

AIMS Materials Science, 7(4): 399–419. DOI: 10.3934/matersci.2020.4.399 Received: 02 March 2020 Accepted: 26 May 2020 Published: 24 June 2020

http://www.aimspress.com/journal/Materials

Research article

Hydrogen as a probe for defects in materials: Isotherms and related microstructures of palladium-hydrogen thin films

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Supplementary

Extending the discussion of the results presented in the main text of the manuscript, we here (1) consider the effect of small changes of the fitting parameters on the σ DOS model fits; (2) present additional fitted isotherms for Pd-H thin films of different thickness and microstructure; (3) discuss the effect of the neglected H-H interaction in the σ DOS model; (4) consider the impact of the site blocking factor *r* on the fitted interstitial site energy, and (5) discuss the impact of dislocations on the chemical potential of bulk Pd-H compared to Pd-H thin films. Finally, we (6) consider the offset-term of the chemical potential of hydrogen, that is often neglected when site energies of hydrogen in metals are discussed, and we (7) investigate the oxide potential of a Pd thin film.

1. Influence of fitting parameter variations in the σ DOS model

Targeting the reconstruction of the density of sites (DOS) hydrogen is occupying in palladiumhydrogen thin films, Eq 14 of the manuscript

$$x_H(\mu_H) = \int_{-\infty}^{\infty} \frac{Z(E)}{1 + \exp\left(\frac{E - \mu_H}{RT}\right)} dE$$

with $Z(E) = (1 - f_1 - f_2) \cdot \delta(E - E_0) + f_0^{il} \cdot \delta(E - E_0^{il}) + \sum_{i=1}^2 \frac{f_i}{\sigma_i \sqrt{\pi}} \cdot \exp\left(-\left(\frac{E - E_i}{\sigma_i}\right)^2\right)$ needs to be fitted to measured chemical potential data of the films. This leaves $E_0, E_0^{il}, E_1, E_2, \sigma_1, \sigma_2, f_1$ and f_2 as fitting parameters to represent the DOS.

Here we first show that considering two Gaussian site energy distributions next to the interstitial sites is mandatory to fit the measured thin film isotherms. Second, we show that the fits are sensitive to small changes of the fitting parameters, yielding considerably small confidence intervals.

Figure S1 shows measured chemical potential data (points) at given hydrogen concentrations of an 80 nm nano crystalline Pd-H thin film, that was corrected by the substrate induced stress impact. The figure reveals modifications of the fitted isotherms resulting from different types of sites taken into account. DOS fits for interstitial sites, grain boundary sites and deep traps, for neglected grain boundary sites as well as neglected deep trap sites are shown, revealing that all three types of sites are necessary to fit the measured chemical potential data. For this film, $f_0^{il} = 0$ by preparation.



Figure S1. Variation of the kinds of sites considered in the DOS fit of the chemical potential of an 80 nm nano crystalline Pd-H film. All kinds of interstitial sites, grain boundary sites and deep traps are necessary to fit the measured data.

In Figure S2 the interstitial site energy E_0 is varied between 0 kJ/mol and 3 kJ/mol. Apparently, small changes in the site energy strongly influence the fitting in the close vicinity of the two-phase region. The best fit is achieved for $E_0 = 1.5(3)$ kJ/mol.



Figure S2. Variation of the interstitial site energy E_0 fitting the σ DOS model to the measured data.

Figure S3 shows fits for modified broad Gaussian distributions around energies E_1 , that we relate to the grain/domain boundaries. For the blues line, E_1 was changed simultaneously with the site energy E_0 . The resulting isotherm is affected at medium H-concentration of the α -phase field. The best fit is achieved for $E_1 = 0.5(1)$ kJ/mol.



Figure S3. Variation of the grain boundary energy E_1 .

Figure S4 shows the sensitivity of the DOS fit regarding the deep trap energy E_2 . This contribution affects the isotherm at lowest H-concentrations. The best fit results for $E_2 = -48.3(5)$ kJ/mol.



Figure S4. Variation of the deep trap energy E_2 .

2. Fitted isotherms of Pd-H thin films of different thickness and microstructure

Additional to the 80 nm nano crystalline Pd-H film in Figures 1a and 4 of the main manuscript, Figure S5 shows fitted isotherms according to the quasi-thermodynamic approach and to the σ DOS model for Pd-H thin films of different microstructures and different film thicknesses. The figures reveal reasonable σ DOS model fits of the chemical potential data in the solid solution regime, with the fitting parameters given in Table 1 of the main text.



Figure S5. Measured chemical potential data of epitaxial Pd-H thin films with (a) 24 nm, (b) 80 nm and (c) 200 nm film thickness, as well as (d) 80 nm multi-oriented Pd-H, fitted with the quasi-thermodynamic approach of Eq 4 and with the σ DOS model of Eq 14 of the main manuscript.

3. Influence of the H-H interaction on the fitting parameters of the σ DOS model

To investigate the impact of neglecting the H-H interaction contribution $E_{HH}x_H$ on the fitted model parameters of Eq 14 in more detail, Figure S6 shows the chemical potential of the 80 nm nano crystalline Pd-H film with different corrections: The orange data points represent the original measured data without correction. For the black data points the measured stress impact $\Delta\mu_{\sigma} =$ $-v_0\eta_H\sigma_{ii}$ was subtracted from the data, like in Figure 3 and Table 1 of the main text. The black line shows the corresponding fit of the data points. The purple dashed line, on the other hand, represents a fit of the data with subtracted $\Delta\mu_{\sigma}$ and $\Delta\mu_{HH} = -E_{HH}x_H$, with the parameter $E_{HH} = 20.5$ kJ/mol as determined from the fit of the quasi-thermodynamic model approach to the data, see Figure 1a of the main manuscript. To plot the purple line together with the black data points, $\Delta\mu_{HH}$ was added back to the fitted isotherm after the fit. All resulting model parameters are summarized in Table S1.



Figure S6. Chemical potential and H-concentration of an 80 nm nano crystalline Pd-H film, sequentially corrected for the mechanical stress impact $\Delta \mu_{\sigma}$ and the H-H interaction effect $\Delta \mu_{HH}$ on μ_{H} . The data points were fitted according to Eq 14 of the main text.

Table S1. DOS fit parameters of Eq 14 for the chemical potential data of an 80 nm nano crystalline Pd-H film, corrected sequentially for the stress impact and the H-H interaction impact on the chemical potential. For this film $f_0^{il} = 0$.

Correction	E_0 (kJ/mol)	E_1 (kJ/mol)	σ_1 (kJ/mol)	f_1	E_2 (kJ/mol)	$\sigma_2 (kJ/mol)$	f_2
none	3.2(3)	0.4(1)	15.7(3)	0.080(1)	-47.2(5)	6.3(3)	0.0020(1)
$\Delta \mu_{\sigma} + \Delta \mu_{HH}$	2.5(3)	0.5(1)	15.7(3)	0.100(1)	-48.3(5)	6.3(3)	0.0020(1)
$\Delta \mu_{\sigma}$	1.5(3)	0.5(1)	15.0(3)	0.118(1)	-48.3(5)	6.3(3)	0.0021(1)

Apparently, the different corrections change the energy scale of the chemical potential to different amounts. Regarding the model parameters, the largest relative effects of preliminary data correction appear in the fitted interstitial site energies E_0 and in the grain boundary fractions f_1 with peak energy E_1 . The relative change of the other parameters is small. The shift of the site energy E_0 by +1.7 kJ/mol is largest for the uncorrected data compared to the data corrected by $\Delta\mu_{\sigma}$, shifting

 E_0 towards that of the 80 nm films with other microstructures, see Table 1 of the main text. E_0 takes a medium value with a shift of +1.0 kJ/mol for the correction of $\Delta\mu_{\sigma} + \Delta\mu_{HH}$.

While fitting the chemical potential without any corrections yields too large site energies E_0 with respect to the assumptions of the σ DOS model, the correction of $\Delta \mu_{HH}$ is meaningful from a physical point of view, since the H-H interaction is the initiator of the phase transition in the Pd-H thin films. This is also supported by the consideration of the slopes of the fitted curves in Figures S6 and S7 with respect to the data points close to the solid solution limit x_{α}^{max} : There, the fit is best for the curve corrected for the H-H interaction, because the H-H interaction gradually decreases the slope of the measured chemical potential in that region, indicating the onset of phase transition.



Figure S7. Impact of the choice of the site blocking factor r on the fitted interstitial site energy E_0 of bulk palladium.

However, since the value of E_{HH} was taken from the quasi-thermodynamic model approach but cannot be determined with Eq 14, it is usually neglected in the data evaluation in the present paper. This yields slightly too small site energies E_0 and slightly too large grain boundary fractions f_1 , compare the second and the third lines of Table S1.

Thereby, the effect of $\Delta \mu_{HH}$ on the model parameters needs to be compared to the effect of an assumed site blocking factor of r = 1 H/Pd. As shown below, r = 1 H/Pd results in slightly too large site energies E_0 , compensating for the effect of $\Delta \mu_{HH}$.

4. Impact of the site blocking factor r on model parameters

In the DOS fits in the main text the site blocking factor r, describing the blocking of sites for the occupation by hydrogen atoms for electronic and microstructural reasons, was set to r = 1. In Figure S7 we evaluate the effect of setting = 1 H/Pd, allowing for the occupation of all octahedral sites in the Pd metal, compared to the correct value of r = 0.6 H/Pd. Chemical potential data of 100 µm bulk Pd-H are shown, together with a fit of the quasi-thermodynamic approach of Eq 4 in the main manuscript.

One can see that the choice of r affects the magnitude of the fitted site energy E_0 , yielding smaller site energies for smaller blocking factors. For the fitting of the quasi-thermodynamic approach the blocking factor was set to r = 0.62 H/Pd as well, yielding a similar site energy like the DOS model fitted with the same r. In total, we find $E_0 = 5.7 \text{ kJ/mol}$ for r = 1 H/Pd, but $E_0 = 4.6 \text{ kJ/mol}$ for r = 0.6 H/Pd. This effect balances the E_0 -increase due to the negligence of $\Delta \mu_{HH}$ in the σ DOS model, see above.

5. Impact of dislocations on the measured chemical potential

In the fit of the density of site energies to the measured chemical potentials of Pd-H thin films we neglected the influence of dislocations. This is justified by the observation that the chemical potential of thin films increases much slower with the hydrogen concentration in the film than predicted by the dislocation impact. Hence, dislocations seem not to play a major role as trapping sites affecting the chemical potential in Pd-H thin films.

This is shown in Figure S8, where the increase of the chemical potential with hydrogen concentration is compared for strongly deformed bulk Pd to that of an 80 nm nano crystalline Pd thin film. The bulk data were adapted from [1].



Figure S8. Comparison of the chemical potential μ_H increase with hydrogen concentration x_H of heavily deformed bulk Pd [1] and of an 80 nm nano crystalline Pd thin film.

The bulk sample possesses a fitted areal dislocation density of $\rho = 7.4 \times 10^{10} \text{ cm}^{-2}$ [1], close to the maximum geometrically possible dislocation density of metals. It is shown in [1] that the deviation of the chemical potential increase from the ideal slope, which is represented by $RTln(x_H)$ in Figure S8, is caused by the trapping of hydrogen atoms in the dislocations in the bulk sample. This is also shown in Figure S9.

The chemical potential of the nano crystalline Pd thin film, however, increases much slower with hydrogen concentration than that of the bulk sample; the chemical potential increase is shifted

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by two orders of magnitude in concentration. This hints on thin film trap sites different from dislocations.



Figure S9. Comparison of the chemical potential of bulk Pd of [1] with the approximation of Eq 19 in the main manuscript. Different from the Pd thin film data in Fig. 8 of the main text, Eq 19 fits the bulk data reasonably well.

6. Offset of the chemical potential

The chemical potential of hydrogen in metals contains half of the standard potential of gaseous hydrogen [2,3],

$$\mu_{H2}^{0}(T)/2 = -\frac{RT}{2} ln\left(\frac{p_{0}(T)}{p_{0}(T_{0})}\right) - E_{d}/2$$

with $p_0(T_0) = 1.013$ bar at $T_0 = 7.55$ K, $p_0(T) = b \times T^{7/2}$, constant $b = 8.57 \times 10^{-4}$ bar/K^{7/2} and the dissociation energy $E_d = 4.476 \text{ eV}/H_2 \cong 431.9 \text{ kJ/mol}_{H_2}$ of H_2 molecules. Hence, the chemical potential of hydrogen in a metal is proportional to an equivalent outside hydrogen gas pressure. Targeting site energies of hydrogen in metals, the energy scale often is shifted by $-\mu_{H_2}^0/2$, practically neglecting the offset term. Thereby it is $-\mu_{H_2}^0(T)/2 = 231.8 \text{ kJ/mol}$ at T = 297 K.

7. Oxide potential of a Pd thin film

All Pd thin films investigated in the present manuscript were electrolytically charged with hydrogen in an electrolyte consisting of 2/3 distilled water and 1/3 80% phosphoric acid. The electromotive force (EMF) of the samples was measured in reference to a saturated Ag/AgCl electrode. The *pH* of the electrolyte was pH = 4. To investigate the oxide potential, Pd thin films were oxidized by anodically discharging. This is shown in Figure S10 for the example of a 100 nm nano crystalline Pd thin film. There, the EMF as well as the corresponding chemical potential μ are plotted as a function of the negative electric charge applied to the sample. The oxide potential starts at $\mu = -45$ kJ/mol and possesses a plateau at $\mu = -70$ kJ/mol.



Figure S10. Oxide potential of an anodically discharged 100 nm nano crystalline Pd thin film at T = 297 K. The oxide potential was measured in an electrolyte of pH = 4 in reference to a saturated Ag/AgCl electrode.

References

- 1. Kirchheim R (1981) Interaction of hydrogen with dislocations in palladium—II. Interpretation of activity results by a Fermi-Dirac distribution. *Acta Metall* 29: 845–853.
- 2. Fukai Y (1993) The Metal-Hydrogen System: Basic Bulk Properties, Berlin: Springer-Verlag.
- 3. Züttel A (1988) Metall-hydride. Vorlesungsskript.