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Temperature influence on hydrogen sorption in palladium limited-volume electrodes (Pd-LVE)

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Abstract The effect of temperature on hydrogen and deuterium electrosorption into a palladium LVE (limited-volume electrode) has been investigated. A decrease in hydrogen capacity (H/Pd ratio) with increasing temperature has been observed. Temperature strongly influences the plots of measured H(D)/Pd values vs. potential scan rate. In addition, hydrogen absorption was found to be dependent on the composition of the surrounding electrolyte solution. These results have confirmed the hypothesis that two different mechanisms of hydrogen desorption from the palladium electrode take place, namely electrochemical oxidation and non-electrochemical recombination. Further, the ratio between the rate constants for these two processes has been found to change with temperature.

Keywords Deuterium electrosorption · Hydrogen electrosorption · Palladium

Introduction

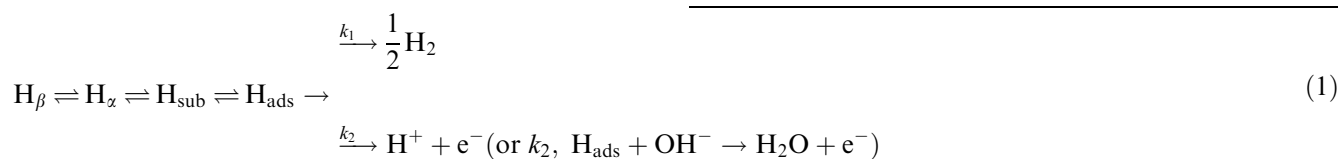
Recent investigations into a palladium-hydrogen system detected unusual behavior of hydrogen electrochemically absorbed in palladium. It was found that the amount of

hydrogen oxidized electrochemically during cyclic voltammetry depends on the potential scan rate [1, 2, 3, 4]. With an increase in the potential scan rate (v) the measured H/Pd value first increases to a maximum and then decreases. This phenomenon was explained on the basis of the existence of dual mechanisms of hydrogen desorption [1, 2, 3, 4, 5]. Hydrogen can be desorbed from Pd and other hydrogen-absorbing materials by either electrochemical reaction and/or a non-electrochemical recombination process. The former process proceeds via the Volmer reaction, while in the latter process absorbed hydrogen is removed from the electrode by participation in the Tafel reaction, i.e. $2H_{\text{abs}} \rightarrow 2H_{\text{ads}} \rightarrow H_2$ [6]. The relative importance of each mechanism in the overall hydrogen desorption process depends on the potential scan rate. The shape of measured H/Pd vs. v plots was strongly influenced by the thickness of the Pd layer as well as by the electrolyte composition [1, 2, 3, 4]. Generally, the smaller the Pd layer thickness, the greater the amount of absorbed hydrogen. This effect was explained on the basis of the existence of a layer of hydrogen dissolved just beneath the surface, i.e. “subsurface hydrogen.” The hydrogen dissolved in this layer behaves in a different way than that dissolved in the bulk of the metal. The differences concern both the concentration and the thermodynamics of the generation of this form of hydrogen. According to the literature [7, 8, 9, 10, 11, 12, 13, 14], the thickness of the layer of subsurface hydrogen varies from one layer to a value of 200–500 Å. This thickness as well as the concentration of hydrogen dissolved in the subsurface layer depend on the adsorption of ions and poisons on the electrode surface [11, 13, 14]. This observation indicates that the existence of a subsurface layer of absorbed hydrogen cannot be the effect of the existence of unique surface morphology, e.g. a Pd-black-like structure. Thus, subsurface hydrogen can be treated as a separate phase (H_{sub}), similar to the α and β phases of absorbed hydrogen. The following diagram presents the general scheme of the hydrogen absorption/desorption process with participation of “subsurface hydrogen” [2, 3]:

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The process of hydrogen desorption can be controlled either by the rate of the surface reaction or by bulk diffusion, depending on the electrode polarization, while the amount of hydrogen desorbed with charge transfer depends on the relative rate of the two processes described above, i.e. k_1/k_2 . The values for k_1 and k_2 might represent a function of the diffusion coefficient (for diffusion as the rate-determining step) or they might be equal to classical rate constants (for desorption limited by the surface process). The temperature should then influence both values in a different manner, hence changing the k_1/k_2 ratio.

In this paper, we report results from a study of the influence of temperature on hydrogen sorption in palladium limited-volume electrodes (Pd-LVEs).

Experimental

All experiments were performed in 0.1 M LiOH and 0.5 M H₂SO₄ solutions prepared using high purity water (Millipore or 99.9% D₂O) and pure LiOH or H₂SO₄ (BDH). It has been shown [15, 16] that at this D/H ratio in electrolyte solution [D/(H + D) = 0.991] the enrichment of absorbed hydrogen with the light isotope is negligible. A platinized platinum foil was used as an auxiliary electrode. The Ag/AgCl electrode was used as the reference electrode, but all potentials in the paper are referred to RHE at room temperature (25 °C).

The working electrode was a gold wire (99.9%, diameter = 0.5 mm) covered with palladium. Palladium was electrochemically deposited at a constant current density ($j = 1 \text{ mA cm}^{-2}$) in an acidic (4 M HCl) PdCl₂ (0.1 M) solution using a Pd wire as the anode. The length of the part of the wire covered with the Pd deposit was 1 cm. The whole Pd deposit was immersed in solution without any contact with gas above the solution level. The working cell was equipped with a water jacket and the temperature controlled in the range 273–361 K via a thermostat (WLM U2C, Germany). The LV electrodes used in this work were obtained under identical conditions, i.e. the geometry of the matrix electrode (gold) and the deposition parameters. The roughness factor of the electrodes used was calculated on the basis of the charge of the reduction of the surface oxides, according to the method described elsewhere [17, 18]. The obtained roughness factor values were ca. 10, with the differences between the electrodes studied not greater than 20%.

At the beginning of each experiment, the old palladium layer was dissolved in concentrated nitric acid and a new palladium deposit was plated on the gold electrode. During the experiments the palladium electrode was first held at a constant potential ($E_{\text{abs}} = -0.26 \text{ V vs. RHE}$) for 30 min in basic solution and 5 min ($E_{\text{abs}} = -0.13 \text{ V vs. RHE}$) in acidic solution to complete the electrode saturation with hydrogen [15, 19]. This time was sufficient for the saturation of all the electrodes used. The potential values were chosen to ensure full saturation of the electrodes with absorbed hydrogen in both solutions studied. To avoid the influence of ageing, the electrode was subjected to a few tens of cycles of hydrogen absorption and desorption at the beginning of the measurements.

The amount of absorbed hydrogen was calculated from the charge obtained from the integration of the anodic peak currents of the cyclic voltammogram taken after the saturation of the palladium electrode with hydrogen. CV curves were recorded at a potential sweep rate of 20 mV s^{-1} unless indicated otherwise. It was stated before [5] that the amount of hydrogen adsorbed and absorbed in/on the palladium electrode calculated from integration of the hydrogen oxidation peak is not influenced by the oxidation of hydrogen gas formed during electrode polarization at potentials in the hydrogen evolution region. The thickness of the deposited Pd layer ranged between $0.2 \mu\text{m}$ to $1.6 \mu\text{m}$ (1000–8000 Pd layers).

The purity of the solutions used was checked using the platinum electrode. Both continuous cyclic voltammetry and CV curves recorded after a long period of cathodic polarization show that the solutions were free from impurities. This method also confirmed the effectiveness of solution deoxygenation. The amount of hydrogen adsorbed and absorbed in/on the palladium electrode calculated from the oxidation peak is not influenced by the evolution of hydrogen gas during the electrode polarization at applied potentials [3].

The measurements were performed with a CH Instruments electrochemical analyzer, model 604 (Cordova, USA), coupled with an IBM compatible computer.

Results and discussion

Temperature effect with continuous cycling of the palladium electrode

Figure 1 presents cyclic voltammograms of the Pd electrode recorded at a sweep rate of 0.01 V s^{-1} in 0.5 M H₂SO₄ in the temperature range from 273 to 341 K. The thickness of the palladium electrode was ca. $1.6 \mu\text{m}$. The electrode potential was swept continuously without any interruption at any potential value for complete electrode saturation with hydrogen. An increase in temperature shifted the peak for oxidation of absorbed hydrogen to more negative potential values. Moreover, the separation between peaks for hydrogen sorption and desorption decreased with increasing temperature. This effect suggests an increase in the reversibility of the hydrogen absorption/desorption process. Both these effects are due to the influence of temperature on the diffusion of hydrogen in palladium and the rate of electrochemical reaction. These results are in agreement with conclusion of Zhang et al. [20] that an increase in temperature accelerates hydrogen absorption into palladium under both galvanostatic and potentiostatic charging conditions.

Influence of potential scan rate

A study of the influence of temperature on the amount of electrode-sorbed hydrogen/deuterium (maximum

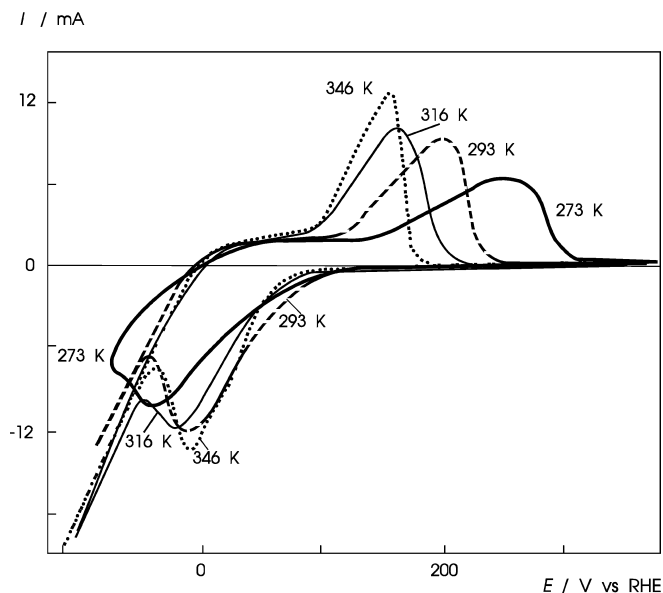


Fig. 1 Cyclic voltammograms, at 0.01 V s^{-1} , of a limited-volume (1.6 m thickness) palladium electrode (Pd-LVE) in $0.5 \text{ M H}_2\text{SO}_4$ at various temperatures. The electrode potential was not stopped at any value for Pd saturation with hydrogen

saturation) was performed for both hydrogen isotopes studied with various Pd layer thicknesses, various electrolyte solutions and for various potential scan rates for hydrogen electrodesorption. The hydrogen and deuterium concentrations in palladium are shown as a H(D)/Pd ratio. For the experiments presented in Figs. 2, 3, 4, 5 the electrode was conditioned at a negative potential (5 or 30 min, according to the procedure described in the Experimental section) prior to the potential sweep to ensure full saturation of the electrode with hydrogen and deuterium. Then the electrode potential was swept in the anodic direction to 0.6 V vs. RHE and the hydrogen (deuterium) oxidation current peak was recorded. One can see that for both hydrogen isotopes an increase in temperature is connected with a decrease in the concentration of absorbed hydrogen (deuterium) in palladium

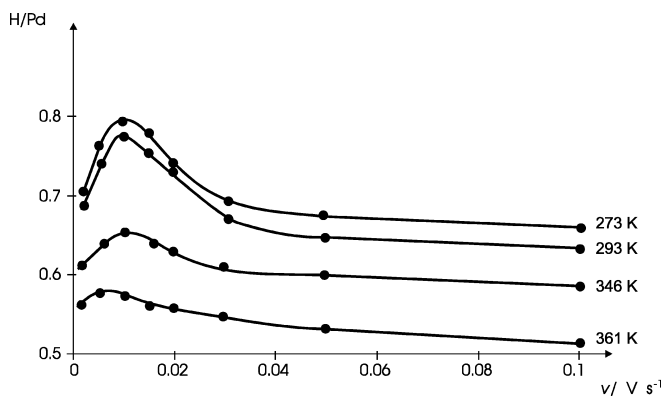


Fig. 2 Influence of the potential scan rate on H/Pd ratios at various temperatures. $0.5 \text{ M H}_2\text{SO}_4$; thickness of Pd layer ca. $1.6 \mu\text{m}$

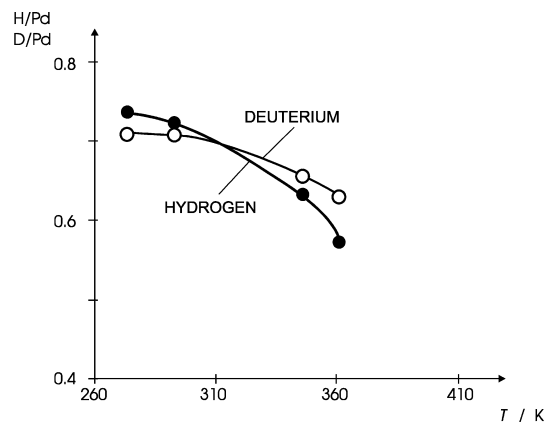


Fig. 3 Influence of the temperature on the amount of absorbed hydrogen and deuterium. $0.5 \text{ M H}_2\text{SO}_4$; absorption potential -0.1 V vs. RHE

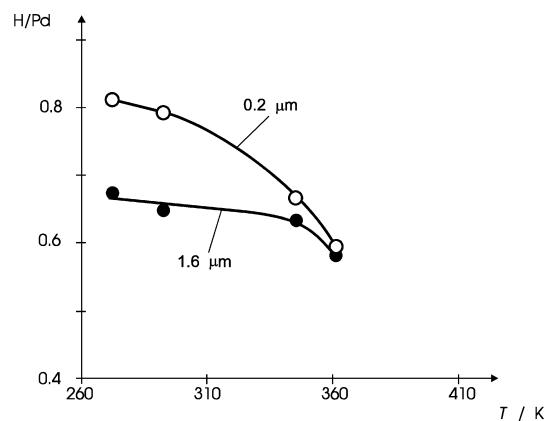


Fig. 4 The influence of the temperature on the amount of hydrogen absorbed from basic solution in samples with various thickness. 0.1 M LiOH ; absorption potential -0.26 V vs. RHE

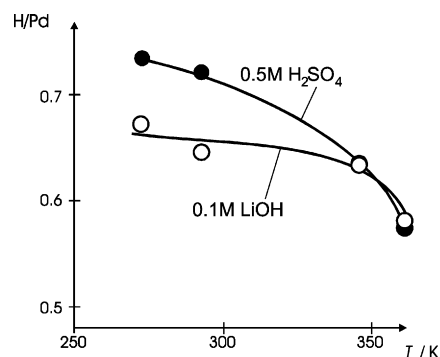


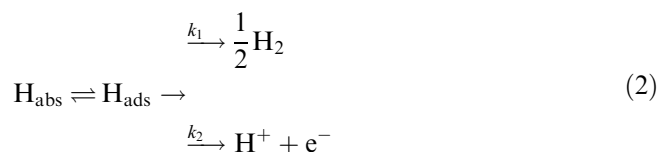
Fig. 5 Influence of the temperature on the amount of hydrogen absorbed from various electrolyte solutions. Pd layer thickness ca. $1.6 \mu\text{m}$

[H(D)/Pd value]. This effect is in agreement with thermodynamic data [21, 22, 23, 24, 25]. The decrease in concentration of hydrogen and deuterium in palladium with an increase in temperature is a general feature

characteristic of various thicknesses of Pd samples and various electrolyte solutions (vide infra).

Figure 2 shows the influence of the potential sweep rate on the amount of electrooxidized hydrogen recorded in 0.5 M H₂SO₄. These plots were taken at various temperatures for a constant palladium layer thickness of 1.6 μm. The temperature ranged from 273 to 346 K. Hydrogen was absorbed at a constant potential value ($E_{\text{abs}} = -0.13$ V vs. RHE). When the absorption process was complete, the absorbed hydrogen was electrooxidized from palladium with various potential sweep rates (from 0.1 to 0.01 V s⁻¹). A characteristic feature of the H/Pd plots shown in Fig. 2 is the maximum visible at relatively slow sweep rates, i.e. below 0.02 V s⁻¹. It has been shown [2, 3] that the maximum amount of hydrogen electrooxidized from a Pd-LVE depends significantly on the thickness of the Pd layer and the potential sweep rate. These experiments show that the maximum amount of hydrogen electrooxidized from a Pd-LVE also significantly depends on the temperature. With an increase in temperature, one observes a decrease in the difference between peak H/Pd values and those on the semi-plateau observed for higher values of potential scan rates. For the highest temperatures studied, the peak is shifted towards lower ν values.

Since the amount of hydrogen absorbed at a constant potential must be scan rate independent, another hydrogen desorption pathway must be introduced. As we stated, the position of the peak on the H(D)/Pd vs. ν plot depends on the ratio of the two rate constants for the concurrent hydrogen desorption reactions (k_1/k_2):



The decrease in the size of the peak observed in Fig. 2 at potential sweep rates below 0.01 V s⁻¹ suggests that participation of both processes of hydrogen desorption from the electrode varies with a change in the potential sweep rate. The smaller the potential scan rate, the greater the amount of hydrogen desorbed without charge transfer and, as an effect, a lower H/Pd value is electrochemically measured. This is explained by the fact that k_2 increases with the electrode potential, while k_1 is potential independent. Thus, the decrease in potential scan rate causes an increase in the k_1/k_2 ratio. This means that more hydrogen is desorbed non-electrochemically and hence the measured H/Pd value decreases. In the vicinity of the peak the k_1/k_2 ratio reaches a minimum and most probably all the hydrogen is desorbed electrochemically. With a further increase in ν , however, due to the slowness of the diffusion process, not all hydrogen reaches the electrode surface during the potential scan. Thus, some part of the absorbed hydrogen cannot be desorbed electrochemically and a decrease of the H/Pd value is observed. These results support our

earlier conclusions regarding the existence of two paths of hydrogen desorption [1, 2, 3, 4, 5]. The influence of temperature on the shape of the H/Pd vs. ν plots indicates changes in the importance of both desorption pathways with temperature. We can propose the following explanations of this effect:

1. The effect could be explained by changes of the k_1/k_2 ratio, which is temperature dependent. This means that the rate constants describing the rate of electrochemical desorption and chemical desorption (without charge transfer) are affected by the temperature in a different manner.
2. The other explanation is based on the complexity of the overall mechanism of hydrogen desorption. We have presented (Eq. 1) a model of the overall hydrogen desorption process. This is a simplified scheme and it is possible that other steps may be involved in the process. One could suggest that the last stage of desorption is more complex. If more than one step is involved in desorption of H_{ads}, it is possible that the temperature can change the rate-determining step.
3. The temperature can influence the energetics of various forms of hydrogen adsorbed on the electrode surface (H_{ads}) and participating in the hydrogen desorption process. If energetically different forms of H_{ads} participate in each of the desorption mechanisms, this effect could change the importance of both hydrogen desorption pathways at various temperatures.

Isotopic effect on hydrogen absorption

Data in Fig. 3 show the influence of temperature on the amount of hydrogen and deuterium absorbed in palladium. For temperatures not greater than ca. 310 K, the maximum concentration of absorbed hydrogen was slightly greater than deuterium, which agrees with known thermodynamic data about the isotopic effect in Pd/H₂ and Pd/D₂ systems (see e.g. [26, 27]). For temperature values greater than 310 K, an increase in temperature caused a smaller decrease in the D/Pd value than in the case of absorbed hydrogen. In this temperature range the difference between the concentration of absorbed deuterium and hydrogen increased with an increase in temperature. Finally, at temperatures greater than 310 K the concentration of deuterium dissolved in Pd was greater than the concentration of hydrogen. Studies of temperature influence on absorption of gaseous hydrogen and deuterium in massive palladium samples much thicker than those used in our study have shown the concentration of absorbed hydrogen to be greater than the concentration of deuterium in the temperature range studied in our work (see e.g. [26, 27]). This comparison indicates that the temperature-related

behavior of hydrogen and deuterium dissolved in thin Pd layers (0.2–0.6 μm) differs from that observed in bulk samples. We propose an explanation for this phenomenon based on differences in the behavior of the subsurface layer of hydrogen and deuterium. The concentration of both isotopes in the subsurface layer can vary, and, in addition, variations can occur with respect to the thickness of the subsurface layer in palladium saturated with hydrogen and deuterium. Since the behavior of hydrogen dissolved in very thin layers of palladium is determined mainly by the hydrogen present in the subsurface region (see discussion for Fig. 2), this layer should also be responsible for the observed isotopic effect. Thus, bearing in mind all the above-mentioned factors and taking into account that the process of deuterium absorption in palladium is less exothermic than the absorption of hydrogen [16, 26, 27, 28, 29], it is possible that hydrogen/deuterium dissolved in relatively thin palladium layers behave in a different way than in much thicker samples, and that this absorption is more strongly affected by temperature changes. Results from the following experiment confirm this.

Influence of thickness of the Pd layer

The influence of temperature on hydrogen absorption in palladium samples with two different thicknesses is shown in Fig. 4. The experiments were carried out in 0.1 M LiOH. In the temperature range 273–361 K for 1.6 μm and 0.2 μm of Pd the maximal steady state of hydrogen concentration decreases by ca. 14% and 27%, respectively. This decrease in H/Pd value for the thinner Pd layer suggests that in a thin layer of palladium a greater relative amount of hydrogen is absorbed more exothermally than in the case of a thicker layer. This hydrogen can be located in the subsurface layer where the concentration of dissolved hydrogen is greater than in the bulk [8, 9, 12]. After comparison of the possible thickness of the subsurface layer (see Introduction) with the thickness of the overall Pd layer, it is obvious that the percentage of hydrogen absorbed in the subsurface layer with respect to the total amount of hydrogen absorbed in the overall volume of the electrode is greater for thinner layers. Thus, this observation implies that the absorption of hydrogen in the subsurface layer should be more exothermic than the generation of other forms of hydrogen absorbed in the bulk of the palladium.

Influence of the electrolyte solution composition

Figure 5 shows the influence of temperature on hydrogen absorption from various electrolyte solutions. In the temperature range 340–361 K the slope of the change of the H/Pd value with an increase in temperature is very similar in both acidic (0.5 M H_2SO_4) and basic (0.1 M LiOH) solutions (Fig. 5). For the lower temperature values, however, a faster decrease in the

amount of absorbed hydrogen is observed in acidic solution. In the discussion of Fig. 5, two effects must be considered:

1. Alkali metal atom/ion inclusion. It is known that during saturation of palladium in aqueous solutions of alkali metal hydroxides the atoms or ions of these metals are irreversibly incorporated into the palladium lattice [30, 31, 32, 33, 34]. This effect is probably responsible for most of the differences occurring during absorption of hydrogen in basic and acidic solutions. This process is very slow [30, 31]. Thus, in the time scale of our experiments we can assume that the concentration of included alkali metal is far from the equilibrium state. This leads us to conclude that the profile of the concentration of incorporated alkali metal atoms/ions presented schematically in fig. 6 in [3] is governed mainly by the kinetics of the process of incorporation. Although the rate-determining step of this process is not clear, we can assume that both the rate constant and diffusion coefficient increase with an increase in temperature according to the Arrhenius formula. Thus, the rate of incorporation of alkali ions should also increase. As a result, the concentration profile for incorporated metal atom/ion should vary with temperature. Thus, it is possible that, due to the increase of the rate of incorporation of alkali ions, both the concentration of alkali metal atom/ion and the depth of penetration in the bulk of palladium increase with an increase in temperature. Since most of the incorporated alkali metal atoms/ions are located just beneath the surface, the changes in their concentrations must strongly influence the behavior of the subsurface hydrogen. It is known that the interaction between absorbed hydrogen and alkali metal atoms present inside the Pd lattice increases the stability and the concentration of absorbed hydrogen [35, 36]. Thus, increasing the concentration of incorporated lithium with an increase in temperature can improve the stability of a greater amount of subsurface hydrogen and, therefore, below ca. 350 K a smaller decrease in the H/Pd value is observed.
2. Thermodynamic factor. Hydrogen absorption in palladium is an exothermic process [26, 27]; thus the increase in temperature impedes hydrogen absorption. It is likely that at higher temperatures the exothermic effect of hydrogen absorption prevails. As a consequence, the decrease of H/Pd with an increase in temperature is similar in both solutions.

Conclusions

1. The temperature has a strong influence on each of the two mechanisms of removal of absorbed hydrogen/deuterium from palladium. These two mechanisms

- are: an electrochemical oxidation step, and a non-electrochemical recombination process.
- The amount of absorbed hydrogen and deuterium in palladium decreases with an increase in temperature. The influence of temperature on hydrogen and deuterium absorption is more significant at small thicknesses of the Pd-LVE. This is due to the more significant contribution of subsurface hydrogen to the total hydrogen concentration. Generation of this form of absorbed hydrogen is probably more exothermic than formation of hydrogen absorbed in the bulk of the metal.
 - The decrease of hydrogen content with an increase in temperature is smaller in basic than in acidic solutions. This is probably due to variation with temperature of the concentration profile of the alkali metal atoms/ions incorporated into the Pd lattice during hydrogen electrosorption.

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