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Metal-metal (hydr)oxide heterostructures for electrocatalysis of hydrogen electrode reactions

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Abstract

Metal/metal (hydr)oxide heterostructures have been proposed as an efficient means to enhance the kinetics of hydrogen electrode reactions (the hydrogen evolution, and the hydrogen oxidation reaction) on Pt, Ni and other electrodes in alkaline medium. However, the reasons for the faster electrode kinetics are still not fully understood. By considering two electrode materials, namely Pt and Ni, widely studied in hydrogen electrode reactions in alkaline media, this review brings to light differences in their pH-dependent behavior and likely different genesis of the enhancement in the presence of 3d transition metal oxides.

Introduction

Stimulated by recent progress in the development of anion-exchange membranes (AEM) and the ensuing interest in AEM fuel cells and electrolyzers, hydrogen electrode reactions in alkaline media have recently attracted close attention of the scientific community. It has been found that the kinetics of both the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER) on Pt and some other PGM (platinum group metals) is considerably slower in alkaline than in acid electrolytes. Various hypotheses were put forward to explain this kinetics slowdown and various means were proposed for increasing the rates of the HOR/HER in alkaline medium. Markovic and coworkers [1,2] discovered that deposition of Ni(OH)₂ islands on the surface of a Pt(111) electrode allows to significantly increase the rate of the HER in 0.1 M KOH [1] and proposed 'bifunctional mechanism' with transition metal hydroxide sites facilitating dissociative

adsorption of water. Later they found that Co hydroxide was also effective towards the HER enhancement, while deposition of Mn and Fe hydroxides led to a further increase of the HER overpotential [2]. Wang et al. also reported HER enhancement for Pt nanocrystals on 2D Ni(OH)₂ nanosheets [3]. An enhancement of the hydrogen electrode kinetics in alkaline media has also been demonstrated for other PGM electrodes in the HER but also in the HOR. Liao et al. studied Pd/FeO_x(OH)_{2-2x} core/shell nanoparticles with the highest activity around 40% coverage by Fe oxyhydroxide [4]. Kundu et al. prepared a Rh-Rh₂O₃/C catalyst and compared its HOR/HER activity with that of the Rh/C counterpart [5]. The authors discovered an activity enhancement, its magnitude increasing with the electrolyte pH. The latter was attributed to an enhanced formation of reactive OH_{ad} species on Rh₂O₃ and a decrease of the Rh-H_{ad} binding energy in the presence of the oxide [5]. Owing to its stability within a wide potential interval, CeO₂ species received particular attention as a component of M/MO_x heterostructures [6]. The positive effect of CeO₂ species on the alkaline HOR/HER activity was demonstrated for Pd/CeO_x and Pt/CeO_x electrodes [7–9]. A negative shift of the H_{UPD} peak in the presence of CeO_x encouraged the authors to propose weakening of the Pd-H_{ad} binding energy being responsible for the HOR enhancement on Pd/CeO_x [7]. Such decrease of the H_{ad} binding energy was assigned by Bellini et al. to the specific structure of Pd/CeO₂ interface, which consists of oxidized Pd atoms coordinated by four oxygen atoms of closely located CeO₂ [9].

Finally, it was reported that alkaline HOR/HER activity could also be enhanced by modifying Pt with metallic (for example Ru [10]) rather than (hydr)oxide species. By combining in situ X-ray absorption spectroscopy (XAS) with electrochemical measurements, it was shown that close to the HOR/HER equilibrium potential the interfacial water was oriented with the oxygen-down on Ru by oxygen-up on Pt. Thus, it was proposed that metallic Ru enhances the HOR on Pt by attracting H₂O from the electrolyte onto the surface with the configuration energetically more favorable for the HOR/HER, subsequently facilitating the removal of H_{ad} species on the Pt neighboring sites. It was suggested that the electronic effect should also be taken into consideration, and that for the Pt-Ru system it might be predominant [11].

Enhancement of the alkaline HER/HOR has also been observed for non-PGM electrodes. Thus, Danilovic et al. reported on the improved HER kinetics in alkaline medium for IB group (Cu, Ag, Au), the Pt group (Pt, Ir, Ru), and the 3d transition metal (V, Ti, Ni) electrodes in the presence of Ni(OH)₂ [12]. For polycrystalline Cu, it was concluded that presence of surface Cu oxides also results in the enhancement of the HER activity [13]. The most studied between non-PGM electrodes is Ni due to its relatively high HER/HOR activity. Already in early publications it was noticed that the HER overpotential depends on the state of the Ni surface [14]. Oshchepkov et al. thoroughly studied the influence of surface oxidation on the activity of Ni in the HOR (and HER at low overpotentials) and concluded that the enhancement was due to the change of the energy of H_{ad} binding on Ni in the presence of surface (hydr)oxides rather than the above-mentioned bifunctional mechanism [15,16]. Based on these findings, Oshchepkov et al. developed a highly active HOR catalyst by depositing Ni on carbon and subsequently subjecting the latter to anodic oxidation pulses in order to produce hybrid Ni/NiO_x nanostructures [17]. The HOR/HER exchange current density could be increased from ca. 6 on metallic Ni/C catalyst to 56 μA.cm⁻² on Ni/NiO_x/C, reaching values comparable to those of Pd/C catalysts. Significant HOR/HER enhancement has also been reported for various Ni/MO_x heterostructures [18–24].

Bates et al. investigated several systems, prepared via deposition of Ni on composite metal oxide (TiO_2 , CeO_2 , Cr_2O_3 , ZrO_2 , WO_3 , and MoO_x) – carbon supports, with the highest HER activity observed for the Ni-NiO_x/Cr₂O₃/C catalyst [19]. Detailed study of a composite M/MO_x interface by XRD and in situ XAS revealed that the active sites are composed of Ni and NiO_x interface. The nearby Cr₂O₃ sites, although not providing the synergistic HER enhancement, were required to stabilize the NiO_x component thus creating an active Ni/NiO_x heterostructure [19]. Combined XAFS and AP-XPS data of Dinh et al. [21] revealed that the presence of CrO_x strongly affects the oxidation behavior of nearby Ni atoms, stabilizing surface NiO_x, which is in agreement with the conclusions of Bates et al. Similar enhancement of Ni activity in the HER in the presence of Cr₂O₃ species was also reported by Gong et al. [22], who proposed formation of NiCrO_x phase at the Ni/NiO_x interface during long-term operation, which helps to maintain the high HER performance. Weng et al. reported Ni/CeO₂-CNT hybrid material that exhibits an improved activity in the HER [23] in alkaline medium. On the basis of DFT calculations the authors assigned this high activity to the Ni/CeO₂ interface, which promotes water dissociation and, most importantly, renders optimum hydrogen adsorption energy [23]. Similar conclusions were made by Yang et al. (Figure 3e) [20], who studied CeO₂(r)-Ni/C catalysts with partially reduced CeO₂ and suggested that the oxide moieties on the surface serve as active sites for OH_{ad} adsorption (due to the presence of oxygen vacancies), while nearby located Ni sites are characterized by weaker adsorption of H_{ad} species (compared to the pure Ni surface).

To conclude, approach based on combining metal with metal (hydr)oxide sites seems very promising for the development of PGM-based but also PGM-free catalysts for the HER/HOR in alkaline medium. Various hypotheses have been put forward to explain this enhancement effect, among them the above-mentioned bifunctional mechanism and variation of the H_{ad} binding energy. However, despite numerous publications there is no agreement regarding the origin of the enhancement effect. Furthermore, the phenomena at stake likely depend on the nature of the metal and the transition metal (hydr)oxide and on their association. The objective of this paper is to provide a short and critical overview of various hypotheses, which have been proposed to explain the enhancement of the hydrogen electrode kinetics on metal-metal (hydr)oxide heterostructures. In order to do so we have chosen to focus this review on two electrode materials: Pt and Ni-based, and on their comparison. This choice is justified by the differences in the electronic properties of Ni and Pt, and the ensuing differences in the point of zero charge (pzc), H adsorption and HER/HOR mechanisms, making of these two metals interesting examples. Furthermore, among studies published to date, those which delve deeply into the origin of the HER/HOR activity enhancement on M₁/M₂(OH)_x heterostructures, mostly deal with either Pt or Ni-based electrodes. The review is arranged as follows. We start with a quick overview of the influence of pH on the hydrogen electrode kinetics (Section 1), where along with the recent publications we recall some early works. Section 2 is devoted to a short presentation of the most common hypotheses to explain high HER/HOR activity of Pt metal-metal (hydr)oxide heterostructures. In Section 3, the HOR/HER enhancement on hybrid Ni/Ni(OH)_x electrodes will be analyzed and confronted to the Pt/Ni(OH)_x electrodes.

1. Influence of pH on the hydrogen electrode reactions

Recent publications widely discuss slowdown of the HER/HOR kinetics when switching from acid to alkali. Figure 1a represents the exchange current density (i_0) of the hydrogen electrode on carbon-supported Pt particles depending on pH. Indeed, one may see that i_0 continuously decreases from pH0 to pH13. Similar behavior was reported for Ir/C, Pd/C and Rh/C [25].

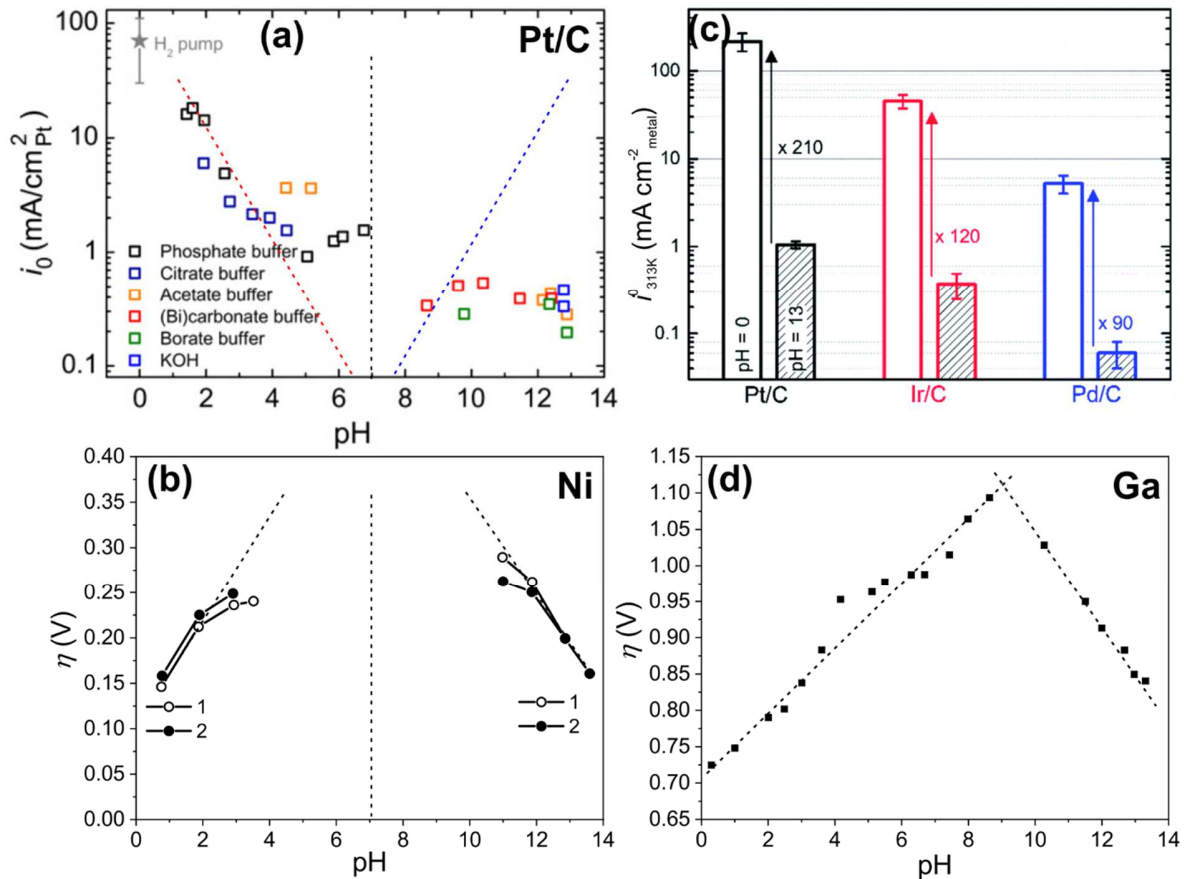


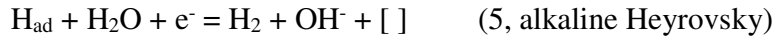
Figure 1. (A) Exchange current density for the hydrogen electrode on Pt/C. Represented with permission from Ref. [25]. Dashed lines are guides for the eye plotted following Eq. 8 (red) and 9 (blue) assuming $\text{const}_1 = \text{const}_2$. (B) Absolute value of the HER overpotential on Ni at current density of $1.6 \cdot 10^{-4} \text{ A cm}^{-2}$ in HCl and NaOH without (1) and with (2) addition of supporting electrolyte. Represented with permission from Ref. [26]. Dashed lines are guides for the eye, which closely follow Eqs. 10 and 11. (C) HOR/HER exchange current densities at 313K obtained in a proton exchange membrane fuel cell (PEMFC) in a hydrogen pump mode (empty columns) and 0.1 M NaOH (hatched columns). Represented with permission from Ref. [27] (D) Absolute value of the HER overpotential as a function of pH on a Ga electrode at a current density of $10^{-3} \text{ A cm}^{-2}$ in the presence of supporting electrolyte. Replotted based on the data from Ref. [28]. Dashed lines are guides for the eye.

The mere fact that the exchange current density of the hydrogen electrode is pH-dependent is not surprising since water and its fragments (H^+ and OH^-) participate in the HOR/HER. The

mechanism of the HER/HOR in acid is fairly well understood and consists of Volmer, Tafel, and Heyrovsky steps [29,30]:



Assuming similar mechanism of hydrogen reactions in alkaline medium, one can write:



The current density at the hydrogen electrode is a complex interplay of the Tafel, Volmer and Heyrovsky step kinetics and depends on the nature of the electrode, its overpotential, temperature and electrolyte composition. It should be noted however that both the Volmer and the Heyrovsky steps are intrinsically pH-dependent. Let us express, for example, the exchange current density for the Volmer step (see e.g. M. W. Breiter [31]) in acid (Eq. 6) and alkaline medium (Eq. 7) assuming high concentration of supporting electrolyte, and thus neglecting the potential (ξ^1) of the diffuse double layer:

$$i_{0,V,acid} = Fk_{acid}^0(1-\theta_H)^\alpha \theta_H^{(1-\alpha)} (C_{\text{H}^+})^\alpha \quad (6)$$

$$i_{0,V,alkaline} = Fk_{alkaline}^0(1-\theta_H)^\alpha \theta_H^{(1-\alpha)} (C_{\text{H}_2\text{O}})^\alpha (C_{\text{OH}^-})^{(1-\alpha)} \quad (7)$$

Assuming $\alpha=0.5$ and independence of the hydrogen coverage of the pH (*vide infra*) one might expect the following pH dependence for acid (Eq. 8) and alkali (Eq. 9) correspondingly.

$$\log(i_{0,V,acid}) = \text{const}_1 - 0.5\text{pH} \quad (8)$$

$$\log(i_{0,V,alkali}) = \text{const}_2 + 0.5\text{pH} \quad (9)$$

Similar behavior is expected for the Heyrovsky step. One may see that in the interval from pH0 to pH4 the exchange current density closely follows the dependence expected within slow discharge theory but then deviates, and an expected increase of the exchange current density is not observed. Deceleration of the HER/HOR in alkaline medium has also been documented by Durst et al. (Figure 2b) [27], who used a proton exchange fuel cell in a hydrogen pump mode to accurately measure the exchange current density in acid medium² and compare it with the one measured in 0.1 M NaOH. Such a kinetic slowdown has been widely discussed in the literature as a common phenomenon, which accompanies transition from acidic to alkaline electrolytes.

Before moving to the next sub-sections, which discuss various means to accelerate the HER/HOR kinetics in alkaline medium, let us turn our attention to early publications [32,33],

¹ Note that in the absence of supporting electrolyte ξ depends on the pH, which affects the form of Eq. 6-9 [32].

² Note that in acidic medium the HOR/HER on Pt and some other PGM is so fast that its kinetics cannot be properly measured using a rotating disc electrode.

which thoroughly discussed the influence of pH on the HER on various (and in particular high overvoltage) electrode materials. Hydrogen overpotential on Hg, and in particular its dependence on pH, concentration of supporting electrolyte, and anion adsorption, was thoroughly discussed by Frumkin [32]. In the presence of supporting electrolyte and constant ξ , the pH dependence on Hg in acid (H_3O^+ as a proton source) and alkaline electrolytes (H_2O as a proton source) could be described with Eq. 10 and 11³ correspondingly.

$$|\eta| = \text{const}_3 + \frac{2.3 RT}{F} \text{pH} \quad (10)$$

$$|\eta| = \text{const}_4 - \frac{2.3 RT}{F} \text{pH} \quad (11)$$

Along with Hg, similar behavior was observed for other metals. Indeed, Figure 1c shows overpotential of the HER measured for a metallic Ni electrode⁴ at constant current density as a function of pH. One may notice that for acidic electrolytes the overpotential increases with pH following Eq. 10, for alkaline electrolytes it decreases with pH following Eq. 11, in both cases in agreement with the slow discharge theory. It should be stressed however that hydrogen overpotential is very sensitive to the presence of specifically adsorbed anions, type of cations, presence of impurities, and that the slope in Eqs. 10 and 11 doubles in the absence of supporting electrolyte. This can partly explain discrepancies in the literature data regarding the pH dependence (see e.g. pH dependence for a Ga electrode in Figure 1d).

Note that no HER slowdown is observed on metallic Ni in alkaline medium, and the alkaline branch mirrors the acidic one questioning "...intrinsically larger barriers for the splitting of water with respect to hydronium..." being the cause of slow HER kinetics in alkaline medium [34]. Thus, the widely discussed slowdown of the hydrogen electrode kinetics when switching from acid to alkaline medium may not be a common phenomenon. Such a slowdown was documented both for carbon supported PGMs (Pt, Ir, Pd) [25,27] and for single crystal Pt(111) [35] but does not seem to occur for high overpotential electrodes like Hg. Ni is an interesting case, obeying Eq. 10 and 11 at high overpotentials, as demonstrated in early publications (Figure 1c) and recently confirmed by Faid et al. [36] but demonstrates anomalous behavior at low HER overpotential and in the HOR interval [37], as discussed in more detail in Section 3. This information should be considered in the following discussion of the HOR/HER kinetics enhancement at metal-metal (hydr)oxide heterostructures.

2. HOR/HER enhancement on Pt electrode modified with 3d transition metal (hydr)oxides

Pt is the most active HER/HOR material in acid, being material of choice (in the form of carbon-supported nanoparticles) at the anode of PEM fuel cells and cathode of PEM electrolysis cells. However, in alkaline media the HER/HOR kinetics slows down both for Pt nanoparticles and Pt(111). Several publications attributed this kinetics slowdown to the change in the H_{ad}

³ Note that Eq 10 and 11 are only valid in the presence of a supporting electrolyte, otherwise the pH dependence of ξ may change the numerical coefficient in front of the pH term.

⁴ Prior to the measurements the authors of Refs. [26] reduced Ni surface in situ in the H_2 atmosphere at 400-420 °C following by its cool down to room temperature.

adsorption energy when switching from acid to alkaline medium [27,38]. However, Ledezma-Yanez et al. [39] demonstrated that the position and shape of the H_{UPD} (underpotential deposition) peaks are not affected by the NaOH concentration between pH 11 and 13, suggesting that the thermodynamic properties of the H_{ad} species do not depend on the pH. Several studies suggested that it is not the H_{UPD} , but another, a weakly adsorbed hydrogen, which participates in the HOR/HER as an intermediate [40]. It is however unlikely that its adsorption energy changes with pH while H_{UPD} is unaltered. In the meantime, a significant decrease of the HER activity as well as slower H_{UPD} formation/oxidation kinetics could be evidenced with increasing NaOH concentration.

Since the HER kinetics on Pt can be enhanced by deposition of 3d transition metal (hydr)oxides, a question arises whether the latter alters the adsorption energy of the HOR/HER intermediate. Cyclic voltammograms of a Pt(111) electrode before and after deposition of various amounts of $Ni(OH)_2$ are displayed in Figure 2a. The CV profiles reveal a decrease of the charge in the hydrogen UPD region with increasing $Ni(OH)_2$ coverage, resulting in a decrease of the accessible Pt surface area. However, the position of the hydrogen UPD peaks remains almost unaltered by the presence of $Ni(OH)_2$ at least for coverages up to 0.22.⁵ This suggests that the H_{UPD} binding energy (and likely the binding energy of the HER/HOR intermediate) on Pt is almost unaffected by the presence of $Ni(OH)_2$. In the meantime, the HER activity substantially increases (Figure 2b) questioning variation of the hydrogen adsorption energy as a reason for the HER enhancement. While the energy of H_{UPD} does not seem to depend on the $Ni(OH)_2$ coverage, its rate of formation is clearly enhanced in the presence of $Ni(OH)_2$, compared to bare Pt(111) (Figure 2c).

⁵ However, for a $Ni(OH)_2$ coverage of 0.37 the position of the H_{UPD} peak seems to shift negatively and thus a decrease of the H_{UPD} binding energy cannot be excluded at a high Ni hydroxide coverage.

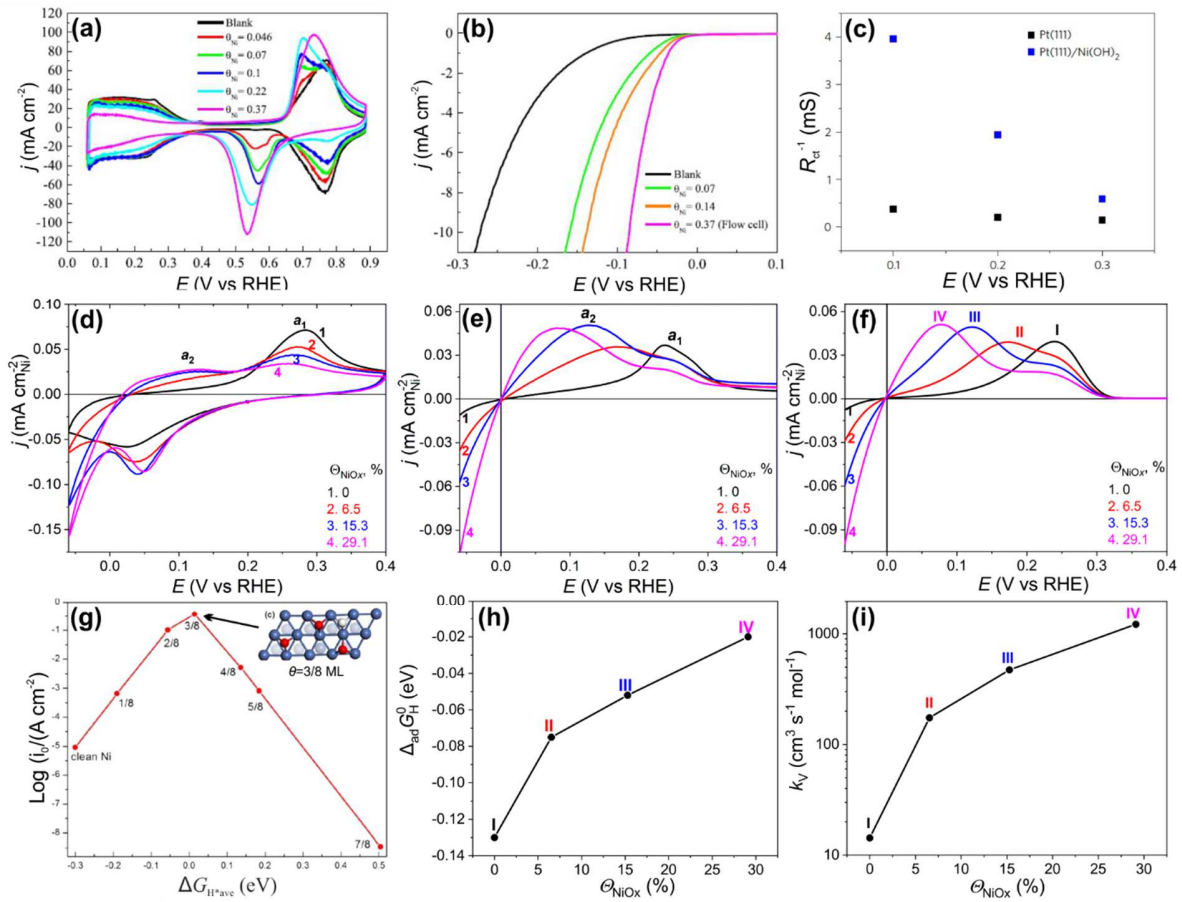


Figure 2. (a) Cyclic voltammograms of the Pt(111) surface modified with different Ni(OH)₂ coverages and (b) corresponding HER currents obtained at $v = 50 \text{ mV s}^{-1}$ in 0.1 M NaOH. Represented with permission from [41]; (c) Inverse of the charge transfer resistance as a function of potential for Pt(111) and a Pt(111) electrode decorated with 10% Ni(OH)₂ in 0.1 M NaOH. Represented with permission from [39]; (d) Cyclic voltammograms of Ni/NiO_x electrodes at various NiO_x coverages obtained in (d) Ar-saturated at $v = 20 \text{ mV s}^{-1}$ or in (e) H₂-saturated 0.1 M NaOH at $v = 5 \text{ mV s}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$. (f) Simulated CV curves for various degree of oxidation of Ni/NiO_x electrodes in H₂ atmosphere at pH 13 and $v = 5 \text{ mV s}^{-1}$; (h) and (i) represent variation of the free energy of the adsorbed H_{ad} intermediate and Volmer rate constant k_v^0 , respectively. The figures (d) – (e), (h) and (i) are represented with permission from [15]; (g) Volcanic curve of the HOR exchange current density (i_0) as a function of the average ΔG_{H^*ave} at different oxygen coverage ($\theta = 0/8, 1/8, 2/8, 3/8, 4/8, 5/8, \text{ and } 7/8 \text{ ML}$) on the Ni(111) surface. Represented with permission from [42].

Moreover, the OH adsorption interval (Figure 2a) changes significantly with the Ni(OH)₂ coverage. Even if these changes are not fully understood yet [41], they provide a hint to water and/or OH interaction with the electrode surface being responsible for the enhancement of the HER kinetics in the presence of Ni(OH)₂.

The source of H_{ad} is different in acid (H_3O^+) and alkaline electrolytes (H_2O). This, along with the observation of significant enhancement of the HER for Pt modified by $Ni(OH)_2$ clusters in base [1], led Markovic and coworkers to propose the bifunctional mechanism of the HER in alkaline media. According to it, two types of surface sites are required for an efficient H_2 production, the first provides optimal $M-H_{ad}$ energetics and the second facilitates dissociative adsorption of water molecules (step 12). Such a bifunctional mechanism implies Volmer step (step 4) to occur in a sequence of two steps (12 & 13).



This concept was extended to Pt(111) modified with other 3d transition metal oxides (Co, Fe, Mn) [2], whose alkaline HER activity was found to increase in the order $Pt(111)/Mn(OH)_2 < Pt(111)/FeO(OH)_x < Pt(111) < Pt(111)/Co(OH)_2 < Pt(111)/Ni(OH)_2$ (Figure 3a), being thus opposite to the strength of OH_{ad} adsorption on the considered transition metals.

The HOR was proposed to involve the same steps (12 & 13) but in the backward direction, decoration of a metal surface with metal (hydr)oxide species facilitating the kinetics of the Volmer step by enhancing of surface oxophilicity and providing OH_{ad} reactive intermediates (step 13) which then recombine with adsorbed hydrogen (recombination step 12). In the case of Pt- $Ni(OH)_2$ system such mechanism would mean that H_{ad} intermediates are adsorbed on Pt sites, while OH_{ad} species are adsorbed on the neighboring $Ni(OH)_2$ sites. By varying surface oxophilicity it should be possible then to modify the HOR activity of the Pt- MO_x catalysts, as was recently demonstrated by Liu et al. [11].

While many publications quote bifunctional mechanism as the main reason of the HER/HOR enhancement on metal/metal (hydr)oxide heterostructures, several studies questioned the validity of such mechanism. By combining single-crystal voltammetry and microkinetic modeling, it was found that participation of OH_{ad} species in the Volmer step on Pt(110) electrodes in alkaline solution is rather unlikely. Furthermore, increasing the OH_{ad} binding energy rather results in a decrease of the number of available Pt active sites and then a decrease of the HOR current [43].

Some recent studies attributed the lower HOR/HER activity in alkaline solution to less facile reorganization of the interfacial water in alkaline compared to acidic media, the enhancement in the presence of transition metal (hydr)oxide being thus attributed to a modification of the potential of zero total charge (pztc)⁶. [39,41,44]. Indeed, the pztc of Pt electrodes in acidic media lies in the H_{UPD} interval, close to the HOR/HER equilibrium potential. In this case, the low intensity of the interfacial electric field enables fast reorganization of the water molecules facilitating proton transport in the electrochemical double layer during the HER/HOR [44]. In alkaline media the pztc of Pt is significantly higher on the RHE scale, its value being close to 0.7 V vs. RHE. Then, at 0 V vs. RHE, i.e. the HOR/HER equilibrium potential, the Pt surface is negatively charged and the increased strength of the interfacial electric field results in a more

⁶ That is the electrode potential at which the total excess charge on the electrode is null.

rigid water adlayer, a slower rate of the interfacial water reorganization upon OH⁻ migration and hence slower HOR/HER kinetics [39,41].

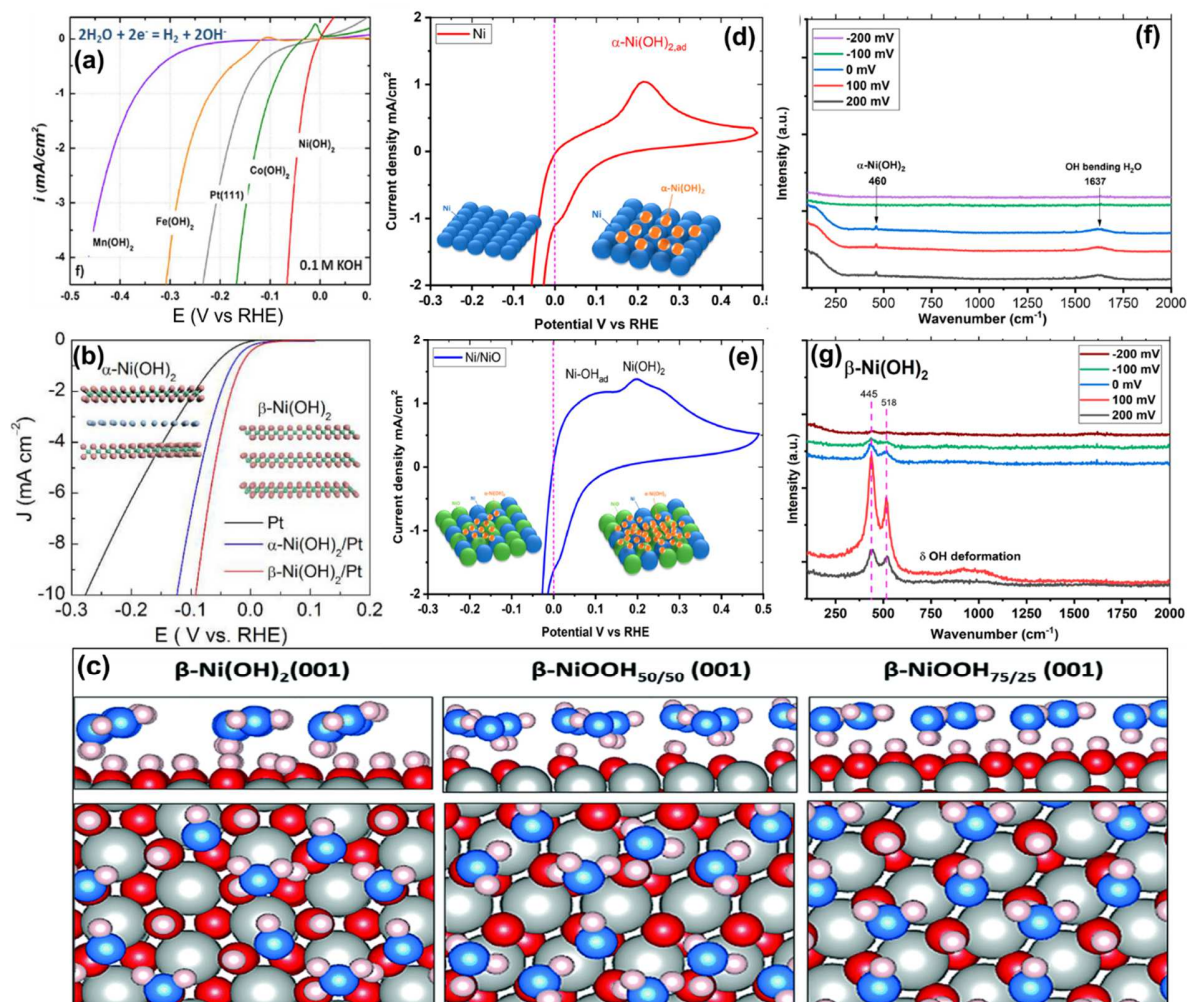


Figure 3. (a) HER polarization curves in 0.1 M KOH for Pt(111) surface modified with different transition metal hydroxides. Represented with permission from [45]; (b) LSV curves of Pt, α -Ni(OH)₂/Pt, and β -Ni(OH)₂/Pt electrodes for HER in 0.1 M KOH. Represented with permission from [46]; (c) Snapshots of the side and top views of the structure of water bilayer taken from the Molecular Dynamic simulations of water at 140 K on β -Ni(OH)₂(001), β -NiOOH(001) terminated with 50% OH–50% O, and β -NiOOH(001) terminated with 75% OH–25% O. Represented with permission from [47]; Cyclic voltammetry of (d) Ni and (e) Ni/NiO nanosheets catalyst synthesized by chemical reduction in 1 M KOH. The corresponding in situ Raman spectra taken at different applied overpotentials are shown in (f) and (g) for Ni and Ni/NiO, respectively. Represented with permission from [36].

Ryu and Surendranath argued for the influence of pH on the magnitude of the interfacial electric field at the Pt/water interface by employing the hydrogenation/hydrogenolysis of cis-2-butene-1,4-diol as a reaction probe sensitive to the interfacial proton concentration [48]. The potential

drop at the Pt/water interface was found to increase by ca. 60 mV per pH unit in the solution bulk, the interfacial electric field associated to this potential drop increasing from a value close to 0 at pH 1 to 10^8 V m^{-1} at pH 7, and probably even higher at pH 14 [48]. However, the presence of hydroxides and oxides at the electrode surface might lead to a decrease of the magnitude of the potential drop at the interface and then of the interfacial electric field. Thus, in alkaline media the reactivity of the interfacial water may be influenced by the presence of transition metal (hydr)oxides [39,41]. Indeed, laser-induced temperature-jump and CO displacement experiments demonstrated that deposition of Ni(OH)_2 clusters on a Pt(111) electrode at submonolayer coverage results in a negative shift of the potential of maximal entropy (and then of the pztc) from 0.675 V vs. RHE for bare Pt(111) in alkaline media to the hydrogen potential region for Ni(OH)_2 -covered Pt(111) [39,41]. Furthermore, a negative shift of the onset potential of CO oxidation on Pt(111) was observed in the presence of Ni(OH)_2 clusters, revealing the formation of adsorbed hydroxide species on Pt at low potential, already in the hydrogen UPD region.

It should be stressed that the water activation, the modification of the pztc of the electrode and/or the structure of the interfacial water might depend on the chemical nature and on the structure of the transition metal (hydr)oxide. Yu et al. compared activities of Pt electrodes modified with either α - or β - Ni(OH)_2 and demonstrated that the latter one not only provides larger enhancement in the HER activity (Figure 3b), but is also more stable at the Pt- Ni(OH)_2 electrode surface at negative potentials, likely due to its more compact structure compared to the α -phase [46]. Note also that α - Ni(OH)_2 should be easily reduced at HER potentials [49]. In contrast, β - Ni(OH)_2 is a passivating Ni hydroxide, which is more difficult to reduce under electrochemical conditions. On the basis of the analysis performed using ex situ XPS and XANES as well as in situ Raman spectroscopy and DFT calculations the authors concluded that β - Ni(OH)_2 provides stronger hydrogen bonding between lamellar hydroxyl and water molecule compared to the α - Ni(OH)_2 , in which the interlamellar water molecules cause shortening of the Ni-O bonds, thus lowering their interaction with water molecules at the outmost surface.

In a yet another study, the interaction between water and two types of Ni oxide, β - $\text{Ni(OH)}_2(001)$ and β - $\text{NiOOH}(001)$ was investigated by first-principles calculations. Water was found to interact weakly with β - Ni(OH)_2 , resulting in a disordered water adlayer, with small surface dipole moment (Figure 3c). In contrast, surface water layers are more strongly interacting with β - NiOOH surface, showing enhanced degree of ordering and a large surface polarization [47]. Such differences might then affect the reactivity of water molecules at the metal/ Ni(OH)_x junction.

3. HOR/HER enhancement on Ni electrode modified with 3d transition metal (hydr)oxides

As mentioned in Section 1, the HER on Ni at high overpotentials does not show any anomaly when switching from acid to alkaline electrolyte (Figure 1b). However, at low overpotentials the behavior of Ni is different. Indeed, recently Kuznetsov et al. investigated hydrogen electrode reactions on a polycrystalline Ni electrode as a function of NaOH concentration in a pH window between 12 and 14 [37]. Figure 4a shows CVs in the absence and in the presence of H_2 . The

anodic peaks observed around 0.25 V vs. RHE in Ar-saturated solution (dashed curves in Figure 4a) were attributed to the electrochemical desorption of strongly adsorbed hydrogen immediately followed by (and thus overlapping with) a surface α -Ni(OH)₂ layer. In H₂-saturated solutions (full curves in Figures 4a) H₂ oxidation occurs in the same potential interval. The slow HOR/HER kinetics can be assigned to the strong binding of the H_{ad} reaction intermediate to the surface of metallic Ni [40]. It is worth noticing that the peak position does not depend on the NaOH concentration either in Ar- or in H₂-saturated solutions suggesting that the binding energy of H_{ad} on metallic Ni is not affected by the NaOH concentration, similar to what was discussed for Pt(111). The HER/HOR activity of metallic Ni (expressed in terms of the exchange current density) does not decrease with pH, but rather slightly increases from pH 12 to 14 [37].

Interestingly, the Ni/Ni(OH)_x heterostructured electrodes demonstrate different behavior. While at high HER overpotential the current density clearly increases with the OH⁻ concentration in agreement with the slow discharge theory, as recently confirmed by Faid et al. [36] (Figure 4c), the HOR/HER activity in the low overpotential region decreases by a factor of two with the pH increase from 12 to 14 (Figure 4b) [37]. The latter is similar to j_0 decrease in alkaline electrolytes documented for Pt and other PGM electrodes. However, at ca. -0.2 V, the HER curves measured at various NaOH concentrations intersect (not shown), the HER current increasing with pH below -0.2 V vs. RHE in agreement with Faid et al. [36]. To the best of our knowledge, such behavior has not been observed either for metallic Ni and Pt or Pt/Ni(OH)_x electrodes.

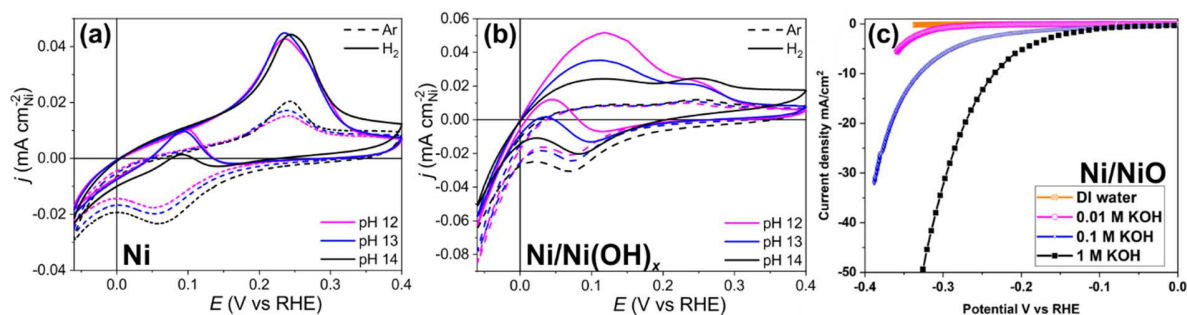


Figure 4. Cyclic voltammetry curves on (a) a metallic Ni or (b) Ni/Ni(OH)_x disk electrodes measured at 5 mV s⁻¹ in H₂-saturated (full curves) or Ar-saturated (dashed curves) 0.01 M (magenta), 0.1 M (blue) and 1 M (black) NaOH. Represented with permission from [37]; (c) HER polarization curves of Ni/NiO catalyst obtained in various electrolytes. Represented with permission from [36].

As discussed above, on Pt, the hydrogen adsorption energy does not seem to be altered upon deposition of transition metal oxide clusters on the electrode surface, their main role being either activation of water molecules (during the HER) or OH_{ad} species (during the HOR) or modification of the pztc of the Pt electrode. However, different behavior has been reported for Ni/NiO_x electrodes. Indeed, several groups have shown that the modification of the Ni surface by NiO_x species strongly affects the energetics of the Ni-H_{ad} bond, weakening the strength of adsorption of H_{ad} [16,42,50,51]. The latter was concluded on the basis of DFT calculations (Figure 2g) [42,51] and microkinetic modeling [15,16]. This accounts for a drastic difference in

the pH dependence of the HOR/HER on metallic Ni and on Ni/Ni(OH)_x heterostructures (Figures 4a and b).

Figure 2d shows CVs of a polycrystalline Ni electrode with different coverage of β -Ni(OH)₂ obtained through anodic potential cycles. While only one anodic peak (denoted a₁) is observed for a metallic Ni electrode at 0.25 V vs. RHE, a second anodic peak (denoted a₂) appears at lower potentials for a partially oxidized Ni surface and grows with the β -Ni(OH)₂ coverage. The peak a₂ was assigned to the electrochemical desorption of weaker bonded H_{ad} species accompanied by OH adsorption. This decrease of the hydrogen adsorption energy results from the influence of β -Ni(OH)₂ on the neighbor Ni sites. In the presence of H₂ the shift of the peak a₂ with the β -Ni(OH)₂ coverage to more negative values can be clearly seen (Figure 2e). Microkinetic modeling (*cf.* Figure 2f) allowed Oshchepkov et al. to attribute the observed changes to a systematic decrease of the hydrogen adsorption energy by about 0.1 eV (*cf.* Figure 2h) in the presence of Ni(OH)_x. [15,16,50]. This conclusion is supported by DFT calculations (Figure 2g) [42,51]. Microkinetic modeling results [15,16,50] suggest that in addition to the decrease of the H_{ad} binding energy, the rate constant of the Volmer step (k_v°) is increased by a factor of 10 at the optimal NiO_x coverage (*cf.* Figure 2i), both hydrogen binding energy and k_v° being responsible for the enhanced HOR/HER activity of Ni/Ni(OH)_x compared to metallic Ni. Maximum HOR/HER activity was observed for Ni metal/metal (hydr)oxide heterostructures at a Ni (hydr)oxide surface coverage ranging between 30 and 50 %, depending on the type of Ni electrode (either polycrystalline or carbon supported Ni/NiO_x nanoparticles) [15,17,51,52]. Interestingly, Lovell et al. [53] reported similar dependence of the HER activity on Ni/NiO heterostructures at neutral pH with an optimum around Ni:NiO = 1:1.

With regard to the bifunctional mechanism involving recombination step 12 as part of the HOR, such a mechanism is rather unlikely on metallic Ni (even if H_{ad} and OH_{ad} co-exist on the Ni surface in the same potential interval) due to the strong H_{ad} binding and the ensuing high activation barrier of step 12 according to DFT calculation [54]. However, when the H_{ad} binding energy is decreased on Ni/Ni(OH)_x heterostructured surfaces, the activation barrier of the recombination step is expected to decrease, making this step feasible. Note however that even if the recombination step cannot be fully excluded, alone, it cannot explain the HOR enhancement on the Ni/Ni(OH)_x heterostructures [15,54]. Moreover, similar to the Pt(110) case discussed above, the formation of OH_{ad} on Ni is a fast process, competing with H_{ad} adsorption for Ni surface sites. This competition accounts for the abrupt decrease of the HOR current on Ni at potentials above ca. 0.2 V (Figures 4a, b) further questioning bifunctional HOR mechanism on Ni/Ni(OH)_x heterostructures.

The question arises whether the enhancement of the HER/HOR kinetics on Ni/Ni(OH)_x could be explained by the modification of the interfacial water structure in the presence of Ni(OH)_x. Unfortunately, the pzc of metallic Ni is not as well established as that of Pt, likely due to difficulties associated with the preparation of Ni free from surface oxides. However, the pzc values available in the literature [55,56], the notably lower work function values for Ni compared to Pt surfaces [57,58], along with the OH adsorption and surface α -Ni(OH)₂ formation on Ni starting slightly above 0 V vs. RHE, suggest that the pzc of metallic Ni is significantly lower

than of Pt. Thus, the consideration of slow HOR/HER in alkaline media due to strong interfacial electric field might not be relevant for Ni electrodes. Nevertheless, upon anodic polarization in the HOR potential range water molecules are expected to be drawn toward the surface [59]. In such case, the interaction of water molecules with metallic Ni sites and then the kinetics of the Volmer step might be affected by the presence of Ni hydroxide islands on the surface. Indeed, depending on the type of Ni (hydr)oxide and on the supporting electrolyte concentration the isoelectric point (pH_i) lies between 8 and 11 [60,61]. Thus Ni (hydr)oxide surface is negatively charged at $\text{pH} > 12$ and this might induce a modification of the interfacial water orientation at the junction between metallic Ni and NiO_x islands in comparison to metallic Ni.

It should be stressed that the heterojunction between metallic and transition metal oxide phases (which are often semiconducting phases) might induce charge redistribution at the heterointerface and modification of the pzc of the electrode and/or the chemical properties of the metallic and metal oxide phases depending on the thickness and the size of the metal oxide phase. Such concept was recently discussed in the field of catalysis [62,63] and in electrocatalysis for the HER and urea oxidation on $\text{CoMn}/(\text{CoMn})\text{O}_x$ electrodes [64].

Furthermore, one should consider different influence of α - or β - $\text{Ni}(\text{OH})_2$ on the HOR/HER enhancement on Ni. This can be grasped by examining the shape of the current-potential curves of metallic Ni and Ni/ NiO_x electrodes in H_2 -saturated NaOH solution displayed in Figures 4a and b. When the electrode potential is kept below 0.5 V vs. RHE, it is commonly accepted that the surface of a Ni electrode can be reversibly oxidized and reduced into α - $\text{Ni}(\text{OH})_2$. Comparing the anodic and cathodic potential scans reveals the transient enhancement of the HOR/HER activity on metallic Ni in the cathodic scan (compared to the HOR/HER activity in the anodic scan) when the reduction of α - $\text{Ni}(\text{OH})_2$ formed during the forward scan occurs. The effect is even more pronounced at higher temperature [16]. Thus the coexistence of α - $\text{Ni}(\text{OH})_2$ with metallic Ni sites on the surface of the electrode is leading to significant HOR/HER current enhancement even if it rapidly vanishes due to the α - $\text{Ni}(\text{OH})_2$ reduction. In contrast, when the potential is increased above 0.5 V vs. RHE, α - $\text{Ni}(\text{OH})_2$ is transformed into β - $\text{Ni}(\text{OH})_2$, which is more difficult to reduce, even under HER conditions. In such case, stable enhancement of the HOR/HER current can be achieved (*cf.* Figure 4b). Indeed, in situ Raman spectro-electrochemistry showed that β - $\text{Ni}(\text{OH})_2$ is maintained in Ni/ NiO_x heterostructures during HER at -0.4 V vs. RHE in contrast to α - $\text{Ni}(\text{OH})_2$ (*cf.* Figures. 3 d-f, e, g). However even β - $\text{Ni}(\text{OH})_2$ is thermodynamically unstable under HER conditions slowly vanishing with time.

Conclusions and Outlook

We have shown that the widely discussed slowdown of the hydrogen electrode kinetics with pH is not a common phenomenon, but is only manifested by some electrode materials, among them platinum and other platinum group metals. Whether this different pH behavior is related to the strength of hydrogen adsorption, HER/HOR mechanism or pzc of electrode materials, is still to be unfolded.

Combining metal with transition metal oxides has been proposed as the means to increase HOR/HER activity in alkaline medium, and has proven to be effective for various metal/metal (hydr)oxide couples. We have considered two specific cases, notably Pt and Ni, and demonstrated that while HOR/HER on both can be enhanced in the presence of Ni (hydr)oxides, the underlying phenomena may be quite different. Indeed, while deposition of Ni(OH)_x islands does not seem to affect the hydrogen adsorption on Pt, it leads to weakening of H adsorption on Ni. These differences may result from different strength of hydrogen adsorption on Pt and Ni, and possibly also the co-existence of strongly and weakly adsorbed hydrogen on Pt, while on Ni only one type of hydrogen adsorbate is likely to be formed.

The bifunctional mechanism is an elegant hypothesis suggested by the group of Nenad Markovic in 2011, and since then evoked by numerous publications, to account for the HER/HOR enhancement on metal/metal (hydr)oxide heterostructures. However, this hypothesis is not capable to explain the HER/HOR enhancement on Ni/NiO_x, and requires complementary experimental and/or computational efforts to either confirm or discard it for Pt/M(OH)_x electrodes.

Combining metallic with metal (hydr)oxide sites likely influences the interfacial water structure both for Pt and Ni electrodes. However, the fine structure of the interfacial layer is still poorly understood. In this context, computational methods, including molecular dynamics, are expected to help uncovering the interfacial water structure. Elucidation the interface between metal/metal (hydr)oxide heterostructures and aqueous electrolytes is hindered by the heterogeneity of the surface comprising metal and metal (hydr)oxide patches, where water molecules and electrolyte ions are likely to be differently oriented. Spatially resolved probe microscopies might be useful to probe such interface heterogeneities.

To conclude, metal/metal (hydr)oxide heterostructures deserve further investigations in order to unveil the cause of their efficiency in electrocatalysis of hydrogen and other electrode reactions.

Conflicts of interest

The authors have no conflicts of interest to declare.

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