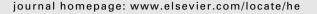
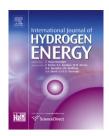


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# Fabrication of AlLi and Al<sub>2</sub>Li<sub>3</sub>/Al<sub>4</sub>Li<sub>9</sub> intermetallic compounds by molten salt electrolysis and their application for hydrogen generation from water

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#### ARTICLE INFO

Article history:
Received 29 November 2011
Received in revised form
6 March 2012
Accepted 7 March 2012
Available online 5 April 2012

Keywords:
Hydrogen
Aluminum
Lithium
Intermetallic
Molten salt
Hydrotalcite

#### ABSTRACT

The concept of "hydrogen on demand" has been widely publicized. More importantly, the materials used to produce hydrogen on demand should be in themselves safe to handle. In present work, Al-Li intermetallic compounds (IMC) were fabricated in air by electrolysis from LiCl–KCl molten salt at 480  $\pm$  25  $^{\circ}$ C. Bulk AlLi IMC and the bulk compound with mixture of Al<sub>2</sub>Li<sub>3</sub> and Al<sub>4</sub>Li<sub>9</sub> (Al<sub>2</sub>Li<sub>3</sub>/Al<sub>4</sub>Li<sub>9</sub> IMC) were not pyrophoric and can be safely handled in air. When both compounds in contact with water, vigorous reaction occurred and H2 was directly produced. The by-products after H2 generation from AlLi IMC were a mixture of Li-containing α-Al and Li-Al hydrotalcite (hereafter referred to as Li-Al LDH). The by-product after H<sub>2</sub> generation from Al<sub>2</sub>Li<sub>3</sub>/Al<sub>4</sub>Li<sub>9</sub> compound was a mixture of LiOH·H<sub>2</sub>O and Li-Al LDH. Those by-products can be easily separated from water and may be reused as a resource. Approximately 500-860 ml of H2 per weight (g) of the IMC compounds was generated in deionized water at room temperature. Experimentally, AlLi IMC powder and Al<sub>2</sub>Li<sub>3</sub>/Al<sub>4</sub>Li<sub>9</sub> compound exhibit gravimetric hydrogen capacity of 7.0 wt.% and 5.4 wt.%, respectively. Although the energy consumed for fabricating Al-Li IMC compounds is a little larger than the energy provided by the generated H2, the Al-Li IMC compounds are promising materials for producing hydrogen on demand without the necessity of hydrogen storage.

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### 1. Introduction

Whether it is possible to gradually change from the carbon energy cycle based on current fossil supplies to the hydrogen energy cycle has attracted considerable attention [1–4]. Hydrogen can be burned in a conventional  $H_2$ – $O_2$  combustion

chamber [5] or used in a fuel cell to produce electrical power [6]. Although hydrogen exists in the earth shell under specific conditions, it is rarely abundant and is difficult to mine or recycle. Therefore, artificial manufacturing methods have been utilized to produce hydrogen. Currently, large-scale production of hydrogen mainly depends on high-temperature treatment of

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fossil fuels such as natural gas, petroleum and coal [7-9]. According to statistical data, these processes for producing hydrogen consume 2% of available global energy [10]. Additionally, large-scale hydrogen production methods that use fossil fuels produce by-products such as CO, CO<sub>2</sub> and other contaminants. Therefore, methods of producing hydrogen without emitting pollutant are needed such that  $H_2$  can become a clean energy [11,12].

Several studies [11–15] generated hydrogen using metallic powder with high chemical activity as the raw material for hydrogen production. These powders include Al [11,12] and Mg [13–15]. However, preparation of metallic powder generally uses the high-energy ball-milled method with ball-milling time as long as 8 h [13,14]. Hence, additional energy is utilized and costs are incurred when preparing the metallic powder.

Li-rich Al-Li alloys or Al-Li intermetallic compounds generate gaseous hydrogen in contact with water [16]. Generally, Li-rich Al-Li alloys or Al-Li intermetallic compounds are fabricated by vacuum induction melting furnace under controlled atmosphere of argon gas [17-19]. However, when lithium metal is used, careful handling and storage are needed because of its high activity. Al-Li alloys [16,20] and AlLi intermetallic compound (AlLi IMC, hereafter) [21,22] can also be fabricated from Al and Li powders. Hypoeutectic Al-Li alloys were obtained by mixing aluminum powder with lithium powder, and then compacting in a hydraulic press [20]. AlLi IMC can be fabricated after 10 h of ball-milling for Al-27.84 wt.% Li mixing powder under argon atmosphere [22]. Instead of using the vacuum melting process [17-19] and the ball-milling process [16,20-22], Watanabe et al. [23] reported that Al-18-20 wt.% Li alloy (composed of intermetallic compound AlLi phase) can be prepared by molten salt electrolysis using bulk aluminum rod as cathode. According to the process, the high lithium content Al-Li intermetallic compounds can be fabricated without using Al and Li powders or pure lithium metal. Additionally, the molten salt electrolysis is a well known commercial process for extracting metals (e.g., Al [24] and Mg [25]) from molten metal salts. However, little is reported about the preparation of Al-Li intermetallic compound with lithium content higher than 20 wt.% by molten salt electrolysis. Furthermore, study on hydrogen generation from the reaction of Al-Li intermetallic compounds with water and evaluation of by-product formed during the reaction is few.

This work explored processes of fabricating AlLi IMC (Al-19.15 wt.% Li) and Al $_2$ Li $_3$ /Al $_4$ Li $_9$  compound (Al-33.32 wt.% Li) in air by molten salt electrolysis. Hydrogen generation from the reaction of water with the AlLi compound and Al $_2$ Li $_3$ /Al $_4$ Li $_9$  compound was studied. The hydrogen generation from the reaction of bulk AlLi, powdered AlLi and bulk Al $_2$ Li $_3$ /Al $_4$ Li $_9$  compound with water was measured. By-products formed during the hydrogen reaction were evaluated.

## 2. Materials and methods

#### 2.1. Al-Li intermetallic compounds

Molten LiCl–KCl salt was electrolyzed in air at 480  $\pm$  25  $^{\circ}$ C in an electrolytic cell. The arrangement of the electrolytic cell

was referred from previous studies by Smolinski [26] and Lin et al. [27,28]. The electrolyte contained a mixture of 45 wt.% LiCl and 55 wt.% KCl. A graphite bar was used as the anode. Commercial 1050 Al alloy strip (~99.5 wt.% purity) was adopted as a cathode material. In fact, commercially pure Al scraps can also meet the goals of this study, and could be used as a cathode material for producing Al-Li intermetallic compound. The cathodic strip sample was 1 mm thick, 20 mm wide and 80 mm long. It has been reported that the theoretical decomposition voltage of LiCl is 3.65 V at 500 °C [29]. As electrolysis voltages higher than 3.65 V between the cathode and the anode were applied, the lithium ions were reduced to lithium atoms. The lithium atoms deposited on the cathode, and then diffusion into Al matrix. The following three-step electrolysis was performed, using a DC power supply unit, which applied a current to the electrolytic cell. First, the electrolysis current was set to  $\sim$  4.3 V for 1 h. Then, the current was maintained at ~4.0 V for another 1 h. It was then turned down to  $\sim$ 3.7 V to complete the final electrolysis for 20 min. The fully charged as-deposited Al-Li strip sample (denoted as ALI-1 hereafter) was expanded to a thickness of 1.8 mm and a width of 22 mm. Approximately 6.42 g of ALI-1 was obtained after the three-step electrolysis. The weight increase of the asdeposited ALI-1 is 2.10 g. On the other hand, based on the above electrolysis process but with a relatively longer time of electrolysis, a high lithium content Al-Li intermetallic compound could be obtained. The high lithium content Al-Li compound was hereafter designated as ALI-2. However, since ALI-2 compound was provided by a private Taiwanese company, weight increase after the longer time of electrolysis was not accessible. ALI-1 and ALI-2 samples were not pyrophoric and could be safely handled in air.

X-ray diffraction (XRD; MAC MO3X-HF, Bruker AXS) analysis was performed using Cu  $K_{\alpha}$  radiation at 40 kV at a scanning speed of  $1^{\circ}$ min<sup>-1</sup> to identify the crystal structure of 1050 Al strip, the ALI–1 and the ALI–2 samples. The lithium content of the samples was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Ultima 2000, Jobian-Yvon, Horriba).

### 2.2. Hydrogen generation experiment

The ALI-1 was dipped in deionized (DI) water for H2 generation at room temperature. The condition of  $H_2$  gas evolution from the ALI-1 was visually examined. The sample vigorously reacted with DI water to form hydrogen gas. The hydrogen generation from the surface of ALI-1 sample was gradually ceased within 10 min immersion in DI water. The crystalline structure of the surface reaction products of the ALI-1 was analyzed by glancing angle X-ray diffraction (GAXRD; MAC MO3X-HF, Bruker AXS). Some ALI-1 samples were broken into powder for H<sub>2</sub> generation. The powder was easily obtained owing to the compound's brittle nature and weak fracture strength. The powder could completely react with DI water to generate H2 gas. The by-product of the reaction was dried at 80 °C, and then examined by X-ray diffraction (XRD) and fieldemission scanning electron microscope (FESEM; JSM-6700F, JEOL). The hydrogen generation amounts of ALI-1 bulk and powder were each measured. ALI-1 powder (0.05 g) and ALI-1 bulk (0.05 g) each was placed in 100 ml DI water to evolve

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