
HYDROGEN-INDUCED STRESSES IN PALLADIUM-RUTHENIUM ALLOYS*

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Abstract: Stresses induced by hydrogen electroabsorption in Pd-rich Pd-Ru alloys were studied with the use of an Electrochemical Quartz Crystal Microbalance. The total frequency shift was found to be much larger than the frequency shift calculated on the basis of the Sauerbrey equation. The mass frequency shift was subtracted from the total frequency shift to isolate the frequency change due to the formation of the stresses in the alloys lattice. The magnitude of the stresses in the Pd-Ru alloys lattice depends on the amount of absorbed hydrogen (H/M) and the sample composition. The slope of stress-related frequency change vs. H/M plots varies with hydrogen to metal atomic ratio in the whole range of the absorbed hydrogen concentrations studied. The stresses which accompany the absorption process play an important role in the hydrogen absorption/desorption hysteresis effect.

1. Introduction

A constant demand for energy stimulates the search for new power sources. The new power source should be economically advantageous and, above all, environmentally friendly. The use of hydrogen as an easily-available, high-energy, non-toxic energy carrier seems to be a good solution (Schlapbach and Züttel, 2001). However, due to a high risk of explosion and other storage problems hydrogen is not commonly used. Fortunately, there is a completely safe way of storing hydrogen— metal hydrides. In addition, metal hydrides can also be used in other safe devices, such as hydride batteries (Kleperis et al., 2001) or supercapacitors (Łukaszewski, Hubkowska, Koss and Czerwiński, 2012).

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It has been known for 150 years that palladium can absorb large amounts of hydrogen (Lewis, 1967). However, pure palladium cannot be widely used due to its high weight, expensiveness and the existence of hydrogen absorption/desorption hysteresis which has adverse effects when commercial use is considered. On the other hand, palladium and its alloys constitute an important model of a metal-hydrogen system used for understanding the processes of hydrogen sorption in metallic materials. Precise knowledge of the mechanisms of hydrogen absorption and desorption will help to develop advanced materials for commercial use in industry.

Addition of a noble metal to Pd can improve hydrogen absorption parameters, such as the potential of hydrogen oxidation or the size of the absorption/desorption hysteresis loop. On the other hand, there is an unfavorable effect related to the decrease of the amount of absorbed hydrogen as a result of Pd alloying with a non-absorbing hydrogen metal. However, there are two types of Pd binary alloys which do not have this effect – Pd-Rh (Koss et al., 2011) and Pd-Ru (Hubkowska et al., 2013).

Palladium-ruthenium alloys are extremely important due to the fact that alloys with low Ru content exhibit the highest capability towards hydrogen absorption of all other binary Pd alloys. Moreover, a Pd-Ru alloy with an atomic Pd content of ca. 99 % is able to absorb ca. 15 % more hydrogen than pure Pd (Hubkowska et al., 2013). It is connected with the fact that ruthenium possesses some free electron states around the Pd Fermi level.

The electrochemical quartz crystal microbalance (EQCM) is one of the most interesting methods used in hydrogen absorption in solid electrodes under in-situ electrochemical conditions. In EQCM it is possible to simultaneously record frequency changes accompanying electrode processes and electrochemical signals, such as current and potential. The EQCM response is determined by several factors (Butry and Ward, 1992). In the case of hydrogen electrosorption the most important factors are: electrode mass changes resulting from changes in the amount of electrosorbed hydrogen and the stresses in the crystal lattice of the absorbing material induced by hydrogen absorption (Bucur and Flanagan, 1974). Therefore, the following equation is valid:

$$\Delta f = \Delta f_{mass} + \Delta f_{stress} \quad (1)$$

where Δf is the total measured frequency shift, Δf_{mass} is the contribution due to mass change and Δf_{stress} is the contribution due to stress generation. The frequency shift due to pure mass changes is described by the Sauerbrey equation (Sauerbrey, 1959):

$$\Delta f = -\frac{2 \cdot f_0^2}{A \cdot \sqrt{\mu_q \cdot \rho_q}} \cdot \Delta m \quad (2)$$

- f_0 – resonance frequency of the resonator,
- Δm – change of mass which causes change of f_0 ,
- μ_q – quartz transverse elasticity modulus: $2.95 \cdot 10^{11} \text{ g} \cdot \text{cm}^{-3}$,
- ρ_q – quartz density: $2.65 \text{ g} \cdot \text{cm}^{-3}$,
- A – resonator cross sectional area.

Equation (2) can be used for recalculating the frequency shift into mass units and



vice-versa. In the case of electrochemical experiments described in this paper the mass of the absorbed hydrogen can be determined on the basis of the charge consumed in the process of electrochemical absorption with assumed hydrogen absorption efficiency equal to 100 %. Introducing the mass of absorbed hydrogen into equation (2) makes it possible to calculate the frequency shift due to pure mass changes, Δf_{mass} . Knowing Δf_{mass} one can easily calculate the stress contribution, Δf_{stress} , using equation (1).

2. Experimental design

All experiments were performed at room temperature in 0.5 M H_2SO_4 solutions which were deoxygenated using an Ar stream. An $\text{Hg}|\text{Hg}_2\text{SO}_4|0.5 \text{ M } \text{H}_2\text{SO}_4$ and a Pt gauze were used as counter and reference electrodes, respectively. 10 MHz AT-cut Au (or Pt)-plated quartz crystals were used in the electrochemical quartz crystal microbalance (EQCM) experiments. Pd and Pd-Ru alloys were deposited electrochemically on the Au/Pt-plated surfaces of the crystals from baths containing various volumetric ratios of aqueous solutions of RuCl_3 (0.32 M) and PdCl_2 (0.11 M) dissolved in 1 M HCl. The thickness of the electrodeposited layers was ca. 0.1 – 0.3 μm . The EQCM calibration constant determined using Pd deposition and adopted in further calculations was equal to 1.2 $\text{ng}\cdot\text{Hz}$ and was close to the theoretical value of 1.14 $\text{ng}\cdot\text{Hz}^{-1}$ calculated from the Sauerbrey's equation (1). The bulk composition of the alloys was determined by EDX measurements. The Quantax 400 energy dispersive X-ray spectrometer (Bruker) was used in the EDX measurement. Electron beam energy used for X-ray excitation was 15 keV and spectrum acquisition time was ca. 120 s. For quantitative EDX data processing a standardless procedure was applied with the use of software supplied by Bruker. Energy calibration was performed with a pure Cu sample. Efficiency of the alloys deposition was determined on the basis of Atomic Emission Spectroscopy measurements.

3. The influence of hydrogen absorption/desorption process on the magnitude of stresses in Pd and Pd-Ru alloys lattice

Fig. 1 shows the dependence of the total frequency change on the amount of electroadsorbed hydrogen, the latter expressed as hydrogen to metal atomic ratio, H/M , where $\text{M} = \text{Pd}$ or $\text{Pd} + \text{Ru}$. Data (solid lines) was obtained in a chronoamperometric absorption experiment: absorption of hydrogen took place when -0.026 V was applied to the working electrode; desorption of hydrogen occurred at 0.374 V. Application of a sufficiently low value of the potential (-0.026 V) ensured the formation of β -phase (hydride) or α -phase (solid solution), whereas a sufficiently high value of the potential (0.374 V) led to hydrogen desorption – at such a high value of potential no hydrogen was present in/on the electrode. In Fig. 1 one can see two types of lines: solid lines derived from the experiment and dashed lines which express theoretical frequency changes calculated on the basis of the Sauerbrey equation (see the introduction).

The Sauerbrey equation can be used to calculate the frequency shift due to pure mass changes only. The experimental mass changes due to hydrogen absorption can be calculated from hydrogen absorption/desorption charge (Q) on the basis of Faraday's



law. Thus, the Sauerbrey equation (2) can be rewritten as equation (3):

$$\Delta f_{mass} = -\frac{Q \cdot M}{F \cdot C} \quad (3)$$

Q – hydrogen absorption/desorption charge,

M – hydrogen molar mass,

F – Faraday's constant,

C – experimental calibration constant: $1.2 \text{ ng} \cdot \text{Hz}^{-1}$.

Assuming that total frequency change originates only from mass change and the magnitude of the stresses generated during hydrogen sorption, it is possible to isolate the frequency shift due to the stress formation in Pd and Pd-Ru alloys crystal lattice. In Fig. 2 the dependence of the stress-related frequency changes on the amount of absorbed/desorbed hydrogen is presented. An analysis of Δf_{stress} vs. H/M plots shown in Fig. 2 indicates that for H/M > 0.1 three main sections of the plots can be distinguished. Thus, for pure Pd a rapid linear drop of frequency is visible in regions of α -phase and α , β -phase coexistence, up to H/M of ca. 0.2. In contrast, in the range of H/M = 0.2 – 0.55 a slight increase followed by a small decrease of the frequency can be noted. Three sections of the Δf_{stress} vs. H/M curves can be

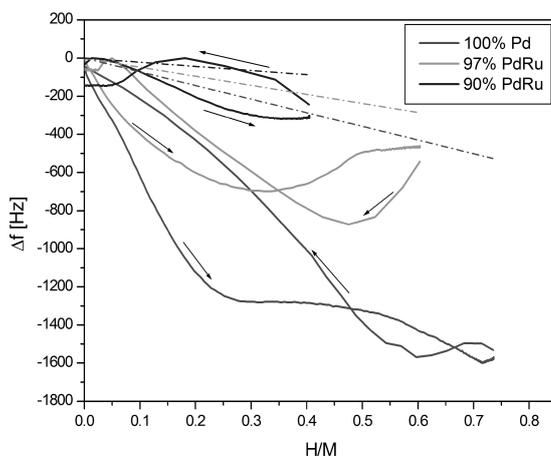


Fig. 1. Dependence of the total frequency changes on the amount of electroadsorbed hydrogen (expressed as a hydrogen to metal atomic ratio) in Pd and Pd-rich Pd-Ru alloys during chronoamperometric absorption (-0.026 V) and desorption (0.374 V); dashed lines – theoretical dependence calculated on the basis of the Sauerbrey equation (see equation (2)); arrows show the direction of changes in the hydrogen content.



distinguished also for the hydrogen desorption: an initial small frequency increase for the highest values of H/M; a small frequency decrease for H/M range of ca. 0.68 – 0.60 and almost linear frequency increase for lower values of H/M. The general shape of Δf_{stress} vs. H/M/ plots obtained for 97 % Pd-Ru is quite similar to the one observed for pure Pd, they differ with respect to the values of the slopes. On the other hand, for the 90 % Pd-Ru sample both the minimum and the maximum on, respectively, absorption and desorption curves are not visible. It should be noted that various sections of Δf_{stress} vs. H/M/ plots with different slopes (presented in Fig. 2) cannot be directly linked with a certain form of absorbed hydrogen, in agreement with the results reported for other hydrogen absorbing Pd-noble metal alloys (Grdeń et al., 2006). Moreover, the magnitude of the stresses depends on the composition of the alloy. The maximum value of the frequency change due to the formation of the stresses in a metal/alloy crystal lattice equals to ca. 1200 Hz for pure Pd and decreases with Ru addition. Hence, for the 97 % Pd-Ru sample the maximum value of Δf_{stress} is equal to ca. 800 Hz while for 90 % Pd-Ru it reaches only ca. 300 Hz. The value of the stress-related frequency change obtained for pure Pd is close to this reported in the literature (Łukaszewski and Czerwiński, 2006). It should be noted that the shape of Δf_{stress} vs. H/M curves for absorption and desorption do not coincide, which implies that stress distribution in Pd and Pd-Ru samples is different during absorption and desorption.

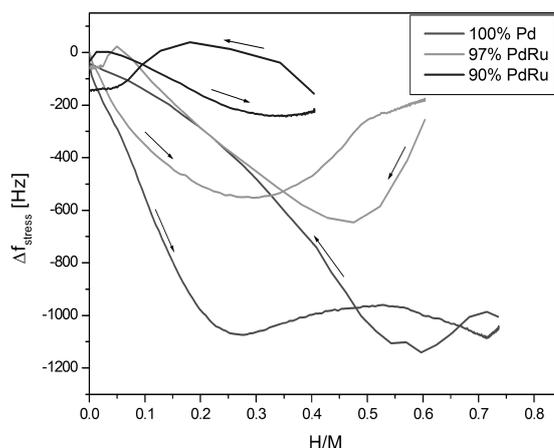


Fig. 2. Dependence of the stress-related frequency changes, Δf_{stress} , on the amount of electroadsorbed hydrogen (expressed as a hydrogen to metal atomic ratio) in Pd and Pd-rich Pd-Ru alloys during chronoamperometric absorption (-0.026 V) and desorption (0.374 V).

The increase/decrease of the frequency observed for the Pd-Ru sample for low values of the hydrogen to metal ratio ranging from H/M = 0 to ca. H/M = 0.1



cannot be attributed to the generation of the stresses inside the alloy lattice. For this range of H/M values the departure from theoretically predicted frequency shift is caused by adsorption/desorption of sulfate/bisulfate ions on/from the surface of the electrode. Prior to applying the potential of the hydrogen sorption (-0.026 V) the electrode was polarized at 0.374 V. It is known (Grdeń et al., 2008) that adsorbed sulphate/bisulphate anions are present at the electrode surface at the latter potential value. When the potential of the hydrogen sorption (-0.026 V) is applied, the charge of the electrode surface becomes more negative and the first process which occurs is the one connected with anions desorption. As a result, a frequency increase is observed immediately after the potential jump to -0.026 V. This frequency increase is followed by a frequency decrease due to the bulk hydrogen absorption, the process which is slower than anions desorption. Subsequently, after application of 0.374 V to the electrode containing absorbed hydrogen, the first process to occur is an oxidative removal of the hydrogen from the electrode, which is connected with a frequency increase. A frequency decrease observed at 0.374 V after completing the hydrogen desorption can be attributed to re-adsorption of the anions. Thus, the latter process starts when almost all hydrogen is desorbed. The described behavior is not visible for pure Pd. Several explanations for this difference between Pd and the alloys can be proposed, for example, it may be suggested that the surface coverage with adsorbed anions is lower for Pd surface compared to the Pd-Ru sample surface. On the other hand, the discussed effect can be attributed to the fact that the studied Pd samples were thicker than Pd-Ru alloy samples and, in case the of Pd the surface processes contribute less to the overall frequency change. Finally, the surface of Pd-Ru alloys is rougher than the surface of pure Pd samples which might affect the surface ability towards the anions adsorption.

The magnitude of the stresses can be also expressed as an „apparent molar mass” and calculated according to the following equation:

$$M_a = -\frac{\Delta f \cdot C \cdot F}{Q} \quad (4)$$

M_a – „apparent molar mass” of absorbed hydrogen,

Δf – total frequency shift,

Q – hydrogen absorption/desorption charge,

F – Faraday’s constant,

C – experimental calibration constant: 1.2 ng·Hz⁻¹.

The deviation of the „apparent molar mass” from the real molar mass of absorbed hydrogen (1 g·mol⁻¹) can be treated as an indicator of the influence of the lattice stresses accompanying hydrogen absorption on the frequency response of EQCM during hydrogen electrosorption. For pure Pd and 97 % Pd-Ru alloy the deviation of the apparent molar mass from the value of 1 g·mol⁻¹ reaches the highest level for H/M below 0.1 and M_a decreases with H/M increase. In the case of the 97 % Pd-Ru sample the lowest value of M_a is close to 1 g·mol⁻¹ (for H/M = 0.6), whereas for pure Pd the minimum value of M_a is ca. 3 g·mol⁻¹. For the 90 % Pd-Ru sample the M_a value is close to the unity when H/M ratio is ca. 0.05, for higher values of



H/M the M_a goes through the maximum ($M_a = 5 \text{ g}\cdot\text{mol}^{-1}$) when H/M equals ca. 0.25 after that a decrease of the M_a value is observed with increasing H/M value. For the maximum value of H/M equal to 0.4 the M_a is close to ca. $4 \text{ g}\cdot\text{mol}^{-1}$. The variation of the „apparent molar mass” of absorbed hydrogen plotted as a function of hydrogen-to-metal atomic ratio gives one information about the relation between various phases of absorbed hydrogen on the magnitude of the stresses in alloy crystal lattice. In Fig. 3 it is clearly visible that when hydrogen is absorbed in α -phase (for Pd and 97 % Pd-Ru alloy) the deviation of the „apparent molar mass” from the real molar mass of hydrogen of $1 \text{ g}\cdot\text{mol}^{-1}$ is greater than in the case of hydrogen absorbed in β -phase. When hydrogen is absorbed in α -phase the charge of absorbed hydrogen is relatively small and any change of the total frequency causes a meaningful change in the apparent molar mass. A completely different behavior can be seen for the 90 % Pd-Ru alloy. Amongst the analyzed electrodes the 90 % Pd-Ru alloy is characterized by the lowest magnitude of stresses accompanying hydrogen absorption, mostly because of the fact that only the α -phase of absorbed hydrogen is formed in this sample.

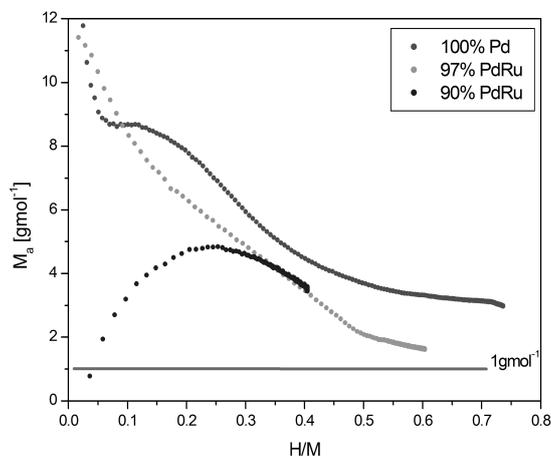


Fig. 3. Apparent molar mass of electroadsorbed hydrogen as a function of the hydrogen content expressed as a hydrogen-to-metal atomic ratio (absorption in a chronoamperometry experiment; potential step between 0.374 V and -0.026 V).

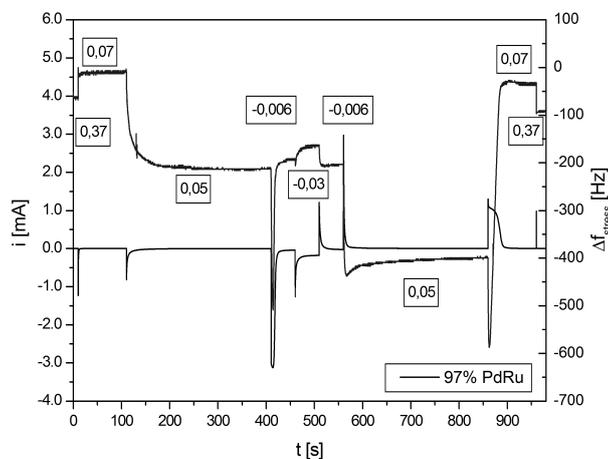


Fig. 4. Chronoamperograms and stress-related frequency changes for the 97 % Pd-Ru electrode during potential steps in the coexistence of α and β -phase (the area of hysteresis). Black line – chronoamperometry signal; blue line – frequency change. Applied potential values (in volts) are presented in the boxes.

4. The stresses accompanying hydrogen absorption/desorption hysteresis effect in Pd-Ru alloys

Fig. 4 and Fig. 5 present a chronoamperometry (current vs. time) signal and stress-related frequency changes recorded during a multi-step experiment. The first part of the experiment is connected with hydrogen absorption. The following values of the potentials applied to the electrode were selected on the basis of an analysis of H/M vs. potential dependences: (1) the value of potential where no hydrogen is absorbed, (2) hydrogen absorbed in α and β -phase, (3) hydrogen absorbed in β -phase (for a Pd-rich sample). Measurement starts from the potential where the electrode is free of both absorbed and adsorbed hydrogen, i.e. 0.37 V. However, at 0.37 V sulphate/bisulphate anions are adsorbed on the electrode surface, as discussed in the previous paragraph. Thus, the decrease of frequency observed at 0.37 V should be attributed to anions adsorption and not to hydrogen adsorption/absorption. In relation to the described phenomenon the potential value of 0.07 V should be selected as a starting point ($\Delta f_{stress} = 0$). In 0.07 V no stresses caused by hydrogen sorption occur in the Pd-Ru alloy material (H/M of ca. 0). In Fig. 4 one can see that application of 0.05 V leads to a rapid decrease in frequency which is followed by frequency stabilization indicating that no more hydrogen can be dissolved in the 97 % Pd-Ru alloy at 0.05 V. The subsequent potential change to -0.006 V results in an initial sharp decrease of Δf_{stress} , followed by an increase of its value with final stabilization at the value



very similar to the one for 0.05 V. A slight increase of Δf_{stress} is also visible for -0.03 V. It indicates that less stress is generated in the sample where hydrogen is only in β -phase compared to the region of α - β -phase coexistence. The second part of the experiment is connected with hydrogen desorption, where reverse direction of potential changes was applied. One can note in Fig. 4 that for 0.05 V the value of the stress-related frequency change obtained in absorption experiment is different than the one calculated for the desorption. This potential value is located in the region of hysteresis between $\alpha \rightarrow \beta$ (absorption) and $\beta \rightarrow \alpha$ (desorption) phase transitions for 97 % Pd-Ru. For the 97 % Pd-Ru sample the difference in magnitude of stresses for absorption and desorption processes equals ca. 200 Hz. An analogous experiment was carried out for the 90 % Pd-Ru sample where no hysteresis between hydrogen absorption and desorption was observed. The potential values for the 90 % Pd-Ru sample were selected in the same way as for the 97 % Pd-Ru sample. In Fig. 5 it can be seen that at 0.024 V, i.e. at the potential where an abrupt increase of hydrogen content is observed (Hubkowska et al., 2013) the magnitude of the stresses in absorption and desorption experiment is the same. Results showed in the Fig. 4 and Fig. 5 confirm the fact that the lattice stress accompanying hydrogen absorption plays a very important role in the hysteresis phenomenon in Pd-Ru alloys.

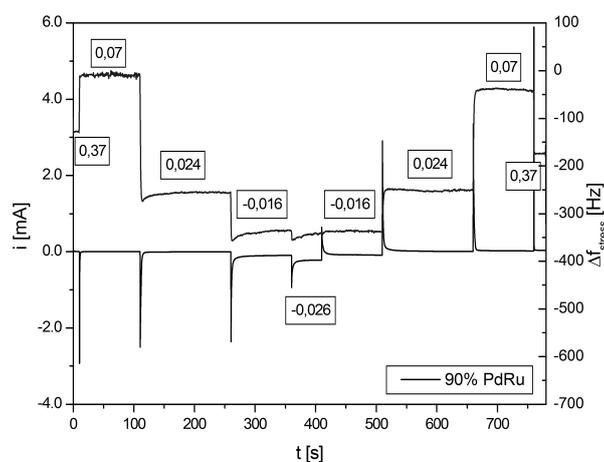


Fig. 5. Chronoamperograms and stress-related frequency changes for the 90 % Pd-Ru electrode during potential steps in the α -phase existence region (no hysteresis effect). Black line – chronoamperometry signal; blue line – frequency change. Applied potential values are presented in the boxes.



5. Conclusions

The total frequency shift recorded during hydrogen electrosorption in Pd-Ru alloys is affected by stresses generated in the alloy crystal lattice. Moreover, the magnitude of the stresses in Pd-Ru alloys lattice depends on the amount of absorbed hydrogen (H/M) and sample composition:

- the slope of stress-related frequency change vs. H/M plots vary in the whole range of hydrogen-to metal atomic ratio and cannot be attributed to any specific form of absorbed hydrogen;
- the magnitude of the stresses is the highest for pure Pd and decreases with increasing Ru content.

Stresses play an important role in hydrogen absorption/desorption hysteresis effect. Furthermore, total frequency shift and stress-related frequency shift in electrodeposited Pd-Ru alloys can be affected by the electrolyte ions adsorption/desorption process.

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