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## Study of hydrogen electrosorption in Pd-Ni alloys by the quartz crystal microbalance

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**Abstract** The electrochemical quartz crystal microbalance (EQCMB) method has been used to study the processes of hydrogen absorption/desorption in Pd-Ni alloy electrodes. It was found that hydrogen electrosorption is accompanied by an additional frequency shift, attributed to the stresses generated inside the alloy. The influence of stresses on the EQCMB response depends on the amount of absorbed hydrogen and the alloy composition. From the comparison of the EQCMB results with Pd-Ni alloy absorption capabilities data, it was concluded that the decrease of the hydrogen sorption capacity at a Ni content of ca. 25–30 at% is due to an excessive generation of stresses in the alloy lattice. Also, a dependency of the rate of hydrogen absorption in Pd-Ni alloys on potential is reported.

**Keywords** Electrochemical quartz crystal microbalance · Hydrogen absorption · Palladium-based alloys

### Introduction

The electrochemical quartz crystal microbalance (EQCMB) allows us to record in situ frequency changes resulting from electrochemical processes accompanied by electrode mass changes together with the current and potential signals. The microbalance has been useful in various fields of electrochemistry [1, 2]. In theory, the frequency changes can be recalculated into mass changes using the Sauerbrey equation [3]. Unfortunately, the microbalance response is determined also by factors other than pure mass changes. Additional effects, like

changes of the viscosity of the solution, non-rigidity of the film deposited on the crystal oscillator, or stresses generated inside the electrode, obscure the pure mass response, making the analysis of the signal complicated [1, 2]. One example is the difficulty of studying hydrogen absorption in metals and its alloys. It was found that this process is accompanied by the generation of stresses inside the lattice of the metal or alloy [4, 5, 6]. The measurements performed both in the gas phase (QCMB) and under electrochemical conditions (EQCMB) show that the frequency response of the quartz oscillator during hydrogen absorption/desorption inside the metal/alloy is strongly affected by stress generation [7, 8, 9, 10, 11, 12, 13, 14, 15, 16].

Although the EQCMB results are difficult to interpret, additional information about the created stresses might be found from comparison of the results obtained with different techniques. In this work we compare the EQCMB results obtained for Pd-Ni binary alloys with those reported previously [7, 8] for the pure Pd electrode. Palladium and nickel form a series of binary alloys without a miscibility gap [17, 18]. The lattice constant of the alloy decreases monotonically with the increase of the nickel content [17, 19, 20, 21]. Under electrochemical conditions (aqueous solutions), different authors report a different threshold value from ca. 10 to ca. 25 at% of the Ni content, above which the pure  $\beta$ -phase of absorbed hydrogen is not formed [17, 22, 23, 24, 25, 26]. A different situation occurs during saturation from the gas phase, in which the pure  $\beta$ -phase is formed over the whole alloy composition range [19, 21], although with the increase of the Ni content the process becomes more endothermic [27].

### Experimental

The Pd-Ni alloys were potentiostatically deposited from a bath containing PdCl<sub>2</sub> and NiSO<sub>4</sub> dissolved in an ammonia solution [22, 28]. The composition of the deposited alloy was determined using an EDAX analyser (Röntec EDR286) coupled with a SEM microscope (LEO 435VP).

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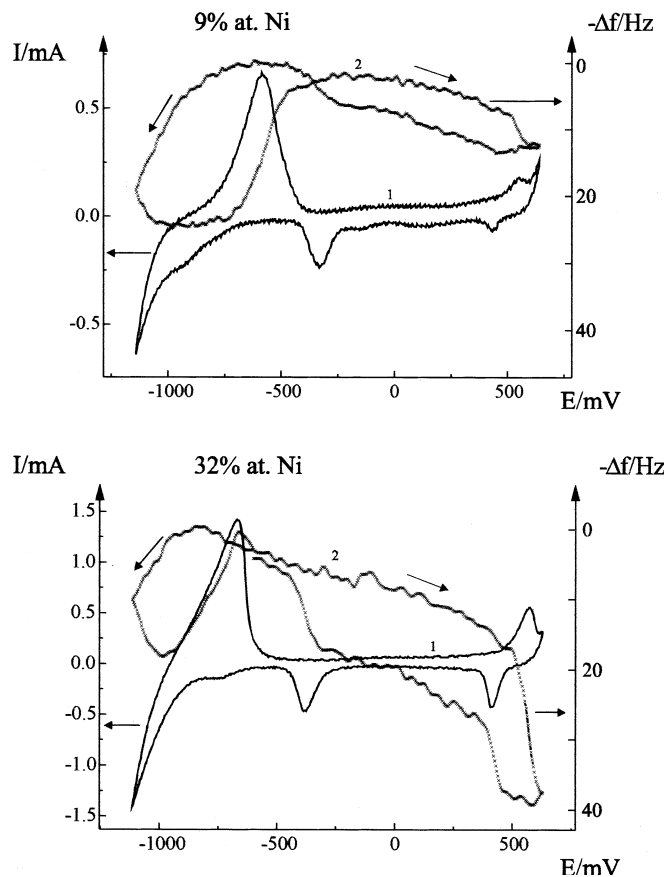
The EQCM was designed in the Institute of Physical Chemistry of the Polish Academy of Sciences (model 234) [29]. The microbalance was coupled with a frequency counter (Hewlett-Packard HP 53131A), a potentiostat (Elpan EP20A) and a generator (Elpan EG20). 5 MHz AT-cut quartz crystals covered with gold electrodes (from Phelps) were used. The microbalance was calibrated in an aqueous solution of  $\text{AgNO}_3$  (silver deposition and stripping) in the same way as in our previous work [7, 8]. The obtained calibration coefficient was close to the one calculated theoretically from the Sauerbrey equation. Hydrogen was absorbed at a constant potential. The amount of absorbed hydrogen was calculated from the charge of the hydrogen oxidation peak recorded during a subsequent CV positive scan [7, 8, 22, 30]. The hydrogen concentration is reported here as the  $\text{H}/(\text{Pd} + \text{Ni})$  atomic ratio. Solutions were deoxygenated with an argon stream. During the experiments an argon atmosphere was kept over the solution surface. The hydrogen absorption data were collected after a few cycles of hydrogen absorption-desorption in order to diminish the ageing effects. All potentials are referred to the SCE electrode. The measurements were conducted in 1 M KOH solution at room temperature.

## Results and discussion

### The electrochemical behavior of Pd-Ni alloys

Figure 1 presents chronovoltammetric curves with accompanying frequency changes for the Pd-Ni alloy electrode. The shape of the CV curve is the same as previously reported for a Pd-Ni alloy deposited on an Au wire [22] and a Pd matrix [31]. Two potential regions can be distinguished on both curves: the hydrogen adsorption/absorption and the surface oxidation regions. The shape of the frequency changes curve in the hydrogen adsorption/absorption potential region is similar to that previously reported for the pure Pd electrode [7]. During the cathodic scan, when hydrogen absorption takes place, an increase of the electrode mass is observed, which is an effect known from other microbalance studies of Pd and its alloys [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. Hydrogen desorption (oxidation) is accompanied by a simultaneous mass decrease (frequency increase). At more positive potentials, where the surface oxidation of palladium begins, a mass increase (frequency decrease) is observed. This observation agrees with previous reports about the behavior of a Pd electrode in solutions of various pH [16, 32]. The obtained gravimetric curve is a closed loop, which means that after the full potential scan encompassing the entire oxygen-hydrogen potential region there is no irreversible changes of the mass of the electrode that could be caused by the dissolution of the alloy. This observation supports previous reports about insignificant dissolution of both palladium [7, 33] and nickel electrodes [34, 35, 36] in basic solution.

A couple of sharp current peaks observed in the potential region  $E > 400$  mV can be attributed to the formation and reduction of nickel compounds with the metal in a higher valence state, probably  $\text{NiOOH}$  [37]. The shape of the gravimetric curve in this potential region is similar to that reported in the litera-



**Fig. 1.** Cyclic voltammetry (solid line, 1) and gravimetric curves (dotted line, 2) for Pd-Ni alloys with 9 and 32 at% Ni. Sweep rate  $25 \text{ mV s}^{-1}$ , 0.1 M KOH

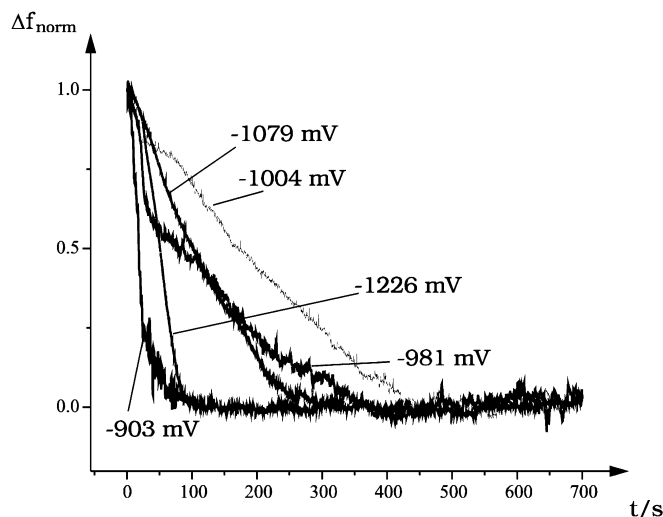
ture for the redox couple  $\alpha\text{-Ni}(\text{OH})_2/\gamma\text{-NiOOH}$  [38, 39, 40]. This result is especially interesting if we take into account that this curve was recorded after ca. 30 cycles of potential scan encompassing the entire hydrogen-oxygen region. Under the same conditions on the pure nickel electrode,  $\alpha\text{-Ni}(\text{OH})_2$  is usually irreversibly transformed to  $\beta\text{-Ni}(\text{OH})_2$  [38, 41]. It suggests that, on Pd-Ni alloys,  $\alpha\text{-Ni}(\text{OH})_2$  is perhaps more stable than in the case of the pure nickel electrode. The explanation of this phenomenon, however, needs further detailed experiments. The high-frequency change connected with the mentioned processes suggests that, similar to the Ni electrode, also in the case of the Pd-Ni alloys the processes are accompanied by the transport of alkali metal cations inside the electrode material [42, 43, 44].

Because the formation and reduction of Pd oxide is accompanied by a mass increase and decrease, respectively, we can conclude that, during the processes, species are respectively attached or removed from the electrode surface. This means that, in the process of Pd oxide formation, not only the molecules or anions originally adsorbed on the electrode surface are involved but also some additional molecules (oxygen species) from the solution.

## The kinetics of hydrogen absorption

Some information about the rate (kinetics) of the hydrogen absorption process can be extracted from the gravimetric profiles (mass or frequency versus time plots). Figure 2 presents normalized frequency changes recorded during the hydrogen absorption process in a Pd-Ni alloy. The time needed for obtaining a steady-state saturation of the electrode with absorbed hydrogen is the time during which the electrode attains a constant mass (frequency of oscillations). It is clearly seen that this time first increases with decreasing absorption potential and, after a maximum, starts to decrease. The decrease of the absorption time at negative potentials was also reported for pure Pd and Pd-Ag alloys [9, 10].

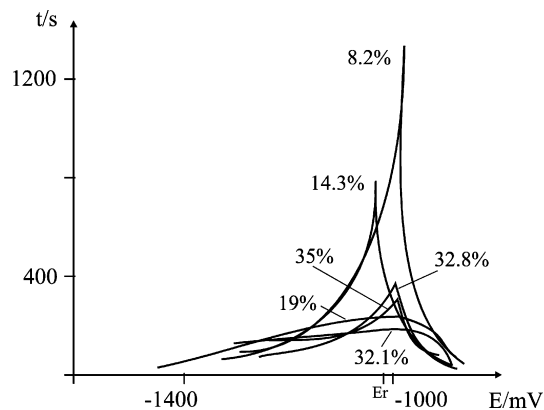
Figure 3 presents absorption time versus absorption potential relationships for various alloy compositions. It is interesting that for the alloys investigated by us the maximum is located in the vicinity of the reversible hydrogen potential. After approaching this potential value the absorption time decreases, which means that the rate of the absorption process increases. We can exclude the  $\alpha$ - $\beta$  phase transition as the reason for the acceleration of the overall absorption process because the  $\beta$ -phase starts forming at potentials positive to the equilibrium hydrogen potential, i.e. before the acceleration of hydrogen absorption is observed (Fig. 4). Moreover, the pure  $\beta$ -phase is not formed for alloys containing more than ca. 25 at% Ni [22], and the increase of the absorption rate is observed in Fig. 4 also for the alloys containing more than 30 at% Ni. According to the literature data [45], an abrupt change of the effective (i.e. calculated from the Fick equation for a continuous hydrogen concentration gradient) hydrogen diffusion coefficient does not take place in the vicinity of the potential at which the change of the absorption rate is observed, and it is a continuous function of the hydrogen content. As a result, an abrupt increase of the rate of the diffusional transport should also be ruled out. Thus, we postulate that the only physical phenomenon that can be responsible for the abrupt change of the hydrogen absorption rate is the generation of a new form of adsorbed hydrogen, namely OPD (overpotentially deposited) hydrogen. This form of adsorbed hydrogen is generated on Pd-Ni alloys [46] and participates in the hydrogen evolution reaction. This form of hydrogen can also participate in the overall hydrogen absorption process in this range of potentials (negative to the hydrogen reversible potential). The surface coverage of the Pd electrode with OPD hydrogen increases with the decrease of electrode potential [47]. Thus, the increase of the rate of hydrogen absorption observed at more negative potentials can be linked to the increasing electrode surface coverage with OPD hydrogen. The problem of the dependence of the rate of hydrogen absorption on the electrode potential will be discussed in detail in another paper concerning hydrogen absorption in Pd-Pt alloys, where this effect was also observed [48].



**Fig. 2.** Changes of the oscillation frequency of the Pd-Ni electrode with time at different potentials of hydrogen absorption. Pd-Ni alloy with 14.3 at% Ni in 0.1 M KOH. The frequency scale is normalized:  $\Delta f_{\text{norm}} = (f_0 - f) / (f_s - f_0)$ , where  $f$  is the actual (time-dependent) frequency of the electrode,  $f_0$  is the frequency of the hydrogen free electrode, and  $f_s$  is the frequency of the electrode fully saturated with absorbed hydrogen (potential-dependent value). The  $\Delta f_{\text{norm}}$  value includes a frequency shift caused by the stresses generated in the alloy during hydrogen absorption

## Interpretation of the frequency response to hydrogen absorption

The frequency change can be recalculated into mass according to the Sauerbrey equation. The number of moles of the species participating in the investigated process can be found from the respective charge, taking into account the number of the electrons exchanged by one molecule. Dividing the mass change by the number of moles, we obtain a parameter in units of grams per mole. Because more than one species can participate in the mass exchange process and additional effects, like changes of the solution density or stresses inside the metal lattice, can influence the frequency response of the oscillator, this value is further called “the apparent molar mass”,  $M_a$ , as was used in our previous work [7]. For the hydrogen absorption-desorption process the expected  $M_a$  value should be equal to 1 g/mol. The obtained values are, however, much greater than unity. A similar disagreement between the expected and the experimental values was observed previously for pure Pd [7, 8, 11, 13, 14, 15, 16, 49]. The effect was explained in terms of stresses produced inside the metal/alloy lattice during the hydrogen uptake. These stresses can strongly influence the frequency of the crystal resonance oscillation and add to or subtract from, depending on the kind of crystal, the frequency changes caused by pure mass exchange [14, 15, 50]. This effect has been explained theoretically by EerNisse [50]. The  $M_a$  value obtained by us with the same amount of absorbed hydrogen [in H/Pd or H/(Pd+Ni) units] for the Pd-Ni alloy is usually greater than for pure palladium (reported in our

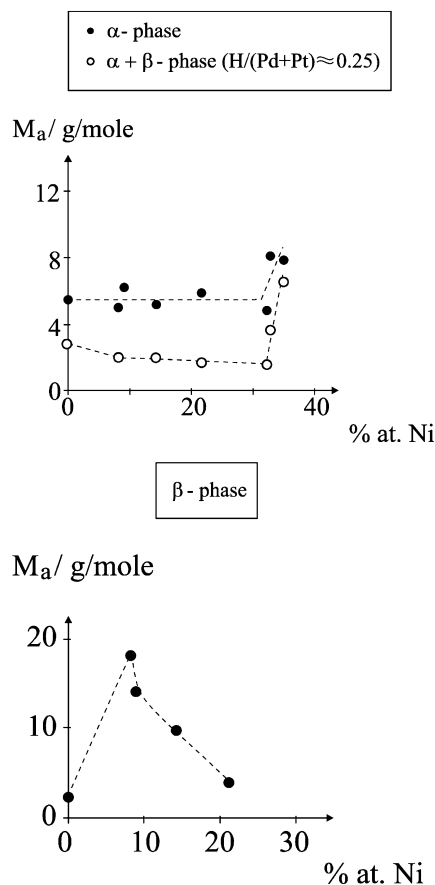


**Fig. 3.** The influence of the electrode potential on the time needed for obtaining steady state saturation with absorbed hydrogen. Alloy compositions (at% Ni) are indicated on the graph.  $E_r$  = reversible hydrogen potential; 0.1 M KOH

previous papers [7, 8]). This difference can be explained as follows. The hydrogen atom/proton located in an interstitial site can be thought of as exerting mechanical forces on the alloy lattice (Kanzaki forces). These forces increase the lattice constant and hence generate stresses in the solid [51]. The magnitude of these forces should be proportional to the change of the lattice constant ( $\Delta a_0$ ) with Young's modulus or the Poisson ratio as the proportionality coefficient. It is known that the lattice constant of the alloy decreases with an increase of the Ni content ( $a_0$ , contractive alloys) [17, 19, 20] and the value of Young's modulus or the Poisson ratio can also be expected to increase with Ni content [52].

Based on the above considerations, one can expect that upon the same increase of the lattice constant the stresses generated inside the Pd-Ni alloy should be greater than in the case of pure Pd. The increase of the experimental value of  $M_a$  with the Ni content can be underlain by the same reasons. These considerations are further supported by the results obtained for the Pd-Ag alloys for which the lattice constant increases with the Ag content (expansive alloys) [19, 53]. EQCMB results for the Pd-Ag alloys show that the  $M_a$  values are lower than in the case of pure palladium and closer to unity [9]. It is explained that the stresses generated inside the lattice with a higher value of  $a_0$  (Pd-Ag alloy) are weaker than in the case of smaller values of  $a_0$  (Pd). Thus, the influence of stresses on the microbalance response is weaker for Pd-Ag than for pure Pd. This observation clearly indicates that the deviations of the  $M_a$  values observed during hydrogen absorption are strictly related to the properties of the crystal lattice of the alloys.

The  $M_a$  values obtained for various alloy compositions with a pure  $\alpha$ -phase [ $H/(Pd + Ni) \approx 0.03$ ], a mixture of  $\alpha$ - and  $\beta$ -phases [ $H/(Pd + Ni) \approx 0.25$ ], and a pure  $\beta$ -phase [ $H/(Pd + Ni) \approx 0.65$ , only for Ni content below 25 at%] are presented in Fig. 4. The composition of the alloys was determined using EDAX analysis, as explained in the Experimental section. The amount of absorbed hydrogen was calculated from the integration



**Fig. 4.** The influence of the Pd-Ni alloy composition (at% Ni) on the values of “apparent molar mass”,  $M_a$ , for different amounts of absorbed hydrogen

of the respective oxidation peak. In consequence, the  $M_a$  values for absorbed hydrogen were calculated as the ratio  $M/N$ , where  $M$  is the mass change calculated from the Sauerbrey equation for the frequency change corresponding to the hydrogen desorption process and  $N$  is the number of moles of absorbed hydrogen from the charge of the hydrogen desorption peak. The shapes of the  $M_a$  versus %Ni curves obtained for the pure  $\alpha$ -phase and the mixture of  $\alpha$ - and  $\beta$ -phases are different from that obtained for the pure  $\beta$ -phase. In the case of hydrogen concentrations lower than in the pure  $\beta$ -phase, for a Ni content below ca. 30 at% the  $M_a$  value is constant and almost independent of the alloy composition. After approaching 30 at% Ni the “apparent molar mass” abruptly increases because of the generation of higher stresses inside the alloy. An opposite behavior is observed for the pure  $\beta$ -phase. After an initial increase, for a Ni content below 9 at% the  $M_a$  value decreases, reaching a value similar to the one observed for pure palladium. At first this is surprising if we assume that the value of  $a_0$  decreases monotonically with the increase of the Ni content in the alloy. However, as presented by Sakamoto et al. [19] for the pure  $\beta$ -phase, the relative change of the lattice constant caused by hydrogen absorption ( $\Delta a_0\%$ , corresponding to the difference of  $a_0$  of

the alloy with and without absorbed hydrogen) decreases with the increase of the Ni content, provided that the Ni concentration does not exceed 30 at%. As a result, lower stresses should be generated and the microbalance response should be close to the one caused by pure mass changes. Thus, the shape of the  $M_a$  versus %Ni dependence observed for the pure  $\beta$ -phase (for the Ni content greater than 9 at%) can be satisfactorily explained in terms of the relative lattice constant changes.

It is known that alkali metal cations (e.g. potassium) can adsorb specifically on the surface of the Pd electrode [54, 55]. Calculations based on surface coverage data show that the influence of this process on the total EQCMB response should not exceed 5% in the case of the pure  $\alpha$ -phase of absorbed hydrogen and should be below 1% for the pure  $\beta$ -phase. Thus, the influence of cation adsorption on the behavior of the EQCMB in the potential region of hydrogen absorption can be disregarded.

In our previous paper [22] we have presented a drastic decrease of the maximum hydrogen loading for thin layers of Pd-Ni alloys with a Ni content of ca. 25–30 at%. For a nickel concentration higher than 25 at% there was no generation of the pure  $\beta$ -phase. Interestingly, this threshold value is close to the nickel concentration for which an increase in the  $M_a$  value for the  $\alpha$ - and the mixture of  $\alpha$ - and  $\beta$ -phases is observed in Fig. 4. According to the above discussion, at this alloy composition, higher stresses inside the alloy lattice are generated. Generally, two factors can be responsible for the changes in the hydrogen sorption capabilities of the Pd alloys: changes of the electronic structure of the alloy (the electronic factor) and/or the geometrical factor [56, 57, 58, 59, 60, 61]. The latter effect is strictly connected with the changes in the lattice constant of the alloy (different volume of the interstitial site) and/or changes of the elastic properties of the alloy. In the case of pure nickel it was suggested previously [56, 57] that the main reason for poorer hydrogen solubility is the smaller lattice constant compared to palladium. Thus, the ingress of the same amount of absorbed hydrogen requires additional energy for increasing the volume of the interstitial site. The results presented in Fig. 4 suggest that the intake of even a very small amount of hydrogen, as in the pure  $\alpha$ -phase, is subject to a very high resistance for alloys containing more than 25 at% Ni. Thus, we can conclude that the decrease of the hydrogen loading at higher nickel content is mainly because of the stresses generated inside the alloy lattice. This reasoning can be translated into the language of thermodynamics. The chemical potential of an absorbed hydrogen atom (proton) can be represented by a sum of two terms: the pure chemical term and the term reflecting the existence of the stresses inside the metal/alloy lattice [4, 62, 63]. An analogous expression must be considered for the energetic effects of absorption,  $\Delta G$ . The increase of the stresses generated inside the alloy with the increase of the nickel content should increase the free energy term

describing the influence of the stresses. This means that the increase of the stresses raises the demand for additional energy during the hydrogen ingress into the alloy lattice. As a result, the overall process of hydrogen absorption should be more endothermic. This agrees with the calorimetry data obtained during saturation of Pd-Ni alloys from the gas phase [64, 65]. It is interesting that, at a similar nickel content (ca. 25–30 at%), other physical properties of the Pd-Ni alloys also change significantly, e.g. the electromagnetic properties [66, 67, 68, 69] or the electronic structure [68].

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## Conclusions

The following conclusions can be drawn:

1. The EQCMB response of the Pd-Ni electrode recorded during the hydrogen absorption/desorption process is strongly affected by the stresses generated inside the alloy lattice. This effect is dependent on the amount of absorbed hydrogen (the pure  $\alpha$ - and  $\beta$ -phases or the mixture of both of them) and on the alloy composition.
2. The EQCMB data suggest a greater stability of  $\alpha$ -Ni(OH)<sub>2</sub> on Pd-Ni electrodes than on pure Ni. The dissolution of Pd-Ni alloys during cyclic polarization in basic solution (0.1 M KOH, room temperature) is negligible.
3. The sharp decrease of the Pd-Ni alloy capability for hydrogen absorption is related to the increase of the stresses generated inside the alloy, as recorded with EQCMB. This suggests that the main reason for the decrease of the hydrogen absorption capability with the increase of the Ni content in the Pd-Ni alloy is the geometrical factor connected with changes of the lattice constant.
4. The rate of hydrogen absorption depends on the electrode potential. The increase of the rate of absorption at potentials lower than the reversible hydrogen potential is probably connected with generation of overpotentially adsorbed (OPD) hydrogen.

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