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Hydrolysis of ball milling Al–Bi–hydride and Al–Bi–salt mixture for hydrogen generation

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Abstract

In this paper, an effective method to produce hydrogen via the hydrolysis of the milled Al–Bi–hydride (or salts) in pure water at room temperature has been found. The result shows that the Al–Bi–hydrides (or salts) prepared by 5 h milling appear very effective to improve their hydrolysis reactivity. And the milled Al–Bi–hydrides (or salts) have high hydrogen yield in pure water, especially the Al–10 wt.% Bi–10 wt.% MgH_2 mixture or Al–10 wt.% Bi–10 wt.% $MgCl_2$ mixture all can produce 1050 ml/g within 5 min. The improvement mainly comes from three factors: (1) the additives (MgH_2, CaH_2, LiCl, $MgCl_2$, KCl, etc.) play an important role to decrease the mean size of the mixture particles; (2) the exothermic dissolution of the salt additive such as $MgCl_2$ can increase the temperature of aqueous solution, favoring the reaction between Al–Bi composite and water; (3) the hydrolysis of the additives can also offer conductive ions on the work of the micro-galvanic cell of Al–Bi composite. Furthermore, the high conductive ions around the Al–Bi composite are the uppermost effect for increasing the hydrogen yield and hydrogen generation rate.

Keywords: Hydrolysis; Hydrogen generation; Ball milling; Chemical hydride

1. Introduction

Hydrogen will be directly used in internal combustion engines or fuel cells because hydrogen is a clean energy and has a large combustion value. But now the expensive production and storage cost limit its application. Many types of hydrogen source (e.g. coal [1], chemical hydrides [2–10], metals [11–16]) are introduced to find an efficient and low cost method for storing and supplying hydrogen. One of the most attractive means of hydrogen storage is the use of compound $NaBH_4$, which can produce a large lot of pure H_2 and display a more controllable reactivity by reacting with water in the presence of a catalyst. So $NaBH_4$ is widely studied and expected to be scalable for systems providing power from 5 W to kW levels. For example, Kojima et al. [4] has developed a hydrogen generator that generates high purity hydrogen gas from the aqueous solution of $NaBH_4$ and it successfully provided a maximum H_2 generation rate of 120 nl/min. Assuming a standard PEM (polymer electrolyte membrane) fuel cell operated at 0.7 V, generating 120 nl/min was equivalent to 12 kW. However, the price and availability of catalyzed $NaBH_4$ is a considerable barrier for mass markets when the catalyst has the inconvenient to be a dead weight and may be degraded upon hydrolysis [6].

Simple and complex hydrides of early second- and third-row metals [10–17], which can produce hydrogen in reactions with water, hold promise as hydrogen sources for their high theoretic hydrogen yields. The yield and kinetics of hydrolysis of MgH_2 for hydrogen generation can be improved by using MgH_2–X (X = Ca, Li, $LiAlH_4$, CaH_2) [12,13] composite materials prepared by ball milling. The best performance was obtained with MgH_2 + 20 mol% CaH_2 powder mixture milled for 10 h, leading to a reaction yield close to 80% after 30 min of hydrolysis with excess water. Grosjeana et al. [14] found that hydrolysis reaction of Mg and Mg–Ni composite, which obtained by high-energy ball milling of 30 min, was faster and extensive when they were

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immersed in 1 M KCl. It is related to the creation of micro-galvanic cells between Mg and dispersed Ni elements, which accelerates greatly Mg corrosion in highly conductive aqueous media. Moreover, Mg or MgH_2 milled with some salts (LiCl, $MgCl_2$, KCl) has high hydrolysis reactivity in pure water. It is found that the 0.5 h milled MgH_2–3 mol% $MgCl_2$ composite can produce 964 ml/g hydrogen in pure water at room temperature. To compare that 1 g Mg reacts with water to produce 933 ml H_2, Al has a higher hydrogen yield of 1245 ml/g. Although Al is highly inert to water, Al alloys can be activated by ball melting with light metals (Sn, Ga, Bi, Zn, etc.) and reacts with water to produce hydrogen in hot water. Kravchenko et al. [15] developed the aluminum-based metal composites doped with Ga, In, Zn and Sn, and found the alloy had high reactivity and produced 1060 ml/g hydrogen in pure water at 82 °C. Zhu et al. [16] also found that the annealed melted Al–9.4 wt.% Bi alloy could react with water slowly at room temperature. In the recent work, we have found that the milled Al–Bi alloys have high reactivity and fast hydrolysis rates in pure water at room temperature, especially in the presence of chloride ions. This performance was explained by the accentuation of the pitting corrosion of Al due to the creation of numerous defects and fresh surfaces through the milling process, the formation of micro-galvanic cell between the anode (Al), cathode (Bi), and high ionic conduction.

In this work, we investigated the hydrolysis properties of Al–Bi–hydride and Al–Bi–solid salt mixtures treated by ball milling. The aim is to accelerate the hydrolysis rate and improve the hydrogen yields of the mixtures in pure water at room temperature.

2. Experimental

The starting materials are elemental powders of pure Al, Bi, MgH_2 (98 wt.%), CaH_2 (97 wt.%), KCl, NaCl, LiCl and $MgCl_2$ salts. The Al powder size is approximately 13 μm and the powder size of other materials is confined in 100–300 μm. The composites were mixed in an argon-filled glove box. Then ball milling was performed by QM-1SP planetary ball miller under 0.2–0.3 MPa argon atmosphere. Ball-to-powder mass ratio corresponds to 30:1. The hydrolysis reaction of the mixture (0.1 g) with pure water was carried out in a stainless steel chamber attached to a gas burette graduated in 0.1 ml increments at room temperature. The gas produced was flowed through a condenser and drierite to remove all water vapour before measurement of H_2 volume. The hydrogen volume was measured by the water trap method and the generation rate was calculated from the amount evolved from the beginning of the test. Hydrogen production is expressed as conversion yield (%) defined as the volume of produced hydrogen over the theoretical volume of hydrogen that should be released, assuming that all material is hydrolyzed. Microstructure studies (EDX analysis) were performed on a CAMEBAX-microbeam electron microprobe equipped with a KEVEX energy–dispersive analyzer.

3. Results and discussion

3.1. Hydrolysis properties of milled Al–Bi–CaH_2 mixture

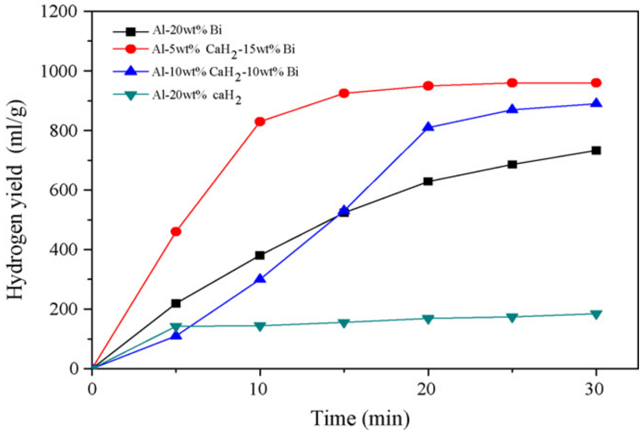

Fig. 1. Hydrogen generation of the hydrolysis of Al–Bi–CaH_2 mixture in water.

Fig. 1 shows the kinetics curves of hydrogen evolution for the milled Al–Bi–CaH_2 mixtures with different contents of Bi and CaH_2 at room temperature. The hydrolysis reactions of the milled Al–20 wt.% CaH_2 mixture with water proceeded very slowly. It can be seen that the Al–CaH_2 mixture produces 120 ml/g hydrogen in hydrolysis of 30 min as shown in Fig. 1, and continues slowly to generate 450 ml/g hydrogen in 24 h. The hydrogen firstly comes from the hydrolysis of CaH_2 ($CaH_2 + 2H_2O = Ca(OH)_2 + H_2$) and then it is from the hydrolysis of Al in the presence of alkali solution ($Ca(OH)_2$). The Al–20 wt.% Bi alloy holds quicker hydrolysis rate, and produces 73.13% (733 ml/g) of the expected amount of hydrogen in 0.5 h of the hydrolysis as Al–Bi alloy displays the low hydrogen overpotential, and improves Al reactivity. The positive effect of the added Bi can be explained as the formation of the micro-galvanic cell composed of Bi cathode and Al anode, which speeds up the Al anode corrosion. When Bi is substituted by CaH_2 partially, it is found that the hydrolysis reaction of Al–Bi–CaH_2 mixture has a higher hydrogen generation rate than that of Al–Bi alloy as indicated in Fig. 1 and it also provides a larger hydrogen yield. The hydrogen yield reaches 91.42% (960 ml/g) for Al–15 wt.% Bi–5 wt.% CaH_2 mixture, and 80.76% (890 ml/g) of Al–10 wt.% Bi–10 wt.% CaH_2 mixture in 0.5 h of the hydrolysis. The higher reactivity of the mixtures is obviously related to the hydrolysis of CaH_2. The hydrolysis of CaH_2 can provide an alkali medium and releases the heat of 186 kJ/kg when Al–Bi–CaH_2 mixture contacts with water. The hydrolysis of CaH_2 can produce many conductive ions on the surface of Al–Bi composite in very short time, which favors the work of micro galvanic cells and results to a higher hydrolysis rate. But the hydrogen yield can be decreased from 960 to 890 ml/g with the increasing content of CaH_2 from 5 to 10%.

The mass ratio of the milled Al–Bi–CaH_2 mixture to water has a great effect on the hydrogen generation rate. It can be seen from Fig. 2 that the hydrolysis reaction ceases in 3 min and produces 1020 ml/g hydrogen when the mass ratio of the milled Al–10 wt.% Bi–10 wt.% CaH_2 mixture to water is 1:10, while there are only 1010 ml/g hydrogen generated in 5 min when the mass ratio changes from 1:10 to 1:20. Furthermore, the hydrogen generation rate continues to decrease when the mass ratio changes from 1:20 to 1:50. The reason is that the hydrolysis reaction of Al–10 wt.% Bi–10 wt.% CaH_2 mixture can release a lot of heat, including hydrolysis heat 186.3 kJ/mol of CaH_2 [9] and 444.4 kJ/mol of Al [17]. A higher temperature can be obtained at a larger mass ratio of the milled A–10 wt.% Bi–10 wt.% CaH_2 mixture to water, which results in a faster hydrogen generation

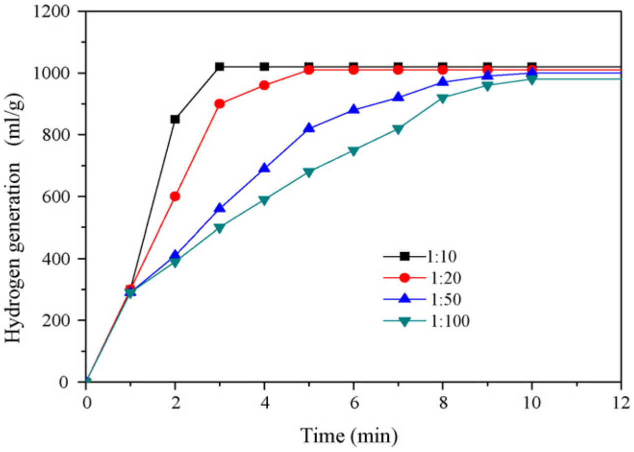

Fig. 2. Influence of different mass ratio of Al–10 wt.% Bi–10 wt.% CaH_2 mixture and water on hydrogen generation in the hydrolysis.

rate, as the kinetic of hydrolysis reaction is improved with the temperature increasing.

Milling time has some effects on the Al reactivity. It is confirmed in Fig. 3, which presents the hydrolysis rates of Al–15 wt.% Bi–5 wt.% CaH_2 mixture and Al–10 wt.% Bi–10 wt.% CaH_2 mixture in pure water as a function of milling time. The hydrolysis rate and hydrogen generation of Al–Bi–CaH_2 mixtures are increasing with the increase of milling time, and the hydrolysis efficiency reaches maximum for 5 h milling, then the hydrolysis rate and hydrogen generation of Al–Bi–CaH_2 mixtures decrease over 5 h milling. Indeed, the 5 h milled Al–Bi–CaH_2 mixture has the highest hydrogen yield of 89% for Al–10 wt.% Bi–10 wt.% CaH_2 mixture and 92% for Al–15 wt.% Bi–5 wt.% CaH_2 mixture in the hydrolysis of 30 min. Furthermore, Al–Bi–CaH_2 mixtures have the highest hydrogen production rate of 186 ml/g for Al–10 wt.% Bi–10 wt.% CaH_2 mixture and 190 ml/g for Al–15 wt.% Bi–5 wt.% CaH_2 mixture in the first 5 min of hydrolysis reaction. The improvement of mixture reactivity is partly resulted from the decrease of the particles size (already proved by the MgH_2–CaH_2 mixtures [13]). Fig. 4a and b show the SEM of 5 h milled Al–20 wt.% Bi alloy and Al–15 wt.% Bi–5 wt.% CaH_2 mixture. The results confirm that many defects and fresh surfaces are created in the milling process, compared to the unmilled Al powder in Fig. 4d. It can be seen that the shapes of Al particles change from the initial round (Al powder) to platelet (Al–20 wt.% Bi alloy of milled 5 h, Fig. 4a) and its mean size increases markedly from 13 to 100 μm. But Al particles become smaller when Al–Bi composite is milled with CaH_2. For Al and Bi powders during 5 h milling, the large alloy platelets have mean sizes above 100 μm, but when Al and Bi powders milled with CaH_2 for 5 h, the mixture powders have mean sizes about 10 μm. And the additional CaH_2 has been homogeneously distributed in the Al–Bi alloy, which is also confirmed from the EDX (shown in Fig. 4b).

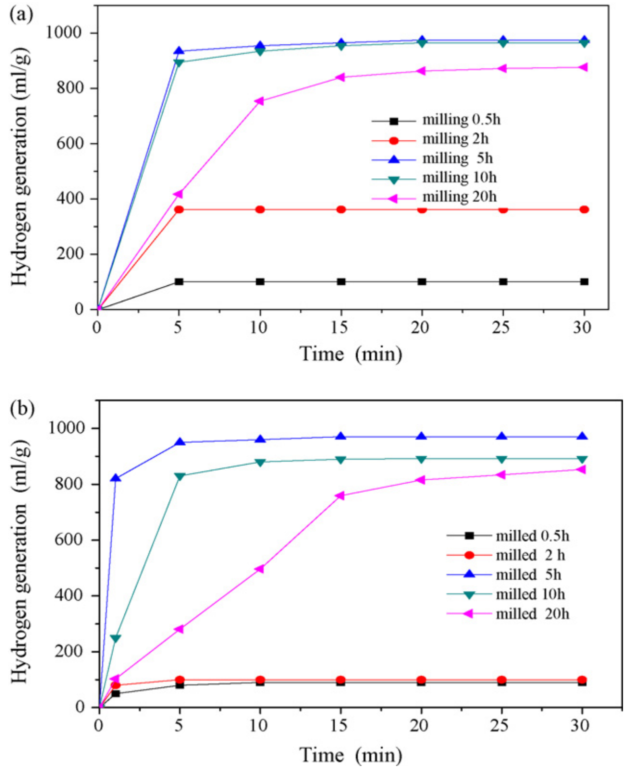

Fig. 3. Hydrogen generation of the hydrolysis of aluminum alloy in water at different milling time; (a) Al–15 wt.% Bi–5 wt.% CaH_2 mixture; (b) Al–10 wt.% Bi–10 wt.% CaH_2 mixture.

3.2. Hydrolysis properties of Al–Bi–MgH_2 mixture

Fig. 4c displays the SEM of Al–10 wt.% Bi–10 wt.% MgH_2 mixture of 5 h milling. It can be seen that the mixture has a mean size about 10 μm. Therefore, the hydride (CaH_2, MgH_2) additives have great influence on the mean size of Al and Bi particles in the ball milling which includes the repeated fracturing and cold welding processes. The hydride additives play an important role for preventing the necessary contact in cold welding for Al-to-Al and Bi-to-Bi, so the fracturing performance of mixture powder is promoted. The same effect was also found by Grosjean et al. [11] who studied the relation of specific surface area of Mg–KCl mixtures with the milling time.

Fig. 5 shows the hydrogen production curves for reaction of 5 h milled Al–10 wt.% Bi–10 wt.% hydride (MgH_2, CaH_2) mixtures with pure water. It can been seen that the Al–Bi–hydride mixtures have great reactivity in the first 15 min of the hydrolysis, especially that Al–10 wt.% Bi–10 wt.% MgH_2 has a very faster hydrolysis rate of 200 mL/min in the first 5 min. Al–10 wt.% Bi–10 wt.% MgH_2 and Al–10 wt.% Bi–10 wt.% CaH_2 produce hydrogen 1050 ml/g and 960 ml/g in the end, respectively. The high hydrogen yields and good kinetics of the mixtures come from the following reasons. In addition to that the smaller mean size of the mixtures particles can speed up the hydrolysis reaction, the hydrolysis reaction releases a lot of heat (277 kJ/mol for MgH_2; 186.3 kJ/mol for CaH_2 [9]), which also increase kinetics of the hydrolysis of Al–Bi composites. For example, the heat of the hydrolysis of MgH_2 can lead to increase about 1 °C for 100 mg Al–10 wt.% Bi–10 wt.% MgH_2 mixture immersed in 20 ml of pure water by the calculation. And there is a peak temperature on the surface of the mixture in a very short time when MgH_2 begins to hydrolysis. Furthermore, the

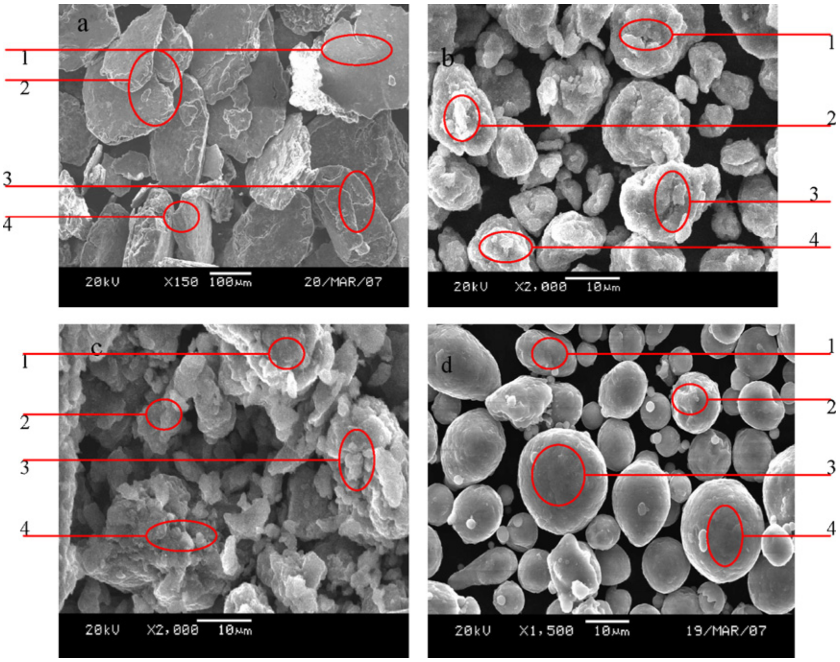

Fig. 4. SEM of 5 h milled materials (a) Al–20 wt.% Bi alloy; (b) Al–15 wt. Bi–5 wt.% CaH_2 mixture; (c) Al–10 wt.% Bi–10 wt.% MgH_2 mixture; (d) the unmilled Al powder. Compositions in designed fields (mass%). (a)—(1) Al-74.63, O-8.49, Bi-14.48; (2) Al-81.51, O–6.25, Bi-14.58; (3) Al-69.52, O-2.7, Bi-27.78; (4) Al-70.68, O-2.76, Bi-26.56. (b)—(1) Al-76.37, O-7.29, Ca-7.99, Bi-8.35; (2) Al-76.14, O- 7.47, Ca-7.76, Bi-8.63; (3) Al-75.10, O-7.85, Ca- 8.05, Bi-9; (4) Al-75.74, O-7.86, Ca-7.87, Bi-8.54. (c)—(1) Al-77.37, O-9.34, Mg-6.59, Bi-6.7; (2) Al-76.84, O-9.87, Mg-7.06, Bi-6.23; (3) Al-76.70, O-9.15, Mg-7.12, Bi-7.03; (4) Al-78.04, O-8.86, Mg-6.75, Bi-6.35. (d)—(1) Al-75.34, Bi-22.87, O-1.79; (2) Al-70.17, Bi-27.48, O-2.36; (3) Al-75.3, Bi-21.63, O-3.07; (4) Al-76.49, Bi-21.71, O-1.8.

hydrolysis of MgH_2 produces conductive ions (Mg^{2+}, OH^-), which are helpful to the formation of the galvanic cell between the anode (Al) and cathode (Bi).

3.3. *Hydrolysis properties of milled Al–10 wt.% Bi–10 wt.% salt composites*

Fig. 6 shows the influence of the salts (KCl, NaCl, LiCl, $MgCl_2$ and $AlCl_3$) on the hydrolysis reactivity of 5 h milled Al–10 wt.% Bi–10 wt.% salt composites with pure water. The salt addition has great effects on the hydrogen yield and kinetics of hydrolysis reaction of the Al–Bi–salt composites with water. Especially, $MgCl_2$ addition makes the Al–Bi–$MgCl_2$ composite produces 1050 ml/g in 5 min of hydrolysis, in comparison to 1040 ml/g, 840 ml/g, 870 ml/g and 900 ml/g for Al–Bi composite with LiCl, NaCl, KCl and $AlCl_3$, respectively. The improvement of hydrolysis reactivity of the Al–Bi–salt composite is concerned with the addition of salt (already confirmed in [14]). The addition of salt has an important role to decrease the mean size of Al–Bi alloy, and their enthalpy of dissolution in water (−155 kJ/mol for $MgCl_2$, −40 kJ/mol for LiCl, 4 kJ/mol for NaCl, 18 kJ/mol for KCl) can heighten the temperature of the aqueous solution. At the same time, it plays a crucial role

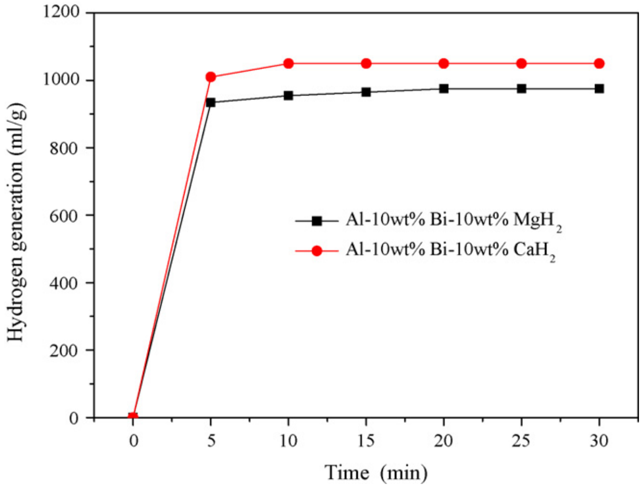

Fig. 5. Hydrogen generation of the hydrolysis of Al–Bi–CaH_2 (MgH_2) mixture in water.

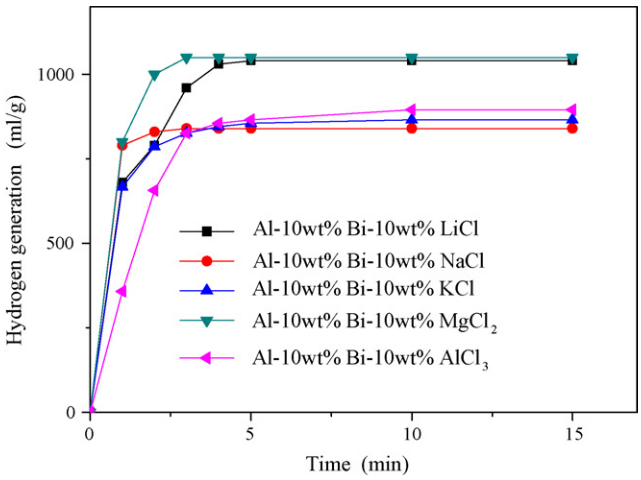

Fig. 6. Hydrogen production profiles for reaction of 5 h milled Al–10 wt.% Bi–10 wt.% salts (KCl, NaCl, KCl, $MgCl_2$ and $AlCl_3$) mixture with water.

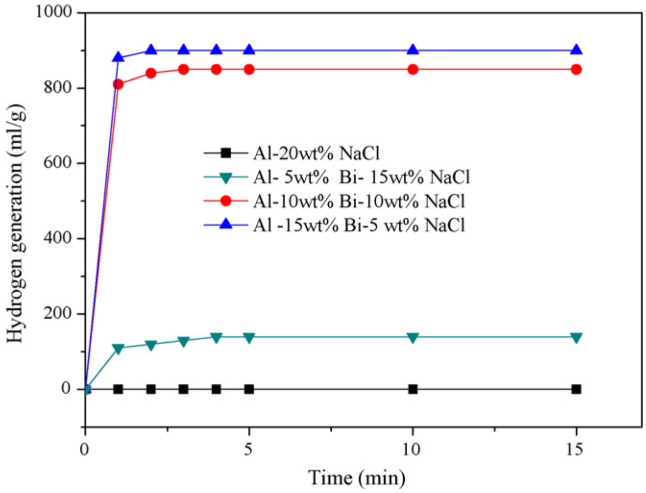

Fig. 7. Hydrogen generation of the hydrolysis of Al–10 wt.% Bi–10 wt.% NaCl mixture in water.

that the dissolution of salts offers high conductive ions accelerated on the formation of micro-galvanic cell of Al–Bi alloy. As shown in Fig. 7, the milled Al–20 wt.% NaCl composite can not hydrolyze to produce hydrogen, but the milling Al–5 wt.% Bi–15 wt.% NaCl composite can generate 140 mL/g hydrogen in pure water. When Bi content increases, it has been found that both the milling Al–10 wt.% Bi–10 wt.% NaCl composite and Al–15 wt.% Bi–5 wt.% NaCl composite can produce much more hydrogen with faster hydrolysis rates.

The hydrolysis mechanism of Al–Bi–X (hydrides, salts) is based on the work of micro-galvanic cell in the following formulas (1) and (2):

$$3H_2O(Bi) + 3e^- \Rightarrow \frac{3}{2}H_2 + 3OH^- \quad (1)$$

$$Al + 3OH^- - 3e^- \Rightarrow AlOOH(Bauxite) + H_2O \quad (2)$$

From the above formulas, increasing OH^- is very favorable to the hydrolysis reaction. As compared with salts, the metal hydrides can firstly produce hydrogen by hydrolysis, and then release OH^- (see formulas (3) and (4)) which also accelerates hydrolysis reaction process.

$$MH_x + xH_2O \Rightarrow M(OH)_x + xH_2 \quad (3)$$

$$M(OH)_X \Rightarrow M^{x+} + xOH^- \quad (4)$$

This explains the additional hydrides are important to the Al hydrolysis. As to the salts, the Cl^- can change the hydrolysis approach of the anode Al as follows [18].

$$Al + Cl^- - e^- \Rightarrow AlCl^- \quad (5)$$

$$AlCl^- + 2H_2O \Rightarrow AlOOH + H_2 + Cl^- \quad (6)$$

4. Conclusions

It is an effective method to produce hydrogen from the hydrolysis of the milled Al–Bi–hydride or Al–Bi–salt mixtures in pure water. Al–Bi alloy was ball milled with different hydrides or solid salts. Depending of the synthesis parameters (mass ratio of Al alloy and water, milling duration, hydride or salt amount and composition), a great improvement of hydrolysis reactivity for the Al–Bi alloy was observed. The results indicate the mixtures have a high hydrogen yield and hydrolysis rate. The improvement of reactivity for Al–Bi–hydride or salt mixtures is explained by three factors: (1) the decrease of mean size of the mixture; (2) the driving force related to the exothermic dissolution of the additive such as MgH_2, $MgCl_2$; (3) the conductive ions is helpful for the formation of micro-galvanic cell of Al–Bi alloy. The 5 h milled Al–10 wt.% Bi–10 wt.% MgH_2 mixture and Al–10 wt.% Bi–10 wt.% $MgCl_2$ mixture have very fast hydrolysis rate, and all can produce 1050 ml/g hydrogen that corresponds to a hydrogen yield of 93.4 wt.% when the water weight is not included in the calculation.

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