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# Study on hydrolysis property of Mg-8Li alloy for hydrogen production

To cite this article: Wang Tao *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **242** 042008

IOP Conf. Series: Earth and Environmental Science **242** (2019) 042008 doi:10.1088/1755-1315/242/4/042008

# Study on hydrolysis property of Mg-8Li alloy for hydrogen production

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**Abstract**. Vacuum induction melting technology was used to prepare Mg-8Li alloy. Magnesium and lithium alloy chips were reacted with aqueous solution. The hydrogen production rate and hydrogen production rate of the alloy were tested and characterized by drainage method. The effect of $NH_4Cl$ solution with different concentration and temperature on hydrogen production rate and reaction degree of Mg-8Li based alloy was investigated. The results showed that with the increase of $NH_4Cl$ concentration and hydrogen production, $NH_4^+$, $Cl^-$, and $H^+$ could promote the hydrolysis reaction. Hydrogen production volume at 25 ℃ and 45 ℃ range increases with temperature decrease, high hydrogen content increases with the temperature when it is higher than 65 ℃.

## 1. Introduction

The promotion of hydrogen energy is limited by hydrogen production technology, storage and transportation technology [1]. Most industrial hydrogen uses fossil fuels to produce hydrogen and electrolytic water to produce hydrogen, which has low efficiency, high energy consumption and serious environmental pollution[2-3]. New hydrogen production methods, such as solar photolysis water method, have disadvantages such as low utilization rate of light energy, small amount of hydrogen production [4], and low production of biological hydrogen [5-6]. Hydrolysis of active metals and their hydrides is a promising hydrogen production technology, among which hydrolysis reaction of aluminum-based, magnesium-based and NaBH4 for hydrogen production has attracted much attention [7].Magnesium is abundant in the earth, the surface protection layer is loose, the reaction with water is easy to start, and the storage conditions are stable. The magnesium-based material has a high theoretical hydrogen production volume, which is the low cost, cost-effective hydrogen production material ideal choice.

However, with the progress of the hydrolysis reaction, the by-product $Mg(OH)_2$ forms an inert layer, which hinders the continuous hydrolysis reaction[8] and reduces the hydrolysis hydrogen production rate and conversion rate, resulting in a decrease in the kinetic performance and incomplete $Mg/H_2O$ reaction at low temperature. It is of great significance to improve the reactivity of magnesium water, safely and effectively remove the hindrance of $Mg(OH)_2$ layers on the hydrolysis reaction, and increase the hydrolysis hydrogen production rate and conversion rate for the application of hydrolysis hydrogen production technology of magnesium base alloy.

Lithium metal and water will have violent chemical reactions to release hydrogen. Under the standard state of 1 gram of lithium, 1760mL of hydrogen will be generated and a large amount of heat will be released. China is rich in lithium resources, and low-grade Li can be used as raw material, but the same storage conditions are relatively poor. If Mg-Li alloy is made, it is a very meaningful and exploratory work to produce hydrogen by hydrolysis reaction of Mg-Li alloy. The hydrolysis of magnesium - lithium alloy for hydrogen production is still less. Hydrolysis of Mg-8Li alloy with α+β two-phase microstructure was studied.

Magnesium-lithium alloy ingots are fused and cast in a vacuum induction melting furnace under the protection of argon. The hydrogen production rate and hydrogen production rate of the alloy were measured and characterized by the drainage method in the hydrogen production and measurement device of metal. The influence of $NH_4Cl$ solution with different concentration and temperature on the hydrogen production rate and reaction degree of Mg-Li based alloy hydrolysis was discussed.

## 2. Influence of $NH_4Cl$ solution concentration on hydrogen production performance of Mg-8Li based alloy by hydrolysis

Ammonium chloride solution is used to expect to enhance the Mg-8Li alloy hydrolysis reaction activity at 25 ℃ water. Ammonium chloride solution with different concentration was used as reaction medium. The hydrolysis volume/time curve of hydrogen production per gram of Mg-8Li based alloy in ammonium chloride solution of different concentrations is as follows in the Fig.1.

As shown in Fig.1, hydrogen production volume increases with the increase of NH4Cl concentration. Fig.2 is the Mg-8Li alloy hydrolysis speed curve for producing hydrogen with different concentrations of NH4Cl solution in 25 ℃ water. It can be clearly seen from Fig.2 that the peak velocity increases gradually with the increase of NH4Cl concentration.

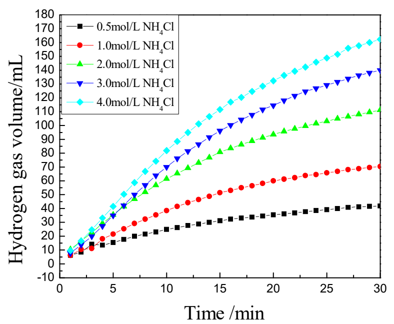


Fig 1 25 ℃ NH4Cl solution of different concentrations of Mg- 8 Li alloy hydrolysis to produce hydrogen volume curve

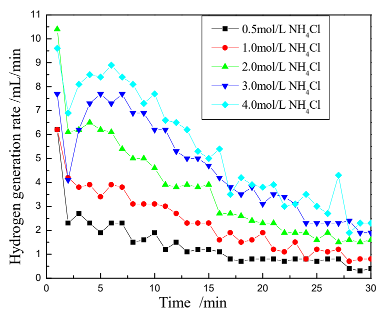


Fig.2 NH4Cl solution of different concentrations of Mg - 8 li alloy hydrolysis to produce hydrogen speed curve in 25 ℃ water

Under the room temperature of 25 ℃, the greater the concentration of NH4Cl, the hydrolysis of hydrogen production performance is more excellent. It is generally believed that the reaction of NH4Cl solution with magnesium and lithium releases $H_2$, because the hydrolysis of NH4Cl solution is acidic. However, the experimental results showed that the acidity of 0.5mol/LNH4Cl, 1mol/L$NH_4Cl$, 2mol/LNH4Cl, 3mol/L$NH_4Cl$, and 4mol/L$NH_4Cl$ solutions were similar, but the reaction rate was 0.5 mol/L $NH_4Cl$ <1 mol/L $NH_4Cl$<2 mol/L $NH_4Cl$<3 mol/L $NH_4Cl$<4 mol/L$NH_4Cl$. The reason for these experimental results is that when $NH_4Cl$ reacts with Mg-8Li basedd alloy, it not only directly reacts with $H^+$, but also directly participates in the reaction of $NH_4^+$ when $[NH_4^+]> [H^+]$ is in solution. $H^+$ and $NH_4^+$ are protic acids. The essence of its chemical reaction is:$2NH_4^+ + Mg + H_2O = Mg^{2+} + H_2\uparrow + 2NH_3 \bullet H_2O$, $Mg^{2+} + 2OH^- = Mg(OH)_2\downarrow$.

Thus, it can be concluded that the hydrolysis rate of Mg-8Li basedd alloy increases with the concentration of $NH_4Cl$ solution increasing.

## 3. Effect of temperature on hydrogen production performance of Mg-8Li based alloy by hydrolysis

In order to further study the influence of $NH_4Cl$ solution at different temperatures on the hydrolysis performance of Mg-8Li based alloy, $NH_4Cl$ solution at different temperatures was used as the reaction medium. Hydrolysis volume/time curve of hydrogen production per gram of Mg-8Li based alloy in $NH_4Cl$ solution at different temperatures is shown in Fig.3.

Hydrolysis volume of hydrogen production decreases with increasing temperature when the temperature is 25 ℃ to 45 ℃ as shown in Fig.3.

In the more than 65 ℃ with the increase of temperature hydrolysis hydrogen production volume increases. Figure 2.2 shows the hydrolysis rate/time curve of hydrogen production per gram of Mg-8Li based alloy in NH4Cl solution at different temperature.

The Fig.4 shows that when the temperature is 25 ℃ to 45 ℃, peak velocity is near with temperature rises; In more than 65 ℃ with temperature rises, peak speed increase. That the temperature increases will accelerate the hydrolysis reaction speed and increase the hydrogen production, thus preventing $Mg(OH)_2$ from binding densification on the unreacted particles. Increasing the temperature will release a lot of heat, so that part of the formed $Mg(OH)_2$ film will undergo redissolution and crystallization, which will affect its densification, thus facilitating the hydrolysis reaction. In a word: in less than 45 ℃, the temperature does not significantly promote the Mg–8Li alloy hydrolysis hydrogen production speed, but in more than 45 ℃ temperature, Mg–8Li alloy hydrogen production speed will be promoted.

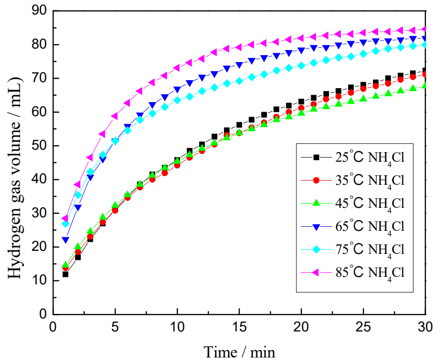


Fig.3 hydrolysis volume curve of hydrogen production of Mg-8Li based alloy in NH4Cl solution at different temperature

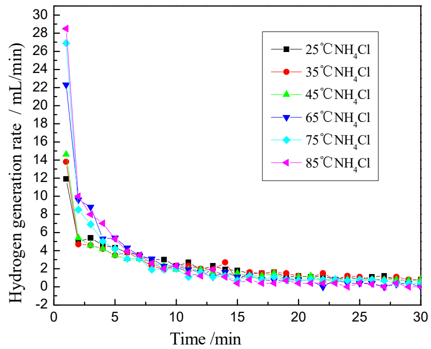


Fig.4 Hydrolysis rate curve of hydrogen production of Mg-8Li based alloy in $NH_4Cl$ solution at different temperature

## 4. Effects of different concentrations of HCl on hydrogen production performance of Mg-8Li based alloy by hydrolysis

In order to further study the effect of HCl (NH4Cl with the same concentration) mixed solution on the densification of hydrolysate $Mg(OH)_2$, the mixed solution with different concentrations of HCl (NH4Cl with the same concentration) was used as the reaction medium. Hydrolysis volume/time of hydrogen production per gram of Mg-8Li based alloy in HCl solution of different concentrations is shown in Fig.5.

As seen from Fig.5, with the increase of HCl solution concentration, hydrogen volume increases. Hydrolysis rate/time curve of hydrogen production per gram of Mg- 8Li base alloy in HCl solution of different concentrations is shown in figure 3.2.

Figure 6 is hydrolysis to produce hydrogen speed curve for Mg-8Li based alloy at different HCl concentration in 25 ℃ (with the same $NH_4Cl$ concentration) mixture reaction. It can be clearly seen from the figure that the peak velocity increases gradually with the increase of HCl solution concentration. Under the room temperature is 25 ℃, the greater the concentration of HCl solution, its performance is more excellent. The main reasons are as follows: in the reaction between acid of different concentrations and Mg-8Li based alloy in ammonium salt aqueous solution, $Mg^{2+}$ is generated by the reaction of the negative electrode, and the positive electrode consumes $H^+$ to produce $OH^-$. With the reaction going on, $[Mg^{2+}]$ and $[OH^-]$ in the solution increase continuously. When the

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reaction goes on to a certain extent, $[Mg^{2+}][OH^{-}]$ is greater than or equal to Ksp $Mg(OH)_2$, $Mg(OH)_2$ will be precipitated. Deposition prevents further reflection of the alloy. Therefore, the reaction rate between acidic ammonium chloride solution and alloy is as follows:0.7 mol/L.

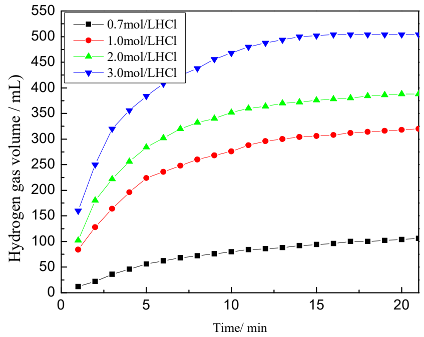


Fig.5 Mg- 8Li alloy hydrolysis to produce hydrogen volume curve in 25 ℃ with different concentration of HCl solution

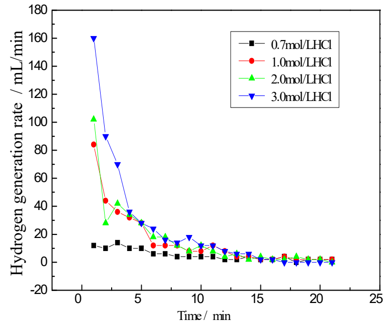


Fig.6 Hydrolysis rate curve of hydrogen production of Mg-8Li based alloy in $NH_4Cl$ solution at different temperature

HCl（$NH_4Cl$）<1.0 mol/LHCl（$NH_4Cl$）<2.0 mol/LHCl（$NH_4Cl$）<3.0mol/LHCl（$NH_4Cl$）

The adsorption on the surface of the alloy adsorbs the relatively small $Cl^-$ on its surface, $Cl^-$ can penetrate the oxide protective film on the metal surface, and $Cl^-$ replaces the oxygen ions in the oxide film to make the protective film become soluble chloride, activate the metal surface, and promote the metal oxidation reaction. Therefore, the oxidation rate of metals in the presence of $Cl^-$ accelerates in chemical reactions in which metals participate. It can be concluded that the hydrolysis rate of Mg-8Li based alloy increases with the concentration of HCl solution increasing.

## 5. XRD analysis

Figure 7 XRD diagram of Mg-8Li based alloy under different corrosion conditions.

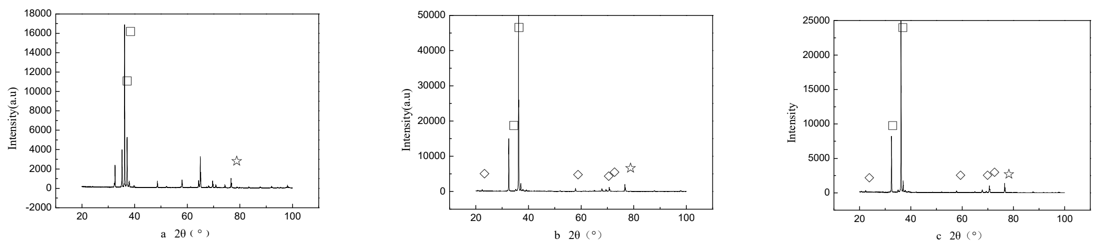


Fig.7 XRD pictures of Mg-8Li based alloy under different conditions

a) XRD diagram of the original microstructure of Mg-8Li based alloy b) XRD diagram of $NH_4Cl$ solution corrosion c) XRD diagram of water corrosion

As seen from Fig.7, the surface of the alloy before corrosion is α-Mg matrix (□) and β-Li phase (☆).The concentration of β-Li phase is lower than that before and in water corrosion, which fully indicates that the β-Li phase in the alloy is preferentially corroded. $Mg(OH)_2$ (◇) in the corrosion products can adhere to the alloy surface, play a role in preventing corrosion, and the corrosion of $Li^+$ is in the solution, resulting in an increase in the pH of the solution. Because $Mg(OH)_2$ does not adequately cover the substrate, alpha Mg and beta Li phases remain on the alloy surface. This also indicates that $H^+$、$NH_4^+$ and $Cl^-$ have obvious destructive effects on the protective film of the alloy surface, making it difficult for the alloy to be passivated in $NH_4Cl$ solution.

## 6. Electrochemical corrosion analysis of Mg-8Li based alloy

Fig.8 shows the polarization curves of corrosion of Mg-8Li based alloy in 0.5mol/LNH4Cl solution, 1.0mol/LNH4Cl solution, and 2.0mol/LNH4Cl solution.

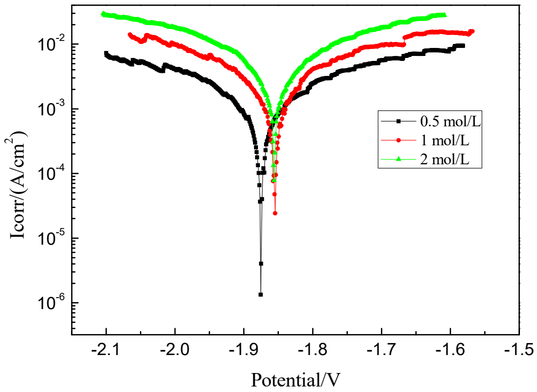


Fig.8 Tafel curve of Mg-8Li based alloy A) corrosion of 0.5 mol/L NH4Cl solution b) corrosion of 1.0 mol/L NH4Cl solution c) corrosion of 2.0 mol/L NH4Cl solution

Fig.8 illustrates that the increasing the concentration of a solution of ammonium chloride hastened Mg-8Li alloy hydrogen production speed, one can see from the potential polarization curves of Mg-8Li alloy in 2.0 mol/L ammonium chloride solution corrosion electrode potential is very big, that the overall destruction more serious can be speculated, to surface corrosion pitting corrosion development, $Cl^-$ seep into the alloy surface, corrosion depth, destroy the hydrate formation of protective film, outer hydroxide film became loose, promote effectively the corrosive medium contact with the magnesium alloy substrate. With the increase of ammonium chloride solution concentration, the more serious the corrosion is, the higher the hydrogen production speed is, and the corrosion electrode potential of Mg-8Li based alloy in 0.5mol/L ammonium chloride solution is lower. This is consistent with the hydrolysis hydrogenation performance curve of Mg-8Li based alloy in $NH_4Cl$ solution of different concentrations.

## 7. Conclusion

The hydrogen production rate law of Mg-8Li based alloy in $NH_4Cl$ solution with different $H^-$ contents, concentrations and temperatures was studied. The hydrogen production rate, corrosion products and corrosion mechanism of Mg-8Li based alloy in solution were analyzed by velocity curve, XRD analysis and polarization curve, and the following conclusions were drawn.

(1) With the increase of HCl solution concentration, hydrogen production increased and the peak velocity gradually increased. The higher H+ concentration is, the more hydrolytic reaction is promoted.

(2) As the concentration of NH4Cl increases, the hydrogen production increases and the peak velocity gradually increases. The higher the concentration of NH4+ and Cl-, the higher the hydrolysis reaction.

(3) When the temperature is 25 °C to 45 °C, high hydrogen volume reduces with temperature rising and speed peak is close. In the more than 65 °C, hydrogen and peak speed produced by hydrolysis increase with the increase of temperature, the more obstacles alloy surface hydrolysis of protective film and indirectly promote the hydrolysis reaction.

## Acknowledgment

**Fund project:** Heilongjiang university students innovation and entrepreneurship training program project (201410222032);Basic research project of basic scientific research operating fee of Heilongjiang education department (2016-KYYWF-0555); Key project of science and technology of Jiamusi university (lz2014-001).

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