# Comparative study on activation of aluminum with four liquid metals to generate hydrogen in alkaline solution

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## ARTICLE INFO

## ABSTRACT

Based on a latest finding on Al-water reaction, we studied the hydrogen production behaviors activated by gallium based liquid metal where the mass percentage of Al was less than 1% in an alkaline environment. Three kinds of room temperature liquid binary alloy including Ga–In, Ga–Sn and Ga–Zn were tested and compared with pure gallium. It was shown that the hydrogen production rate activated by Ga–In alloy was far below than that of pure gallium, while Ga–Sn and Ga–Zn run slightly slower. Aiming to optimize the catalytic performance of pure gallium, we further performed researches to clarify its practical features. We divided five times to add equivalent Al block into pure gallium and found that the rate and quantity of hydrogen production kept unchanged in each batch addition, which suggested that liquid metal as catalyst was activated continuously without impurities mixing to impede catalytic effect. In addition, components analysis of the residual precipitates after reaction with XRD also indicated that there was only $Al(OH)_3$ but no gallium or its derivatives. These findings as clarified by this article can help guide future high performance hydrogen generation and reuse of the liquid metal catalyst.

## Introduction

With the exhaustion of fossil energy and the accompanying growing environmental problems, hydrogen power is widely regarded as highly efficient and clean secondary energy source. Generally, the utilization mode of the hydrogen is similar to oil which contains procedures like receiving, storage, transportation, and utilization. But there exist problems over the process in storage and transportation of hydrogen such as requesting extremely low temperature to maintain hydrogen in liquid state. In addition, potential explosion hazard is another major concern because even a tiny electricity discharge would lead to big danger. Therefore, the method storing the hydrogen in a chemical-power form and

releasing it on demand is clearly a desirable way from practical aspect.

Hydrogen can be produced through various strategies including biological [1], water electrolysis [2] or photocatalytic hydrolysis [3]. Compared with such approaches, the lightweight metals (second- or third-row) or intermetallic hydrides are high power density hydrogen sources because they can generate hydrogen based on reaction with aqueous solution. E.g.: aluminum (1 g−1.245 l), magnesium (1 g−0.95 l), and their hydrides (2.24 and 1.88 l of hydrogen). In these lightweight metals, aluminum holds high promise as hydrogen generation materials due to its abundant amount on earth. However, aluminum cannot react with water actively under natural conditions due to its formed thin oxide film during the process. To resolve this problem, tremendous efforts have been devoted, which can generally be classified into three typical categories [4]: ball milling with salts, metal oxides [5−8], reacting with strongly alkaline solution [9,10] and making Al based alloy through adding low melting point metal such as Ga, In, Sn, Zn through mechanical methods [11−16]. The ball milling methods utilized aluminum particles that could be chopped by sharp edges of salt during milling [6] which lead to newly created surfaces of aluminum particles. The salt covered in aluminum particles would be dissolved when the mixed powder were immersed in water, leading to the contacting of non-oxide aluminum with water. The second way adopted strongly acidic or alkaline solution to remove the oxide surface film and guaranteed that aluminum was free to react with water. Another way was to mix certain low melting point metal with aluminum particle to circumvent the passive oxide on aluminum. Activation mechanism in this method lies in that the aluminum lattice structure would be embrittled with the diffusion of these metals.

Now we focused on the low melting point metal to directly activate Al-water reaction for hydrogen production at room temperature. The conventional investigation was usually established on an Al based solid alloy in which aluminum percentage account for more than 90%. This compound alloy was agglomerated at high temperature in inert atmosphere and then stored in vacuum. All these procedures were relatively complicated and need critical condition. In latest works [17,18], researchers found that in alkaline atmosphere, the hydrogen generation could be easily realized through a rather straightforward way after adding small amount Al into liquid metal. In this way, the liquid metal (Ga−In alloy) can be continuously utilized rather than being used for only once as Al-based alloy is horribly difficult to recycle. However, the rate of hydrogen generation activated by Ga−In alloy was still somewhat slow.

In the present work, aiming at further increasing the hydrogen production rate, we systematically studied the performance of several gallium binary alloys: Ga−Sn, Ga−Zn, Ga−In and compared them with pure gallium. The quantitative results showed that hydrogen generation activated by Ga−In alloy was much slower than other three liquid metals and Ga−Sn and Ga−Zn alloy runs slightly slower. Meanwhile, the rate of hydrogen evolution under different temperatures was also clarified. At last, we demonstrated the continuous utilization results of the liquid metal in hydrogen generation.

## Experimental section

In this experiment, the samples of 1 ml liquid metal, 50 mg aluminum block and 100 ml NaOH solution were put into a closed reactor. And $GaSn_{10}$, eutectic $GaZn_{3.6}$, $GaIn_{10}$ were chosen to compare with pure gallium. Because the gallium melt point was 29.6 °C, all experiments were conducted above 30 °C to ensure the gallium in a liquid state. A thermostat water bath was used to keep the reaction vessel at steady state temperature during the experiments. In order to perform quantitative analysis, the volume was recorded in real-time with a soap film flowmeter to obtain the rate of hydrogen production. X-ray diffraction analysis was carried out to evaluate the residues after reaction.

## Results and discussions

### Processes of aluminum block dispersed in different liquid metals

When dispersed in alkaline electrolyte, the surface oxide layer of aluminum block will be removed due to the reaction: $Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O$. Then through contacting with the liquid metal, two processes occurred simultaneously. With the crystal lattice of aluminum block penetrated by the liquid metal, Al block gradually broke into tiny granules, part of which dispersed in the liquid metal interior and the other part spreads over the liquid metal surface. The aluminum granules that spread over the liquid metal surface would react with water easily and produced hydrogen rapidly: $Al + 3H_2O \rightarrow Al(OH)_3\downarrow + 3/2H_2\uparrow$. In this process, the alkali acted as catalytic action, but was not consumed. Initially, the hydrogen generation reaction consumed sodium hydroxide due to reaction: $Al + 3H_2O + OH^- \rightarrow Al(OH)_4^- + 3/2H_2\uparrow$. However, when the aluminate concentration exceeded the solid saturation limit, aluminate underwent a decomposition reaction that regenerated the alkali: $Al(OH)_4^- \rightarrow OH^- + Al(OH)_3\downarrow$ [10].

Here, we focused on the differences among various liquid metals when a portion of aluminum block was broken into granules and dispersed across the surface of liquid metal and generated hydrogen. Fig. 1 showed the comparisons between four kinds of liquid metals: pure gallium, $GaSn_{10}$, $GaZn_{3.6}$ and $GaIn_{10}$. In the case of pure gallium and $GaZn_{3.6}$, aluminum block could be readily resolved and spread to the surface and internal of liquid metal (1−2 min). Then, the accumulated Al granules covering the surface reacted vigorously to generate hydrogen, which continued for more than 10 min until the surface reaction finished and the liquid metal restored shiny. Remarkably, the reaction time was relatively short for pure gallium than for $GaZn_{3.6}$, as shown in Fig. 1(a) and (c).

It was plainly visible that the surface of $GaSn_{10}$ liquid metal could not restore bright after reaction, as is usually the case of pure gallium and $GaZn_{3.6}$. In terms of $GaSn_{10}$, aluminum block was also dispersed across the whole surface, but the reaction of generating hydrogen could last for half an hour. After finishing the reaction, the surface of $GaSn_{10}$ still remained dark dull unlike the original as shown in Fig. 1(b).