

EFFECT OF NANOPARTICLES SIZE ON CORROSION BEHAVIOR AND HYDROGEN EVOLUTION REACTION ACTIVITY OF Ni MODIFIED SCREEN-PRINTED CARBON ELECTRODES

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Abstract

The great research interest of electrochemical analyst in electromodification includes increasing the surface area, enhancing the electrode conductivity, facilitating the electron transfer and improving the analytical sensitivity and selectivity. We present the screen-printed carbon-based electrodes (SPCEs) coated with nickel nanoparticles (NiNPs) as a novel alternative to the unmodified electrodes. The electrochemical potentiostatic deposition was used as a convenient, cost-efficient and time-saving method for NiNPs-SPCEs preparation. Modified electrodes acquire very specific behavior in corrosion tests and also electrocatalytic properties to hydrogen evolution reaction (HER) even being re-useable. The morphology of NiNPs-SPCEs was characterized by scanning electron microscopy (SEM). Corrosion tests and HER measurements were performed in a highly acidic media of H₂SO₄ using potentiodynamic polarization methods. The electrochemical kinetic parameters such as corrosion potential and corrosion current density and also equilibrium potential values in HER were determined. Corrosion resistance was influenced by grain density boundary. Electrocatalytic characteristics of Ni nanoparticles play important role in their following sensing applications opening the way to rapid 'in-situ' analyses.

Keywords:

Corrosion, Electrocatalytic Activity, Hydrogen Evolution Reaction, Screen-Printed Carbon Electrodes, Nickel Nanoparticles

1. INTRODUCTION

In an effort to meet the growing need to perform rapid "in situ" analyses the disposable screen-printed electrodes (SPEs) present a suitable choice [1, 2]. The great versatility presented by the SPEs lies in the wide range of ways, in which the electrodes may be modified. These modification techniques can convert relatively inexpensive and disposable substrate electrodes into very specific electrocatalytically active and even re-useable electrochemical sensors [3]. Nanocrystalline materials are the main subject of interest in industrial applications due to their unique properties. Nanocrystalline materials with comprehensive combination of excellent mechanical properties increased corrosion resistance and good adhesion ability with substrate, that are considerably needed for design or operation of devices, machine and structural systems [4]. The surface morphology at both microscopic and nanoscopic levels exerts a marked influence on the electrocatalytic activity of an electrode. At nanoscopic levels, a change in the superficial ordering of the metal atoms can produce a significant effect in the kinetics of reactions involving adsorbed intermediates [5]. Though recent developments in the synthesis method of nanocrystalline materials it is difficult to summarize and predict their corrosion properties. Actually, different synthesis methods lead to difference in microstructure and properties of nanocrystalline materials. A good understanding of the relation between the

corrosion property of the nanocrystalline materials and their microstructure is important for both prospective engineering applications and knowing of fundamental physicochemical properties [6]. Electrodeposited Ni is widely used in many fields to improve surface finishing, corrosion resistance and wear properties [4]. Nickel and nickel alloys are used for a wide variety of applications in electroanalysis and electrocatalysis. These potential usages require corrosion and heat resistance. The hydrogen evolution reaction (HER) is historically very important and has been widely studied using both a broad range of solution conditions, and electrode materials. It is well established that the HER on a metallic electrode M, in acidic media, proceeds according to the following reaction mechanism:



The Volmer step (reaction 1) is the primary electron transfer step with formation of adsorbed hydrogen on the electrode surface ($M\text{H}_{\text{ads}}$) from H_2O molecule. It is followed by the Heyrovsky step or/and the Tafel step with the formation of H_2 molecule. The occurrence of Heyrovsky step (reaction 2) suggests the formation of H_2 molecule by desorption of adsorbed hydrogen and a simultaneous reduction of H_2O molecule. The Tafel step (reaction 3) suggests the formation of H_2 molecule by a combination of two neighbouring adsorbed hydrogen atoms. A fraction of atomic hydrogen ($\text{H}_{\text{ads}} \cdot$) may undergo adsorption in a surface layer of nickel, thus altering its catalytic properties. The adsorbed hydrogen atom ($M\text{-H}_{\text{ads}}$) plays a key role in the mechanism and kinetics of the HER, changing both its thermodynamics and kinetics [7, 8].

The goal of this investigation was electrochemical corrosion behavior of nickel NPs-SPCE in acidic solution. We report also the study of the current – potential dependence for HER on electrodeposited nickel as a low cost electrocatalyst in sulphuric acid solution. The influence of various NiNPs electrodeposition time on electrochemical corrosion parameters and enhancing activity in HER was studied. The electrocatalytic characteristics of Ni nanoparticles modified SPCEs play very important role in their following biosensing applications.

2. EXPERIMENTAL DETAILS

2.1 Apparatus and electrodes

The electrodeposition process, corrosion tests and hydrogen evolution reaction studies were performed with the same electrochemical cell at room temperature and at atmospheric pressure. The electrochemical measurements were carried out with screen-printed carbon electrode system consisting of three electrodes: graphite working electrode (diameter 4.0 mm), Ag/AgCl reference electrode and graphite auxiliary electrode. A three-electrode SPCE system was fabricated with a semi-automatic screen-printing machine DEK 248 (DEK International, Switzerland). The reagents used for this process were: Autostat HT5 polyester sheet (McDermid Autotype, UK), Electrodag 423SS carbon ink, Electrodag 6037SS silver/silver chloride ink and Minico 7000 Blue insulating ink (Acheson Industries, The Netherlands). The electrochemical experiments were performed with an Autolab PGSTAT 302N potentiostat/galvanostat connected to a PC and controlled by Autolab Nova software. All measurements were realized with a working electrolyte volume of 50 μL , which was enough to cover the three-electrode system connected to the potentiostat by an edge connector module. The morphology and homogeneity of nano-scaled surface Ni-modified SPCEs were observed by Merlin Zeiss scanning electron microscope (SEM EVO MA 10 ZEISS).

2.2 Reagents and solutions

All used chemicals were obtained from REACHEM or Laboratory Chemicals - Milan Adamík (Slovakia) and were of the highest grade available and used without other purification. All measurements were made at 20 ± 2 °C and atmospheric pressure.

2.3 NiNPs modified SPCEs Preparation

In an effort to achieve reproducible Ni nanoparticles modified SPCEs we used potentiostatic electrochemical deposition as a suitable and time-saving method for preparation of Ni-SPCEs. The solution, in which the nickel deposition was carried out, typically consisted of 0.7 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.6 mol/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.6 mol/L H_3BO_3 and 0.05 mol/L sodium citrate. The electrochemical deposition of metallic nickel was made using constant potential value of -2.0 V in a working electrolyte containing the nickel sulphate, with the following deposition times of 5 s, 10 s, 30 s, 50 s.

3. RESULTS AND DISCUSSION

3.1 Characterization of NiNPs modified SPCEs

The obtained electrodeposited NiNPs onto SPCEs were studied by scanning electron microscopy at different magnifications. It is important to choose the optimal magnifications to obtain the best images in which some agglomeration of nanoparticles in the electrodeposited layers was observed. The size of electrodeposited nanoparticles depends on the period of electrodeposition process. Scanning electron microscopy was used for investigation the surface morphology and homogeneity of electrodeposited nickel nanoparticles. In Fig. 1 the representative SEM images of Ni nanoparticles modified SPCEs are displayed for different deposition periods of 5 s, 10 s, 30 s and 50 s.

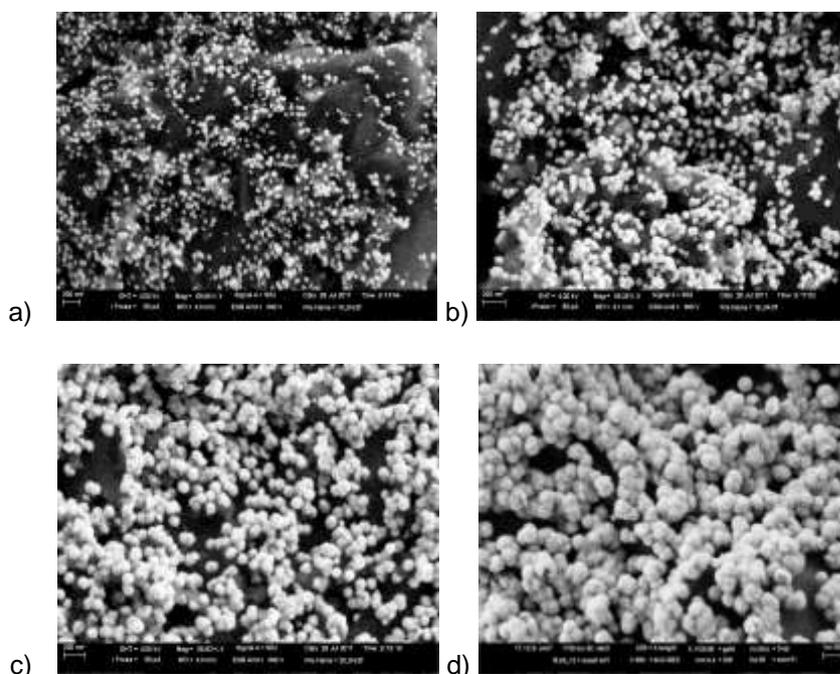


Fig. 1 Representative SEM micrographs of NiNPs modified SPCEs electrodeposited after deposition period of a) 5 s; b) 10 s; c) 30 s; d) 50 s.

The surface of SPCE working electrode was covered with Ni nanoparticles with different size distribution. Similar oval-shaped nickel nanoparticles about 20 nm in diameter were homogeneously distributed onto SPCE after 5 s (Fig. 1a)). Though there was the lower coverage of SPCE with Ni nanoparticles at this deposition time. As it can be clearly seen in SEM images, we observed the increase in both the size (from ca. 80 nm to 250 nm in diameter) and density of NiNPs with increasing electrodeposition time (Fig. 1b), c), d)). With an increase of deposition time, Ni nanoparticles also became more aggregated. Ni nanoparticles electrochemically synthesized after 50 s showed the highest density and coverage of working electrode.

3.2 Electrochemical Corrosion Behavior

Corrosion tests were performed for nickel nanoparticles substrates in sulphuric acid solution. Before all the measurements, the samples were immersed into electrolyte for 120 s to stabilize the open circuit potential (OCP). The anodic polarization curves $i = f(E)$ were obtained applying following conditions: the potential range from -0.6 V to +0.1 V at scanning rate of 0.5 mV/s. The representative Tafel plots are shown in Fig. 2. The reproducibility of Tafel plots was also good. The obtained Tafel plots displayed shift of corrosion potential to the more negative values associated with an increase in corrosion rate.

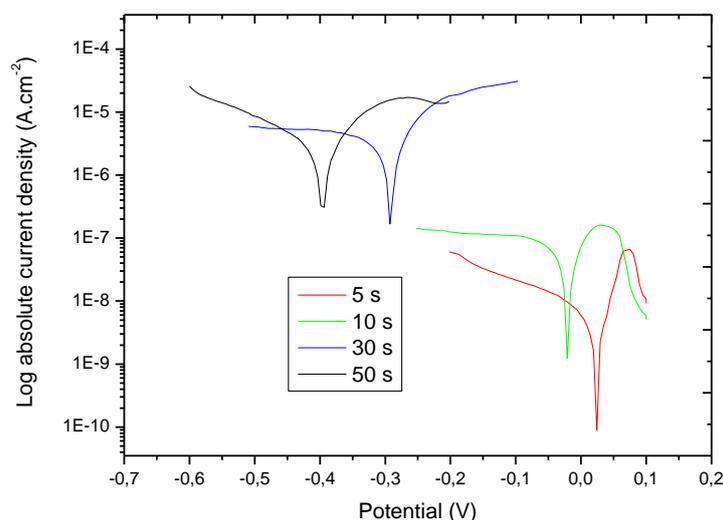


Fig. 2 Potentiodynamic polarization curves of NiNPs modified SPCEs in 1 mol/L H₂SO₄ solution at room temperature.

The electrochemical kinetic parameters such as corrosion potential (E_{corr}) and corrosion current (i_{corr}) were determined and calculated from the intersection of the anodic and cathodic Tafel lines extrapolation. The corresponding numerical values are summarized in Table 1.

Table 1 Determined values of E_{corr} , i_{corr} and corrosion rates obtained from potentiodynamic polarization curves of NiNPs modified SPCEs in 1 mol/L H₂SO₄ solution at room temperature.

NiNPs deposition time (s)	E_{corr} (mV)	i_{corr} (μ A)	Corrosion rate (mm/year)
5	13.85	3.491×10^{-4}	4.057×10^{-6}
10	-35.20	5.469×10^{-3}	6.355×10^{-6}
30	-290.5	4.351×10^{-1}	5.056×10^{-3}
50	-389.8	1.913	2.223×10^{-2}

The highest positive potential was observed for Ni nanoparticles electrodeposited after 5 s. The significant decrease of corrosion potential was observed for Ni nanoparticles electrodeposited during 30 s. Furthermore, the polarization curves indicate, that the corrosion current increased with the increasing deposition time. Potentiodynamic polarization curves demonstrated the decrease in electrochemical stability with increasing NPs size. The best electrochemical stability in corrosive aqueous media showed NiNPs electrodeposited onto SPCE after 5 s.

3.3 Electrocatalytic Activity

The HER activity of resulting NiNPs-SPCEs was evaluated depending on electrodeposition time of nickel. For the purpose of nickel oxides on the electrocatalytic layer reduction, the NiNPs-SPCEs were polarized in 1 mol/L H₂SO₄ at -500 mV for 180 s. The representative current versus potential plots recorded during hydrogen evolution in 1 mol/L H₂SO₄ solution applying a slow potentiodynamic sweep of 0.5 mV/s in the range of potentials from 0.2 V to -0.6 V are in graph below (Fig. 3).

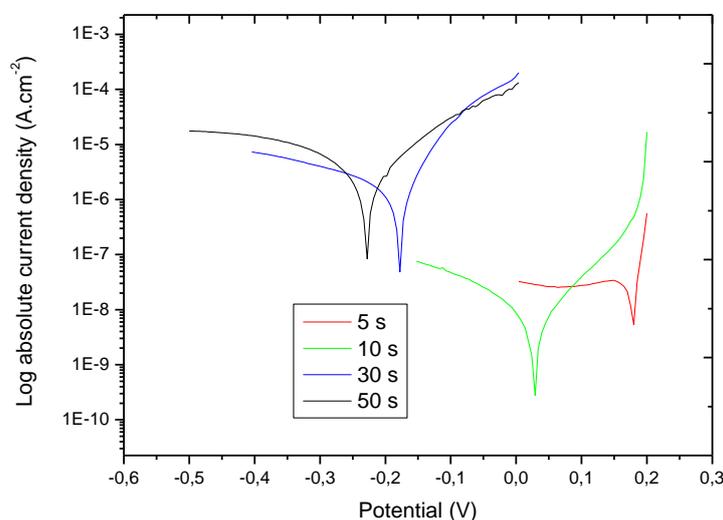


Fig. 3 Tafel curves of electrodeposited NiNPs onto SPCEs in 1 mol/L H₂SO₄ solution at room temperature.

The equilibrium potential values obtained from Tafel plots are listed in Table 2. It is clearly seen, that there is an equilibrium potential shift to more negative potential values with increasing Ni nanoparticles deposition time. We observed decrease of catalytic activity of nickel nanoparticles with increasing electrodeposition time.

Table 2 Values of equilibrium potentials and Tafel slopes of the HER derived from linear plots on NiNPs modified SPCEs in 1 mol/L H₂SO₄ solution at room temperature.

NiNPs deposition time (s)	E_{eq} (mV)	b (mV·dec ⁻¹)
5	177.9	17.21
10	27.86	36.95
30	-183.5	53.34
50	-230.1	81.71

CONCLUSION

In an effort to develop metal nanoparticles with corrosion stability and enhanced electrocatalytic activity we prepared NiNPs modified SPCEs by electrodeposition process. Ni nanocrystalline structure was characterized by scanning electron microscope. We studied corrosion tests and also electrocatalytic properties to hydrogen evolution reaction (HER) in 1 mol/L H₂SO₄ using potentiodynamic polarization methods. Electrochemical corrosion behavior of NiNPs-SPCEs is strongly affected by nanoparticles size. We observed an increase in corrosion rate with increasing electrodeposition time associated with shift of corrosion potential to the more negative values. HER measurements showed a potential shift to more negative equilibrium potential values with increasing NiNPs deposition time. The best electrochemical corrosion resistance and the highest activity in HER was registered for Ni nanoparticles deposited after 5 s. Combination of electrochemical screen-printed sensors with nanoscale nanoparticles and films presents a considerable step for improved sensitivity, longer stability of the bioelement in biosensors and new detection possibilities of these disposable microanalytical devices.

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