



The hydrogen electrode in the “dry”: A Kelvin probe approach to measuring hydrogen in metals

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ABSTRACT

Hydrogen mobility plays an important role in the storage and release of hydrogen in hydrogen fuel applications, but also constitutes the main problem in materials prone to hydrogen embrittlement. Hence, the ability to perform high-sensitivity, quantitative measurements of mobile hydrogen in metals is of crucial importance. Here we present a novel approach utilizing the Kelvin probe technique that provides unprecedented sensitivity by measuring the work function of an ultrathin palladium film evaporated on the sample of interest. We show that the measured work function can be interpreted as electrode potential of a hydrogen electrode in the “dry”, depending logarithmically on the amount of hydrogen released from the metal beneath it.

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1. Introduction

Previously, it has been reported that work function measurements on steel and palladium by using the Kelvin probe technique can be utilized to detect hydrogen [1,2] even at a high lateral resolution down to a few tens of nanometers [2], however no quantification was possible. Further, the work function of iron oxides and the changes related to the uptake of hydrogen, caused by hydrogen induced reduction of Fe^{3+} states to Fe^{2+} states, were found difficult to reproduce [1]. In view of the extensive work, which has already been published about the effect of hydrogen on the work function of palladium under UHV conditions, it seemed unlikely that such measurements could be used for a quantitative hydrogen detection [3,4].

However, the situation is different in electrochemistry: defined by the Nernst equation the electrode potential of a Pd:H electrode depends sensitively on the hydrogen concentration in the palladium [5–7]. In this paper, we show that a similar behavior is found for the work function of palladium under non-UHV conditions. Thus, the work function can be used to determine the concentration of hydrogen in metals and its permeation through metals with an unprecedented sensitivity, which is much higher than e.g. achievable with the widely used Devanathan–Stachurski cells [8].

2. Materials and methods

The Kelvin probe measurements that led to the results presented in Figs. 1 and 2a) were performed in a custom made combined electrochemistry and Kelvin probe set-up. The KP needle (SS 304) had a diameter of 400 μm . The measurements for the data shown in Fig. 2b) were performed with a commercially available set-up (Wicinski&Wicinski Surface Scanning Systems, Germany). The KP needle (SS 304) had a diameter of 100 μm . The 100 μm thick iron membrane (99.5% purity, temper: hard) and the 25 μm thick palladium foil (99.99% purity, temper: as rolled) were both purchased from Goodfellow. 1000 nm iron and 100 nm palladium films were deposited by PVD in a Leybold Univex 450. The Fe-0.233 wt.%Zr samples were cut to 1 mm thick slabs from the solidified melt [9] and then surface finished by grinding down to 4000 grit paper.

3. Results and discussion

As can be seen in Fig. 1a) the work function measured on the one side of a palladium membrane exposed to a dry nitrogen atmosphere (r.h. < 0.1% r.h.), and whose other side forms the working electrode of an electrochemical cell, behaves in line with the applied electrode potential in a wide range, i.e. it seems that we can “look through” the palladium membrane and directly measure the applied electrode potential. This is what would be expected in the case of an electrochemical double cell where both sides of a palladium membrane are in contact with electrolyte. Due to the high solubility of hydrogen in palladium and the high reactivity of the hydrogen electrode on palladium equilibrium establishes across the whole system. Hence, the

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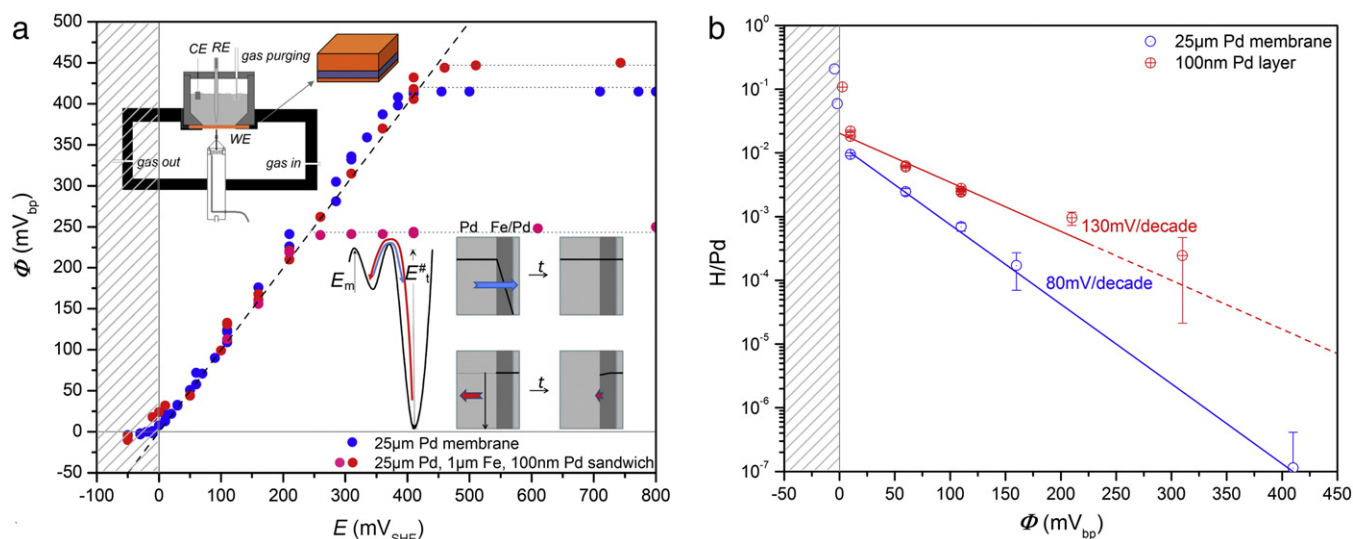


Fig. 1. Measuring electrode potentials through metal: a) work function measured by Kelvin probe on the exit side of a membrane, exposed to a dry nitrogen atmosphere (<0.1% r.h.), vs. applied potential on the entry side, exposed to an aqueous electrolyte of 0.1 M H_2SO_4 (see inset on the upper left). The work function is referenced as potential vs. the onset potential of the binary phase (bp) region of α - and β -Pd-H. The measurements were performed with a 25 μm thick palladium membrane and with a sandwich sample consisting of a 25 μm palladium membrane, coated by 1 μm of iron and 100 nm palladium, the latter exposed to the dry atmosphere. In one experiment the sandwich sample was already pre-loaded (pink circles). The insets show schematics illustrating the set-up and the sandwich sample, as well as sketches of the chemical potential for hydrogen throughout the system at initial and later stages of loading and draining. b) Concentration of hydrogen in a 25 μm thick palladium membrane and a palladium film of 100 nm thickness evaporated on a glass sample plotted as function of the work function measured in the dry nitrogen atmosphere, referenced as electrode potential vs. the onset of the binary phase.

application of a certain electrode potential on one side (entry side) also leads to the establishment of a corresponding electrochemical equilibrium on the other side (exit side) of the membrane. This can indeed be measured in a double cell, but only if the diffusion of hydrogen from the palladium into the electrolyte is kept at a low level by using highly viscous electrolytes [7].

Obviously, the same is happening here. It is known that ultrathin adsorbed water layers remain on the surface even under dry conditions, as it has been demonstrated e.g. for silica [10]. Hence, the

palladium surface exposed to the dry nitrogen atmosphere is still covered by a nanoscopic water layer, which seems to enable the establishment of electrochemical equilibrium. *In other words: we have a hydrogen electrode in the dry!* The correlation between the work function on the dry side and the applied electrode potential at the entry side is observed for a wide potential range. Only at very high applied potentials, i.e. above 400 mV_{SHE} , the work function does not correlate anymore, as most likely the corresponding hydrogen activities are too low. Also at potentials below 0 mV_{SHE} the correlation between the

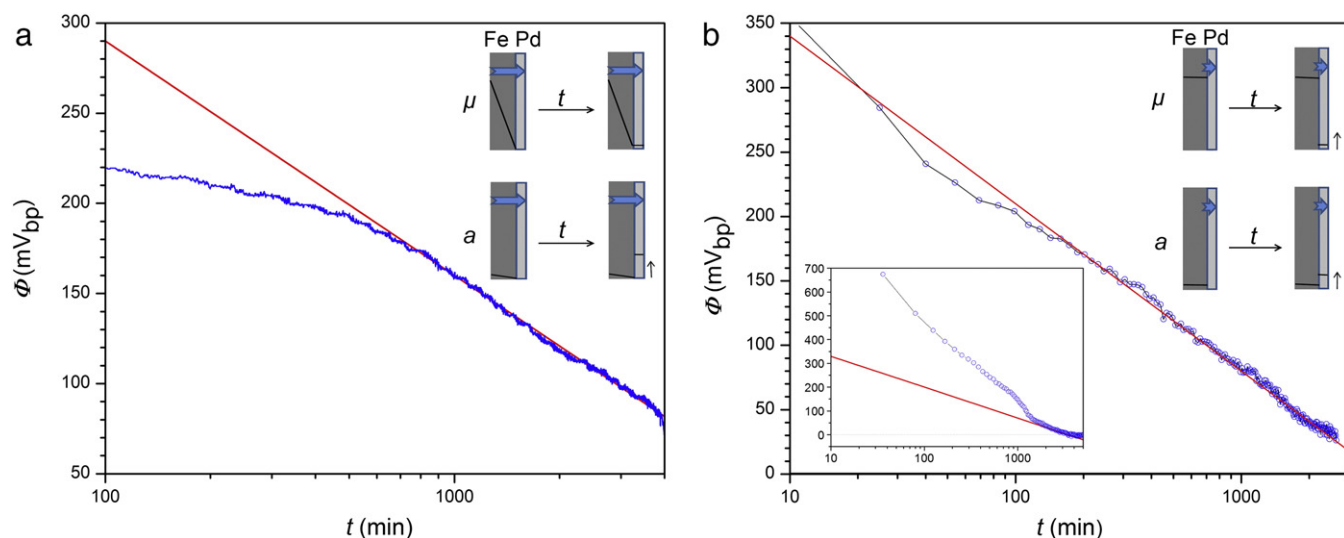


Fig. 2. Ultra-sensitive measurement of hydrogen: a) permeation: change in work function measured on the exit side, coated by 100 nm Pd, of a 100 μm iron membrane exposed on the entry side to aqueous 0.1 M NaCl solution of pH 8.5 and polarized to $-730 \text{ mV}_{\text{SHE}}$. After an initial time lag period (here: 800 min), necessary for filling the traps in the iron and hence for establishing a gradient in activity across the iron film, a constant flow of hydrogen into the palladium thin film is observed, as can be seen from the linear slope of 130 mV/decade . Using the calibration (Fig. 1b)) gives a corrosion current of about 1 nA/cm^2 . The inset schematically shows that due to the low chemical potential of hydrogen in palladium the hydrogen flow will remain constant for a while even though the hydrogen activity in the Pd increases. b) Change in work function measured on a 100 nm Pd film evaporated on a Fe-0.23 wt.%Zr sample pre-loaded with hydrogen. Fe-Zr is known to contain a high density of trap states [9] that are slowly releasing the hydrogen into the palladium. The insets show the initial behavior after starting the measurements in the dry nitrogen atmosphere and a sketch of the chemical potential and the activity of hydrogen throughout the system. Initially, the hydrogen has to fill the traps in the grain boundaries of the palladium and at the interface to the substrate. After re-exposure to air, which drains the hydrogen from the palladium, and reestablishing nitrogen atmosphere, a linear behavior is observed right away, with the slope of 130 mV/decade (release rate about 1.9 nA/cm^2 , measured on about 0.01 mm^2 !).

work function and the applied potential is lost. This is due to the formation of a binary phase of α -Pd-H, i.e. of Pd with dissolved hydrogen, and β -Pd-H, i.e. palladium hydride, which are coexisting in a wide concentration range of hydrogen. This pins the hydrogen activity to the equilibrium level of these coexisting phases (see Fig. 1). Note that since it is difficult to perform a defined calibration under non-UHV conditions in the dry nitrogen atmosphere, the onset of this binary phase region was chosen as reference point for the work function, reported here as an electrode potential. Due to the choice of 0.1 M sulfuric acid as electrolyte, the onset potential of this region is also about 0 mV_{SHE} at the entry side [11].

As shown in Fig. 1a) (“sandwich” sample) equilibrium is also found to be established through layers of other materials, such as iron. However, when the sandwich sample has been loaded with hydrogen beforehand, applying a higher potential at the entry side, i.e. emptying the Pd membrane from hydrogen, does not have an effect at the exit side, i.e. on the thin Pd film, at least not within a reasonable time. The reason lies in the high density of deep trap sites for hydrogen in the evaporated iron film. While filling the traps is quick, depletion of these traps is slow, due to the high activation energies for escaping a trap site (see inset of Fig. 1a)). Diffusible, i.e. interstitial, hydrogen exists only at very low concentrations in the iron, steadily re-supplied from the traps. Hence, only a very shallow gradient in chemical potential will form from the interface between the palladium membrane and the iron layer. This results in a decoupling of the ultrathin palladium film at the exit side from the palladium membrane at the entry side (see sketch in inset of Fig. 1a)). The hydrogen will be drained from the traps very slowly only, governed by the binding energy of hydrogen in the different trap sites. This opens up the possibility to measure the release rates from trap sites: when a thin layer of palladium is evaporated on a material containing hydrogen, the palladium will take up the hydrogen released from the trap sites due to its lower chemical potential for hydrogen and thus the potential measured on its surface will change accordingly. If the correlation between the potential and the concentration of hydrogen in the palladium layer is known, a direct quantification of local hydrogen release rates from any sample of interest will be possible. In Fig. 1b) such calibration curves are shown: a palladium membrane and a 100 nm thin palladium film, evaporated on a glass slide, were immersed in 0.1 M sulfuric acid and polarized to different potentials. After a sufficient equilibration time the potential was ramped up to oxidize the hydrogen. The corresponding anodic charge is a measure for the equilibrium hydrogen content taken up into the palladium at the potential applied prior to the jump.

Because of the equilibrium between the hydrogen absorbed into the palladium and the hydrogen adsorbed on the surface of the palladium we can use the Nernst equation and write:

$$E = E^{\circ}_{\text{SHE}} + R \cdot T / F \cdot \ln \left(a(\text{H}^+_{\text{el}}) / a(\text{H}_{\text{ad}}) \right) = E^* + R \cdot T / F \cdot \ln \left(a(\text{H}^+_{\text{el}}) / a(\text{H}_{\text{Pd}}) \right),$$

where $a(\text{H}_{\text{ad}})$ is the activity of the adsorbed hydrogen, $a(\text{H}_{\text{Pd}})$ the activity of absorbed hydrogen in the palladium and $a(\text{H}^+_{\text{el}})$ the activity of H^+ in the electrolyte, i.e. the ultrathin layer of adsorbed water. Hence, a slope of about 60 mV per decade of hydrogen activity is expected for the potential. For annealed palladium immersed in highly viscous sulfuric acid electrolyte this was indeed confirmed by Kirchheim [7]. The high viscosity was found to be necessary in order to sufficiently suppress the loss of hydrogen from the palladium. The results depicted in Fig. 1b) clearly show a linear dependence of the potential and the hydrogen concentration in the palladium membrane, but with a slope of about 80 mV/decade. For the 100 nm palladium film the error bars are quite high, due to the extremely low hydrogen amounts involved at high potentials. However, a linear dependence of 130 mV/decade is suggested in the full range depicted, as this is supported by additional results. For instance in Fig. 2a) a permeation experiment is shown where at the entry side of a

100 μm thick iron membrane hydrogen is taken up at an applied potential of -730 mV_{SHE} in aerated aqueous 0.1 M NaCl electrolyte. This simulates the condition of steel cathodically protected by zinc. Due to the high oxygen reduction rates under these conditions a high surface pH is expected, which leads to low hydrogen activity. Accordingly, the permeation currents are very low. This is why up to now hydrogen uptake during corrosion was usually investigated for more severe conditions at acidic pH where the hydrogen activity and hence the permeation rates are much higher [9]. In Fig. 2a) we can see that after an initial time lag period the potential decrease at the exit side, coated by 100 nm Pd, is linear with the logarithm of time, at 130 mV per decade. This is interpreted as being due to a constant permeation current j :

$$E = E^{*'} - 130 \text{ mV} \cdot \lg(c) = E^{*'} - 130 \text{ mV} \cdot \lg(j \cdot t) = E^{*''} - 130 \text{ mV} \cdot \lg(t).$$

The observed slope of 130 mV per decade confirms the suggested linear fit for the calibration (Fig. 1b)). Based on this, the linear potential decrease vs. time found here corresponds to a permeation current of just about 1 nA/cm²!

Similarly, as already indicated above, also hydrogen draining from trap sites can be measured. An example is shown in Fig. 2b). A Fe-0.23 wt.%Zr sample was loaded with hydrogen, then a 100 nm thin palladium film was evaporated on one side and the sample was transferred into the SKP chamber. As can be seen, also here the same dependence of 130 mV/decade can be found. However, in this case the slope cannot be measured right from the beginning, as the palladium layer was freshly evaporated, i.e. at first trap sites in the palladium film itself and at the interface between the substrate and the palladium have to be saturated (see inset of Fig. 2b), which shows the first measurement). In the case shown in Fig. 2a), the palladium was already pre-charged by hydrogen released from the iron sample during storage prior to the corrosion experiment.

4. Summary and conclusions

In summary, we have found that the work function on the surface of the palladium charged with hydrogen behaves like a hydrogen electrode, depending logarithmically on the hydrogen concentration. The deviation from 60 mV per decade is due to the simple fact that the Nernst equation applies for activities and not concentrations. Kirchheim et al. showed that the chemical potential deviates significantly from the Nernst behavior for nano-crystalline and also for deformed palladium [12,13]. Approximately linear regions with slopes of about 100 mV per decade and more can be found in their data [12,13]. This is due to the fact that a considerable part of the hydrogen is trapped at grain boundaries. Therefore, we suggest that the much higher slope for the ultrathin palladium film is due to trap sites at grain boundaries within the nano-grained ultrathin films and at the interface between the substrate and the palladium film.

In conclusion, we believe that this novel method will have a great impact in a wide range of applications, especially because also a high spatial resolution can be reached [2]. The achievable sensitivity for hydrogen permeation is assumed to be higher than pA/cm² and the sensitivity for releasable hydrogen in steel should be well below 0.01 atomic ppm.

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References

- [1] M. Krasemann, H. Streckel, K. Hoffmann, H.J. Grabke, M. Stratmann, *Proceedings of the Electrochemical Society* 97 (1998) 207.
- [2] C. Senöz, S. Evers, M. Stratmann, M. Rohwerder, *Electrochemistry Communications* 13 (2011) 1542.

- [3] R.J. Behm, K. Christmann, G. Ertl, *Surface Science* 99 (1980) 320.
- [4] M.G. Cattania, V. Penka, R.J. Behm, K. Christmann, G. Ertl, *Surface Science* 126 (1983) 382.
- [5] M.J. Vasile, C.G. Enke, *Journal of the Electrochemical Society* 112 (1965) 865.
- [6] T.H. Yang, S.I. Pyun, *Electrochimica Acta* 41 (1996) 843.
- [7] R. Kirchheim, R.B. McLellan, *Journal of the Electrochemical Society* 127 (1980) 2419.
- [8] M.A.V. Devanathan, Z. Stachurski, *Proceedings of the Royal Society A* 270 (1962) 90.
- [9] E. Riecke, B. Johnen, H. Liesegang, A. Thorns, B. Reynders, H.J. Grabke, *Materials and Corrosion* 39 (1988) 525–533.
- [10] X. Deng, T. Herranz, C. Weis, H. Bluhm, M. Salmeron, *Journal of Physical Chemistry C* 112 (2008) 9668.
- [11] M.J.N. Pourbaix, J. van Muylder, N. de Zoubov, *Platinum Metals Review* 3 (1959) 100–106.
- [12] T. Mütschele, R. Kirchheim, *Scripta Metallurgica* 21 (1987) 1101–1104.
- [13] R. Kirchheim, *Progress in Materials Science* 32 (1988) 261–325.