IV.A.8 Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis using Ordered Polymer Templates

Technical Targets

The objective of this project is to achieve tunable thermodynamics and/or kinetics by confining metal hydrides within the chemically and geometrically well-defined pores of templates such as metal-organic frameworks (MOFs) and porous carbons, thus allowing faster \( \text{H}_2 \) desorption at a lower temperature than bulk. The project addresses the following DOE technical target (Table 1), as outlined in the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DOE 2010 Target</th>
<th>Project Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Delivery Temperature</td>
<td>85°C</td>
<td>Tunable kinetics demonstrated for nano-confined NaAlH(_4) and LiBH(_4). Size-dependent desorption enthalpy observed for NaAlH(_4).</td>
</tr>
</tbody>
</table>

FY 2011 Accomplishments

- Demonstrated size-dependent thermodynamics for LiBH\(_4\) infiltrated into porous carbon templates: the bulk orthorhombic-to-hexagonal phase change is not observed, no melting transition occurs, and the material is amorphous.
- Showed that nano-confined NaAlH\(_4\) thermodynamics are tunable: reaction to form the stable intermediate Na\(_3\)AlH\(_6\) is not observed. The enthalpy of \( \text{H}_2 \) desorption for the one-step decomposition to form NaH, Al, and H\(_2\) is size dependent, consistent with theoretical results.
- Nano-confined NaAlH\(_4\) decomposes more than an order of magnitude faster than bulk hydride.
- Predicted that (MgAlH\(_3\))\(_n\) clusters are destabilized relative to MgH\(_2\) and that compositional tuning of \( \Delta H^o \) is feasible.

Introduction

Some of the most attractive hydrogen storage materials, such as MgH\(_2\), AlH\(_3\), and LiBH\(_4\), have unfavorable desorption thermodynamics and are either too stable (e.g. MgH\(_2\) and LiBH\(_4\)) or too unstable (e.g. AlH\(_3\)) in bulk form to be of use for vehicular transport applications. However, recent theoretical and experimental results indicate that decreasing particle size can substantially reduce the stability of metal hydrides, leading to lower desorption temperatures. The key challenges that must be addressed
are to: 1) develop synthetic routes that provide controlled size and composition; 2) stabilize particles over time; and 3) develop computational tools to guide synthesis that can accurately address particle sizes spanning the micro-to-meso length scales. This project addresses all three challenges and, if successful, will create for the first time nanoscale hydrogen storage materials with tailorable composition and size compatible with fuel-cell materials over a wide range of operating temperatures.

**Approach**

We are using highly ordered, chemically tailorable nanoporous templates to create particles ranging in size from <1 nm to 20 nm, the critical size range at which nanoscale effects are anticipated. These templates are infiltrated with hydride precursors or hydrides themselves, using mild synthetic routes that eliminate template degradation. The resulting template-satabilized nanoparticles are characterized to determine particle size, composition, and desorption thermodynamics and kinetics. Validated computational modeling tools guide synthesis. This approach allows nanoparticle dimensions and hydride composition to be systematically varied, enabling the effects of nanoscale dimensions on hydride thermodynamics to be determined.

**Results**

**Tunable Thermodynamics and Kinetics for Nano-Confined NaAlH₄**

NaAlH₄ is perhaps the most thoroughly characterized hydride in terms of its thermodynamics and kinetics of H₂ desorption. As such, it is an excellent test case for determining the influence of size and confinement environment on hydride thermodynamics and kinetics. This year, we performed detailed measurements to determine both ΔH° and E_a using an infiltrated MOF with 1.3-nm pores and a melt-infiltrated porous carbon with uniform 4-nm diameter pores. The results show that both thermodynamics and kinetics are modified and suggest that these properties can be tuned by adjusting pore size.

Our experiments show that confining NaAlH₄ to ≤4 nm pores has several effects on the reaction. The H₂ desorption data for particles in the 1.3-nm MOF template (Figure 1) display evidence of at least two distinct reaction zones: a thermodynamic vapor-solid equilibrium at low reaction extent (<110°C) and a kinetically limited regime at temperatures up to 170°C. We characterized the reactant-product mixture obtained from vapor-solid equilibrium regime, using the 1.3-nm templated hydride, and see no evidence of Na₃AlH₆. This shows that under these conditions the reaction proceeds by a one-step process, which is different from the bulk behavior.

We also measured the temperature dependence of the H₂ vapor pressure to determine the heat of desorption (ΔH°).

The pressure-composition isotherms of NaAlH₄ confined in 4-nm nanoporous carbon (Figure 2) are not completely flat and exhibit only one plateau, whereas bulk Ti-catalyzed NaAlH₄ exhibits two flat plateaus corresponding to a two-step mechanism that forms first Na₃AlH₆ followed by NaH formation. Hydride confined to 4-nm pores has a lower ΔH° than bulk (Table 2), while hydride confined to the 1.3-nm pores of the MOF actually has a higher ΔH°. The increased ΔH° for small particles agrees with the results of both our nano-prototype electrostatic ground state/density functional theory (DFT) calculations and with a report in the literature for NaAlH₄ within a porous (0.5–4 nm) carbon template [1]. This is the first quantitative evidence that hydrogen desorption thermodynamics can be tuned by controlling particle size. However, our results below concerning LiBH₄ show that this behavior is very specific to the particular hydride.
The behavior of the 1.3-nm NaAlH₄ (Figure 1) nanoparticles in the kinetic regime is consistent with a one-dimensional diffusion model. The measured activation energy (Table 2) is considerably smaller than the uncatalyzed bulk value and somewhat smaller than the value previously reported for 2–10 nm NaAlH₄ particles on carbon nanofiber [2]. This trend indicates that size has a stronger effect on the desorption kinetics than the chemical environment of the template. The activation energies obtained using the MOF template and the carbon nanofibers are rather similar, although the chemical environments are different; in fact, it is not clear that NaAlH₄ is actually “confined,” but rather is “supported” on the surface of the carbon nanofibers, differentiating this template even further from the enclosed pores of the MOF.

Controlling the Decomposition Pathway of LiBH₄ via Confinement in Highly Ordered Nanoporous Carbon

We find that nanoporous LiBH₄ melt-infiltrating into 4-nm nanoporous carbon (NPC; 4-nm hexagonally packed cylindrical pores) is kinetically destabilized relative to bulk, but the thermodynamics are unchanged relative to bulk. The PCT for LiBH₄@NPC were measured at three different temperatures (Figure 3). The PCT has a clearly identified plateau region, from which we obtain ΔH° and entropy ΔS° of 70 kJ mol⁻¹ H₂ and 104 J K⁻¹ mol⁻¹ H₂⁻¹, respectively. This strongly suggests that in contrast to NaAlH₄ confinement, or particle size alone, has no effect on the thermodynamics of LiBH₄ decomposition. This result may be somewhat surprising in light of the many theoretical studies on nanoscale materials such as MgH₂ and other simple saline hydrides. It suggests, therefore, that decomposition of this hydride is thermodynamically limited by the strength of the B-H bonds in the BH₄⁻ anion, which Fourier transform infrared data (not shown) indicate are similar to those of the bulk.

The benefits of incorporating LiBH₄ into ordered 4-nm pore frameworks are twofold. First, the desorption behavior up to six cycles is clearly reversible [3]. Second, the release of diborane per gram of infiltrated LiBH₄ can be dramatically reduced compared with both bulk hydride and hydride confined in 15 nm or 9 nm NPC. These observations clearly show that confining hydrides within a nanoporous material can change a material that is unusable in bulk form to one that could have practical utility in some applications. Importantly, the differences between the behavior of NaAlH₄ described above and LiBH₄ in these hard-carbon frameworks indicate that the interactions with the framework are hydride dependent, suggesting that a proper choice of hydride and framework chemistry can lead to a storage material having the desired properties.

### Computational Modeling of Hydride Nanoparticles

The narrow range that ΔH° can assume for a successful vehicular hydrogen storage material (20–50 kJ mol⁻¹) lies roughly between two physical bounds: chemical bonds that are usually too strong, and hydrogen bonds that are usually too weak. One strategy for modulating ΔH° is to use compositional tuning in conjunction with nanoscale confinement. Our prior work demonstrated that MgH₂ nanoclusters are destabilized, but only at extremely small sizes (<5 formula units). Here, we describe high-accuracy fixed-node diffusion quantum Monte Carlo (DMC) calculations to evaluate the change in energy for the removal of H₂ from mixed Mg-Al clusters, which we hypothesized would have stability intermediate between MgH₂ and AlH₃. Our results show that this is indeed the case and show that ΔH° values between 20–50 kJ mol⁻¹ can be obtained.

The DMC calculations confirm our hypothesis. First, they indicate that mixed Mg-Al nanoclusters are stable, i.e., ΔE is greater than zero (Figure 4). Second, the desorption

#### TABLE 2. Comparison of Measured ΔH° and E°

<table>
<thead>
<tr>
<th>Reaction</th>
<th>1.3 nm</th>
<th>4 nm</th>
<th>Bulk</th>
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<tbody>
<tr>
<td></td>
<td>ΔH°</td>
<td>E°</td>
<td>ΔH°</td>
</tr>
<tr>
<td>NaAlH₄ → NaH + 0.33Al + 1.5H₂</td>
<td>47</td>
<td>47–53</td>
<td>35±10</td>
</tr>
<tr>
<td>NaAlH₄ → 0.33NaAlH₄ + 0.67Al + 1.0H₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Cu-BTC (MOF) template, solution infiltrated; Porous carbon, melt-infiltrated; Uncatalyzed; N/A – not applicable.
energy of these clusters is intermediate between the pure materials. For example, the MgAl/MgAlH$_2$ stoichiometry in addition to the MgAl/MgAlH$_2$ stoichiometry, as is evident in Figure 4. This can be understood from the fact that the hydrides are ionic and the pure metallic clusters have metallic bonding. As a result, there are no bond networks to create nonlinear effects as a function of size. There are only magic numbers in the binding energy of the metals for small sizes, but this effect diminishes with increasing size and does not change the overall trend.

The size range at which $\Delta E$ is predicted to reach a value between 20 kJ mol$^{-1}$ and 50 kJ mol$^{-1}$ range is given in Table 3. From the DMC results, the estimated size range for the MgAl alloy is from ~74 metal atoms up to the bulk, whereas Al alone has only a very small range between 10 and 40 atoms. This confirms that alloying can significantly alter the size range in which nanoparticles have the desired desorption energies. However, the effects of errors in DFT predictions are very evident here. The estimated size ranges are dramatically different for the various functionals. It is thus clear that the accuracy of the method used to obtain $\Delta E$ is critical.

**TABLE 3.** Estimated Size Range with $\Delta E$ in the Range 20-50 kJ mol$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>DMC</th>
<th>B3LYP</th>
<th>LDA</th>
<th>M06</th>
<th>PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl</td>
<td>74 – $\infty$</td>
<td>Never</td>
<td>44 – $\infty$</td>
<td>Never</td>
<td>16 – $\infty$</td>
</tr>
<tr>
<td>Al</td>
<td>10 – 40</td>
<td>17 – 2,000</td>
<td>13 – 100</td>
<td>15 – 80</td>
<td>7 – 20</td>
</tr>
</tbody>
</table>

**Conclusions and Future Directions**

- Our results show that 1–4 nm NaAlH$_4$ nanoclusters undergo single-step decomposition with fast kinetics, effectively increasing the storage capacity by 50% under fuel cell conditions.
- We predict that MgH$_2$ H$_2$ desorption thermodynamics can be shifted to a more favorable thermodynamic regime by creating Mg-Al-H nanoclusters.
- During the remainder of the project, we will develop a synthetic method to make mixed Mg-Al-H nanoclusters, and will complete H$_2$ desorption measurements for NaAlH$_4$, MgH$_2$, LiBH$_4$, LiNH$_2$, and Ca(BH$_4$)$_2$ in MOFs and nanoporous carbons.

**FY 2011 Publications/Presentations**


**References**