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# Experimental study on the effect of low melting point metal additives on hydrogen production in the aluminum–water reaction

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ABSTRACT

Aluminum (Al) is a promising hydrogen carrier. Continuous reaction of pure Al and water ($H_2O$) cannot proceed smoothly because Al particles are covered with a protective oxide layer. Thus, 20% Mg, Li, Zn, Bi, and Sn content were added as additives to Al–$H_2O$ reaction at high temperature. Thermogravimetric experiments were conducted to determine the reactivity of pure Al and five other samples with additives in a vapor atmosphere. Experiments indicated that Mg and Li drove the Al–$H_2O$ reaction, but Zn, Bi, and Sn had little effect. Thus, Mg and Li were selected as activators in the hydrogen generation of the Al–$H_2O$ reaction conducted on a specially designed experimental facility. Hydrogen was monitored in the reaction of Al-based composites with $H_2O$ vapor in real time. Among them, Al–20%Li achieved the fastest hydrogen generation rate (309.74 ml $s^{-1}$ $g^{-1}$) and the largest hydrogen amount (1038.9 ml $g^{-1}$). XRD (X-ray diffraction), SEM (scanning electron microscopy), and TEM (transmission electron microscopy) were used for product analyses to identify the influence of adding Mg and Li. This method of Al energy utilization may be used in underwater propulsion systems.



## 1. Introduction

Hydrogen, as a renewable and environmentally friendly fuel with high heating value, has gained extensive research attention [1,2]. This gas is in urgent demand because of the air pollution caused by the combustion of fossil fuels. However, hydrogen storage is one of the key challenges in developing a hydrogen economy [3]. Aluminum (Al) is recognized as one of the most suitable hydrogen carriers because of its high hydrogen capacity of 0.11 g/g [4]. Al and its alloys have been studied as sources of hydrogen [1,4–7].

In neutral conditions, the release of hydrogen was observed through cutting, drilling, or grinding of freshly exposed Al surfaces in water ($H_2O$) [8,9]. However, this reaction soon stopped because of the rapid passivation of the Al surface [9]. The main problem in this method is the passive surface oxide film and its by-products [e.g., Al(OH)]. Removing the protective film is the key to overcoming this problem. Metal particles with small sizes and mechanical treatments, such as ball milling, are investigated to increase the specific surface area and pitting corrosion on Al [4,10–13]. Hydroxide ions ($OH^{-1}$) in alkaline solutions can destroy the protective oxide layer on the Al surface. The most commonly used hydroxide is sodium hydroxide (NaOH) [4]. Other hydroxides are also used as the reacting base, such as potassium hydroxide and calcium hydroxide [14,15]. Milling Al with different oxide modifiers, including $Bi_2O_3$, $Cr_2O_3$, $MoO_3$, $TiO_2$, and ZnO, has proven to be an effective method to improve reaction efficiency [16–18].

One of the most commonly used methods to promote Al–$H_2O$ reaction is chemical activation through the modification of the composition of Al alloys. Gallium and its liquid alloys preclude the formation of a protective oxide film on Al and improve Al activity [19]. Al–Ca alloy was also used in hydrogen production, in which hydrogen yield was 47.87% when Ca content was 20% [20]. A small fraction of Li enables a spontaneous reaction of activated Al particles with $H_2O$ and results in an almost 100% yield of hydrogen generation [21]. The Al–In–Zn–salt–$H_2O$ system can produce hydrogen at room temperature. The Al–5%In–3%Zn–2%NaCl mixture in $H_2O$ has the highest hydrogen yield of 1035 ml/g in 4 min when the ball milling time is 10 h [22]. Hydride is added to Al in the process of ball milling, which greatly improves the hydrolysis of Al powder [23]. The formation of $LiAl_2(OH)_7 \cdot xH_2O$ proves to be the key in enhancing the hydrogen generation of Al–$H_2O$ reaction. Hydrogen generation from the reaction of Al–Bi–NaCl and $H_2O$ is used in a portable hydrogen generator for fuel cell applications [24].

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Different metals, such as Zn, Bi, Mg, and Sn, are added to Al to react with pure $H_2O$. Al–Bi alloy has a faster hydrolysis rate than other alloys at room temperature [25]. The reason behind the improved hydrolysis of Al through the addition of Bi is the micro-galvanic cell formed between the anode (Al) and the cathode (Bi).

The reaction of Al–$H_2O$ is exothermic (15.4 kJ/g), and this heat can hardly be utilized in aqueous solutions at room temperature. This study focused on the reaction of molten Al with $H_2O$ vapor at an elevated temperature. In this hydrogen generation method, the produced hydrogen and released heat can be utilized simultaneously. Thus, the whole energy utilization efficiency of the system will be improved. The different additives, such as Li, Mg, Zn, Bi, and Sn, were selected as activators because of their role in promoting the Al–$H_2O$ reaction in the aqueous solutions of previous studies. These metals and their oxides are all nontoxic. Their properties are listed in Table 1. The experiments on thermogravimetric analyzer and special setup were conducted to study the effects of low-melting-point metal on Al reactivity. XRD (X-ray diffraction), SEM (scanning electron microscopy), and TEM (transmission electron microscopy) were used to analyze the products and to explore the activation mechanism.

## 2. Experimental

All the reagents are listed in Table 2, including the suppliers, particle sizes, and chemical purity. Deionized water was used in the experiments. Different composites were made through hand mixing, except for the Al–Li mixture. Different Li contents were prepared through mixing Al and Al–Li alloy (Al–20%Li). Experiments were conducted with a high-temperature thermogravimetric analyzer (CAHN THERMAX500, Thermo Electron Corporation, USA) to investigate the reactivity of different Al-based samples at a heating rate of 25 K/min up to 1000 °C. The samples (10 mg) were placed in a crucible, which was in the argon atmosphere. The flux of argon and $H_2O$ vapor were 500 and 100 ml/min respectively.

The samples with relatively high activities were used to generate hydrogen in a PDEF (particularly designed experimental facility, Fig. 1). The stainless steel reactor was cylindrical with an inner diameter of 5 mm and a height of 10 mm. The reactor was kept sealed, and the argon was sent into the reactor to exclude air. Samples (1.5 g) were placed in the reactor and heated to 700 °C to ensure they were in a molten state. A K-type thermocouple that was anchored to the reactor and inserted in the middle of the sample monitored the temperature inside the reactor. To avoid oxidation and hydrolysis of the sample, only argon was fed into the reactor when heating the sample. Once the temperature rose to 700 °C, $H_2O$ (5 ml/min) was pumped into the reactor using an injection pump. The flux of water was controlled through the linear velocity of injector with an error less than 0.5%. $H_2O$ and argon were heated to approximately 200 °C after they mixed, and then flowed into the reactor. Upon being exposed to $H_2O$ vapor, samples reacted with $H_2O$ immediately. Hydrogen, $H_2O$ vapor, and argon were removed from the reactor, and then the gas was cooled, dried, and measured using a gas analyzer with a precision of 1%. The output

**Table 2**
Samples used for the experiments.

| Reagents | Supplier | Mean particle size | Purity (%) |
|---|---|---|---|
| Al | Aladdin | 10 μm | 99.9 |
| Al–Li alloy | Zhoushan Copper | 45 μm | 99.0 |
| Mg | Sinopharm Chemical Reagent Corp | 45 μm | 99.9 |
| Zn | Alfa Aesar | 45 μm | 99.0 |
| Bi | Sinopharm Chemical Reagent Corp | 45 μm | 99.5 |
| Sn | Shanghai HUSHI | 45 μm | 99.5 |

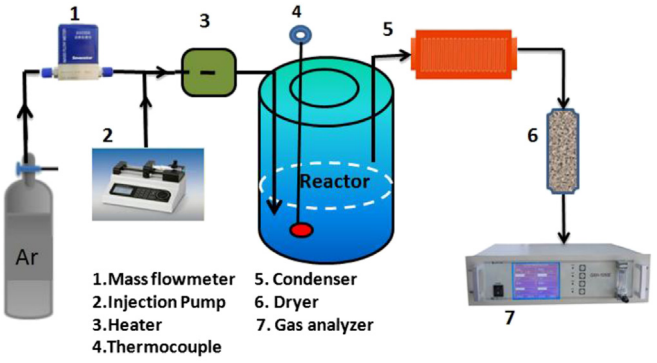


**Fig. 1.** Schematic diagram of the experimental setup.

data of hydrogen were automatically recorded in a notebook computer every second. The fluxes of $H_2O$ and argon were 5 and 500 ml/min respectively for the whole experiment. The precision of the injection pump was 0.05%, and the flow meter that measured the argon flow was 1%. After the test, the final weight was obtained through an electronic balance with the precision of 0.001 g.

The products were collected after the test ended and then measured using XRD (X'Pert PRO, Netherlands), SEM equipped with an energy Dispersive X-ray Spectrometer (SEM-EDX, SU-70, Japan), and TEM (Tecnai G2 F20 S-TWIN, America).

## 3. Results

### 3.1. Effect of metal elements

Fig. 2 shows the thermogravimetric results of six samples: pure Al, Al–20%Li, Al–20%Mg, Al–20%Zn, Al–20%Bi, and Al–20%Sn. The sample of pure Al presented the least final WG (weight gain) and the reaction was weak below 900 °C. WG is defined as the final weight to the initial weight. The Al–20%Li sample demonstrated the best reactivity and gained the highest DTG (derivative thermogravimetric) peaks. Second to Al–20%Li, Al–20%Mg had a WG of 140% and a DTG peak at approximately 600 °C. Except for the samples of Al–20%Li and Al–20%Mg, the others all obtained the fastest WG rate at the temperature of 1000 °C, which is the highest temperature limit. For all these samples, the WG process

**Table 1**
Physical properties of metals.

| Metal | Melting point (°C) | Boiling point (°C) | Melting point of oxide (°C) | $H_2$ capacity (ml $g^{-1}$) |
|---|---|---|---|---|
| Al | 660 | 2519 | 2054 | 1244 |
| Li | 180 | 1342 | 1205 | 1600 |
| Mg | 648 | 1107 | 2825 | 933.3 |
| Zn | 420 | 907 | 1973 | 344.6 |
| Bi | 271 | 1564 | 824 | 160.8 |
| Sn | 231.9 | 2602 | 1630 | 377.7 |