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A hydrogen traffic jam in YH_x

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Abstract

Electromigration of hydrogen in the YH_x switchable mirror system is studied with a simple optical technique. The $YH_{3-\delta}$–$YH_{2+\varepsilon}$ phase boundary moves towards the anode with a velocity v_{pb}, that becomes constant for large t. A spectacular effect takes place when the phase boundary reaches an artificial discontinuity in the electric field: a 'hydrogen traffic jam' is formed. This phenomenon is succesfully simulated using the exact solutions of a non-linear electromigration equation and a large wind force coefficient $K = -23$ mΩcm. It is in principle possible to reach very high chemical potentials, comparable to those in high pressure experiments, in the traffic jam area.

Keywords: Hydrogen in metals; Switchable mirrors; Electromigration

1. Introduction

Electromigration, material transport in the presence of an electric field, has been a subject of intensive research for many decades [1]. Usually, two contributions to the force $\mathbf{F} = Z^*e\mathbf{E}$ on a migrating particle are considered: (*i*) the 'direct' force $\mathbf{F}_d = Z_d e\mathbf{E}$ due to the field $\mathbf{E}$ acting directly on the charged impurity, (*ii*) the 'wind' force $\mathbf{F}_{wind} = Z_{wind}e\mathbf{E}$, due to a net momentum transfer by scattering charge carriers. In contrast to the direct force, the theory of the wind charge is well established in metallic systems: $Z_{wind} = K/\rho$, where ρ is the total resistivity and K is constant.

In this study, we focus on YH_x, one of the so-called switchable mirrors. This class of materials (YH_x and LaH_x and the rare earth hydrides) shows a metal–insulator (MI) transition accompanied by spectacular optical changes [2–8]. The virgin materials (α-phase) and their dihydrides (β) are good metals; the trihydrides (γ) are optically transparent insulators. The nature of the insulating ground state has been a subject of recent debate [9].

2. Experiment

Our samples are prepared by electron gun evaporation on room temperature sapphire substrates in ultra high vacuum (base pressure: $\sim 5 \cdot 10^{-9}$ mbar). First, we deposit a 200-nm Al layer at one side of the substrate using a shadow mask. Next, a 200-nm, polycrystalline Y layer is evaporated, covering the entire sample area. Third, a 30-nm Pd strip is deposited in such a way that the Al and Pd areas do not overlap (see Fig. 1a). The samples are completed by an oxidation step in air, leaving a superficial oxide layer on top of the bare Y. For an experiment, the sample is mounted in a chamber equipped with optical windows, temperature control, and electrical leads. The chamber itself is placed onto the positioning table of an optical microscope (Olympus BX60F5) on top of which a 3-CCD (RGB) camera is mounted. When 1 bar of H_2 gas is introduced, the Pd-covered Y absorbs hydrogen immediately, because Pd is an excellent catalyst for H_2 dissociation. However, the oxide-covered Y, does not take up any hydrogen [5–7]. Therefore, within a few seconds the concentration profile is a step function, with x in YH_x equal to $x \approx 2.81$ (at 383 K) beneath the Pd (by definition $z \leq 0$) and $x \approx 0.1$ beneath the oxide ($z > 0$) [4]. As time passes, lateral H migration into the Y underneath the transparent oxide layer takes place with boundary condition $x(z = 0,t) \approx 2.81$. (The actual H concentration c is related to x, Avogadro's number N_A and the H molar volume V_m by $c = x \cdot N_A / V_m$.). We study electromigration by applying a current between the Al and Pd strips. As shown in Fig. 4 of Ref. [5], the migration of the β and γ phase fronts is easily observed (see also Fig. 1a). Before the experiment described below, we have tuned the

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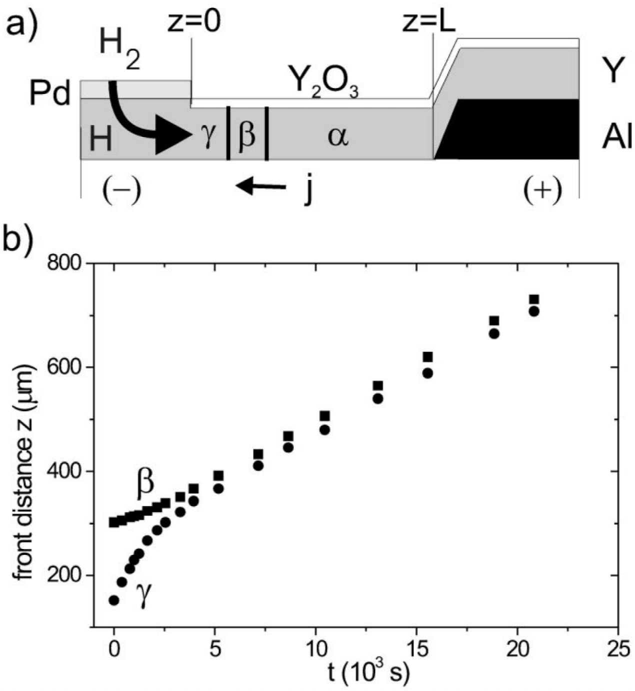

Fig. 1. Sample lay-out and experiment. (a) A 200-nm Al strip (right) on a sapphire substrate is covered by a 200-nm Y layer. A 30-nm Pd strip protects the Y at the left. The uncovered Y, however, is superficially oxidized. In 1 bar H_2, H enters via the Pd only and $YH_{3-\delta}$ is formed locally. This initiates lateral migration of H in the film, which is followed optically. After the α–β and β–γ phase boundaries are initially tuned to $z_{\alpha\beta} = 302$ μm and $z_{\beta\gamma} = 152$ μm (where z denotes the distance to the Pd edge), a current is applied from Al to Pd. (b) Phase front distances $z_{\alpha\beta}$ and $z_{\beta\gamma}$ versus time ($j = 1.37 \cdot 10^4$ A/cm², $T = 383$ K).

distances of the α–β and β–γ phase boundaries to the Pd strip edge, so that $z_{\beta\gamma} = 152$ μm and $z_{\alpha\beta} = 302$ μm.

3. Results and discussion

At $t = 0$, we apply a current ($j = 1.37 \cdot 10^4$ A/cm²) from the Al (+) to the Pd (−) strip ($T = 383$ K). Immediately, the α–β and β–γ phase boundaries start moving towards the anode. Fig. 1b shows the distance of both phase boundaries to the Pd strip edge at $z \equiv 0$. For $t < 5000$ s, the migration of the γ-front seems diffusion-like, its velocity decreasing with time. However, the β-front distance increases more than linearly with time. For $t > 5000$ s, the β and γ fronts pair up to travel at a constant velocity $v_{\mathrm{pb}} = 21.6$ nm/s.

For a qualitative analysis, we turn to the theory of electromigration. Within the context of irreversible thermodynamics, the hydrogen flux J_{H} is described by $\mathbf{J}_{\mathrm{H}} = -L_{\mathrm{HH}}(\nabla\mu - Z^{*}e\mathbf{E})$ [10], where μ is the chemical potential of H in YH_x, and $\mathbf{E}$ denotes the electric field. If $\mathbf{E} = 0$, this reduces to Fick's first law with $D = L_{\mathrm{HH}} \cdot \partial\mu/\partial c$. Applying the continuity equation $\partial c/\partial t = -\nabla \cdot \mathbf{J}_{\mathrm{H}}$, we obtain:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[D\frac{\partial c}{\partial z}\right] - \frac{\partial}{\partial c}\left[\frac{D}{\partial\mu/\partial c}\left(Z_{\mathrm{d}} + \frac{K}{\rho}\right)eE\right]\frac{\partial c}{\partial z} \qquad (1)$$

For a multi-phase system, continuity at the phase boundaries demands additionally [11]:

$$J_{q\rightarrow p} - J_{p\rightarrow q} = (c_{qp} - c_{pq}) \cdot \mathrm{d}X_{pq}/\mathrm{d}t \qquad (2)$$

where $(p,q) = (\alpha,\beta)$ or (β,γ), and $J_{p\rightarrow q}$ denotes the H flux from phase p to phase q at the phase boundary location $X_{pq}(t)$. Furthermore, $c_{qp} - c_{pq}$ is the miscibility gap between phases p and q ($x_{\alpha\beta} \approx 0.2$, $x_{\beta\alpha} \approx 1.8$, $x_{\beta\gamma} \approx 2.0$, and $x_{\gamma\beta} \approx 2.1$ following Ref. [4]). With Eqs. (1)–(2) we can explain Fig. 1b qualitatively. At small $t > 0$, the concentration profile within the γ-phase is steep, and the first term in Eq. (1) dominates. This leads to diffusion-like ($z \propto t^{0.5}$) behavior of the γ-front. However, as time passes two phenomena occur. First, the γ front approaches the β front, so that the coupling via Eq. (2) becomes increasingly important. Consequently, the β-front gets accelerated by the γ-front. Second, within the γ-phase, Eq. (1) is increasingly governed by the field term. These two effects eventually yield a dynamically stable situation: both fronts move at constant velocity $v_{\mathrm{pb}} = \mathrm{d}X_{\beta\gamma}/\mathrm{d}t = \mathrm{d}X_{\alpha\beta}/\mathrm{d}t$. From Eq. (1) one expects $v_{\mathrm{pb}} \propto E \propto j$. Varying the current density j between $6 \cdot 10^3$ and $4.2 \cdot 10^4$ A/cm², we find that this relation is indeed satisfied.

In the rest of this study, we explore the effect of a local drop in E. In Fig. 2a), a schematic picture is given of the

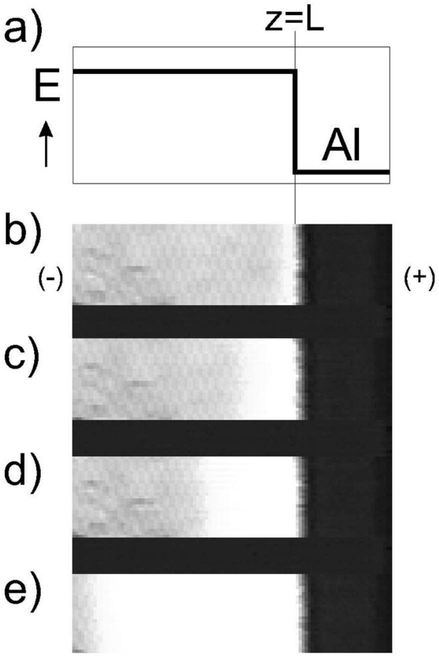

Fig. 2. The local electric field $E(z)$ has a discontinuity at $z = L$ as shown schematically in (a). When the γ-front reaches $z = L$, a 'traffic jam' of H becomes visible, its tail moving opposite to the direction of the incoming H. (b)–(e): Optical transmission pictures taken at (b): $t - t_L = 130$ (c): 580 (d): 990 and (e): 2370 s. ($j = 1.02 \cdot 10^4$ A/cm², $T = 383$ K).

field around the Al edge at $z \equiv L$. Here E has a discontinuity due to the low resistivity of the Al: $E(0<z<L) = \rho_{\mathrm{YH}_x}(c(z)) \cdot j \gg E(z>L) \approx \rho_{\mathrm{Al}} \cdot j$. Figs. 2b–e show pictures in transmission of the area just after the γ-front reaches $z = L$ ($T = 383$ K, $j = 1.02 \cdot 10^4$ A/cm^2). A spectacular effect is observed: a much more transparent phase appears at $z = L$, and apparently moves back to the Pd strip at constant velocity. Before doing a mathematical analysis, we explain this qualitatively. We note that at $z = L$, there is not only a drop in E, but also in J_{H}, i.e. more H is transported to $z = L$ than away from $z = L$. Consequently, H piles up locally, until the H concentration reaches the highest possible level ($x \approx 3$). As H is still transported towards $z = L$, a 'H traffic jam' is formed. Just as in 'car' traffic jams, there is a high density region close to a bottleneck, whose tail moves opposite to the direction of the incoming entities (cars or H) [12].

We now give a mathematical description of this inherently non-linear problem, based on the work by S.D. Majumdar [13]. Although the problem treated by Majumdar is slightly different than ours, we show below that it includes all important physical features. The dynamics of the 'traffic jam' are again described by Eq. (1). This time however, we are only interested in the situation after the γ-phase reaches $z = L$ (at $t \equiv t_L$), so that we do not need Eq. (2). First we focus on the second term of Eq. (1). For a precise description, one should use the isotherms of Ref. [4]. Unfortunately, this would lead to a differential equation which cannot be solved exactly. In order to have a tractable form, we take the expression of a non-interacting lattice gas, with $x_{\beta\gamma} = 2.1$ as a lower boundary [14], i.e. $\mu(x) = k_{\mathrm{B}} T \ln[(x-2.1)/(3-x)] + \varepsilon_0$, where again $c = x \cdot N_{\mathrm{A}}/V_{\mathrm{m}}$. As shown in Ref. [15], the Z_{d} term in Eq. (1) is small compared to the K/ρ term, so that we neglect it here. Furthermore, we assume that D is constant. Transforming to $\Theta \equiv (c \cdot V_{\mathrm{m}}/N_{\mathrm{A}} - 2.1)/0.9 = (x-2.1)/0.9$, we obtain:

$$\frac{\partial \Theta}{\partial t} = D \frac{\partial^2 \Theta}{\partial z^2} - H(1-2\Theta)\frac{\partial \Theta}{\partial z} \tag{3}$$

where $H = DKej/k_{\mathrm{B}}T$. Second, we focus on the 'initial' distribution $c(z,t-t_L=0)$, which is a consequence of the experimental history and thus of both Eqs. (1)–(2) and the condition $c(z=0,t) = 2.81 \cdot N_{\mathrm{A}}/V_{\mathrm{m}}$. To connect to Majumdar's work, we focus on a small region $0.9 \cdot L < z < L$, and assume that here $c(z,t-t_L=0) = c_{\gamma\beta} + 0.1 \cdot (3 \cdot N_{\mathrm{A}}/V_{\mathrm{m}} - c_{\gamma\beta}) = 2.19 \cdot N_{\mathrm{A}}/V_{\mathrm{m}} \equiv c_0$, neglecting the initial concentration gradient. (Note that concentration variations on $0.9 \cdot L < z < L$ are small compared to $3 \cdot N_{\mathrm{A}}/V_{\mathrm{m}} - c_{\gamma\beta}$). Furthermore, we take $J_{\mathrm{H}}(z \geq L,t) = 0$. With these assumptions, our problem has taken the form considered by Majumdar [13]. He showed that the transformation $\Theta(\lambda,\tau) = 1/2 + \partial \ln w(\lambda,\tau)/\partial\lambda$, where $\lambda \equiv z \cdot H/D$ and $\tau \equiv t \cdot H^2/D$ are dimensionless variables, reduces Eq. (3) to $\partial w/\partial\tau = \partial^2 w/\partial\lambda^2$. A solution of Eq. (3), subject to the conditions $\Theta(\tau=0,\lambda) = \Theta_0 \equiv (c_0 \cdot V_{\mathrm{m}}/N_{\mathrm{A}} - 2.1)/0.9 = 0.1$, $\Theta(\tau,\lambda=0) = \Theta_0$, and $J_{\mathrm{H}}(z>L) = 0$ is found via the Laplace transformation technique:

$$\begin{aligned} w(l,\tau) = {} & \exp(-\sigma l + \tau/4) \cdot \frac{\Theta_0 e^{\lambda/2} + (1-\Theta_0)e^{-\lambda/2}}{\Theta_0 e^{l/2} + (1-\Theta_0)e^{-l/2}} \\ & + \sum_{n=1}^{\infty} \frac{(1/4-\sigma^2)\cdot 8s_n}{\sigma \cdot (1-4s_n^2)\cdot[1-\sigma l(1-s_n^2/\sigma^2)]} \\ & \cdot \exp(-\sigma l + s_n^2 \tau) \cdot \sinh s_n(l-\lambda) \end{aligned} \tag{4}$$

where s_n denotes the nth root ($\in C$) of the equation $\tanh(s_n l) = s_n/\sigma$ with $l = L \cdot H/D$, and $\sigma = 1/2 - \Theta_0$. Transforming Eq. (4) back to c via Θ, we obtain the desired result.

To compare the analytical solution to the experiment, we determine the optical transmission T_{opt} for the pictures

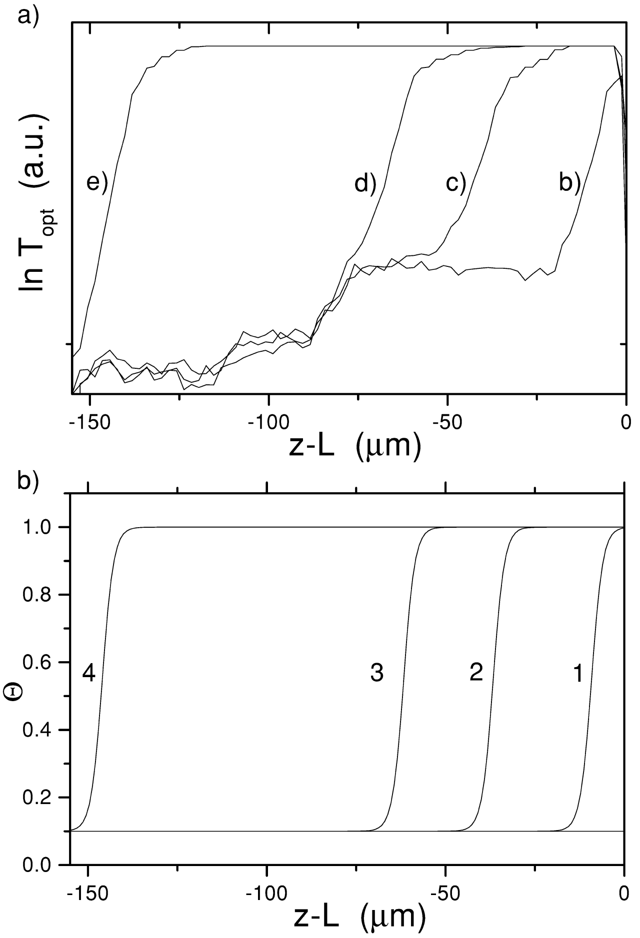

Fig. 3. (a) Vertically averaged optical transmission T_{opt} (for the green part, 490 nm $\lesssim \lambda \lesssim$ 560 nm, of the RGB signal) as a function of $z-L$, on a semilog scale. The curves are taken from the pictures in Fig. 2b–e. Note that roughly $\ln T_{\mathrm{opt}} \propto c$. The step in the curve is a result of optical inhomogeneities in the low concentration γ-phase (see Fig. 2b–e). Unfortunately, in the traffic jam region, the signal saturates. A check at lower intensities, however, confirms the optical homogeneity of this area, i.e. $\ln T_{\mathrm{opt}}$ is constant here. (b) Rescaled concentration Θ as a function of $z-L$ using Eq. (4). Curves 1, 2, 3, and 4 correspond to $t - t_L = 130$, 580, 990 and 2370 s, respectively.

in Fig. 2. Fig. 3a shows ln T_{opt}, which is approximately proportional to c [4], as a function of $z-L$, the distance to the Al edge. Fig. 3b displays an exact solution $\Theta(z,t)$ using $H=6.1\cdot10^{-7}$ m/s and $D=8.6\cdot10^{-13}$ m^2/s, where the latter value is taken from Ref. [15]. We find good correspondence between experimental and theoretical curves. From the value of H, we obtain $K=-23$ mΩcm, i.e. the wind force coefficient is 3 orders of magnitude larger than in the archetypical metalhydride systems (PdH_x,VH_x, NbH_x) [10]. This remarkably high value is in reasonable agreement with Ref. [15] who report $K\approx-50$ mΩcm at $T=383$ K, considering that Eq. (4) is only an approximate description of electromigration of H in $YH_{3-\delta}$.

Finally, we discuss the steady state, i.e. when the jam region has filled the entire sample. In that case, $J_{\mathrm{H}}(z)=0$, so that $\nabla\mu=Z^*eE$ and $\mu(z)=\mu(z=0)+\int_0^z\mathrm{d}z\ Z^*eE\approx\mu(z=0)+Kejz$. This means that very high chemical potentials, comparable to those in high pressure experiments, can in principle be reached. In this particular case, we obtain $\mu\sim10$ eV, which corresponds to pressures of as much as $p_{\mathrm{H}_2}=10^6$ bar [16]. Interestingly, a 'traffic jam' like effect can also be obtained in samples which have two Pd strips opposite of each other (at distance L) and no Al (see Fig. 4a of Ref. [5]). These samples are very suitable for H vacancy migration experiments as shown in Refs. [8,15]. In this case, however, the boundary conditions are different, as $J_{\mathrm{H}}(z,t)\neq0$ in steady state and $c(z=0,t)=c(z=L,t)\approx2.81\cdot N_{\mathrm{A}}/V_{\mathrm{m}}$ (at 383 K). In other words, H can move in and out at both sides of the sample.

4. Conclusions

Lateral electromigration of the β- and γ-phase fronts in α-phase YH_x is investigated. After initial diffusion dominated behavior, both fronts move with one velocity v_{pb}. This is explained within the theory of irreversible thermodynamics, demanding continuity at the phase boundaries. We show that once the γ-front reaches a local discontinuity in the electric field, a sort of H traffic jam is formed: H piles up in a highly concentrated trihydride region. This phenomenon is well described using a non-linear differential equation that incorporates the essential physics of the problem. Comparing its analytical solution to the experiment, we find an anomalously large wind force coefficient $K\approx-23$ mΩcm. This value is orders of magnitude larger than in the archetypical metalhydrides such as PdH_x, but comparable to recent results on $YH_{3-\delta}$. In the steady state, very high chemical potentials, comparable to those in high pressure experiments, can be reached in the traffic jam area.

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