Technical Communication

Evolution of hydrogen from magnesium alloy scraps in citric acid-added seawater without catalyst

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A B S T R A C T

This work employed a mixture of low-grade Mg scraps (LGMS) and citric acid-added seawater to generate hydrogen gas. Metal catalyst was not required for accelerating the reaction of H2 generation in the Mg scraps/citric acid solution. LGMS in 20 wt% citric acid-added seawater could produce substantially higher H2 volume than the LGMS in 5 wt% citric acid-added seawater. Purity of the generated H2 was about 99% (after dehumidification). By filling H2-production reactor every 30 min with fresh seawater to which citric acid has been added, ~70 l of hydrogen could be produced in 100 min.

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1. Introduction

Hydrogen (H2) is likely to become a main source of fuel in the near future. H2 can be produced using many techniques [1], including the steam reforming of hydrocarbons, the electrolysis of water and the gasification of heavy oil, coal or biomass [2]. H2 is only an energy carrier and not a source of energy, and, therefore, differs from oil and gas for example. Hydrogen must be produced using energy from other sources [3]. Accordingly, hydrogen production actually consumes more energy than that contained in the resulting hydrogen [4]. To ensure long-term sustainability and supply, a renewable H2 generator must be developed. Amendola et al. [5] studied a new method of generating hydrogen gas from a mixed solution of sodium borohydride (NaBH4), sodium hydroxide (NaOH) and H2O, with Ru-based powder as a catalyst. When aqueous NaBH4 comes into contact with the catalyst, it spontaneously hydrolyzes to produce H2 gas and sodium borate (NaBO2) [5]. This process is important to the production of high-purity hydrogen without the emission of pollutants. However, when NaBO2 is generated at the same time as the H2 is generated, a problem arises, as the NaBO2 adheres to the catalyst [6], slowing the generation of H2. The current high price of NaBH4 of which 1 kg costs about US$ 40–55 [7], NaBH4 systems may be useful in less cost-sensitive applications, such as the powering of portable electronics [8]. On the other hand, some studies [9–13] have employed metallic powders as raw materials in the production of hydrogen in NaOH solution [9,10] or KCl solution [11–13]. These powders include Al [9,10] and Mg [11–13]. The metallic powder is usually prepared by high-energy ball-milling with a ball-milling time of as long as 8 h [11,12]. Therefore, additional energy is consumed and costs are
incurred in preparing the metallic powder. The production of hydrogen from metallic waste has recently been studied [14–17]. Martinez et al. [14] proposed the use of used aluminum beverage cans (Al UBC) in a 6 M NaOH solution to yield H₂. Their results revealed the feasibility of using metallic powder as a portable and safe hydrogen gas generator. The authors of this work have studied the generation of H₂ by the reaction of low-grade magnesium scraps in aqueous NaCl [16–18]. However, in our earlier investigation [16–18], a metallic catalyst is required to improve H₂ yield. The catalyst net has to be pressed on the scrap Mg during the generation of H₂ [17] or the Mg scraps must be remelted at high temperature to produce Mg scrap/catalyst net couples [18]. A non-catalyst approach should be explored to enable this resource (low-grade Mg scraps) to be re-used in a relatively highly efficient and convenient way.

The recycling or re-use of magnesium scrap has become increasingly important [19,20]. Most Mg products are coated with metallic coatings that contain Ni and Cu, and then with an organic coating for both aesthetic reasons and protection against corrosion. However, end-of-life or post-consumer Mg products cannot presently be recycled into secondary Mg ingots efficiently and economically [22–24]. Hence, an important Mg source remains unused. According to Javaid et al. [21], because of the inability of current sorting and refining approaches to separate and clean the variety of scrap produced, only clean scrap is recycled into secondary Mg ingots. More than half of Mg scraps and end-of-life Mg products cannot be recycled economically [21]. Clean Mg scraps are produced in a process that is associated with die-casting [25]. The clean scraps include runners, biscuits, trimmings and rejected cast parts [25]. Mg alloy castings that contain steel/aluminum inserts, painted parts, and/or machine turnings are not clean Mg scrap [25]. This work addresses an aqueous solution that can be mixed with Mg scraps to produce H₂ at a high rate without a catalyst. The chemical evolution of hydrogen from aqueous solution thus occurs with the cathodic reduction of H⁺ or the hydrogen atom in H₂O molecules. The cathode reaction may be:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1) \]

and/or

\[ 2H^+ + 2e^- \rightarrow H_2 \quad (2) \]

The anodic reaction should be:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (3) \]

Therefore, in order to increase the anodic reaction rate, Mg scraps should be in a highly corrosive environment. Severe corrosion of Mg is well known to occur in a highly conductive aqueous media such as chloride solution. However, chloride solution is not sufficiently corrosive for the generation of H₂ with the consumption of Mg scraps. Aqueous HCl, H₂SO₄, HNO₃ and other acids are extremely corrosive toward magnesium. Such solutions are toxic and dangerous because of their highly corrosive nature. The solution adopted herein is citric acid in seawater. The supply of seawater is almost inexhaustible. Citric acid (C₆H₈O₇), a tricarboxylic acid, is a weak organic acid. The acid is a white crystalline powder at room temperature, and dissolves easily in water. The global production of citric acid in 2004 was around 1.4 million tones [26]. Owing to its high solubility, palatability and low toxicity, citric acid is used extensively in the food and beverage industries as an acidifying and flavor-enhancing agent, and in other industries such as the pharmaceutical industry [26–28]. The price of citric acid is about US$1–1.3 per kg [26].

The purpose of this work is to study a new technique for reusing Mg scraps. The Mg scraps, especially low-grade Mg scraps and post-consumed Mg products, were heavily corroded in seawater to which citric acid had been added, with the simultaneous evolution of hydrogen. Experimental results reveal that H₂ can be generated at a high rate without the use of catalytic materials.

2. Experimental procedure

In this work, low-grade Mg scrap (LGMS) (post-consumed or end-of-life Mg products, Fig. 1) was used to produce hydrogen. Fig. 1(a) shows some broken pieces of magnesium gearbox, magnesium parts covered in coatings and paint used in cell phones. Fig. 1(b) illustrates a magnesium part (a die-cast Mg housing) from a post-consumed notebook computer and the broken pieces from the part. Fig. 1(c) shows crucible Mg sludge and dross, and some copper-coated Mg parts, etc. In this investigation, LGMS was remelted and was cast into an LGMS plate with a mass of 70 g (See the plate in Fig. 2). The author’s earlier works [17,18] have stated that the metallic catalytic net such as a 304 stainless-steel net (S.S. net) strongly affects H₂ yield by accelerating the hydrolysis of LGMS in 3.5 wt% NaCl solution. In this work, LGMS/S.S. couples (in Fig. 2) were prepared to evaluate the ability of the metal catalytic net on improving H₂ yield in the newly explored aqueous solution. Table 1 presents the solutions that are adopted herein. Fig. 3 presents the equipment that is used in this experiment. One LGMS plate was placed in a sealed stainless-steel reactor. The aqueous solution was natural seawater or seawater to which citric acid has been added (Table 1). The solution was pumped from a storage tank until it filled the stainless-steel reactor (Fig. 3). The air valve (Fig. 3) was not shut off until the reactor was filled with the aqueous solution. The generated hydrogen then passed through a low-temperature dehumidifier (−15 ± 1 °C) (Fig. 3) to condense the most water vapor out of the H₂ streams. The generation rate (liter/min) of the dehumidified H₂ gas was measured using a mass flow meter (M-10SLPM-D) (Alicat Scientific Co., Ltd.) and recorded using a personal computer with a data acquisition device. The total volume of generated H₂ was calculated by integrating the experimentally measured H₂ generation rate over time. The composition of generated gas was analyzed by gas chromatography (GC) (GC-8900) (China Chromatography Co., Ltd.). The GC was equipped with a 198 cm by 3.16 cm column packed with stainless-steel and a thermal conductivity detector. Hydrogen samples taken from different periods during H₂ generation were quantitatively measured by the gas chromatography. The temperature of the NaCl solution in the reactor increased during the reaction. A water-cooled jacket (Fig. 3) was buried in the reactor exterior to maintain a temperature of 25 ± 2 °C.
3. Results and discussion

Fig. 4 plots cumulative H₂ volume versus time. LGMS/S.S. couples and the LGMS plate were each placed in 1.5 l of seawater to produce H₂. As presented in the figure, about 1 l of H₂ was generated in 3 h by the reaction of LGMS scrap plate. For comparison, the LGMS/S.S. (sample in Fig. 2) produced much more H₂ in the same electrolyte in the same period. The stainless net, functioning as a catalyst [18], promoted the production of H₂ in the seawater. The chemical reaction was:

\[
\text{Mg}(s) + 2\text{H}_2\text{O}(\text{in seawater}) \xrightarrow{\text{a net catalyst}} \text{H}_2(g) + \text{Mg(OH)}_2(s) \quad (4)
\]

LGMS/S.S. couples and the LGMS plate were also each placed in citric acid-added seawater (1.5 l) to generate H₂. Fig. 5(a) plots the cumulative volume of the generated H₂ in citric acid-added seawater against time. As presented in the figure, the LGMS/S.S. sample in a 5 wt% citric acid seawater bath produced \(~201\) H₂ in 3 h. The LGMS plate in the same 5 wt% citric acid bath produced as much as \(19\) l of H₂. Restated, a high yield of H₂ was obtained by the reaction of LGMS in a 5 wt% citric acid bath, even when no S.S. catalyst net was employed. Fig. 5 also plots results obtained using the 20 wt% citric acid seawater bath, revealing that \(~501\) of H₂ were generated. A similar volume of H₂ was generated between the LGMS plate and the LGMS/S.S. As shown in Fig. 5(b), during the initial 0–30 min of the reaction, the H₂ generation rate in seawater with 20 wt% citric acid exceeded that in seawater with 5 wt% citric acid. Although the data in Fig. 4 show that a stainless-steel net, functioning as a catalyst, markedly increased the volume of H₂ generated in the electrolyte – seawater, the stainless-steel net did not act as a catalyst in the bath of seawater + citric acid (Fig. 5). Restated, the metal catalyst was not required for generating H₂ from Mg scraps in

![Fig. 1 – Different kinds of LGMS: (a) broken pieces of Mg gearbox and Mg parts in paint; (b) the post-consumed Mg part from notebook computer and the broken pieces of the Mg scrap material from the part; (c) crucible Mg sludge and dross, and Mg parts in copper coating.](image)

![Fig. 2 – LGMS plate (~70 g) coupled with stainless-steel net (LGMS/S.S.) (left) and the LGMS plate (~70 g) (right) without the S.S. net (i.e., metallic catalytic net).](image)

![Table 1 – The solutions employed in this work.](image)
the citric acid-added seawater bath. With respect to practical application and energy conservation, the data in Fig. 5 are important in the efficient and economical re-use of Mg scraps since Mg scraps can be directly added to the electrolyte for generating H₂ without pretreatments, such as re-melting of the scraps at high temperature. Fig. 6 plots data on the generation of H₂ using Mg scraps from a post-consumed magnesium part (see the scraps in Fig. 1(b)). When the scraps were directly mixed with seawater to which 20 wt% citric acid had been added in the reactor, 70 g of the scrap produced at least 40 l of hydrogen, as displayed in Fig. 6. Furthermore, 140 g of the scrap in the same bath produced at least 55 l of hydrogen. Since some scraps remained after the 3-h reaction, more hydrogen could be produced when the reaction was continued for more than 3 h. The purity of the generated hydrogen after dehumidification was as high as ~ 99%. Fig. 7 presents another example of the generation of H₂ from crucible Mg sludge (see them in Fig. 1(c)). Fig. 7 plots the amount of hydrogen generated by mixing sludge (70 g and 140 g, respectively) with seawater in a bath to which 20 wt% citric acid had been added. As indicated, relatively large amount of H₂ was produced by the reaction between the Mg sludge and the citric acid seawater.
According to the plot of H2 generation rate as a function of time (Fig. 5(b)), the generation rates from 30 min to 180 min are relatively low – perhaps because of the degradation of the solution to which citric acid had been added. Also, the 70 g Mg scrap sample did not completely react in 3 h with the solution to which citric acid had been added. In the reaction between the LGMS plate in 20 wt% citric acid seawater, for example (Fig. 5(a)), around 42.5 g of the LGMS plate was reacted and converted to H2 in 3 h. About 27.5 g of residual LGMS remained. To convert all scraps into H2 in a short period, the citric acid solution in the chamber was refreshed every 30 min. The old citric acid solution was removed from the reactor immediately before each recharging operation. Fig. 8 plots the cumulative volume of H2 against time. For comparison, the data in Fig. 6 are also presented in Fig. 8. After the fresh citric acid solution was recharged twice into the reactor, the total conversion of the Mg scraps into hydrogen took about 100 min. About 70 l of H2 was generated in 100 min using the recharging method. Comparing the data from Fig. 6 (no recharging was performed), approximately 30 l of H2 was produced in 100 min.

Materials used for the hydrogen production system were LGMS, citric acid, and seawater. The cost per kg of Mg scraps is about US$ 1.1 [16] while LGMS should charge less than it. The price of citric acid, as was pointed above, is US$ 1–1.3 per kg [26]. Moreover, the system does not need any catalyst, and can be carried out easily. For comparison, NaBH4 has high cost (US$ 40–55 per kg [7]), and NaBH4 system needs catalyst to have good H2 generation volume. Therefore, the hydrogen generation system by this work is possibly to be a new hydrogen-on-demand system. In the near future, studies on practical applications of the H2 generation system will be carried out. H2-production reactor (as shown in Fig. 3) was designed for possible future application in large-scale model. Based on the schematic of the experimental apparatus (Fig. 3), a new large-scale reactor can possibly be built, simply increasing the size of each unit in Fig. 3. Experimentally, the data of Fig. 8 were obtained by continually removing old solution in the reactor, followed by recharging fresh solution in the reactor during H2 generation every 30 min. In other word, Fig. 8 suggests that the H2-production reactor (Fig. 3) could likely be operated continuously. Future research will also address the by-product of H2 generation. For example, formaldehyde (CH2O) may be a by-product of the H2 generation process in citric acid solution. In this work, formaldehyde was qualitatively identified in the post-H2 generation solution using an MBTH color comparison method (reagent: 3-methyl-2-benzothiazolinone-hydrazone hydrochloride) (Kyoritsu Chemical-Check Lab., Corp., Tokyo, Japan). Accurate measurements will be addressed for the CH2O in the Mg/citric acid-added seawater H2 generation system. Moreover, future work will study the degradation of the formaldehyde in the post-H2 generation solution by oxidizer, e.g., hydrogen peroxide (H2O2) [29].
4. Conclusions

Low-grade Mg scraps, Mg slag/dross and post-consumed Mg products cannot currently be recycled efficiently and economically as secondary Mg alloy ingots. In this study, such Mg scraps were converted into hydrogen. Citric acid is a weak organic acid, which is cheap and almost non-toxic. Since citric acid markedly improves the volume and rate of H₂ generation, no catalyst net is required. The purity of the generated hydrogen following dehumidification was as high as ~99%. Fresh seawater to which citric acid is added can be recharged into the H₂ reactor to ensure that Mg scraps fully react in a short period to generate a considerable volume of hydrogen.

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