IV.H.13 Theory of Hydrogen Storage in Complex Hydrides

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Objectives

Using first-principles methods, determine the atomic-level processes that are rate limiting in hydrogen storage reactions involving complex hydrides. The energetics of point defects are calculated in order to find those that form in the largest concentrations and the mobility of these defects is obtained from stochastic Kinetic Monte Carlo methods. The activation energy from these calculations is used to determine whether mass transport may be rate-limiting in various storage reactions, both during dehydrogenation and rehydrogenation. Methods are also being developed to study nucleation and to determine its role in the kinetics of hydrogen storage reactions.

Technical Barriers

The slow kinetics observed during absorption and desorption of hydrogen in complex hydrides limits their applicability in real system. However, it is not clear in many cases what the rate-limiting processes are in these reactions. Identification of these rate-limiting processes will aid the improvement of reaction rates and the design of new catalysts.

Abstract

Complex metal hydrides are attractive as potential storage media due to the large volumetric and gravimetric hydrogen densities. However, the absorption and desorption of hydrogen is generally too slow for practical applications under the conditions that exist in systems using proton exchange membrane fuel cells. It is therefore important that an understanding of the kinetic processes in these reactions be developed in order to guide further improvement of reaction rates. Experimental evidence has shown that mass transport may be rate limiting in some hydrogen storage reactions. In particular, metal-containing point defects have been identified as a potential mechanism for this transport in the sodium alanate system [1,2]. Methods have been developed to study the role of point defects during mass transport at the atomic level using properties obtained from ab-initio density functional theory (DFT) calculations. In this model, chemical potential gradients that are developed in a system that is out of equilibrium (that is, at temperatures other than the equilibrium temperature for the reaction) drive diffusion of defects between regions of different phases. These differences in chemical potentials are manifested as concentration gradients of defects, which are obtained after calculating the associated formation energies. Where necessary, the mobility of these defects is studied using Kinetic Monte Carlo simulations that are parameterized using DFT calculations. Together, these provide the necessary parameters to find the flux of defects through the phases involved in a particular reaction. The activation energy of this flux is compared to experimentally determined activation energy for the reaction in order to determine if mass transport may be rate limiting. In systems for which there is no experimentally measured activation energy, the calculated value can be used to screen for those reactions that may be kinetically limited, assuming that bulk diffusion is a requisite for the reaction.

Progress Report

We have developed a model that describes mass transport via the diffusion of point defects during hydrogen storage reactions using properties from first-principles calculations. In this model, chemical potentials are set by local equilibrium conditions. At temperatures other than the equilibrium temperature for the reaction, this leads to gradients in the chemical potentials between interfaces of different phases, which drives mass transport. Using DFT, we calculate the formation energies of native point defects in all of the phases involved in a reaction and use Kinetic Monte Carlo simulations to determine their diffusivities. From this we calculate the flux of defects as $J = -D\nabla C$, where D is the diffusivity and ∇C is the concentration gradient between interfaces. Comparing then to the Arrhenius equation, the activation energy is equal to

$$E_{act} = -k_B \frac{\partial \ln J}{\partial \left(1/T \right)}$$

We have applied this model to the storage reactions involving NaAlH$_4$, Li$_3$AlH$_6$ and B$_{20}$H$_{16}$.

The first step in the dehydrogenation of sodium alanate follows

$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_1$$
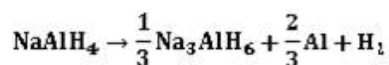
where there is experimental evidence that mass transport may be rate limiting when doped with small amounts of Ti [1,2]. We have calculated the formation energies of native defects in all three solid phases. From this, we identify neutral AlH$_3$ vacancies, negatively charged Na vacancies, and positively charged AlH$_4$ vacancies as the metal-containing defects that form in the largest concentrations in NaAlH$_4$. In Na$_3$AlH$_6$, the metal defect with the largest concentration is negatively charged Na vacancies, which are balanced by positively charged H vacancies. We have calculated the diffusivities of these defects and the resulting fluxes are shown as a function of temperature in Figure 1. Of these defects, the one with the largest flux is the Na vacancy in Na$_3$AlH$_6$ (a product phase of the reaction), which we identify as the defect that facilitates

mass transport during this reaction. The calculated activation energy for the formation and migration of this defect is 70 kJ/mol, near to the experimentally obtained activation energy for the reaction of 80 kJ/mol in Ti-doped systems [3]. From this we conclude that mass transport is the rate-limiting step in the dehydrogenation of Ti-doped sodium alanate.

The second step in the dehydrogenation of lithium alanate is

$$Li_3AlH_6 \rightarrow 3LiH + Al + \frac{3}{2}H_1$$
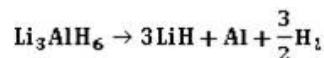
where the measured activation energy is 100 kJ/mol [4]. In this system, the relevant mass flux is through the initial phase, Li$_3$AlH$_6$. Four defects have been found to have large concentration gradients in this system: positively charged H vacancies and Li interstitials, negative Li vacancies, and neutral LiH vacancies. Of these, the two Li defects have the largest gradients and are therefore expected to dominate mass transport. The calculated formation enthalpy for both of these defects is equal to 86 kJ/mol. With the addition of the diffusion barrier (the calculation of which is ongoing),
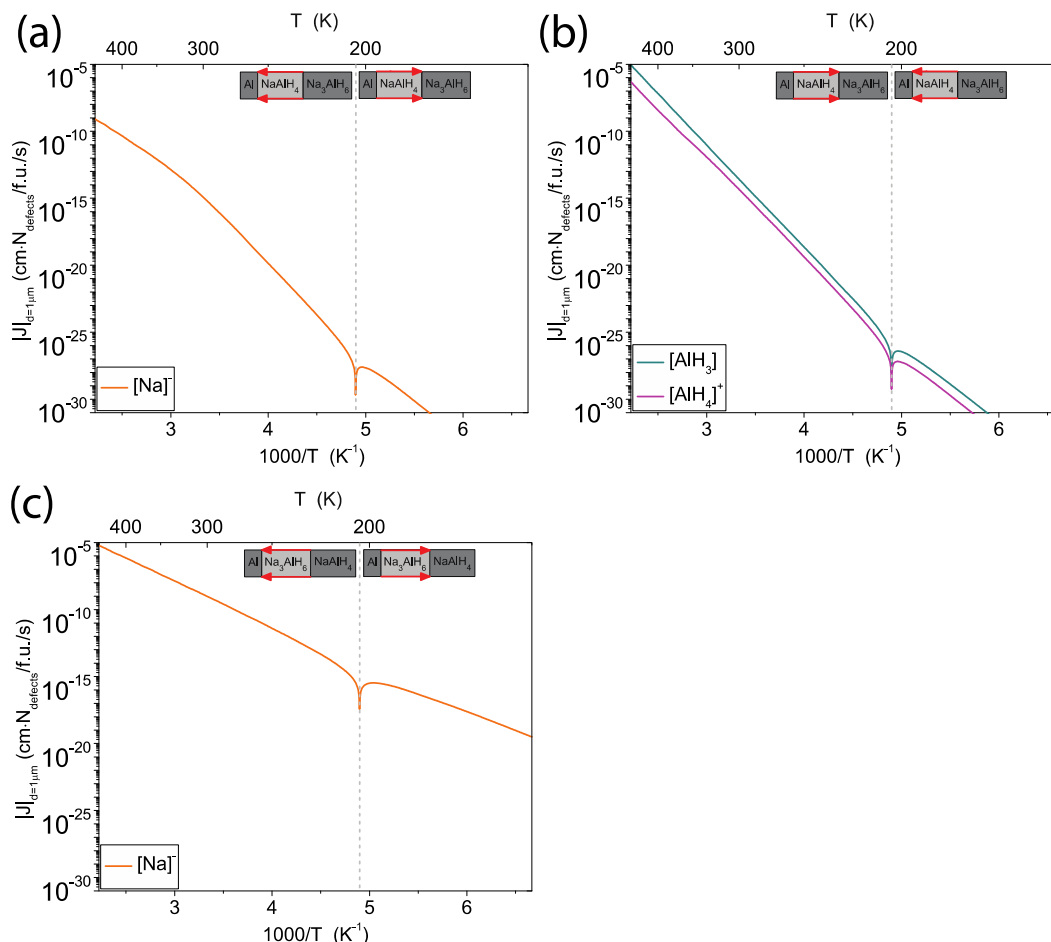

FIGURE 1. Calculated flux of defects in NaAlH$_4$ (a, b) and Na$_3$AlH$_6$ (c).

the activation energy for this flux will likely be near to the measured activation energy for the reaction. It is therefore likely that mass transport is also rate limiting in this reaction.

Finally, we have calculated the formation energies of native defects in the dehydrogenation of $B_{20}H_{16}$ into pure boron and hydrogen gas. We find that the formation energy of atomic hydrogen in boron is much larger than the defect formation energies in $B_{20}H_{16}$ so that diffusion through this phase does not facilitate mass transport. Of the defects in $B_{20}H_{16}$, the lowest formation energy is of interstitial H_2 in a neutral charge state and all other defects are predicted to occur in negligible concentrations compared to it. The formation enthalpy for this defect is equal to 51 kJ/mol under dehydrogenation conditions. Even with the addition of the diffusion barrier, this likely represents a relatively low activation energy. Therefore, if mass transport is rate limiting in this reaction, it should proceed relatively rapidly compared to other storage reactions. However, it is still possible that some other process besides bulk diffusion is limiting the reaction.

Future Work

Having examined mass transport in a number of reactions, we will begin to study nucleation as another possible kinetically limiting process. There is experimental evidence that nucleation may be rate limiting in the MgH_2 + $2LiNH_2$ system where seeding with the product phase, $Li_2Mg(NH)_2$, has been shown to lower the activation energy [5]. We are in the process of developing a stochastic model to study such systems. In particular, a seed of the product phase in modeled in the host and a search is performed for the ground-state configuration. We plan to use classical potentials to model the energetics that are fit to each system individually using properties from first-principles calculations. The goal is to search for additional reactions that may be kinetically limited by nucleation.

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