining one. However, as the surface coverage by adsorbed hydrogen should increase with increase in negative overpotential, the rate limiting step should be that of Heyrovsky. Thus, the r.d.s. for HER on the studied electrodes could not be distinguished, the Tafel slopes being between 100 mV/dec (pure nickel coating) and 187 mV/dec. (Ni/TiO₂ (20 gL⁻¹)).

3.2. Electrochemical impedance spectroscopy measurements at cathodic potential

The nanocomposites and pure nickel coatings were comparatively studied for hydrogen discharge by electrochemical impedance spectroscopy (EIS) measurements at cathodic potentials in 0.5 M NaOH solution. The Nyquist representation of experimental diagrams performed at E = -1000 mV cathodic potential, is presented in Fig. 7 (a-d) and Fig. 8 (a-d) at E = -1200 mV cathodic potential.

In order to analyze the value of each circuit element in the impedance spectroscopy, the measured data were simulated using nonlinear-least square fitting analysis (NLS) software. The electrical circuit model selected to investigate the HER electrochemical process is shown in Fig. 9, which is similar to elsewhere proposed [2, 24]. In the equivalent circuit, R_s is the solution resistance. R_{ct} is the electrochemical charge transfer resistance. CPE₁ is associated with the double layer capacitance (C_{dl}). R_p is related to the resistance of the adsorbed intermediate H_{ads}, and CPE₂ is the constant phase element of the pseudo-capacitance.

Due to the solid electrodes dispersion effect, resulted from the inhomogeneous surfaces of the modified nanocomposite and pure nickel coating the double layer capacitance C_{dl} is substituted by a constant phase element (CPE). Its impedance is given by the equation [2]:

$$Z_{\text{CPE}} = \frac{1}{T(j\omega)^\varphi}$$

Where: ω is the angular frequency in rad/s of the AC voltage, and φ corresponds to the depression angle $90(1-\varphi)$ of the semicircle. T is a constant which is related to the double layer capacitance, C_{dl}, of the coating electrodes [16, 20].

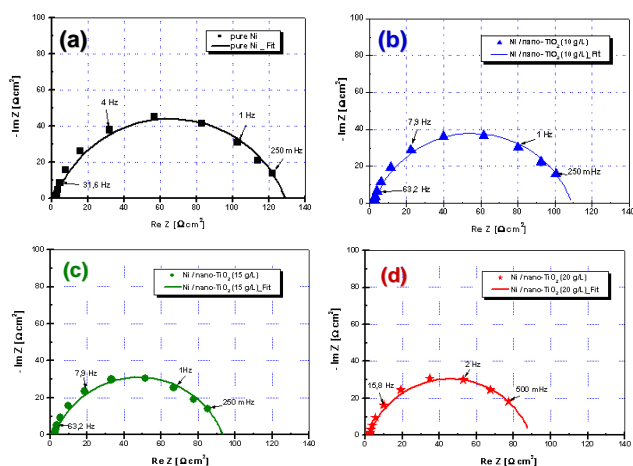


Fig. 7. Nyquist representation of the EIS measurements for HER reaction in 0.5 M NaOH solution on Ni/nano-TiO₂ nanocomposites (b-d) and pure nickel coatings (a) at an overpotential of E=-1000 mV: plain symbol – experimental data; full line – fitted diagram.

At overpotential of E=-1000mV, for the same electrode geometric surface (4 cm²) the charge transfer resistance on pure nickel coating surface is 130 Ω·cm² and lower on Ni/TiO₂ nanocomposite surfaces: from 110 Ω·cm² at 10 gL⁻¹ nano-TiO₂ to 87 Ω·cm² at 20 gL⁻¹ nano-TiO₂ in electrolyte.

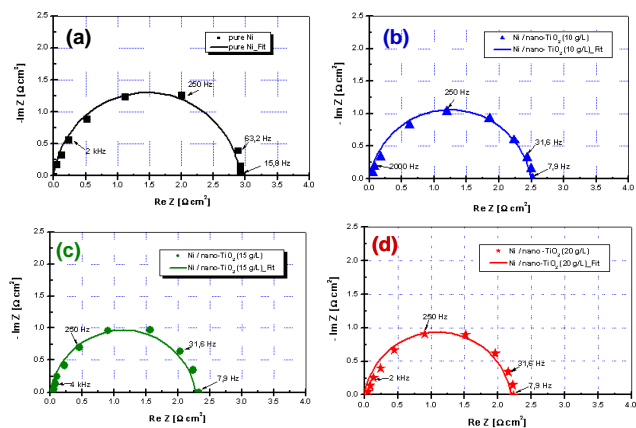


Fig. 8. Nyquist representation of the EIS measurements for HER reaction in 0.5 M NaOH solution on Ni/nano-TiO₂ nanocomposites (b-d) and pure nickel coatings (a) at an overpotential of E=-1200 mV: plain symbol – experimental data; full line - fitted diagram.

At the overpotential of E=-1200 mV, for the same electrode geometric surface (4 cm²) the charge transfer resistance on pure nickel coating surface is 3 Ω·cm² and lower on Ni/TiO₂ nanocomposite surfaces: from 2.5 Ω·cm² at 10 gL⁻¹ nano-TiO₂ to 2.25 Ω·cm² at 20 gL⁻¹ nano-TiO₂ in electrolyte.

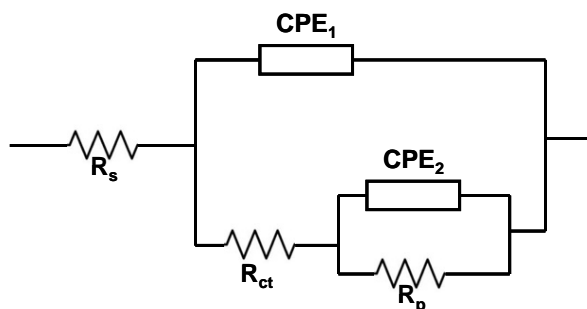


Fig. 9. Equivalent circuit used for fitting the impedance results.

The electrochemical charge transfer resistance (R_{ct}) values decreased from pure nickel coating to Ni/nano-TiO₂ nanocomposite coating (10 - 20 gL⁻¹ TiO₂). The effect of increasing the TiO₂ nanoparticle concentration in the nickel plating electrolyte is observed to be in decreasing the charge transfer resistance of Ni/nano-TiO₂ nanocomposite surface for HER in alkaline solution.

4. Conclusions

-Hydrogen reduction overvoltage is less on the composite surface of Ni/nano-TiO₂, as compared with the pure nickel surface, confirming the improved effect of electro catalytic activity for HER of the TiO₂ nanoparticles inclusion into nickel matrix.

-The analysis of electrochemical impedance spectroscopy measurements shows the following:

-The electrochemical charge transfer resistance (R_{ct}) values decreased from pure nickel coating to Ni/TiO₂ nanocomposite coatings (10-20 gL⁻¹ nano-TiO₂).

-The effect of increasing the TiO₂ nanoparticles concentration in the nickel plating electrolyte is observed to decrease the charge transfer resistance of nanocomposite surfaces for HER in alkaline solution.

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