Hydrogenography on palladium-copper thin films as a tool for finding new hydrogen separation membranes

Christijn den Besten

Supervision of Martin Slaman and Bernard Dam

Condensed Matter Physics Group VU Amsterdam

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# Contents

Contents ........................................................................................................................................... 3  
Abstract ........................................................................................................................................ 5  
Introduction.................................................................................................................................. 7  
Objective ...................................................................................................................................... 8  
Outline .......................................................................................................................................... 9  
Theoretical background .................................................................................................................. 10  
Palladiumhydrides .......................................................................................................................... 10  
PdCu hydride system ....................................................................................................................... 15  
Cluster Variation Method ............................................................................................................... 19  
Experimental ................................................................................................................................ 22  
Hydrogenography .......................................................................................................................... 22  
Thin film deposition and analysis .................................................................................................... 25  
Hydrogenography Results ............................................................................................................... 28  
The influence of alloying Pd with Cu .............................................................................................. 28  
Influence of temperature on Pd_{100-y}Cu_{y} ..................................................................................... 36  
Finding the plateau pressures ......................................................................................................... 39  
Finding the critical copper concentration ....................................................................................... 42  
Electrochemistry on Pd and PdCu .................................................................................................... 49  
Electrochemistry: Theoretical background ..................................................................................... 49  
Electrochemistry: Experimental ...................................................................................................... 52  
Electrochemistry: Results for Pd ..................................................................................................... 55  
Electrochemistry: Results for PdCu ................................................................................................. 62  
Discussion and Conclusion ............................................................................................................. 66  
Shape of isotherms ......................................................................................................................... 66  
Critical Cu concentration ................................................................................................................ 67  
Lambert Beer relation ...................................................................................................................... 67  
Plateau width.................................................................................................................................. 68  
More substrate related effects ......................................................................................................... 70  
Literature ....................................................................................................................................... 72  
Acknowledgements ......................................................................................................................... 74
Abstract

Separating hydrogen from a gas mixture is done with membranes based on palladium. Pd can ab- and desorb hydrogen very selectively, but below a critical temperature it goes through a phase transition affined with a volume change of approximately 11% when doing so. This creates cracks and reduces the lifetime of the membrane. In order to lower the working temperature and to extend the membranes usage the material properties can be improved by alloying palladium with copper. By doing so, the critical temperature decreases as has been found in literature and by theoretical work on this system.

In this thesis a technique to rapidly study many PdCu compositions in one batch will be employed. This so called hydrogenography is based on the change in optical transmission of visible light through a thin film as it hydrogenates. The method is used to compare material properties like $T_C$ with literature data on bulk systems and with findings by theoretical studies.

In hydrogenography the relation between the transmission and the hydrogen concentration in the sample is given by the Lambert Beer law. To confirm this and to also gain insight in the amount of hydrogen that can be absorbed in a PdCu thin film, electrochemistry is used. Films are galvanostatically (dis-)charged while the transmission is measured.

Results indicate that there is a difference between PdCu thin films and bulk, but that this can be explained by substrate effects. The composition at which $T_C$ is 308 K (thin film) is Pd$_{71.5}$Cu$_{28.5}$, while Böttger et al. found Pd$_{67}$Cu$_{33}$ at 298 K (theoretical work). This small underestimation of the Cu amount measured with hydrogenography can be explained by a clamping to the substrate which is inevitable in thin film research, although it can be tuned. The calculated width of the plateau of various PdCu compositions (literature) is reproduced by hydrogenography.

The electrochemical measurements show that the linearity between the concentration of H in a film and the log of the transmission is confirmed for charging but not for discharging. For PdCu films there is a large influence of the current of loading on the discharge capacity. Because of that there is some deviation from the values that were found in literature (bulk).

Since hydrogenography shows that for the PdCu model system material properties like $T_C$ are reproducible, this technique can be exploited in the search for even better materials (like ternary PdCuM) for long-lived hydrogen separation membranes.
Introduction

Changing a fossil fuel based economy to one based on renewable energy sources like sunlight and derivates needs time. The Annual Energy Outlook 2007 from the Energy Information Administration states that coal will still be a major source for energy production in the next decades. [1] Using coal without dumping too much carbon dioxide into the atmosphere needs new strategies. In the integrated coal gasification combined cycle (IGCC) coal is being transformed into hydrogen and carbon monoxide. Adding a consecutive water gas shift step to this reaction enhances the reaction of steam with CO to produce CO$_2$ and H$_2$. An essential step in this process is the separation of these two products. If that can be done, both can be used in their own unique ways. Hydrogen can be used to produce electricity instantly, or it can be used in mobile applications. CO$_2$ can be as a commodity for the greenhouse industry, or else it can be stored underground in order not to pollute the atmosphere.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$ (Water gas shift)

Transforming natural gas by the steam reforming reaction is another way of producing hydrogen. That reaction also leads to the creation of a CO$_2$/H$_2$ gas mixture. Thus finding a way to effectively separate these gasses is an essential step for transforming both coal and natural gas into hydrogen.

The water gas shift reaction is limited by its chemical equilibrium. A classical way to separate the reaction products is by low temperature CO$_2$ removal from the mixture, which needs a cooling step in the process. [2] Continues H$_2$ removal during the reaction by the use of a membrane reactor not only avoids this cooling step, but also lets the equilibrium go to completion. It increases the overall reaction yield. The equilibrium reaction will go to completion if the hydrogen is removed from the products. Palladium’s unique property to selectively ab- and desorb hydrogen is used for this purpose. In membranes a thin layer of this metal is adhered to a ceramic base. The ceramic base is merely for the stability, the palladium is doing all the separating work. The adhesion of the metal to the ceramic can be tuned by the type of adhesion material and the size of the pores. This can influence the flow and the lifetime of the membrane throughout switching the reactor on and off (or going from high to low H$_2$ pressures). The products of the water gas shift reaction are fed into a membrane reactor where the hydrogen selectively diffuses through the membrane (hydrogen is the permeate), whereas the other gasses (unconverted CO, unseparated H$_2$, and mainly CO$_2$) stay behind (that gas mixture is called the retentate). For electricity production the H$_2$ mixture is fed to a gas turbine. The retentate is burnt to produce only CO$_2$, which then can be used for other purposes or it can be stored underground.

Ab- and desorption of H$_2$ (which translates to switching the process on and off) leads to stress in the Pd. Because of this cracks will appear in the Pd layer which ultimately will
destroy the membrane. An example of a Pd membrane that has suffered from stress and developed cracks is shown in Figure 1. Working at elevated temperatures reduces this effect, but one likes to work at low temperatures to save operating costs. The key solution seems to be the tuning of the material properties in such a way that one can combine the high selectivity of Pd with the stability of palladium alloys. It has already been found that doping Pd with Cu or Ag enhances the lifetime of the membranes. [3] The problems with Pd that are encountered in the membrane technology can be understood by looking at the way at which H$_2$ is absorbed. This will be explained in detail in the paragraph about theory on palladium hydrides, page 10.

![Figure 1: Aging of a Pd membrane. Absorbing and desorbing H$_2$ creates phase transitions and sudden volume changes leading to the formation of cracks.](image)

**Objective**

In this thesis I will study the interaction of H$_2$ with palladium copper thin films. This will be done with a relatively new method called hydrogenography, which exploits the optical properties of metalhydride thin films. Hydrogenography is a very fast method that can give insight in numerous PdCu compositions in a short time. It has already proven to be very useful in metalhydride research illustrated by publications on hydrogen storage materials [4][5] and hydrogen sensors [6][7]. Typically the transmission of light through a metal thin film is measured while the surrounding hydrogen pressure is controlled at an equilibrated temperature. Palladium and alloys of it go to a more transparent phase upon hydrogenation. Below a certain critical temperature there is a second order phase transition affined with a large change in the optical transmission at a well defined pressure. That pressure, which from now on will be called the plateau pressure $p_{plat}$, in combination with the known temperature allows us to derive interesting thermodynamic properties of the material.

The PdCu system has already been studied quite extensively, both experimentally and theoretically. Because of that PdCu is used as model system to compare hydrogenography data with the PdCu system in bulk [8][9] and theoretical studies on the same system [10]. In their study Burch and Buss [8] use samples that have a
thickness of 200 µm which defines “bulk”, in contrast to thin films which are typically thinner than micrometers.

The first aim of this research is to find the temperature at which there is no more phase transition in the isotherms, defined as the critical temperature $T_C$, for PdCu films with various copper composition. Next these values will be compared to bulk and theoretical data. At the same time the isotherm characteristics (shape of the isotherms, plateau pressure and width of the plateau) are compared with bulk data.

According to the Lambert Beer law there is a linear relation between the concentration of H in a thin film $c_H$ and the log of the transmission of light going through it. Therefore an optical method is possible to study the material properties upon hydrogenation. The Lambert Beer relation has been confirmed by electrochemical hydrogenation of a Mg$_{70}$Ti$_{30}$ thin film in combination with in situ measurement of the transmission [11].

The second aim of this work is to find if the linear relation between the concentration of H in a thin film and the log of the transmission of light going through it is valid for Pd and PdCu with varying Cu content. For this thin films are electrochemically (de-)hydrogenated while the transmission is measured. In an electrochemical measurement at which the current is constant we “count” the protons that are absorbed by the material while measuring the transmission. This allows us to check whether or not there is a linear relation between $c_H$ and the log of the normalized transmission.

Besides that, in an electrochemical dehydrogenation the potential reveals how much H can be stored in a film. The outcome for Pd will be compared with results from electrochemistry by others. For PdCu it will be compared with my hydrogenography results and with literature (bulk measurements and theoretical work).

If the results from hydrogenography can confirm the results that are previously found with other methods for the PdCu model system, similar studies can be done on other (ternary) palladium alloys. Theoretical studies can be helpful by pointing in the right direction of which elements to use. In this way new materials for the hydrogen separation membrane industry will be at hand.

Outline

This paper is build up as follows: first there is a chapter about the theoretical background of hydrides followed by an experimental section on thin films and hydrogenography. Next the hydrogenography results are discussed. I have chosen to keep the electrochemistry in this paper together in a separate chapter, including the theoretical background and the experimental details. In the discussion/conclusion the results of both techniques are brought together, and the questions put forth in the objective are answered. At last there is separate chapter about substrate effects.
Theoretical background

Palladiumhydrides

Already in 1866 the Scottish chemist Thomas Graham found that palladium can ab- and desorb hydrogen. Since then this interaction has been studied extensively. The hydrogenation isotherms show that with increasing pressure Pd goes through a phase transition from the low hydrogen concentration α-phase to the metalhydride β-phase. In the α-phase there is not much space for hydrogen, and a large pressure is needed for a little absorption. At some point the metal lattice expands and the absorption goes very fast until the β-phase is reached.

By measuring the pressure and the amount of hydrogen that is absorbed by a metal at constant temperature so called pressure-composition-isotherms (pci’s) can be created. This is shown for Pd in Figure 2.

Figure 2: pressure-composition-isotherms (pci’s) for PdH. When the temperature is below critical temperature of approximately 571 K there is a transition between the α- and the β-phase, marked with a plateau at a well defined pressure: the plateau-pressure. Graph taken from [12].

These measurements are done with the so called Sieverts’ method. The Pd is kept under vacuum, and a small amount of hydrogen is introduced. Once equilibrium has reached, the weight of the sample and the surrounding pressure are measured. Then one knows how much H₂ is absorbed by the sample. By slowly increasing the pressure and
accurately measuring the H concentration in the film through the mass, the points as shown in Figure 2 are plotted. The pci’s are used to construct the phase diagram of PdH$_x$. It is shown in Figure 3 and is taken from the work of Frieske and Wicke [12].

![Figure 3: PdH$_x$ and PdD$_x$ phase diagram taken from [12]. Below the critical temperature there is a distinct α- and β-phase, and a α/β-mixed region.](image)

This phase transition takes place at a certain equilibrium pressure (0.005 atm for Pd at room temperature) where the α- and β-phase are coexisting. Increasing the temperature lifts the plateau’s to higher pressures, up until the so called critical temperature at which the system stays in the α-phase. The phase transition upon hydrogenation is accompanied with a volume expansion of about 10% [13].

The interesting behaviour of the pci’s deserves a closer look. The following is based on the master course “Hydrogen in Metals” and the accompanying lecture notes by Ronald Griessen [14]. Considering a simple lattice gas model which describes the energy of hydrogen atoms H in a metal containing metal atoms M we need an interaction between H and M and between H and H.

\[ E = N_H \varepsilon_0 + N_{HH} \varepsilon \]

where \( N_{HH} \) is the number of nearest neighbour H-pairs, \( N_H \) the number of H atoms absorbed by M, \( \varepsilon_0 \) the zero energy and \( \varepsilon \) the H-H pair interaction energy. Now we use the Bragg William approximation to say that there is no short range order around the H atoms.
\[ N_{HH} = N_H n \frac{N_H}{N} \times \sqrt{2} \]

where \( n \) is the number of nearest neighbour interstitial sites, \( N_H/N \) is the probability of finding a nearest neighbour around H, and this ratio is from now on labelled \( c_H \).

In this formula we count for the first two H atoms the interaction of \( N_{H,1} \) with \( N_{H,2} \) and also \( N_{H,2} \) with \( N_{H,1} \). That will result in double counting, so to prevent that we divide by 2.

From this the free energy \( F \) can be determined, and taking the derivative of \( F \) with respect to \( N_H \) one finds the chemical potential to be

\[ \mu_H = kT \ln \frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H. \]

The chemical potential of the surrounding hydrogen gas is

\[ \mu_{H_2} = \varepsilon_b + kT \ln \frac{p}{p_0} \]

where \( \varepsilon_b \) equals the binding energy of a \( H_2 \) molecule. In equilibrium

\[ \frac{\sqrt{2}}{2} \mu_{H_2} = \mu_H \]

which leads to an expression of the hydrogen pressure as a function of the hydrogen dissolved in the metal.

\[ \ln \left( \frac{p}{p_0} \right) = \frac{2\varepsilon_0 - \varepsilon_b}{kT} + \frac{2\varepsilon n}{kT} c_H + 2 \ln \left( \frac{c_H}{1-c_H} \right) \]

Figure 4 shows what this function looks like for \( 0 < c_H < 1 \).

Figure 4: Lattice gas model for MH: where \( -\varepsilon_0 = -\varepsilon_b = kT = 1 \) and \( \varepsilon n = -8 \). The region between the 2 maxima is unphysical.
The region between the local maximum around 0.1 \( c_H \) and the local minimum around 0.9 \( c_H \) represents unphysical behaviour because the derivative of the chemical potential to the hydrogen concentration is smaller than 0. A necessary condition for thermodynamic equilibrium is

\[
\frac{\partial \mu}{\partial c_H} \geq 0
\]

In a physical system shown by the pci’s in Figure 2 this leads to a plateau. When drawing a horizontal line from \( \ln(p/p_0) \) at which the unphysical behaviour starts to \( \ln(p/p_0) \) with the same value at which \( \mu \) is positive, a plateau is created. This construction is shown in Figure 5.

![Figure 5: The lattice gas model with -\( e_b = -e_b = kT = 1 \) and \( c_H = -8 \). From point A at which there is no more physical behaviour there is the dotted line which goes to the next point at the same pressure where the derivative is positive. This happens at a different pressure B when desorbing H₂, leading to a hysteresis. From this model it is obvious that there is a difference between going from low to high pressure and vice versa. In the first case the local maximum is reached and the system goes to the β-phase. When desorbing H the other local minimum is reached at a very different pressure, leading to a hysteresis which is observed in experiments with metalhydrides.

The hysteresis that is found in hydrogenation and dehydrogenation of metals can only partially be explained by the hysteresis found from the lattice gas model. There is also a clamping effect induced by the growth of β-phase nucleation sites in the surrounding α-phase. Since the β-phase has a larger lattice than the surrounding α-phase, there is a pressure counteracting the growth of the β-phase, resulting in a higher hydrogen pressure. [15]
From the lattice gas model it can be seen that there is an apparent influence of temperature on the shape of the isotherms, following the pci’s. The plateau pressure increases when measured at higher temperature. This is also represented by the model as shown in Figure 6.

At the critical temperature the hysteresis between absorbing and desorbing hydrogen disappears. This fact is used when a so called van ‘t Hoff plot is constructed to determine the critical temperature. According to the van ‘t Hoff relation

$$\frac{1}{2} \ln \frac{p_{plat}}{p_0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Here $\Delta H$ and $\Delta S$ are the enthalpy and entropy of formation and $p_{plat}$ is the plateau pressure. So a plot of the log of the plateau pressure against the reciprocal temperature gives a value for $\Delta H$ and $\Delta S$. Furthermore, making this construction for H$_2$ ab- and desorption creates two straight lines that intersect at the reciprocal critical temperature. See Figure 7 for a construction of a van ‘t Hoff plot.
Figure 7: Construction of a van ‘t Hoff plot for loading and unloading, resulting in a value for $T_C$. With courtesy of Y.Pivak.

From this paragraph we have learned that at temperatures lower than $T_C$ every time Pd ab- or desorbs H there is a phase transition. The problems of palladium membranes that were revealed in the introduction can be explained by these phase transitions and accessory changes in volume. Palladium membranes that experience large changes in hydrogen pressure undergo the above mentioned phase transitions and changes in volume. This creates stress in the membrane which leads to embrittlement and therefore a reduced lifetime of the membrane.

**PdCu hydride system**

A solution to the problem mentioned above is to keep the membrane above the critical temperature. This is an expensive solution because a lot of energy is needed to keep the system at high temperatures. Another solution is to influence the material properties in such way that $T_C$ is lowered. This is done by alloying Pd with metals like Ag or Cu. There is a twofold influence of alloying Pd with Cu.

1. The elastic effect is related to the size of the metal that is replacing the Pd. We realize that the Cu atom has a smaller atomic volume than Pd (7.11 and 8.85 cm$^3$/mol respectively). The more Pd atoms are being replaced by Cu atoms, the less space there is for H atoms in the lattice. With that a higher surrounding H$_2$ pressure is needed for the system to absorb H.

2. The electronic effect considers the interaction of the hydrogen electron with the collective band structure of Pd. This effect is based on the fact that copper, being in the period on the right with respect to the period that contains palladium in the periodic table, brings in an extra d-electron to the band structure. In PdCu the d-band will be filled sooner upon hydrogenation, and the hydrogen solubility will be less than in pure Pd. [16]
Taking these two effects together, Figure 8 shows the overall effect of Cu on the characteristic of hydrogen absorption in PdCu for various Cu concentrations, measured by [8].

Figure 8: Pci’s of loading a PdCu sample at 303K measured by Burch and Buss. [8] The influence of Cu on the isotherms, measured for bulk samples by Sieverts’ method.

The lattice structure of PdCu at Cu concentrations less than 40 at.% is Face Centred Cubic (FCC) and between 65 and 53 at.% Cu Body Centred Cubic (BCC). Figure 9 shows the PdCu phase diagram. Around 60 at.% Cu the equilibrium phase is BCC with a larger lattice parameter and a very high diffusivity. That might be useful for increasing the hydrogen diffusion through a PdCu membrane, but that is outside the scope of this research. To reach this equilibrium phase one needs to anneal at high temperature, and the PdCu films that I used in this work didn’t go to the BCC phase. Also the α- to β-phase transition is reached at elevated pressures compared to pure Pd. This effect brings the metal closer to a critical temperature.
The doping of copper in palladium has a twofold effect on thepci’s: the system absorbs less hydrogen at low and high hydrogen concentration, and the equilibrium pressure plateaus are shifted to higher values. The replacement of hydride forming atoms with non hydride forming atoms scales linearly with the decrease of hydrogen absorption in both α- and β-phase, as can be seen in Figure 10 taken from [8]. The intersection in the graph marks the critical concentration. That means that at the temperature of 303 K at less than 31% Cu there still is a phase transition, whereas at higher concentrations there is none.

Figure 10: Hydrogen concentration at phase boundaries for some PdCu compositions. There is a linearity, and the lines cross at around the critical concentration of 31% Cu. Data at 303 K taken from Burch and Buss [8].
From Figure 8 it seems as if the relation between the log of the plateau pressure and the amount of copper in the film is linear. When discussing the critical point I will come back to this, but for now the lattice gas model might give insight in this peculiarity. To model the influence of copper, we take the lattice gas model and introduce a reduction of available sites by reducing the number of nearest neighbour interstitial sites by the amount of Cu labelled $y$, assuming that non-hydrogen absorbing Cu atoms are just replacing hydrogen absorbing Pd atoms:

$$\ln\left(\frac{p}{p_0}\right) = \frac{2\varepsilon_0 - \varepsilon_h}{kT} + \frac{2\varepsilon n}{kT} c_H (1 - y) + 2 \ln\left(\frac{c_H}{1 - c_H}\right)$$

For increasing values of $y$ in Pd$_{1-y}$Cu$_y$ we find a very similar influence as an increase in temperature as is shown in Figure 6. Now we are interested in the pressure at the plateau, which is defined by the local maximum for loading and the local minimum for unloading. Thus, setting the derivative of $\ln(p/p_0)$ with respect to $c_H$ to zero results in a hydrogen concentration of

$$c_H = \frac{1}{2} \pm \frac{1}{2} \sqrt{1 + \frac{4kT}{\varepsilon_n(1-y)}}$$

The first solution to this equation is the plateau at low concentration, the second solution the plateau at high concentration. The pressure at these concentrations defines the plateau pressure, where the first solution is for loading and the second one for unloading.

$$\ln\left(\frac{p_{\text{plat}}}{p_0}\right) = \frac{2\varepsilon_0 - \varepsilon_h}{kT} + \frac{\varepsilon n(1-y)}{kT} \left(1 \mp \sqrt{1 + \frac{4kT}{\varepsilon_n(1-y)}}\right) + 2 \ln\left[1 \mp \sqrt{1 + \frac{4kT}{\varepsilon_n(1-y)}}\right]$$

This looks as straightforward as it is, but plotting these plateau pressures for some Cu concentrations provides some clarity. In Figure 11 these maxima are given for values of $y$, where $-\varepsilon_0 = -\varepsilon_h = kT = 1$ and $\varepsilon n = -10$. 

18
Figure 11: Plateau pressures versus $y$ (the amount of Cu) according to the lattice gas model, with $-\varepsilon_0 = -\varepsilon_b = kT = 1$ and $\varepsilon_{n} = -10$. The points are fitted with a straight line and the $R^2$ value shows that there is only a small deviation from a linear function.

Now we see that plotting the local maximum and local minimum of the pressure at different values of $y$ in Pd$_{1-y}$Cu$_y$ results in an almost linear relation. The intersection of both lines marks the critical Cu concentration.

Membranes that stay above the critical temperature do not go through a phase transition and the related sudden volume change. When avoiding this abrupt volume change, the system suffers less from stress. So by using palladium-copper instead of pure palladium in a membrane the system stays above the critical temperature. By doing so there is no phase change when cycling between hydrogen pressures, and no negative effects related to this phase change. This increases the lifetime of the membrane.

On top of all that, palladium-copper shows a remarkable resistance against sulphur poisoning which is a major problem in membrane technologies when dealing with sulphur rich fuels such as coal. [18]

**Cluster Variation Method**

As mentioned in the introduction the experimental results will be compared with theoretical work. In their work Amarante Böttger and Diana Nanu from Delft University use a statistical thermodynamics approach to obtain several properties of Pd alloy hydrides, including PdCu [10].

The palladium system with low substitutions of copper has a face centred cubic lattice. The octahedral interstitial sites may contain hydrogen atoms (H) or nothing (Vac). The whole system is thus divided in two overlapping sub lattices, namely the Substitutional metal Sub lattice (SS) where we find Pd or Cu atoms and the Interstitial Sub lattice (IS) which comprises the H or Vac sites. Figure 12 shows both sub lattices.
Figure 12. The face centred cubic lattice for Pd or M (Substitutional metal Sub lattice) with positions where H can sit. These (possibly occupied) vacancies also form an FCC lattice (Interstitial Sub lattice). Taken from [10].

The tetrahedron made up by hydrogen or no-hydrogen (H or Vac) in IS is used for the Cluster Variation Method (CVM). The CVM method uses effective pair interaction parameters between H-H, H-Vac and Vac-Vac for minimizing the energy in order to find thermodynamic properties and phase transformations. These effective pair interaction parameters are taken directly from experimental data, or they are estimated from the extrapolation of the linear dependence of the parameters on the Cu content. Nanu and Böttger have done these calculations and found phase boundaries for PdCu with varying Cu. Results are plotted, together with bulk measurements, in Figure 13.
Figure 13: Phase boundaries between α- and αβ-mixed-phase and αβ-mixed- and β-phase calculated by CVM (lines) for PdCu with various Cu concentrations (0, 5, 10, 15, 20, 33 %Cu). The full lines are phase boundaries calculated with interaction parameters from experiments, dotted lines are calculated with predicted values. These data are compared with data measured in bulk (symbols).
Experimental

Hydrogenography
As mentioned before, the pci’s which are shown in Figure 2 are obtained by Sieverts’ method. This method relies on accurate measuring very small mass differences, which is difficult. Also it takes a lot of time to let the ab- or desorption reach equilibrium. Besides that, the preparation of bulk samples is not straightforward, and often involves an annealing step. Burch and Buss need 1 week annealing at 800°C for preparing their samples. [8] In this project thin films are studied with hydrogenography. Thin films are easy to prepare by sputter deposition techniques. Gradient compositions, multilayers and reactive sputtering in for instance oxygen or hydrogen are just a few of the numerous possibilities with this technique for preparing thin films. Hydrogenography is a combinatorial method that has already proven to be a powerful tool for studying metal-hydrogen systems. It makes use of the fact that some metals undergo a transition from a highly reflective to a more transparent state upon hydrogenation.

A thin film on glass substrate is placed in a vacuum cell, and the surrounding hydrogen pressure is controlled by an input and an output valve. A PC controls the valves to create a hydrogen (or mixed hydrogen) gas pressure inside the cell. The cell is put in an oven where the temperature can be controlled from 35°C up to 300°C and higher. The temperature in the oven is stabilized, but possible variations might be checked afterwards since the PC stores the temperature for every measuring step. From below the oven the cell is lit by a columnated DC-stabilized halogen lamp and above the oven the light shining through is recorded by a 3CCD camera. Within the image of the camera a region of interest can be selected. Normally this will be the part of the sample where interesting behaviour is expected. For this region of interest, the transmission of light through the sample at every position is sent to the PC. For the sake of data reduction there is the possibility to first average the transmission of the region of interest in one or both directions before storing it.

Before the actual measurement a photo of the region of interest is taken which yields the transmission in the metallic state T₀.

With the Lambert Beer law in mind (see next paragraph) in every measuring step the log of the normalized transmission is calculated, and with the raw data these values are stored in a data file on the PC. This data file also contains data on the pressure set point, the actual pressure in the cell, the temperature and information of the light source. From these files pressure-optical transmission-isotherms (pti’s) can be made for the thin film. A measurement typically takes half a day, depending on the time it takes for a material to reach equilibrium with the surrounding pressure. For the measurements presented here, data are written to the PC every 10 seconds.

As an example of the type of data delivered by hydrogenography, an output image of a PdCu composition thin film measured at 308 K is shown in Figure 14. In (A) there is the image of the region of interest covering most of the 70 x 5 mm glass thin film before the
measurement. The dark regions at both ends, best visible on the left side, show the sample holder. From the left to the right side the composition ranges from Pd$_{50}$Cu$_{50}$ to Pd$_{93}$Cu$_7$ respectively, as measured by Rutherford Back Scattering spectroscopy (see paragraph on thin film deposition later in this chapter). The thickness profile of the film which is inevitable with a varying composition, makes the film more transparent on the left side. This variation in transmission caused by the thickness profile is withdrawn by normalizing the data by the transmission in the metallic state.

In Figure 14 (B) an image is build up by showing the image in (A) averaged in the vertical direction, creating a horizontal line. These lines are normalized by the image in the metallic state. The log of $T/T_0$ is plotted for all 1400 measure steps. During the measurement the surrounding hydrogen pressure is cycled from 1 mbar to 1000 mbar and back. Each line in (B) corresponds to its own hydrogen pressure which is plotted in the left side.

The vertical lines in (B) can be explained by thin film defects which sometimes can be seen in the film. They don’t show an optical change.

![Diagram](image)

**Figure 14:** Hydrogenography output data for a PdCu film ranging from Pd$_{93}$Cu$_7$ (position 536) to Pd$_{50}$Cu$_{50}$ (position 15). The Cu concentration is not linear dependant on the position, but as $[Cu] = 88.9 \times 10^{-6} \times Position^2 - 0.131 \times Position + 51.96$. The coloured lines correspond to lines with the same colour plotted in Figure 22.

The measured transmission can give insight in the concentration of hydrogen in the film. This can be explained by the Lambert Beer relation.

In the next derivation the concentration of $\alpha$- and $\beta$-phase is the starting point. Simply said, there is a concentration of $\alpha$-phase in $\beta$-phase medium. We don’t assume anything about the H concentration, only that it causes the metal to be in the $\alpha$-phase or in the $\beta$-phase. Both phases add up to one. Light going through the metal interacts with both phases, and the intensity is
\[ I(x_\alpha, x_\beta) = I_0 \times \exp\{(-\mu_\alpha \times x_\alpha - \mu_\beta \times x_\beta)t\} + I_B \]

where \( I \) is the intensity, \( I_0 \) is the intensity of the light before it reaches the sample, \( I_B \) the background intensity of the CCD camera, \( x \) is the fraction of a phase, \( \mu_\alpha \) the absorption coefficient at the maximum \( c_H \) before the dual-phase region, \( \mu_\beta \) the absorption coefficient at the minimum \( c_H \) after the dual-phase region and \( t \) is the thickness of the film. Now it is nice to define a transmission \( T \)

\[ T \equiv \frac{I(x_\alpha, x_\beta)-I_B}{I_0} = e^{(-\mu_\alpha \times x_\alpha - \mu_\beta \times x_\beta)t} \]

and a transmission before any absorption of hydrogen

\[ T_0 \equiv T(x_\alpha = 1; x_\beta = 0) = e^{-\mu_{\alpha,0}x_\alpha t} \]

Here \( \mu_{\alpha,0} \) is the absorption coefficient at the as deposited metallic state, and please note that \( \mu_{\alpha,0} \) is not equal to \( \mu_\alpha \). Using the fact that the system is either in the \( \alpha \)- or in the \( \beta \)-phase, \( x_\alpha + x_\beta = 1 \). In hydrogenography we do not know the intensity of the light shining into the sample, so we divide out the factor \( I_0 \) by

\[ \frac{T}{T_0} = \frac{e^{(-\mu_\alpha \times x_\alpha - \mu_\beta \times x_\beta)t}}{e^{-\mu_{\alpha,0}x_\alpha t}} = \frac{e^{(-\mu_\alpha x(1-x_\beta) - \mu_\beta x_\beta)t}}{e^{-\mu_{\alpha,0}x_\alpha t}} \]

\[ = e^{(-\mu_\alpha x(1-x_\beta) - \mu_\beta x_\beta)t + \mu_{\alpha,0}x_\alpha t} = e^{\mu_{\alpha,0}x_\alpha t - \mu_\alpha x(1-x_\beta) - \mu_\beta x_\beta t} \]

\[ \ln \frac{T}{T_0} = (\mu_{\alpha,0} - \mu_\alpha)t + (\mu_\alpha - \mu_\beta)x_\beta \]

Formally, this equation (which states that the hydrogen concentration scales linearly with the logarithm of the normalized transmission) only holds in the dual-phase region. Outside this region there is an influence of hydrogen on the transmission which cannot be described by Lambert Beer. The absorption coefficient is an unknown function of the hydrogen concentration.

Nevertheless, it is worthwhile to plot \( \ln(T/T_0) \) also outside the plateau region and to compare it with the hydrogen concentration. We find that it produces isotherms that are comparable with pressure composition isotherms, though one should realize that Lambert Beer formally only holds inside the plateau region.

When measuring a thin film (TF) with a gradient composition or any other film with varying thickness, one needs to correct for this when converting the transmission to a hydrogen concentration. So on the “H concentration” axis, we plot

\[ c_H \sim \ln\left(\frac{T}{T_0}\right)/t \]

The relation between the transmission through and the concentration of hydrogen in a film can be experimentally proven by the electrochemical hydrogenation of a thin film. The loading is controlled by the constant current and in time H atoms that are absorbed by the thin film are counted. By in situ measuring the transmission of light through the film the Lambert Beer relation is checked. For this see the results on electrochemistry presented later.
**Thin film deposition and analysis**

Thin films have been prepared by high vacuum magnetron sputtering. Palladium and copper targets are placed at opposite positions facing the 70 × 5 mm glass substrate that is attached to a wafer held by the sample holder. In this way a gradient sample is made. In order to know the film thickness and the PdCu composition at all locations tooling samples have been made. On a glass substrate the material was deposited and the thickness of the films is measured by a DEKTAK profilometer. This is done separately for Pd and Cu, so we know at what rate the deposition takes place. From these data the total thickness of the PdCu film is calculated by adding the thicknesses of Pd and of Cu resulting in the points in Figure 16.

These points are fitted with an exponential fit:

\[ t(nm) = 89.6 \times e^{-0.121x(cm)} \]

From the thickness profiles the PdCu composition at the position on the wafer is calculated using the atomic volumes of Pd (8.85 cm³/mol) and Cu (7.11 cm³/mol). The results are shown in Figure 17 and the data are fitted with an exponential and also with a second order polynomial. For both fits the \( R^2 \) value lies close to 1, but especially at the high Cu concentration side of the film the fits differ a lot from each other.

In order to determine which fit is best to be used and to confirm the DEKTAK profilometer measurement, the Cu/(Pd+Cu) ratio has been measured with Rutherford Back Scattering spectroscopy.

In RBS spectroscopy He nuclei are shot on a sample and under an angle of 15 ° the reflected nuclei are detected. The velocity of the reflected particles give information about the mass of the atoms in the sample and the positions with respect to the surface.
of atoms in the film. Heavy atoms let the light He-nuclei bounce back fast, whereas light atoms give less velocity to the reflected particles. The energy is directly depending on the atomic number \( Z \) of the atoms in the film. The detection takes place at a certain channel which corresponds to an energy, and integration of the peaks returns the number of atoms present. Figure 16 shows the data of an RBS measurement of the \( \text{Pd}_{50}\text{Cu}_{50}-\text{Pd}_{93}\text{Cu}_{7} \) thin film at 0.5 cm from the low copper concentration side of the glass substrate, together with a simulation of the same experimental conditions of that spot on such a film. Peak integration gives a value of \( 4.69 \times 10^{17} \) and \( 4.64 \times 10^{16} \) \( \text{at/cm}^2 \) for respectively Pd and Cu, resulting in a copper concentration of 9.0 at.%. Also at 3.5 and 6.2 cm from the low copper concentration side of the substrate RBS was done resulting in a concentration of 22.9 at.% Cu and 46.5 at.% Cu.

![Figure 16: RBS result for a PdCu thin film. The data (black line) are fitted with a model (red line).](image)

A copper concentration \( \frac{n_{\text{Cu}}}{n_{\text{Pd}} + n_{\text{Cu}}} \) has been determined. The results are plotted in Figure 17 with the results from the DEKTAK measurement. Clearly the RBS data coincide with the profilometer data, and the DEKTAK data are best fitted with a second order polynomial:

\[
\text{Comp}(s) = 0.53x^2 + 2.8x + 7.0
\]

where \( s \) is the position on the substrate from the low copper content side in cm.
From the assumption that the thickness profile of a sputtered thin film is exponential, the composition profile of the Cu ratio can be calculated. If the thin film thickness is
\[
t_M = a_M \exp(b_M s)
\]
where \(a\) and \(b\) are deposition constants and \(s\) is the position, then
\[
\frac{n_{Cu}}{n_{Pd} + n_{Cu}} = \frac{1}{1 + \frac{AV_{Cu} \times b_{Pd}}{AV_{Pd} \times b_{Cu}} \exp\{(b_{Pd} - b_{Cu})s\}} = \frac{1}{1 + A \exp(Bs)}
\]
where \(AV_M\) is the metal atomic volume, and \(A\) and \(B\) fitting parameters. However, there is only a very small deviation from this fit and a second order polynomial.

It is known that sometimes there might be an influence on the deposition rate when two sputter sources are working at the same time (Pd and Cu). In the case of this sample the sources were opposite of each other in the chamber so we assume that there is no such an influence.

One sample has been prepared exactly as the Pd\(_{50}\)Cu\(_{50}\)-Pd\(_{93}\)Cu\(_7\) sample sputtered on a 3 nm Pd layer on glass, and is referred to as (Pd)PdCu.
Hydrogenography Results

The interaction of hydrogen with palladium copper alloys has been studied extensively. [8][9][10][16][19][20][21] According to Huang et al. [21] where they refer to [22] Cu can only absorb hydrogen to a very small amount at extreme conditions. Those are not the working conditions of the experiments presented in this paper, so we assume no copper hydride formation.

The influence of alloying Pd with Cu

First of all the kinetics of the PdCu thin film system at 308 K is studied. We want to find out how the response is of the intensity to the surrounding H₂ pressure, and if the diffusion of hydrogen in the alloy is not limiting the experiment. For this a Pd₁₀₀₋ₓCuₓ gradient thin film on a 5×70 mm glass substrate has been prepared with 8 < x < 50. In the first hydrogenation cycle the hydrogen pressure in the cell is increased in 10 steps from 1 mbar to 2 bar and back to 1 mbar hydrogen. After each step, there is a relaxation time of 10 minutes to observe the system response time (kinetics) to hydrogen. It was found that within this period the system completely relaxes. As for all data presented here, every 10 seconds data are stored in a file on the PC.

The 5 steps for hydrogenation from 1 to 2000 mbar are taken logarithmically, meaning that the increase of hydrogen pressure gets bigger with each consecutive step. The 4th step goes from 95 mbar to 440 mbar, and the pressure set point and actual pressure in combination with response in intensity of the Pd₉₅Cu₁₅ (70 nm) composition on the film are plotted in Figure 18. From the graph it can be seen that the intensity nicely follows the hydrogen pressure. For these rather large pressure steps the actual hydrogen pressure needs to adjust for some time before stabilizing at the desired pressure set point.
Figure 18: Loading of a thin film at 308 K. The measured H₂ pressure needs some time to respond to the (large) pressure step set point. The intensity in Analog to Digital Converter units follows the pressure.

The hydrogenation is not limited by kinetic effects for this PdCu composition. There is a rather large overshoot of the pressure which might cause problems in the transmission data in case there is a hysteresis. In all following measurements the hydrogen setpoint steps are much smaller and no overshoot has been noted. Normally the unloading of a metalhydride causes more difficulties than the loading. For that reason in Figure 19 the data of a pressure step in dehydrogenation is presented.
Figure 19: Dehydrogenation step of Pd$_{85}$Cu$_{15}$. Intensity is related to left side axis, pressure and setpoint pressure to right side axis.

A change in pressure is followed by an instant change in intensity. The response to the first rather large pressure steps is smaller than the change in intensity when the pressure drops below 200 mbar. This is no kinetic effect, it is just telling us that the response of the intensity to the hydrogen pressure is not linear. As the pressure reaches the pressure set point, the intensity also reaches a value which is constant in time. There is delayed effect in the intensity after the pressure has stabilized.

The kinetics might be affected by the amount of alloying with copper in PdCu. By studying various compositions on the film it is found that there is no significant influence of the amount of alloying with Cu in the range of 7-50% on the systems kinetics.

All further experiments are done with pressure steps smaller than 25 mbar per 30 seconds. Based on the results shown above these steps are not limiting the systems kinetics.

Knowing this, we did three exactly similar cycles lasting 5 hours per cycle at 308K to examine the systems reproducibility. For the Pd$_{83}$Cu$_{17}$ composition the results are shown in Figure 20. One expects the intensity to go back to the same value as before the cycle. Then the log of the normalized intensity has the value 0. In the plot it can be seen that this is not the case. The value goes to less than 0, which means that the sample is darker than before. It is not understood why this happens but it might be related to reorganisation of the microstructure in the film.
Figure 20: Optical response to three PdCu hydrogenation cycles (2,3 and 4). In each cycle the pressure goes from 1 mbar to 1 bar and back. Note that the starting value changes in cycle 2.

Since one of the key properties of the isotherms is the plateau pressure, the development of the pti’s is plotted in Figure 21 for the three cycles at the same composition. There is no large change in behaviour, except for the deviation from 0 which was already mentioned. Inside the graph the isotherm in the plateau region is plotted, and a small deviation appears between the 2nd and 3rd cycle. The 4th cycle is exactly the same as the 3rd cycle, from which it is concluded that the system is stable upon cycling.

Figure 21: Pti’s showing the reproducibility of 3 consecutive cycles (2,3 and 4) at 308 K for Pd$_{83}$Cu$_{17}$. The inlay shows the same data in the plateau region for the hydrogenation. There is a difference in transmission for the value at low hydrogen pressure between cycle 2 and 3, as well as a difference in plateau pressure for absorption (see inlay). Both effects don’t appear between cycle 3 and 4.
Being sure that the PdCu system is not limited by kinetics and that it shows reproducibility the influence of alloying with copper is examined. This is done by plotting pti’s for several copper compositions in one graph, from the same data presented in the image in Figure 14. The colours of the isotherms correspond with the lines in that image. Figure 22 shows pti’s of compositions of the sample being cycled (for the fourth time) at 308 K between from 1000 mbar to 1 mbar in 300 logarithmic pressure steps.

Figure 22: Fourth hydrogenation cycle of some Pd$_{100-y}$Cu$_y$ compositions at 308 K. The amount of copper is shown in each isotherm. Note the transition of a dual phase region clearly showing a plateau (Pd$_{90}$Cu$_{10}$ and Pd$_{85}$Cu$_{15}$) or sloping plateau (Pd$_{90}$Cu$_{15}$) to a single phase region at Pd$_{72}$Cu$_{28}$. The critical point is expected somewhere between 20 and 28 % Cu. The unexpected shape of the 23% and 25% Cu data are not yet understood.

The Pd$_{90}$Cu$_{10}$ isotherm shows very clearly a dual phase region. There is a plateau pressure of 50 mbar, and the effect of inserting more copper makes this pressure go up. Besides that, the shape of the isotherms changes. The plateau transforms into a more “sloping plateau” with increasing copper content. For Pd$_{77}$Cu$_{23}$ and Pd$_{75}$Cu$_{25}$ we see some unexplained behaviour. It is exactly in this region that we expect the plateau and with that the α/β-mixed-phase region to disappear.

An explanation why the plateaus are not horizontal lies in the fact that these are thin films. The adhesion of thin films to a glass substrate is to a certain extend influenced by the film material. Palladium, being a noble metal, doesn’t form a strong bond with the siliciumoxide. The less noble copper makes stronger bonds with it, so the more doping with Cu, the better the sticking of a PdCu film to the substrate. This sticking to the substrate is the reason of clamping and an elevated plateau pressure in hydrogenation
because the system is constrained by the substrate when it wants to expand in order to absorb $H_2$.

The closer to the substrate the stronger this clamping effect gets. So in the region close to the substrate there will be absorption at a relatively high plateau pressure, and in the region further from the substrate there will be less suffering from clamping and a “normal” $p_{plat}$. This is explained in the schematic isotherm in Figure 23. The film is divided in 4 layers where the difference lies only in the proximity of the substrate, so we get an isotherm with 4 plateau pressures. Since in an experiment there are infinite sublayers the 4 steps will be seen as an average of many steps just like the blue line in Figure 23.

The more copper there is to clamp to the substrate, the larger this effect will be. So in Figure 22 the $Pd_{90}Cu_{10}$ plateau is horizontal and at 20 % Cu there is a sloping plateau.

Figure 23: Schematic representation of the construction of a sloping plateau. Close to the substrate a thin film will be loaded at a higher plateau (1) because of a clamping to the substrate. Further from the substrate the film will be loaded at lower pressure (4).

The hysteresis is much smaller than the one seen for the bulk data measured by Burch and Buss. An explanation will be given in the discussion about the influence of critical points on page 45. The graph in Figure 24 compares the hysteresis for a PdCu thin film with bulk data.
Figure 24: Hysteresis for Pd$_{85}$Cu$_{15}$ for TF (symbols, this work) and bulk data (full lines). Data are taken from Burch and Buss [8]. In both cases absorption is at higher pressure.

Knowing that absorption data underestimate the plateau pressure Figure 25 compares dehydrogenation data of TF’s by hydrogenography with bulk data with Sieverts type measurement for copper compositions that are found in literature [8]. In there, the $x$ axis is normalized by the film thickness. This is done to have a linear relation between the hydrogenography output data ($\ln(T/T_0)$, lower axis) and the hydrogen concentration (upper axis) measured in bulk.
Figure 25: Comparing TF hydrogenography pti’s with bulk data pci’s measured by Burch and Buss in a Sieverts type measurement [8]. The film thickness is 80 nm (Pd$_{90}$Cu$_{10}$), 70 (Pd$_{85}$Cu$_{15}$) and 63nm (Pd$_{80}$Cu$_{20}$) and the scaling between both horizontal axes is $c_H = 36.7 \times \ln(T/T_0)/t$

Both the plateau pressures for these thin film compositions and the shape of the isotherms don’t deviate too much from bulk data. The data are fitted in such a way that the data for the hydrogen rich side for 15% Cu coincide.

For some reason the data from Burch and Buss [8] show a somewhat rounded edges. That’s why hydrogenography data are also compared to dehydrogenation of PdCu samples in bulk by a Sieverts’ method by Sakamoto and colleagues [9]. Data are put in the same graph in Figure 26. Note that the measurement by hydrogenography is at 5 degrees higher temperature, though this should not affect the outcome a lot. It is striking that the data for both 15 and 20 % Cu follow the same shape at the hydrogen poor and rich side. Only the plateau is lower and more sloping in the case of thin film. When not taken the Pd$_{90}$Cu$_{10}$ composition into account, the width of the plateau is exactly equal. We have seen before that Burch and Buss [8] find a linearity in the relation between phase boundary and Cu content.
We have seen that there is a large influence of the temperature on the shape of the isotherms, as it is shown for Pd in Figure 2. The simple lattice gas model can explain the range of this impact. The influence of temperature as it is found for Pd is the same for PdCu.

To investigate the influence of the temperature an experiment was set up where a Pd$_{100-y}$Cu$_y$ gradient composition TF with a Cu concentration between 3-30%. The film is cycled at 307 K (cycle 11), 323 K (cycle 9) and 353 K (cycle 10), and the dehydrogenation data for the Pd$_{95}$Cu$_5$ composition (38 nm) are shown in Figure 27. In the same graph reference data measured by Sakamoto and coworkers in a Sieverts type method at (almost) the same temperature [9] are plotted.
Figure 27: Dehydrogenation of Pd$_{95}$Cu$_5$ at various temperatures. Symbols only show data at the end of each pressure step in hydrogenography. Bulk data refer to the upper axis and are measured by Sakamoto et al. [9].

After cycling at 308 K the Pd$_{93}$Cu$_7$-Pd$_{50}$Cu$_{50}$ sample has been loaded and unloaded with hydrogen at 323 K and 373 K. The data are presented as images that are build up as described before Figure 14.
Figure 28: Hydrogenography data at 323 K showing $\ln(T/T_0)$ plotted on a logarithmic pressure axis with a range from 32 to 1000 to 32 mbar. On the horizontal axis is the PdCu composition ranging from Pd$_{50}$Cu$_{50}$ (position 15) to Pd$_{33}$Cu$_{7}$ (position 536). The copper concentration is almost linear versus the position, but it is best described by a polynomial shown below Figure 14.
Finding the plateau pressures

Hydrogenography allows us to obtain pti’s of hundreds of compositions at the time. In order to extract the plateau pressure for many of these compositions, a fitting procedure is followed. By plotting the $\ln(T/T_0)$ on the y-axis and $p$ on the x-axis a Boltzmann curve can be fitted through the plateau region, and the plateau pressure is defined as the $p$-value where the derivative has its maximum. It is necessary to mention that not all composition have a clear plateau but some (Cu-rich) have more sloping plateaus. By using a Boltzmann curve fitting procedure the plateau pressure in the sloping plateaus is also found. A Boltzmann function is described by

$$\ln(T / T_0) = \frac{A_1 - A_2}{1 + \exp\left(\frac{p - p_{PLAT}}{dp}\right)} + A_2$$

where $A_1, A_2$ and $dp$ are constants and $p_{PLAT}$ is the plateau pressure.
Normalizing all data in a way that for each composition the minimum is 0 and the maximum is 1 makes the fitting procedure easier. As an example fitting data for Pd$_{100-x}$Cu$_x$ for the 4$^{th}$ dehydrogenation at 308 K are presented in Figure 30.

Figure 30: Normalized isotherms against pressure that are fitted with a Boltzmann function in the plateau area.

Clearly there is a transition between 24% and 28% Cu. The fitting has been done for the cycles at 308 K, 323 K and 373 K, and the data are presented in Figure 31, Figure 32 and Figure 33. On the x-axis is plotted the copper concentration and on the y-axis the plateau pressure extracted from the isotherms by the Boltzmann procedure.
Figure 31: Plateau pressures at 308 K for loading and unloading PdCu. Obtained by fitting a Boltzmann curve through isotherms in the plateau region, as shown in Figure 30.

Figure 32: \( p_{\text{plat}} \) for PdCu at 323 K.
Finding the critical copper concentration

The plot as shown in Figure 22 suggests the existence of certain copper concentration at which there is no more hysteresis and where the plateau or sloping plateau has disappeared. With other words, there is a PdCu composition at which there is no phase change when absorbing hydrogen. There are several ways to find this composition.

1. In a van ’t Hoff plot the disappearing hysteresis marks the critical point. As explained earlier on page 14 by measuring at different temperatures and plotting the plateau pressure’s versus the reciprocal temperature one can find a critical temperature where the absorption and desorption plateau pressure are equal.

2. The hydrogenography output image suggests a point where there is no more sudden increase in transmission, or a disappearing plateau. The phase change takes place where we see the difference between the dark region and the light one. Unfortunately there is no theoretical theory that suggest where to find this point.

3. By plotting the plateau pressure against the Cu concentration a relation is found and this reveals a critical concentration. Flanagan and colleagues show in there paper [20] that there is a linear relation between the log of the plateau pressure and the copper concentration. Like in the case of a van ’t Hoff plot a hysteresis shows up and it’s disappearance marks the critical Cu concentration, $c_C$. The fundamental difference between this method and the first one is that here we measure various Cu concentrations at a single $T$ and find a $c_C$ whereas with the van ’t Hoff method we measure at a single PdCu composition at various $T$ and find a $T_C$. Now the critical point unites the critical temperature and the critical copper concentration, so both methods should gain the same result.
Figure 34: Plateau pressure’s against copper composition in Pd$_{1-x}$Cu$_x$. The values at higher pressure are for absorption (open symbols) and the ones at lower pressure for desorption (filled symbols). Graph is taken from Flanagan et al. [20], who used the data from Sakamoto for Pd$_{95}$Cu$_5$-Pd$_{80}$Cu$_{20}$ [9]. The authors measured at 30% Cu and at this composition the hysteresis almost vanishes. Compare this with relation based on the lattice gas model in Figure 11.

From Flanagan's data [20] shown in Figure 34 we would expect a larger difference between the loading and unloading. Already we have seen that the data measured by hydrogenography show a much smaller hysteresis than bulk data, see Figure 24. Putting the data of Flanagan with the data of hydrogenography in one graph results in Figure 35. As we have seen before we note that the pressure for unloading for thin films coincide with bulk, but for loading this is not the case.
Figure 35: Comparing plateau pressures of hydrogenography with bulk, taken from [20] as shown in Figure 34. Thin film data show a much smaller hysteresis, the unloading data coincide.

Because of the small deviation between load and unload there is no distinct point at which both lines cross and thus that is not the way to define the critical composition. These points are plateau pressures defined by plotting a Boltzmann curve, where the plateau is defined by the pressure at which the derivative of the Boltzmann curve has its maximum. If the system is in the β-phase there is no plateau, but still the fitting procedure finds a value for the plateau at higher H\textsubscript{2} pressure than was measured at. This is the case for compositions 28 and 32 as shown in Figure 30. In Figure 31 we can see that this leads to a plateau pressure of $10^{3.4} = 2500$ mbar, which shows a large divergence from the linearity of the smaller plateau pressures. The critical point is defined as the composition at which the pressure for the first time shows a large deviation from the linearity between log $p$ and the Cu concentration of the other points. For the plateau pressures at 308 K this means that we find a critical Cu composition of 26%, at 323 K it is Pd\textsubscript{74.5}Cu\textsubscript{25.5} and at 373 K it is Pd\textsubscript{81}Cu\textsubscript{19}.

These critical points data are plotted in a graph together with the critical points taken from the work of Böttger and Nanu [8]. They derived the critical points by an estimation of the temperature at which the phase boundaries come together at various compositions, as plotted in Figure 13. For pure Pd a critical temperature has been determined experimentally by Frieske and Wicke [12] and that value from is added to the graph. On top of that this plot shows the critical temperature of a Pd thin film, taken from Gremaud et al. [5]
From Figure 36 we note that the critical temperature that we find in thin films by hydrogenography is lower than the values found by CVM.

Except for a publication by Sakamoto and colleagues where they show a disappearing gap between the α- and β-phase for Pd$_{67}$Cu$_{33}$ at room temperature by using X-ray diffraction and electrochemical introduction of hydrogen [19] there are no bulk measurements explicitly showing a critical temperature for PdCu compositions. The phase boundaries calculated by Böttger and Nanu [10] fit very well with the measured bulk phase boundaries [9][12][23] at high hydrogen concentration and rather good at low hydrogen concentration, see Figure 13.

Thin films tend to clamp to the substrate and because of this there is a reduced H-H interaction and a reduced $T_C$ [5], so it is not surprising that we find lower critical temperatures.

There seems to be a linearity in the plot of the CVM data in Figure 36. For the hydrogenography data this is not the case. At lower temperature we find a relatively lower critical Cu concentration. As mentioned before, the sticking of Cu to the substrate is larger for Cu than for Pd. So increasing the copper in a sample increases the sticking to the substrate and the clamping. Since clamping lowers the H-H interactions we expect to find a reduced $T_C$ at higher Cu compositions, and this is what we see for the sample at 308 K. The data at 323 K and 373 K are equal in the deviation from the bulk $c_C$.

Since for PdCu thin films we are closer to $T_C$ there is a smaller hysteresis as it was shown in Figure 24. This follows from the construction of a van ‘t Hoff plot as shown in Figure 7.

To exclude sticking of Cu to the substrate and effects thereof on criticality, we prepared another sample which is exactly the same except for a 3 nm interlayer of Pd between
the substrate and film. This layer is present to eliminate the composition dependant interactions between substrate and thin film. All experiments as described above are done simultaneously for both samples. First the influence on the plateau pressure is shown, since this is supposed to be influenced by the clamping to the substrate. Figure 37 shows that a 3 nm Pd interlayer has a large effect on the plateau pressure.

![Graph showing the difference between PdCu compositions on substrate and on a 3 nm Pd layer on the same substrate.](image)

**Figure 37:** 4th dehydrogenation at 308 K showing the difference between PdCu compositions on substrate and on a 3 nm Pd layer on the same substrate.

The effect of lowering the plateau pressure by a Pd interlayer increases as the amount of copper in the PdCu composition increases. Especially at 28% Cu there is still something which hints at a plateau visible for (Pd)PdCu and not for PdCu. As for the PdCu sample the plateau pressure’s have been determined at various temperatures for the PdCu on Pd interlayer sample. The results for the critical temperature are shown in Figure 38, Figure 39 and Figure 40.
From Figure 38, Figure 39 and Figure 40 the critical concentrations at 308 K, 323 K and 373 K are determined to be 28.5, 25.5 and 19.5 at.% Cu respectively. Together with the concentrations found by CVM [10] these values are plotted in In Figure 41. There we can see that the critical points run more parallel to the “bulk” critical concentrations from CVM calculations. This is explained by the elimination of the effect that alloying with copper has on the substrate effect, end thus on the critical points.
Figure 40: $p_{\text{plat}}$ for (Pd)PdCu at 373 K.

Figure 41: Critical Cu concentration and critical temperatures. Data by Nanu et al. (CVM) [10], Frieske et al. (bulk) [12], Gremaud et al. (TF) [5] and this work. The effect of a Pd interlayer - shielding the Cu interactions with the substrate- is that it reduces clamping and brings the thin film values closer to bulk.

It is known that in thin films clamping to the substrate reduces long range H-H interactions and therefore the critical temperature. This effect is confirmed by these results. The influence of a 3 nm palladium layer between film and substrate reduces the clamping effect and produces $T_C$ values closer to bulk.
**Electrochemistry on Pd and PdCu**

*Electrochemistry: Theoretical background*

Hydrogenography is based on the relation between the transmission of light through a metal thin film (TF) and the amount of hydrogen absorbed in that film. Lambert Beer law tells us that this is a linear relation for the dual phase region. To find out if this is the case for Pd and PdCu TF’s, experiments are done where samples are hydrogenated by electrochemical charging and discharging while at the same time the transmission of light through the film is measured.

There are several ways to use electrochemistry for comparing it with hydrogenography. One way is to link the hydrogen surrounding pressure with a potential. There for one applies a rather high current for a short time to change the oxidation state of a sample, followed by a relaxation time. The potential goes to an equilibrium value and it can be converted to a hydrogen pressure. With this so called Galvanostatic Intermittent Titration Technique (GITT) one knows the amount of hydrogen in the film and the pressure (from the potential) whereas in hydrogenography the $c_H$ is measured indirectly by the transmission through the film. R.Niessen has used this technique to measure the discharge potential for Pd and found a maximum discharge value of PdH$_{0.7}$. [24]

In this study I have chosen another way to link the transmission with the hydrogen concentration, namely the galvanostatic technique. In these measurements a current which is constant in time is applied and the output potential is not in equilibrium. This means that we accurately know the amount of hydrogen in the film. The potential is not in equilibrium and doesn’t provide any quantitative information, but, as will be seen later, the change in the potential marks an important point. During the measurement the transmission through the film is assessed.

The galvanostatic technique will give results that can confirm the linear relation between $c_H$ and $\ln(T/T_0)$ as predicted by the Lambert Beer law. The galvanostatic measurements are much faster since there is no relaxation time needed for the potential to reach equilibrium. For that reason I have chosen to do galvanostatic measurements. Besides, the discharge potential from the galvanostatic measurement can show the total amount of hydrogen that was stored in the film. This can tell us the H concentration at the $(\alpha+\beta)/\beta$-phase boundary for PdCu films with varying Cu concentration. These can be related to similar data measured by others, as is shown in Figure 42.
Figure 42: Image taken and edited from Burch and Buss [16] showing solubility of hydrogen (loading) at 1013 mbar and 303 K as a function of alloy composition in Pd$_{100-x}$Cu$_x$.

Measuring the potential between two electrodes while applying a constant current through the electrolyte allows us to study the (de-)hydrogenation of a thin film. Literally meaning "current constant" a galvanostatic measurements allows us to count hydrogen atoms that are ab- or desorbed by the electrode. Every electron arriving at the thin film corresponds to one hydrogen ion from the electrolyte being absorbed by the metal. Knowing the current and the time Faraday’s law allows us to calculate the amount of hydrogen that has reacted.

$$n_H = \frac{I \cdot t}{F}$$

where $n_H$ is the amount of hydrogen in mol, $I$ the current, $t$ the time and $F$ Faraday’s constant.

As mentioned the hydrogen pressure at which ab- or desorption takes place can be related to an electrochemical potential through the chemical potential.

$$\mu_{MH} = \frac{1}{2} \mu_{H_2} = \frac{1}{2} \mu_{H_2}^0 + \frac{1}{2} RT \ln \frac{p_{H_2}}{p_{ref}}$$

Here, $\mu_{MH}$ is the chemical potential for a hydride forming compound, $\mu_{H_2}^0$ is the standard chemical potential for hydrogen gas, which is zero, and $p_{ref}$ is 1 bar. Now the chemical potential is related to the electrochemical potential through

$$\mu_{MH} = -FE_{MH}^{eq}.$$ Combining these two we find that

$$E_{MH}^{eq}(V) = -\frac{RT}{2F} \ln \frac{p_{H_2}}{p_{ref}}$$
For the hydrogenation of Pd the equilibrium pressure is 20 mbar at room temperature so \( E = 0.051 \text{ V} \). For unloading the pressure is 5 mbar which converts to a potential of 0.069 V.

A potential is measured between two electrodes. In electrochemistry these are defined as the working electrode (the sample under investigation) and the counter electrode (a Pt foil). The electrodes are in contact with each other by the electrolyte liquid, which is a 0.5 M H\(_2\)SO\(_4\) solution in water. The reactions that take place during and after charging and discharging, with the corresponding standard potential, are summarized in Figure 43.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Working electrode</th>
<th>Counter electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>Pd + H(^+) + e(^-) \rightarrow PdH</td>
<td>2H(^+) + 2e(^-) \rightarrow H(_2)</td>
</tr>
<tr>
<td>Desorption</td>
<td>PdH \rightarrow Pd + H(^+) + e(^-)</td>
<td>2H(_2)O \rightarrow O(_2) + 4H(^+) + 4e(^-)</td>
</tr>
<tr>
<td>E(^0) (V)</td>
<td>0.051</td>
<td>0.000</td>
</tr>
<tr>
<td>E(^0) (V)</td>
<td>0.069</td>
<td>-1.23</td>
</tr>
</tbody>
</table>

**Figure 43**: Chemical reactions that take place in electrochemical (de-)hydrogenation of Pd in acidic electrolyte.

From the palladiumhydride pressure-composition-isotherms we know that about 60 at% of the Pd is hydrogenated at the end of the plateau. Then the system is in the \( \beta \)-phase where the pressure goes up steeply with hydrogenation. What marks this transition in electrochemistry? When a reduction reaction (Pd + H\(^+\) + e\(^-\) \rightarrow PdH) comes to an end in electrochemistry the potential goes to another value corresponding to a different chemical reaction. In case of an 0.5M H\(_2\)SO\(_4\) electrolyte that is the reduction of protons with the formation of H\(_2\) gas.

From Figure 43 it is found that the potential difference between the reaction during absorption \( (E^0(V) = 0.051) \) and the reaction after absorption \( (E^0(V) = 0.000) \) is not large which makes this transition hard to determine. In contrast to that, the change in potential going from desorbing hydrogen to oxidizing water is large and easily noticed in the potential characteristic. Because of that the determination of the width of the plateau is easier for unloading than for loading.

A potential is always measured versus a reference electrode. To convert the measured potential versus a reference potential r.e. (labelled \( E(\text{vs.r.e.}) \)) to a potential versus the natural hydrogen electrode \( E(\text{vs.NHE}) \), at which \( E^0 \) is defined as zero, one must add the potential of the reference electrode, \( E^0(\text{r.e.}) \):

\[
E(\text{vs.NHE}) = E(\text{vs.r.e.}) + E^0(\text{r.e.})
\]

In case of a Ag/AgCl in 1 M KCl reference electrode \( E^0(\text{Ag/AgCl}) \) is 0.235, so

\[
E(\text{vs.NHE}) = E(\text{vs.Ag/AgCl}) + 0.235
\]

51
Figure 44 shows a typical charge-potential galvanostatic cycle for palladium, measured as in all data presented in this work versus a Ag/AgCl r.e. In there we can clearly see the difference between the transition in the potential between charging (small) and discharging (large transition).

![Graph showing galvanostatic charge and discharge curves for PdH at 303 K.](image)

Figure 44: Characteristic galvanostatic charge ($I = -20 \mu A$) and discharge ($I = 20 \mu A$) curve for PdH at 303 K. On the vertical axis the potential versus a silver/silverchloride reference electrode, on the horizontal axis the sum of the charge normalized by the thin film mass for load and unload. The vertical line marks the maximum discharge capacity for Pd at room temperature as found by R.Niessen to be PdH$_{0.7}$. [24]

**Electrochemistry: Experimental**

The electrochemical cell is designed to study electrochemical hydrogenation while in situ measuring optical characteristics of thin films. The cell is build up from two connected compartments containing the liquid electrolyte, separated by a salt bridge. These compartments are fitted in a larger compartment where cooling water is running through. On top of the cell there are airtight connections for the electrodes. Figure 45 shows a schematic drawing of the electrochemical cell.

The thermostated cell has room for three electrodes that are in contact with a conducting liquid electrolyte. The sample to be investigated is defined as the Working Electrode (WE) and the Counter Electrode (CE) can be any material that doesn’t change its oxidizing or reducing reaction during the measurements. In the experiments described here a Pt foil is used. In order to obtain quantitative results on the potential a Reference Electrode (RE) is added to the system. It is placed very close to the WE to reduce the Ohmic drop of the electrolyte. The RE is made from a substance with invariant potential and high input impedance in order to have an open circuit situation.
Very little current goes through the RE to allow almost all current to interact with the working electrode during experiments.

A Potentiostat/Galvanostat controls the current while the potential is measured or vice versa. The P/G is controlled by a PC that is running a HP/VEE program, and at the same time the PC stores the data that are received from the P/G. The design of the cell allows for the thin film to hang between two flat windows creating an optical path through the cell. 635 nm Laser light shines through the optical path in the cell and is partly transmitted by the sample into a photodiode which is linked to a Keithley multimeter. The light that’s reflected by the material under investigation can be also collected by another photodiode. While the program is running the Keithley collects the signals of both photodiodes and together with the data obtained by the P/G (current, potential and time) it is sent to the PC, that stores all data in a file.

Even small amounts of oxygen interfere with measurements [25] so the electrolyte is purged with argon before (1 hour) and in between (15 minutes) measurements. The cell contains three water locked gas compartments to let Ar enter the cell and one water locked compartment to let gas go out while preventing air from coming into the chamber. To avoid the risk of interfering with the flow of current through the electrolyte, Ar is not blown through but only over the electrolyte during the measurement.

Reactions are possible in basic and acidic electrolyte. All measurements described in here are done in 0.5 M H₂SO₄ unless mentioned otherwise. The potential is measured
versus a 1 M KCl Ag/AgCl reference electrode, $E = 0.235\text{V}$. All measurements are done at a temperature of 303 K.

Three sets of samples have been prepared by sputter deposition on 10 × 20 mm quartz substrates. Before the actual deposition of the samples the sputter rates are determined by sputtering for some time and determination of the thickness with a DEKTAK profilometer. In this way the film thickness is known for all layers. The first set consists of 60 nm Pd films. In the next set there is a 3 nm Ti interlayer between the 60 nm Pd and the substrate, which should improve the sticking of Pd to the substrate. Ti, being less noble than Pd, makes a better adhesion to the quartz than Pd and Pd sticks better to Ti than to the substrate. In case the Pd samples fall off the substrate through charging cycles the (Ti)Pd films might withstand by better sticking properties.

Last of all PdCu films with varying Cu composition are deposited on Ti (3 nm) on quartz. We aimed at making PdCu films with 5, 10 and 15 % Cu by repeating the sputtering routine while the power of the sputter sources was adjusted each time. Next to the quartz 10×20 mm substrates on the wafer a small 5×5 mm carbon substrate is put, which is used to check the compositions with RBS. In Figure 46 the RBS data are plotted and by peak integration it is found that the compositions are Pd, Pd$_{96.2}$Cu$_{3.8}$, Pd$_{91.6}$Cu$_{8.4}$ and Pd$_{86.6}$Cu$_{13.4}$.

![RBS graph of 4 samples on a carbon substrate. r101 is a pure Pd sample, samples r102, r103 and r104 are PdCu samples with respectively increasing Cu content. The peak at channel 620 is Pd, the one at 550 is Cu. Integration of the peaks has shown that the compositions are Pd$_{96.2}$Cu$_{3.8}$, Pd$_{91.6}$Cu$_{8.4}$ and Pd$_{86.6}$Cu$_{13.4}$.

The sample needs to be connected to a platinum wire which runs through a glass plug that fits airtight to the electrochemical cell. To do so the film side of the sample will be
connected to a pre-shaped Pt wire by a conductive silver paste (Ag in methyl-isobutylketone). This is let dry for 15 minutes in air and subsequently the connection is covered with adhesive (Uhu 2 component epoxy adhesive) to prevent any contact between the silver and the electrolyte. After checking that the glued part is dry and completely insulating the remaining conductive parts, except for the thin film and the end of the Pt wire, are covered with glue. In this way only the thin film is in contact with the electrolyte.

Now on one end of the Pt wire we have the sample, and the other end is connected to the Pt wire running through the glass plug. This connection, which hangs well above the electrolyte level, is stabilized with teflon tape. One needs to know the exact surface area of the thin film in order to calculate the hydrogen concentration in units of hydrogen atoms per metal atom. A photo is taken from the sample and it is analyzed with photo editing software to determine the thin film surface area by counting the pixels.

Electrochemistry: Results for Pd

To be able to show a proof of principle the galvanostatic absorption behaviour of a palladium thin film was studied in order to compare hydrogen absorption values to reference data. Applying a negative current corresponds to the reduction of H\(^+\) and consequently the absorption of H by Pd at the working electrode. Figure 48 shows for the hydrogenation of a Pd thin film the potential versus time with a current of \( I = -20 \mu A \) .
Figure 48: Galvanostatic loading of 60 nm Pd TF with in situ measurement of transmission of Laser light (635 nm) through the film at 303 K. On the right side axis the potential versus a Ag/AgCl r.e., on the left side the normalized transmission. As a guide to the eye the blue straight line shows linearity between $\ln(T/T_0)$ and $c_H$.

The log of the normalized transmission shows a relation with the charge which is not far from linear.

It is not obvious to determine from the potential when the sample is fully loaded. For this we need the data from the dehydrogenation, as shown in Figure 49. Now on the vertical axis the discharge capacity in mAh/g is plotted.
As can be seen in Figure 49 there is a sharp transition from a low potential to a higher potential. This is at a value of 168 mAh/g which corresponds to an $H/M$ value of 0.66. The log of the transmission for discharging the Pd film as plotted in there shows a nonlinear relation with the charge per mass (which is linear with the H concentration) where linearity is predicted from the Lambert Beer law stating that $\ln \frac{T}{T_0} \propto c_H$. It is not understood why this is the case. In all measurements the predicted linearity between the log of the normalized transmission and the hydrogen concentration is approximated in charging but for discharging it is not found in the whole region of discharging.

Figure 49: Unloading of the same sample as in Figure 48. Unlike in the case of the hydrogenation here we do see a sharp transition in the potential. This marks the end of the plateau and the start of the oxidation of water. The increases of the transmission after the transition is not understood. As a guide to the eye the blue straight line shows linearity between $\ln(T/T_0)$ and $c_H$. Only in a small range this linearity is found.
Galvanostatic hydrogenation has been done with the Pd TF on a 3 nm adhesive Ti layer on quartz. The charging potential and transmission has been plotted in Figure 51, the discharging in Figure 52. To be able to find the influence of this sticking layer, the same data as presented earlier on Pd TF’s is also plotted in the same graphs.

Figure 51: Charging Pd and (Ti)Pd TF with electrochemistry at 303 K. The grey vertical line marks the point where, if all current is used for hydrogenation, $\text{PdH}_{0.7}$ is reached.
There is a clear difference between the Pd on glass and Pd on Ti on glass in unloading. After the transition in potential (end of PdH unloading) the Pd electrode stays constant but the (Ti)Pd electrode has another transition. Since the only difference between the electrodes is the lack or presence of the Ti interlayer, the change in potential corresponds to a reaction taking place in that layer. It is known that titanium forms a dihydride at very low pressures. Unloading TiH$_2$ is very difficult with hydrogenography, but it seems to be possible with electrochemistry. The charge per thin film mass that is related to this second transition in Figure 52 where the potential goes from $E = 0.9$ V to $E = 1.2$ V is about $\frac{220 - 190}{166} = 18\%$ of the $Q/m$ for unloading the PdH. Knowing that the film contains 60 nm Pd and 3 nm Ti and the stoichiometric factors of the hydrides (TiH$_2$ and PdH$_{0.7}$) this factor is about the same: $\frac{2 \times 3 \text{nm}}{0.66 \times 60 \text{nm}} = \frac{10}{60} = 15\%$. So from this it is concluded that the second transition in the potential when galvanostatic unloading a (Ti)PdH film is caused by the dehydrogenation of titaniumhydride.

To be able to compare galvanostatic cycles for Pd and (Ti)Pd these are plotted together in Figure 53. The vertical axis is decreasing from bottom to top in order to relate directly with a log of the H$_2$ pressure axis. In this way the plot can be compared with pressure concentration isotherms or pressure optical transmission isotherms, as it has been done in the chapter on substrate effects on page 70. Since the potential has not reached equilibrium, this comparison is only qualitatively. Clearly the hysteresis between loading
and unloading increases with adding the Ti interlayer. This has also been found in hydrogenography. See the discussion on substrate effects in the Discussion.

![Graph showing galvanostatic charging and discharging of Pd and Pd on Ti films.](image)

Figure 53: Galvanostatic charging and discharging of Pd and Pd on Ti films. There is a remarkable increase in the hysteresis when adding a Ti adhesion layer in between Pd film and substrate.

The Pd film degraded from the sample after one cycle, but for the (Ti)Pd film it has been possible to do multiple cycles. In Figure 54, the sample has been charged for the first second and third time with a current of respectively -20 μA, -80 μA and -80 μA for at least 1 H/M equivalent. The discharging was done with respectively I = 15 μA, 80 μA and 80 μA. So there is exactly no difference in the conditions between unload 2 and 3 while the results show an earlier transition related to the end of the dual phase region. This might be related to the slow degradation of the film. Less material on the film translates to a smaller discharge capacity.

The titaniumhydride unloading regime shifts to higher charge through cycling. The reason is not known. In further experiments the discharge is stopped before unloading the TiH₂ layer because it is found that unloading this layer makes the thin film degrade.
A Pd sample has been covered with a 50 nm protective hydrophobic teflon based polymer which we name Special Protective Coating (SPC). Result show that this layer blocks the immediate charging of the Pd, but that after some the charging does take place. This can be seen from the results in Figure 55 where the transmission and reflection show a transition only after 45 minutes. It can be that the SPC is degraded from the interaction with the (acidic) electrolyte, but unpublished experiments by M.Slaman have shown that SPC is stable in an acidic environment. Probably there is a retardation effect caused by the slow kinetics in SPC, so it takes some time before the hydrogenation at the Pd surface can take place. The time in between the horizontal optical regions (from 45 mins to 1 hour 15 mins) is equal to about 0.38 $H/M$. The film shows a almost equal discharge capacity of $H/M = 0.4$. This confirms that loading takes place between 45 mins and 1 hour 15, marked by optical data.
After the discharge of the Pd-SPC film the film fell of the substrate. This is exactly what happened with the Pd films and it is caused by the poor sticking of Pd on the substrate.

**Electrochemistry: Results for PdCu**

Hydrogenography has shown that alloying Pd with Cu influences the width of the plateau and that there is a linear relation between the amount of Cu and the plateau width. To confirm this relation, and more importantly to confirm the relation between the amount of hydrogen in and the transmission of light through a PdCu film of various Cu compositions electrochemistry is done. In the same manner as shown for Pd TF’s now the transmission of light through the PdCu film is measured while (de-) hydrogenating the film in a controlled way.

First the charging and discharging potentials is shown for a Pd$_{96.2}$Cu$_{3.8}$ film in Figure 56. On the vertical axis the value of H/M is plotted. For the charging that doesn’t mean that that value represents the amount H absorbed by the film, but it means the maximum value that can be absorbed. It show that the charging has been long enough for maximum charging. The charging has been done with different currents, and it seems that there is a relation between the $I_{\text{charge}}$ and the $H/M_{\text{discharge}}$. 
Since there is an influence of the current of loading on the total discharge, this is further investigated. Going to a lower potential in charging corresponds to a higher hydrogen pressure. From hydrogenography we know that in the β-phase even the pressure goes up steeply there still is absorption of hydrogen. To find out if this can explain the increase on the Pd$_{96.2}$Cu$_{3.8}$ film as shown in Figure 56, the potential is converted to a H$_2$ pressure. Officially this is not allowed since the potential is not in equilibrium but still it might be helpful. In Figure 57 a linear fit through the H rich phase is fitted for the Pd$_{90}$Cu$_{10}$ composition to relate log $p$ with $c_H$. Note that the slope is not influenced much with varying Cu content, especially for the Cu poor curves. Next the increase in hydrogen absorbed in the film by an increase of log $p$ as found in hydrogenography is plotted together with the increase of $c_H$ caused by an increase in pressure (calculated from the potential) in electrochemistry. The increase in H/M caused hydrogenography is added to the first discharge concentration from electrochemistry. Both curves are shown Figure 57. It is found that the increase in discharge concentration caused by the decrease in charging potential cannot be explained by the related increase in hydrogen pressure when as we translate a potential to a H$_2$ pressure.
Figure 57: Relating the hydrogen concentration caused by hydrogenography or electrochemistry with respectively the H\(_2\) pressure or the potential. This being a galvanostatic measurement the potential is not in equilibrium so the pressure calculated from it is only qualitative.

The “current of charging effect” has been seen for all compositions Pd\(_{96.2}\)Cu\(_{3.8}\), Pd\(_{91.6}\)Cu\(_{8.4}\) and Pd\(_{86.6}\)Cu\(_{13.4}\). So instead of showing a maximum discharge capacity of these films I also have to show what the current of charging is. Like that the data are plotted in Figure 58. During the measurements it was found that there is maximum current for loading of -200 µA so the influence could only be measured up till that value.

Figure 58: Influence of \(|I_{\text{load}}|\) on \(H/M\) for three compositions at 303K.
Still the largest discharge value for all measured PdCu compositions are taken and plotted together with the points as shown before in Figure 42 and the value found by R. Niessen [24]. Only for the lowest Cu concentration H/M is far away from the literature value. This might be from the fact that only in cycle 8 and 9 a high $|I_{\text{load}}(\text{charge})|$ is reached. For the other compositions cycles 4, 5, 6 and 7 (8.4%Cu) and 5, 6 and 7 (13.4%Cu) are shown. Already for Pd it has been seen that through cycling films degrade. So for further research it might be useful to measure all compositions at higher $|I_{\text{load}}(\text{charge})|$ from the beginning, and also at higher values than 200 µA.

![Graph showing H/M vs %Cu](image)

*Figure 59: Minimum hydrogen capacity in the β-phase per metal atom for several Cu compositions. Data from Burch et al. [8] and Niessen [24].*
Discussion and Conclusion

Shape of isotherms

With the optical method hydrogenography pressure-optical transmission-isotherms (pti’s) for a PdCu thin film were determined, as was shown in Figure 22. The shape of the isotherms for the compositions Pd$_{90}$Cu$_{10}$ (80 nm), Pd$_{85}$Cu$_{15}$ (70 nm), Pd$_{80}$Cu$_{20}$ (63 nm) and Pd$_{72}$Cu$_{28}$ (54 nm) resemble the shape of the pressure-concentration-isotherms (pci’s) that were measured in bulk with a Sieverts’ method. Hydrogenography pti’s have a sloping plateau which differs from the more horizontal plateau that Sakamoto et al. found as shown in Figure 26. This can be explained by the clamping to the substrate of thin films as it was outlined on page 32. Thin films are clamped by the substrate leading to an increased plateau pressure. Close to the substrate this effect is larger than further away, which results in not one single plateau pressure but the sum of various regions in the thin film with each their own plateau pressure. That leads to a sloping plateau.

In Figure 22 hydrogenography results revealed an unexpected shape of the isotherms at 23 % Cu (59 nm) and 25 % Cu (57 nm) at 308 K. The shape of the unloading pti is different from the shape of the loading isotherm. This behaviour might be related to reorganisation of the microstructure in the film. These composition lie close to the critical composition that was found at that temperature, which might be a part of the answer.

Hydrogenography on PdCu thin films revealed a hysteresis between hydrogenation and dehydrogenation. It is a smaller hysteresis than was found in measurements on bulk samples. The smaller hysteresis for PdCu thin films is related to the effect that clamping has on the critical temperature ($T_C$). Since $T_C$ is defined as the temperature at which the hysteresis disappears in a van ‘t Hoff plot (see page 15), closer to the critical point we find a smaller hysteresis.

In the electrochemical hydrogenation cycles it was found that adding a 3 nm Ti interlayer tremendously improves the adhesion of 60 nm Pd and PdCu thin films to the substrate. The titaniumhydride is formed instantly upon hydrogenation, and dehydrogenation of the TiH$_2$ layer quickens the degradation of the film. However keeping the Ti in the charged state makes it possible to cycle a PdCu film more than 9 times.

At the same time it is found with both hydrogenography and electrochemistry that adding a 3 nm Ti layer between Pd/PdCu films and the substrate largely increases the hysteresis (see chapter on substrate effects on page 70). So in conclusion thin films have a smaller hysteresis than bulk samples because clamping brings it closer to $T_C$, but a Ti interlayer which increases the clamping and thus lowers $T_C$, shows a larger hysteresis. So these two effects that are pointing in opposite directions leave an open question about the effect a Ti interlayer has on the sticking, hysteresis and $T_C$. 
**Critical Cu concentration**

There are several ways to find a critical temperature for a metal hydride. As explained on page 39 one of those is by constructing a van’t Hoff plot for hydrogenation cycles at various temperatures and defining the temperature at which the hysteresis disappears as critical.

The plateau pressure versus the amount of Cu in the PdCu film shows a linearity for loading and unloading (as seen in Figure 34) and the intersection of both lines defines a critical Cu content at the temperature of the measurement. This corresponds to a critical temperature for that specific Pd_{100-x}Cu_x composition.

In this study a very small hysteresis was found and it has not been effective to use this hysteresis for finding the critical temperature for none of both techniques mentioned above. Because of that a method described on page 44 was used which is not based on theory but evolved through trial and error and turned out to be working well. In this method the normalized isotherms have been fitted with a Boltzmann curve in the plateau region. The pressure in the middle of the (sloping) plateau is given by the value at which the derivative of the Boltzmann function has a maximum, and this defines the plateau pressure ($p_{plat}$). These plateau pressure form a linear relation with the Cu concentration in PdCu thin films. At a certain Cu concentration there is a large deviation from linearity, and that point marks the critical concentration.

A 3 nm Pd interlayer between PdCu and the substrate (referred to as (Pd)PdCu) lowers the pressure for loading, because it is withdraws the interaction of Cu clamping at the substrate. With other words, a Pd interlayer reduces the “thin film effect” and approaches bulk behaviour, as was seen in the change in the critical Cu concentration at 308 K from 26 % Cu for PdCu to 28.5 % Cu for (Pd)PdCu. No influence of this interlayer on the hysteresis was seen.

For (Pd)PdCu critical Cu concentrations have been found to be 28.5 at.% Cu at 308 K, 25.5 at.% Cu at 323 K and 19.5 at.% Cu at 373 K. There is a small deviation with CVM [10].

**Lambert Beer relation**

The electrochemical measurements on Pd and on PdCu have shown that a linear relation between the log of the normalized transmission and the amount of H absorbed or desorbed by the film is not always found. That is however what Lambert Beer predicts. For the discharging of both the Pd as the (Ti)Pd and the (Ti)PdCu the transmission decreases in a non-linear fashion. For charging the linear relation has been found.

There might be side reactions taking place during the discharging, related to oxygen in the electrolyte. The Pd film can act as a catalyst for these side reactions. For the PdCu films, Cu has the possibility to get oxidized during discharge reactions. A Pd cap layer should be able to prevent this.
**Plateau width**

From the CVM calculations shown in Figure 13 and unpublished data by A. Böttger the width of the plateau is compared with hydrogenography data at 308 K. For this the phase boundaries are estimated by a construction that has been used before by others. 3 Straight lines are fitted through the dilute phase, the (tilted) plateau region and the high H concentration part of the isotherms. This is done for several PdCu compositions at 308 K and the intersections mark the phase boundaries. The difference between $\ln(T/T_0)$ normalized by the film thickness at both phases determines the plateau width, and these values are plotted together with the CVM data in Figure 60.

![Figure 60: Width of the plateau which is defined as the minimum hydrogen capacity per metal atom at the β-phase minus the maximum H capacity in the α-phase. Published [10] and unpublished CVM data (303 K) are supplied by A. Böttger and refer to the left axis, hydrogenography points (308 K) to the right axis.](image)

The axis are set such that the points at 20 % Cu coincide. Unfortunately because of the increased slopyness of the plateau’s it is not possible to obtain more phase boundaries, so this technique will not lead us to a critical Cu concentration. From the CVM point we learn that there seems to be a linear trend except for the last point marking the critical concentration at 303 K which lies at a lower value than what might be suspected would the linear trend continue.

In the galvanostatic determination of the maximum discharge capacity a large influence of the current of loading on the discharge capacity of the PdCu samples with 3.8, 8.4 and 13.4 % Cu has been found. This effect needs further research. Nevertheless the discharge capacity found for Pd and for these compositions has been compared with plateau widths obtained with hydrogenography as described above. This is shown in Figure 61 where the same scaling is used as in Figure 60. Also plateau width from bulk measurements from Burch and Buss [8] are plotted in there.
Figure 61: Minimum hydrogen concentration at the β-phase for hydrogenography and electrochemistry. Reference data are taken by Niessen [24] (GITT discharging of Pd film) and Burch et al. [8] (bulk hydrogenation by a Sieverts’ method). Scaling between $\ln(T/T_0)/t$ (right axis) and $H/M$ (left axis) is the same as in Figure 60. Points are obtained as described on page 68.

The PdCu is studied as a model system. From the good resemblance of the isotherms, critical concentration, plateau pressures and plateau widths of PdCu thin films we conclude that it is valid to use hydrogenography, possibly in combination with electrochemistry, to study PdMH systems, where M can be one or more elements. Especially by knowing that substrate effects can be tuned by interlayers as Pd and Ti, thin films are a valid option to rapidly study material properties for hydrogen separation membranes. Possible interesting materials can be put forward by theoretical studies. Some Pd based ternary systems can have improved properties like a low critical temperature and enhanced diffusion which makes them excellent membrane materials. In this work hydrogenography has proven to be the ultimate tool to rapidly scan these materials in numerous compositions.
More substrate related effects

In electrochemistry we have seen the effect of a Ti interlayer between a 60 nm Pd layer and a substrate on the hysteresis and potential. When these data are compared qualitatively with hydrogenography on a Pd$_{91}$Cu$_{9}$ film on glass and on 3 nm Ti on glass we find very similar behaviour. The hydrogenography data for the cycling (9$^{th}$ time) of these films at 295 K are shown in Figure 62.

![Figure 62: Hydrogenography pti's for 9$^{th}$ cycling of PdCu on glass and on 3 nm Ti on glass.](image)

The difference in hysteresis between Pd and (Ti)Pd that was found with electrochemical hydrogenation is also found in hydrogenography, as shown in Figure 63.

![Figure 63: Hydrogenography data by Y.Pivak.](image)
To directly compare these results, the pressure axis is converted to a potential. In the
galvanostatic hydrogenation the potential is not in equilibrium, so the comparison in
just qualitatively and not quantitatively. The effect of the Ti interlayer is completely
similar, but might be exaggerated in the galvanostatic charging.

Figure 64: Copy of Figure 53.

Figure 65: Copy of Figure 63 where the pressure is converted to a potential according to

\[ E(\text{vs Ag / AgCl}) = -0.235 - \frac{RT}{2F} \ln \frac{p_{H_2}}{p_{ref}} \]
Literature


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Graag wil ik nog wat mensen bedanken die mij hebben geholpen bij dit onderzoek, en die het mogelijk hebben gemaakt. Laat ik dat maar doen aan de hand van uitspaken die mij bij zullen blijven.

Bernard: “Dat had ik nou altijd al gehoopt dat er een scheikundestudent hier zou komen.”

Ronald: “Na overleg met Bernard heb ik besloten dat wij deze koffieronde niet in het boek hoeven op te schrijven.”

Jan: “Nieuwe studenten kiezen niet op basis van kwaliteit. Je moet gewoon een goed feest organiseren.”

Martin: “Now I want to sit in the garden and drink a beer.”

Student: “Heb je nog leuke vogeltjes gezien op je vakantie op de wadden?”
Kier: “Ja. Ik heb ook nog een wiskundig probleem onder de hand genomen, en op weten te lossen.”

Yevgheniy: “Ik trakteer!”

Lennard: “Het is geen leuk feest en daarom moet je juist wel gaan.”

Bernard wil ik hartelijk bedanken dat ik dit project heb kunnen doen. Martin wil ik bedanken voor de hulp bij metingen en voor zijn nuchtere kijk op dingen. Ik wil Ronald bedanken voor de erg leuke colleges. Herman wil ik bedanken voor de hulp bij het maken van samples, het opruimen van kwik dat iemand had gemorst, maar belangrijker nog voor het gezelschap tijdens de trainingsrondjes in het Amsterdamsche Bos! Jan bedankt voor het meten van de RBS. Ruud, Amarante en Wim bedankt voor het samenwerken in het membranen project. For all the people in the condensed matter group thanks for the nice time and also for the hearty reactions when I was (lost in translation) in Japan and Marika was born.