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# Hydrogen Generation of Al-La-Bi Alloy in Aqueous Inorganic Salt Solutions

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***Abstract:*** *A method for obtaining hydrogen from Al-La-Bi alloy in different solutions was investigated for the production of inexpensive, pure, and safe hydrogen for micro-fuel cells. The hydrogen generation amount and rate could be regulated by changing composition design or salt solutions. Combined with X-ray diffraction (XRD), scanning electron microscopy (SEM) and hydrogen generation experiments, the hydrolysis byproduct* $La(OH)_3$ *and inorganic salt solution stimulated the hydrolysis reaction of Al-La-Bi alloy and water, which was mostly based on micro galvanic cell between Al and Bi in the previous work. Increasing La content led to decrease particle size in the milling process which led to large special surface area and contact area of aluminum and water. Using inorganic salt solution such as* $Na_2SnO_3$ *solution might produce metal Sn which covered on Al surface and functioned as a cathode of a micro galvanic cell. The Al-13 wt%La-10 wt%Bi alloy yielded 1113 ml/g hydrogen with 100 % efficiency with 60 min at 343 K.*

*Keywords: Hydrogen generation; Aluminum; Lanthanum; Bismuth*

## 1. INTRODUCTION

The development of proton exchange membrane fuel cell (PEMFC) in vehicles and portable electronics is helpful to decrease the problems of environmental pollution and energy crisis as electricity can be generated by consume of hydrogen energy and oxygen in PEMFC. Hydrogen is a non–polluting energy which can be generated by water electrolysis, methane reform, etc, with a low cost, but hydrogen storage still meets many problems such as hydrogen storage density, cost, efficiency and security. Large scales of hydrogen storage with high efficiency and low cost is a key problem to limit the commercial application of PEMFC. There are many achievements in developments of solid–state hydrogen materials and technologies in the past decades [1]. However, they cannot supply reversible above 5 wt% hydrogen at mild conditions to fulfill the practical operation of PEMFC. For example, some new hydrogen storage materials such as $NH_3BH_3$, $LiBH_4$, etc., have high theoretic hydrogen storage value but have to release hydrogen at temperature higher than 373 K [2]. In comparison with the reversible hydrogen storage materials, on–board hydrogen generation from aluminum hydrolysis may provide a more realistic alternative for near–term hydrogen storage applications.

Hydrogen generation from aluminum hydrolysis has been paid attention widely due to its advantages such as high theoretic hydrogen generation density, safe, controllable and mild operating conditions. The hydrolysis byproduct AlOOH or $Al(OH)_3$ are eco–friendly and easily recyclable. Many achievements showed that Al–based hydrogen generation system attached to PEMFC can provide 2 W–10 kW powers [3, 4]. However, Al has a disadvantage that alumina layer covered on Al surface reduces Al reactivity and prevents the sustainable aluminum hydrolysis in water.

It is a good method that aluminum–based mixtures doped with some metals [5, 6], metal salts [7, 8] and oxides [9] had high reactivity in neutral aqueous solution at moderate temperature. The additives could destroy the alumina layer covered on Al surface or make Al potential shift negatively in the hydrolysis process. Kravchenko found that Al–Ga alloy had 100% efficiency at 333 K and its hydrolysis rate could be enhanced by In and Zn additives [5]. Czech [7] found that aluminum powder milled with water−soluble inorganic salts released 1095 ml hydrogen/1g Al in 1 hour of reaction at 333 K and hydrogen production could be further increased up by increasing ball−milling duration and global temperature. Dai [10] found that $Na_2SnO_3$ solution could dramatically improve the hydrogen generation kinetics of the Al–$H_2O$ system. It is a pity that the additives cannot react with water and more additive content leads to lower hydrogen generation density.

Recently, hydrogen generation from aluminum alloys doped with rare earth metals [11], alkaline metals [12] and alkaline earth

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metals [13] are considered. Theses metals can react with water at mild conditions and produce hydrogen and alkaline solution. The alkaline solution further acts as a good catalyst to accelerate aluminum hydrolysis. Compared to other additive metals, Metal lanthanum is a good choice as hydrogen generation material due to its abundance in the earth and strong reducibility. It has a controllable hydrolysis rate, and its hydrolysis byproduct $La(OH)_3$ presents alkaline, which accelerates the hydrolysis kinetic of magnesium [14].

In this work, environment–friendly and highly activated Al-La-Bi composite materials have been prepared by ball milling method to obtain high, safe and portable hydrogen. The hydrogen generation performance of Al-La-Bi alloy in different solutions is illustrated in detail to explore the effect of La content and salt. It was thought that the strong reducibility of La and the microstructure of La and Bi distributed into Al matrix improved hydrogen generation efficiency.

## 2. EXPERIMENTAL

### 2.1. Preparation of Al-La-Bi alloys

Aluminum powder (mean size, 70μm, common grade), La powder (250 um, 99.9% purity) and Bi powder (1 mm, 99.9% purity) supplied by Tianjin Delan Chemical Company, were used as the starting materials. The powders were mixed and put in 50 mL stainless steel jars with stainless steel milling balls, which were fixed in an argon−filled glove box. The ball to alloy weight ratio is 26:1. Finally the alloys were milled for 5 h in a QM-3SPO$_4$ planetary ball miller at 450 r min$^{-1}$ under 0.2 MPa argon atmospheres.

### 2.2. Measurement of hydrogen evolution

The hydrolysis properties of Al-La-Bi alloys were carried out in different solutions at 343 K. The weight of Al alloy was 0.5 g and the volume of solutions was 4 mL. NaOH, $Na_2SnO_3$, NaCl, $InCl_3$, $CuCl_2$ (AR) were bought from Chinese reagent Company. The alloy powder was pressed into tablets in a stainless steel mould (Its diameter is 10 mm) under 2 ton pressure before the hydrolysis reaction. At the set temperature, the Al alloys was thrown in solutions and the produced gas was flowed through a condenser prior to measurement of the hydrogen volume. The produced hydrogen volume was measured by monitoring water displaced from a graduated cylinder as the reaction proceeded. The reaction time was beginning with the first bubble and the final volume of the produced hydrogen was collected in 1 h of the reaction at 298 K and 1 atm. Efficiency was defined as the generated hydrogen volume over the theoretical hydrogen volume of 1g alloy, which can react with water completely.

### 2.3. Characterization

Powder X−ray diffraction patterns (XRD) of the as−prepared samples were collected by an X−ray diffractometer (RIGAKU, Japan, model, D/MAX2550V/PC) over a range of diffraction angle (θ) from 2θ = 10° to 2θ = 80° with Cu Kα radiation filtered by a monochromater.. Scanning electron microscopy (SEM) observations were performed using the model JSM−5610LV from JEOL Company which was equipped with INCA energy dispersive X−ray spectroscopy measurements (EDS). Particle size distribution of the as–prepared samples was measured by a particulate size description analyzer (Dandong Better size, China, specification, BT−2003). Surface area was collected by a surface area and porosity analyzer (Micromeritics, USA, model ASAP2020). The solid hydrolysis byproduct in the reactor was filtered using a vacuum pump and then dried in an oven at 313 K.

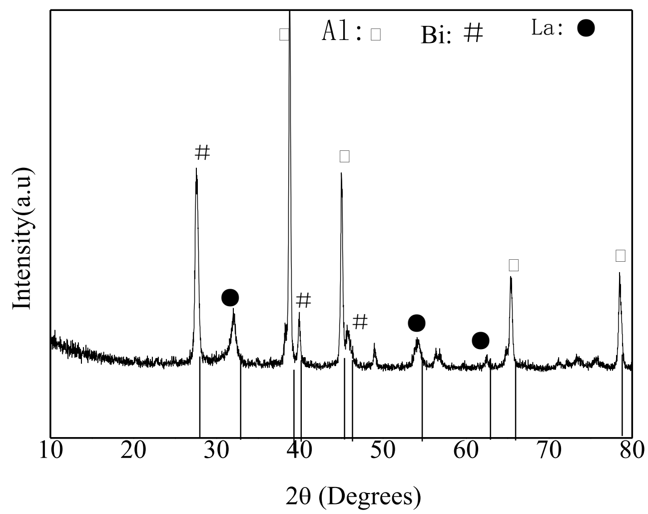


Figure 1. XRD patterns of milled Al-13 wt%La-10wt%Bi alloy

## 3. RESULTS AND DISCUSSION

### 3.1. Characteristic of milled Al-La-Bi alloy

Fig. 1 shows XRD patterns of milled Al-13 wt%La-10wt%Bi alloy. The peaks of La, Al and Bi are identified, reflected that they have not formed alloy compound in the milling process. There exists a slight shift between the results and the peaks of pure metals, showing that the solid solution between Al, Bi and La is obtained. The solid solubility of La and Bi in Al was 0.01 and 0.03 at% at 913 K, respectively [15, 16]. Averaged solubility data indicated that 0.02 at% La was soluble in Bi at 573 K and 1.2 at% at 873 K [17]. The formation of the solid solution prevents the combination of Al-Al, Bi-Bi and La-La, resulting in the decreased particle size in the milling process. So it can be found that the particle size is decreased with increasing La content in Fig. 2. The milled Al-1 wt%La-10 wt%Bi alloy has averaged 500 um particle size. With La content increased to 5 wt%, the milled alloy has averaged 200 um particle size. With La content further increased to 13 wt%, the alloy only has averaged 100 um particle size. Decreased particle size of the alloy means to uniform mixing of Al and Bi. In addition, Decreased particle size also leads to large special surface area and contact area of aluminum and water.

### 3.2. Kinetics of the hydrogen generation

Fig. 3 shows effect of La content on hydrogen generation performance of Al-La-Bi alloys at 343 K. Hydrogen generation amount and rate are increased with increasing La content. The Al-1 wt%La-10 wt%Bi alloy yields 678 ml/g hydrogen within 60 min, with 194 ml/g.min maximum hydrogen generation rate and 56% efficiency. The Al-13 wt%La-10 wt%Bi alloy yields 1113 ml/g hydrogen at the same conditions, with 927 ml/g.min maximum hydrogen generation rate and 100% efficiency. La metal can react

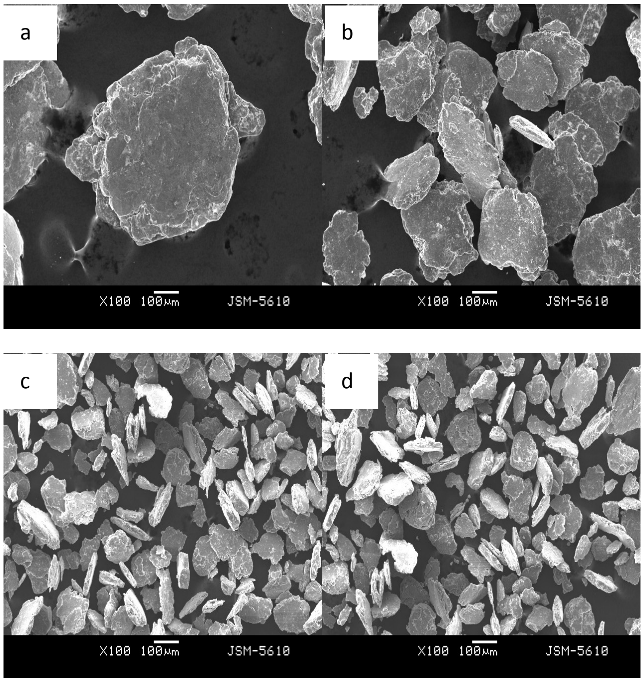


Figure 2. SEM images of milled Al-La-Bi alloys. a, Al-1 wt%La-10 wt%Bi alloy; b, Al-5 wt%La-10 wt%Bi alloy; c, Al-9 wt%La-10 wt%Bi alloy; d, Al-13 wt%La-10 wt%Bi alloy

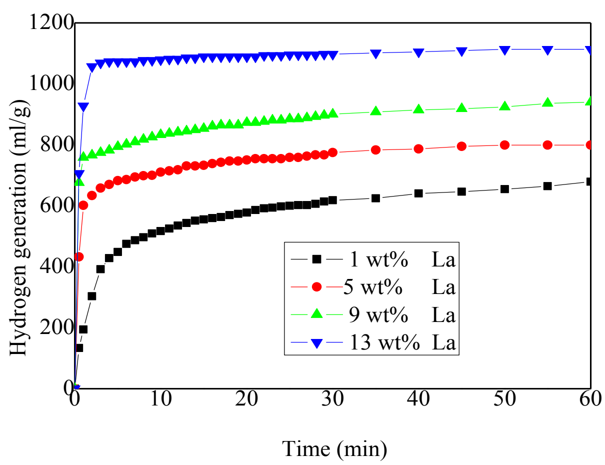


Figure 3. Hydrolysis characteristic of Al-10 wt%Bi alloy with different La content in water.

with water to produce hydrogen and its hydrolysis byproduct presents alkaline, which may accelerate the hydrolysis kinetic of aluminum and water. With La content increasing from 1 wt% to 13 wt%, the pH value of the hydrolysis byproduct of the Al-La-Bi alloys increases from 8.7 to 9.6. Therefore, the increased alkaline concentration stimulates the hydrolysis reaction of Al-La-Bi alloy and water.

Fig. 4 shows hydrolysis characteristic of Al-10 wt%Bi alloy with different La content in 1 M NaCl solution and 0.1 M $Na_2SnO_3$ solution. The alloys have better hydrogen generation performance in 1

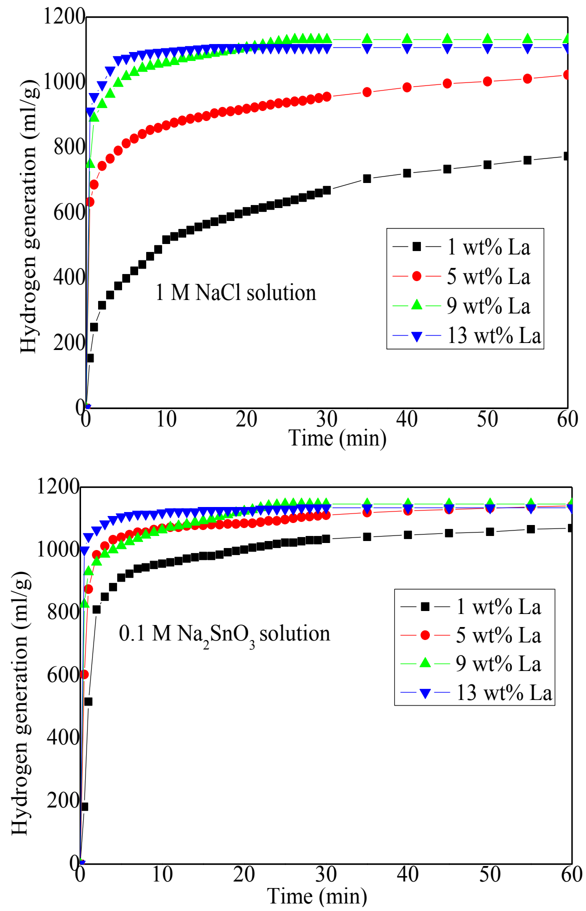


Figure 4. Hydrolysis characteristic of Al-10 wt%Bi alloy with different La content in different solutions.

M NaCl solution and 0.1 M $Na_2SnO_3$ solution than that in pure water. Combined with Fig. 3, the inflection points of hydrogen generation curves in Fig. 4 are brought forward, reflecting that the hydrogen generation rate is increased and the hydrolysis reaction needs less time. The hydrogen generation amount is also increased (except Al-13 wt%La-10 wt%Bi alloy), especially to the alloys with lower La content. There exists a same trend that the hydrogen generation performance is improved with increasing La content in pure water, 1 M NaCl solution and 0.1 M $Na_2SnO_3$ solution. But the effect of La content is decreased in the solutions with the order of pure water, 1 M NaCl solution and 0.1 M $Na_2SnO_3$ solution. For example, Al-5 wt%La-10 wt%Bi alloy, Al-9 wt%La-10 wt%Bi alloy and Al-13 wt%La-10 wt%Bi alloy have more similar hydrogen generation performance in 0.1 M $Na_2SnO_3$ solution than that in pure water.

In order to elaborate the effect of the solutions on hydrogen generation performance of Al-La-Bi alloys, Fig. 5 further shows their efficiencies of the alloys and pH values of their hydrolysis byproducts. Al-1 wt%La-10 wt%Bi alloy has the efficiencies of 59%, 68% and 89%, corresponded to the order of pure water, 1M NaCl solution and 0.1 M $Na_2SnO_3$ solution. Al-9 wt%La-10 wt%Bi alloy has the efficiencies of 84%, 100% and 100% in the solutions with the

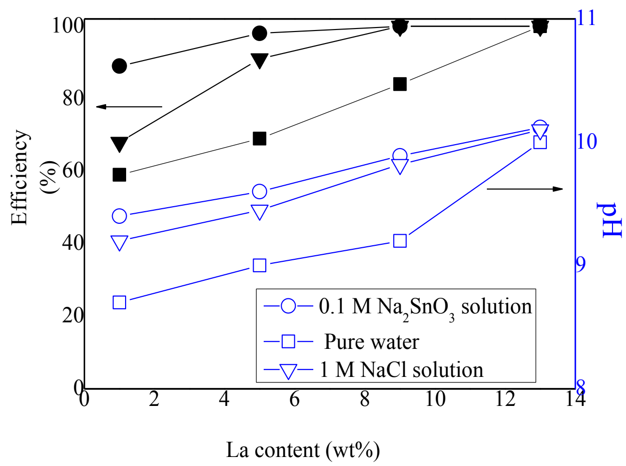


Figure 5. Efficiency and pH of Al-10 wt%Bi alloy with different La content in different solutions.

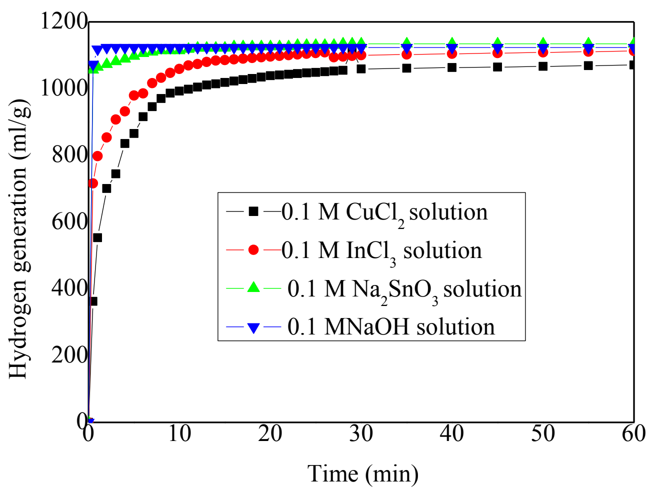


Figure 6. Hydrolysis characteristic of Al-9 wt%La-10 wt%Bi alloy in different solutions.

same order. That means that the different solutions have great effect on the hydrogen generation amount and rate on Al-La-Bi alloys with low La content, but the solutions only have the effect on the hydrogen generation rate of Al-La-Bi alloys with high La content. The pH values of the hydrolysis byproducts of Al-La-Bi alloys are proportional to La content, but the solution property also affects pH values of the hydrolysis byproduct of the alloys with low La content. The hydrolysis byproducts of Al-xwt%La-10 wt%Bi alloys (1<x<9) has higher pH values in 1M NaCl solution and 0.1 M $Na_2SnO_3$ solution than those in pure water.

Fig. 6 shows hydrolysis characteristic of Al-9 wt%La-10 wt%Bi alloy in different solutions. The solutions have great effect on hydrogen generation performance of the alloy and make the efficiency arrived to 100%, except $CuCl_2$ solution. Meanwhile, the maximum hydrogen generation rate of the alloy in 0.1 M NaOH solution and 0.1 M $Na_2SnO_3$ solution reach 1118 ml/g.min and 1064 ml/g.min. That means above 95% hydrogen was generated in the first minute

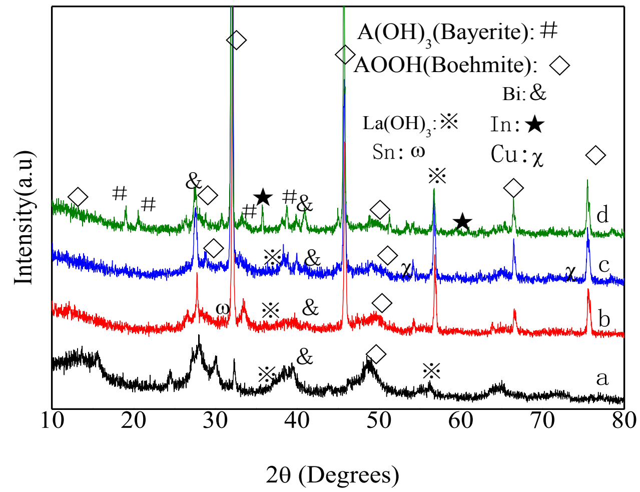


Figure 7. XRD patterns of hydrolysis of Al–9 wt%La–10 wt%Bi alloys in different solution within 60 min. a, water; b, 0.1 M $Na_2SnO_3$; c, 0.1 M $CuCl_2$; d, 0.1 M $InCl_3$.

of the hydrolysis process, so the controllable hydrogen generation rate can be further obtained via decreasing the concentration of NaOH and $Na_2SnO_3$ solution. In contrast, the alloy in o.1 M $CuCl_2$ solution and 0.1 M $InCl_3$ solution have relatively stable hydrogen generation rate. The Al-La-Bi alloy has the gradually improved reactivity according to the order of NaOH> $Na_2SnO_3$> $InCl_3$> $CuCl_2$.

### 3.3. Hydrolysis mechanism of Al-La-Bi alloy in different solutions

The hydrolysis of Al-Bi alloy was based on micro galvanic cell between anode Al and cathode Bi, according to Eq.1-5[18]. The activated Al particle firstly combined with hydroxide ions to produce AlOH and release electrons. The unstable AlOH species had a significant oxidation potential and quickly converted to the AlOOH (Boehmite) [19, 20]. Meanwhile, electrons were transferred from Al anode to Bi cathode and hydrogen gas was generated on Bi surface where hydrogen ions obtained electrons to produce hydrogen atoms and the hydrogen atoms were combined to produce hydrogen molecule.

There are peaks of $Al(OH)_3$ and AlOOH identified in XRD patterns of hydrolysis byproducts of Al-La-Bi alloys in water in Fig. 7a, showed that the addition of La metal can change the hydrolysis mechanism of Al-Bi alloy in some degrees. La metal can react with water to produce $La(OH)_3$ and $H_2$. Hydrolysis byproduct $La(OH)_3$ presents alkaline which is a good promoter for hydrolysis reaction of aluminum and water in Eq. 6. The alkaline solution also stimulates the micro galvanic cell of Al-Bi alloy and changes reaction process of AlOH in Eq. 7 [21]. Fig. 7 b,c,d show XRD patterns of hydrolysis byproducts of Al-La-Bi alloys at different salt solutions. The peaks of AlOOH become stronger and some new peaks of Sn, In and Cu are identified in the XRD patterns of hydrolysis byproducts of Al-La-Bi alloys in $Na_2SnO_3$, $CuCl_2$ and $InCl_3$ solution. The Al particles react with salt solutions ($Na_2SnO_3$, $CuCl_2$ and $InCl_3$) to produce Sn, In and Cu metals which

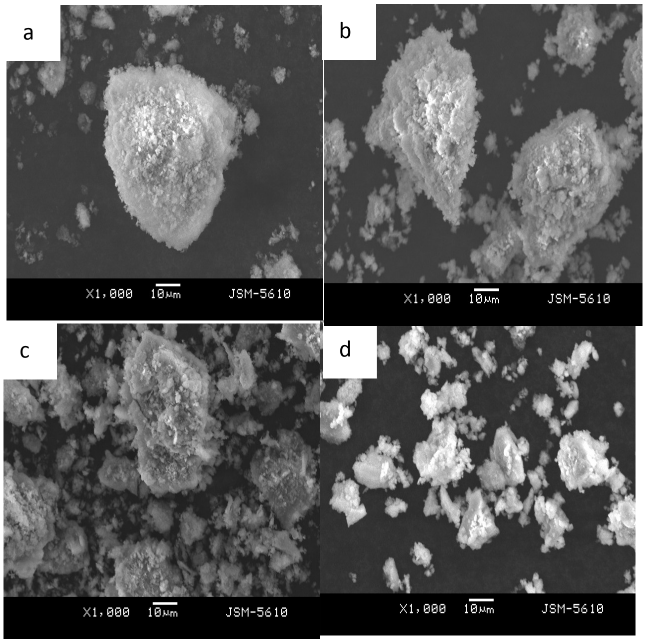


Figure 8. SEM images of hydrolysis byproduct of Al–9 wt%La–10 wt%Bi alloys within 60 min. a, water; b, 0.1 M $Na_2SnO_3$; c, 0.1 M $CuCl_2$; d, 0.1 M $InCl_3$.

cover on Al surface and function as a cathode of a micro galvanic cell. The hydrolysis mechanism of Al-La-Bi alloy in neutral solution is mostly based on micro galvanic cell due to low solubility of $La(OH)_3$ in water. As Al-Sn alloy has higher standard potential than those of Al-In and Al-Cu, Al-La-Bi alloy in $Na_2SnO_3$ solution has better hydrogen generation performance than those in $CuCl_2$ and $InCl_3$ solution. Combined with the results in Fig. 6, the improved hydrogen generation performance of Al-La-Bi alloys in salt solution comes from the formation of more micro galvanic cells.

Fig. 8 shows SEM images of hydrolysis byproduct of Al-La-Bi alloy in different solutions. The particle size of hydrolysis byproducts is distributed from several um to tens of um, compared with approximate 100 um particle size of the alloy before hydrolysis. The decreased particle size of hydrolysis byproduct was due to the continuous fracture of Al-La-Bi alloy in the hydrolysis process, which occurred in the combined junction of Al and Bi. That is, the electrochemical corrosion of aluminum based on micro galvanic cell stimulates the rupture of Al-La-Bi alloy. More micro galvanic cells uniformly distributed on Al matrix leads to more small particles. Therefore, there are more small particles could be found in the SEM images of hydrolysis byproducts of Al-La-Bi alloy in $Na_2SnO_3$, $CuCl_2$ and $InCl_3$ solution than those in pure water.

## 4. CONCLUSIONS

The Al-La-Bi alloy exhibits good hydrogen generation performance at 343 K. The Al-13 wt%La-10 wt%Bi alloy yields 1113 ml/g hydrogen with 100 % efficiency and 927 ml/g.min maximum hydrogen generation rate. The hydrogen generation performance including hydrogen generation amount and rate can be regulated by changing La content or inorganic salt solutions. Increasing La content is helpful to decrease particle size of Al-La-Bi alloy in the milling process, which induces that large special surface area and contact area of aluminum and water are obtained. The Al-La-Bi alloy in inorganic salt solution such as $Na_2SnO_3$ can generate metal Sn, which covers on Al surface and functions as a cathode of a micro galvanic cell. Al-La-Bi alloy may be applied as safe and pure hydrogen generation source for portable micro fuel cell. Its cost can be further reduced if inexpensive materials, appropriate preparation technology, and recycling are adopted.

## 5. ACKNOWLEDGMENTS

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