

ORIGINAL PAPER

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Behavior of a nickel electrode in the presence of carbon monoxide

Received: 21 May 1997 / Accepted: 9 June 1997

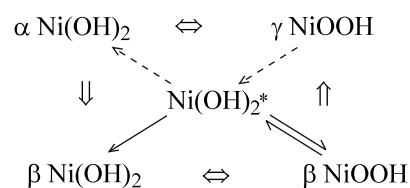
Abstract The electrochemical behavior of a nickel electrode with limited volume (LVE) electrodeposited as a thin layer on gold has been studied. The influence of the gold matrix on the electrochemical Ni electrode behavior has been considered. The electrosorption and oxidation of carbon monoxide on the Ni surface and its influence on hydrogen sorption has also been demonstrated.

Key words Nickel electrode · Carbon monoxide adsorption · Hydrogen sorption in/on nickel · Limited volume electrode

Introduction

In our previous papers it was shown, with palladium as an example [1, 2], that a thin layer of metal deposited on a neutral matrix is suitable for measurements of the electrochemical behavior. In our studies with palladium, currents obtained during absorption of hydrogen or oxidation of absorbed hydrogen are a few orders of magnitude higher than currents originating from other surface processes, i.e. formation or reduction of surface oxides. This problem was eliminated by the use of a thin layer of palladium deposited on gold. Because the term “thin layer” is also used in the case of studies of deposits with one or a few atomic layers of material, we proposed to name our thin layer electrode a “limited volume electrode” (LVE) [3]. The use of this kind of electrode (LVE) allows the current ratio for the oxidation of absorbed hydrogen and for the oxidation of chemisorbed species to be limited and controlled by electrode thickness.

Another problem can be seen in the study of electrochemical behavior of nickel. After a few cycles over the full range of anodic-cathodic polarization potentials, the fresh Ni electrode changes its behavior irreversibly, i.e. the surface oxide-hydroxides are not fully reduced during the cathodic scan. The procedure of mechanical cleaning does not always restore the electrochemical behavior of a fresh nickel electrode, and the electrochemical activity of the electrode surface differs in the subsequent cycling sweeps of polarization. The main electrochemical reactions which take place on a nickel electrode during cycling polarization are shown on the Bode and Arvia diagram [4, 5] demonstrated in the paper by Hahn et al. [6]:



As in the case of palladium, we decided to use a thin layer of Ni electrode, which can be replaced by freshly deposited metal after each experiment. This method allows us always to obtain an “electrochemically clean” nickel electrode without any effect from previous experiments. The hydrogen absorption in thin layers of nickel with and without the presence of surface poisons (thiourea and arsenic) was studied by Baranowski and Śmiałowski [7–9]. Nickel was electrochemically deposited on a copper matrix, which had to be specially prepared before electrode material deposition. Some papers on Ni electrochemical behavior are devoted to the nature and structure of various hydroxides Ni(OH)_2 and oxyhydroxides NiOOH [10, 11]. Visscher and Barendrecht [11], using electrochemical (CV) and ellipsometrical methods, investigated the behavior of a thin film of α - and β - Ni(OH)_2 deposited on Pt, C and Ni substrates. Also, Gomez et al. [12] studied nickel electrodeposition on different substrates (Pt, Ni, Fe, C). For

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the study of anodic corrosion films on nickel, in situ Raman spectroscopy was used [13–15]. Some authors [16, 17] also showed an effect of crystal structure on electrochemical behavior of nickel hydroxides formed on nickel single crystals. Conway et al. [18] studied the decomposition of a hydride phase at nickel cathodes by measurements of open-circuit potential data. The electrochemical behavior of nickel and nickel hydrides was intensively studied by Żóltowski [19, 20] by impedance spectroscopy. Fleischman and Saraby-Reintjes [21] found that during nickel electrolysis on vitreous carbon two hydrogen-rich nickel phases were deposited.

The system CO/Ni was mainly a subject of studies in the gaseous phase [22, 23]. A smaller number of papers have been devoted to CO adsorption on Ni electrodes [24–29]. It was found that CO adsorbed on nickel from water solutions has a significant influence on electrode surface processes. Castro Luna and Arvia [26] found that adsorbed CO in acidic solutions shifts the electro-dissolution of nickel to more positive potentials. Also, the presence of adsorbed CO decreases the formation of surface nickel hydroxides in alkaline solution. Hori et al. [24, 25, 27], after studies of CO adsorption from phosphate buffer, concluded that adsorbed product prevents hydrogen evolution on nickel electrode. In our previous work [30, 31] it was also demonstrated that adsorbed carbon monoxide on a palladium surface strongly inhibits sorption and desorption of absorbed hydrogen. Cuesta and Gutierrez [28], using PMR Spectroscopy, indicated that CO molecules adsorbed from 1 M NaOH solution are chemisorbed on the electrode surface in the on-top position. Zinola et al. [29] concluded from mass spectroscopy measurements (DEMS) that carbon monoxide adsorbs strongly on a Ni surface, but the concentration of adsorbed CO molecules is 6–12 times higher in acidic solutions than in phosphate buffer solution.

In this paper we would like to show the electrochemical behavior of LVE (ca. 1 μm thickness) deposited on gold, a matrix which in our opinion is very convenient for the electrodeposition and easy removal of deposited metals. We have compared the obtained results to our data and data from literature obtained on solid nickel electrodes (Ni wire, foil etc.). We have also studied the influence of adsorbed CO on reactions which occur on/in a Ni-electrode in 1 M KOH solution.

Experimental

Experiments were performed in 1 M KOH solution. All experiments were carried out at room temperature ($20 \pm 1^\circ\text{C}$). Solutions were prepared from high purity water (Millipore). The solutions were replaced after each experiment. Platinum foil and saturated calomel electrodes (SCE) were used as auxiliary and reference electrodes, respectively. Cyclic voltammetry was performed with a nickel electrode which was electrodeposited on gold wire (99.9%, 0.5 mm diameter) at constant current from a borate bath (Na_2SO_4 83 g/l, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 83 g/l, H_3BO_3 10 g/l). The deposit thickness was ca. 1 μm . The efficiency of the nickel

deposition, as estimated in separate experiments from the weight of the electrodes before and after electrolysis, was between 90 and 95%. In order to obtain reproducible conditions and to avoid generation of, Ni-Au alloys a new deposit was layered on the gold electrode before each experiment. The old deposit was removed with nitric acid immediately after finishing the experiment.

Carbon monoxide was prepared by the reaction of formic acid with sulfuric acid, and was passed through 1 M KOH by means of a bubbler [32].

For the study of the electrochemical behavior of the Ni thin-layer electrode, the cyclic voltammetry technique has been used. The measurements were taken in different regions of polarization potentials. Mainly, the cyclic voltammograms were taken in the "hydrogen region" between -1.20 V and -0.20 V or the full region of polarization (oxygen-hydrogen region) from -1.20 V to $+0.60$ V. Before cycling, the electrode was kept for 2 min at -1.2 V to reduce surface nickel oxides and hydroxides. This nickel surface cleaning method was proposed by Weininger and Breiter [16]. All potentials are referred to the saturated calomel electrode (SCE).

Results and discussion

Figure 1 presents the voltammograms obtained on the Ni electrode (LVE) in 1 M KOH solution. The electrode was cycled over the potential range between -1.20 V and 0.6 V at a sweep speed of 100 mVs^{-1} . The reactions which occurred on the surface are labeled with the letters on the cycling voltammogram. The shape of the obtained cyclic voltammograms on the Ni electrode (LVE) is almost the same as that of the voltammograms on a solid nickel electrode demonstrated in the literature [6] and also obtained in our laboratory on Ni wire

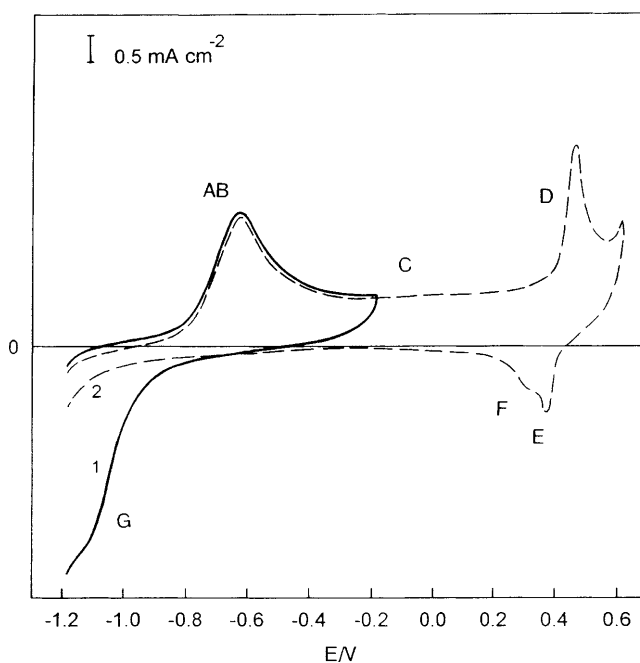
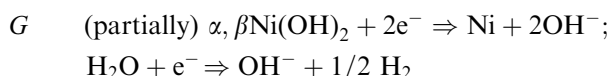
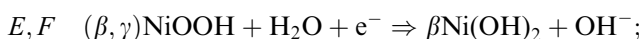
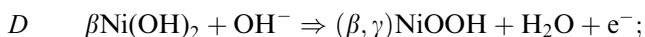
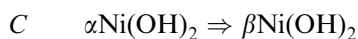
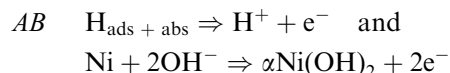


Fig. 1 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential range from -1.20 V to -0.20 V at sweep rate 100 mV s^{-1} , (1-solid line) first sweep, and from -1.20 V to 0.60 V in 1 M KOH, sweep rate 100 mV s^{-1} (2-dashed line)

(99.99), i.e. no influence of the gold matrix on the deposited nickel has been observed. The current waves can be attributed to the following reactions:



After the first cycle of the nickel electrode taken over the full range of potentials (-1.2 V to 0.6 V vs SCE), the waves responsible for surface oxidation to $Ni(OH)_2$ and its reduction totally disappeared, i.e. there are irreversible changes (passivation) after surface oxidation to $\beta Ni(OH)_2$ and $NiOOH$. According to Hahn et al. [6], the first anodic wave (AB on Fig. 1) should not only represent the generation of $\alpha Ni(OH)_2$ but also the oxidation of sorbed hydrogen. In our opinion, the first part of wave AB on Fig. 1 is responsible for hydrogen sorption reactions, which is in agreement with other authors, e.g. [33–35]. The first voltammogram (curve 1) was obtained in the potential range between -1.2 V and -0.2 V after two minutes of cathodic polarization at -1.2 V. The second voltammogram (curve 2) was obtained in the wider potential region, i.e. between -1.2 V and 0.6 V. On both obtained curves, reproducible waves originated from the oxidation of sorbed hydrogen, $H_{\text{ad}(\text{ab})} \Rightarrow H^+ + e^-$ are observed, and the reversible process $Ni + 2OH^- \Rightarrow \alpha Ni(OH)_2 + 2e^-$ (ca -0.90 V vs SCE) should occur. After Ni electrode polarization towards more positive potentials on surface transformation, α - to β - $Ni(OH)_2$ forms occur (see curve 2 in Fig. 1) and oxidation to $NiOOH$ surface compound takes place.

The cyclic voltammograms on Ni obtained in the potential region (from -1.20 V to -0.20 V at sweep rate $100 \text{ mV} \cdot \text{s}^{-1}$) without stopping during anodic and cathodic polarization, i.e. without longer cathodic polarization at -1.2 V, are shown in Fig. 2. No irreversible surface changes occur during the electrode cycling in the potential region between -1.2 V and -0.2 V.

Different Ni electrode behavior (Fig. 3) was observed in the experiment cycling over the full range of potentials (between -1.2 V and 0.6 V), i.e. without potential stopping at -1.2 V. The plot of the second (and next) following sweep differs from the shape of the plot during the first cycle. The wave AB responsible for sorbed hydrogen oxidation and $\alpha Ni(OH)_2$ generation disappears. The wave AB does not disappear even after the second sweep (Fig. 4a) if the electrode was polarized for some period of time (ca. 30 min) at maximal cathodic potential, i.e. -1.2 V. Obtained waves do not decrease during subsequent polarization sweeps. If the

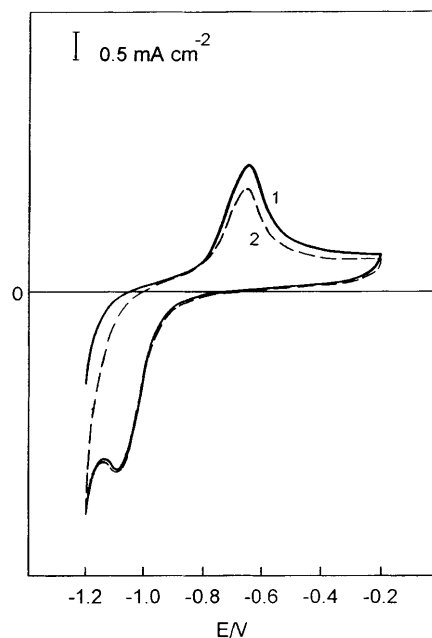


Fig. 2 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential range from -1.20 V to -0.20 V at sweep rate $100 \text{ mV} \text{ s}^{-1}$; (1-solid line) first sweep, (2-dashed line) second sweep

same electrode was kept again at potential -1.2 V for another 30 min, the obtained waves AB in subsequent sweeps are larger (Fig. 4b). Also, during electrode cycling, the obtained wave (AB) does not decrease. The potential value of the peak is shifted towards the cathodic potential in comparison to the wave obtained in

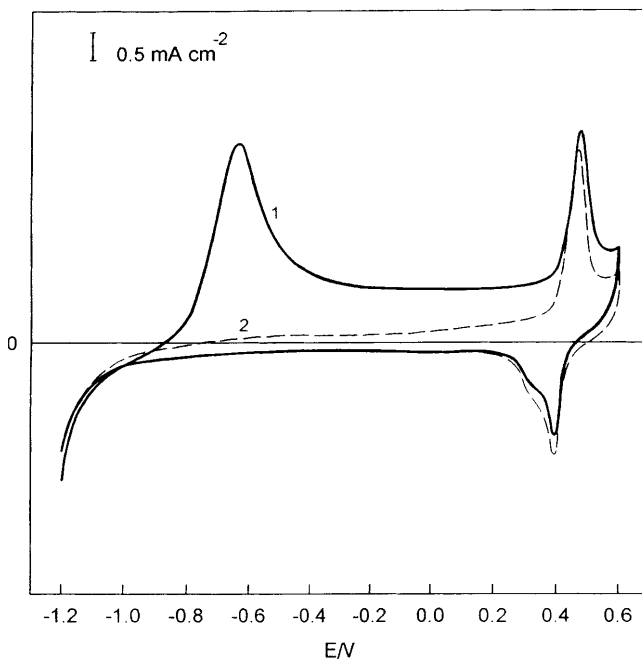
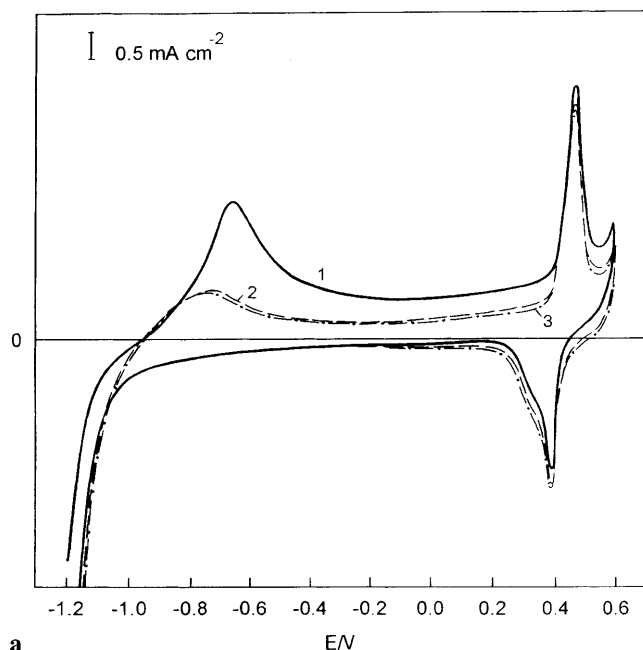
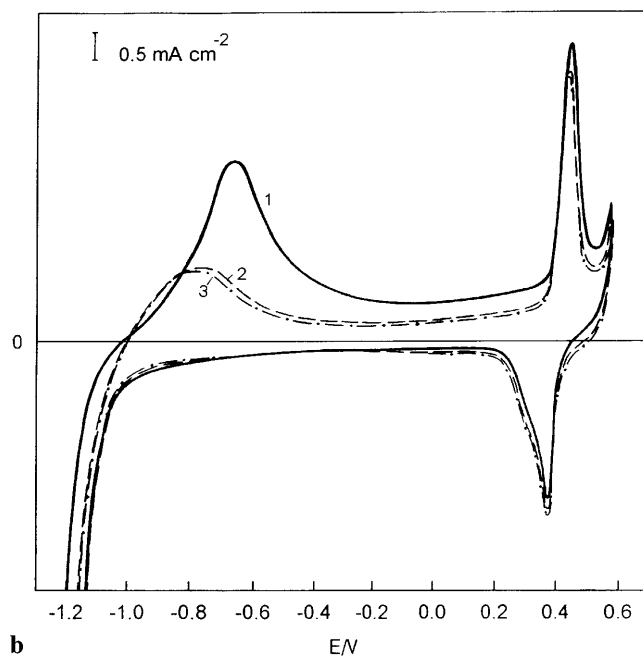


Fig. 3 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential range from -1.20 V to 0.60 V at sweep rate $100 \text{ mV} \text{ s}^{-1}$; (1-solid line) first sweep, (2-dashed line) second sweep



a



b

Fig. 4a, b Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential range from -1.20 V to $+0.60$ V at sweep rate 100 mV s^{-1} ; **a** The electrode from Fig. 3 was kept for 30 min at -1.20 V; first sweep (solid line-1), second sweep (dashed line-2), third sweep (dashed-dotted line-3), and **b** The electrode from Fig. 4a was kept for 30 min at -1.20 V; first sweep (solid line-1), second sweep (dashed line-2), third sweep (dashed-dotted line-3)

the first cycle. This wave can be attributed mostly to oxidation of sorbed hydrogen. Keeping the electrode at the potential of hydrogen reduction allows the reduction of surface nickel hydroxides to form nickel, which more easily sorbs hydrogen than nickel electrochemically deposited (as at the beginning of the experiment). It has to be noted that charges needed for $\beta\text{Ni}(\text{OH})_2$

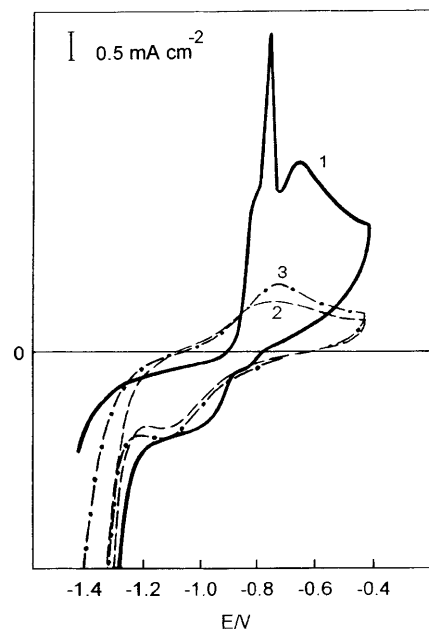


Fig. 5 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential range from -1.20 V to -0.20 V at sweep rate 100 mV s^{-1} . The electrode was kept at -1.4 V for 1 64 hours (solid line), 2 20 min (dashed-dotted line); and 3 0 min (dashed line)

oxidation to NiOOH do not significantly change in subsequent experiments with the same electrode (Fig. 4a, b). It means that surface of the electrode during the subsequent sweep does not change. These results (Fig. 4a, b) showed that nickel hydroxides are reduced by hydrogen during cathodic polarization, and/or the nickel electrode surface is activated for hydrogen sorption after longer cathodic polarization.

Figure 5 shows the cyclic voltammograms in the potential range -1.4 V to -0.4 V. Before cycling, the electrode was kept at -1.4 V for different periods of time (64 h and 20 min). At potentials -1.4 V, strong hydrogen generation is observed (gas bubbles). The influence of hydrogen on electrode behavior in the range of potentials where hydrogen sorption in/on nickel occurs was expected (changes of wave A shape in Fig. 1). After a longer time of electrode polarization at -1.4 V, a growing oxidation wave was observed on obtained cyclic voltammograms. The potential of the obtained peak (ca. -0.7 – 0.6 V vs SCE) is close to the value (ca. -0.8 V) obtained on cyclic voltammograms over the full range of polarization potentials after keeping the electrode at -1.2 V. It supports the conclusion that this current is mainly from the oxidation reaction of sorbed hydrogen. The large waves obtained after 64 h of electrode polarization (Fig. 5a) decrease during subsequent sweeps. After several sweeps, the voltammogram shape become the same as it was before the experiments (Fig. 5b). It means that during hydrogen sorption the real electrode surface does not grow. The value of the oxidation peaks is also close to those obtained by Kleperis et al. [35] who studied hydrogen

absorption in Raney nickel. The shape and potential region shows that, together with hydrogen sorption-desorption reaction, the nickel hydroxide reaction also takes place.

In Fig. 6 is shown the influence of adsorbed carbon monoxide on sorbed hydrogen desorption. The background solution 1 M KOH was saturated with CO during polarization of the electrode at constant potential (-1.2 V). After some time of electrode polarization, CO was removed by passing nitrogen through the solution. Then, a new cyclic voltammogram was taken. On the basis of obtained voltammograms, one can say that adsorbed carbon monoxide blocks the nickel electrode surface against hydrogen sorption and reactions generating surface hydroxides. During electrode polarization towards the anodic side, we observe adsorbed carbon monoxide oxidation first, and surface hydroxide generation occurs subsequently. We can expect that the production of CO adsorption is the result of its reaction with adsorbed hydrogen, as was suggested by Koga and Hori [24]. In the next experiment, the cyclic voltammogram was taken after keeping the electrode at -1.20 V in the presence of CO in solution (without removing it). A higher (but narrower) oxidation wave was observed at the same potential region as in previous experiment (in which carbon monoxide was removed before cyclization), but the charge needed for adsorbed carbon monoxide oxidation with and without its presence in solution is almost the same ($\pm 10\%$). The small

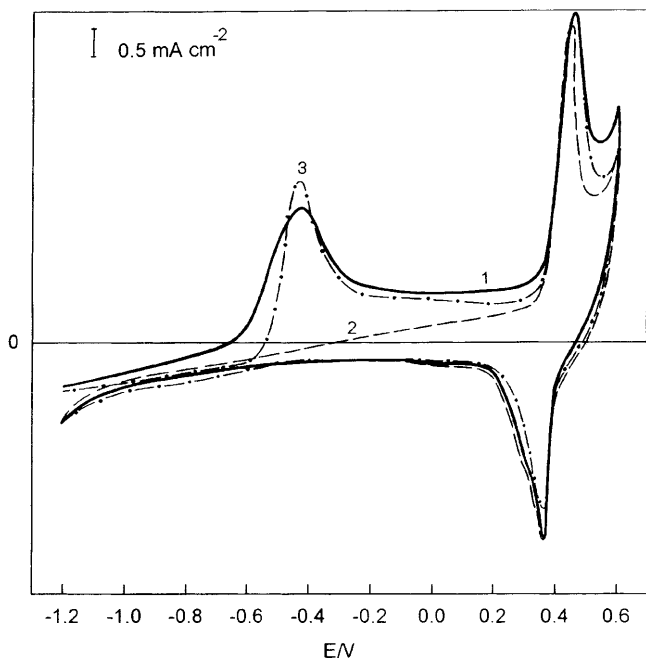


Fig. 6 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH solution. Solution was saturated with CO at -1.20 V for 30 min. Then CO was removed by N_2 and electrode was cycled towards anodic side of potentials (between 1.2 V and 0.6 V); (1-solid line) first sweep, (2-dashed line) second sweep. The cyclic voltammogram (3-dashed-dotted line) was obtained at the same conditions as previously (1 and 2) but without purging CO from the solution

difference between potentials of oxidation of adsorbed and of not adsorbed carbon monoxide (directly from solution) means that no carbon monoxide oxidation from bulk solution takes place. Oxidation of carbon monoxide starts at the beginning of the range of potentials where the Ni surface is oxidized to nickel hydroxides ($\alpha Ni(OH)_2$). The conclusion that the adsorbed form of carbon monoxide is a product (as on platinum group metals [32]) of the carbon monoxide reaction with sorbed hydrogen is supported by the experiment in which the electrode was kept at open circuit in the presence of carbon monoxide in the solution (Fig. 7). At open circuit, the Ni electrode potential in the background solution (1 M KOH) was stabilized at 0.0 ± 0.1 V vs SCE, i.e. and no adsorbed hydrogen on electrode surface was observed. Carbon monoxide was then removed by passing nitrogen through the solution and a cyclic voltammogram was taken. After keeping the Ni (LVE) electrode at open circuit in the presence of CO in solution, only a small oxidation wave from adsorbed CO was observed.

This effect is the opposite of that in the CO/Pt system, where at open circuit carbon monoxide is strongly and irreversibly adsorbed on a platinum electrode [32, 36]. It is known that a non-polarized Ni electrode is covered with nickel hydroxides. This was proved by the Raman spectroscopy method by Melendres and Xu [13]. We may suspect that the layer of nickel hydroxides protects the surface against CO sorption. In the experiment in which the Ni electrode was cathodically polarized at -1.2 V and immediately after opening the

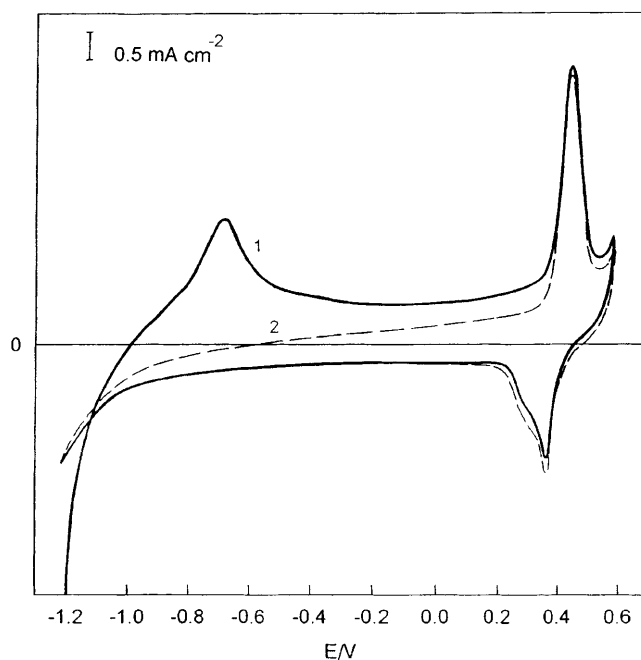
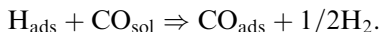


Fig. 7 Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH solution. Solution was saturated with CO at open circuit for 30 min. Then CO was removed by N_2 and electrode was cycled firstly towards anodic side of potentials, (1-solid line) first sweep, (2-dashed line) second sweep

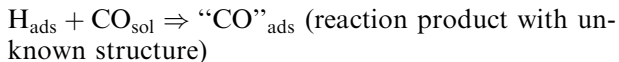
circuit CO was introduced into bulk solution, the results were also negative as previously, i.e. without cathodic polarization (Fig. 7). It can be an effect of the rapid generation of a layer of nickel hydroxide.

On the basis of obtained results and literature data [24–29], we conclude that the carbon monoxide adsorption reaction with adsorbed hydrogen takes place in two paths:

1. Adsorbed hydrogen and carbon monoxide molecular exchange



2. Reaction of carbon monoxide with adsorbed hydrogen



At this moment we are not able to establish the ratio between products of these proposed reactions.

It should be noted that in the presence of carbon monoxide in solution and/or the products of carbon monoxide adsorption on the nickel surface we have not observed the increase of the amount of adsorbed hydrogen in the electrode (as was observed by Baranowski et al. [7, 8] in the presence of other surface poisons). We have also not observed the “blocking” effect of adsorbed hydrogen oxidation by adsorbed CO (large positive shift of potential oxidation of adsorbed hydrogen) which was observed in our previous work with palladium [37, 38]. In Fig. 8 are demonstrated cyclic voltammograms taken after CO adsorption at -1.20 V with (a) and without (b) removing CO from the solution. The electrode was polarized in the region of the potential where the surface is not irreversibly changed by surface hydroxides $[\alpha Ni(OH)_2]$, i.e. -1.20 V and

-0.20 V. As in Fig. 6, the oxidation peaks, obtained with and without removal of carbon monoxide from solution, are situated almost at the same potentials. The oxidation wave taken in the absence of CO in solution is wider than in the presence of CO in bulk solution. It is interesting that in the presence of CO in solution (Fig. 6b) practically no oxidation waves (except a small current in the second sweep which is due to oxidation of the rest of the adsorption product not removed) are present during cycling after oxidation of the CO adsorption product from the electrode surface. It supports the earlier conclusion that no CO oxidation directly from bulk solution occurs. It is difficult to explain the origin of the wider oxidation wave after passing N_2 . Maybe during the longer time of electrode polarization on the surface, a small amount of additional product formed from hydrogen and CO is produced and this is catalyzed by the Ni electrode. We suppose that the wider oxidation wave during oxidation of the adsorption product after CO removal from solution could be due to the shift of the reaction equilibrium: $H_{\text{ads}} + CO \Rightarrow \text{“adsorption products”}$ (i.e. CHO_{ads}), and/or some small amount of hydrogen is adsorbed on sites unoccupied by CO. This effect is also observed in the presence of Ar, which means that nitrogen does not take part in the surface reaction. This effect needs additional study. For the purpose of checking the influence of potential on CO adsorption, experiments where the solution was saturated at different electrode potentials: -0.95 V, -0.85 V, -0.75 V and -0.65 V have been performed. The results are represented in Fig. 9. From the plots of obtained voltammograms (Fig. 7) it can be concluded that, at electrode potentials higher than -0.95 V, CO adsorption on the Ni electrode does not occur. It is observed that the presence of adsorbed

Fig. 8 a Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH solution. Solution was saturated with CO for 30 min at -1.20 V. Then CO was removed by N_2 (15 min) and cyclic voltammograms taken between -1.20 V and -0.20 V; (solid line) first sweep, (dashed line) second sweep, (dashed-dotted line) third sweep and (dotted line) fourth sweep. **b** Procedure the same but without purging CO from the solution

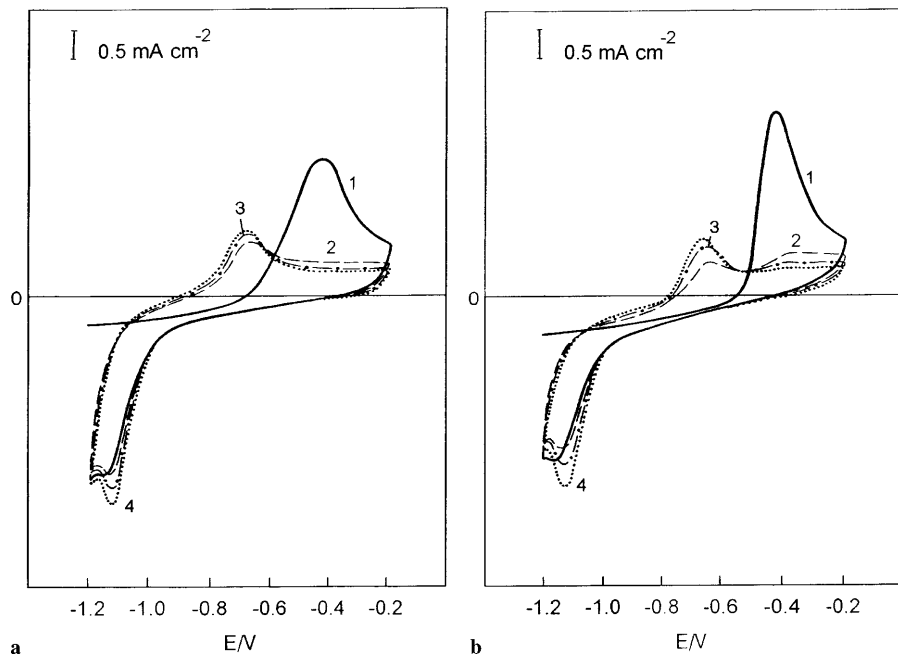
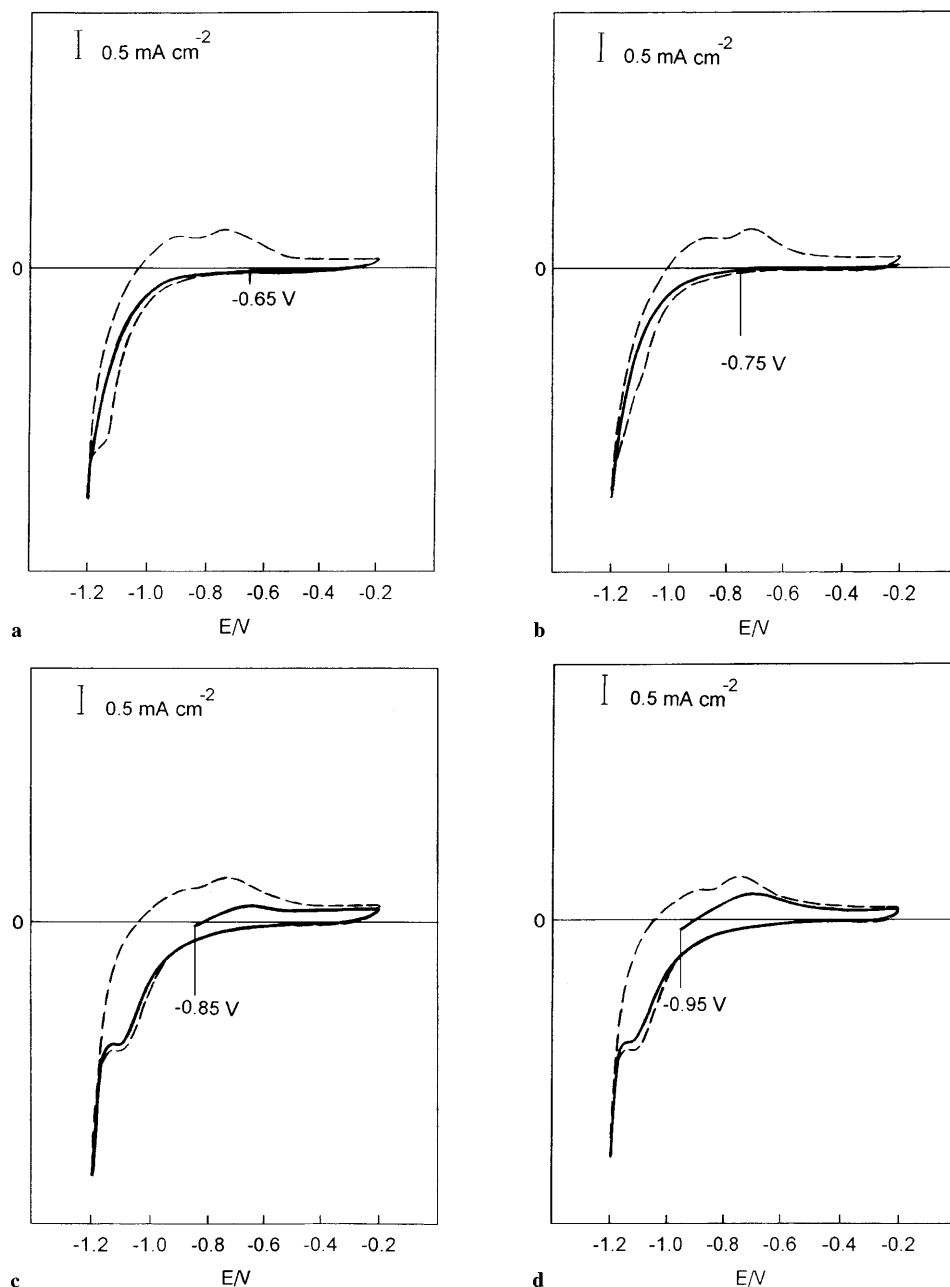


Fig. 9a–d Cyclic voltammograms of thin-layer Ni electrode in 1 M KOH in potential ranges between 1.20 V and -0.20 V. Solution was saturated with CO at potentials **a** -0.65 V, **b** -0.75 V, **c** -0.85 V, **d** -0.95 V; (solid line) first sweep, (dashed line) second sweep. Sweep rate 100 mV s⁻¹



carbon monoxide (or adsorption products) on the nickel surface prevents hydrogen absorption and nickel hydroxide generation by the electrode. The effect of preventing significant hydrogen evolution by adsorbed CO in cathodic region in phosphate buffer solution (pH = 6.8) was also reported by Hori et al. [24, 25].

Summary

1. Thin-layer Ni electrodes (LVE) are more convenient for use in electrochemical experiments than solid Ni electrodes.

2. No influence of the gold matrix material on the electrochemistry of the deposited thin layer of nickel has been found.
3. The oxidation current of sorbed hydrogen overlaps with the current of $\alpha\text{Ni}(\text{OH})_2$ generation on the nickel electrode surface
4. A longer time of cathodic polarization (at potentials of hydrogen generation) activates the nickel electrode for hydrogen sorption even if the electrode was covered before with $\beta\text{Ni}(\text{OH})_2$ and NiOOH. This effect is not observed if the electrode is continuously cycled, i.e. nickel hydroxides from the Ni electrode surface were not totally reduced.

5. Carbon monoxide is adsorbed on the nickel electrode surface by reaction with hydrogen sorbed on the nickel electrode surface, and this takes place by at least two reaction paths.
6. Carbon monoxide is adsorbed on the nickel surface at potentials below -0.95 V. At higher potentials, the electrode is covered with hydroxides which block carbon monoxide access to the nickel surface
7. Carbon monoxide adsorbed on the nickel surface prevents hydrogen sorption in/on the electrode and generation of nickel hydroxide.

Acknowledgements This work was financially supported by the Warsaw University 12-501-03-BST-562/19/97.

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