

# Hydrogen production from highly corroding Mg-based materials elaborated by ball milling

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## Abstract

It is universally known that the reaction between magnesium or magnesium hydride and water produces hydrogen. However, this reaction stops rapidly due to the formation of a passive  $\text{Mg}(\text{OH})_2$  layer onto the reactive material. In this paper, we present an investigation of the hydrogen production by hydrolysis of Mg-based materials elaborated by high-energy ball milling. The best performance is obtained with a Mg–10 at.% Ni composite material milled for 30 min, which leads to a conversion yield of 100% after 1 h of hydrolysis in neutral aqueous solution containing chloride ions.

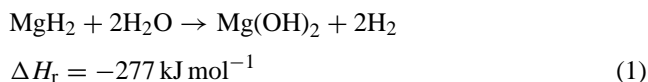
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**Keywords:** Hydrogen storage materials; Magnesium; High-energy ball milling; Hydrolysis reaction; Corrosion

## 1. Introduction

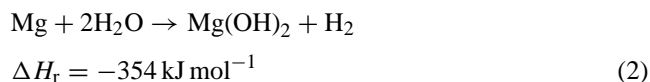
The conception of a compact, safe and inexpensive hydrogen source is a key issue for the development of fuel cells. Different sources of hydrogen can be considered, including compressed  $\text{H}_2$ , carbon-based  $\text{H}_2$  storage, metal hydrides, chemical hydrides and methanol. Among them, chemical hydrides (e.g.  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ ,  $\text{MgH}_2$ ) [1–6] appear very promising due to their high theoretical hydrogen yield by weight.

For example, pure hydrogen can be obtained by reacting  $\text{MgH}_2$  with water through the reaction:



The hydrogen yield of this reaction is 6.4 wt.% when water is included in the calculation. The hydrogen yield increases to 15.2 wt.%, if the water produced by the fuel

cell is recovered for the hydrolysis reaction. Moreover, this reaction has the advantage to produce residual  $\text{Mg}(\text{OH})_2$ , which is environmental friendly. It is also possible to produce hydrogen by using very cheap Mg material by the following reaction:



In this case, the hydrogen yield is 3.3 wt.% (considering water mass) and 8.2 wt.% (no water included in the calculation). However, the hydrolysis reaction using conventional Mg or  $\text{MgH}_2$  is rapidly interrupted because of the formation of a passive magnesium hydroxide layer onto the reactive material. Acid can be added to form soluble  $\text{Mg}^{2+}$  species but this is detrimental to the equipment and provides a potential hazard for users.

In this work, we present an investigation of the hydrogen production by the hydrolysis of Mg-based materials elaborated by high-energy ball milling. The aim is to conceive highly corroding materials to assure a full completion of the hydrolysis reaction in neutral aqueous solution.

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## 2. Experimental

MgH<sub>2</sub> (95 wt.% MgH<sub>2</sub>, 5 wt.% Mg, 20 μm), Mg and Ni (99.8 wt.%, –325 mesh) were used as starting materials. Ball milling was performed under argon atmosphere with a ball-to-powder mass ratio of 8:1 using a SPEX 8000 ball mixer. The milling time was varied from 0.5 to 10 h.

The specific surface area of the powders was measured by N<sub>2</sub> adsorption (multipoint BET).

The hydrolysis reactions were carried out in flask reactor of 1000 ml with two openings, one for water addition and the other one for hydrogen exhaust. The produced gas was flown through a condenser and drierite to remove all water vapour before passing through a flowmeter (ADM 3000, Agilent Technologies). One-hundred millilitres of aqueous solution were added to react with 250 mg of powder.

## 3. Results and discussion

Fig. 1 shows the hydrogen production profiles of Mg and MgH<sub>2</sub> powders reaction in pure water and in 1 M KCl solu-

tion for different milling times. The hydrogen production is expressed as a conversion yield (%) defined as the volume of produced H<sub>2</sub> over the theoretical volume of hydrogen that should be released assuming that all material is hydrolysed.

As seen in Fig. 1a, the ball milling treatment has no effect on the Mg reactivity in pure water. All curves show a very rapid H<sub>2</sub> release in the first 30–60 s of hydrolysis followed by a drastic interruption of the reaction, leading to a very low conversion yield (<15%). The abrupt stop of the hydrolysis reaction is due to the well-known formation of passive Mg(OH)<sub>2</sub> layer onto the Mg powder surface, which prevent further contact between water and un-reacted Mg material. The formation of Mg(OH)<sub>2</sub> occurs although the bulk pH of the solution is lower than the pH predicting the appearance of Mg(OH)<sub>2</sub> (i.e. pH ≥ 10–11) [7] because the pH at the powder/solution interface is greater than 10 due to the hydrogen evolution reaction leading to the formation of hydroxide ions (2H<sub>2</sub>O + 2e<sup>-</sup> = H<sub>2</sub> + 2OH<sup>-</sup>).

In contrast, the ball milling affects the MgH<sub>2</sub> hydrolysis reactivity in pure water as seen in Fig. 1b. The highest reactivity is obtained with 30 min milled MgH<sub>2</sub>, which displays a

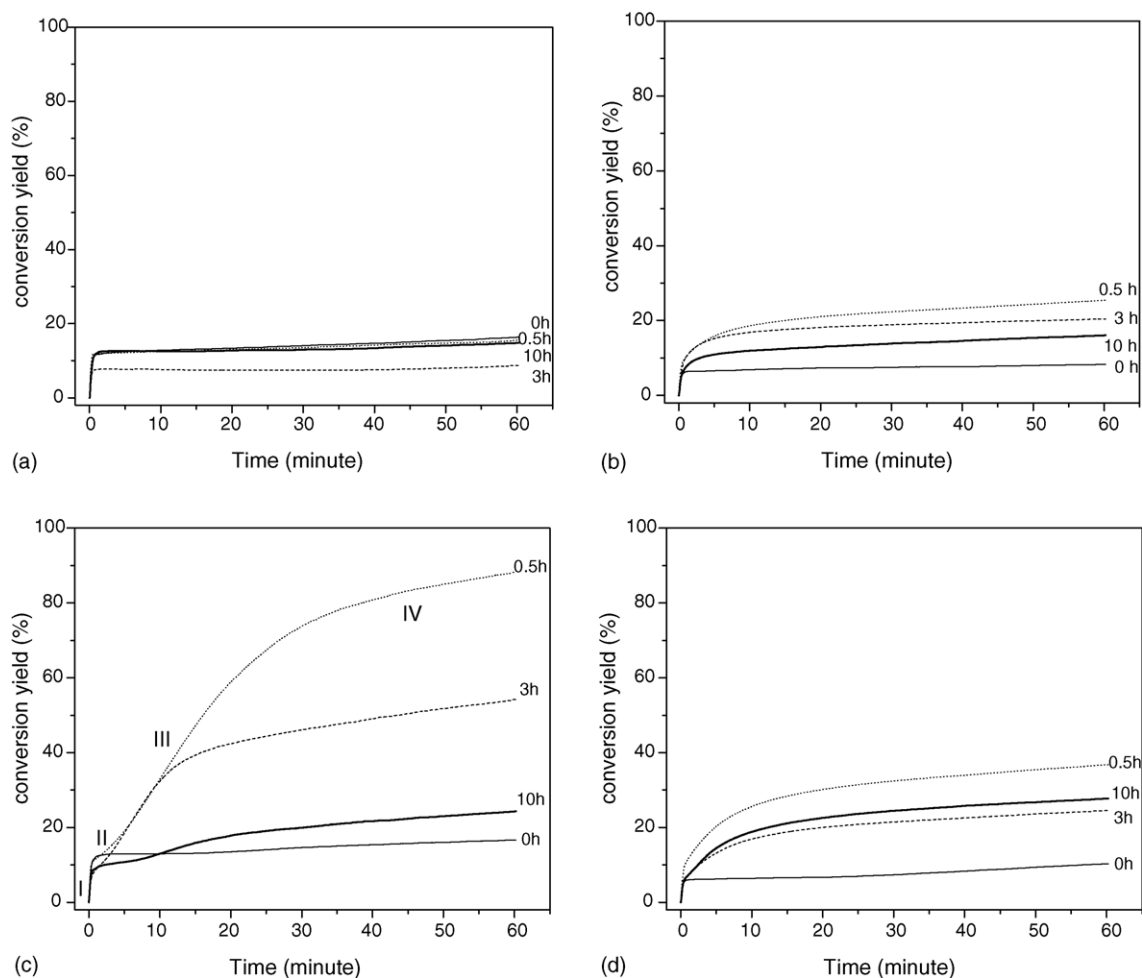


Fig. 1. Hydrogen production curves of (a) Mg in pure water, (b) MgH<sub>2</sub> in pure water, (c) Mg in 1 M KCl, (d) MgH<sub>2</sub> in 1 M KCl for different milling times (0, 0.5, 3 and 10 h).

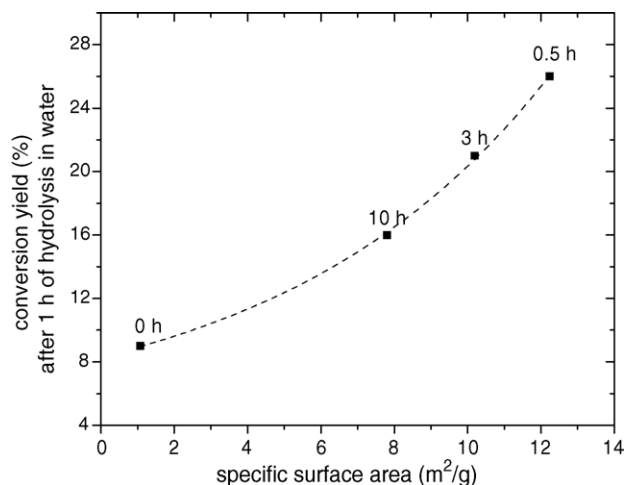


Fig. 2. Conversion yield of MgH<sub>2</sub> powders after 1 h of hydrolysis in pure water as a function of the powder effective surface area.

conversion yield of 26% compared to 9% for unmilled MgH<sub>2</sub> powder. Actually, the more the specific surface area of the powder is increased by the milling treatment, the more the fraction of powder likely to react with pure water before its passivation is large. Indeed, a correlation can be clearly established between the conversion yield of the MgH<sub>2</sub> powders and their effective surface area (see Fig. 2). The specific surface area of MgH<sub>2</sub> powder displays a maximum of 12.2 m<sup>2</sup>/g after 30 min of milling – indicating that the powder fracturing is predominant in the first stages of the milling – and then decreases to 7.8 m<sup>2</sup>/g after 10 h of milling due to formation of particle agglomerates for longer milling period. In contrast, the specific surface area of Mg powder decreases almost linearly from ~0.7 m<sup>2</sup>/g for as-received Mg powder to ~0.1 m<sup>2</sup>/g for 10 h milled Mg powder. This reflects the major difference in the mechanical properties between MgH<sub>2</sub> and Mg, i.e. the brittle characteristic of MgH<sub>2</sub> powder favours its fracturing during ball milling whereas with ductile Mg material the cold welding phenomenon predominates.

When hydrolysis is performed in 1 M KCl aqueous solution rather than pure water, the results are drastically different for Mg powders as seen in Fig. 1c. The Mg powder milled 30 min displays the best efficiency with a conversion yield reaching 89% after 1 h of hydrolysis compared to 54, 25 and 17% for 3 and 10 h and unmilled powders. In addition, the hydrolysis curves for milled Mg in KCl solution presents a distinctive shape with the appearance of an induction period. That is, after the first 30 s of rapid hydrolysis (region I in Fig. 1c), the hydrolysis rate decreases for few minutes (region II) and reaccelerates again (region III) before stopping progressively (region IV). The duration of this induction period (region II) differs with milling time (i.e. ~1 min for 0.5 h Mg powder compared to ~3 min for 3 h Mg powder and ~7 min for 10 h Mg powder). This period may correspond to the incubation time for pit initiation.

The increase of the Mg conversion yield with KCl addition is associated with the destabilization of the Mg(OH)<sub>2</sub>

passive layer by chloride ions as demonstrated by corrosion studies [8,9]. The Cl<sup>-</sup> ions substitute OH<sup>-</sup> ions to form MgCl<sub>2</sub>. This salt is more soluble than Mg(OH)<sub>2</sub> (the solubility of MgCl<sub>2</sub> in water at 20 °C is 542 g/l compared to 0.009 g/l for Mg(OH)<sub>2</sub> [10]). Then, localized breakdown of the passive layer occurs leading to a pitting corrosion process. Thus, the increase of the H<sub>2</sub> production with milled Mg powders (in particular with 30 min milled Mg sample) may reflect their higher susceptibility to pitting corrosion. It can be ascribed to the formation of defects (grains boundaries, dislocations, vacancies, etc.) through the milling process, which may favor localized chloride enrichment accentuating the pitting corrosion. The breaking of the native surface oxide layer on Mg powder during milling may also create fresh active surfaces for corrosion. On the other hand, the fact that Mg powders milled 3 and 10 h are less reactive than 0.5 h milled Mg powder can be ascribed to the accentuation of the powder oxidation during prolonged milling [11] in addition to the decrease of its specific surface area as indicated previously. Prolonged milling may also induce a more uniform distribution of the defects compared to the 30 min Mg sample, resulting in a better distribution of Cl<sup>-</sup> on the powder surface and thus, localized chloride enrichment favorable to pitting corrosion might be less marked.

In contrast, KCl addition has a weak effect on the improvement of the hydrolysis activity of MgH<sub>2</sub> powders as shown in Fig. 1d. For example, the conversion yield of the MgH<sub>2</sub> powder milled for 30 min is 37% in 1 M KCl compared to 26% in pure water. It can be related to the insulator characteristic of the MgH<sub>2</sub> material that must limit the corrosion process.

It is well known that magnesium is highly susceptible to impurities that promote internal galvanic attacks [9]. Nickel constitutes an appropriate cathode material to cause severe galvanic corrosion in Mg due to its low hydrogen overpotential. Thus, in order to increase the conversion yield of Mg and to accelerate the hydrolysis reaction, Mg–Ni composite materials were elaborated. Optimization procedure (results not shown) by varying the milling time (from 0 to 10 h), the proportion of Ni (from 1 to 25 at.%) and the Ni particles size (from ~0.1 μm to –325 mesh) indicated that milling of Mg powder with 10 at.% Ni (–325 mesh) for 30 min are appropriate synthesis parameters to obtain highly active Mg-based material for H<sub>2</sub> production. This is illustrated in Fig. 3, which compares the hydrogen production profiles in 1 M KCl of 0.5 h milled Mg and 0.5 h milled Mg–10 at.% Ni powders. A conversion yield of 100% is obtained after 1 h of hydrolysis with a mean hydrogen production rate of 70 ml/min per gram of powder in the first 10 min of reaction compared to a conversion yield of 89% with a mean hydrogen production rate of 30 ml/min per gram of powder in the first 10 min of reaction for 0.5 h milled Mg alone. However, due to the presence of unreactive Ni material, the 0.5 h milled Mg–10 at.% Ni powder produces less hydrogen per gram of material than the 0.5 h milled Mg powder, i.e. 763 ml H<sub>2</sub> compared to 856 ml H<sub>2</sub>, corresponding to a hydrogen yield of 6.8 and 7.6 wt.%

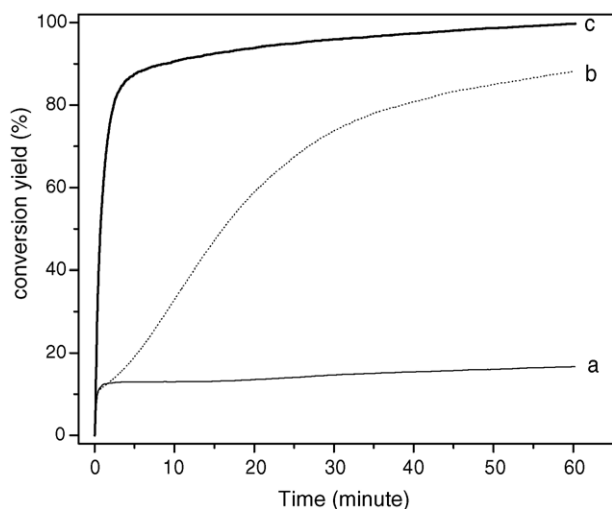


Fig. 3. Hydrogen production profiles in 1 M KCl of (a) unmilled Mg, (b) 0.5 h milled Mg and (c) 0.5 h milled Mg–10 at.% Ni.

respectively (the KCl solution weight is not included in the calculation).

#### 4. Conclusion

We have elaborated a very effective and cheap H<sub>2</sub> source material, which consisted of a mixture of Mg + 10 at.% Ni milled for 30 min. The high reactivity of this material for hydrolysis is explained by the presence of fresh active surfaces with numerous defects in addition to the creation micro-

galvanic cells between close Mg and Ni components that accentuate greatly the corrosion process.

#### Acknowledgements

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#### References

- [1] R. Aiello, M.A. Matthews, D.L. Reger, J.E. Collins, *Int. J. Hydrogen Energy* 23 (1998) 1103.
- [2] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, *Int. J. Hydrogen Energy* 24 (1999) 665.
- [3] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, *Int. J. Hydrogen Energy* 28 (2003) 205.
- [4] Y. Kojima, K.I. Suzuki, Y. Kawai, *J. Mater. Sci.* 39 (2004) 2227.
- [5] Y. Kojima, K.I. Suzuki, K. Fukimoto, Y. Kawai, M. Kimbara, H. Nakanishi, S. Matsumoto, *J. Power Sources* 125 (2004) 22.
- [6] J.P. Tessier, P. Palau, J. Huot, R. Schulz, D. Guay, *J. Alloys Comp.* 376 (2004) 180.
- [7] M. Pourbaix, in: *Atlas of the Electrochemical Equilibria in Aqueous Solutions*, second ed., National Association of Corrosion Engineers, Houston, Texas, 1974, p. 143.
- [8] G.L. Makar, J. Kruger, *Int. Mater. Rev.* 38 (1993) 138.
- [9] G.L. Song, A. Atrens, *Adv. Eng. Mater.* 1 (1999) 11.
- [10] *Handbook of Chemistry*, 73rd ed., CRC Press, Boca Raton, Florida, 1992, pp. 4–71.
- [11] M.H. Grosjean, M. Zidoune, L. Roue, J. Huot, R. Schulz, *Electrochim. Acta* 49 (2004) 2461.