Concentration-dependent hydrogen diffusion in hydrogenation and dehydrogenation of vanadium-coated magnesium nanoblades

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ABSTRACT

We carry out a computational investigation to show how the exponential concentration dependence of hydrogen diffusion, which was recently verified in a combined experimental and analytical study, could affect the characteristics of hydrogenation and dehydrogenation of a vanadium-coated magnesium nanoblade. A reaction model is built that separates hydrogen surface sorption and interior diffusion during the hydrogenation/dehydrogenation process. For the hydrogenation process, the hydrogen surface adsorption is much faster than the hydrogen diffusion, resulting in high hydrogen concentration buildup at the surface at a relatively low temperature. With increasing temperature, the hydrogen diffusion time decreases more rapidly than the hydrogen surface adsorption time. This leads to a relatively low-gradient diffusion field in the nanoblade during most time of the hydrogenation process, and no shell−core structure with a finite hydride layer is observed. However, for the dehydrogenation process, when hydrogen molecules are released at the surface, a hydride core is formed inside the nanoblade and the interface recedes gradually. The receding rate of the hydride core is determined by the hydrogen molecule release rate. In a two-dimensional simulation with decorated vanadium catalyst islands on the surface, isolated interior hydride islands are sometimes observed before the hydride core entirely fades away. The hydride core boundary is sharper at lower temperature when the surface reaction rate is high relative to the interior diffusion rate.

1. Introduction

Hydrogen storage is one of the bottlenecks for using hydrogen energy in on-board vehicle applications. Various methods have been proposed to store hydrogen, such as pressurized gas, cryogenic liquid state storage, and solid state storage through metal hydrides, complex hydrides, and high surface area adsorbents. The safest and most promising one is the solid state materials. Among different materials, magnesium hydride is considered to be a good candidate for this purpose based on the consideration of its lightweight, low cost, non-toxicity, and high theoretical storage capacity of 7.6 wt% [1−3]. However, the practical application of magnesium hydride is severely inhibited due to its high thermodynamic stability (with enthalpy $\Delta H = -75$ kJ/mol hydrogen) [4], high hydrogen desorption temperature (>623 K), and extremely slow

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hydrogen sorption kinetics in and out of magnesium [4–7]. Researches show that such limitations could be relaxed by tailoring magnesium and magnesium hydride into nanostructures and incorporating an appropriate transition metal catalyst [8–20]. For example, by making magnesium into a nanoblade shape with a blade thickness $h \leq 100$ nm, hydrogenation begins at ~523 K [11]. In addition, if a catalyst is coated on the surface of individual nanoblades, both thermodynamics and kinetics of hydrogen absorption and desorption can be improved significantly [12–14]. We have fabricated 4.6 at.% vanadium surface-decorated magnesium nanoblades, in a physical vapor deposition system, by combining an oblique angle deposition (OAD) technique to form magnesium nanoblades and dynamically swinging the substrate within a certain range of deposition angle (vanadium vapor flux with respect to the substrate normal) to coat vanadium onto the two sides of individual magnesium nanoblades uniformly [14]. The as-deposited sample shows a well-aligned vertical nanoblade array structure with an average blade thickness $h \approx 100$ nm. The catalyst vanadium exists in the form of randomly oriented nanocrystals of ~5 nm in diameter on both sides of individual magnesium nanoblades. For this structure, the hydrogen uptake and release began at an even lower temperature, below 500 K [14]. The improved hydrogen sorption kinetics is attributed to both the catalytic effect of the vanadium coating and the unique nanoblade morphology with large surface area and small hydrogen diffusion length [12–14]. However, a quantitative theory accounting for both effects has been scarce for magnesium nanoblades [21]. We have most recently introduced a model separating the two effects, as schematically shown in Fig. 1, and applied it to analyze the hydrogenation process of vanadium-coated magnesium [22]. In the model,

the hydrogen diffusion is approached as a field problem, and the surface reaction is taken as the boundary condition. It is shown that the hydrogen adsorption and hydrogen diffusion rates are comparable for ~100 nm thick magnesium nanoblades between 500 K and 570 K. More importantly, the hydrogen diffusion coefficient depends exponentially on its concentration in the magnesium nanoblades.

The present paper aims to extend the model to both hydrogenation and dehydrogenation processes of vanadium-coated magnesium and computationally facilitate insights into how this concentration dependence of diffusion coefficient could significantly affect the characteristics of diffusion field in magnesium. The paper is organized as follows. In Section 2, an initial-boundary value problem is formulated for hydrogen diffusion in a vanadium-coated magnesium nanoblade. The finite concentration, or saturation effect, is taken into account in the chemical potential [23,24], compared to the formulation for dilute diffusion [24–29]. We also consider the relationship of hydrogen flux to potential gradient [24–29]. It turns out that the flux equation derived on these assumptions is in the classical form of Fick's first law. The law is symmetric and is applicable to both dilute and near-saturation hydrogen diffusion. A rate equation of surface sorption is imposed as the boundary condition, which models the catalytic effect of surface vanadium. In Section 3, a finite difference method is applied to solve the above problem in one and two dimensions. In Section 4, calculation results are presented and analyzed. It is shown that the hydrogen diffusion is the limiting process to the hydrogenation and dehydrogenation of magnesium nanoblade. The vanadium catalyst can effectively provide fast enough surface hydrogen sorption and desorption below 600 K. In the simulations, no shell-core structure with a finite hydride layer is observed in the hydrogenation process. In contrast, such a structure occurs in the dehydrogenation process. The characteristic difference in diffusion field is attributed to the exponential concentration dependence of hydrogen diffusion in magnesium. Section 5 draws the conclusions.

2. Problem formulation

Hydrogen atoms upon absorption are assumed to occupy interstitial sites between magnesium atoms. They diffuse by hopping from current interstitial sites to adjacent interstitial sites if the latter are vacant or available. The specific chemical potential is given by [23,24]

$$\mu = \mu_0 + RT\ln\left(\frac{c}{c_s - c}\right), \tag{1}$$

where T is the temperature, c is the hydrogen concentration per unit volume, c_s is the total interstitial site concentration, i.e., the hydrogen saturation concentration in the magnesium matrix, R is the universal gas constant, and μ_0 is the equilibrium chemical potential, which may be a function in terms of temperature and stress state but not of c. Since c is the concentration of occupied interstitial sites by hydrogen atoms, $c_s - c$ measures the concentration of vacant interstitial sites. The diffusion of hydrogen atoms can also be viewed as
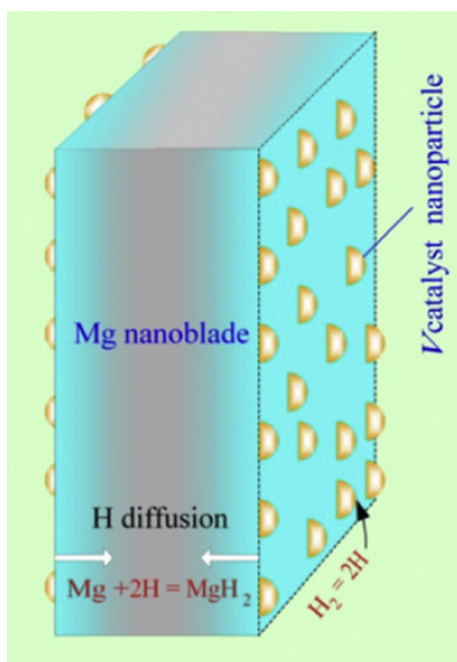

Fig. 1 – A schematic showing a vanadium-coated magnesium nanoblade undergoing hydrogen surface reaction and interior diffusion.