Evaluation of a New Hydrogen Generating System: Ni-Rich Magnesium Alloy Catalyzed by Platinum Wire in Sodium Chloride Solution

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Fuel cells are often seen as a long-term solution to environmental problems such as CO₂ emission associated with transportation. To ensure long-term sustainability and the supply of fuel, new renewable of hydrogen (H₂) generator have to be introduced. In this study, Ni-rich AZ91D magnesium alloy ingot, which was considered as waste material, was used as a H₂ generator in sodium chloride (NaCl) solution with catalyst. The chemical reaction $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Mg}(\text{OH})_2$ occurred in NaCl aqueous solution. The H₂ evolution rate depended on the solution's temperature (25 or 70°C), length of catalyst (0.9 or 1.8 m) and the concentration of NaCl solution (5 or 10 mass%). The H₂ evolution rate increased with increasing the solution's temperature. The catalyst (Pt wire) could significantly improve the H₂ generation rate. In addition, the by-product of this method is Mg(OH)₂, a non-toxic chemical compound which is usually used as flame retardant.

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1. Introduction

The challenge for automotive industry is to develop a clean and energy efficient vehicle to meet the need of CO₂ reductions. Various options have been considered not only from the environmental aspect but also with respect to what they cost. Fuel cell is seen as a long-term solution to the environmental problems associated with transportation.¹⁾ Currently, PEMFC (proton exchange membrane fuel cell) is regarded as the most suitable for fuel-cell-driven automobiles. Hydrogen (H₂) is a power source of the PEMFC. The H₂ can be provided by several methods,²⁾ including steam reforming of hydrocarbons, electrolysis water and gasification of heavy oil, coal or biomass.³⁾ However, H₂ is only an energy carrier, not a source of energy such as oil, gas or natural gas, etc. It must be manufactured using energy from other sources.⁴⁾ For this reason, hydrogen production actually consumes more energy than that contained in the resulting hydrogen itself.⁵⁾ To ensure long-term sustainability and the supply of fuel, a new renewable of H₂ generator have to be introduced. Amendola *et al.*^{6,7)} have explored a new method to generate hydrogen gas from sodium borohydride (NaBH₄), sodium hydroxide (NaOH) and H₂O mixed solution with Ru-based catalyst. When NaBH₄ aqueous solution contacted with the catalyst, it spontaneously hydrolyzes to form H₂ gas and sodium borate (NaBO₂).^{6,7)} Such investigations are significant for producing high quality hydrogen without polluting emissions. However, a disadvantage is that NaBH₄ is made from borax, a material that is found in substantial natural reserves globally. Currently, the production cost of NaBH₄ is still high, which is about 80 US dollars per kilogram.⁷⁾

2. Background of H₂ Generation from Ni-rich AZ91D Magnesium Ingot

Magnesium alloy was considered as an environment-

friendly material; one of the reasons is that the alloy is recyclable. In ASTM B93 standard for magnesium alloy ingot, the maximum Ni content should be less than 10 ppm. It is because the Ni element causes the formation of Mg-Ni compound in Mg matrix, leading to an extremely deleterious effect on corrosion resistance of magnesium alloys.⁸⁾ Once the Ni content in recycled ingot exceeds this limit, the ingot is usually discarded and considered as a waste. Thus, the Ni-rich ingot is inexpensive. The handling charge for magnesium scraps in recycling casthouse is approximately 1.1 US dollars per kilogram.⁹⁾

Electroless Ni plating is a common process for surface coating of AZ91D magnesium product.^{10,11)} For the recycling of the magnesium scraps, it is difficult to remove Ni from the molten magnesium due to strong affinities between Ni and Mg.¹²⁾ In present work, Ni-rich AZ91D magnesium ingot, which was considered as waste material, was used as a H₂ generator. Previous studies^{13,14)} have suggested that the overall reaction for the corrosion of magnesium is:

To promote H₂ generation rate, the overall reaction in NaCl solution with catalyst for the H₂ production may be expressed below:

In addition, the by-product, Mg(OH)₂, is a non-toxic chemical compound which is usually used as flame retardant.¹⁵⁾ Song¹⁶⁾ and Lunder¹⁷⁾ reported that a more direct way to determine corrosion rate is to measure the total amount of H₂ evolution from the magnesium specimen. Experimental results showed that the total amount of H₂ was increased with increasing the corrosion rate.^{16,17)} Figure 1 depicts a stack of Ni-rich AZ91 ingots and a qualified AZ91 ingot. The Ni-rich AZ91 ingot, due to careless scrap classification, was oxidized with dark surface. Figure 2 shows the curves of electrochemical polarization of Ni-rich and qualified AZ91 samples. As elucidated in Fig. 2, the Ni-rich AZ91 sample

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Fig. 1 The recycled Ni-rich AZ91D ingots and a qualified AZ91D ingot.

Fig. 2 Polarization curves of the qualified AZ91D and the Ni-rich AZ91D.

had corrosion current density ($I_{\text{corr}} \sim 2.7 \text{ A/m}^2$), which is about 2 order higher than the qualified ones ($\sim 8 \times 10^{-2} \text{ A/m}^2$). The experimental result revealed that the Ni-rich AZ91D magnesium ingots had inferior corrosion resistance.

This article addressed the hydrogen generation from the Ni-rich AZ91D magnesium ingot in NaCl solution with catalyst. The solution's temperature, length of catalyst and the concentration of NaCl solution were studied to investigate the H_2 generation rate. The weight loss of Ni-rich AZ91 sample was examined. The findings in this report not only suggest a method to generate hydrogen but also promote the recycling of the used magnesium products that were plated with Ni.

3. Experimental Procedures

Table 1 presents the chemical compositions of the Ni-rich AZ91D magnesium specimen. The Ni content in the specimen was 10 times greater than that in a qualified AZ91D magnesium ingot. The dimension of the Ni-rich AZ91D sample was 3 mm in thickness, 20 and 40 mm for the width

Table 1 Chemical compositions of the Ni-rich AZ91D magnesium alloy.

Composition	Al	Zn	Mn	Si	Cu	Fe	Ni	Mg
mass%	9.09	0.63	0.24	0.02	0.002	0.002	0.0148	Bal

Fig. 3 The Ni-rich AZ91D sample and the catalyst (Cu or Pt wire).

Fig. 4 The schematic illustration of hydrogen generation set-up.

and length. The samples were cleaned with ethyl alcohol, and then dried in furnace (70°C). Platinum (Pt) and copper (Cu) were used as catalyst. The Pt wire were 0.9 or 1.8 m in length and both with diameter 0.3 mm. The Cu wire was 0.9 mm in length and 0.3 mm in diameter. Figure 3 shows the catalyst (Pt or Cu wire) was being fastened to the sample. The sample was dipped in NaCl aqueous solution for H_2 generation. The concentration of the NaCl solution was 5 or 10 mass%. As the schematic illustration indicated in Fig. 4, an inverted graduated cylinder filled with the NaCl solution was immersed in a beaker containing the solution. The sample with catalyst wire fixed with a float ball was then put into the cylinder. The liquid in cylinder would be drained out, owing to the hydrogen generation (Figs. 4 and 5). In addition, ultrasonic vibration equipment was applied to study the vibration effect on H_2 generation rate. The weight loss of the Ni-rich AZ91D specimen after H_2 generation experiment was measured. To obtain the weight loss data, corrosion product on the sample after H_2 generation was cleaned using the

Fig. 5 The Ni-rich AZ91D sample with catalyst, generating H_2 in the inverted graduated cylinder.

Fig. 6 H_2 generated from the Ni-rich AZ91D sample vs. time in 5 mass%NaCl solution in the absence of catalyst. Hereafter, the plot of $NaBH_4 + NaOH + H_2O$ /catalyst Ru at $25^\circ C$ was redraw according to the data of a previous study.⁶⁾

procedures as described elsewhere.¹⁸⁾ An X-ray diffractometer using $Cu K_\alpha$ radiation operated at 40 KV was employed to examine the chemical reaction product after the reaction for H_2 generation. An X-ray scanning speed of 1 degree/minute was used.

4. Results and Discussion

Figure 6 shows the H_2 volume generated from the Ni-rich AZ91D sample in 5 mass%NaCl aqueous solution in the absence of catalysts. As elucidated in Fig. 6, the temperature of the NaCl solution was able to affect the H_2 generation rate. The rate of the $70^\circ C$ experiment was about three times higher than that of the sample in the $25^\circ C$ solution. The weight loss of the Ni-rich AZ91D sample after the H_2 generation experiments was about 0.22 and 0.47 g for the 70 and $25^\circ C$ experiments, respectively. The data of a previous study⁶⁾

Fig. 7 H_2 volume generated from the Ni-rich AZ91D sample catalyzed by Cu wire vs. time in 5 mass%NaCl solution at $25^\circ C$.

about H_2 generation from the aqueous borohydride ($NaBH_4$) solution and Ru catalyst were also plotted in Fig. 6. The H_2 generation rate of present study was lower, as compared to the previous result.

The data of H_2 volume generated from the Ni-rich AZ91D in the presence of Cu catalyst were depicted in Fig. 7. For exploring the effect of ultrasonic vibration on the H_2 production rate, the H_2 generation set-up (see Fig. 4) was placed into an ultrasonic vibration cleaner. The data points shown in Fig. 7 elucidated that ultrasonic vibration could effectively promote the H_2 generation rate. The H_2 generation rate from the Ni-rich AZ91D catalyzed by Cu wire was much higher than that from the same alloy without catalyst (*cf.*, data in Fig. 6). Nevertheless, it is only about one half of the H_2 generation rate by $NaBH_4$ solution/Ru catalyst.⁶⁾ Figure 8 presents the significant improvement of the H_2 production from the Ni-rich AZ91D sample catalyzed by Pt wire. The data points in Fig. 8 were obtained from the

Fig. 8 H_2 from the Ni-rich AZ91D sample catalyzed by Pt wire vs. time in 5 and 10 mass%NaCl solutions.

experiments under ultrasonic vibration. As indicated in this figure, there are three groups of data sets: (a), (b) and (c). The data set “(a)” presented the H_2 generation rate of the AZ91D sample catalyzed by 1.8 meters Pt wire (e.g., see the sample in Fig. 3) in the solution of 70°C . The sample in 10%NaCl solution generated H_2 in a higher rate than the sample in the 5% solution did. Similar results were obtained for the samples tested in the NaCl solution at 25°C (see the data set “(b)” in Fig. 8). The H_2 generation rate was substantially improved by using Pt wire as the catalyst for the reaction: $\text{Mg}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \text{Mg}(\text{OH})_{2(s)}$. For the H_2 volume created from zero to $\sim 550\text{ mL}$, the data set “(a)” and “(b)” showed a good efficiency that spent no more than 800 s to achieve. The H_2 generation rate is as good as the result of previous study *via* NaBH_4 solution/Ru catalyst at 25°C .⁶⁾ The weight losses of the samples for the H_2 generation in Fig. 8 were in the range between 0.29 and 0.62 g.

One of the by-products of the catalyzed reaction is magnesium hydroxide ($\text{Mg}(\text{OH})_2$), which is non-toxic, non-corrosive¹⁹⁾ and is one of the most widely used metal hydroxide flame retardant additives for polymers.²⁰⁾ As the AZ91D sample being generating H_2 in NaCl solution, some solid compound was being condensed in beaker, as schematically shown in Fig. 4. The compounds were collected and rinsed in distilled water to dilute the NaCl concentration. Figure 9 is the X-ray diffraction pattern of the compound, showing that the compound is $\text{Mg}(\text{OH})_2$. Another by-product, which was being synchronically mixed in the H_2 gas stream during the hydrogen generation, is water vapor. Prehumidified H_2 is needed in proton exchange membrane fuel cells,⁶⁾ since the electric conductivity depends significantly on the water content in the fuel cell, especially in the membrane.^{21,22)} As indicated in Fig. 10, several ice cubes were continually put on the top of the cylinder that containing the H_2 gas produced by present method at 25°C . The condensed water drop (as shown in Fig. 10) was not seen until three hours were spent in keeping the container's top cooled down. The experimental result suggested that the total gas volume not only contained H_2 but also had a few water vapor. However, the present report did not examine the volume fraction of water vapor existing in the H_2 gas stream.

Fig. 9 X-ray diffraction pattern of the by-product compound after H_2 generation, showing that the compound is magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

Fig. 10 A water drop condensed by ice cubes, showing the existence of water vapor in the generated hydrogen volume.

Fig. 11 (a) and (b), a set-up to view the hydrogen flame. The H_2 was generated in the NaCl solution at 25°C .

It was believed that the gas volume produced at 70°C (see Figs. 6 and 8) contained more water vapor than that at 25°C .

Figure 11 shows a set-up to view the hydrogen flame, and to see how long the flame could last. Hydrogen ignited and produced a bark-like noise, when mixed with the oxygen of the air.²³⁾ This reaction is the positive test for hydrogen gas.²³⁾

The hydrogen was coming from the Ni-rich AZ91 sample catalyzed by Pt wire at the solution temperature of 25°C. Figures 11(a) and (b) reveal the hydrogen flame, which could keep burning for about 1 h.

5. Conclusion

- (1) The corrosion rate of the Ni-rich AZ91D ingot can be greatly bigger than that of the qualified AZ91D alloy. The corrosion current density of the former material is 2.7 A/m², which is two order higher than that of the latter material.
- (2) Ni-rich AZ91D magnesium ingot can be used to generate hydrogen (H₂) in NaCl aqueous solution. The NaCl concentration in the solution evidently affects the hydrogen generation rate. More NaCl dissolved in the solution resulted in a superior rate of H₂ generation. The rate of H₂ generation was experimentally confirmed to be increased by ultrasonic vibration.
- (3) Platinum wire can be employed as the catalyst for the reaction: $\text{Mg}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \text{Mg}(\text{OH})_{2(s)}$. Given the sample size ($3 \times 20 \times 40 \text{ mm}^3$) and the Pt wire used herein, ~550 mL of H₂ was produced in 10 minutes after the above chemical reaction at 25°C.

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