On Development Of Hydrogen Storage Material For Vehicular Application

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Abstract: Transportation is a major sector that consumes energy. At present 24.6% of total energy is consumed in transportation sector around the globe. In India, the percentage of total energy consumed in transportation is 15%. At present, the major fuel for transportation is fossil fuel, which produces a lot of pollution (carbon imprint) in the environment. Hence the society must move towards the use of electric vehicles or adopting a clean fuel for vehicle. Hydrogen is an alternate fuel which can be stored in a vehicle directly or in the form of negative electrode material of nickel metal hydride (Ni-MH) battery. In the hydrides some of the important parameters are the heat of formation and plateau pressure. Until now, the search of optimum material properties is based on trial and error method by substituting other elements in basic alloy. In the present study, a semi-empirical formula has been proposed to calculate the heat of formation of AB_5 - type multi-component hydrogen storage alloy. The formula has been applied to calculate heat of formation of binary hydrides, ternary hydrides and multi-component hydrides. Very good agreement with experimental values has been achieved. The heat of formation has also been correlated with the plateau pressure. This model will help in predicting important thermodynamic parameters of novel hydrogen storage materials.

Keywords: Metal hydride battery, Multicomponent metal hydride, Heat of formation.

1. INTRODUCTION

Hydrogen storage materials can be utilized in electric vehicles directly or in form of negative electrode material or nickel metal hydride (Ni-MH) battery [1, 2]. Heat of formation of hydride and plateau pressure of pressure-composition isotherm are important parameters of hydrogen storage material [3, 4]. One of the basic alloys for this application is $LaNi_5$ which is similar to $MnNi_5$. The hydrogenation properties of these two alloys do not fulfil all the requirements for specific applications. Therefore they need to be tailored. Till now, the search of appropriate material properties has been based on trial and error methods by substituting other elements in the basic alloy [5]. Although multi-component alloys offer better hydrogenation characteristics in comparison to basic alloys, no model is known to calculate heat of formation of hydrides of multi-component hydrogen storage alloy properly. In the present paper, a semi-empirical formula to calculate the heat of formation of AB_5 - type multi-component hydrogen storage alloy is proposed. This formula has been applied to calculate the heat of formation of binary hydrides, ternary hydrides and multi-component hydrides.

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2. SEMI-EMPIRICAL FORMULA FOR HEAT OF FORMATION

To calculate heat of formation (ΔH) of a hydride, Van Mal et al. have given rules of reverse stability as given below [3]. ΔH for a ternary hydride AB_nH_{2m} can be given in terms of the ΔH values of associated binary compounds by the equation

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta H(AB_n) \quad (1)$$

2.1 Proposed formula for multi-component alloy

We want to consider a system where A and H_{2m} are fixed and make an alloy at the B site by substituting some of the B atoms by C atoms. The proposed semi-empirical formula of heat of formation of a multi-component hydride alloy $AB_{n-p}C_pH_{2m}$ is given by

$$\Delta H(AB_{n-p}C_pH_{2m}) = \Delta H(AH_m) + (1-x)\Delta H(B_nH_m) + x\Delta H(C_nH_m) - \Delta H(AB_{n-p}C_p) \quad , \quad (2)$$

where $x = \frac{p}{n}$ and p takes values $0,1,\dots,n$.

This equation interpolates between $\Delta H(AB_nH_{2m})$ and $\Delta H(AC_nH_{2m})$ when p takes values from 0 to *n* i.e. x goes from 0 to 1. The heat of formation of the ternary $AB_{n-p}C_p$ can be interpolated between the corresponding values for the binary compounds AB_n and AC_n using the equation

$$\Delta H(AB_{n-p}C_p) = (1-x)\Delta H(AB_n) + x\Delta H(AC_n) \quad (3)$$

Most of the time the values of the heat of formation of binary hydrides AH_m, B_nH_m and C_nH_m, for general values of *m* are not known, but the values for AH_3, B_nH_3 and C_nH_3 etc. are known. We suggest a simple equation to get the unknown values as

$$\Delta H(AH_m) = \left(\frac{m}{3}\right)\Delta H(AH_3);\ \Delta H(B_nH_m) = \left(\frac{m}{3}\right)\Delta H(B_nH_3);\Delta H(C_nH_m) = \left(\frac{m}{3}\right)\Delta H(C_nH_3) \quad (4)$$

2.2 Calculation of heat of formation of alloy hydrides using equations 2, 3 and 4

Based on the calculation from above mentioned equations 2, 3 and 4 following results have been obtained.

Table 1. Heat of formation **(H)** of binary hydrides in units of kcal/mole and verification of proposed Eq. 4.

No.	Compound	Heat of formation Reported	Reference of reported value	Heat of formation calculated using Eq. 3
1.	LaH_3	-60	3	-
2.	LaH_2	-49.6	3	-40
3.	Ni_5H_3	+1.0	3	-
4.	Ni_5H_2	+0.7	3	0.67
5.	Co_5H_3	+7	3	-
6.	Co_5H_2	+5	3	4.67

Table 2 - Heat of formation **(H)** in units of kcal/mole of ternary and multi-component alloy and verification of proposed Eq. 3.

No.	Compound	Reported value of Heat of formation	Reference of reported value	Heat of formation calculated using Eq. 3
1.	$LaNi_5$	-40	3	-
2.	$LaCu_5$	-24.0	4	-
3.	$LaCo_5$	-17.5	3	-
4.	$LaFe_5$	+4	3	-
5.	$LaCr_5$	+12	3	-
6.	$LaAl_5$	-44.4	4	-
7.	$LaMn_5$	+1.2	4	-
8.	$LaNi_4Cu$	-34.2	4	-36.8
9.	$LaNi_4Co$	-		-35.5
10.	$LaNi_4Fe$	-31.0	4	-31.2
11.	$LaNi_4Al$	-40.6	4	-40.88
12.	$LaNi_4Mn$	-32.0	4	-31.64
13.	$LaNi_4Cr$	-		-29.6

Table 3- Heat of formation **(H)** in units of kcal/mole H_2, of ternary and multi-component hydrides as calculated through proposed Eq. 2.

S. No.	Alloy	Heat of formation Reported	Reference of the reported value	Heat of formation Calculated
1.	$LaNi_5H_6$	-7.3	4	-6.33
2.	$LaNi_4CoH_6$	-7.56	4	-7.43
3.	$LaNi_4CuH_6$	-8.1	4	-8.068
4.	$LaNi_4FeH_6$	-8.2	4	-8.87
5.	$LaNi_4CrH_6$	-10.2	4	-10.0
6.	$LaNi_4MnH_6$	-11.6	4	-11.6
7.	$LaNi_4AlH_6$	-11.4	4	-13.1

In summary, a good agreement can be seen in the calculated and reported values of heat of formation of multi-component hydrogen storage alloy using Eq. 2, 3 and 4 in Tables 1, 2 and 3.

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