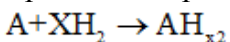


Strontium Alanate and Barium Alanate as Effective Hydriding Alloys for Hydrogen Storage

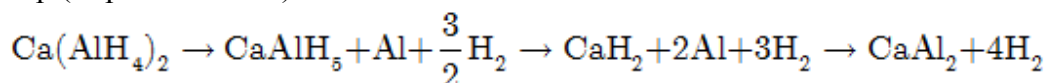
Hydrogen fuel cell vehicles have the potential to be extremely efficient, zero-emission vehicles and may serve to be a central component in the battle against global warming.¹ However, one major issue of the viability of hydrogen fuel cell vehicles is the logistics of hydrogen storage on board the car. The alternative to storing hydrogen in its gaseous form, a dangerous and inefficient process, is to find a solid state alloy that absorbs hydrogen at low temperatures and desorbs it at high temperatures.² This summer I will be working with the Wolverton Group at Northwestern University to search for effective candidate materials for this process. I will do this by using the VASP program, which utilizes a first-principles computational approach with density functional theory, to calculate the electronic-structure total energy of the candidate materials strontium alanate ($\text{Sr}(\text{AlH}_4)_2$) and barium alanate ($\text{Ba}(\text{AlH}_4)_2$). Computational materials science has been shown to be effective in predicting the performance of materials before they are synthesized in laboratories,³ and the prediction of likely candidates will save time, energy, and resources in synthetic laboratories by focusing search efforts early on.

A solid state hydriding alloy [A] will undergo the reaction **1** at low temperatures and proceed in the reverse direction at high temperatures. When absorbed, the metal atoms will form strong covalent bonds with the hydrogen atoms, and the release process requires heating the metal hydride to decompose and release the H_2 gas. In order for a metal to be commercially viable, A should be lightweight and have high hydrogen storage density. However, it is also extremely important for this temperature window to be near ambient vehicle operation temperatures. Initial studies, for example, found lithium borohydride (LiBH_4) and sodium alanate ($\text{Na}(\text{AlH}_4)$) to be possible candidates based on their hydriding abilities, but were also found to desorb hydrogen outside the range of practical vehicle temperatures, and they were also found to only store up to 2.5 wt% hydrogen, as opposed to the minimum target ratio of at least 6.5 wt%,⁴ and so were found to be ineffective. To test different materials, scientists have replaced sodium with many other cations, such as lithium, calcium and magnesium. One benefit of +2 cations (e.g. calcium) is that they synthesize to form $(\text{X}^{2+}(\text{AlH}_4)_2)^-$, which provides higher H_2 density. Magnesium alanate, unfortunately, was found to desorb hydrogen and rehydride poorly with respect to the operation parameters.⁵



Reaction 1: The general reaction for a hydriding metal alloy.

A study conducted by Wolverton and Ozolins⁶ on the use of calcium alanate ($\text{Ca}(\text{AlH}_4)_2$) as a hydrogen storage material found the reaction undergone by calcium to decompose in a weak endothermic step, a weak exothermic step, and then a strong endothermic step (as per reaction **2**).

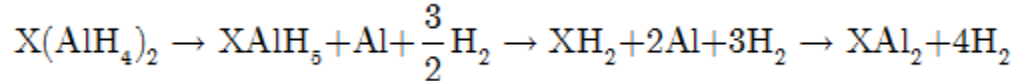


Reaction 2: The decomposition process for calcium alanate to release hydrogen gas.

Although the material weight and hydrogen storage density was very good, it was found that the binding of the calcium to the hydrogen was not strong enough for practical use. It is known that larger elements in the periodic table have stronger binding properties.⁷ In this case, it makes sense to look towards the heavier elements in the same group as calcium, such as

strontium and barium, as alanate alloys, to use in place of calcium. Although these metals are significantly heavier and thus have lower hydrogen densities, this may be a necessary compromise for the required hydriding enthalpies. Sr_2AlH_7 has already been studied as a material for hydrogen storage⁸, but strontium alanate ($\text{Sr}(\text{AlH}_4)_2$) and Barium Alanate ($\text{Ba}(\text{AlH}_4)_2$) would have much higher hydrogen density than Sr_2AlH_7 , and is thus the focus of my study.

In order to determine the competitiveness of strontium and barium alanate as a means of hydrogen storage, I will be calculating their reaction enthalpies by finding the enthalpy of the crystal structures of each component of their reactions. Because barium and strontium have similar electronic properties to calcium, I will base the new alanates' reactions on calcium's (2), resulting in analogs of reaction 3.



Reaction 3: Replace the Ca from 2 with X, where X may be Sr. or Ba.

My first step will be to find the ground state crystal structure of each of the components in the reaction based upon chemical intuition, which is derived from knowledge of the crystallography of structures with similar stoichiometries (AB_2C_8). I will use data for low-energy crystal structures from the International Crystal Structures Database as candidates for each reaction step. From the database, I must consider several hundred competitive crystal structures for these two reactions. This part of the study may take several weeks and will take up a majority of the time and effort of the project.

Using the VASP program, I will then perform frozen-phonon calculations ($T = 0\text{K}$) on individual crystal structures in order to find the lowest energy crystal structure for the alloy, and thus the ground state enthalpy of that component. This will be done by computer and should take no more than a week. I will then have a ΔH for every step in the decomposition process, and using this information, I will calculate the reaction enthalpy using Hess' Law. Once I know the crystal structures, I will study their high temperature thermodynamic properties, a more computationally expensive procedure, to verify the accuracy of the frozen phonon calculations. I will then find the vibrational properties of the alloys to determine their stabilities. The analysis should take several more weeks. Understanding all of these properties will allow me to create conclusions on the effectiveness of strontium and barium alanate as alloys to be used in hydrogen storage.

Since spring quarter, I have collaborated with the Wolverton Group and familiarized myself with the VASP interface and have already completed some simple calculations of the enthalpies of different crystal structures. I have also taken Introduction to Materials Science and Engineering (MSE 301), Thermodynamics for Materials Scientists (MSE 314), and Phase Transformations and Diffusion (MSE 315), courses that will be central to understanding the thermodynamics of the reactions. I have also been self-studying quantum mechanics and solid state physics in order to better understand the VASP calculations. All of this preparation will form the fundamental knowledge basis for the project. Professor Chris Wolverton will provide a 144-CPU linux cluster that will form the computational resources, free of charge. Following the project, I will submit a summary of my findings, which will be published in a solid state physics journal. I hope to continue as a scientist in computational and theoretical materials science by later attending graduate programs after Northwestern, and eventually continue into academia as a professor of Materials Science and Engineering. This research experience will prove invaluable to the actualization of my goals.