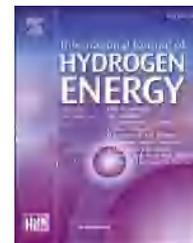


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# A comparative study of hydrogen generation by reaction of ball milled mixture of magnesium powder with two water-soluble salts (NaCl and KCl) in hot water

Takshak Shetty, Jerzy A. Szpunar, Omar Faye\*, Ubong Eduok

Department of Mechanical Engineering, University of Saskatchewan, S7N5A9, Saskatoon, Saskatchewan, Canada

## HIGHLIGHTS

- Mg–KCl generates 200 mL more hydrogen than Mg–NaCl for 1 g Mg at 15 h milling time.
- The KCl salt is more favorable for hydrogen generation than NaCl salt.
- The rate of H<sub>2</sub> is correlated with the degree of penetration of the salt into Mg particles.
- The increase of the milling time increased the hydrogen generation rate.

## ARTICLE INFO

### Article history:

Received 29 September 2019

Received in revised form

13 March 2020

Accepted 17 March 2020

Available online xxx

### Keywords:

Hydrogen generation

Ball milling

Mg–NaCl

Mg–KCl

Hot water

## ABSTRACT

Magnesium powder was ball milled with different weight percentages of NaCl and KCl. These mixtures were added to hot water (80 °C) and the hydrogen generation rate was measured. The results show that the hydrogen generation rate increased with an increase of the presence of both salts. Moreover, increase of the time of milling increased the hydrogen generation rate. The structure of magnesium salt mixtures was further investigated using SEM and EDS and it was demonstrated that higher hydrogen generation rate is correlated with the degree of penetration of the salt into magnesium particles. In addition, we determined that for the 15 h milled composite samples, Mg–KCl mixture generates 200 mL more hydrogen than Mg–NaCl for every 1 g Mg used. These results show that KCl salt addition is promising for hydrogen generation in presented experimental system.

Crown Copyright © 2020 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. All rights reserved.

## Introduction

The depletion of fossil energy resources (coal, crude oil and natural gas) and environmental pollution generated by their extensive used, requires the scientific community to search

for efficient ways to develop high-performance, low cost and environmentally friendly energy storage and production systems. Different energy sources like wind, solar and nuclear have been extensively explored. Because of weather constraint in some places and environmental concern, wind, solar and nuclear cannot provide enough energy for a

\* Corresponding author.

E-mail addresses: [omf071@mail.usask.ca](mailto:omf071@mail.usask.ca), [omsfaye@yahoo.fr](mailto:omsfaye@yahoo.fr) (O. Faye).

<https://doi.org/10.1016/j.ijhydene.2020.03.156>

0360-3199/Crown Copyright © 2020 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. All rights reserved.

worldwide green economy [1,2]. However, due to high energy content, cleanness and abundance, hydrogen is a promising energy vector for future economy and can contribute to a solution of the problem's greenhouse gases emission and environmental pollution. In fuel cells its byproduct is only  $H_2O$ . However, worldwide hydrogen use as an energy vector is restrained by lack of convenient hydrogen production. There are various methods for hydrogen productions that have been proposed including electrolysis of water [3], steam reforming of hydrocarbons gasification of heavy oil, coal or biomass [4–8]. Nevertheless, these methods have some holdup such as high energy input, low efficiency and high price. However, hydrogen generation through hydrolysis reaction is showed to be a promising method due to its low cost, safety and possible recyclability of the hydrolysis products [9–11]. So far, many studies have been performed on many kinds of the materials including metals [12], metal hydrides [13–15] and metal alloys [16,17]. But the main problem with these methods is the oxide layer that is formed on the surface of the metal which stops the reaction from completing [18,19]. Therefore, to overcome these barriers scientists have suggested various methods such as changing the pH of the solution [14,20] ball milling [18,19,21–23], use of catalysts [24], ultrasonic irradiation [25,26], and addition of carbon materials [27]. The most effective methods for improving the reaction are ball milling and alloying [28,29]. Magnesium in its purest form has not been successfully adopted for producing hydrogen due to formation of oxide layer during hydrolysis [30]. Moreover, Mg, Al, their hydrides and composites have shown promising results for hydrogen generation by hydrolysis through ball milling [9,30,31]. In addition, ball milling of aluminum powder in the presence of water-soluble salts is considered effective and safe [32]. Also, water-soluble salts (NaCl, KCl, etc.) can be considered in this process as they are cost effective and significantly shorten the completion time of the reaction [31]. According to Grosjean et al. [33] the hydrolysis reaction of Mg and Mg–Ni composite, by high-energy ball milling of 30 min, was faster and more extensive when they were immersed in 1 M KCl. They explain this phenomenon assuming the creation of micro-galvanic cells between Mg and dispersed Ni elements, this should accelerate greatly Mg corrosion in highly conductive aqueous media. Moreover, they also claim that Mg or  $MgH_2$  milled with salts like LiCl,  $MgCl_2$ , KCl has high hydrolysis reactivity in pure water. It is found that the 0.5 h milled  $MgH_2$ –3 mol%  $MgCl_2$  composite can produce 964 mL/g hydrogen in pure water at room temperature [33]. In addition, Tan et al. [34] showed that 466 mL  $g^{-1} H_2$  in 10 min and 616 mL  $g^{-1} H_2$  in 30 min at 25 °C was produced by reacting  $Mg_2Si$  and  $NH_4F$ . Ma et al. [35] also demonstrated that plasma-assisted milling of Mg and 20 wt% expanded graphite (EG) can significantly enhance the hydrolysis properties of Mg, and the obtained composite may generate 614.3 mL  $g^{-1} H_2$  with a hydrolysis conversion rate of 83.5% in 25 min. Moreover, Tan et al. [36] showed that composite in 0.5 M  $MgCl_2$  solution generated 445 mL/g hydrogen in 5 min, 688 mL/g hydrogen in 10 min and 889 mL/g hydrogen (conversion rate 99%) in 40 min at 328 K. In addition, Huang et al. [37] stated that Mg-5 wt%  $MoO_3$  and  $Fe_2O_3$  demonstrate the best hydrolysis performance (above 888 mL/g and 95.2% of theoretical hydrogen generation yield in 10 min) in comparison to Mg– $Fe_3O_4$ ,

Mg– $TiO_2$ , Mg– $Nb_2O_5$  and Mg–CaO composites. Also, they showed that  $MgH_2$ -4.5 wt%  $NH_4Cl$  system showed the fastest hydrolysis rate, producing 1310 mL/g hydrogen in 5 min, 1604 mL/g hydrogen in 10 min, and 1660 mL/g hydrogen in 30 min at 60 °C [38]. Also, Huang et al. [39] demonstrated that the hydrogenated  $Mg_3La$  with smaller particle size of [ $<12$ ]  $\mu m$  had a higher hydrolysis yield of 863 mL/g (7.70 wt%) hydrogen. He also showed that H– $Mg_3CeNi_{0.1}$  has been identified, which can generate 276 mL  $g^{-1} min^{-1}$  hydrogen in the first 1.5 min and achieve a total yield of 1088 mL/g [40]. Zhong et al. [41] developed a simple regeneration process via ball milling with Mg–Al alloys as the reducing agent for  $NaB(OH)_4$  under an argon atmosphere. Under optimized conditions, a high yield of about 72% of  $NaBH_4$  could be obtained. Moreover, Huang et al. [42] showed that the introduction of  $Mg_2Si$  increases the  $NaBH_4$  regeneration yield to 86%, which is the highest regeneration yield reported for  $NaBH_4$  until now. Also Zhong et al. [43] showed that using a mixture of magnesium silicide and dihydrate sodium metaborate is reacted via ball milling under ambient conditions without the requirements of additional hydrogen sources a 30-fold reduction in cost over a previous study that used  $MgH_2$  as the reduction agent. In addition, Nabid et al. [44] proposed a new route to synthesis  $Fe_2O_3$  nanosheets using glucose, urea and ferric nitrate. By coating  $Fe_2O_3$  core sheet with nitrogen doped carbon materials shell, they showed excellent catalytic activity with hydrogen production rate of 637 mL ( $H_2$ )  $min^{-1} \cdot g_{cat}^{-1}$ . Furthermore, Pighin et al. [45] reported that the as-milled  $MgH_2$  shows average hydrolysis properties with good hydrogen production capacity (1390 mL/g  $H_2$ ) and kinetics (50% of the total yield in 2.3 min). Chehade et al. [46] demonstrates a unique method of hydrogen production via water plasmolysis and investigates the energy and exergy efficiencies for applications involving the collection of hydrogen gas as an alternative fuel source.

Despite of the various research on production of hydrogen the magnesium ball milling with two control agents (NaCl and KCl) with hot water has not been investigated. We will report here the hydrogen production using ball milled mixture of magnesium powder and water-soluble salts with hot water. We will also optimize the hydrogen production efficiency by analyzing the role of milling times and optimizing the weight percentage of the added NaCl and KCl salts.

## Experiment procedures

### Ball milling

The Magnesium powder was purchased from Alfa Aeser of 99.8% purity (particle size  $-20 + 100$  mesh). After mixing sodium chloride (purity: 99%) with the magnesium powder, the mixture was ball milled with different weight percentages of NaCl (25%, 50%, 75%). Ball milling was performed with a ball to powder mass ratio of 30:1 in an inert argon atmosphere using planetary ball mill (Torrey Hills- ND2L) with stainless steel cups (285 mL capacity) and balls (28 of 16 mm and 6 of 18 mm diameter). The milling speed was maintained at 200 RPM for durations of 1, 3, 7 and 15 h to evaluate the effect of the milling time. To assess the influence of the type of salts, mixtures of 25 wt% KCl- 75 wt% Mg, 75 wt% KCl-

25 wt% Mg and 50 wt% KCl- 50 wt% Mg were ball milled for 1, 3, 7 and 15 h.

### Hydrogen measurement

Hydrogen was measured using a similar setup as discussed in Ref. [47]. Powdered mixtures equivalent to 1 g of Magnesium was added to an Erlenmeyer flask containing 200 mL of distilled water at  $80 \pm 2$  °C at a constant stirring rate of 120 rpm. The hydrogen gas produced was passed through a desiccant (CaSO<sub>4</sub>) to absorb moisture, and then to an ADM1000 flowmeter to measure its flow rate. The flowmeter was connected to a computer running ADM Trend software to acquire the data. A baseline curve was obtained by measuring the flow rate from 200 mL of distilled water at 80 °C with a constant stirring rate of 120 rpm with no powder added. This flow rate was then subtracted from the data obtained from the test with powder to ensure that the results obtained do not contain any contribution from water moisture or the air in the flask during heating. Maximum amount of generated hydrogen was for 15 h Mg–NaCl mixture more than 75% and that is very close to the theoretical value of hydrogen generation (900 mL) for 1 g of Mg.

### Scanning electron microscopy

SEM examinations were made using Hitachi SU6600 field emission scanning electron microscope. A small amount of

each milled powder was mixed with a conductive carbon resin powder mixed and mounted. The mounted samples were then polished using abrasive grinding papers ranging from 600 to 2000. Average particle sizes were calculated using Image J software.

## Results and discussion

### Effect of ball milling time and NaCl on hydrogen generation

#### Hydrogen measurement

Milled pure magnesium powder did not generate any hydrogen. This was most likely because the oxide layer formed on the surface of the particles. Another reason was that the magnesium powder was difficult to wet making it float on the water. The as received and non-milled Mg and NaCl powder without ball milling also failed to generate hydrogen.

Figure 1 shows hydrogen generation in ml with as function of ball milling time for 50% magnesium and 50% NaCl mixture. From Fig. 1 we can see that mixture milled for 1 h produced a small amount of H<sub>2</sub>, below 100 mL. Furthermore, increasing the milling time to 3 h increased production considerably to around 300 mL. As the milling time was increased to 7 h and later to 15 h the amount of generated hydrogen increased significantly. Further milling of the mixture to 25 h and 50 h resulted in cold welding of Mg particles and hence they were not fit for hydrolysis. The results obtained that no hydrogen

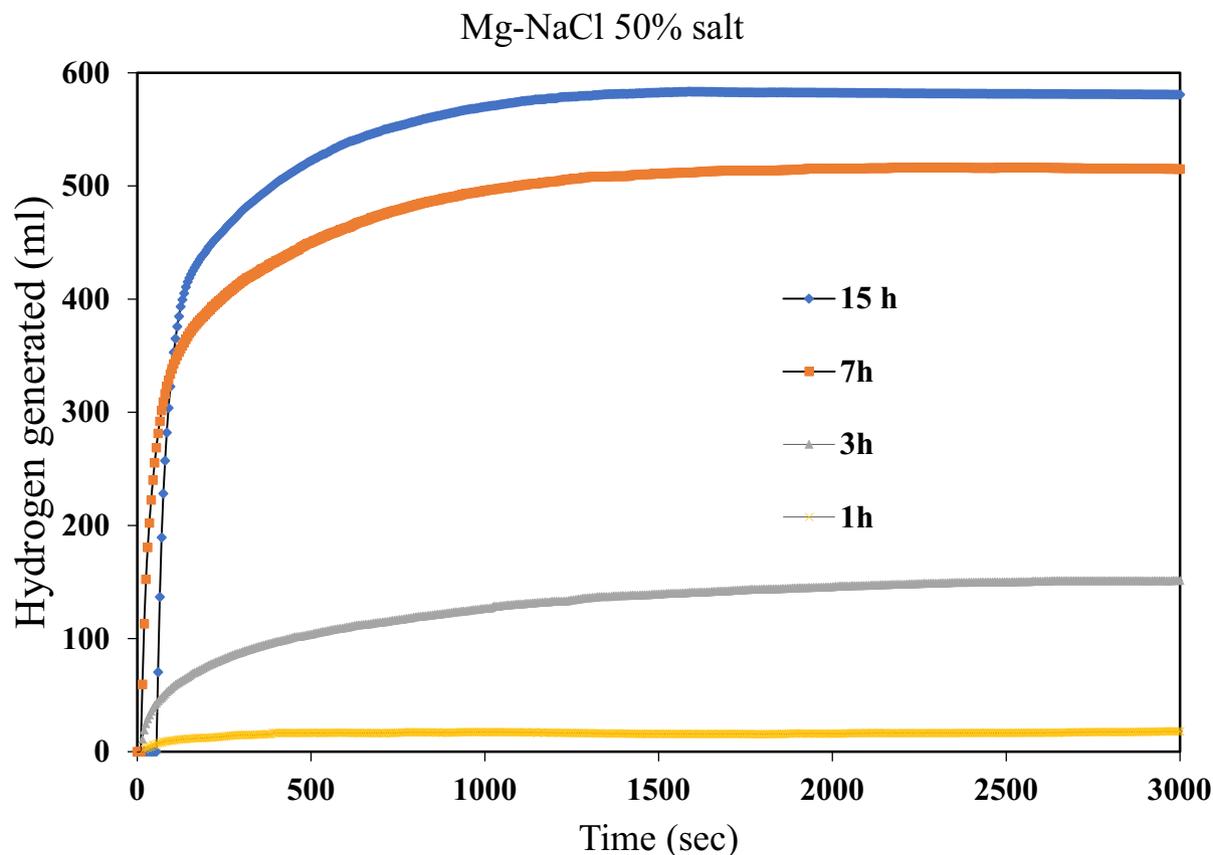


Fig. 1 – Hydrogen generated for Mg -NaCl 50% mixture for 1 h, 3 h, 7 h and 15 h milling period.

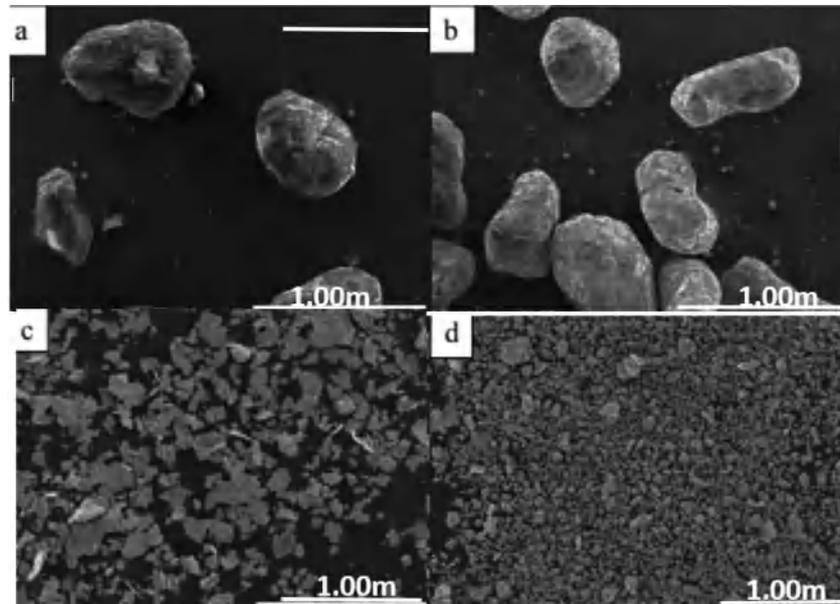


Fig. 2 – SEM images of the Mg 50%-NaCl 50% mixtures milled for 1 h, 3 h, 7 h, and 15 h.

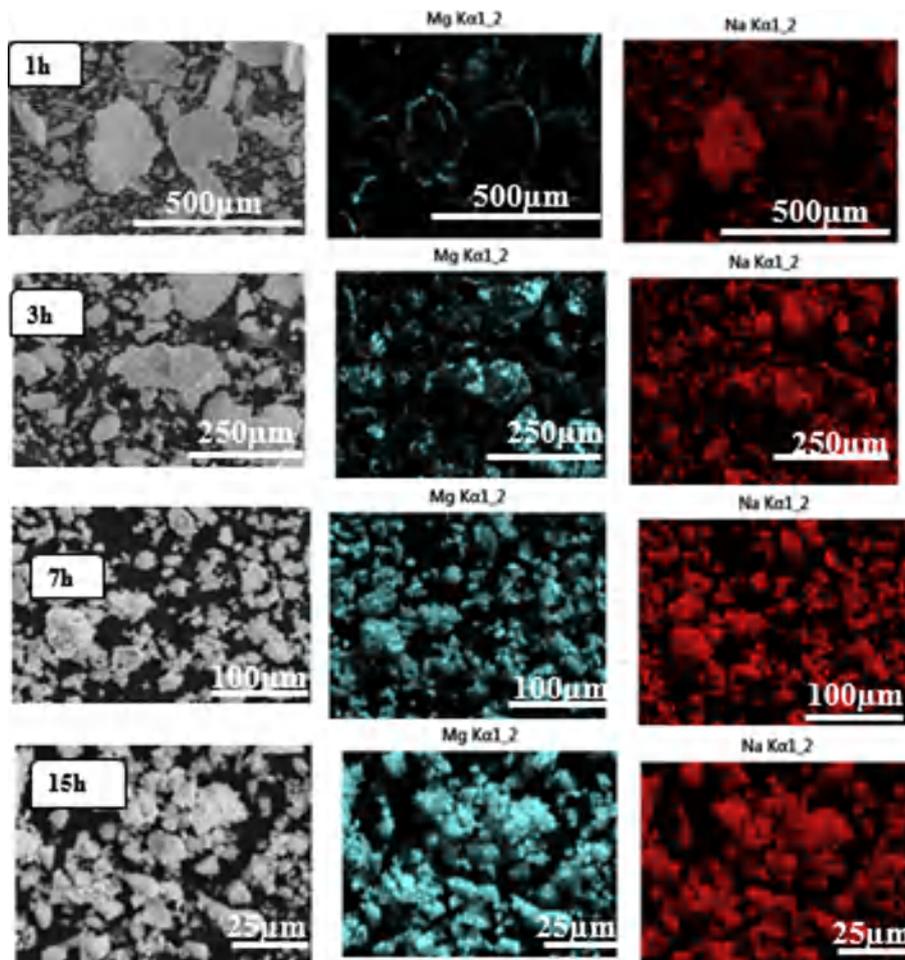


Fig. 3 – Elemental mapping of mixture showing the homogeneity of Mg and NaCl for different ball milling times (1 h, 3 h, 7 h and 15 h).

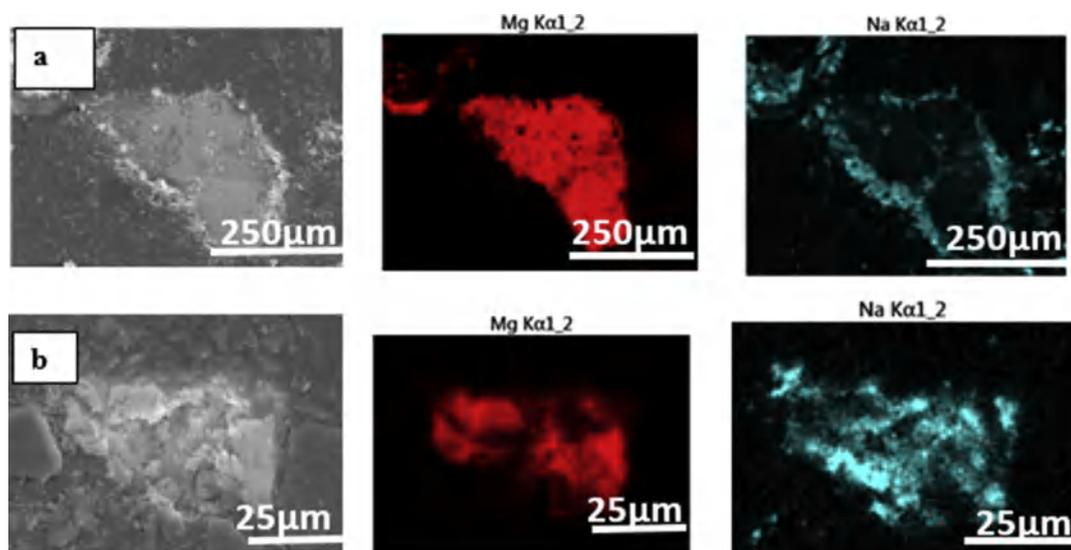


Fig. 4 – EDS scan of cross section of Mg50%-NaCl50% mixture ball milled for a) 1 h b) 3 h

was produced with just ball milled pure magnesium nor with the as received magnesium and NaCl mixture. The fact that NaCl alone is not effective in hydrogen generation nor is it effective when it is not present during milling brings us to conclusion that the presence of salt during ball milling plays an important role and secondly the presence of Cl ions does not play a significant role in pitting corrosion of magnesium unlike it was suggested by Grosjean et al. [13].

#### Microstructure

SEM was used to examine the ball milled mixture in order to understand the mechanics behind the improved hydrogen generation with increased milling time. The SEM images in Fig. 2 show a change in the morphology and particle sizes after ball milling. After 1 h of ball milling, we see that magnesium particles which were initially spherical are deformed to form flat disks like structures with an average particle size of 690  $\mu\text{m}$ . Furthermore, milling deforms the particles until a

point of fracture is reached and smaller particles are formed. The average particle size of magnesium which was ball milled for 3 h, 7 h and 15 h is 277  $\mu\text{m}$ , 65  $\mu\text{m}$  and 46  $\mu\text{m}$  respectively. It was possible to distinguish between the salt and magnesium particles for mixtures milled for 1 h and 3 h, however for higher milling times i.e. for 7 h and 15 h it was not possible to distinguish as the particles formed Mg–NaCl composite. The results obtained are in good agreement with ‘what is reported by Grosjean et al. [48].

As mentioned earlier in Fig. 1, the highest amount of hydrogen was obtained after milling for 15 h, longer milling time does not enhance hydrogen production. The increase in produced hydrogen can also be attributed to the decrease in particle size after longer milling time.

In addition, when Mg–NaCl mixture is milled, NaCl acts as a process control agent which prevents cold welding of magnesium and assists in forming smaller particles [49]. Initially the NaCl particles cover the surface of the Mg matrix which are

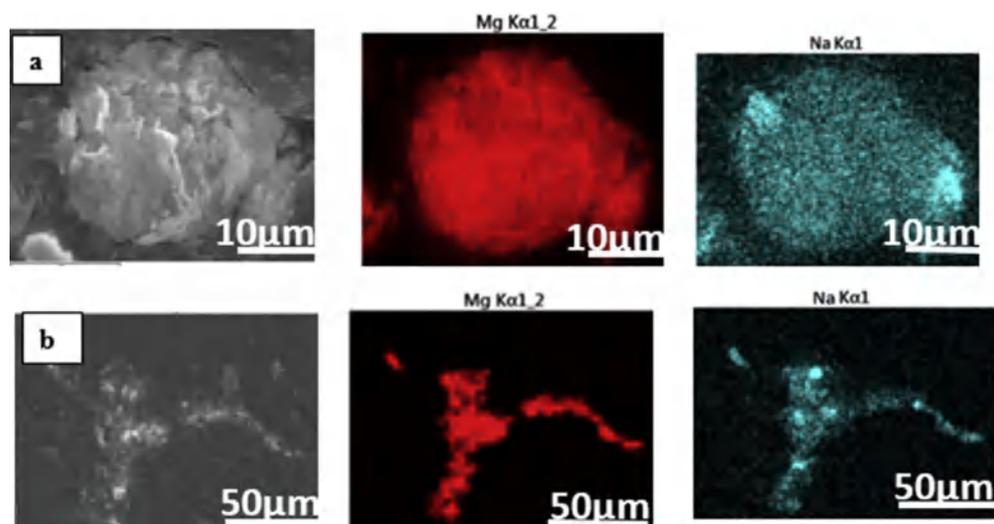
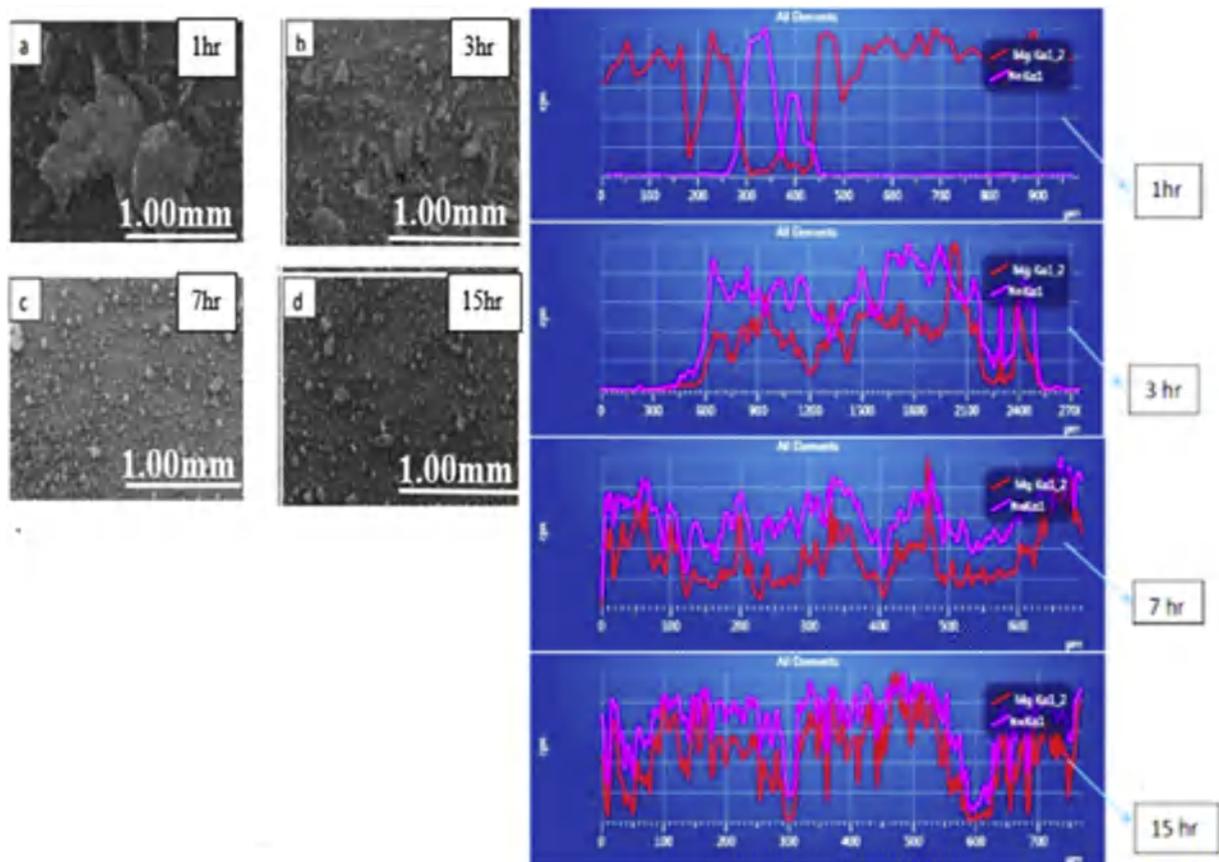
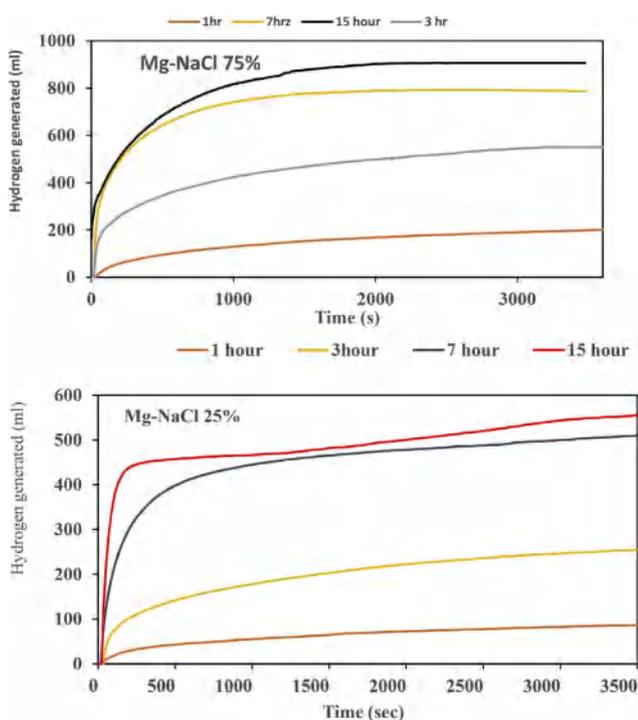


Fig. 5 – EDS scan of cross section of Mg–NaCl 50% mixture ball milled for a) 7 h b) 15 h.



**Fig. 6** – Represents the SEM and the line scan showing the occurrence of Mg and NaCl on the cross section of the particle for different ball milling time.



**Fig. 7** – Hydrogen generation profile for Mg–NaCl 25% and Mg–NaCl 75% mixture ball-milled for 1 h, 3 h, 7 h, 15 h.

seen in the EDS mapping in Fig. 3, Fig. 4 and Fig. 5. However, the embedding of NaCl in magnesium is the most important, this helps create voids and when dissolved in water generates fresh surfaces for hydrolysis. However further increasing the milling time above 15 h resulted in cold welding as all NaCl was embedded in the matrix leading to coalescence of particles. The EDS scans in Fig. 3 shows the distribution of Mg and Na elements. The green color represents Mg while Na is mapped red. For the mixture milled for 1 h, NaCl is seen covering the surface on the Mg particles. As the milling time was increased to 3 h, there were still some dark spots observed on the Mg particles which corresponded to Na. Furthermore, increasing the milling time from 7 h to 15 h shows a homogenous distribution of both Mg and NaCl phases. This shows that the particles form now Mg–NaCl composite in which the two phases are well mixed as illustrated in Fig. 5.

The SEM in Fig. 6 reveals the characteristic changes in particulate morphology and sizes after milling. After 1 h, the Mg particles which were initially spherical are deformed to form flat disk structures with an average particle size of 690  $\mu\text{m}$ . Further milling deforms the particles until a point of fracture is reached and smaller particles are formed. The average particle size of Mg which was ball milled for 3 h, 7 h and 15 h is 277  $\mu\text{m}$ , 65  $\mu\text{m}$  and 46  $\mu\text{m}$  respectively.

The EDS line scan in Fig. 6 shows the presence of Mg and NaCl for 1 h, 3 h, 7 h and 15 h milled mixtures. The red line represents Mg and the violet line represents Na. These scans

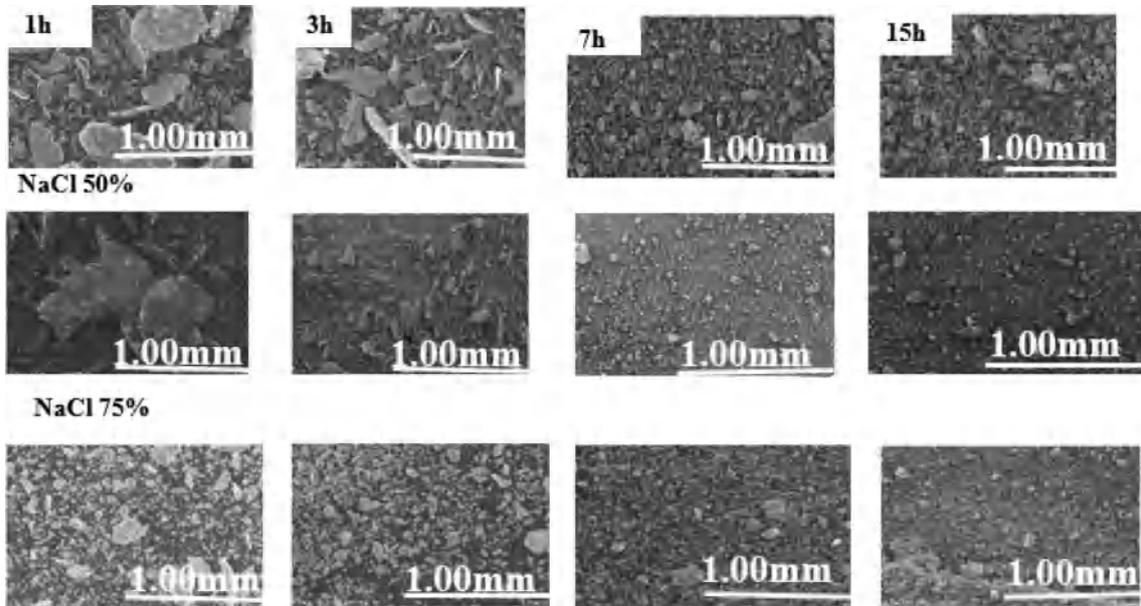


Fig. 8 – SEM images comparing the Mg–NaCl mixtures with different weight % of NaCl milled for 1 h, 3 h, 7 h, and 15 h.

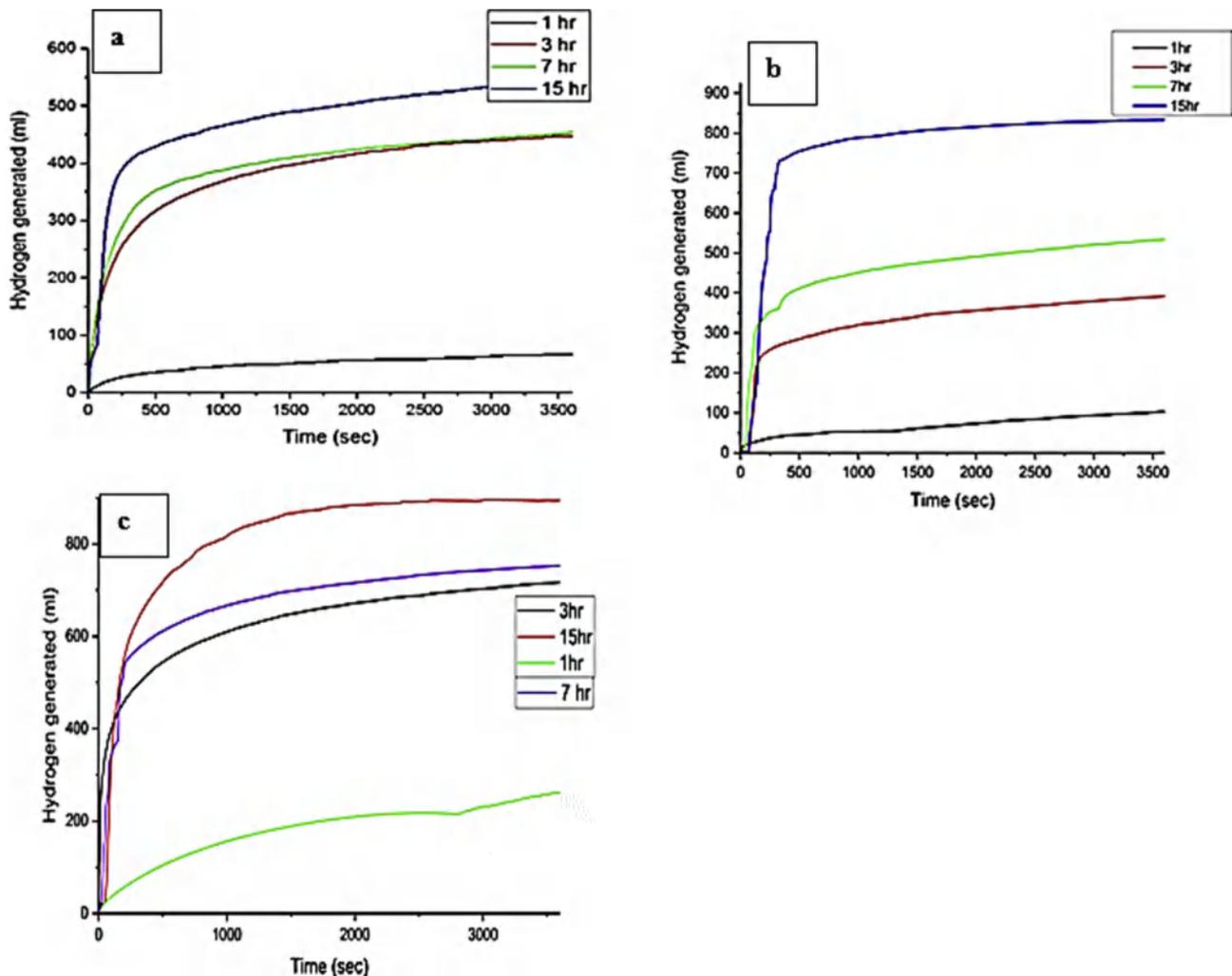
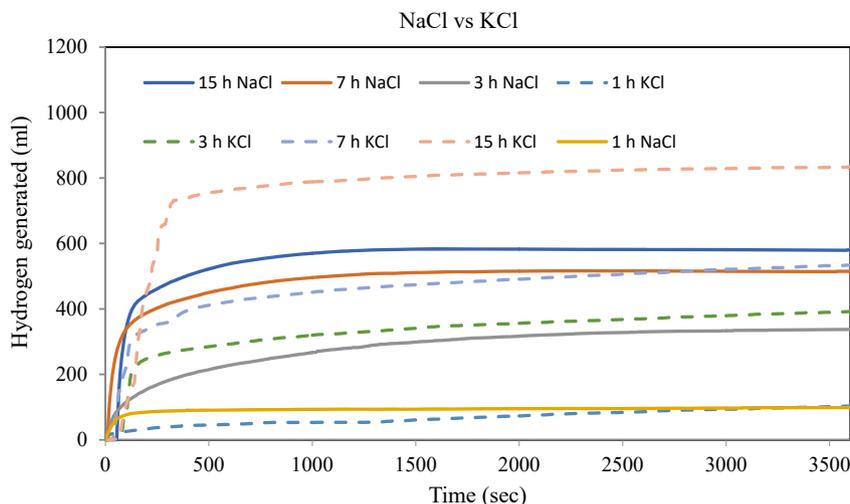


Fig. 9 – Hydrogen generation profile for (a) Mg 75%-KCl 25% (b) Mg 50%-KCl 50% (c) Mg 25%KCl 75% mixture ball-milled for 1 h, 3 h, 7 h, 15 h.



**Fig. 10** – Comparison of hydrogen generation between Mg 50%-NaCl 50% and Mg 50%-KCl 50% mixture ball-milled for 1 h, 3 h, 7 h, and 15 h.

were obtained across the cross section of a particle and they represent the distribution of the elements. For shorter milling times (1 h and 3 h) the of Mg and Na elements are distributed in selected areas and do not mix. When the milling time increases Mg and NaCl mixed more evidently and at time of milling of 15 h form homogenous composite structure.

#### Effect of weight percentage of NaCl

Figure 7 shows hydrogen generation of ball milled Mg–NaCl 25% and Mg–NaCl 75% for durations 1 h, 3 h, 7 h and 15 h for 1 g of Mg. It is evident from the result that the amount of hydrogen generated increases with increased amount of salt content in the mixture. Comparing Figs. 1 and 4, for the same time period of milling the amount of hydrogen generated is higher. This increase in the amount of generated hydrogen is due to higher amounts of NaCl embedded in the matrix and associated increase in permeation of salt and water into Mg particles. This led to an increase in area of Mg contact with water which explains the improved kinetics of the reaction.

The SEM images in Fig. 8, reveals that the average particle size changes with time of milling for three different concentrations of NaCl, which are 25%, 50% and 75%.

The SEM micrographs in Fig. 8 illustrate a decrease in average particle size as the wt% of NaCl increase while the milling time is constant. This can be explained by the role of NaCl in preventing cold welding of Mg particles as showed by Zidoune et al. [49].

#### Role of KCl in hydrogen generation

Figure 9 shows the hydrogen generation for Mg–KCl mixtures with different wt% ball milled for 1 h, 3 h, 7 h and 15 h. The results follow a similar trend as already reported with NaCl i.e. increased amount of hydrogen produced with increasing milling time and with increase of wt % of KCl. The SEM and EDS results were also like the Mg–NaCl results and show better refinement of particles with increased milling time and higher KCl wt%.

However, based on results presented in Fig. 9, KCl showed slightly higher amount of hydrogen produced as compared with NaCl. To compare the results obtained with both agents (NaCl and KCl), we present in Fig. 10 the weight percentage of salts obtained under similar processing conditions.

We see that for the 15 h milled samples, Mg–KCl mixture generated approximately 200 mL more hydrogen than Mg–NaCl for every 1 g Mg used. In addition, Razavi-Tousi et al. [50] showed that the formation of interlayer spaces within the investigated Al particles effectively increases hydrogen yield.

## Conclusion

The presence of salt (NaCl and KCl) enhanced the hydrogen generation rate by facilitating the ingress of the salty water into magnesium particles. The milling process is optimized to allow complete mixing of the salt and the metal. The milling time also plays an important role in the hydrogen generation as it creates a special particle structure that allows ingress of the salt. The best results were obtained for Mg–KCl 75% composite ball milled for 15 h and resulted in 80% hydrogen generation in less than 10 min. The SEM and EDS results show that with increasing milling time particles were more refined with Mg and salt phases having a uniform distribution. The EDS maps of the cross section of the particles proves that salt particles were embedded inside the metal matrix. During hydrolysis, the salt dissolves in water thus increasing the surface area for the reaction and the hydrogen production rate. The type of salt used also had an influence on the hydrogen generation rate. Both salts that were used are abundant, however there is still room for research on KCl additions to improve the effect of this salt on hydrogen generation.

## Acknowledgments

This work was supported by the National Engineering Research Council of Canada and the Canada Research Chair program.

## REFERENCES

- [1] Irankhah A, Seyed Fattahi SM, Salem M. Hydrogen generation using activated aluminum/water reaction. *Int J Hydrogen Energy* 2018;43:15739–48.
- [2] Fanghanel T, Rondinella VV, Glatz JP, Wiss T, Wegen DH, Gouder T, Carbol P, Serrano-Purroy D, Papaioannou D. Reducing uncertainties affecting the assessment of the long-term corrosion behavior of spent nuclear fuel. *Inorg Chem* 2013;52:3491–509.
- [3] Fiegenbaum F, Martini EM, De Souza MO, Becker MR, De Souza RF. Hydrogen production by water electrolysis using tetra-alkyl-ammonium- sulfonic acid ionic liquid electrolytes. *J Power Sources* 2013;243:822–5.
- [4] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: a review and analysis. *Int J Hydrogen Energy* 2009;21:8799–817.
- [5] Kumagai S, Alvarez J, Blanco PH, Wu C, Yoshioka T, Olazar M, Williams PT. Novel Ni-Mg-Al-Ca catalyst for enhanced hydrogen production for the pyrolysis-gasification of a biomass/plastic mixture. *J Anal Appl Pyrolysis* 2015;113:15–21.
- [6] Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int J Hydrogen Energy* 2007;13:2367–73.
- [7] Izquierdo U, Barrio VL, Cambra JF, Requies J, Güemez MB, Arias PL, Kolb G, Zapf R, Gutiérrez AM, Arraibi JR. Hydrogen production from methane and natural gas steam reforming in conventional and microreactor reaction systems. In: *Int. J. Hydrogen energy*, vol. 8; 2012. p. 7026–33.
- [8] Sánchez-Sánchez MC, Navarro RM, Fierro JLG. Ethanol steam reforming over Ni/Mx Oy-Al<sub>2</sub>O<sub>3</sub> (M = Ce, La, Zr and Mg) catalysts: influence of support on the hydrogen production. *Int J Hydrogen Energy* 2007;10–11:1462–71.
- [9] Tan ZH, Ouyang LZ, Huang JM, Liu JW, Wang H, Shao HY, Zhu M. Hydrogen generation via hydrolysis of Mg<sub>2</sub>Si. *J Alloys Compd* 2019;770:108–15.
- [10] Kojima Y, Haga T. Recycling process of sodium metaborate to sodium borohydride. *Int J Hydrogen Energy* 2003;9:989–93.
- [11] Park EH, Uk Jeong S, Ho Jung U, Kim SH, Lee J, Woo Nam S, Hoon Lim T, Jun Park Y, Ho Yu Y. Recycling of sodium metaborate to borax. *Int J Hydrogen Energy* 2007;14:2982–7.
- [12] Zidoune M, Grosjean MH, Rou L, Huot J, Schulz R. Comparative study on the corrosion behavior of milled and unmilled magnesium by electrochemical impedance spectroscopy. *Corrosion Sci* 2004;46:3041–55.
- [13] Grosjean MH, Zidoune M, Roué L, Huot JY. Hydrogen production via hydrolysis reaction from ball-milled Mg-based materials. *Int J Hydrogen Energy* 2006;1:109–19.
- [14] Hiraki T, Hiroi S, Akashi T, Okinaka N, Akiyama T. Chemical equilibrium analysis for hydrolysis of magnesium hydride to generate hydrogen. *Int J Hydrogen Energy* 2012;17:12114–9.
- [15] Tayeh T, Awad AS, Nakhl M, Zakhour M, Silvain JF, Bobet JL. Production of hydrogen from magnesium hydrides hydrolysis. *Int J Hydrogen Energy* 2014;39:3109–17.
- [16] Eom K, Cho E, Kwon H. Feasibility of on-board hydrogen production from hydrolysis of Al-Fe alloy for PEMFCs. *Int J Hydrogen Energy* 2011;19:12338–42.
- [17] Oh SK, Kim MJ, Eom KS, Kyung JS, Kim DH, Cho EA, Kwon HS. Design of Mg-Ni alloys for fast hydrogen generation from seawater and their application in polymer electrolyte membrane fuel cells. *Int J Hydrogen Energy* 2016;10:5296–303.
- [18] Petrovic J, Thomas G. Reaction of aluminum with water to produce hydrogen. *US Dep. Energy*; 2008. p. 1–26.
- [19] Huang M, Ouyang L, Chen Z, Peng C, Zhu X, Zhu M. Hydrogen production via hydrolysis of Mg-oxide composites. *Int J Hydrogen Energy* 2017;35:22305–11.
- [20] Kojima Y, Suzuki KI, Kawai Y. Hydrogen generation by hydrolysis reaction of magnesium hydride. *J Mater Sci* 2004;6:2227–9.
- [21] Alinejad B, Mahmoodi K. A novel method for generating hydrogen by hydrolysis of highly activated aluminum nanoparticles in pure water. *Int J Hydrogen Energy* 2009;34:7934–8.
- [22] Wang C, Yang T, Liu Y, Ruan J, Yang S, Liu X. Hydrogen generation by the hydrolysis of magnesium-aluminum-iron material in aqueous solutions. *Int J Hydrogen Energy* 2014;39:10843–52.
- [23] Razavi-Tousi SS, Szpunar JA. Effect of addition of water-soluble salts on the hydrogen generation of aluminum in reaction with hot water, vol. 679; 2016. p. 364–74.
- [24] Uan J-Y, Cho C-Y, Liu K-T. Generation of hydrogen from magnesium alloy scraps catalyzed by platinum-coated titanium net in NaCl aqueous solution. *Int J Hydrogen Energy* 2007;32:2337–43.
- [25] Hiroi S, Hosokai S, Akiyama T. Ultrasonic irradiation on hydrolysis of magnesium hydride to enhance hydrogen generation. *Int J Hydrogen Energy* 2011;2:1442–7.
- [26] Hiroi S, Hosokai S, Akiyama T. Ultrasonic irradiation on hydrolysis of magnesium hydride to enhance hydrogen generation. *Int J Hydrogen Energy* 2011;36:1442–7.
- [27] Awad AS, El-Asmar E, Tayeh T, Mauvy F, Nakhl M, Zakhour M, Bobet J-L. Effect of carbons (G and CFs), TM (Ni, Fe and Al) and oxides (Nb<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>) on hydrogen generation from ball milled Mg-based hydrolysis reaction for fuel cell. *Energy* 2016;95:175–86.
- [28] Wu D, Ouyang L, Wu C, Wang H, Liu J, Sun L, Zhu M. Phase transition and hydrogen storage properties of Mg-Ga alloy. *J Alloys Compd* 2015;642:180–4.
- [29] Li HW, Kikuchi K, Nakamori Y, Miwa K, Towata S, Orimo S. Effects of ball milling and additives on dehydrogenating behaviors of well-crystallized Mg(BH<sub>4</sub>)<sub>2</sub>. *Scripta Mater* 2007;8:679–82.
- [30] Huang M, Ouyang L, Chen Z, Peng C, Zhu X, Zhu M. Hydrogen production via hydrolysis of Mg-oxide composites. *Int J Hydrogen Energy* 2017;35:22305–11.
- [31] Razavi-Tousi SS, Szpunar JA. Effect of addition of water-soluble salts on the hydrogen generation of aluminum in reaction with hot water. *J Alloys Compd* 2016;679:364–74.
- [32] Ho CY, Huang CH. Enhancement of hydrogen generation using waste aluminum cans hydrolysis in low alkaline de-ionized water. *Int J Hydrogen Energy* 2016;6:3741–7.
- [33] Grosjean MH, Zidoune M, Huot JY, Roué L. Hydrogen generation via alcoholysis reaction using ball-milled Mg-based materials. *Int J Hydrogen Energy* 2006;9:1159–63.
- [34] Tan ZH, Ouyang LZ, Huang JM, Liu JW, Wang H, Shao HY, Zhu M. Hydrogen generation via hydrolysis of Mg<sub>2</sub>Si. *J Alloys Compd* 2019;770:108–15.
- [35] Ma M, Yang L, Ouyang L, Shao H, Zhu M. Promoting hydrogen generation from the hydrolysis of Mg-Graphite composites by plasma-assisted milling. *Energy* 2019;167:1205–11.
- [36] Tan Z, Ouyang L, Liu J, Wang H, Shao H, Zhu M. Hydrogen generation by hydrolysis of Mg-Mg<sub>2</sub>Si composite and enhanced kinetics performance from introducing of MgCl<sub>2</sub> and Si. *Int J Hydrogen Energy* 2018;5:2903–12.
- [37] Huang M, Ouyang L, Chen Z, Peng C, Zhu X, Zhu M. Hydrogen production via hydrolysis of Mg-oxide composites. *Int J Hydrogen Energy* 2017;35:22305–11.
- [38] Huang M, Ouyang L, Chen Z, Peng C, Zhu X, Zhu M. Hydrogen production via hydrolysis of Mg-oxide composites. *Int J Hydrogen Energy* 2017;35:22305–11.

- [39] Huang JM, Duan RM, Ouyang LZ, Wen YJ, Wang H, Zhu M. The effect of particle size on hydrolysis properties of Mg3La hydrides. *Int J Hydrogen Energy* 2014;25:13564–8.
- [40] Huang JM, Ouyang LZ, Wen YJ, Wang H, Liu JW, Chen ZL, Zhu M. Improved hydrolysis properties of Mg3RE hydrides alloyed with Ni. *Int J Hydrogen Energy* 2014;13:6813–8.
- [41] Zhong H, Ouyang L, Zeng M, Liu J, Wang H, Shao H, Felderhoff M, Zhu M. Realizing facile regeneration of spent NaBH<sub>4</sub> with Mg–Al alloy. *J Mater Chem* 2019;17:10723–8.
- [42] Chen K, Ouyang L, Zhong H, Liu J, Wang H, Shao H, Zhang Y, Zhu M. Converting H<sup>+</sup> from coordinated water into H<sup>-</sup> enables super facile synthesis of LiBH<sub>4</sub>. *Green Chem* 2019;4380–7.
- [43] Zhong H, Ouyang LZ, Ye JS, Liu JW, Wang H, Yao XD, Zhu M. An one-step approach towards hydrogen production and storage through regeneration of NaBH<sub>4</sub>. *Energy Storage Materials* 2017;7:222–8.
- [44] Nabid MR, Bide Y, Kamali B. Hydrogen release from sodium borohydride by Fe<sub>2</sub>O<sub>3</sub>@ nitrogen-doped carbon core-shell nanosheets as reasonable heterogeneous catalyst. *Int J Hydrogen Energy* 2019;44:25662–70.
- [45] Pighin SA, Urretavizcaya G, Bobet JL, Castro FJ. Nanostructured Mg for hydrogen production by hydrolysis obtained by MgH<sub>2</sub> milling and dehydriding. *J Alloys Compd* 2020;154000.
- [46] Chehade G, Lytle S, Ishaq H, Dincer I. Hydrogen production by microwave-based plasma dissociation of water. *Fuel* 2020;264:116831.
- [47] de Souza RF, Padilha JC, Gonçalves RS, de Souza MO, Rault-Berthelot J. Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: towards the best device. *J Power Sources* 2007;164:792–8.
- [48] Grosjean MH, Roué L. Hydrolysis of Mg–salt and MgH<sub>2</sub>–salt mixtures prepared by ball milling for hydrogen production. *J Alloys Compd* 2006;(1–2):296–302.
- [49] Zidoune M, Grosjean MH, Roué L, Huot J, Schulz R. Comparative study on the corrosion behavior of milled and unmilled magnesium by electrochemical impedance spectroscopy. *Corrosion Sci* 2004;12:3041–55.
- [50] Razavi-Tousi SS, Szpunar JA. Effect of structural evolution of aluminum powder during ball milling on hydrogen generation in aluminum–water reaction. *Int J Hydrogen Energy* 2013;38:795–806.