Influences of Y_2O_3 Doping on Hydrogen Release Property of LiAlH_4

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Abstract: The dehydrogenation properties of LiAlH_4 doped with Y_2O_3 were investigated by PCT (Pressure-Composition-Temperature) equipment. The results show that with the increase of amount of Y_2O_3 , the dehydrogenation amount of LiAlH_4 increases, however, when the doping amount reaches a certain value, the hydrogen release amount decreases with the increase of doping amount. Compared to the LiAlH_4 sample, the dehydrogenation starting time of the samples doped with Y_2O_3 is significantly brought forward. In addition, it can be found that the dehydrogenation rates of all the doped samples are higher than that of the original sample. The change trends of the dehydrogenation rates of all the doped samples are similar in the whole dehydrogenation process, namely, with the extension of time, the dehydrogenation rates increase firstly, and then decrease gradually.

Key words: hydrogen release amount; hydrogen release rate; LiAlH_4 ; Y_2O_3

Since the energy crisis, the environmental pollution and the greenhouse effect have been caused by a large amount of energy consumption, people have been studying the efficient energy. Hydrogen is recognized as the ideal future energy due to high calorific value. In addition, hydrogen is a potential major alternative as an environment friendly energy carrier. Importantly, hydrogen is the most abundant element in the universe. It can be produced through water decomposition by solar energy, wind energy and geothermal energy and other natural energies, and it is an inexhaustible secondary energy [1-3] which will be never used up. However, due to the lack of convenient and effective hydrogen storage materials and hydrogen storage technology, the application of hydrogen energy has been greatly hindered for a long time. Therefore, in order to realize the application of hydrogen as an energy carrier, the hydrogen storage problem must be solved. At present, for the researches on hydrogen storage materials there are mainly three kinds of categories: metal hydrogen storage materials, porous adsorption hydrogen storage materials and organic liquid hydrogen storage materials. Among them,

the hydrogen storage alloys attract more and more people's attention due to their high hydrogen storage capacity, no pollution, safety and reliability. According to the different combination type, the hydrogen storage alloys can be divided into two categories: one is the metal hydride hydrogen storage alloy, the other is the complex hydride hydrogen storage alloy.

Compared with the metal hydride hydrogen storage alloy, the complex hydride hydrogen storage alloy has much higher hydrogen storage amount. For example: the hydrogen storage amounts of NaAlH_4 and LiAlH_4 have achieved 7.4 wt% and 10.5 wt%, respectively. Up to now, a great deal of researches has focused on finding better catalysts. For example, Resan M [4] and other scientists studied TiH_2 , TiCl_3 , TiCl_4 , AlCl_3 , FeCl_3 , Fe, Ni, V, Ti and C. In addition, some new catalysts were studied, such as NH_4Cl [5], TiF_3 [6], nano fiber [7], nano nickel [8], NH_3 [9] etc. In this work, the dehydrogenation properties of LiAlH_4 doped with Y_2O_3 will be studied.

1 Experiment

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LiAlH_4 with purity $\geq 93\%$ was purchased from J & K Chemical Ltd. NaAlH_4 was used as the received with no additional purification. The main purpose of this experiment is to study the influences of different rare earth compounds on the hydrogen release property of LiAlH_4 . The selected rare earth compound was Y_2O_3 . The ball milling device adopted is planetary ball mill, all samples were milled for 1h at a gyration rate of 200 r/min, and the ratio of ball to powder was 22:1. In order to prevent the samples from oxidation, the loading of the samples and sampling process were carried out in a glove box filled with argon. The hydrogen release properties of the samples were tested by PCT (Pressure-Composition-Temperature) equipment. Firstly, the samples were heated to 200 °C, and then kept under this temperature for 150 min. The doping amounts (mol%) of the dopants were 0.5, 1, 2, 3, 4, 5 and 6. The microstructure was analyzed by SEM (scanning electron microscope)

2 Results and Discussion

Fig.1 shows the curves of the dehydrogenation amount vs the time of the LiAlH_4 samples doped with 0.5 mol%~6 mol% Y_2O_3 and the pure LiAlH_4 sample. It can be seen that all the samples show obvious two-step decomposition. At the same time, the experimental results indicate that the sample doped with 1 mol% Y_2O_3 has the largest amount of hydrogen release, while the sample doped with 5 mol% Y_2O_3 has the smallest amount of hydrogen release. And as the doping amount increases from 1 mol% to 5 mol%, the dehydrogenation amount of the samples decreases gradually, but the dehydrogenation amount of the sample doped with 6 mol% Y_2O_3 increases, which is same to the dehydrogenation amount of the sample doped with 3 mol% Y_2O_3 . The final dehydrogenation amount of the LiAlH_4 samples doped with 0.5 mol%, 1 mol%, and 2 mol% is larger than that of the original sample under the same conditions, while the final dehydrogenation amounts (mol%) of the samples doped the 3, 4, 5, 6 are smaller than that of the original sample. In addition, from the slope of the curves in Fig. 1, it can be seen that, the dehydrogenation rate of the doped samples are higher than that of the original sample.

Fig.2 show the changing relations between the maximum dehydrogenation amount and the doping amount. It is easy to see that only the dehydrogenation amounts of the samples doped with 0.5 mol% and 1 mol% are larger than that of the original sample, when the doping amount is among 1 mol%~5 mol%, with the increase of the Y_2O_3 doping amount, the dehydrogenation amount of the samples decreases gradually. The dehydrogenation amount of the sample doped with 1 mol% Y_2O_3 is the largest, while the dehydrogenation amount of the sample doped with 5 mol% Y_2O_3 is the least.

Fig.1 Curves of the dehydrogenation amount vs the time of the LiAlH_4 samples doped with 0 mol%~6 mol% Y_2O_3

Fig.2 Curve of the dehydrogenation amount of the LiAlH_4 samples doped with 0 mol%~6 mol% Y_2O_3 and the concentration of Y_2O_3

Fig.3 shows the relational curves between the dehydrogenation rate and the dehydrogenation time of the samples doped with Y_2O_3 . It can be seen that the dehydrogenation rate of the samples doped with Y_2O_3 are higher than that of the original sample, and dehydrogenation starting time of the doped samples is significantly earlier, namely maximum peaks of the dehydrogenation speed of the samples doped with 0.5 mol%~6 mol% Y_2O_3 appear earlier than that of the original sample. Furthermore, the original sample and the samples doped with 0.5 mol%~6 mol% Y_2O_3 all show, with the extension of time, the dehydrogenation rate increases firstly, when the dehydrogenation rate is increased to a certain value, it begins to decrease. The dehydrogenation rate of the sample doped with 2 mol% Y_2O_3 is the highest.

Fig.4 gives the amount of dehydrogenation of the samples doped with 0.5 mol%~6 mol% Y_2O_3 in the first and second steps. It is obvious that the dehydrogenation amount of the sample doped with 1 mol% Y_2O_3 is the largest in the first and second steps. With the increase of amount of Y_2O_3 , except for the sample doped with 6 mol% Y_2O_3 , the dehydrogenation amounts of the samples present firstly an increase and then a decrease.

Fig.3 Curves of the dehydrogenation rate and the time of the LiAlH₄ samples doped with 0 mol%~6 mol% Y₂O₃

Fig.4 Dehydrogenation amount of the LiAlH₄ samples doped with 0 mol%~6mol% Y₂O₃ in the first and second steps

In this part work, the microstructure of the samples doped with Y₂O₃ was analyzed. Fig.5 gives the SEM images of LiAlH₄ sample and the samples doped with Y₂O₃. It can be found that the microstructure of all samples present a kind of flocculent structure. In addition, a lot of pores are found on the surface of the powder of all samples. We consider these pores may be left by overflowing hydrogen when the samples were milled.

Table 1 compares the dehydrogenation amount and maximum dehydrogenation rate of the LiAlH₄ samples doped with Y₂O₃. Among the samples doped with Y₂O₃, the sample doped with 1 mol% Y₂O₃ has the largest dehydrogenation amount of 7.23 wt%, while the sample doped with 2 mol% has the maximum dehydrogenation rate of 0.51 wt%/min.

Fig.5 SEM images of the samples doped with different amount of Y₂O₃: (a) 0 mol%, (b) 0.5 mol%, (c) 1 mol%, (d) 2 mol%, (e) 3 mol%, (f) 4 mol%, (g) 5 mol%, and (h) 6 mol%

Table 1 Dehydrogenation amount and maximum hydrogen release rate of the samples doped with different amount of Y₂O₃

Y ₂ O ₃ doped/ mol%	Dehydrogenation amount/wt%	Maximum hydrogen release rate/wt% min ⁻¹
0.5	6.57	0.41
1	7.23	0.50
2	6.35	0.51
3	5.63	0.35
4	5.21	0.44
5	5.19	0.39
6	5.66	0.38
0	6.03	0.31

3 Conclusions

1) With the increase of doping amount, the dehydrogenation amount of LiAlH₄ increases, however, when the doping amount reaches a certain value, the dehydrogenation amount begins to decrease.

2) Compared to the LiAlH₄ sample, the dehydrogenation starting time of the samples doped with Y₂O₃ is significantly brought forward.

3) The dehydrogenation rates of all the doped samples are higher than that of the original sample. And, the change

of the dehydrogenation rates of all the doped samples are similar in the whole dehydrogenation process, namely, with the extension of time, the dehydrogenation rates increase rapidly, and then decrease gradually.

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掺杂 Y_2O_3 对 $LiAlH_4$ 放氢性能的影响

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摘要: 主要通过 PCT 设备研究了掺杂 Y_2O_3 的 $LiAlH_4$ 试样的放氢性能。结果显示, 随着 Y_2O_3 掺杂量的增加, $LiAlH_4$ 的放氢量增加, 然而, 当掺杂量达到某一值时, $LiAlH_4$ 的放氢量随着掺杂量的增加而降低。和 $LiAlH_4$ 原样相比, 掺杂 Y_2O_3 的试样初始放氢时间提前。此外, 关于 Y_2O_3 对 $LiAlH_4$ 放氢速率影响的研究还发现, 所有掺杂试样的放氢速率都比未掺杂原样的放氢速率快。并且所有掺杂试样的放氢速率的变化趋势都是相似的, 即: 随着时间的延长, 放氢速率快速增大之后逐步降低。

关键词: 放氢量; 放氢速率; $LiAlH_4$; Y_2O_3

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