

IV.H.14 Computational Studies of Hydrogen Interactions with Storage Materials

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Objectives

Building on our accumulated knowledge of hydrogen interactions with semiconductors and insulators we have been conducting computational studies with the goal of developing new insights for hydrogen interactions with hydrogen storage materials. Using state-of-the-art density functional calculations, our research addresses the energetics and electronic structure of hydrogen atoms interacting with potential storage materials. In contrast to previous computational studies of bulk quantities, our investigations explicitly address the behavior and interactions of individual hydrogen atoms with the host material. Our **overall goal** is twofold: (1) to provide direct insight into the processes of hydrogen uptake and release, and help in developing guidelines for designing storage media with improved storage capacity; and (2) to generate new fundamental knowledge, for instance, about mechanisms that govern ionic transport, the shape of reaction curves, or reaction rates as a function of particle size.

Abstract

Our studies comprise two classes of materials: metal hydrides and complex hydrides. **Metal hydrides** can store large amounts of hydrogen, but due to the high atomic mass of the host element(s) the weight-percent efficiency is typically low. We are focusing on materials in which the atomic mass of the metal is low, such as MgH_2 and AlH_3 . Comprehensive studies of point defects and migration enable us to identify the dominant diffusion mechanisms. We are also performing Kinetic Monte Carlo simulations of the dehydrogenation process. For **complex hydrides**, a major result of our studies is that the point defects that are relevant for transport are all *charged*. Their formation energy (and hence the kinetics of diffusion and decomposition) thus depends on the electron chemical potential, which in turn

is affected by the presence of additives. This explains, for instance, the effect of transition metal impurities on the kinetics. Our recent work has focused on LiBH_4 , LiAlH_4 , and $\text{Li}_2\text{NH/LiNH}_2$. For the latter, we have been able to explain the particle-size dependence of the activation energy for decomposition.

Progress Report

We investigate the kinetics of hydrogen uptake and release in high-capacity hydrogen storage materials using first-principles calculations based on density functional theory. Our approach takes into account that defects and impurities in non-metallic systems can occur in charge states other than the neutral state; this important aspect of the problem had not been addressed in previous computational studies performed by other groups. Our investigations showed that this has extremely important consequences for defect concentration and diffusion, and other groups have now started to apply this methodology as well.

We are constantly expanding our methodology. To more accurately model the electronic structure of materials with a band gap, we have employed the screened hybrid functional of Heyd, Scuseria, and Ernzerhof [1], an approach we successfully applied to AlH_3 [2]. We have also implemented a multiscale approach that combines *ab initio* calculations with Kinetic Monte Carlo simulations, enabling us to model the complete dehydrogenation reaction. Both of these developments go beyond the current state-of-the-art methodology.

1. Dehydrogenation of AlH_3 via Vacancy Clustering Mechanism

Aluminum hydride (AlH_3) has emerged as a prime candidate for hydrogen storage applications [3,4]. We have performed density functional calculations as well as Kinetic Monte Carlo simulations in order to develop a systematic understanding of the hydrogen uptake and release in this material. Though thermodynamically unstable at room temperature, AlH_3 does not decompose and remains stable on a timescale of years [5]. Above 150°C , however, it rapidly decomposes into Al and H_2 [3,6]. The origin of the kinetic barriers responsible for the metastability of AlH_3 has been widely debated [7-9].

We have first used density functional theory calculations to investigate the role played by point defects in the dehydrogenation of AlH_3 . We used a hybrid functional [1], which provides an accurate description of the electronic

structure. Positively charged hydrogen vacancies (V_{H}^+) turn out to play the dominant role in the dehydrogenation of the hydride. We also found that the hydrogen vacancy defects have a strong tendency towards clustering, with binding energies of 0.5 to 1.6 eV. Vacancy clusters of sizes ranging from 2 to 12 were analyzed. The clusters establish the nuclei of a local Al phase which forms inside the hydride during dehydrogenation.

We subsequently performed Kinetic Monte Carlo simulations to model the overall dehydrogenation process, using parameters obtained from first principles. Our results allow us to identify the contributions of the various microscopic mechanisms that govern the dehydrogenation reaction. The overall activation energy for the dehydrogenation process, $E_a = 1.62$ eV, is dominated by the activation energy for self-diffusion of the positively charged hydrogen vacancies, 1.21 eV; this accounts for mass transport and growth of the Al phase cores which drive the AlH_3/Al phase transformation. A second, smaller contribution to the activation energy is related to the nucleation of the Al phase cores. These results clearly indicate that the reaction is diffusion limited, and produce reaction curves that agree well with the experimental observations.

Our research has also produced insights that go well beyond the specific case of dehydrogenation of AlH_3 . Systematic and general classifications of solid-state reactions were presented by Avrami [10] and later by Sharp *et al.* [11], who derived nine different equations for the reaction kinetics, i.e., the fraction of decomposed material as a function of time. Sharp *et al.* classified these as either diffusion controlled (identified by a “square-root-like” onset of the reaction curve) or phase-boundary controlled (“S-shape-like” onset). These classifications have subsequently been widely used in the literature. In the case of dehydrogenation of AlH_3 , an S-shape-like onset is observed, and on this basis it was previously reported that the kinetics must be phase-boundary controlled and that diffusion can be ruled out as a rate-limiting factor (e.g., [12]). Our study, however, clearly demonstrates that the self-diffusion of point defects is the rate-limiting step—and still the reaction curves have an S-shape! This example illustrates that the classification proposed by Sharp *et al.* [11] is too restrictive and can be misleading when used to infer conclusions about microscopic mechanisms.

The Kinetic Monte Carlo simulations and results about shapes of reaction curves have been submitted to the *Journal of Chemical Physics*.

2. Particle-Size Dependence of the Activation Energy for Decomposition of Lithium Amide

Lithium amide (LiNH_2) is a promising material for reversible hydrogen storage [13], yet atomistic mechanisms behind the dehydrogenation process are unknown. The

activation energy for LiNH_2 decomposition has been observed to strongly vary with ball milling [14–16], suggesting a dependence of the thermodynamics and kinetics of the decomposition on the particle size. We have examined these mechanisms based on first-principles calculations for native point defects and defect complexes in LiNH_2 .

Our results show that the decomposition of LiNH_2 into lithium imide (Li_2NH) and ammonia (NH_3) occurs through two competing mechanisms, one involving the formation of native defects in the interior of the material and the other at the surface. As a result, the prevailing mechanism and hence the activation energy depend on the surface-to-volume ratio, or the specific surface area, which changes with the particle size. These insights allow us to explain the observed variations of activation energy.

The results were published in *Angewandte Chemie* and in *Physical Review B*.

Once again this study has implications that go beyond the case of the specific material studied (LiNH_2), but sheds light on kinetics of reactions in bulk *versus* nanoscale systems in general, i.e., not just in hydrogen storage materials. A dependence on particle size has often been observed but a rigorous explanation has been lacking. Our model attributes the differences to the formation of native defects (which are always necessary for diffusion and reactions) in the *bulk* as opposed to on the *surface*. This leads to specific, verifiable differences in activation energies.

3. Decomposition Mechanisms of LiBH_4 and LiAlH_4

Lithium borohydride (LiBH_4) has a high hydrogen density (18.4 wt%) [17] but its high decomposition temperature and slow hydrogen desorption kinetics prevent practical use [18]. Incorporation of certain metal additives has been reported to lower the decomposition temperature and enhance the kinetics [17,19,20], but the mechanisms are poorly understood. Our first-principles calculations show that Li vacancies and interstitials have low formation energies and are highly mobile. These defects can participate in Li-ion conduction, and act as accompanying defects in H and B mass transport. We propose a specific mechanism for the decomposition: LiBH_4 releases borane (BH_3) at the surface or interface, leaving negatively charged H interstitials in the material, which then act as nucleation sites for LiH formation. The diffusion of H interstitials in the bulk is the rate-limiting step in the decomposition kinetics. Li vacancies and interstitials have low formation energies and are highly mobile, and are responsible for maintaining local charge neutrality as other charged defects migrate along the material, as well as assisting in the formation of LiH. Based on this mechanism, the effects of metal additives on hydrogen desorption kinetics can also be explained. This research has been published in the *International Journal of Hydrogen Energy*.

Lithium alanate (LiAlH_4) has a relatively low decomposition temperature [21]. We find that the compound is prone to Frenkel disorder on the Li sublattice: lithium interstitials and vacancies have low formation energies and are highly mobile. They can participate in lithium-ion conduction, and act as accompanying defects in hydrogen mass transport. We have proposed a specific mechanism for the decomposition of LiAlH_4 that involves the formation and migration of negatively charged hydrogen interstitials, Li Frenkel pairs, and AlH_4 vacancies, with the latter constituting the rate-limiting step. Our results also suggest that it is the structure of the negatively charged hydrogen interstitial that determines the hydride phase (Li_3AlH_6 or LiH) in the decomposition products, a relationship that should be further explored in other complex hydrides.

Future Directions

a) Role of hydrogen-related Frenkel pairs for the dehydrogenation kinetics

The aim is to compile the results that we have already obtained for Frenkel pairs in a variety of systems, and carry out calculations for additional materials. The materials include NaAlH_4 , LiBH_4 , $\text{Li}_4\text{BN}_3\text{H}_{10}$, LiNH_2 , Li_2NH , MgH_2 , Mg_2Fe -hydride, Mg_2Ni -hydride, Na_3AlH_6 , LiAlH_4 , and Li_3AlH_6 . The hypothesis is that Frenkel-pair formation may be the rate-limiting step to dehydrogenation and/or mass transport in some cases, while in other cases Frenkel pairs play the role of enabling local charge neutrality. Systematic studies will elucidate the physics.

b) Role of transition metal doping in MgH_2

We are investigating two prominent and effective transition-metal additives, Ni and Fe. The effects on formation energies and migration barriers of point defects will be studied.

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Publications acknowledging the grant (since August 2010)

1. “Point-defect-mediated dehydrogenation of AlH_3 ”, L. Ismer, A. Janotti, and C.G. Van de Walle, *Appl. Phys. Lett.* **97**, 201902 (2010).
2. “Stability and mobility of native point defects in AlH_3 ”, L. Ismer, A. Janotti, and C.G. Van de Walle, *J. Alloys Compd.* **509S**, S658 (2011).
3. “The particle-size dependence of the activation energy for decomposition of lithium amide”, K. Hoang, A. Janotti, and C.G. Van de Walle, *Angew. Chem. Int. Ed.* **123**, 10352 (2011).
4. “Mechanisms for the decomposition and dehydrogenation of Li amide/imide”, K. Hoang, A. Janotti, and C.G. Van de Walle, *Phys. Rev. B* **85**, 064115 (2012).
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6. “Decomposition mechanism and the effects of metal additives on the kinetics of lithium alanate”, K. Hoang, A. Janotti, and C.G. Van de Walle, *Phys. Chem. Chem. Phys.* **14**, 2840 (2012).
7. “Dehydrogenation of AlH_3 via vacancy clustering mechanism”, L. Ismer, A. Janotti, and C.G. Van de Walle, submitted to *J. Phys. Chem.*