

THE ROLE OF CARBON IN THE HYDROGEN STORAGE KINETICS OF LITHIUM METAL HYDRIDES

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Abstract

A feasible solution to the problem of urban pollution is hydrogen propelled zero-emission vehicles. The US Department of Energy (DoE) has set the target of 6.5 wt% of H₂ storage capacity and a volumetric energy density of 1.5 kWh/L at an operating temperature and pressure conditions of 50°C and 2.5 bar respectively by 2010.[1] The storage media being studied until now have not been able to successfully achieve these targets and therefore, a compact, light weight hydrogen-storage system for transportation is not available currently. Hydrogen storage is therefore the key enabling technology that should be significantly advanced in terms of performance and cost effectiveness if hydrogen is to become an important part of the world's energy economy.

In the present work, fundamental studies of the processes involved in hydrogen adsorption and release by carbon beryllium-containing lithium hydrides are carried out, to enable the design of efficient hydrogen storage materials for transportation applications. This is obtained by studying geometric, energetic, and thermodynamic properties such as the enthalpy of formation ΔH_f of ionic metal hydrides Li(C_nBe_y)H_x and Li₂(C_nBe_y)H_x. Our results indicate that the presence of (C-Be) dopants in Li-H complexes, enhances the desorption kinetics of these compounds lowering the enthalpy of dehydrogenation tremendously.

Introduction

Complex metal hydrides have been studied for decades as unique materials capable of incorporating hydrogen into their lattice. Many metal hydrides [2] have been reported to be capable of meeting the aforementioned gravimetric and the volumetric storage densities; however, favorable kinetics and thermodynamics (dehydrogenation at room temperature) is an issue that needs to be resolved in order to make these materials available for hydrogen storage. Recent research has shown that dopant additions to complex metal hydrides can enhance hydrogen desorption kinetics. The dopants are theorized to introduce vacancies leading to increase in the mobility of hydrogen atoms and are also responsible for weakening of bonds within the material. Hence, the overall goal of this research is to advance fundamental knowledge of C-Be doped Li hydrides as hydrogen storage materials.

The energy released during this chemical reaction associated to the formation of a metal hydride is called the formation enthalpy or the heat of formation (ΔH_f) of the metal hydride.[3] The larger its heat of formation, the more stable it is, and the higher is the temperature needed to desorb hydrogen from the metal hydride. A good hydrogen storage material, must have promising thermodynamic properties and have sufficiently rapid kinetics of hydrogen charging and discharging.[4] According to Alapati et al. the ΔH_f of a metal hydride should be between -30

and -60 kJ/Mol of H₂, for it to be useful as a hydrogen storage medium. A ΔH_f less than -30 kJ/Mol will result in the adsorption/desorption hydrogen kinetics being not easily reversible, and a ΔH_f greater than -60 kJ/Mol will lead to an extraordinary stability of the metal hydride, which implies higher hydrogen desorption temperatures.[4]

Procedure and Method

Calculation of Heats of Formation and Hydrogen Weight Percentage

In this work, a large number of metal hydrides of the type LiC_nBe_yH_x (0 ≤ n ≤ 3 for every y value under consideration) are investigated. The corresponding heats of formation are calculated based on their formation (or decomposition) reactions as suggested by Alapati et al. [4] where the decomposition reaction for a metal hydride LiC_nBe_yH_x is given by equation (1).



For each system, the normalized form of reaction (1) is taken so as to obtain the heat of formation of 1 mol of H₂. Quantum mechanical calculations are conducted using the program Gaussian'03 using the Density functional B3PW91 and the basis set 6-31++G**. The ground state geometry of each of these systems is also calculated at this level of theory. The enthalpy of reaction (1) is calculated as shown in equation (2), where E is the total energy plus the correction to the enthalpy at 298.15K and 1 bar ($\epsilon_0 + H_{\text{corr}}$) of each product/reactant as specified in the Thermochemistry part of the corresponding outputs of the ground states.[5]

$$\Delta H_f = E(\text{LiC}_n\text{Be}_y\text{H}_x) - E(\text{LiH}) - E(\text{C}_n\text{Be}_y) - E(\text{H}_{x-1}) \quad (2)$$

The weight percentage of hydrogen in each of these metal hydrides is calculated according to equation (3).

$$\text{wt\% of H}_2 \text{ in LiC}_n\text{Be}_y\text{H}_x = \left[\frac{x * (\text{At.Wt})_H}{(\text{At.Wt})_{\text{Li}} + n * (\text{At.Wt})_C + y * (\text{At.Wt})_{\text{Be}} + x * (\text{At.Wt})_H} \right] * 100 \quad (3)$$

Results and Discussion

Tables 1 to 4 show the various systems that were studied, including their normalized formation reactions, their heats of formation ΔH_f and the weight percentage of hydrogen. Tables 1, 2, and 3 show the reactions corresponding to the formation of LiC_nBe_yH_x for y=1, y=2, and y=3 respectively. Table 4 corresponds to the results obtained for Li₂C_nBe_yH_x.

Table 1. Systems with one beryllium atom

System	Normalized Formation Reactions	ΔH_f (kJ/mol H ₂)	wt% H
LiBeH ₃	LiH+Be+H ₂ →LiBeH ₃	-362	15.96
LiCBeH ₃	LiH+CBe+H ₂ →LiCBeH ₃	-1125	9.78
LiCBeH ₅	1/2LiH+1/2CBe+H ₂ →1/2LiCBeH ₅	-571	15.30
LiC ₂ BeH ₃	LiH+C ₂ Be+H ₂ →LiC ₂ BeH ₃	-478	7.05
LiC ₂ BeH ₅	1/2LiH+1/2C ₂ Be+H ₂ →1/2LiC ₂ BeH ₅	-311	11.22
LiC ₂ BeH ₇	1/3LiH+1/3C ₂ be+H ₂ →1/3LiC ₂ BeH ₇	-215	12.61
LiC ₃ BeH ₃	LiH+C ₃ Be+H ₂ →LiC ₃ BeH ₃	-763	5.51
LiC ₃ BeH ₇	1/3LiH+1/3C ₃ Be+H ₂ →1/3LiC ₃ BeH ₇	-324	11.97
LiC ₃ BeH ₉	1/4LiH+1/4C ₃ Be+H ₂ →1/4LiC ₃ BeH ₉	-244	14.88

From the table 1 can be seen that the heat of formation ΔH_f of lithium beryllium hydride (LiBeH₃) is -362 kJ/ mol of H₂ and even though the gravimetric storage density of hydrogen in this hydride is 15.96 wt%, this does not seem to be practically feasible due to its high ΔH_f . This heat of formation is seen to be significantly lowered by using the C-Be complex for the formation of hydride. It can be noted from the same table I that the ΔH_f of LiC₂BeH₇ is down by a considerable amount to -215 kJ/mol of H₂ with respect to ΔH_f (LiBeH₃). The gravimetric storage density of hydrogen in LiC₂BeH₇ is 12.61 wt% which more acceptable according to the DoE requirements.[1]

It is interesting to note that the ΔH_f of LiCBeH₃ and LiCBeH₅, which contain only one carbon atom are -1125 and -571 kJ/mol respectively being those values much higher than that corresponding to LiBeH₃. Similarly the ΔH_f of LiC₃BeH₃, LiC₃BeH₇ and LiC₃BeH₉ are -763, -324 and -244 kJ/mol of H₂ respectively. This shows that the heat of formation of a metal hydride is thoroughly dependant on the amount of carbon in the hydride.

Even though the hydrides with (C-Be) complexes presently studied do not meet the requisition of a ΔH_f within -30 kJ/mol to -60kJ/mol, still can be seen that the presence of carbon in the Li-Be hydrides significantly lowers the formation enthalpy, which suggests better adsorption and desorption kinetics.

Similarly, Table 2 shows the systems with two beryllium atoms and the number of carbon atoms varying from 1 to 3. The wt % of hydrogen in LiBe₂H₃ is found to be 10.82% whereas its ΔH_f is -476 kJ/mol of H₂. It is observed from our calculations that the ΔH_f of this type of hydrides goes down to -179 kJ/mol and the gravimetric storage density of H₂ increases to 12.97% for the metal hydride LiC₃Be₂H₉. Again here, it is seen that the ΔH_f of these systems is a function of the number of carbon atoms.

Table 2. Systems with two beryllium atoms

System	Normalized Formation Reactions	ΔH_f (kJ/mol H ₂)	wt% H
LiBe ₂ H ₃	LiH+2Be+H ₂ →LiBe ₂ H ₃	-476	10.82
LiCBe ₂ H ₃	LiH+CBe ₂ +H ₂ →LiCBe ₂ H ₃	-674	7.57
LiCBe ₂ H ₅	1/2LiH+1/2CBe ₂ +H ₂ →1/2LiCBe ₂ H ₅	-436	12.02
LiC ₂ Be ₂ H ₃	LiH+C ₂ Be ₂ +H ₂ →LiC ₂ Be ₂ H ₃	-464	5.83
LiC ₂ Be ₂ H ₅	1/2LiH+1/2C ₂ Be ₂ +H ₂ →1/2LiC ₂ Be ₂ H ₅	-359	9.35
LiC ₂ Be ₂ H ₇	1/3LiH+1/3C ₂ Be ₂ +H ₂ →1/3LiC ₂ Be ₂ H ₇	-283	12.61
LiC ₃ Be ₂ H ₃	LiH+C ₃ Be ₂ +H ₂ →LiC ₃ Be ₂ H ₃	-679	4.73
LiC ₃ Be ₂ H ₇	1/3LiH+1/3C ₃ Be ₂ +H ₂ →1/3LiC ₃ Be ₂ H ₇	-258	10.39
LiC ₃ Be ₂ H ₉	1/4LiH+1/4C ₃ Be ₂ +H ₂ →1/4LiC ₃ Be ₂ H ₉	-179	12.97
LiC ₄ Be ₂ H ₃	LiH+C ₄ Be ₂ +H ₂ →LiC ₄ Be ₂ H ₃	-550	3.99
LiC ₄ Be ₂ H ₅	1/2LiH+1/2C ₄ Be ₂ +H ₂ →1/2LiC ₄ Be ₂ H ₅	-428	6.47
LiC ₄ Be ₂ H ₇	1/3LiH+1/3C ₄ Be ₂ +H ₂ →1/3LiC ₄ Be ₂ H ₇	-204	8.83
LiC ₄ Be ₂ H ₉	1/4LiH+1/4C ₄ Be ₂ +H ₂ →1/4LiC ₄ Be ₂ H ₉	-251	11.07
LiC ₄ Be ₂ H ₁₁	1/5LiH+1/5C ₄ Be ₂ +H ₂ →1/5LiC ₄ Be ₂ H ₁₁	-209	13.21

Table 3. Systems with three beryllium atoms

System	Normalized Decomposition Reactions	ΔH_f (kJ/mol H ₂)	wt% H
LiBe ₃ H ₃	LiH + 3Be + H ₂ → LiBe ₃ H ₃	-637	8.19
LiCBe ₃ H ₃	LiH + CBe ₃ + H ₂ → LiCBe ₃ H ₃	-547	6.18
LiCBe ₃ H ₅	1/2LiH + 1/2CBe ₃ + H ₂ → 1/2LiCBe ₃ H ₅	-384	9.90
LiC ₂ Be ₃ H ₃	LiH + C ₂ Be ₃ + H ₂ → LiC ₂ Be ₃ H ₃	-533	4.97
LiC ₂ Be ₃ H ₇	1/3LiH + 1/3C ₂ Be ₃ + H ₂ → 1/3LiC ₂ Be ₃ H ₇	-302	10.87
LiC ₃ Be ₃ H ₅	1/2LiH + 1/2C ₃ Be ₃ + H ₂ → 1/2LiC ₃ Be ₃ H ₅	-292	6.73
LiC ₃ Be ₃ H ₇	1/3LiH + 1/3C ₃ Be ₃ + H ₂ → 1/3LiC ₃ Be ₃ H ₇	-269	9.17
LiC ₃ Be ₃ H ₉	1/4LiH + 1/4C ₃ Be ₃ + H ₂ → 1/4LiC ₃ Be ₃ H ₉	-233	11.49

Table 3 shows the systems studied with three beryllium atoms, which again shows the same kind of results as mentioned before: the presence of carbon in Li-Be hydrides is seen to lower their formation enthalpy without much compromising the gravimetric storage density.

The presence of two Li atoms in then investigated and results from our calculations are reported in Table 4. From this table, the formation enthalpy of those systems is more responsive to the amount of carbon present rather than the amount of Lithium. For instance, the ΔH_f of Li₂CBeH₄ is more than 200% of the ΔH_f of Li₂BeH₄, whereas Li₂C₂BeH₆ has considerably lower ΔH_f .

Table 4. Systems with two lithium atoms

System	Normalized Decomposition Reactions	ΔH_f (kJ/mol H ₂)	wt% H
Li ₂ BeH ₄	2LiH + Be + H ₂ → Li ₂ BeH ₄	-524	15
Li ₂ CBeH ₄	2LiH + CBe + H ₂ → Li ₂ CBeH ₄	-1302	10.37
Li ₂ CBeH ₆	LiH + 1/2CBe + H ₂ → 1/2Li ₂ CBeH ₄	877	14.79
Li ₂ C ₂ BeH ₄	2LiH + C ₂ Be + H ₂ → Li ₂ C ₂ BeH ₄	-382	7.93
Li ₂ C ₂ BeH ₆	LiH + 1/2C ₂ Be + H ₂ → 1/2Li ₂ C ₂ BeH ₆	-313	11.44

Based on our Density Functional Theory calculations we have identified a few ionic LiCBe hydrides with promising characteristics (kinetic/thermodynamics) to be considered as hydrogen storage materials. In Table 5 we summarized their information regarding number of Be (y), C (n), and H (x) atoms, valence of C atoms in the complexes, proposed stoichiometry, and calculated ground state geometry.

Table 5. Promising Ionic CBe-containing Li Hydrides for hydrogen storage applications. Electrostatic potential energy surfaces mapped over an isodensity of 0.001 eV corresponding to cases.

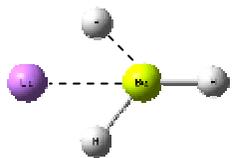
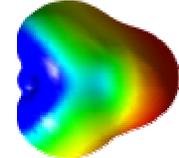
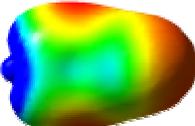
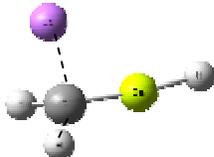
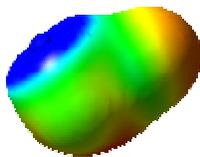
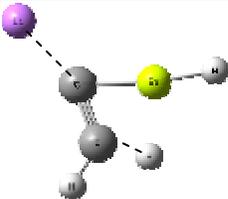
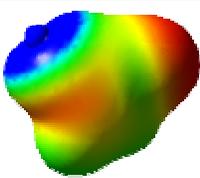
y	n	C valence	x	Stoichiometry	Geometry Found	PES
1	0	-	3	Li ⁺ (BeH ₃) ⁻		
1	1	2	1	Li ⁺ (CBeH) ⁻		
			3	Li ⁺ (CBeH ₃) ⁻		
1	2	4, 4	3	Li ⁺ (C ₂ BeH ₃) ⁻		

Table 5 shows cluster geometry and electrostatic potential surfaces mapped over isodensities of 0.001 eV for proposed (promising) Li⁺(C_nBeH_y)⁻ hydrides. These surfaces allow the direct visualization of the formation of chemical bonds. Note that not only a slice or isosurface of the electron density was examined, but the entire volumetric data to get to this conclusion. It is observed that in those cases (Table 5) strong adsorption takes place since only one electrostatic surface is observed and the electrons are always localized in the vicinity of

beryllium atoms, indicating the formation of a strong bond within the entire hydride (Chemisorption).

Conclusions

It is clear that the C-Be containing Li Hydrides are better than just the Li-Be hydrides in terms of their adsorption and desorption kinetics. From the results on these systems, it can be seen that a specific ratio of carbon to beryllium needs to be present to lower the formation enthalpy of the hydrides. Further studies are required to establish the optimum C/Be ratio for hydrogen storage applications.

References

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