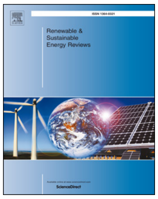
Renewable and Sustainable Energy Reviews 92 (2018) 17–37

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Liquid metal activated aluminum-water reaction for direct hydrogen generation at room temperature

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ARTICLE INFO

Keywords:
Clean energy
Hydrogen source
Liquid metal catalyst
Room temperature Al-H_2O reaction
Self-propelled machine
Oxide layer
In-demand mass production

ABSTRACT

In light of high energy density, hydrogen has been recognized as a promising clean energy carrier to defuse the coming energy crises. Among the many technological strategies ever tried, the Al-H_2O reaction is a rather favored way to produce hydrogen although it is always hindered by a layer of passive film on Al surface. Recently, a class of gallium-based room-temperature liquid metal (RTLM) is found to effectively activate the Al-water reaction which draws attentions to such an extremely simple hydrogen production method. To push forward further investigations of this newly emerging area, this article is dedicated to present an overview of the latest advancement of the hydrogen production from the RTLM activated direct Al-H_2O reaction. Meanwhile, it also comprehensively interprets the mechanisms of the RTLM activated Al-H_2O reaction in terms of electrochemistry, phase constituents, interface actions and energy transfer process, and then discusses four influencing factors dominating the reaction. Next, several unique phenomena of RTLM fed with Al driven by releasing hydrogen are also illustrated, offering a glimpse on the development of soft robots. In addition, theoretical and technological challenges lying behind such a hydrogen generation scheme are prospected. It is anticipated that the RTLM triggered Al-H_2O reaction for an in-time and on-demand hydrogen generation will witness a ever bright future in the coming time.

1. Introduction

There is no doubt that energy system constitutes the backbone of civilization, which boosts the progress of technology and human living standard. Over the long river of history, every transition of energy structure would breed an unprecedented industrial revolution [1,2]. As Fig. 1 shows, in the last century, fossil fuels [3] has remained dominant in energy resources. As a result, immeasurable emissions of carbon dioxide extremely exacerbated the Greenhouse effect which endangered the survival of terrestrial life [4–6]. Additionally, the storage of fossil fuel is rather limited on earth [7]. Therefore, it has been an unstoppable trend to explore alternative energy sources. At the G20 Summit in 2016 [8], a low-carbon, intelligent and shared energy future is especially appealed for. In order to realize the sustainable development [9,10], it is essential to find an alternative renewable clean energy to substitute for the fossil fuel.

Composed of the most abundant and lightest element in the world, hydrogen energy becomes a preferential power candidate by virtue of high gravimetric energy density of 122 kJ/g [11], large heating value of combustion of 141.8 kJ/g [12], free carbon emission, renewable affordability, and more other merits [13–20]. The earliest research of hydrogen dated back to 1766 when Henry Cavendish [21] discovered the inflammable air. Then Antntoine Lavisier [22] named it as hydrogen in 1787 and obtained hydrogen via decomposition of water. Half a century later, William Grove and Christian Friedrich Schönbein [23] published their study on hydrogen-supplied fuel cells. Since then, hydrogen has been praised as a promising green energy carrier for clean development [24]. With the progress of science and technology, great strides have been made, and hydrogen production has gradually been industrialized.

Based on status quo, there are main six approaches [25–29] to produce hydrogen as Fig. 2 displays: electrolysis of water [30–34], water splitting by photo-catalysis [35–42], reforming of fossil fuels [43–46], nuclear hydrogen production [47–52], biomass processing techniques [53–58], reaction between active metal and aqueous solution [59–64]. Electrolysis and photolysis of water have long been hot research areas, but their energy efficiencies stay low, and the production capacities should be significantly enhanced. At present, hydrogen production from reforming of fossil fuels occupies over 90% of hydrogen market share [65]. However, in this method, the raw material is

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https://doi.org/10.1016/j.rser.2018.04.052
Received 11 February 2017; Received in revised form 26 November 2017; Accepted 14 April 2018

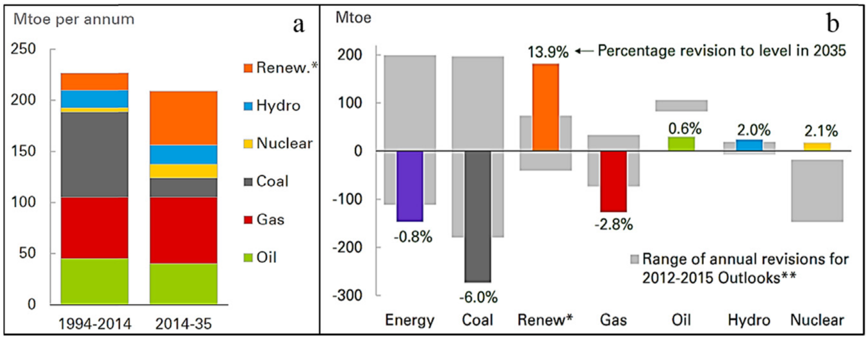

Fig. 1. a. Annual demand growth of different fuel; **b.** Energy demand changes in 2035 relative to previous outlook (Note: *Renewables including biofuels) [3].

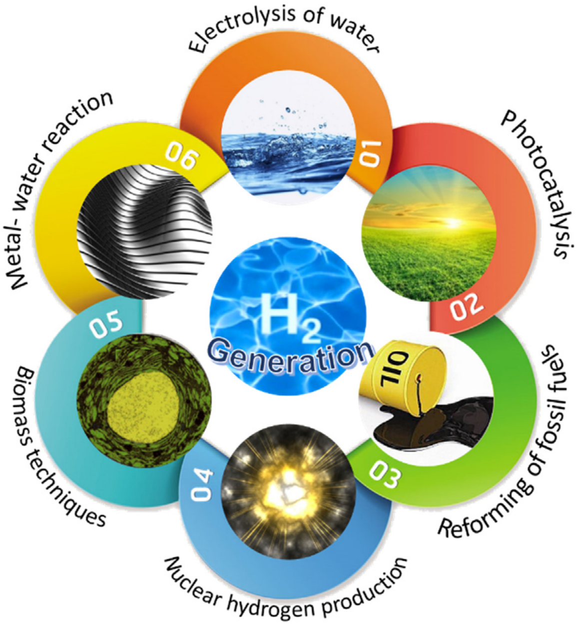

Fig. 2. Typical hydrogen production approaches.

still finite fossil fuel, and enormous CO_2 is released in this complex course. As for the nuclear hydrogen production, excellent corrosion resistance is required for device materials, and the coupling between the nuclear reactor and hydrogen production process is a challenge. Biomass processing technology is still in the stage of laboratorial investigation puzzled by the purification problem. Metal-water reaction was one of the most ancient approaches of producing hydrogen [66]. Once active alkaline earth metals touch water, they react violently with water at ambient temperature, releasing hydrogen [67,68]. Such reaction is so fast that it is risky and difficult to control. As for other relatively stable metals, like iron [69–73], zinc [74–76], magnesium [77–80], they can only react with water steam at extraordinary temperature [81,82] or when activated by certain complicated pre-processes [83], which are not cost-effective.

Aluminum, as the most abundant metal in the earth's crust, approximately 8% (wt) [84], is one of the most appropriate raw materials [85,86] to evolve hydrogen with its low cost [87] and low density. Theoretically, hydrogen yield can be up to 1.244 L/(g Al). However, a layer of dense oxide film [88] fleetly forms once Al is exposed to the air, which impedes the subsequent reaction of inner Al and water. How to remove the passivated alumina film on the surface has puzzled people for many years. So far, there are several activation routes: alkali aqueous activation [89,90], mixing and grinding with special metallic oxide or inorganic salt [91,92], nano/micro-crystallization of Al [59,92–94], alloying of Al and other metals [95–100]. In these methods, the pre-preparation work is either unsafe or time and energy-consuming. Moreover, the prepared alloys is inclined to suffer from aging and lose activities. In addition, the storage and transportation of hydrogen are incredibly costly, which impedes the batch application of hydrogen [101–107]. Therefore, it is critically important to explore a real-time and on-demand hydrogen generation technology.

In recent years, gallium-based liquid metal alloys were found to easily activate Al hydrolysis for hydrogen generation at room temperature. Initially, the raw materials, i.e. Al, RTLM and water, were preserved separately. Once the prepared materials were put together, hydrogen could be instantly obtained. Additionally, owing to the fluidity and unique surface characters of RTLM, the Al-RTLM alloys could be assembled as self-actuated motors with hydrogen impetus, which provided a new insight into future flexible robots. This paper aims to give an overview of the development of hydrogen production from RTLM activated Al-H_2O reaction and its application prospects, expecting more advances in science and technology to meet the challenges.

2. Historical development of liquid metal activated Al-H_2O reaction for hydrogen generation

In the late 1960's, Jerry Woodall et al. [108,109] accidentally discovered that Al-Ga alloys successfully reacted with water to generate hydrogen, heat and aluminum hydroxide. This led to the in-time hydrogen production method with Al-Ga alloy [110–112]. In 1980's, Kolbenev et al. [113] reported the first quantitative research of smelted multi-component Al alloys (Ga 0.07 wt%, Bi 2 wt%, Pb 1 wt%, Sn 1 wt %, the rest is Al.) for Al-H_2O reaction at room temperature to produce hydrogen, affording a hydrogen generation rate up to 4 L/(g·min) and a hydrogen productivity approximate to theoretical value. In the early 21st century, with the assistance of X-ray diffraction, DTA and EDX, Kravchenko et al. [97] studied the chemical properties of Al alloy doped with Ga, In, Sn, Zn which could react vigorously with water. It was inferred that the presence of solid solution of Al and liquid phase eutectic distributed in the grain boundary resulted in the high reactivity of the 'freshly prepared alloys'. Besides, the deactivation of alloys in storage was also investigated. In order to reduce the cost of activating elements, researchers [110] made progress in increasing the Al content to 95% in the alloys. The alloys existing as solid were still able to split water and generate hydrogen. In 2007, Fan et al. [114] proposed a new method, namely mechanical milling, to synthesize Al alloys that could intensely react with water to produce hydrogen. In comparison with the high-temperature melting method, mechanical milling could further improve the activity of Al, and it was much more environmentally friendly. The reaction activities could be optimized by adding different compositions in Al alloys. However, the preparation process was highly energy-consuming, and the Al alloys quickly lost their chemical activity when exposed to air. Later on, Wang et al. [115] developed an arc melting technique to prepare Al-rich ingots. They put considerable effort into investigating the influence of microstructure on the hydrogen generation performance of Al alloys, and evaluated the activation