Electrochemical study of hydrogen diffusion in a vanadium thin film

M. Di Vece [a,*], A. Remhof [b,1], J.J. Kelly [a]

[a] *Debye Institute, Physics and Chemistry of Condensed Matter, Utrecht University, P.O. Box 80 000, 3508 TA Utrecht, The Netherlands*
[b] *Faculty of Sciences, Division of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands*

Abstract

We show that the optical indicator technique used to visualize fast hydrogen migration in thin metal films can also be applied in an electrochemical set-up. Lateral diffusion of hydrogen in a vanadium film under a masking layer could be monitored from the optical change of an yttrium switchable mirror, which served as an indicator for the diffusion front. An electrochemical loading experiment provides a precise measure of the total hydrogen content of the sample. Optical reflectance measurements allow the determination of the diffusion coefficient of hydrogen. Additionally, the electrochemical set-up was used to measure a room-temperature solubility isotherm of the film under investigation. The observed miscibility gap was smaller than that of the bulk metal.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Lateral diffusion; Optical indicator; Hydrogen; Switchable mirror; Electrochemical intercalation

1. Introduction

Hydrogen absorption by thin metal films is important for various technologies [1]. Hydrogen can be introduced either from the gas phase, as in sensors [1], or electrochemically [2], as in batteries and electrochromic devices [3,4]. For the fundamental study of metal hydrides, electrochemical loading has the advantage that the concentration of hydrogen in the film can be easily and accurately controlled and monitored. Atomic hydrogen, produced by electrochemical reduction of water, diffuses into the material; the concentration in the film is proportional to the charge transferred in the electrochemical reaction [5]. In this way pressure–concentration isotherms are obtained which yield information on the loading characteristics, e.g., the capacity of the film and the presence of a miscibility gap. It is known that the thermodynamic properties of thin films can be different from those of the bulk metal or alloy [6].

Hydrogen transport in metal hydride films may be important in determining the dynamic response of a device. Electrochemical techniques can be used to study transport. For example, potential-step experiments provide diffusion coefficients of an intercalating species [7–9]. For metals showing very effective hydrogen transport, such as vanadium, the large diffusion coefficients should result in extremely fast kinetics. As a result it may be difficult to follow experimentally intercalation in a standard electrochemical experiment.

Recently it has been shown that thin films of various metals and alloys become optically transparent on hydrogen intercalation [10]. This "switchable mirror" effect, first observed with yttrium, allows the visualization of hydrogen diffusion [11]. Remhof et al. [12] have demonstrated that the optical properties of the yttrium switchable mirror can be used to measure diffusion coefficients for metals such as vanadium. A thin yttrium layer covers the metal film. The yttrium surface is partly passivated by oxidation. Gas-phase hydrogen enters the system only through a palladium cap-layer on the yttrium and diffuses laterally, under the passivated parts of the film. The hydrogen concentration in the metal changes the optical properties of the yttrium layer, thereby accurately indicating the position of the

---

hydrogen front. The mobility of the diffusion front can be directly calculated from the rate at which the boundary moves. The rather slow diffusivity and the high solubility of hydrogen in yttrium can be used to visualize hydrogen migration in other materials for which similar conditions are valid.

In the present work we describe a novel application of the "optical indicator" technique of Remhof et al. [12]. The approach consists of measuring the current, which accompanies hydrogen transport normal to the exposed surface and underneath a masked thin vanadium film. The optical change in an underlying yttrium layer indicates the position of the diffusion front, from which a diffusion coefficient can be calculated. Hydrogen diffusion in palladium is slower than that in vanadium; this enables the determination of the effective diffusion coefficient of a palladium/vanadium laminate, for transport normal to the sample surface. With this information it is possible to investigate the influence of the palladium cap-layer on the hydrogen diffusion process in metal hydride systems. In addition, we have determined the pressure-concentration isotherm of a vanadium thin film to obtain information about the loading characteristics.

2. Experimental

The active layer was a polycrystalline vanadium film top-coated with a thin palladium layer (nominal thickness 10 nm), which acts as a catalyst for the electrochemical production and oxidation of atomic hydrogen [10] and protects the film from oxidation [10]. The vanadium films for the isotherm and diffusion determination were 200 and 300 nm thick, respectively. In contrast to the sample design used by Remhof et al. [12] the 300 nm film had a 35 nm yttrium indicator layer between the vanadium and the quartz substrate. This protected the yttrium layer from chemical attack by the electrolyte (yttrium corrodes at a pH 10 or lower). The layers were deposited by electron-gun evaporation at 10^{-9} mbar base pressure. A platinum lead was fixed with silver glue (2400 Circuit Works Conductive Epoxy, Agar Scientific) on the vanadium, and both the lead and a part of the vanadium were protected from the solution by wax (Apiezon). A fresh sample was used for each experiment.

The sample geometry for the diffusion experiments is shown in Fig. 1. The vanadium film with the palladium cap-layer was partially masked by wax (Apiezon), which prevented hydrogen uptake. The unmasked active surface area was 0.2 cm^2. The hydrogen produced at the palladium cap-layer first diffuses normal to the sample surface. Calculations with reported diffusion coefficients for the 200 nm vanadium film, capped with 10 nm palladium, indicate that the complete absorption time is too short to measure accurately with the current set-up.
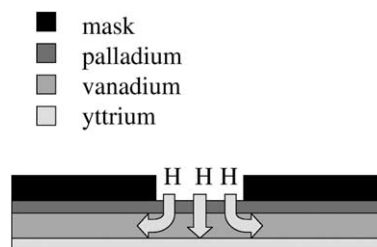

Fig. 1. The geometry of the sample used for the hydrogen diffusion experiment. The yttrium layer, which functions as an optical indicator, is sandwiched between the quartz substrate and the vanadium film. A palladium cap-layer is used for protection and catalytic purposes. Part of the film is masked enabling lateral diffusion.

Diffusion normal to the sample surface is followed by lateral diffusion of hydrogen under the mask. Since the masked length is 3 mm, typical diffusion times are within the detection range of our equipment resolution.

A two-compartment electrochemical glass cell was used for the measurements. The working electrode was positioned together with a Hg/HgO reference electrode in one compartment and a platinum counter electrode was placed in the other compartment. All potentials are given with respect to Hg/HgO. Argon gas was bubbled through the solution in both chambers. The experiments were performed in a 5 mM KOH solution at room temperature. A potentiostat/galvanostat (EG&G Princeton Applied Research (PAR) 273A) was computer-controlled by in-house developed programs (LabView). Changes in the yttrium layer were recorded from the quartz side of the sample with a Panasonic video camera (Model No. NV-MS1E). The pressure-concentration isotherm was determined by the Galvanostatic Intermittent Titration Technique (GITT) [13]; the equilibrium potential, which is measured in open circuit after a current pulse, provides (via the Nernst equation) the equivalent hydrogen pressure, P_{H2}. The electrochemical approach allows one to work at pressures, which are much lower than those possible in conventional gas-phase experiments [5,14].

3. Results and discussion

The absorption isotherm of the 200 nm thick vanadium film is shown in Fig. 2; the pressure is plotted as a function of the hydrogen/metal atomic ratio, x. The first plateau at about 10^{-7} bar corresponds well to literature pressure values for the α–β-phase transition [15]. However, the atomic ratio range of the plateau $\Delta x = 0.3$ is considerably smaller than the miscibility gap reported for bulk vanadium ($x = 0.5$). Although some systems (rare-earth metals, Mg) show evidence of hydrogen contamination during deposition, we can rule this out for our films since vanadium is less reactive with hydrogen. It is known that the range of the miscibility gap
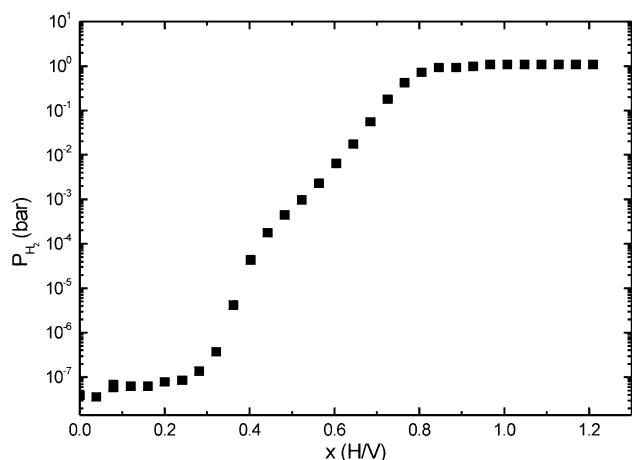
Fig. 2. The atomic ratio-pressure isotherm of a 200 nm thick vanadium film as measured by GITT [7]. Current pulses of 3×10^{-4} A were maintained for 20 s and the relaxation time was 2 min.

depends strongly on the size of the nanocrystals, composing a polycrystalline film [6].

Above $x = 0.4$ the pressure rises sharply to 10^{-4} bar. From this point on the rate of pressure increase is lower. A pressure of 10^{-4} bar corresponds to the β_1–β_2-phase transition reported for the bulk metal. The pressure increases until the plateau at 1 bar is reached at $x = 0.8$; in the plateau range, the adsorbed hydrogen is not absorbed by the vanadium but, instead, forms gas. Hydrogen gas development occurs at an atomic ratio $x = 0.8$, which is in good agreement with that found for isotherms of bulk vanadium [15]. This would indicate that the atomic ratio determination is accurate and that little hydrogen is present initially in the film.

A potential step was applied from open circuit (−0.36 V) to −0.96 V. The latter potential is more negative than the equilibrium hydrogen potential at ambient atmosphere. Since this is not an equilibrium experiment the actual pressure is not known but it never exceeds 1 bar. The yttrium side of the 300 nm sample was filmed and, at the same time, the electric current was recorded. The optical changes due to the hydrogen intercalation in the yttrium film are shown in the photographs of Fig. 3(a). Initially no changes are observed. Within 54 s a brownish colour appears gradually (seen as grey in the photograph) underneath the area exposed to the electrolyte. In agreement with Remhof et al. [12] we ascribe this colour to the presence of yttrium dihydride. From 180 to 220 s another, dark purple coloured phase (black in the photo) appears. We attribute this to the formation of the hydrogen rich, substoichiometric $YH_{3-\delta}$ phase. The brownish colour has extended underneath the mask and the border between the intercalated and virgin parts of the film is clear, as is the border between the brown and purple regions. The progress of the purple front is slower than that of the brown front; lateral diffusion in the phase corresponding to the brownish colour is much
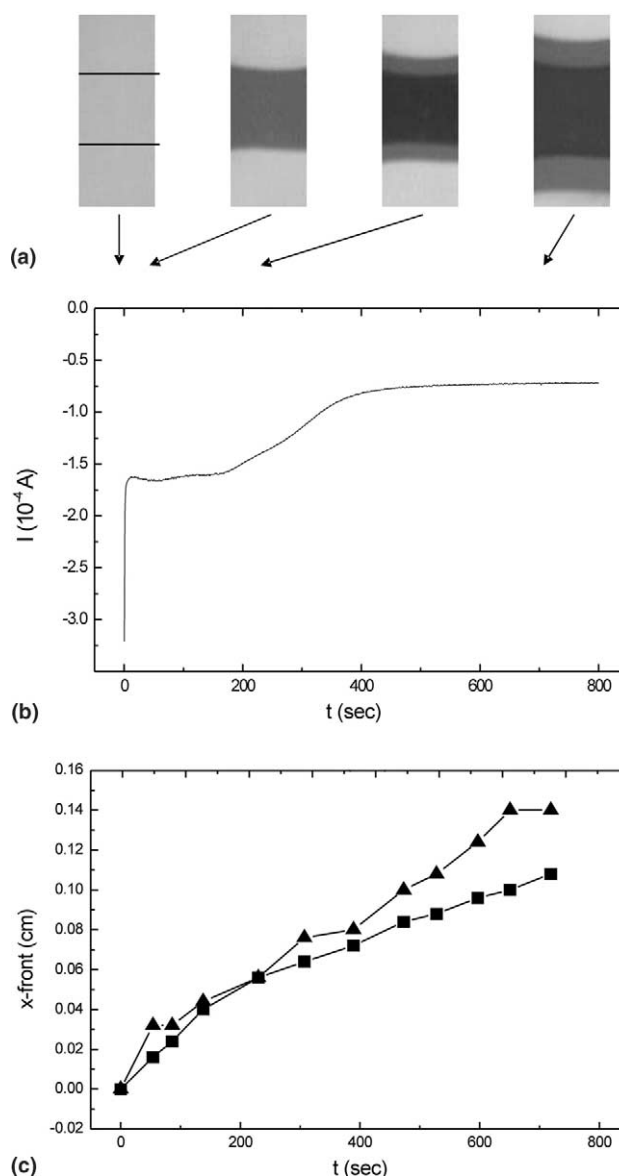

Fig. 3. (a) Photos taken at the yttrium side of the sample, at $t = 0$ s, $t = 54$ s, $t = 230$ s, $t = 719$ s. The grey and black areas correspond to the di- and trihydride states, respectively. The two lines in the picture on the left indicate the positions of the masked edge. (b) The current transient during the electrochemical loading of the sample. (c) The positions of the dihydride fronts (grey) from (a) as a function of time.

faster than that in the phase corresponding to the purple colour. The relative speeds of the different phases depend on the hydrogenation conditions and sample batch. The sharp colour boundaries are fronts dividing thermodynamically stable hydride phases in the hydrogenated yttrium layer, separated by a large miscibility gap.

The purple colour is the result of the transparency of yttrium trihydride in the yellow [10]. Visible light, except that part of the spectral range up to yellow, is reflected by the quartz–yttrium interface giving the purple colour. The yellow light, which passes through the yttrium

layer, is absorbed at the yttrium–vanadium interface. The reflection at the quartz–yttrium interface is, therefore, the only reflection and this reflected light is expected to have a low intensity, which explains the darkness of the purple. A similar explanation holds for the brown colour. The dihydride state is transparent for red light. The reflected light at the quartz/yttrium interface, therefore, originates from the visible spectral range minus the red. The result is a brownish colour.

The corresponding current transient is shown in Fig. 3(b). Before the potential step is applied, the current is zero (open-circuit condition). At $t = 0$ s, the current rises very fast to a high value (not shown in the figure). It is clear that within the first second a rapid decay of the current to about −0.17 mA occurs, after which a constant value is observed. At about $t = 180$ s the current begins to decrease again until it reaches a constant value of approximately −0.09 mA at about 400 s; this background current is ascribed mainly to hydrogen gas evolution. The current integrated from $t = 0.76$ s to $t = 380$ s corresponds to a charge of −53 mC. This is not sufficient to account for the amount of hydrogen needed to bring about the optical changes seen in Fig. 3(a). A charge of −112 mC would be required: this comprises the charge for loading (i) the vanadium to an atomic ratio of 0.8 (see isotherm, Fig. 1) in the unmasked area ($\Delta x_V = 0.8$, −59 mC) and under the mask ($\Delta x_V = 0.8$, −36 mC) and (ii) the yttrium to the trihydride state in the unmasked area ($\Delta x_Y = 3$, −14 mC) and to the dihydride state under the mask ($\Delta x_Y = 2$, −7 mC). The charge necessary to load only the yttrium layer at the unmasked area and the vanadium and yttrium underneath the mask is about −50 mC (lateral loading of vanadium ($\Delta x_V = 0.8$) and yttrium ($\Delta x_Y = 2$), and loading of yttrium ($\Delta x_Y = 3$) at the unmasked surface). Since the purple colour indicates that the unmasked layers are completely loaded, we conclude that intercalation of hydrogen in the vanadium film at the unmasked surface has taken place within the first second after application of the potential step; its charge contribution and double-layer charging are not detected when we integrate the current.

The current reflects processes related to both normal and lateral transport of hydrogen in the system. The presence of the first plateau is explained by the yttrium metal to dihydride transformation since the chemical potential remains constant during the dihydride formation [6]; this is supported by the optical data. Because of this combination of processes we are not able to determine the hydrogen diffusion coefficient from the current transient.

In Fig. 3(c) the position of the dihydride fronts are shown as a function of time. The upper front corresponds to the side at which the electrical contact is made. After about 400 s the lower border moves a little faster than the upper border; the reason for this is not clear. Remhof et al. [12] found a square root dependence of the diffusion front on time for gas-phase loading. The progression of the front in the present experiment does not have a perfect square-root dependence on time. An estimate of the hydrogen diffusion coefficient can be determined by inserting the position of the diffusion front and the corresponding time in the square root dependence. This results in a diffusion coefficient of 1.6×10^{-5} cm^2 s^{-1}. This is in good agreement with the value of 6.7×10^{-6} cm^2 s^{-1} as reported by Remhof et al. [12]; it is also in agreement with NMR results of Orimo et al. [16] on bulk vanadium, at a temperature of 373 K.

Electrochemical experiments on intercalation of lithium and hydrogen in thin metal films show a similar dependence of current on time [2,7,17]. Wen et al. [7] have demonstrated that for electrochemical insertion of lithium in a thin film a relation between the current decay and a diffusion coefficient can be derived with a simple model. The model involves two parallel plates; one side (substrate) is not permeable to the intercalating species while the concentration at the other side (film/solution interface) is constant. Before the potential step, the concentration in the film is uniform and constant. Solving Fick's diffusion equations [18] and taking first order terms, Wen et al. [7] have shown that the current is given by

$$I(t) = FS\Delta C \left[\frac{D}{\pi t} \right]^{1/2}, \quad t < l^2/D, \tag{1a}$$

$$I(t) = \frac{2FSD\Delta C}{l} \exp\left[\frac{-D\pi^2 t}{4l^2} \right], \quad t > l^2/D, \tag{1b}$$

where D is the diffusion coefficient, l the film thickness, F the Faraday constant, S the active surface area and ΔC the difference between the concentration before the potential step and the final concentration, which can be determined from the solubility isotherm. Eq. (1a) is the well-known Cottrell relation [19].

The fast current decay in the transient of Fig. 3(b) contains a capacitive charging and a Faraday contribution. Charging is expected to occur in the (sub)millisecond range. The Faraday contribution is attributed to the filling of vanadium in the unmasked area, i.e., by diffusion normal to the sample surface. In contrast to the current transient for a longer time this is a single loading process, i.e., only the vanadium layer is being loaded with hydrogen (the palladium cap-layer can be disregarded as it constitutes only 3% of the sample volume). Since this process is extremely rapid, the detected current decay in the first seconds can be attributed to the $t > l^2/D$ domain, to which the exponential relation is applicable. Calculating the corresponding diffusion coefficient from the exponential fit of the tail of this exponential decay, and a characteristic thickness of 310 nm, we find $D = 2.2 \times 10^{-9}$ cm^2 s^{-1}. This indicates that the diffusion process normal to the sample surface must be limited by the palladium cap-layer. Hydrogen diffusion coefficients for thin palla-

dium films have been shown to be much lower than for the bulk metal ($D = 10^{-6}$ cm^2 s^{-1}[17]). Li and Cheng [20] report values in the order of $D = 10^{-11}$ cm^2 s^{-1} for a 20 nm thick film [17]. Using the series formula for diffusion in a laminate [18], and our hydrogen diffusion coefficient for vanadium, we find a diffusion coefficient of hydrogen in palladium of $D = 1.0 \times 10^{-10}$ cm^2 s^{-1}. This is an order of magnitude higher than the value found by Li and Cheng [20]; the difference is probably due to a different morphology as a result of different deposition conditions.

A 10 nm palladium cap-layer is commonly used in metal hydride switchable mirrors [5,12,17]. For optical switching, hydrogen diffusion in palladium may be important. On the basis of the good agreement between the hydrogen diffusion coefficient in palladium, determined in this study, and literature values we can conclude that formation of hydrogen and its transport in the palladium do not limit the switching kinetics in yttrium. As in a recent study of the gadolinium switchable mirror [9], a limitation due to a catalytic effect is not expected in the time domain of our experiments. For much shorter times a catalytic effect may be important. A diffusion time of 0.01 s for a 10 nm layer is much smaller than the optical switching times, which are in the order of seconds [17,21].

4. Conclusions

Lateral diffusion of hydrogen in a vanadium thin film could be studied in potential step experiments. The different stages of hydrogen loading and the movement of the diffusion fronts could be monitored by the optical change in an yttrium indicator layer. The diffusion coefficients of the individual layers of a laminate are in good agreement with literature values. By use of the equation that relates diffusion coefficients of individual layers in a laminate to the effective diffusion coefficient, we show that a 10 nm palladium cap-layer does not limit the hydrogen transport process, although it is confirmed that the hydrogen diffusion coefficient is orders of magnitude lower than that of bulk metal.

Acknowledgements

References

[1] L. Schlapbach, A. Züttel, P. Gröning, O. Gröning, P. Aebi, Appl. Phys. A 72 (2001) 245–253.

[2] J.O'M. Bockris, J. McBreen, L. Nanis, J. Electrochem. Soc. 112 (1965) 1025.

[3] C. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, 1995.

[4] P.H.L. Notten, M. Kremers, R. Griessen, J. Electrochem. Soc. 143 (1996) 3348.

[5] E.S. Kooij, A.T.M. van Gogh, R. Griessen, J. Electrochem. Soc. 146 (1999) 2990.

[6] L. Zaluski, A. Zaluska, J.O. Strom-Olsen, J. Alloys Compd. 253–254 (1997) 70.

[7] C.J. Wen, B.A. Boukamp, R.A. Huggins, J. Electrochem. Soc. 126 (1979) 2258.

[8] P. Millet, M. Srour, R. Faure, R. Durand, Electrochem. Commun. 3 (2002) 478.

[9] M. Di Vece, I. Swart, J.J. Kelly, J. Appl. Phys. 94 (2003) 4659.

[10] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nature 380 (1996) 231.

[11] F.J.A. den Broeder, S.J. van der Molen, M. Kremers, J.N. Huiberts, D.G. Nagengast, A.T.M. vanGogh, W.H. Huisman, N.J. Koeman, B. Dam, J.H. Rector, S. Plota, M. Haaksma, R.M.N. Hanzen, R.M. Jungblut, P.A. Duine, R. Griessen, Nature 394 (1998) 656.

[12] A. Remhof, S.J. van der Molen, A. Antosik, A. Doborowolska, N.J. Koeman, R. Griessen, Phys. Rev. B 66 (2002) 020101(R).

[13] W. Weppner, R.A. Huggins, J. Electrochem. Soc. 124 (1977) 1569.

[14] M. Di Vece, S.J.M. Zevenhuizen, J.J. Kelly, Appl. Phys. Lett. 81 (2002) 1213.

[15] C.-H. Fagerstroem, F.D. Manchester, J.M. Pitre, in: F.D. Manchester (Ed.), Phase Diagrams of Binary Hydrogen Alloys, ASM International, Materials Park, 2000.

[16] S. Orimo, F. Kimmerle, G. Majer, Phys. Rev. B 63 (2001) 094307.

[17] M. Di Vece, J.J. Kelly, J. Alloys Compd. 356–357 (2003) 156–159.

[18] J. Crank, The Mathematics of Diffusion, second ed., Oxford University Press, 1999.

[19] F.G. Cottrell, Z. Phys. Chem. A 42 (1902) 385.

[20] Y. Li, Y.T. Cheng, Int. J. Hydrogen Energy 21 (1996) 281.

[21] S.J. van der Molen, J.W.J. Kerssemakers, J.H. Rector, N.J. Koeman, B. Dam, R. Griessen, J. App. Phys. 86 (1999) 6107.