

Hydrogen generation from coupling reactions of AlLi/NaBH₄ mixture in water activated by Ni powder

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Abstract: A novel composition of AlLi/NaBH₄ mixture activated by common Ni powder in water for hydrogen generation was investigated. The composition presents good hydrogen generation performance and an optimized Al–10% Li–10% Ni/NaBH₄ mixture (mass ratio of 3:1) generates 1540 mL/g hydrogen with 96% efficiency at 333 K. Ni powder exhibits dual catalytic effects on the hydrolysis of AlLi/NaBH₄ mixture due to the formation of Ni₂B in the hydrolysis process. The Ni₂B deposited on aluminum surface could act as a cathode of a micro galvanic couple. Ni₂B/Al(OH)₃ also has a synergistic effect on NaBH₄ hydrolysis. Good hydrogen generation performance with stable pH value of hydrolysis byproduct Al(OH)₃/NaBO₂·2H₂O was obtained with successive additions of Al–Li–Ni /NaBH₄ mixture into fixed water.

Key words: hydrogen generation; AlLi alloy; NaBH₄; Ni

1 Introduction

Hydrogen is an ideal energy source for fuel cells where the energy obtained in the reaction of hydrogen and oxygen is converted to electric energy. Hydrogen storage is still a large problem for the application of fuel cell in transportation vehicles and small portable devices [1,2]. Scientists have done much endeavor to solve the problem on two ways: one is to develop hydrogen storage materials which meet the required targets of U.S. Department of Energy (referred as DOE) at moderate pressure and temperature ranges [3]; another is to develop hydrogen generation materials which can supply portable hydrogen source when and where it is needed. Due to no hydrogen storage materials which can be efficiently applied to supplying hydrogen for fuel cells, on board hydrogen generation has been an alternative choice for fuel cells in recent years.

Sodium borohydride (NaBH₄) has been extensively studied nowadays for portable and mobile fuel cell applications with theoretical gravimetric hydrogen generation value of 10.8% [3,4]. The environmentally benign sodium metaborate (NaBO₂) can be recycled [5] and the hydrogen generation rate can be controlled with

catalyst. Unfortunately, there are many engineering problems, such as high cost, low catalyst durability caused by the solubility limitations of sodium by-products borohydride and sodium metaborate (NaBO₂) in an aqueous solution. Aluminum and aluminum alloy have been identified as another attractive candidate for on board hydrogen generation, with a lot of advantages including abundant source, low cost, etc [6]. Some studies [7–9] evidenced that Al has high reactivity in alkali solution. The corrosive nature of alkaline solutions is harmful to the common user; thus, they cannot be easily handled in practical applications. Many literatures have found that milled aluminum alloys including some additives such as light metals, salts and oxides, can react with water in neutral solution at mild condition [10,11]. But these additives would reduce the gravimetric hydrogen generation volume because they could not react with water. Previous work by LIU et al [12] showed that Li additive could significantly improve the hydrolysis rate of Al-based mixtures and increase hydrogen generation amount. It is a pity that the theoretical hydrogen generation density from Al/H₂O system is limited to 3%–4% (mass fraction), which is still far below the target of 6.5% of the DOE [10,11,13]. Recently, SHAFIROVICH et al [14] found a novel

method to supply about 7% hydrogen generation density from $\text{NaBH}_4/\text{nano-Al}$ composite. There was an interaction of Al/NaBH_4 hydrolysis without any catalyst. The hydrolysis by-product $\text{Al}(\text{OH})_3$ from Al hydrolysis has a catalytic effect on the hydrolysis kinetic of NaBH_4 [15]. On the contrary, a lot of heat and protons generated from NaBH_4 hydrolysis also stimulate Al hydrolysis. Some non-ferrous metals or salts, such as Co , Ni , CoCl_2 and NiCl_2 , have dual catalytic effects on the hydrolysis kinetic of Al/NaBH_4 . SOLER et al [8] found that $\text{AlCo}/\text{NaBH}_4$ had better hydrolysis performance than Al/NaBH_4 . The improvement was attributed to the formation of Co_2B in the hydrolysis process, which showed superior catalytic activity on the hydrolysis kinetic of Al/NaBH_4 . But so far, the hydrolysis of Al/NaBH_4 system has to be performed in alkaline solution or using nanoscale Al powder.

In this work, a new composition of Al-Li-Ni and NaBH_4 powder is designed to obtain high hydrogen generation density in neutral aqueous solution with affordable cost. The effects of composition design, preparation method and hydrolysis mechanism of Al/NaBH_4 activated by Li and Ni , are explored and discussed. The aim of the work is to find the best composition with a high hydrogen yield and elaborate the possible application of $\text{AlLi}/\text{NaBH}_4$ as hydrogen generation materials.

2 Experimental

2.1 Preparation of Al alloys

Aluminum powder (mean size of $10\ \mu\text{m}$, common grade, 99.9% purity) (supplied by Beijing Xingry Technology Company Ltd.), Li flakes ($d16\ \text{mm}\times0.5\ \text{mm}$, 99.9% purity), pure Ni powder, sodium borohydride (solid, 95% purity) supplied by Tianjin Delan Chemical Company, China, were used as the starting materials. All reagents were used as-received. A little NaCl was added as a milling-assisted agent. The reagents were weighed and put into 50 mL stainless steel jars including stainless steel balls in an argon-filled glove box. The mass ratio ball to mixture was 26:1. Then 15 h-milling was

performed in a QM-3SPO4 planetary ball miller at 450 r/min under 0.2 MPa argon atmospheres if not specially noted. Two preparation methods of $\text{Al-Li-Ni}/\text{NaBH}_4$ mixture were considered: Method 1, mixture of Al+Li+Ni and NaBH_4 was milled for 15 h; Method 2, Al-Li-Ni milled for 15 h and solid-state NaBH_4 were mixed. The processes are listed in Fig. 1.

2.2 Measurement of hydrogen evolution

The hydrolysis experiments of $\text{Al-Li-Ni}/\text{NaBH}_4$ mixtures were carried out in pure water with a sealed reactor attached a condenser at 333 K and 101.325 kPa. The volume of water was fixed (50 mL) and the mass of the $\text{Al-Li-Ni}/\text{NaBH}_4$ mixture was probably 0.4 g. The mass ratio of $\text{Al-Li-Ni}/\text{NaBH}_4$ mixture was 3:1, unless otherwise indicated. The mixture was pressed into a tablet in a stainless steel mold with diameter of 10 mm, using 49 kN pressure before the hydrolysis reaction because highly dispersed Al-Li alloy easily burned with water even at 298 K. The generated hydrogen gas was monitored by the measurement of the inverted cylinder by water displacement. The generated hydrogen was collected and measured from the water level change in the cylinder at 273 K and 101.325 kPa. The hydrogen generation rate was calculated from the amount evolved from the beginning of the test. As water/ $(\text{Al-Li-Ni}/\text{NaBH}_4\ \text{mixture})$ mass ratio was approximately 500: 1, the hydrolysis kinetics of aluminum mixture in water wholly came from the effect of global temperature.

2.3 Microstructure analysis

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were collected by an X-ray diffractometer (RIGAKU, Japan, model, D/MAX2550V/PC) over a range of diffraction angle $2\theta=10^\circ-80^\circ$ with $\text{Cu K}\alpha$ radiation filtered by a monochromator. Scanning electron microscopy (SEM) observations were performed on a JSM-5610LV from JEOL Company. The solid hydrolysis by-product in the reactor was filtered using a vacuum pump and then dried in an oven at 323 K for 24 h.

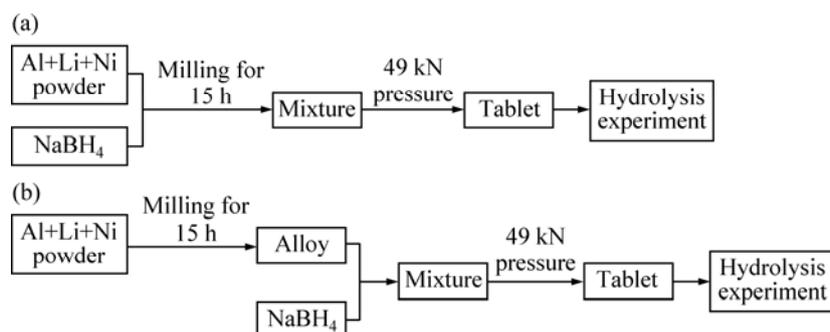


Fig. 1 Flow chart of different preparation technologies of $\text{Al-Li-Ni}/\text{NaBH}_4$ mixture: (a) Method 1; (b) Method 2

3 Results and discussion

3.1 Effects of preparation technology and Ni amount

Figure 2 shows hydrogen generation of Al–10%Li–10%Ni/NaBH₄ (mass ratio of 3:1) by different preparation methods. The mixture prepared by Method 1 has bad hydrolysis performance with less than 800 mL/g hydrogen generation amount within 60 min. However, the mixture with the same composition prepared by Method 2 can generate approximately 1540 mL/g hydrogen within 60 min. NaBH₄ milled with Al–Li–Ni or not seriously affects its hydrolysis performances due to the distribution of NaBH₄ on the surface of Al–Li–Ni alloy. Figure 3 shows XRD patterns of Al–Li–Ni/NaBH₄ by different preparation methods. Microstructure changes can be found with the addition of NaBH₄. The peaks of Al, AlLi, etc, become broadened, reflecting that the particle size decreases. It can be further confirmed from SEM micrograph in Figs. 4(a) and 4(b). The NaBH₄ particle deposited on the surface of the composites impedes the contact of Al, Ni and Li, and results in the uniform distribution of the composition. Large specific area and uniform distribution obtained with milled Al–Li–Ni /NaBH₄ mixture results in fast hydrolysis rate in Fig. 2. Al–10% Li–10% Ni/NaBH₄ mixture prepared by Method 1 has a maximum hydrogen generation rate of 667 mL/(g·min), evidently higher than 158 mL/(g·min) of the same mixture prepared by Method 2.

From Fig. 3, there is also a great difference that the peaks of AlNi alloy cannot be identified in the XRD patterns of Al–Li–Ni/NaBH₄ mixture prepared by Method 1, but observed in the mixture prepared by Method 2. AlNi alloy can easily form micro galvanic cell and react with water and NaBH₄ to generate nano-

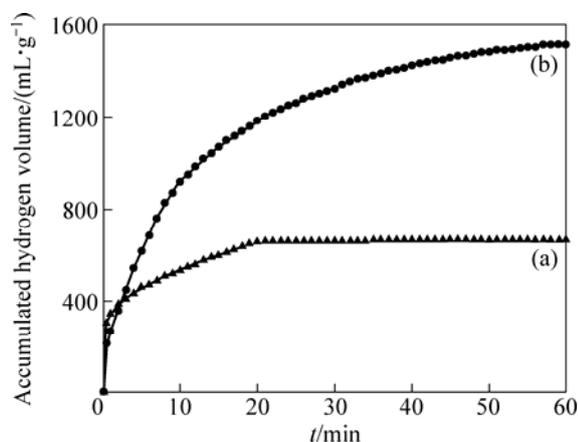


Fig. 2 Hydrogen generation of Al–10%Li–10%Ni/NaBH₄ (mass ratio, 3:1) by different preparation methods: (a) Milled Al–Li–Ni/NaBH₄ (mass ratio 3:1) by Method 1; (b) NaBH₄+milled Al–Li–Ni (mass ratio 3:1) by Method 2

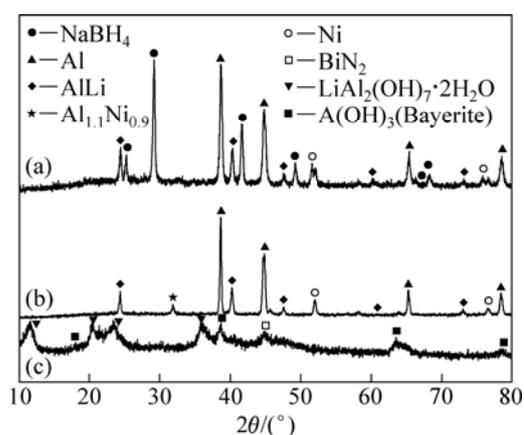


Fig. 3 XRD patterns of Al–Li–Ni/NaBH₄ with mass ratio of 3:1 by different preparation methods: (a) Al–10%Li–10%Ni/NaBH₄ mixture milled for 15 h; (b) Al–10%Li–10%Ni alloy milled for 15 h; (c) Solid hydrolysis product

Ni₂B/Al(OH)₃ catalyst due to the distribution of Ni into Al matrix in AlNi alloy. Figures 4(c) and 4(d) show SEM micrographs and EDS of hydrolysis byproduct of Al–Li–Ni/NaBH₄ mixture prepared by Method 2. The sub-micro platy particles [LiAl₂(OH)₇] distribute in loose solid [Al(OH)₃]. Combined with XRD results in Fig. 3 and Ni map in Fig. 4, it shows that Ni element is uniformly distributed in the hydrolysis by-product, reflecting that Ni₂B is uniformly distributed in Al(OH)₃. The same phenomenon was observed by SOLER et al [8] where AlCo/NaBH₄ had good hydrogen generation performance due to the formation of nano-Co₂B/Al(OH)₃. But common Ni powder prepared by Method 1 has a low catalytic ability to improve hydrolysis of Al–Li–Ni/NaBH₄ mixture, even common Ni₂B/Al(OH)₃ generates in the hydrolysis process. Therefore, all Al–Li–Ni/NaBH₄ mixtures are prepared according to Method 2 if not specially noted.

Figure 5 shows the effect of Ni amount on hydrogen generation performance of Al–Li–Ni/NaBH₄ mixture. Hydrogen generation amount increases from 1135 to 1540 mL/g with Ni amount increasing from 2% to 10% within 45 min. It has been elaborated that Ni has a dual catalytic effect on Al/NaBH₄ mixture. So, more Ni amount results in higher hydrogen generation rate of the Al–Li–Ni/NaBH₄ mixture, as shown in Fig. 5. However, with Ni amount further increasing from 10% to 15%, the hydrogen generation rate is increased when the sacrifice of hydrogen generation amount is decreased from 1540 to 1350 mL/g. Therefore, the suitable Ni amount in the mixture should be pursued.

3.2 Effect of Al–Li–Ni/NaBH₄ mass ratio

Table 1 shows the maximum hydrogen generation rate and amount of Al–10%Li–10%Ni/NaBH₄ mixture

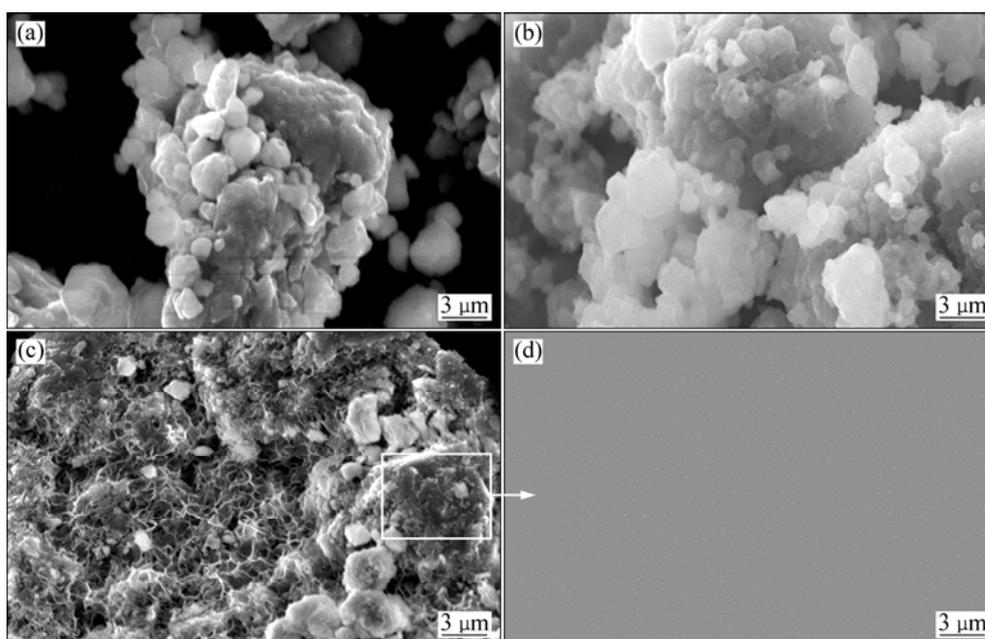


Fig. 4 SEM images (a, b, c) and EDS (d) of Al-10%Li-10%Ni/NaBH₄: (a) SEM, milled Al-10%Li-10% Ni; (b) SEM, milled Al-10%Li-10%Ni with NaBH₄; (c) SEM, hydrolysis by-product of NaBH₄ and milled Al-10%Li-10% Ni; (d) EDS of hydrolysis by-product of NaBH₄ and milled Al-10%Li-10% Ni

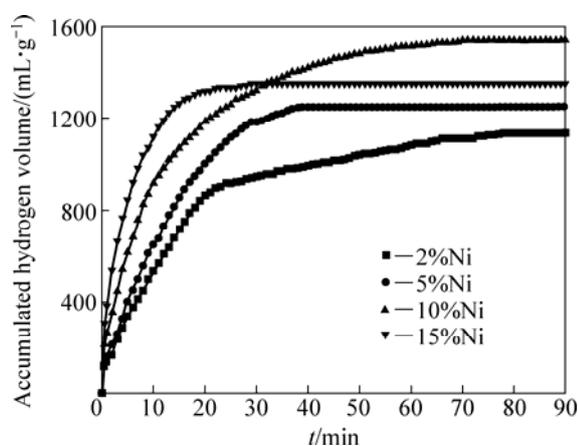


Fig. 5 Hydrogen generation performance of Al-10%Li/NaBH₄ mixtures (mass ratio 3:1) doped with different Ni amounts

with different mass ratios. With Al-10%Li-10%Ni/NaBH₄ mass ratio changing from 4:0 to 0:4, the maximum hydrogen generation rate is decreased from 218 to 115 mL/(g·min). Hydrogen generation amount is increased from 843 to 1715 mL/g with Al-10%Li-10%Ni/NaBH₄ mass ratio changing from 0:4 to 1:3 and then is decreasing with further increased mass ratios. Their conversion efficiency was calculated and the largest value of 96% can be obtained in the mixture with Al-10%Li-10%Ni/NaBH₄ in mass ratio of 3:1. The results confirm that the catalytic effect of Ni powder can be improved with the interaction of Al/NaBH₄ hydrolysis. The hydrolysis of Al-Li-Ni is based on micro galvanic

cell between Al (anode) and Ni (cathode). Li/NaBH₄ hydrolysis generates a lot of protons and heat which stimulate the work of micro galvanic cell and accelerate Al corrosion. Otherwise, the exothermic reaction of Al and Li also improves NaBH₄ hydrolysis with the catalytic effect of Ni₂B/Al(OH)₃. Considering hydrogen generation performance of Al-Li-Ni/NaBH₄ mixture and high cost of NaBH₄, Al-10%Li-10%Ni/NaBH₄ mixture (mass ratio 3:1) may be a good choice for future portable hydrogen sources.

Table 1 Hydrogen generation amount and the maximum rate of Al-10%Li-10%Ni/NaBH₄ with different mass ratios

Al-Li-Ni/NaBH ₄ mass ratio	Maximum hydrogen generation/(mL·g ⁻¹ ·min ⁻¹)	Hydrogen generation amount/(mL·g ⁻¹)	Efficiency/%
0:4	115	1511	58
1:3	125	1715	75
1:1	171	1640	84
3:1	210	1540	96
4:0	218	843	73

3.3 Potential application

Table 2 and Fig. 6 report the hydrogen generation performance of the 11th successive addition of Al-10%Li-15%Ni/NaBH₄ (mass ratio of 3:1) mixture into fixed water. The mixture has hydrogen generation amount of 1303 mL/g and the maximum hydrogen

Table 2 Hydrogen generation amount and the maximum rate of Al–10%Li–15%Ni/NaBH₄ (mass ratio of 3:1) with consecutive runs

Consecutive run	Maximum hydrogen generation rate/(mL·g ⁻¹ ·min ⁻¹)	Hydrogen generation amount/(mL·g ⁻¹)	pH after hydrolysis
1st	710	1303	12.51
2nd	1248	1448	12.82
3rd	1269	1501	13.04
4th	1358	1556	13.11
5th	2359	1582	13.19
6th	2070	1516	13.24
7th	1181	1482	13.28
8th	1323	1448	13.31
9th	1084	1445	13.39
10th	1035	1437	13.43
11th	926	1321	13.44

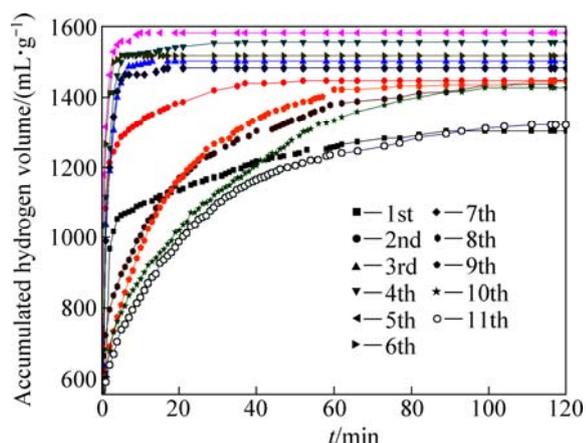
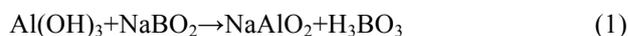


Fig. 6 Hydrogen generation of Al–10%Li–15%Ni/NaBH₄ mixture (mass ratio of 3:1) in consecutive runs

generation rate of 710 mL/(g·min⁻¹) in the first run. The pH value of hydrolysis by-products quickly soars from 7 to 12.51. With the successive addition of Al–10%Li–15%Ni/NaBH₄, the hydrogen generation performance of the mixture is improved evidently and the largest values of hydrogen generation amount and rate appear in the fifth addition. The values are 2359 mL/(g·min) and 1582 mL/g, respectively. The improvement has been explained from the catalytic effect of Ni₂B/Al(OH)₃ and the interaction of Al/NaBH₄ hydrolysis. However, with further successive addition of Al–10%Li–15%Ni/NaBH₄, hydrogen generation amount and rate are undermined. The mixture only yields 1321 mL/g hydrogen with a maximum hydrogen generation rate of 926 mL/(g·min) in the 11th addition, lower than those of the 5th addition. The hydrolysis by-product presents strong alkaline with pH of 12.5–13.5 which

accelerates Al hydrolysis. So, the deteriorated hydrogen generation performance mostly comes from NaBH₄ hydrolysis. Hydrolysis by-product NaBO₂ indicates alkaline and dissolves Al(OH)₃ in Reaction (1). Support failure of the catalyst results in the catalyst deterioration. The problem can be resolved by changing Al/NaBH₄ mass ratio in practical application.



4 Conclusions

1) The mixture of NaBH₄ and milled Al–Li–Ni has excellent hydrogen generation performance and the optimized Al–10%Li–10%Ni/NaBH₄ (mass ratio of 3:1) yields 1540 mL/g hydrogen with 96% efficiency at 333 K.

2) The effect of Ni powder is attributed to nano-Ni₂B generated in the hydrolysis process due to the existence of AlNi alloy in milled Al–Li–Ni mixture. Ni₂B has dual catalytic effects on the hydrolysis of AlLi/NaBH₄ mixture. Ni₂B deposited on aluminum surface can act as a cathode of a micro galvanic couple. Ni₂B/Al(OH)₃ catalyst is also a good promoter to improve the hydrolysis kinetics of NaBH₄.

3) There exists the interaction of Al/NaBH₄ hydrolysis while a lot of heat and protons from NaBH₄ hydrolysis promote the corrosion of aluminum. On the contrary, the highly exothermic Al/H₂O reaction and hydrolysis byproduct Al(OH)₃ improve the hydrolysis performance of NaBH₄.

4) Hydrolysis by-product shows good hydrogen generation performance with stable pH value when successive addition of Al–Li–Ni/NaBH₄ mixture into fixed water is performed.

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金属 Ni 掺杂催化 AlLi/NaBH₄ 混合体系水解析氢

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摘 要: 采用机械球磨法制备 AlLi/NaBH₄/Ni 混合体系。水解测试分析表明, 固态 Al–Li–Ni/NaBH₄ 混合物具有良好的析氢性能。Al–10%Li–10%Ni/NaBH₄(质量比为 3:1)混合物在 333 K 时的产氢值达 1540 mL/g, 产氢效率为 96%。通过 XRD、SEM 等分析 Ni 掺杂改善其水解析氢机制, 金属 Ni 的产物 Ni₂B 对 Al 合金和 NaBH₄ 的水解具有双重催化作用。Ni₂B 沉积在 Al 表面可作为微型腐蚀电池的阴极并促进铝的阳极腐蚀。另外, Ni₂B/Al(OH)₃ 对 NaBH₄ 的水解动力学具有很好的催化作用。连续水解测试结果显示: 水解产物 Al(OH)₃/NaBO₂·2H₂O 具有稳定的 pH 值, Al–Li–Ni/NaBH₄ 混合物具有很好的水解动力学。

关键词: 水解析氢; 铝锂合金; 硼氢化钠; 镍

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