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Topics in Catalysis

ISSN 1022-5528 Volume 59 Combined 15-16

Top Catal (2016) 59:1319-1331 DOI 10.1007/s11244-016-0657-0





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ORIGINAL PAPER



Exploring the Influence of the Nickel Oxide Species on the Kinetics of Hydrogen Electrode Reactions in Alkaline Media

Alexandr G. Oshchepkov^{1,2,3} · Antoine Bonnefont³ · Viktoriia A. Saveleva² · Vasiliki Papaefthimiou² · Spyridon Zafeiratos² · Sergey N. Pronkin² · Valentin N. Parmon^{2,4} · Elena R. Savinova²

Published online: 21 July 2016 © Springer Science+Business Media New York 2016

Abstract The influence of the oxidation of Ni electrodes on the kinetics of the hydrogen oxidation (HOR) and evolution reactions (HER) has been explored by combining an experimental cyclic voltammetry study, microkinetic modeling and X-ray photoelectron spectroscopic analysis. Almost 10 times enhancement of the activity of Ni in the HOR/HER has been observed after its oxidation under the contact with air at ambient conditions and assigned to the presence of NiO species on the surface of metallic Ni. The experimental cyclic voltammetry curves have been analyzed with the help of kinetic model in order to shed light on the mechanism of the HOR/HER for two types of Ni electrodes and its dependence on the presence of NiO on the surface of the electrode. The main features of the experimental current-potential curves can be reproduced with a kinetic model assuming that the free energy of the adsorbed hydrogen intermediate is increased and that the kinetics of the Volmer step is enhanced in the presence of nickel oxide species. The kinetic model provides evidence for the switching from the Heyrovsky-Volmer mechanism on metallic Ni to Tafel-Volmer mechanism on the

Electronic supplementary material The online version of this article (doi:10.1007/s11244-016-0657-0) contains supplementary material, which is available to authorized users.

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activated electrode, where surface oxide species co-exist with metal Ni sites.

Graphical Abstract



Keywords Hydrogen oxidation and evolution reactions · Alkaline solutions · Nickel · Nickel oxide · X-ray photoelectron spectroscopy · Kinetic modeling

1 Introduction

Increase of the global energy demand stimulates an interest in renewable energy sources which *inter alia* are intended to decrease CO_2 emissions in the future. Hydrogen (produced from renewable resources by e.g. water electrolysis and converted into energy in fuel cells) has been perceived as a valid alternative to fossil fuels in many applications because of its high energy density and environmental friendliness (the only product of its oxidation being water) [1]. Thereby the hydrogen evolution (HER) and oxidation reactions (HOR) have attracted strong research interest for many decades. Due to commercial applications of alkaline water electrolyzers, where non-noble metal catalysts can be

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utilized, most of these studies were devoted to the HER and the synthesis of catalysts related to this process [2]. However, recent progress in the development of anion-exchange membranes [3, 4] and the ensuing growing interest in alkaline membrane (AM) fuel cell (FC) technology [5] stimulate studies of the HOR.

Among non-noble metals Ni is perceived as the most promising catalyst for the HOR/HER in alkaline media. Hydrogen evolution over Ni catalysts in alkaline water electrolyzers has long history, in XXth century the studies being largely dedicated to Raney Ni electrodes, while in the past decades the interest has shifted to bimetallic materials [2, 6–12]. Exchange current densities of Ni electrodes reported in the literature may differ by nearly two orders of magnitude [13–18], which may be attributed to differences in the electrode pre-treatment resulting in different surface structure and/or composition. Indeed, by using Ni single crystals Floner et al. [19] have shown that the HOR on Ni is structure-sensitive, decreasing in the order (110) > (100) > (111), with Ni (110) being 6 times more active compared to polycrystalline Ni. Furthermore, Ni is prone to oxidation, already at ambient conditions, which usually results in the formation of a several monolayer thick surface oxide film consisting of a mixture of NiO and Ni(OH)₂ [20–23]. Recently, an increase of the activity has been reported for systems where Ni coexists with surface oxide species such as β -Ni(OH)₂ [24] or NiO [10, 25, 26]. The activity enhancement was attributed to the synergy between Ni oxide species, which serve to enhance the water dissociation step, and nearby metallic Ni sites necessary for H adsorption [24, 25]. All of the above complicate measurements of the catalytic activity of pure Ni in the HOR/ HER. Meanwhile, the latter is necessary for a proper evaluation of the activity enhancement in bi- or trimetallic catalysts as well as the understanding of the role of the additives.

Further insights in the HOR/HER mechanism and kinetics may be gained from the comparison of the experimental data with the predictions of microkinetic modeling. In the last decade, modeling of the experimental HOR/HER current potential curves allowed the extraction of some important parameters such as the free energy of adsorption of the reaction intermediate (H_{ad}), and rate constants of the Volmer, Heyrovsky and Tafel steps for various electrode materials (such as Rh, Ru, Pd and PdAu) in acidic and alkaline solutions [27-34]. In the case of Ni electrodes in alkaline media, microkinetic modeling was used to analyze only the HER part of the experimental current potential curves [17, 35–37], processes occurring in the HOR part being largely ignored. Besides, even if significant differences have been noticed between the HER of freshly polished Ni electrodes and those which were subjected to the electrochemical oxidation, the mechanism of the HER was analyzed only for metallic Ni [17].

In the present work, the influence of the NiO on the kinetics of the HOR and HER on Ni electrodes of different morphology (polycrystalline rod and Ni nanoparticles) is investigated by cyclic voltammetry (CV), ex situ XPS and kinetic modeling. A ten times increase of the HOR/HER activity is observed after exposure of the Ni electrodes in air at ambient conditions which could be correlated with an increase of the NiO amount detected by the XPS. The complex interplay between the hydrogen reactions and the hydroxide adsorption/desorption occurring in the same potential range is rationalized with the help of kinetic model taking into account the Tafel-Heyrovsky-Volmer HOR/HER mechanism and a two-step mechanism of the surface oxidation/reduction. The influence of Ni surface oxide species on the shape of current-potential curve and on the HOR/HER activity could be semi-quantitatively reproduced, assuming that their presence on the surface of metallic Ni results in (i) ca 80 meV increase of the Gibbs energy of adsorption of the strongly adsorbed hydrogen intermediate, and (ii) ca 10 times increase of the rate constant of the Volmer step.

2 Experimental and Modeling Details

2.1 Materials

For electrochemical experiments, all solutions were prepared using ultrapure water produced by ELGA Ultra Analytic apparatus (18.2 M Ω cm, TOC <2 ppb). NaOH (50 % in water, Premium quality, Aldrich), NiSO₄•6H₂O (99.99 %, Aldrich) and (NH₄)₂SO₄ (99.0 %, Aldrich) were used as received.

2.2 Working Electrodes

The working electrode was either a polycrystalline Ni rod (Ø5 mm, Mateck, 99.99 %) or a glassy carbon (GC) cylinder with Ni nanoparticles electrodeposited on its top surface (Ni_{ED}/GC). X-ray photoelectron spectroscopy (XPS) measurements were performed with a Ni foil $(10 \times 10 \text{ mm})$. Prior to use the top flat surface of the Ni rod, GC cylinders and both sides of the Ni foil were thoroughly polished with Al₂O₃ slurries (Alfa Aesar) from 1.0 down to 0.05 μ m and rinsed by H₂O. Ni foil was sonicated in H₂O for 2 min. GC cylinders were cleaned by consecutive sonication in acetone, ethanol and H₂O (10 min in each solvent) and dried in the oven at 80 °C for ca 1 h. Then either a Ni rod or a GC cylinder was fixed in a holder and their lateral surfaces were sealed with the Teflon tape so that only the flat top surface of the electrodes was accessible to the electrolyte. Ni foil was fully immersed in the solution using thin Au wire as a current collector.

For studying the influence of the oxidation of the Ni electrode on its activity towards the HOR/HER, the polycrystalline Ni rod was tested in 0.10 M NaOH electrolyte either immediately after polishing (hereinafter, "non-activated Ni") or after a preliminary oxidation in air for 48 h at ambient conditions (hereinafter, "activated Ni"). Two states of polycrystalline Ni foil were obtained in a similar manner for XPS experiments.

Electrodeposition of Ni on a GC surface was performed at 25 °C in a potentiostatic regime from the deaerated $0.01 \text{ M NiSO}_4 + 0.10 \text{ M} (\text{NH}_4)_2 \text{SO}_4$ solution. The following 3 step potential (time) procedure was applied: $E_{\rm D1} = -1.50 \text{ V}$ (8 s), $E_{\rm D2} = -0.93 \text{ V}$ (2 s), and $E_{D3} = -1.25$ V (120 s), where potential is given versus a Mercury-Mercury Sulphate Electrode. The potential values were chosen so that the nucleation of Ni nanoparticles occurs in the first step, while their growth takes place mainly during the third step. The second step is necessary in order to replenish the electrolyte layer in the vicinity of the electrode surface with NiSO₄. After the deposition, the samples were thoroughly rinsed with water and either studied immediately (hereinafter, "non-activated Ni_{ED}/ GC") or activated before testing by drying them under N₂ flow and oxidizing them in air for 24 h at ambient conditions (hereinafter, "activated Ni_{ED}/GC").

2.3 Electrochemical Measurements

Electrochemical measurements were performed in a threeelectrode glass cell thermostated at 25 °C using a Biologic SP-300 potentiostat. The counter electrode (Pt wire) and the reference electrode (HglHgOl0.10 M NaOH) compartments were connected with the working electrode chamber via a glass frit and a Luggin capillary, respectively. If not otherwise stated, all electrode potentials reported in the manuscript are referred to the reversible hydrogen electrode (RHE). Prior to each experiment, the glassware was cleaned by soaking in a $H_2SO_4:H_2O_2$ (1:1 v/v) mixture and then thoroughly washed with pure water.

After immersion in the electrochemical cell and before the measurement of their electrocatalytic activities, non-activated Ni electrodes (both Ni rod and Ni_{ED}/GC) were cycled 2 times between -0.20 and 0.30 V at a sweep rate 20 mV s⁻¹ in order to remove oxide species formed on their surfaces during the transfer to the cell. Activated Ni electrodes were conditioned by cycling between -0.06 and 0.40 V at a sweep rate 20 mV s⁻¹ until stabilization of the CV profiles. The HOR/HER exchange currents were derived from the anodic scans of linear-sweep voltammograms obtained in H₂-saturated 0.10 M NaOH at the sweep rate of 5 mV s⁻¹ in the potential interval between -0.06 and 0.40 V by the linearization of the micropolarization region.

Electrochemical surface area of Ni was estimated by using the charge required to form a monolayer of surface α -Ni(OH)₂ and the 0.514 mC cm⁻² conversion coefficient [38]. This was accomplished by integrating CVs acquired in the potential interval from -0.06 to 0.40 V in a N₂saturated solution at a sweep rate of 20 mV s⁻¹ and considering the entire value of the anodic charge. The positive potential limit of 0.40 V was selected to minimize transformation of the reversible α - into an irreversible β -Ni(OH)₂ [21, 39].

Prior to the XPS, a freshly polished Ni foil was reduced in 0.10 M NaOH by applying cathodic polarization (E = -0.20 V) for 5 min, and then cycled once between -0.20 and 0.40 V and twice between -0.60 and 0.40 V at a sweep rate of 20 mV s⁻¹ (hereinafter, "non-activated Ni foil"). Ni foil oxidized in air was conditioned by cycling several times between -0.06 and 0.40 V at a sweep rate of 20 mV s⁻¹ (hereinafter, "activated Ni foil"). The final scans in both cases were stopped at 0 V going from negative to positive values and then the electrodes were removed from the solution, rinsed with water and rapidly transferred to the XPS entry chamber with a drop of water on the surface, meant to prevent its contact with air.

2.4 Characterization of Ni and Ni_{ED}/GC Samples

XPS measurements were performed in an ultra-high vacuum chamber (pressure $<5 \times 10^{-6}$ Pa) equipped with a VG Microtech Clam2 electron analyzer, a dual anode (Al and Mg K α) X-ray source. After electrochemical treatments the Ni foil was immediately fixed on the sample holder and protected with a drop of purified water. The temperature was maintained constant throughout the experiment at 30 °C. Survey and narrow scan Ni2p, O1s, C1s spectra were recorded using the excitation photon energy of 1486.6 eV. Characterization of the Ni foil was carried out by means of normal (0°) and grazing (50°) takeoff angle measurements.

In addition to the electrochemically treated Ni foil samples, NiO produced by thermal oxidation of Ni foil in air at 500 °C for 1 h, and pure metallic Ni foil (cleaned by several Ar^+ sputtering and annealing cycles) were used as reference samples.

The binding energy (BE) values are presented without any correction, while the areas of XPS peaks were determined after Shirley background subtraction. In the spectra deconvolution procedure the same peak parameters for Ni^0 , NiO and Ni(OH)₂ components were employed for all processed samples (see ESM for the details). Quantitative calculations were performed using normalized Ni2p, O1s, C1s peak areas, taking into account the atomic sensitivity factors of each element [40]. The simulation of Ni2p XPS spectra was done using SESSA software (Version 2.0) for the "planar" and "island" morphologies with different thickness. The excitation photon energy was set at 1486.6 eV and the mean free paths of the photoelectrons were calculated by the software. The density values of Ni⁰, NiO and Ni(OH)₂ were equal to 9.091, 6.746 and 5.698 g cm⁻³, respectively. The sample, the analyzer, the source orientation as well as the aperture parameters were adjusted to the ones of the experimental set-up. Two take-off angles 0° and 50° were simulated.

The morphology of Ni electrodeposited on GC was studied by Scanning Electron Microscopy (SEM) using a JEOL JSM-6700F microscope at accelerating voltage of 6 kV.

2.5 Equations for the HOR/HER Kinetic Modeling on Ni

The hydrogen oxidation reaction in alkaline medium involves the adsorption of molecular hydrogen either in the Tafel (Eq. 1) or in the Heyrovsky (Eq. 2) step:

$$H_2 + 2Ni \rightleftharpoons 2 Ni - H_{ad} \tag{1}$$

$$H_2 + OH^- + Ni \rightleftharpoons Ni - H_{ad} + H_2O + e^-$$
 (2)

Here Ni denotes a free nickel surface site. The oxidation of the adsorbed hydrogen intermediate H_{ad} according to the Volmer reaction can be written in alkaline medium as:

$$Ni - H_{ad} + OH^{-} \rightleftharpoons H_2O + e^{-} + Ni$$
 (3)

Based on Refs. [16, 19, 39], a two-step $Ni-(OH)_{2,ad}$ formation process is considered:

$$OH^- + Ni \rightleftharpoons Ni - OH_{ad} + e^-$$
 (4)

$$Ni - OH_{ad} + OH^{-} \rightleftharpoons Ni - (OH)_{2,ad} + e^{-}$$
 (5)

The rates for the Tafel, Heyrovsky and Volmer reactions in alkaline aqueous electrolyte can be expressed as:

$$v_1 = k_1^0 C_{\rm H_2} (1 - \theta_{\rm H} - \theta_{\rm OH} - \theta_{\rm (OH)_2})^2 - k_{-1}^0 \theta_{\rm H}^2$$
(6)

$$v_{2} = k_{2}^{0} \exp\left(\frac{(1-\alpha_{2})\text{FE}}{\text{RT}}\right) C_{\text{H}_{2}} C_{\text{OH}^{-}} (1-\theta_{\text{H}}-\theta_{\text{OH}} - \theta_{(\text{OH})_{2}}) - k_{-2}^{0} \exp\left(\frac{-\alpha_{2}\text{FE}}{\text{RT}}\right) \theta_{\text{H}}$$
(7)

$$\upsilon_{3} = k_{3}^{0} \exp\left(\frac{(1-\alpha_{3})\text{FE}}{\text{RT}}\right) C_{\text{OH}^{-}} \theta_{\text{H}} - k_{-3}^{0} \exp\left(\frac{-\alpha_{3}\text{FE}}{\text{RT}}\right) (1 - \theta_{\text{H}} - \theta_{\text{OH}} - \theta_{(\text{OH})_{2}})$$
(8)

Here $C_{\rm H2}$ and $C_{\rm OH-}$ are the concentrations of H₂ and OH⁻ in the solution, which are assumed to be the same in the bulk of the electrolyte and near the electrode surface (*cf* the rotating rate independence of CVs—vide infra). $\theta_{\rm H}$,

 θ_{OH} $\theta_{(OH)2}$ denote the surface coverage of the active intermediate, Ni–H_{ad}, Ni–OH_{ad} and Ni–(OH)_{2,ad}, respectively. A Butler–Volmer dependence on the electrode potential *E* is assumed for the rate constants of the Heyrovsky and Volmer steps, where α_2 and α_3 are the corresponding charge transfer coefficients and *F*, *R*, *T* are the Faraday constant, the ideal gas constant and the temperature respectively.

The rates of Ni–OH_{ad} and Ni–(OH)_{2,ad} formation/reduction in the sequence of reactions (4) and (5) are given by:

$$b_{4} = k_{4}^{0} \exp\left(\frac{(1 - \alpha_{4})FE}{RT}\right) C_{OH^{-}} (1 - \theta_{H} - \theta_{OH} - \theta_{(OH)_{2}}) - k_{-4}^{0} \exp\left(\frac{-\alpha_{4}FE}{RT}\right) \theta_{OH}$$
(9)

$$v_{5} = k_{5}^{0} \exp\left(\frac{(1-\alpha_{5})\text{FE}}{\text{RT}}\right) C_{\text{OH}^{-}} \theta_{\text{OH}} - k_{-5}^{0} \exp\left(\frac{-\alpha_{5}\text{FE}}{\text{RT}}\right) \theta_{(\text{OH})_{2}}$$
(10)

where α_4 and α_5 are the charge transfer coefficients of reactions (4) and (5), respectively. When the potential *E* is scanned at a sweep rate *v*, the simulated current-potential curves can be obtained by solving the following set of differential equations:

$$\frac{d\theta_{\rm H}}{dt} = 2\upsilon_1 + \upsilon_2 - \upsilon_3 \tag{11}$$

$$\frac{d\theta_{\rm OH}}{dt} = v_4 - v_5 \tag{12}$$

$$\frac{d\theta_{\rm (OH)_2}}{dt} = v_5 \tag{13}$$

$$\frac{\mathrm{dE}}{\mathrm{dt}} = v \tag{14}$$

The total Faradaic current density is due to the Heyrovsky and Volmer reactions and to the Ni hydroxide formation/reduction reactions:

$$\dot{v}_F = FS_t(v_2 + v_3 + v_4 + v_5)$$
 (15)

Here S_t is the mole number of active Ni sites per electrode geometric surface area.

3 Results and Discussion

3.1 Electrochemical Properties and Electrocatalytic Activity of Ni in the HOR/HER

CVs of a non-activated Ni rod in N_2 -saturated 0.10 M NaOH (Figs. 1a, S1) exhibit typical features of Ni

electrodes in alkaline medium [21, 39, 41] with an anodic (a_1) and cathodic (c_1) peak usually attributed to the formation and reduction of the surface α -Ni(OH)₂, although some contribution of the NiO formation cannot be fully excluded [20, 42]. Sweep rate dependence (see Fig. S2 of the ESM) suggests that Ni(OH)₂ formation, being chemically reversible, is an electrochemically irreversible surface process. Activation of the Ni rod following the procedure described in the Experimental section results in changes of the shape of the CV and in the appearance of a second anodic peak (a_2) at lower potentials (Fig. 1). These changes are accompanied with ca. 1.5 times decrease of the electrochemical surface area (Fig. S1), presumably due to the passivation of a part of the surface by oxide species, thus decreasing the number of Ni sites accessible for the reversible transformation to α -Ni(OH)₂. Noticeably, a small shoulder in the potential range of peak a_2 also appeared in the CV of the non-activated Ni after its storage in the electrolyte at the open circuit potential (OCP) for a short time. The latter may be attributed to the Ni corrosion in an alkaline solution [43, 44]. Therefore, every time before acquiring a CV curve for the non-activated Ni electrode, the Ni rod was polished and then reduced, following the procedure described in the experimental part, in order to obtain a clean reproducible surface.

Figure 1 compares CVs for a non-activated and an activated Ni rod registered in N₂- and H₂-saturated 0.10 M NaOH at a sweep rate of either 20 or 5 mV s⁻¹. First, we note that anodic currents increase in H₂ compared to N₂ atmosphere both for the non-activated and for the activated electrode, but to a much higher extent for the latter. Second, similar to what was observed in the N₂ atmosphere, two anodic peaks (a_1 and a_2) may be noticed for the activated electrode, even though the positions of these peaks under H₂ are not exactly the same as under N₂. Finally, we observe that, for the activated Ni, the relative contribution of the a_2 peak increases with a decrease of the sweep rate (Figs. 1b, c, S2).

In order to better understand the processes occurring in the potential region of the anodic peak a_2 on activated Ni, experiments were performed at different rotation rates. CVs appeared to be virtually rotation rate independent either under N₂ or H₂ atmosphere (Fig. 2) suggesting that (i) peak a_2 cannot be fully attributed to the oxidation of hydrogen evolved in the cathodic scan, though a small contribution of this process to the currents is observed in N₂-saturated 0.10 M NaOH close to the equilibrium potential; and (ii) HOR is kinetically rather than masstransport controlled. Moreover, the CV profile of non-activated Ni was rotation rate independent in either N₂- or H₂-saturated electrolyte (not shown).



Fig. 1 Cyclic voltammograms for non-activated (*curve 1*, *black*) and activated (*curve 2*, *red*) Ni rod at 25 °C in N₂-saturated 0.10 M NaOH at $v = 20 \text{ mV s}^{-1}$ (**a**) and H₂-saturated 0.10 M NaOH at $v = 20 \text{ mV s}^{-1}$ (**b**) and $v = 5 \text{ mV s}^{-1}$ (**c**)

Peak a_2 was noticed in several studies [16, 19, 38, 45], when Ni electrode was subjected to an oxidation either during cycling up to high positive potentials (around 1 V vs. RHE) or to a prolonged contact with the electrolyte, and was tentatively attributed either to the formation of Ni– OH_{ad} or oxidation of adsorbed hydrogen [16, 19]. These explanations do not contradict the results of this work (vide infra), whereas oxidation of absorbed hydrogen [38, 45] as the main origin of peak a_2 is considered rather unlikely. Indeed, peak a_2 showed up even at relatively fast sweep rates (20 mV s⁻¹), and even if the electrode potential was not decreased below -0.06 V (Figs. 1, 2).

The catalytic activities of non-activated and activated Ni rod for the HOR/HER were estimated in terms of exchange currents normalized to either electrochemical or geometric surface area of the Ni rod (Table 1). First, it is found that metallic Ni rod has very poor HOR/HER activity, which is close to 2 μ A cm_{Ni}⁻² if normalized to the electrochemical surface area of Ni, while activated Ni rod demonstrates ca. 9 times enhancement of the specific activity. It should be stressed that the observed enhancement cannot be fully explained by the decrease of the surface of metallic Ni. Indeed, normalization of the activity to the geometric surface area of the Ni rod also shows more than 5 times enhancement for activated Ni (Table 1). The enhancement of the specific activity is also observed when the potential is scanned in a wider range (from -0.20 to 0.50 V as displayed in Figs. S2, S3), the exchange currents values estimated either in the potential interval close to the equilibrium (micropolarization region) or from the Tafel plots being essentially the same (Fig. S3).

In order to inspect the universality of such catalytic enhancement after oxidation of Ni in air, we have then synthesized Ni nanoparticles using electrodeposition technique. SEM analysis (Fig. 3a) of fabricated Ni_{ED}/GC nanoparticles revealed their narrow size distribution with an estimated surface mean diameter of ca. 25 nm (under the assumption of the spherical particle shape). After that, two states of the surface of Ni_{ED}/GC, namely "non-activated" and "activated" (cf Sect. 2.2), were considered, and the corresponding HOR/HER activities (Table 1) were calculated using the above-mentioned procedure. It appeared that all characteristic features described above for non-activated and activated Ni rod were also observed for the two states of Ni_{ED}/GC nanoparticles (cf Figs. 1, 3b). Besides, almost 9 times enhancement of the specific activity in the HOR/HER was found for the activated Ni_{ED}/ GC electrode compared to the non-activated one. It is worth mentioning that the HOR/HER exchange current density of the activated Ni_{ED}/GC sample is ca. 23 times higher than the activity of non-activated Ni rod (Table 1).

In addition, we tested the HOR/HER activity of an electrochemically oxidized Ni rod. For that non-activated Ni rod was oxidized in N₂-saturated 0.10 M NaOH by applying two potential cycles between -0.30 and 1.0 V at a sweep rate of 50 mV s⁻¹ followed by conditioning described above for a Ni rod activated in air (*cf* in the Sect. 2.3). Two anodic peaks (a_1 and a_2) were observed in the CV of an electrochemically activated Ni rod (Fig. S4).





Fig. 2 Cyclic voltammograms for an activated Ni rod at 25 °C in a N₂- and b H₂-saturated 0.10 M NaOH at 0 (*curve 1, black*) and 1600 (*curve 2, red*) rpm at a sweep rate of 20 mV s⁻¹

Estimation of the catalytic activity of electrochemically activated Ni rod has shown 7 times increase of the specific activity in the HOR/HER (Table 1).

Thus we tentatively conclude that the presence of oxide species on the surface of Ni results in its HOR/HER activity enhancement regardless either the electrode morphology (bulk polycrystalline Ni rod vs. electrodeposited Ni nanoparticles) or the method of surface oxidation (oxidation in air vs. electrooxidation). The higher HOR/HER activity of electrodeposited Ni nanoparticles vs. Ni rod may be explained by the presence of defects or low-coordinated sites on the surface of Ni particles, and the ensuing changes in the adsorption properties of species involved in the reaction [15, 18, 25].

3.2 X-ray Photoelectron Spectroscopy

In order to unveil the differences in the surface state of Ni samples possessing different catalytic activity, non-activated and activated Ni foil (pre-treatment procedure is clarified in the Sect. 2.2) were characterized by XPS. The

Table 1 Catalytic activity ofvarious Ni electrodes in theHOR/HER depending on thepre-treatment conditions

Catalyst	Exchange current density	
	j_0 , μ A cm ⁻² $^{a}_{Ni}$	j_0 , $\mu A \text{ cm}^{-2} _{\text{geom}}^{\text{b}}$
Non-activated Ni rod	2.2	5.6
Activated Ni rod	19.9	32.5
Electrochemically activated Ni rod	14.9	29.2
Non-activated Ni _{ED} /GC	5.8	
Activated Ni _{ED} /GC	50.3	

^a Exchange currents are normalized to the electrochemical surface area of Ni

^b Exchange currents are normalized to the geometric surface area of Ni rod (0.196 cm²)



Fig. 3 a SEM image of Ni nanoparticles electrodeposited on GC, the scale label is 100 nm, the average particle diameter $d_{av} \approx 25$ nm. **b** Cyclic voltammograms for non-activated (*curve 1, black*) and activated (*curve 2, red*) electrodeposited nanoparticles Ni_{ED}/GC at 25 °C in H₂-saturated 0.10 M NaOH at v = 5 mV s⁻¹

Ni2p spectra exhibit several peaks overlapping in a narrow BE region (Fig. 4), which complicates their assignment. Despite this, three components, namely metallic Ni, NiO and Ni(OH)₂, could be distinguished for the analyzed samples, assuming that oxidation of Ni in contact with oxygen and alkaline electrolyte solution mainly results in the formation of NiO and Ni(OH)₂ [20–23].

According to ex situ XPS characterization, surfaces of both samples contain Ni oxide and hydroxide species. While for the activated sample the surface is dominated by NiO, for the non-activated one Ni(OH)₂ prevails (cf composition at 0° take-off angle). Changing of the take-off angle from 0° (sub-surface sensitive angle) to 50° (surface sensitive angle) leads to an increase of the Ni(OH)₂ concentration from 31 to 49 % for the non-activated sample and from 15 to 33 % for the activated one, whereas the NiO amount does not depend on the take-off angle. Finally, the amount of metallic Ni decreases with the increase of the take-off angle for both Ni samples, suggesting its location primarily in the sub-surface of the samples. This angle dependence prompts us to propose the layered structure of the samples, with a continuous nickel hydroxide layer on top (cf increase of the Ni(OH)₂ contribution with the increase of the take-off angle), a NiO layer beneath (cf NiO independence of the take-off angle). and metallic Ni in the bulk. To confirm this, we have performed the simulation of the XP spectra for different location of NiO and Ni(OH)2 layers, their different thickness, and for two morphologies - planar and island (see ESM for the details). The simulation data have proven the layered structure of the surface of Ni samples with a nickel hydroxide on the top, and nickel oxide beneath. According to the simulations the $Ni(OH)_2$ layer is likely to be either continuous or to occupy a significant fraction of the surface (see the ESM). However, on the basis of the modeling data one cannot conclude on whether the NiO layer is continuous or is present in the form of islands overlayered by Ni(OH)₂.

Since the XPS analysis was performed ex situ (after the emersion of the samples from the electrolyte and their transfer to the UHV chamber through air), it allows only some tentative conclusions regarding the state of the Ni surface in electrolyte under the potential control. As mentioned above, the surface of non-activated Ni sample is dominated by the Ni hydroxide, which is likely to be formed during the emersion of the electrode from 0.10 M NaOH, when it is shortly exposed to the OCP. Since the





Fig. 4 X-Ray photoelectron $\text{Ni2p}_{3/2}$ spectra for non-activated (**a**, **b**) and activated (**c**, **d**) Ni foil at two take-off angles: **a**, **c** 0° and **b**, **d** 50°. Spectra were curve-fitted with Ni⁰ (*solid line, green*), NiO

(*dash-dotted line*, *red*) and Ni(OH)₂ (*dashed line*, *blue*) components, their resulting atomic concentrations are indicated in the panels. For the curve-fitting procedure the reader is referred to the ESM

OCP sets in between 0.20 and 0.40 V, we tentatively attribute these Ni hydroxide species to the chemically reversible α -Ni(OH)₂ (see Refs. [21, 39, 43, 46, 47] and CV in Fig. 1). Since α -Ni(OH)₂ is electrochemically reduced close to the equilibrium potential of the hydrogen electrode (see Refs [21, 39] and Fig. 1), it thus cannot influence the HOR/HER kinetics in contrast to either NiO or β -Ni(OH)₂ [10, 24–26].

According to the XPS analysis, the amount of Ni hydroxide on the surface of the activated Ni electrode is considerably decreased at the expense of Ni oxide. We thus conclude that (i) in agreement with the literature data [20–23], oxidation of Ni in air results in NiO formation, (ii) contrary to the chemically reversible α -Ni(OH)₂, the NiO formation under the employed experimental conditions is irreversible, conditioning of the activated electrode resulting only in a *partial* reduction of the NiO layer, and (iii) NiO screens the surface of the Ni electrode, leading to a decrease of the amount of Ni(OH)2. As discussed below, we believe that NiO is a likely reason for the higher catalytic activity of the activated Ni in the HOR/HER. The existence of some amount of NiO on non-activated Ni foil is believed to be due to the sample transfer in air and an incomplete surface reduction under electrochemical conditions (Fig. S5). We infer that in situ the surface of the activated Ni electrode is only partly covered by NiO islands, while the rest of the surface being metallic. At the same time the surface of non-activated Ni electrode mostly consists of metallic Ni sites, which are responsible for the appearance of peak a_1 typical for CV of the Ni metal (Fig. 1).

The surface structure of the activated Ni samples is schematically shown in Fig. 5a and will be discussed in more detail below. It should be stressed again that due to the ex situ character of the performed measurements, a significant part of Ni(OH)₂ detected by XPS might be formed during the emersion of the Ni electrode from 0.10 M NaOH electrolyte at OCP and its transfer to the XPS chamber with a drop of water on the surface (Fig. 5b). The latter may also lead to the partial transformation of NiO into Ni(OH)₂ [20, 21, 23]. Indeed, both theoretical [48–50] and experimental TPD—XPS data [51, 52] suggest that pre-adsorbed oxygen reacts with H₂O to give two adsorbed OH species.

3.3 Kinetics of the HOR/HER and Its Dependence on the Presence of Ni Surface Oxide

Based on the results of XPS measurements we assume that it is the presence of NiO (together with Ni) on the surface of activated Ni electrode, which is responsible for the changes of the CV in the supporting electrolyte, and the enhancement of the kinetics of the HOR/HER (Figs. 1, 2). This assumption can be further supported by the analysis of computational studies devoted to the adsorption of H_{ad}, OH_{ad}, O_{ad} and H₂O_{ad} species on Ni surfaces [48, 53-56] and the influence of pre-adsorbed oxygen atoms on them [48, 54]. Confirming great tendency of Ni towards oxidation, DFT calculations have shown strong adsorption of O_{ad} and OH_{ad} on metallic Ni [48, 53, 54]. Besides, hydrogen is also strongly adsorbed on Ni, which may be considered as one of the likely reasons for its lower (compared to Pt) HOR/HER activity [53, 55, 56]. However, the presence of adsorbed oxygen atoms leads to a decrease of the binding energies of Ni-H_{ad} and Ni-OH_{ad} [48, 54]. Considering a volcano type dependence of the HER exchange current density on the free energy of hydrogen adsorption [56, 57], the presence of NiO on the surface may thus enhance the activity of Ni towards the HOR/HER by decreasing the hydrogen adsorption energy. Besides, the binding energy of H₂O, which is weakly adsorbed on metallic Ni, is increased in the presence of co-adsorbed oxygen [48, 53, 54]. Gentle stabilization of H_2O , being the product of the HOR, can also enhance the activity of Ni in this process.

In order to extract the key parameters entering into the HOR/HER mechanism, and find out how they have to be modified to reproduce the difference in the activity of the two kinds of Ni electrodes (non-activated and activated ones), microkinetic modeling was performed. It should be stressed that given the complexity of the electrochemical processes at Ni electrodes [16, 17, 20, 21, 36, 39, 41, 42], the purpose of the model is not to accurately determine the rate constants of the reaction steps, but rather to propose a self-consistent interpretation of the experimental trends, which does not contradict the literature data regarding the HER kinetics [17, 35–37].

Two sets of rate constants were considered in this work in terms of the variation the Gibbs energy of adsorbed hydrogen intermediate and of the Tafel-Heyrovsky-Volmer mechanism (Table S6). The first set was chosen to reproduce the main features of the current-potential curves obtained for non-activated Ni while the second set of parameters was adjusted to describe the ones obtained for activated Ni. The rate constants k_{4}^{0} , k_{-4}^{0} , k_{5}^{0} , k_{-5}^{0} were adjusted to reproduce approximately the position of the Ni hydroxide formation peak in the CVs of the Ni electrodes in N₂ purged solution and also the decrease of the HOR current in the presence of Ni(OH)₂ on the surface. To reproduce the inhibition of the HOR in the presence of Ni-OH_{ad} and Ni-(OH)_{2 ad} one has to assume relatively fast Ni- OH_{ad} and Ni–(OH)_{2.ad} formation (k_4^0 and k_5^0) in comparison to the rate of the Volmer process. In order to minimize the number of adjustable parameters, the same values of k_{4}^{0} , k_{-4}^{0} , k_{5}^{0} , k_{-5}^{0} were assumed for the activated and non-activated Ni



Fig. 5 Cartoon showing the structure of the activated Ni electrode in situ (**a**) and after its transfer to the UHV chamber (**b**). A tentative HOR activation mechanism is also schematically illustrated in (**a**). Presence of NiO islands results in the (i) decrease of the strength of H_{ad} adsorption at the neighbor Ni sites, and (ii) strengthening of H₂O adsorption at either NiO or neighbor Ni sites. These changes lead to an increase of the rate constant of the Volmer step and transition from the Heyrovsky–Volmer HOR mechanism on metal Ni sites (peak a_1) to Tafel–Volmer HOR mechanism on Ni sites neighboring the NiO islands (peak a_2). See Sect. 3.3 for the details. *Color codes grey* metallic Ni, *red*—NiO, *green*— α -Ni(OH)₂

electrode. The values of k_1^0 , k_2^0 and k_{-3}^0 were adjusted to reproduce the HOR/HER currents, whereas the choice of the rate constants for reverse reactions k_{-1}^0 , k_{-2}^0 and k_3^0 must account for the Gibbs energy of adsorption of the hydrogen intermediate $\Delta_{ad}G^0$. According to the present understanding, two types of adsorbed hydrogen may exist on metal surfaces, namely the strongly adsorbed ($\Delta_{ad}G^0 < 0$) and the weakly $(\Delta_{ad}G^0 > 0)$ adsorbed H_{ad} species. According to the DFT calculations [58], the Gibbs energy of weakly adsorbed hydrogen on Ni is high (above 0.8 eV), which makes its formation as a HOR/HER intermediate unlikely. Furthermore, the presence of co-adsorbed O on the Ni surface is expected to decrease the Ni-H_{ad} binding energy [48, 54], leading to a further increase of the $\Delta_{ad}G^0$. Meanwhile, the strongly adsorbed H_{ad} on Ni is characterized by a rather low $\Delta_{ad}G^0$ (below -0.2 eV) [58], whose increase in the presence of surface oxide is expected to result in the HOR/HER enhancement. Therefore, we assume strongly adsorbed Had as a HOR/HER intermediate on Ni.

Figure 6a, c shows the comparison of the simulated and experimental current-potential curves in N_2 and H_2 purged electrolytes for non-activated Ni (note that currents are

referred to the geometric surface area). The essential experimental features, namely the presence of one anodic (a_1) and one cathodic (c_1) peaks in the CVs, under N₂ atmosphere, and the low HOR/HER activity could be qualitatively reproduced by assuming $\Delta_{ad}G^0 = -0.10 \text{ eV}$ (for other parameters the reader is referred to Table S6). The low HOR/HER activity of non-activated Ni results from the surface blocking by either adsorbed hydrogen (below 0.20 V) or surface hydroxide (Ni-OH_{ad} and Ni-(OH)_{2.ad}) species (above 0.20 V). Indeed, below 0.20 V strong H_{ad} adsorption combined with the relatively slow Volmer step are responsible for low currents either in the absence or in the presence of H_2 (the absence of the peak a_2). The peak a_1 results from the contribution of both the electrochemical desorption of Had and the Ni(OH)2,ad formation, which is in agreement with Hall et al. [21]. Meanwhile, above 0.20 V, it is the fast formation of Ni-OH_{ad} and Ni-(OH)_{2,ad}, which results in the surface blocking and an ensuing low HOR rate. Thus, for nonactivated Ni large overpotential (ca. 0.15 V) is needed to activate the HOR, which mainly occurs through the Heyrovsky-Volmer mechanism in this range of overpotentials.

To explain the experimentally observed changes in the shape of CV and the HOR/HER activity enhancement upon oxidation of the Ni electrode, we assume weakening of the strength of the H_{ad} adsorption in the presence of surface NiO, and the ensuing increase of $\Delta_{ad}G^0$ by ca. 0.08 eV. This allowed us to reproduce the emergence of the peak a_2 (cf Fig. 6b, d) which is now attributed to the H_{ad} oxidation and Ni-OH_{ad} formation in agreement with other authors [16, 19, 39], while the Ni(OH)_{2.ad} formation still occurs in the peak a_1 . It is worth mentioning that the enhancement of the currents in H₂ atmosphere exclusively corresponds to the oxidation of Had, while the Ni-OHad formation currents should be the same both in N₂ and in H₂ atmosphere and could not affect the HOR currents (Fig. 6b, d). We note in passing that while the exact value of $\Delta_{ad}G^0$ cannot be determined by the fitting process due to the large number of unknown parameters, its decrease in the presence of NiO is consistent with the results of this as well as previous publications. Note however that to explain the strong HOR/ HER activity enhancement for the activated Ni the $\Delta_{ad}G^0$ increase alone was not sufficient (see Fig. S7), but also required an order of magnitude increase of the Volmer rate constant k_3^0 (cf Figs. 6d, S7). The simulated CVs showing the influence of either $\Delta_{ad}G^0$ or k_3^0 are displayed in Fig. S7 as supplementary information. The significant variation of the Volmer rate constant implies that the presence of NiO on the surface not only results in the increase of $\Delta_{ad}G^0$, but also considerably affects the metal/electrolyte interface. This is in agreement with the DFT calculations, which suggest that pre-adsorbed O not only influences the binding energies of Ni-Had and Ni-OHad, but also the adsorption of water molecules on Ni [48, 54]. The high HOR/HER activity of the activated Ni electrode at low overpotentials $(|\eta| < 0.10 \text{ V})$ is mainly attributed to the Tafel–Volmer mechanism. Some differences observed between the simulated and the experimental CVs of activated Ni above 0.10 V (*cf* Fig. 6b, d) might be due to an additional HOR pathway, which is probably the reaction between adsorbed Ni–H_{ad} and Ni–OH_{ad}, as it was proposed earlier [16, 19]. This additional step has not been included in the current model for simplicity and will be analyzed in the future if being supported by further experimental evidence.

Along with the co-existence of metallic Ni and NiO sites on the surface of the Ni electrode, surface defects, which may be formed upon (*partial*) removal of nickel oxide species from the surface of the electrode might also affect the HOR/HER activity of Ni. Further advances in characterization (mainly in situ) of the sample structure and composition should improve our understanding of the observed Ni activity enhancement after its oxidation and subsequent *partial* reduction.

4 Conclusions

Significant variations in the electrochemical and electrocatalytic properties of Ni in the hydrogen oxidation and hydrogen evolution reactions were observed depending on the electrode pretreatment. If electrochemical tests are performed shortly after the preparation of Ni electrodes (either by polishing Ni rod or by electrodepositing Ni nanoparticles) and care is taken to minimize their contact with air, their electrocatalytic activity in the hydrogen electrode reactions is low and amounts to ca. 2 μ A cm⁻² for polycrystalline Ni, and ca. 6 μ A cm⁻² for Ni nanoparticles electrodeposited on GC. If, however, Ni electrodes are "activated" by either their exposure to an ambient atmosphere or under controlled electrochemical conditions, their activity in the hydrogen oxidation and hydrogen evolution reactions increases up to ca. 20 μ A cm⁻² for polycrystalline Ni and ca. 50 μ A cm⁻² for electrodeposited Ni.

On the basis of ex situ angle-resolved XPS measurements this difference is explained by the presence of a significant amount of NiO on the surface of activated Ni.

By combining the experimental observations with microkinetic modeling we conclude that the enhancement of the electrocatalytic activity of Ni in the presence of surface NiO can be related to a decrease of the adsorption energy of the hydrogen intermediate participating in the HOR/HER, along with an increase of the rate constant of the Volmer step. This conclusion is supported by the published results of DFT calculations suggesting decrease of the strength of hydrogen adsorption, and increase of the strength of water adsorption in the presence of oxygen



Fig. 6 Comparison of the experimental (**a**, **b**) and simulated (**c**, **d**) cyclic voltammograms for non-activated (**a**, **c**) and activated (**b**, **d**) Ni in N₂-(*curve 1*, *black*) and H₂- (*curve 2*, *red*) saturated 0.10 M NaOH at v = 20 mV s⁻¹ and 25 °C

adsorbed on Ni. We infer that not only the rate of HOR/ HER, but also its mechanism is affected by the presence of surface oxide. While on metallic Ni the HOR/HER largely follows the Heyrovsky–Volmer mechanism, on the "activated" electrode, where Ni metal sites co-exist with the "irreversible" surface oxide species, the HOR/HER predominantly follows the Tafel–Volmer mechanism. Our kinetic model not only explains the experimental results of this work, but also allows to reconcile the inconsistencies reported in the literature regarding the electrocatalytic activity in the hydrogen reactions depending on the electrode pretreatment conditions, as well as different HER kinetics and mechanisms (Heyrovsky–Volmer [17] vs. Tafel–Volmer [35]).

Acknowledgments The authors acknowledge financial support from the grant ERA.Net RUS No. 208 and Russian Academy of Science and Federal Agency of Scientific Organizations (Project No. V.46.4.4). The authors express their gratitude to Dr. Thierry Dintzer for SEM measurements. Valuable discussions with Dr. Olga V. Cherstiouk and Dr. Pavel A. Simonov (Boreskov Institute of Catalysis, Russia) are highly appreciated. A.G.O. acknowledges financial support from RFBR (Project No. 16-33-00331 mol_a) and PhD scholarships of French government.

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