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Hydrogenation of magnesium nanoblades: The effect of concentration dependent hydrogen diffusion

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By assuming the H diffusion coefficient and H adsorption rate to be exponentially and linearly dependent on concentration, a physical model is developed to predict the hydrogenation process of Mg nanoblades. The predicted H uptake curves agree well with the experimental data from V-coated Mg nanoblades. The obtained H diffusion coefficients in MgH_x between Mg and MgH_2 have nearly three orders of magnitude variation. The characteristic time of H surface adsorption is longer than that of H diffusion in Mg but shorter than that in MgH_2 for 100 nm thick nanoblades. A hydride shell is not formed during the hydrogenation. © 2011 American Institute of Physics.

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Recently there has been a great effort in pursuing innovative materials and structures for solid-state H storage applications.¹ Magnesium hydride is considered to be a good candidate for this purpose because of its lightweight, low cost, and high H storage capacity of 7.6 wt % in MgH_2 .¹⁻³ However, its practical application is severely inhibited by its high thermodynamic stability (hydrogenation temperature ~ 623 K) and sluggish H sorption kinetics.⁴⁻⁶ This limitation could be relaxed by tailoring Mg/ MgH_2 into nanostructures and incorporating an appropriate transition metal catalyst.⁶⁻¹² For example, by making Mg into a nanoblade shape with a blade thickness $h \leq 100$ nm, hydrogenation begins at ~ 523 K.⁹ In addition, if a catalyst is coated on the nanoblades, both thermodynamics and kinetics of H absorption can be improved significantly.¹⁰⁻¹² We have fabricated 4.6 at. % V coated Mg nanoblades by an oblique angle deposition technique.¹² The as-deposited sample shows well-aligned vertical nanoblade arrays with an average blade thickness of $h \approx 100$ nm. The catalyst V exists in the form of randomly oriented nanocrystals of ~ 5 nm in diameter on both sides of individual Mg nanoblades. For this structure, the H uptake began at temperature below 500 K.¹² The improved H sorption kinetics is attributed to both the catalytic effect of the V coating and the unique nanoblade morphology with large surface area and small H diffusion length.¹⁰⁻¹² However, a quantitative theory accounting for both effects has not been developed yet for Mg nanoblades.

In this letter, we propose a physical model to examine and interpret the hydrogenation process of Mg nanoblades.¹² It consists of two basic processes: (a) the H adsorption at the nanoblade surface; (b) the concentration dependent diffusion of absorbed H atoms into the nanoblades, as schematically shown in Fig. 1(a). Important microscopic parameters, such as H diffusion coefficients in Mg and MgH_2 , the surface reaction rate, etc., can be obtained indirectly by fitting the calculated results with the experimental data.

The H diffusion flux \mathbf{J} in MgH_x ($x < 2$) and Mg/ MgH_2 mixture systems is assumed to follow Fick's first law,

$$\mathbf{J} = -D \nabla c, \text{ with } D = MRT, \quad (1)$$

where c is the H concentration, D is the H diffusion coefficient, M is the H mobility, R is the universal gas constant, and T is the temperature. During the hydrogenation, the transition of Mg to MgH_2 can induce a significant change in D .¹³ We hypothesize that the D change is due to a c dependence of M . It may be worth noting that the H diffusion at high c may be more reasonably viewed as the diffusion of vacancies. The H diffusion in Mg and the vacancy diffusion in MgH_2 may be fundamentally different. We assume that M depends on c and T as

$$M = M_0 e^{-\beta_1 \hat{c} - \beta_2 \hat{c}^2} e^{(-\Delta E_d / RT)}, \quad (2)$$

where M_0 is the H mobility at $c=0$, $\hat{c} (\equiv c/c_s)$ is the normalized H concentration by the saturation H concentration c_s , and ΔE_d is the activation energy of H diffusion. The exponential factor, $e^{-\beta_1 \hat{c} - \beta_2 \hat{c}^2}$ with dimensionless constants β_1 and β_2 , is assumed to account for the c dependence of M . The mass conservation law requires

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = 0, \quad (3)$$

where t denotes the time. Equations (1)–(3), together with proper initial and boundary conditions, can be assembled to formulate an initial-boundary value problem of the H diffu-

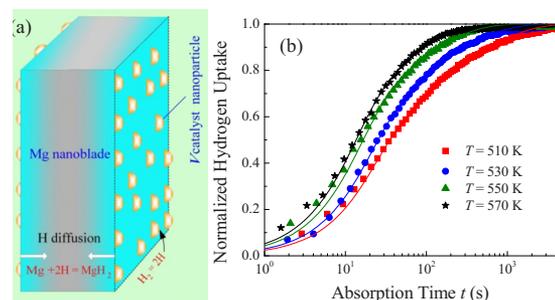


FIG. 1. (Color online) (a) A schematic of the V coated Mg nanoblade with the corresponding H diffusion and surface reaction processes. (b) Normalized H uptake vs. absorption time t at $T=510$, 530, 550, and 570 K for V coated Mg nanoblades. The scattered data are obtained from experiments and the solid curves are calculated from the model.

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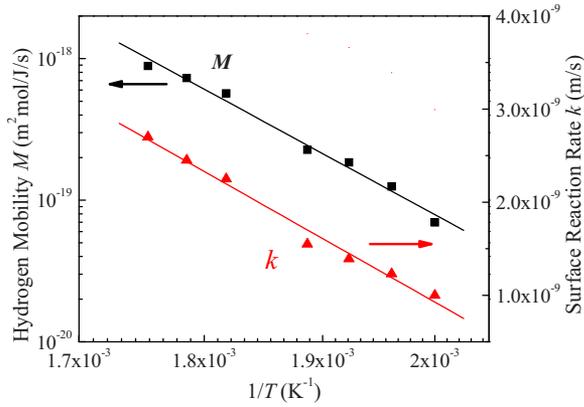


FIG. 2. (Color online) The log-log plots of the H mobility M and the H_2 surface reaction rate k vs T^{-1} .

sion in Mg nanoblades. The boundary condition is determined by the surface reaction of $H_2=2H$ and the nanoblade geometry. The H adsorption process at the surface is rather complicated, involving the dissociation of H_2 molecule into H atoms at V surface, diffusion of H atoms along V surface to bare Mg surface and then into Mg (spillover¹⁴), and diffusion of H atoms into V and then across an interface into Mg. A detailed study of kinetic pathways on surface adsorption is beyond the scope of the present work. Although experimentally the V catalyst is distributed as islands on the Mg surface as shown in Fig. 1(a), in order to use the continuum equations, we assume that the V catalyst is uniformly distributed on both sides of the Mg nanoblade, and the average surface adsorption rate is proportional to the number of available sites for H occupancy at the surface

$$\mathbf{J} \cdot \mathbf{n} = k(c - c_s). \quad (4)$$

where the reaction constant k follows the Arrhenius equation, $k = k_0 e^{(-\Delta E_s/RT)}$, with k_0 being the reaction constant at the infinite temperature, and ΔE_s being the activation energy of H adsorption at the V-coated Mg nanoblade surface. Under the experimental conditions, the H surface adsorption would not stop until $c = c_s$ since the H absorption-desorption equilibrium pressure $P_{eq} \leq 1.12$ bar at $T \leq 570$ K is far below the applied H_2 gas pressure of 10 bar.¹⁰

The above H adsorption and diffusion in a Mg nanoblade is assumed to be one-dimensional through the thickness.¹² The reduced governing equations, Eqs. (1) and (3), together with the boundary condition Eq. (4), are solved by applying a standard implicit backward finite difference method.¹⁵ Because the Mg nanoblade is coated with V particles on both sides [Fig. 1(a)], the problem is symmetric. The Mg nanoblade is initially free of H. It has an average thickness of 100 nm.¹² In order to compare with the experimental results, we adjust four parameters, D_H^{Mg} , β_1 , β_2 , and k in the numerical calculations, where $D_H^{Mg} (= M_0 RT e^{(-\Delta E_d/RT)})$ is the H diffusion coefficient in pure Mg, derived by setting $c=0$ in Eq. (2). Given a set of values of these parameters, the above boundary-initial value problem is solved. The shapes of early and late stages of a H-uptake curve are determined by surface adsorption constant k and by concentration-dependent constants β_1 and β_2 , respectively. The shape of intermediate stage and the magnitude of the entire H-uptake curve are determined by D_H^{Mg} . We finalize the curve fitting by matching the main intermediate stage with the experimental results but leaving slight disagreement at the two ends.

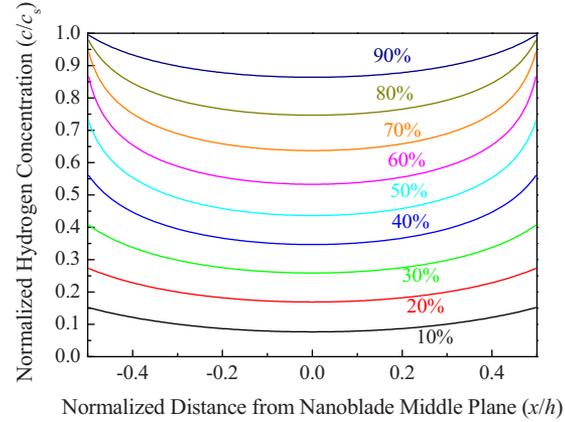


FIG. 3. (Color online) Normalized H concentration profiles vs normalized position in nanoblade at various H uptake stages from 10% to 90% of saturation amount at $T=510$ K.

We have examined the experimental results at temperatures ranging from 500 to 570 K. The predicted normalized H uptake curves at $T=510, 530, 550,$ and 570 K are plotted in semilog scale with corresponding experimental data in Fig. 1(b). The calculated results from the model agree well with the experimental results, except in the very early stage before 20 s and in the very late stage after 1000 s. This excellent agreement demonstrates that the present model has captured the main characteristic features of the hydrogenation process of Mg nanoblades.¹²

For all the fittings of H uptake curves from 500 to 570 K, parameters β_1 and β_2 are found to be 3.8 and 2.7, respectively. This suggests that the c -dependence of H diffusion is pronounced but is insensitive to T as hypothesized in Eq. (2). D is decreased by a factor of ~ 665 when c increases from 0 to c_s . In other words, D is approximately 665 times greater in Mg (D_H^{Mg}) than in its hydride ($D_H^{MgH_2}$), which is consistent with early experimental results by Töpler *et al.*¹³ In addition, both D_H^{Mg} and $D_H^{MgH_2}$ vary with T . When T increases from 500 to 570 K, D_H^{Mg} increases from 2.90×10^{-16} to 4.20×10^{-15} m^2/s , and $D_H^{MgH_2}$ increases from 4.36×10^{-19} to 6.31×10^{-18} m^2/s . This result is around the same order of magnitude as those obtained by Yao¹⁶ but very different (by up to ten orders) from others.^{17,18} It should be noted that the previous measurements were made upon large-scale Mg samples and/or under complicated conditions (such as post-milling). In contrast, the present paper deals with V-coated crystalline Mg nanoblades at the nanoscale, under nearly free-standing condition and well-defined surface condition. The large variation in reported values of D in Mg and MgH_2 itself demands further systematic investigation of the very fundamentals of H diffusion in the materials. In Fig. 2, the magnitude of M found from the fitting curves at the temperature range of 500 to 570 K is plotted in log-log scale against T^{-1} . Compared with Eq. (2), we obtain $M_0 = 7.652 \times 10^{-11}$ $m^2 \text{ mol}^{-1} \text{ J}^{-1} \text{ s}$ and $\Delta E_d = 86.1$ kJ/mol H. The surface reaction constant k found in the analyses is also plotted against T^{-1} in Fig. 2. It follows the Arrhenius law. We obtain $k_0 = 3.61$ $\mu\text{m/s}$ and $\Delta E_s = 34.0$ kJ/mol H. Our previous analysis revealed that the activation energy for the overall H absorption process is $\Delta E_a = 50.6 \pm 0.9$ kJ/mol H,¹² which is located between $\Delta E_s = 34.0$ kJ/mol H and $\Delta E_d = 86.1$ kJ/mol H but relatively closer to the former. This demonstrates that for the V-coated Mg nanoblade, the surface reaction is the rate limiting process.

The above observations can be understood by viewing the H distribution in the nanoblade. For example, at $T=510$ K, the predicted H profiles through nanoblade thickness are plotted in Fig. 3, which are snapshots acquired at various moments with H uptake from 10% to 90% of saturation amount. They show that the surface H concentration gradually increases during almost the entire hydrogenation process. This observation is verified for all other cases of different temperature. It suggests that the characteristic time for surface reaction, t_s , is longer than that of the diffusion process, t_d . This can be confirmed by the following estimate: $t_s^{500\text{ K}} \approx 50$ s at $T=500$ K and $t_s^{570\text{ K}} \approx 18.5$ s at $T=570$ K using $t_s = h/2k$ with $h=100$ nm and k values from Fig. 2; $t_d^{500\text{ K}} \approx 8.6$ s at $T=500$ K and $t_d^{570\text{ K}} \approx 0.6$ s at $T=570$ K by $t_d = h^2/4D_{\text{H}}^{\text{Mg}}$. Note that the obtained t_d values on basis of D_{H}^{Mg} are from the initial hydrogenation stage. Therefore, at the beginning of hydrogenation, the diffusion process is faster than the surface reaction process and thus the hydrogenation is reaction limited. By combining Fig. 3 and Eq. (2), it can be seen that D decreases and $t_d (=h^2/4D)$ increases, with hydrogenation proceeding. For example, at $T=510$ K, when the H uptake reaches 10%, 30%, and 50% of saturation amount, the average value of $t_d^{510\text{ K}}$ across the nanoblade increases from 3.3, 8.9 to 16 s but the local value of $t_d^{510\text{ K}}$ at the nanoblade surface changes from 4.1, 16 to 143 s, values which are comparable to or even longer than $t_s^{510\text{ K}}=40.6$ s. Thus, at a late hydrogenation stage, the surface reaction outruns diffusion and starts to build up H atoms at the nanoblade surface, and the process becomes diffusion limited. Therefore, during the hydrogenation of V-coated Mg nanoblades, it undergoes a transition from a reaction limited process to a diffusion limited process.

From Fig. 3, it can also be seen that no MgH_2 shell is formed with a sharp MgH_2/Mg interface near the surface. This is quite different from the shrink-core model, which assumes that a diffusion retardant layer or a hydride layer is growing or shrinking depending on the process of hydrogenation or dehydrogenation.^{19–23} However, for the Mg nanoblade, since the storage particles are sufficiently small, t_d is comparable to or smaller than the t_s , and the shrink-core model is no longer valid.^{14,24,25} According to Fig. 3, D is higher deep inside the nanoblade with lower c than near the surface with higher c . The H atoms that are generated by the catalyst and that break into Mg surface are diffused at an accelerating rate through the nanoblade to form $\text{MgH}_{x < 2}$ phase, which has been demonstrated by Schimmel *et al.*²⁶ using *in situ* neutron diffraction and is considered to be a characteristic of nanostructured insertion materials. As the hydrogenation continues, the x value increases until $x=2$ when $c/c_s=100\%$. However, experimentally it is challenging to observe the gradual concentration change, especially near the surface (Fig. 3), due to the existence of complications such as the formation of MgO and Mg-based perovskite $[\text{Nb}(\text{Mg}_{0.333}\text{Nb}_{0.667})\text{O}_3]$ at the surface,²⁶ the catalyst itself possibly with less H like $\text{VH}_{0.81}$ in its hydride,¹⁰ etc., which are not considered in the present model. These factors will reduce the surface H amount, as demonstrated by Kumar *et al.*²⁷ regarding Pd/Mg films hydrogenated under different conditions using nuclear resonance reaction analysis: close to the surface, the H concentration into the film surface is higher than that at the surface. However, from the catalyst layer deeper into the interior of the partially hydrogenated

film, they indeed observed and showed gradual H concentration decrease (their Fig. 5), which is consistent with our results (Fig. 3) except the complicated surface region.

In summary, by assuming that the H diffusion coefficient is an exponential function of H concentration and that the surface H reaction plays a nontrivial role in the absorption process, we have shown that the H diffusion in Mg nanoblades is strongly dependent on H concentration. The predicted H uptake history agrees very well with the experimental data from V-coated Mg nanoblades. The effective H diffusion coefficient in Mg is approximately three orders of magnitude greater than that in MgH_2 . Thus, as it proceeds, the hydrogenation process gradually changes from surface reaction-limited to diffusion-limited. Because a hydride shell is not observed during the hydrogenation of the nanoblade, the shrink-core model is unsuitable to describe the process at the nanometer scale. The proposed model provides a genetic principle for hydrogenation of nanostructured materials with concentration dependent H-diffusion. One can use this model to describe the hydrogenation process in other H-storage materials as long as they have the same features.

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