Electrohydrogenation of MgH_2 -thin films

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Mg-metal hydride systems are potential hydrogen storage media and might be used in hydrogen switchable mirrors. However, absorption kinetics are too slow even with appropriate catalysts. The authors demonstrate the enhancement of the formation of MgH_2 by an electric current, thus enabling the hydrogenation of Mg without an external heat source. The effect is explained by the local heating of the Mg together with an electromigration of H^- ions. The electrically supported hydrogen uptake might also be a possibility to enhance the hydrogen uptake rate of complex hydrides due to a similar electronic structure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2695626]

Limited energy resources and increasing pollution associated with classical energy production have stimulated the search for cleaner, cheaper, and more efficient energy technologies. One promising technology involves hydrogen that can be used in fuel cells stored in metal hydrides and switchable mirrors for smart window coatings.^{1,2} Magnesium might be considered to be one promising material for hydrogen storage because of its high hydrogen storage capacity (7.6 mass %), the abundance of magnesium in the earth's crust, and low cost compared with alternative systems. Moreover, it might be used in hydrogen switchable mirrors, as the optical properties required by switchable mirrors are perfectly adapted.³ However, one important problem is the (un-)loading kinetics. At sufficiently high temperatures (>500 K) and pressures, magnesium reacts with hydrogen to form MgH_2 but at moderate temperatures the hydrogen uptake rate is effectively zero. This terminates any application in switchable mirrors and makes hydrogen storage in Mg energy inefficient.

Vegge ascribed the slow formation of MgH_2 to the low dissociation rate of hydrogen on Mg.⁴ His work is based on the calculation of the potential energy surface, revealing an activation barrier of 1.1 eV. His result is experimentally supported by several authors, finding dissociation and adsorption to be activated.^{5–7} The diffusion of hydrogen in magnesium is very low: Renner and Grabke determined a diffusion constant of $D=4.0 \times 10^{-13}$ m²/s at 300 K.⁸ By neutron scattering, the H diffusion in MgH_2 was found to be three orders of magnitude lower than in Mg (at 350 K).⁹ The overall hydrogen diffusion coefficient for the Mg-to- MgH_2 transition (including nucleation and growth) is even lower; $D=1.1 \times 10^{-20}$ m²/s as determined by Spatz *et al.* using x-ray photon spectroscopy.¹⁰

Hydrogen uptake by Mg thin films may occur even at relatively low temperatures if the surface of the Mg film is modified by deposition of a catalytic capping layer (typically

Pd). This procedure is employed in this study. In bulk systems, the same idea is realized by adding catalysts (transition metals¹¹ or oxides¹²). Still, after an initially fast uptake rate the reaction stops and only a relatively thin surface layer of the film (or grain) has reacted to MgH_2 .¹³ Here, the hydrogen absorption of bulk magnesium is controlled by the Mg- MgH_2 interface.¹⁴ The coherent MgH_2 film at the surface blocks further hydrogen uptake because of the low hydrogen diffusion rate through the hydride (see above). At sufficiently high temperatures and/or low pressures the continuous surface hydride film does not form and thermodynamic equilibrium is then reached.¹³ Another possibility of improving the uptake kinetics is the use of nanoparticles (grains) and very small thicknesses for bulk and thin film systems, respectively.^{12,15}

The traditional way to overcome this barrier is to heat the sample. This is somehow a waste of energy, as hydrogen absorption is an exothermic reaction, and the released heat of the once running reaction has to be removed. We will demonstrate in this letter that an electric current and the thereby induced heat and electromigration of hydrogen can start and control the absorption of hydrogen in Mg thin films in a hydrogen atmosphere at room temperature. The results hint toward the use of "electrocatalysis"¹⁶ in hydrogen storage systems.

Polycrystalline of 100 nm thick Mg films are grown on glass substrates using a dc sputtering system. On this film, 6–8 nm thick Pd film is sputtered. The argon pressure is 10^{-2} mbar and the background pressure is less than 10^{-8} mbar. The sample size is 8×30 mm². The hydrogen content of these films are probed optically by monitoring the transmission using a charge coupled device camera. This enables us to map the formation of MgH_2 as a function of time and location. The method is based on the correlation between the optical properties and the hydrogen content of the Mg films.¹⁷ Pure magnesium is a shiny metal, i.e., a 100 nm thick Mg film has essentially zero transmission. Conversely, a MgH_2 film is highly transparent due to its large band gap.³ In images in this letter, black and bright spots represent low and high hydrogen contents, respectively. The sample is exposed to 1 bar hydrogen in a loading cell and simultaneously a voltage in the order of 20–30 V is applied. The current

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FIG. 1. (Color online) Sketch of the experiment. Hydrogen is dissociated and dissolved in the Pd-cap layer. A “passivating” surface hydride is formed and the hydrogenation stops. Hydrogen uptake is still possible after applying a current via the indicated electrodes.

(0–1 A) through the films is supplied by evaporated gold contacts. The experimental setup is sketched in Fig. 1.

Figure 2 shows the hydrogen uptake of a Mg film during the application of an electric current. The top image represents the state of the Mg film after exposing to hydrogen for 10 min. Due to slow kinetics, only a surface layer is hydrided, which is not visible in transmission. The second image shows the evolving MgH_2 front after applying 20 V (corresponds to an averaged electric field of around 200 V/m). The front starts at the narrowest path on the sample and moves toward the positive side. Without a defined bottleneck for the current, the front starts at coincidentally existing imperfections. To avoid this, we added a scratch on the surface (highlighted by a red line in Fig. 2). After the fourth image the polarity is changed and simultaneously a new front evolves, which moves in reversed direction.

FIG. 2. (Color online) Photographs in optical transmission of a typical electrocatalysis experiment. The region of higher hydrogen content (lower H content) in MgH_x is recognizable by its higher (lower) transmission. The top image represents the state of the Mg film after exposing to hydrogen for 10 min. Due to slow kinetics, only a surface layer is hydrided, which is not visible in transmission. The white bar (highlighted by a red line) is an artificial scratch on the surface. The second image shows the evolving MgH_2 front after applying 20 V. The front moves toward the positive side. After the fourth image the polarity is changed and simultaneously a new front evolves, which moves in reversed direction.

FIG. 3. (Color online) Electrocatalytically enhanced hydrogenation of a Mg-wedge sample with a thickness gradient. The subsequent photographs show the development and movement of the MgH_2 front, which starts at a hole in the film (white spot). The sketch illustrates the sample setup and the main directions of the front moving. Two effects have to be considered: heating and electromigration.

The threshold current density, from which on the formation of a front can be observed, is around $1 \times 10^8 \text{ A/m}^2$. This value points to electromigration effects, in which these threshold current densities are commonly observed.¹⁸ The dependence of the front moving on the field direction indicates that the ions are involved. $\text{Mg}^{2\delta+}\text{H}_2^{\delta-}$ is an ionic compound with $\delta=0.26\text{--}0.94$ (Refs. 19 and 20). The electronic structure of hydrogen dissolved in metallic Mg is presently unknown, though a negative state is probable.²¹ As a hydrogen atom (ion) is more mobile than Mg ions, we postulate that H ions are driven by electromigration. It cannot be distinguished whether the effect is due to a field effect inside the ionic hydride or due to the “electron wind” induced by the electric current in the metallic Mg α phase.²² The reason for this is that electromigration is a nonlinear effect, which is influenced both by the charge distribution and electron correlation inside the solid.^{22,23} Microscopy images of the moving front show small Mg channels, i.e., paths through which the electric current can flow (Fig. 3, top). This corroborates the assumption that hydrogen is driven by the electron wind through metallic Mg.

The heat effect induced by the electric current cannot be neglected though. An estimate of the average temperature inside the film assuming only heat losses by radiation reveals a maximum temperature of $T_{\text{rad}} < (P/\sigma)^{1/4} \approx 650 \text{ K}$ with $P \leq 10^{-4} \text{ W/m}^2$ and $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. This estimate matches the dissociation temperature of MgH_2 at $p_{\text{H}_2} = 2 \text{ bars}$: $T_{\text{diss}} \approx 600 \text{ K}$,²⁴ i.e., hydrogen diffusion is enhanced even without assuming a field effect. To provide further evidence for electromigration, we have grown a Mg-wedge sample with a thickness gradient perpendicular to the applied voltage. The Mg thickness varies between 60 and 120 nm. The sample setup is sketched in Fig. 3. The subsequent photographs clearly demonstrate that the direction of the main front follows the regions of highest current density, i.e., first perpendicular to the applied field and then as ex-

FIG. 4. (Color online) Optically derived hydrogen content along the indicated line scan (see image) as a function of time during the electrically enhanced hydrogen uptake. The hydrogenation takes place at constant voltage in 1 bar hydrogen. The top figures show the macroscopic appearance of the film and a microscopy image of the front.

pected parallel to it after hydrogenation of the complete width of the sample. This can be explained by two simultaneously occurring effects: a local heating, which enhances the hydrogen uptake independent of the direction of the electron current, and an electromigration effect, which drives the front along the field direction.

In Fig. 3 as well as in Fig. 2 a darker zone behind the front, i.e., a partially unloaded film, is visible. To investigate this in greater detail, we show the time evolution of the hydrogen uptake in Fig. 4. Line scans along the indicated line are taken every 10 s and plotted as a function of location. During the first seconds an overall increase of the intensity with a broad maximum is visible. At a certain time, a front evolves, which then moves towards the positively charged side. Here, the local current density has become high enough to trigger electromigration. At the same time, a small zone behind the front is partially unloaded. This is indeed expected if a larger amount of hydrogen is driven by electromigration than absorbed through the surface and the negative side of the front is depleted. Still, the total amount of hydrogen absorbed in the film increases. Accordingly, the local current density at the partially depleted region will again reach the critical value and will form a second front. This interplay repeats (see arrows in Fig. 4).

Similar behavior has been observed when a dc current is applied to a polycrystalline bar of yttrium barium copper oxide²⁵ (and other superconducting materials²⁶) a hot zone forms at a certain point along the bar. This phenomenon is

known as direct current zoning. Here, oxygen atoms are moved by electromigration.

In conclusion, we have demonstrated the enhancement of hydrogen uptake of Mg thin film by applying an electric current (electrocatalysis). The electrically supported hydrogen uptake might also be a possibility to enhance the hydrogen uptake rate of other materials. In particular, the alkali alanates and borohydrides are promising candidates as their thermodynamic equilibrium temperatures are relatively low and therefore the kinetics remains slow.²⁷ Indeed, microwave irradiation on hydrides was recently found to increase the desorption kinetics of such materials drastically.²⁸

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