Assessing nanoparticle size effects on metal hydride thermodynamics using the Wulff construction

To cite this article: Ki Chul Kim et al 2009 Nanotechnology 20 204001

View the article online for updates and enhancements.

You may also like

- Thermal stability of titanium hydride modified by the electrochemical deposition of titanium metal
 R N Yastrebinsky, V I Pavlenko, A A Karnauhov et al.
- <u>Metallic and complex hydride-based</u> <u>electrochemical storage of energy</u> Fermin Cuevas, Mads B Amdisen, Marcello Baricco et al.
- <u>Study of Thermal Runaway</u> <u>Electrochemical Reactions in Alkaline</u> <u>Batteries</u> N. E. Galushkin, N. N. Yazvinskaya and D. N. Galushkin





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.117.196.217 on 12/05/2024 at 02:30

Nanotechnology 20 (2009) 204001 (7pp)

Assessing nanoparticle size effects on metal hydride thermodynamics using the Wulff construction

Ki Chul Kim¹, Bing Dai², J Karl Johnson^{2,3} and David S Sholl^{1,4}

¹ School of Chemical and Biomolecular Engineering, Georgia Institute of Technology,

311 Ferst Drive, Atlanta, GA 30332-0100, USA

² Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA

³ National Energy Technology Laboratory, Pittsburgh, PA 15236, USA

E-mail: david.sholl@chbe.gatech.edu

Received 18 August 2008 Published 23 April 2009 Online at stacks.iop.org/Nano/20/204001

Abstract

The reaction thermodynamics of metal hydrides are crucial to the use of these materials for reversible hydrogen storage. In addition to altering the kinetics of metal hydride reactions, the use of nanoparticles can also change the overall reaction thermodynamics. We use density functional theory to predict the equilibrium crystal shapes of seven metals and their hydrides via the Wulff construction. These calculations allow the impact of nanoparticle size on the thermodynamics of hydrogen release from these metal hydrides to be predicted. Specifically, we study the temperature required for the hydride to generate a H₂ pressure of 1 bar as a function of the radius of the nanoparticle. In most, but not all, cases the hydrogen release temperature increases slightly as the particle size is reduced.

S Supplementary data are available from stacks.iop.org/Nano/20/204001

1. Introduction

The high gravimetric and volumetric capacities of light metal hydrides make them appealing candidates for reversible H_2 storage in vehicular applications [1, 2]. The performance of metal hydrides for H_2 storage, however, is limited by thermodynamic and kinetic factors. For many hydrides, the equilibrium conditions required for H_2 release and uptake lie outside those appropriate for fuel-cell powered vehicles. This situation has spurred searches for materials with more appropriate thermodynamic properties [3–8]. Aside from these thermodynamic factors, the kinetics of H_2 uptake and release by metal hydrides are often much slower than would be desirable.

The concept of improving the performance of metal hydrides for H_2 storage by using nanoparticles has received considerable attention [9–14]. This work is most often motivated by the idea that the kinetics of H_2 uptake and release may be improved by decreasing the particle size of the relevant solid phases. This expectation is reasonable if

the reaction kinetics are controlled by diffusion through a bulk phase. It is not yet clear in most light metal hydrides what the rate limiting steps in H_2 uptake or release are, so anticipating the effects of nanosizing on the kinetics of these reactions remains difficult. It is useful to note in this context that examples are known in studies of metal films used as membranes for H_2 purification where reducing the film thickness below a critical thickness yields a limited return in terms of improved device performance because processes other than bulk diffusion become rate limiting [15, 16].

In addition to changing the reaction kinetics, using nanoparticles instead of bulk metal hydrides can also alter the thermodynamics of H_2 uptake and release [17, 18]. Conceptually, the thermodynamics of these processes is governed by energy differences between the metal and metal hydride. Because the energies (on a molar basis) of both materials change in going from bulk materials to nanoparticles, the reaction thermodynamics of these materials must be affected by particle size [19]. The aim of this paper is to estimate the size of this effect for a number of simple metal hydrides. The ultimate aim of work on metal hydride nanoparticles is to generate reliable experimental data with

⁴ Author to whom any correspondence should be addressed.

robust materials. Because the reactions of many metal hydrides have severe kinetic limitations, unambiguously decoupling the kinetic and thermodynamic effects in experimental studies of nanoparticles is challenging. This situation means that estimates of the thermodynamic effects associated with nanoparticles from theoretical methods can play a useful role in understanding the overall properties of these materials.

One useful theoretical approach to examining the energy of nanoparticles is a 'bottom-up' method in which detailed calculations are performed for clusters in which every atom is represented. This approach has been used extensively to explore the geometry of very small metal clusters [20]. Two studies have explored Mg and MgH₂ nanoclusters in this way [19, 21]. Wagemans et al used density functional theory (DFT) to examine clusters with <60 Mg atoms, with most of their calculations focusing on clusters with <20 Mg atoms [19]. Cheung et al used DFT calculations of small clusters and bulk materials to parameterize a classical force field for Mg-H interactions and subsequently applied this force field to study clusters containing up to 101 Mg atoms [21]. Both of these studies provided clear indications that nanoclusters containing <50 Mg atoms could show deviations in their heats of formation from bulk materials, an observation that implies that the reaction thermodynamics of these clusters differs from that of bulk materials. An important limitation of this 'bottom-up' approach is that the computational expense associated with examining clusters grows rapidly with the cluster size. Clusters of Mg with radii of 2 and 5 nm contain \sim 1500 and \sim 23000 atoms, respectively, and the relevant MgH₂ clusters contain three times as many atoms. These system sizes lie far beyond those that are accessible with contemporary DFT calculations, and even using a force field approach, such as the one introduced by Cheung et al, these system sizes are daunting. Calculations based on classical force fields face the additional complication that a large amount of effort must be expended for each new material of interest.

In this paper, we explore the thermodynamics of metal hydride nanoparticles from an alternate 'top-down' viewpoint. In this approach, the crystal structure of each nanoparticle is assumed to be identical to the bulk crystal, aside from relaxation of the atoms in the first few layers near the surface. Differences in energy between nanoparticles and bulk materials arise because of the presence of well defined surfaces. For each surface exposed on a nanoparticle, this energy difference is characterized by a surface energy. We have used DFT calculations to compute the surface energies, including the effects of surface relaxation, of a large number of potentially relevant surfaces for seven elemental metals and their hydrides. The equilibrium crystal shape (ECS) of a material can be predicted using the calculated surface energies and the Wulff construction [22-24]. This makes it possible to calculate the net surface energy of the nanoparticle. Below, we describe the influence of nanoparticle size on the reaction thermodynamics for nanoparticles formed in this way.

2. Results

A useful way to characterize the thermodynamics of hydrogen release or uptake by metal hydrides is to determine the temperature at which the metal hydride is in equilibrium with the metal when the H_2 pressure is 1 bar [25]. Under these conditions the free energies, or equivalently, the grand potentials, of the two systems are equal [7]. For bulk samples, the grand potential can be estimated using DFT calculations by

$$\Omega(T) = E - \frac{1}{2} \left(E_{\rm H_2} + E_{\rm ZPE, H_2} + \tilde{\mu}_{\rm H_2} \right) n^{\rm H}, \qquad (1)$$

where *E* is the total energy for the solid of interest computed from DFT, the quantities inside the parentheses are the energy, zero point energy (ZPE), and chemical potential of molecular H₂, and $n^{\rm H}$ is the number of H atoms per metal atom in the solid [26–28]. This expression neglects the ZPE in the solid and temperature dependent vibrational contributions to the solid's free energy; we return to these approximations below. From this expression for the grand potential, it follows that the bulk metal hydride and metal are in equilibrium when

$$\tilde{\mu}_{H_2}(T, P_{H_2} = 1 \text{ bar}) = \beta = \frac{2}{n^H} \left(E_{MH}^{bulk} - E_M^{bulk} \right) - \left(E_{H_2} + E_{ZPE,H_2} \right).$$
(2)

Here, MH and M denote the metal hydride and metal, respectively. To extend this expression to solid particles of finite size, the influence of surface energy on the overall energy of the solids must be included. Using quantities accessible via DFT calculations based on slab geometries, the surface energy is

$$\gamma = \left[E^{\text{slab}} - N E^{\text{bulk}} \right] / A, \tag{3}$$

(4)

where E^{slab} is the total energy of the slab containing N metal atoms, E^{bulk} is the total energy of the bulk material per metal atom, and A is the total surface area exposed by both sides of the slab [23, 24, 29]. Here, the slab energy is defined using a slab that has been geometry optimized to include the effects of surface relaxation. Nanoparticles of a metal and its metal hydride are in equilibrium when

 $\tilde{\mu}_{\mathrm{H}_2}(T, P_{\mathrm{H}_2} = 1 \text{ bar}) = \beta + \alpha/N,$

where

$$\alpha = \frac{2}{n^{\mathrm{H}}} \left(\sum_{i} \left(A_{\mathrm{MH},i}^{\mathrm{surf}} \gamma_{\mathrm{MH},i}^{\mathrm{surf}} \right) - \sum_{j} \left(A_{\mathrm{M},j}^{\mathrm{surf}} \gamma_{\mathrm{M},j}^{\mathrm{surf}} \right) \right)$$
$$= \frac{2}{n^{\mathrm{H}}} \Delta \left(A^{\mathrm{surf}} \gamma^{\mathrm{surf}} \right).$$
(5)

The summations are necessary here to allow for particles that expose multiple surfaces. Once $\tilde{\mu}_{H_2}(T, P_{H_2})$ is known from either equation (2) or equation (5), the temperature at which the metal and metal hydride are in equilibrium, T_{eq} , is defined. In calculating T_{eq} , we assume that H₂ is an ideal gas.

An alternative way to describe the thermodynamic effects of nanosizing is to use the change in enthalpy between the reaction involving a nanoparticle and the reaction for the bulk materials,

$$\Delta \Delta H = \Delta H(N) - \Delta H(\infty). \tag{6}$$

In terms of the quantities defined above, this enthalpy change is simply

$$\Delta \Delta H = -\frac{\alpha}{N}.$$
 (7)



Figure 1. The predicted equilibrium crystal shapes of Sc, Ti, and their hydrides determined from the Wulff construction as described in the text.

(This figure is in colour only in the electronic version)

To make use of the formalism above, we need to determine the areas and surface energies of the surfaces exposed by each nanoparticle of interest. If the surface energies of each possible surface are known, the Wulff construction can be used to predict the equilibrium crystal shape (ECS) of the material [22–24]. To apply the Wulff construction, we used DFT to calculate the surface energy of each low index surface of seven elemental metals and their hydrides, as summarized in table 1. A complete list of the surface energies from our calculations is given in the supplementary information (available at stacks.iop.org/Nano/20/204001). A convenient feature of these low index surfaces for all the hydrides we considered is that each layer normal to the surface has the same stoichiometry as the bulk hydride. This means that there is no ambiguity in defining the termination of these surfaces [30].

All of our DFT calculations were performed with the PW91 generalized gradient approximation functional [31] using the Vienna *ab initio* simulation package [32, 33]. The core electrons of each atom were described by ultrasoft pseudopotentials [34], and an energy cutoff of 300 eV was used for all calculations. During geometry optimization, all atoms were relaxed until the forces on all atoms were less than 0.03 eV Å⁻¹. All surface calculations used supercells

defined by the DFT-optimized bulk lattice constant in the plane of the surface and a vacuum spacing of at least 10.8 Å. All surfaces were modeled by using (1×1) surface unit cells with six layers in which all atoms are allowed to relax freely. Calculations on the surface unit cells were performed with a $12 \times 12 \times 1$ Monkhorst–Pack mesh in *k*-space. Reciprocal space for the bulk materials was sampled using $8 \times 8 \times 8 k$ points for NaH, LiH, ScH₂, TiH₂, and VH₂, $8 \times 8 \times 12 k$ -points for MgH₂, $12 \times 12 \times 4 k$ -points for AlH₃, $12 \times 12 \times 12 k$ points for Na, Li, and V, $15 \times 15 \times 10 k$ -points for Ti and Sc, $20 \times 20 \times 12 k$ -points for Mg and $20 \times 20 \times 20 k$ -points for Al. All bulk materials were modeled by using a $1 \times 1 \times 1$ supercell.

Using the surface energies calculated from DFT, we applied the Wulff construction for the seven metals and metal hydrides we considered. Two examples of the resulting equilibrium crystal shapes are shown in figure 1. We examined five low index surfaces for Sc, and all of these surfaces appear on the ECS shown in figure 1(a), with the $(10\overline{11})$ and $(11\overline{21})$ surfaces defining about 70% of the entire surface area. The $(11\overline{20})$ surface is predicted to only account for 0.4% of the particle's total surface area. The same set of five surfaces was considered for Ti, whose predicted ECS is shown in figure 1(c). For Ti, only four surfaces feature on the ECS, and

 Table 1. Summary of the surfaces examined for each material in applying the Wulff construction to form the ECS. The final column indicates the fraction of the total surface area on the ECS associated with each surface.

Space group	Material(s)	Surfaces examined	Surfaces on the ECS
Im3m	V Li Na	(111), (110), (100) (111), (110), (100) (111), (110), (100)	(110)—70%, (100)—24%, (111)—6% (110)—53%, (100)—39.3%, (111)—7.7% (110)—78.1%, (100)—21.2%, (111)—0.7%
<i>P</i> 6 ₃ / <i>mmc</i>	Sc	(0001), (1010), (1011), (1120), (1121)	(1011)—38.7%, (1121)—33%, (0001)—15.8%, (1010)—12.1%, (1120)—0.4%
	Ti	(0001), (1010), (1011), (1120), (1121)	(1121)—55.5%, (1011)—24.5%, (0001)—17.2%, (1010)—2.8%
	Mg	$(0001), (10\overline{1}0), (10\overline{1}1), (11\overline{2}0), (11\overline{2}1)$	(1011)—38%, (1010)—37.8%, (0001)—24.2%
$Fm\bar{3}m$	Al	(111), (110), (100)	(111)-75.5%, (100)-24.5%
Fm3m	VH ₂ LiH NaH ScH ₂ TiH ₂	(111), (110), (100) (111), (110), (100) (111), (110), (100) (111), (110), (100) (111), (110), (100)	(111)—100% (100)—100% (100)—100% (111)—100% (111)—100%
$P4_2/mnm$	MgH ₂	(111), (110), (101), (100), (001)	(101)—45%, (110)—38.1%, (100)—16.4%, (001)—0.5%
$R\bar{3}c$	AlH ₃	$(0001), (10\overline{1}0), (10\overline{1}1), (11\overline{2}0), (11\overline{2}1)$	(1121)—100%



Figure 2. The variation in the metal/metal hydride transition temperature relative to the result for a bulk material determined as described in the text.

the $(11\overline{2}1)$ surface defines about half of the total surface area. Our calculated surface energies for Ti differ in several respects from the values reported by Wang *et al* using calculations with the modified embedded atom method (MEAM) [35]. For example, our calculations indicate that the $(11\overline{2}1)$ surface has the lowest surface energy, while Wang *et al*'s calculations suggested that the $(11\overline{2}0)$ surface has a lower surface energy than $(11\overline{2}1)$. Although DFT calculations do not give exact results for surface energies, it seems likely that our DFT results are more reliable than results from the semi-empirical MEAM. The ECSs of ScH₂ and TiH₂ are much simpler than those of their metal counterparts, an observation that can be understood by noting that the partially ionic nature of these materials makes their surface energies much more anisotropic than the surface energies of elemental metals. As shown in figures 1(b)

Table 2. The numerical coefficient, α , that controls nanoparticle thermodynamic effects for the seven systems we have considered, where *N* is the number of metal atoms in the nanoparticle.

System	$\alpha/N^{2/3}$ (eV)
VH ₂ /V	-1.608
LiH/Li	-0.822
ScH ₂ /Sc	-0.667
TiH ₂ /Ti	-0.461
AlH ₃ /Al	-0.107
NaH/Na	0.134
MgH ₂ /Mg	0.296

and (d), these hydrides have only (111) surfaces on their ECSs. The contribution of each surface to the total surface area on the ECS of each of the seven metals and hydrides we have considered is summarized in table 1.

From the calculated surface energies and ECSs, we used equations (4) and (5) to describe the influence on particle size on the thermodynamics of hydrogen evolution. Our results are summarized in figure 2, which shows the difference between the equilibrium temperature, T_{eq} , for a nanoparticle and a bulk material. In this figure, the size of the metallic nanoparticle is shown by converting the volume of the nanoparticle with the predicted Wulff ECS to a spherical particle with the same bulk density. The numerical values of α for each metal/metal hydride pair are defined in table 2 by listing $\alpha N^{-2/3}$, a quantity that is independent of N. An initial observation from figure 2 and table 2 is that both positive and negative deviations of the transition temperature with respect to the bulk material exist. For MgH₂/Mg and NaH/Na, the sign of α is positive, so the transition temperature decreases as the particle size is reduced. The opposite trend is seen for the other five metal/metal hydride pairs.

A second observation from figure 2 is that the changes in the transition temperature relative to the bulk materials are, on the whole, small. For metal particles with radius



Figure 3. The variation in the metal/metal hydride reaction enthalpy relative to the result for a bulk material determined as described in the text.

10 nm, the effects from the exposed surfaces change the transition temperature by less than 20 K for every material. For the two cases where the transition temperature is lower for nanoparticles than for the bulk material, the temperature is only reduced by 33 (16) K for MgH₂/Mg (NaH/Na) for the extreme case of a nanoparticle having a radius of 1 nm. The largest effect of nanoparticle size is predicted for VH2/V. If we consider a V nanoparticle with radius 5 nm as an example, the transition temperature in this case is only 30 K larger than for the bulk system. We note that for most systems it is desirable to reduce the transition temperature or heat of reaction. However, for AlH₃, it would be useful to increase the transition temperature (or equivalently, the heat of reaction) because, at equilibrium, AlH₃ decomposes at temperatures that are too low for practical applications [36]. The nanoparticle transition temperature does indeed increase for the AlH₃/Al system, as seen in figure 2, but the effect is extremely small, increasing T_{eq} by only 13 K for the extreme case of a metal nanoparticle 1 nm in radius.

Our results are shown in figure 3 in terms of the enthalpy instead of temperature. As has already been discussed by focusing on the transition temperatures for these materials, the enthalpy changes associated with even very small nanoparticles are small.

To consider the physical source of the trends in α listed in table 2, we calculated the charge associated with the H atoms in each metal hydride we examined using a Bader charge decomposition [37]. The resulting charges are shown in figure 4. With the exception of LiH, there is a distinct correlation between α and the H atom Bader charge in the hydride, with the most (least) ionic materials being associated with positive (negative) values of α .

The results discussed above relied on surface energies calculated without accounting for zero point energies. Calculating the zero point energy contributions to surface energies is time consuming, so we have only examined the strength of these effects for three representative examples.



Figure 4. Plot of $\alpha/N^{2/3}$ as a function of the charge on the H atom in the bulk hydride as computed by Bader charge analysis, where α is the parameter that controls the nanoparticle thermodynamic effects and *N* is the number of metal atoms in the nanoparticle. The line is a linear fit to all systems except LiH/Li.

Table 3. Surface energies of $MgH_2(101)/Mg(0001)$, LiH(100)/Li(100), and VH₂(111)/V(110) films computed using DFT with and without zero point energy.

Materials	γ^{surf} (J m ⁻²)	$\gamma^{surf} + \gamma^{ZPE}$ (J m ⁻²)	Materials	γ^{surf} (J m ⁻²)	$\gamma^{\text{surf}} + \gamma^{\text{ZPE}}$ (J m ⁻²)
MgH ₂ (101)	0.62	0.79	Mg(0001)	0.52	0.57
LiH(100)	0.33	0.45	Li(100)	0.47	0.55
VH ₂ (111)	1.16	0.84	V(110)	2.48	2.65

In each case, we considered the equilibrium between a twodimensional slab of a metal hydride that exposes one surface facet to a two-dimensional slab of metal that also exposes a single surface facet. We estimated the zero point energy contribution to the surface energy of each surface using

$$\gamma + \gamma^{\text{ZPE}} = \frac{\left(E^{\text{slab}} - NE^{\text{bulk}}\right) + \left(E^{\text{slab},\text{ZPE}} - NE^{\text{bulk},\text{ZPE}}\right)}{A}.$$
(8)

The zero point energies on the right-hand side of equation (8) were calculated using harmonic normal mode frequencies calculated within DFT with finite displacements of each atom in an appropriate supercell. In principle, this treatment could be made more precise by computing the full vibrational density of states [27, 38] for the bulk material and a slab model of a surface, but we have not pursued calculations of this kind.

The zero point energy contributions to the surface energies of the six surfaces we have examined are listed in table 3. As should be expected, the zero point energy effects are larger in magnitude for the metal hydrides than for the metals. Similarly, the zero point energy for the Li surface is larger than for Mg or V. An interesting observation from these results is that values of γ^{ZP} with both negative and positive signs are found, the former for VH₂(111) and the latter for MgH₂(101) and LiH(100). Figure 5 shows the change in the transition temperatures as a function of the thickness of the



Figure 5. The variation in the metal/metal hydride transition temperatures for thin films relative to the result for bulk materials as determined with and without zero point energy.

metal film with and without zero point energy. Results are shown for $MgH_2(101)/Mg(0001)$ and $VH_2(111)/V(110)$. The ZPE terms increase the transition temperature for VH_2 and decrease the transition temperature for MgH_2 . As shown in figure 5, the transition temperatures of $MgH_2(101)/Mg(0001)$ and $VH_2(111)/V(110)$ are changed by about 30–40 K from the values before the consideration of the zero point energy when the film thickness is 1 nm.

The effect of surface energy on the transition temperature for equilibrium between the metal hydride and metal surfaces listed in table 3 is controlled by $\alpha = \frac{2}{n^{\text{H}}} \Delta (A^{\text{surf}} [\gamma^{\text{surf}} + \gamma^{\text{ZPE}}])$. The importance of the zero point energy effects can therefore be quantified by the dimensionless ratio $\alpha^{\text{ZPE}}/\alpha = \Delta (A^{\text{surf}}\gamma^{\text{ZPE}})/\Delta (A^{\text{surf}}\gamma^{\text{surf}})$. For MgH₂(101)/Mg(0001), LiH(100)/Li(100), and VH₂(111)/V(110) films, this ratio is 0.36, 0.01, and 0.34, respectively. These values indicate that it is reasonable to think of the zero point energy contributions as a correction to the results calculated without zero point energies. This observation supports the idea that our calculations for the full ECSs of the seven materials considered above that did not include zero point energies give useful estimates for the influence of nanoparticle size on reaction thermodynamics.

3. Discussion

Our results for MgH₂ nanoclusters provide a useful way to compare our methods to other approaches and to consider the strengths and limitations of our calculations. Possibly the most direct comparison we can make with experimental data is via the experiments of Li and Chen, who examined hydrogen evolution from MgH₂ nanowires of radii 20, 45, and 80 nm [11]. In these experiments, no noticeable difference in the temperatures associated with H₂ evolution was observed between the nanowires of different radii, although the thinner nanowires had better reaction kinetics. Our results are consistent with these observations; the data in figure 2 suggest that the transition temperature for MgH₂ varies only by a few degrees over the size range examined in these experiments. The calculations by Wagemans *et al* [19] and Cheung *et al* [21] for MgH₂ clusters containing up to 50 Mg atoms discussed in section 1 both predicted a reduction in the equilibrium temperature for H₂ evolution relative to bulk MgH₂, but found that this reduction was small once clusters containing ~ 100 Mg atoms were considered. These predictions are consistent in both sign and magnitude with our results.

The experimental results of Aguey-Zinsou *et al* [14], which exhibit H₂ evolution from Mg nanoparticles near room temperature, appear superficially to contradict our theoretical predictions. It is crucial to note, however, that the colloidal particles in these experiments are not Mg nanoparticles in isolation; instead, the metal cores of these particles are coated in tetrabutylammonium bromide and only $\sim 1/5$ of the total mass of the colloidal particles comes from Mg, limiting the hydrogen storage capacity of these particles to less than 1.5 wt%. Because the physical environment of the Mg and MgH₂ in these particles is so different from the isolated environment considered in our model and in other theoretical calculations [19, 21], it is not surprising that our calculations are unable to describe the outcome of these experiments.

There are a number of reasons why our calculations define only an approximate description of metal hydride nanoparticle thermodynamics. To discuss these issues, we first consider the case of nanoparticles that are isolated from a support or surrounding matrix material. Our description is based on the concept of an equilibrium crystal shape (ECS) as predicted for a pure material. It is important to note, however, that the presence of impurities during crystal growth can substantially alter crystal shapes relative to the ECS of the pure material. This phenomenon is frequently used to control particle morphology in crystal growth [39, 40]. These effects may be relevant to the crystal shape in particular experiments, but they are unlikely to change the overall conclusion of our calculations that the effect of nanosizing on the reaction thermodynamics in simple metal hydrides is relatively small because the magnitude of α in equation (5) is not especially sensitive to the precise surface areas of the surfaces making up each crystal. Our treatment of the ECS is also approximate because we neglected the contributions of edge and kink sites defined by the intersections between atomically flat surfaces on the crystal. Examples are known from studies of heterogeneous catalysis on metal nanoparticles where these sites dominate the catalytic properties of practical nanoparticles when the reactivity of these sites greatly exceeds that of sites on flat surfaces [41]. Because applications for nanoparticles in hydrogen storage require removing or adding hydrogen to all sites in a nanoparticle, not just those that might be most reactive, the influence of these undercoordinated sites will be minimal for moderate and large particles. For very small particles, however, where the fraction of all surfaces sites that are edge sites becomes appreciable, then including these sites in assessing the reaction thermodynamics may become important. To give a sense of the number of these edge sites, we consider the TiH_2 crystal shown in figure 1. For a hydride particle associated with a metal particle of radius 10 or 5 nm, approximately 4.5 or 9% of the surface atoms are

edge sites, respectively. If the radius of the metal nanoparticle is reduced to 2 nm, 22% of the surface sites on the ECS shown in figure 1 are edge sites. The Wulff construction is only valid if the internal crystal structure of the particle being considered is identical to that of the bulk material. For nanoparticles containing 20 or fewer atoms, many examples are known where the coordination of atoms in a nanoparticle is not related in a simple way to the material's bulk crystal structure [20]. For nanoparticles in the size range we have considered above, however, treating the crystal structure of the bulk and an isolated nanoparticle as being the same appears to be a reasonable approach.

In practical applications, metal or metal hydride nanoparticles cannot be isolated entities; instead, they must be in contact with an appropriate support material or matrix. This situation creates a number of complications that have not been included in our calculations or in previous 'bottomup' calculations of metal hydride nanoparticle properties. First, when nanoparticles are in contact with a support, even if that support is relatively inert, some of the surface energy contributions to the nanoparticle free energy must be replaced by interfacial energies. These energies can be calculated using DFT, but typically only for examples where the support is highly ordered and there is little strain between the material and the support [30] or, alternatively, for very small nanoparticles [42]. When particle/support interactions create significant strain within a nanoparticle, these effects can play an important role in the nanoparticle's properties [17, 18]. Finally, in hydrogen storage applications where long term cycling of a material between the hydrogenated and dehydrogenated states is envisioned, the possibility of chemical interactions between the nanoparticle and the support material cannot always be ignored. For example, reversible reactions involving LiBH₄ and graphitic carbon with favorable thermodynamics have been identified in theoretical calculations [6]. It is possible that reactions of this kind could play a role in the cycling of LiBH₄ when this material is contained in a nanoporous carbon. The role of chemical interactions of this kind can not be examined by considering isolated nanoparticles.

Acknowledgments

This work was supported by the DOE grant number DE-FC36-05G015066 and performed in conjunction with the DOE Metal Hydride Center of Excellence.

References

- [1] Züttel A 2004 Naturwissenschaften 91 157
- [2] Grochala W and Edwards P P 2004 Chem. Rev. 104 1283
- [3] Orimo S-i et al 2007 Chem. Rev. 107 4111
- [4] Alapati S V, Johnson J K and Sholl D S 2006 J. Phys. Chem. B 110 8769
- [5] Alapati S V, Johnson J K and Sholl D S 2007 Phys. Chem. Chem. Phys. 9 1438
- [6] Alapati S V, Johnson J K and Sholl D S 2008 J. Phys. Chem. C 112 5258
- [7] Akbarzadeh A, Ozolinš V and Wolverton C 2007 Adv. Mater. 19 3233
- [8] Wolverton C et al 2008 J. Phys.: Condens. Matter 20 064228
- [9] Fichtner M et al 2004 Mater. Sci. Eng. B 108 42
- [10] Imamura H et al 2005 J. Alloys Compounds 386 211
- [11] Li W, Li C and Chen H M J 2007 J. Am. Chem. Soc. **129** 6710
- [12] Vajo J J and Olson G L 2007 Scr. Mater. 56 829
- [13] Bérubé V et al 2007 Int. J. Energy Res. 31 637
- [14] Aguey-Zinsou K-F and Ares-Fernández J-R 2008 Chem. Mater.20 376
- [15] Ward T L and Dao T 1999 J. Membr. Sci. 153 211
- [16] Ling C and Sholl D S 2007 J. Membr. Sci. 303 162
- [17] Pundt A 2004 Adv. Eng. Mater. 6 11
- [18] Pundt A and Kirchheim R 2006 Annu. Rev. Mater. Res. 36 555
- [19] Wagemans R W P et al 2005 J. Am. Chem. Soc. 127 16675
- [20] Wang L-L and Johnson D D 2007 Phys. Rev. B 75 235405
- [21] Cheung S et al 2005 J. Phys. Chem. A 109 851
- [22] Wulff G 1901 Z. Krist. Mineral. 34 449
- [23] Shi H Q and Stampfl C 2008 Phys. Rev. B 77 094127
- [24] Soon A et al 2008 Phys. Rev. B 77 125423
- [25] Züttel A 2003 Mater. Today 6 24
- [26] Raybaud P et al 2000 J. Catal. 189 129
- [27] Alapati S V, Johnson J K and Sholl D S 2007 J. Phys. Chem. C 111 1584
- [28] Stampfl C 2005 Catal. Today 105 17
- [29] Rankin R B and Sholl D S 2006 J. Chem. Phys. 124 074703
- [30] Asthagiri A and Sholl D S 2002 J. Chem. Phys. 116 9914
- [31] Perdew J P et al 1992 Phys. Rev. B 46 6671
- [32] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
- [33] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758
- [34] Vanderbilt D 1990 Phys. Rev. B 41 7892
- [35] Wang D-D, Zhang J-M and Xu K-W 2006 Surf. Sci. 600 2990
- [36] Graetz J et al 2007 J. Alloys Compounds 446 271
- [37] Henkelman G, Arnaldsson A and Jonsson H 2006 Comput. Mater. Sci. 36 354
- [38] Ackland G J 2002 J. Phys.: Condens. Matter 14 2975
- [39] Chen D H et al 2008 Mater. Chem. Phys. 109 224
- [40] Poomachary S K, Chow P S and Tan R B H 2008 J. Cryst. Growth 310 3034
- [41] Honkala K et al 2005 Science 307 555
- [42] Wang L-L and Johnson D D 2007 J. Am. Chem. Soc. 129 3658