

## Research Article

The effect of various cations/anions for MgH<sub>2</sub> hydrolysis reactionChongyang Yuan<sup>a</sup>, Wei Chen<sup>a</sup>, Zunxian Yang<sup>b,\*</sup>, Zhenguo Huang<sup>c</sup>, Xuebin Yu<sup>a,\*</sup><sup>a</sup> Department of Materials Science, Fudan University, Shanghai, 200433, China<sup>b</sup> National and Local United Engineering Laboratory of Flat Panel Display Technology, Fuzhou University, Fuzhou, 350002, Fujian, China<sup>c</sup> School of Civil & Environmental Engineering, University of Technology Sydney, Ultimo, New South Wales, 2007, Australia

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## ABSTRACT

MgH<sub>2</sub> is regarded as a potential hydrolysis material for the hydrogen generation due to its high theoretical hydrogen yield, abundant source on earth and environmentally friendly hydrolysates. However, the quickly formed passive magnesium hydroxide layer on the surface of MgH<sub>2</sub> will hinder its further hydrolysis reaction, leading to sluggish reaction kinetics and low H<sub>2</sub> yield. In this paper, we explore the improvement of different anions and cations in solutions for the hydrolysis of MgH<sub>2</sub>. It is found that the cations in the solution promote the reaction rate of MgH<sub>2</sub> hydrolysis through the hydrolysate-induced growth effect, among which the fastest hydrogen yield can get 1664 mL/g within a few minutes in the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution. As for the anions, it enables different microstructures of the Mg(OH)<sub>2</sub> hydrolysate which give rise to enhanced water utilization. Specially, for the mixed 0.5 M MgCl<sub>2</sub> + 0.05 M MgSO<sub>4</sub> solution, the water utilization rate attains the optimum value of 51.3 %, much higher than that of the single MgCl<sub>2</sub> or MgSO<sub>4</sub> solutions. These findings are of great significance for the application of MgH<sub>2</sub> hydrolysis as hydrogen generation.

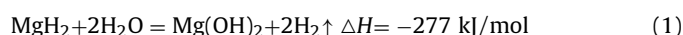
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## 1. Introduction

To improve the ecological environment resulted from the consumption of fossil energy, new clean energy needs to be developed and implemented. Hydrogen, with the advantages of high energy density (142 MJ/kg), benign environmental compatibility, and abundant resources, is the most promising energy carrier for replacing traditional fossil fuels [1–3]. So far, it has contained great challenges for mass production, storage and controlled distribution of hydrogen which could be the critical part of the pursuit for the hydrogen economy [4].

Compared to traditional hydrogen storage methods, such as compressed gaseous hydrogen and low-temperature liquid hydrogen, solid hydrogen storage shows the advantages of high hydrogen storage volume density, high safety, low cost and so forth [5–7]. Among the solid hydrogen storage materials, MgH<sub>2</sub> holds the promise as an energy carrier medium due to its non-toxicity, high hydrogen content (7.6 wt.%) and low price [8,9]. What's more, because of its strong reducibility when MgH<sub>2</sub> reacts with water at room temperature, it will undergo a chemical reaction as shown

in formula (1) and the hydrogen yield can reach to 15.2 wt. % if the weight of water is not calculated, which makes it especially suitable for the fuel cell in supplying hydrogen [10–14].



However, Mg(OH)<sub>2</sub>, which is low solubility in water, is the by-product of MgH<sub>2</sub> hydrolysis and it is usually formed on the surface of MgH<sub>2</sub>. The passive Mg(OH)<sub>2</sub> layer will hinder the further contact of water with fresh MgH<sub>2</sub> and thus leading to sluggish hydrolysis kinetics [14,15]. A number of approaches have been proposed to solve this problem by modifying the MgH<sub>2</sub>, involving in alloying [16,17], designing nanostructure [18–20], ball-milling with other metal hydrides [21], oxides [22], carbon additives [22], chlorides [23] or other chemicals [24]. These methods can improve hydrogen yield and hydrolysis kinetics to a certain extent.

Furthermore, changing the component of aqueous solution is another easy-operated and efficient way to promote the hydrolysis process of MgH<sub>2</sub>. Gan et al. [25] found that a hydrogen generation of 1487 mL/g in 10 min at 303 K was achieved for the MgH<sub>2</sub> powder in 0.5 mol/L AlCl<sub>3</sub> solution. In addition, ammonium salts have been applied in MgH<sub>2</sub> hydrolysis. Huang et al. [26] reported that hydrogen generation via MgH<sub>2</sub> hydrolysis in 4.50 wt. % NH<sub>4</sub>Cl solution produced 1604 mL/g hydrogen in 10 min at 333 K. Chen et al. [15] combined MgH<sub>2</sub> nanoparticles and MgCl<sub>2</sub> solution to promote the hydrolysis process of MgH<sub>2</sub> and discovered near-theoretically

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1820 mL/g of H<sub>2</sub> released within 20 min in 1 mol/L MgCl<sub>2</sub> solution. Sevastyanova et al. [27] adopted mixed solutions of magnesium chloride with aqueous ammonium, copper or potassium chlorides to accelerate the MgH<sub>2</sub> hydrolysis process and observed the highest reaction rate yielding of 100 % hydrogen releasing in 120 min in mixed 0.45 mol/L MgCl<sub>2</sub> and 0.85 mol/L NH<sub>4</sub>Cl solutions. Clearly, the promoted hydrolysis process of MgH<sub>2</sub> in above studies is attributed to the addition of various salts. It has been proposed by Zheng et al. that the cations of the chlorides play a critical role in the hydrolysis reaction and the cations with higher OH<sup>-</sup> affinity are more effective for facilitating the hydrolytic reaction [28]. As for the effect of anions in the reaction, however, there has never been reported yet.

In this work, we first demonstrate that excellent H<sub>2</sub> generation can be achieved by reaction of MgH<sub>2</sub> powder with several chloride and sulfate solutions without any activation procedure, and the role of cations/anions on the improvement of MgH<sub>2</sub> hydrolysis is discussed. And then we put forward the concept of water utilization rate, which means the ratio of measured hydrogen production to theoretical hydrogen production of the total employed water in the MgH<sub>2</sub> hydrolysis reaction. Our results indicate that the mixture of MgCl<sub>2</sub> and MgSO<sub>4</sub> solution can obtain higher water utilization than that of separate MgCl<sub>2</sub> and MgSO<sub>4</sub> solutions. This study lays the foundation for the practical application of MgH<sub>2</sub> hydrolysis.

## 2. Experimental

### 2.1. Materials and characterizations

MgH<sub>2</sub> powder (Shanghai Magnesium Power, 99.0 %, 500 mesh, XRD patterns are shown in Fig. S1 in supplementary material), MgCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·4H<sub>2</sub>O, ZnCl<sub>2</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Shanghai Hushi, AR) and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Macklin, 99.0 %) and Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aladdin, 99.99 %) were used as received commercially.

X-ray diffraction (XRD) patterns are collected using the CuKα line at a scan rate of 10° min<sup>-1</sup> (Rigaku D/max 2000 diffractometer). Scanning electron microscopy (SEM) images are collected with acceleration voltage of 1 kV (Hitachi S4800).

### 2.2. Hydrogen generation test

The hydrogen generation test system is showed in Fig. 1. The hydrolysis was carried at a 100 ml three-necked flask: one sealed with a rubber stopper, one for solution injection and MgH<sub>2</sub> powder addition, the last one for the hydrogen collection and recording. For the measurement of H<sub>2</sub> yield, various solution (20 mL, 0.5 mol/L, hereinafter abbreviated as “M”) was loaded in the flask and was kept at a certain temperature by a water bath. MgH<sub>2</sub> powder (0.1 g) was added into the solution under moderate stirring and the system was rapidly sealed. The generated hydrogen passes through a drier to remove the water vapor, and the volume of H<sub>2</sub> was recorded

by a flowmeter (Ritter MGC-1 V3.4 PMMA) connected with a computer. The rubber tubes were used to connect the flask, the drier and the flowmeter. The hydrogen is exhausted to the outside to ensure safety.

It is common that the amount of H<sub>2</sub>O is far exceeding for MgH<sub>2</sub> hydrolytic reaction and the H<sub>2</sub>O utilization is low which leads to a decreased hydrogen capacity in the whole MgH<sub>2</sub>/H<sub>2</sub>O system. In this situation, we used the term H<sub>2</sub>O utilization rate to describe the hydrogen capacity of the whole MgH<sub>2</sub>/H<sub>2</sub>O system. The H<sub>2</sub>O utilization rate is the ratio of experimentally measured hydrogen yield to stoichiometric hydrogen yield of the total employed water in the MgH<sub>2</sub> hydrolysis reaction. Thus, the higher H<sub>2</sub>O utilization rate means the higher system hydrogen capacity. For the measurement of H<sub>2</sub>O utilization rate, 0.4 g MgH<sub>2</sub> powder was added in batches into 10 mL solution until the hydrogen evolution of the entire system stopped, and the data of the released H<sub>2</sub> was used to calculate the H<sub>2</sub>O utilization rate.

After hydrolysis reaction, the precipitates were centrifuged and washed with water and ethanol three times and dried at 60 °C via dynamic vacuum on a Schlenk line.

## 3. Results and discussion

### 3.1. The influence of cations in MgH<sub>2</sub> hydrolysis

Fig. 2 shows the hydrogen generation of MgH<sub>2</sub> hydrolysis in different chloride and sulfate solutions with the same volume and concentration. It is obviously that the total amount of H<sub>2</sub> yield and the H<sub>2</sub> release rate have been improved greatly due to the existence of chloride/sulfate compared with the MgH<sub>2</sub> hydrolysis in pure water, for which only 5.0 % (94.0 mL/g) theoretical H<sub>2</sub> is released after 2 h. The slow reaction kinetics in the case of MgH<sub>2</sub>/pure water is caused by the formation of passivated Mg(OH)<sub>2</sub> layer on the surface of the MgH<sub>2</sub> particles as previous reports [29]. In Fig. 2(a), it can be clearly seen that the FeCl<sub>3</sub> solution shows the highest reaction rate, releasing 1632.0 mL/g H<sub>2</sub> in 6.2 min. CuCl<sub>2</sub> also delivers a good activity and releases 810.3 mL/g H<sub>2</sub> in 20 min, while the H<sub>2</sub> generation for ZnCl<sub>2</sub> and MgCl<sub>2</sub> solutions is 561.2 mL/g and 491.4 mL/g, respectively. The H<sub>2</sub> generation data from MgH<sub>2</sub> in various sulfate solutions gives the analogous promoting rules as shown in Fig. 2(b). What's more, 89.0 % (1664.0 mL/g) theoretical H<sub>2</sub> is released in the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution in 5 min and the CuSO<sub>4</sub> solution provides 816.7 mL/g H<sub>2</sub> in 20 min. The H<sub>2</sub> generation after 20 min in ZnSO<sub>4</sub> solution is 378.6 mL/g, higher than that in MgSO<sub>4</sub> solution (244.5 mL/g). Hence, integrating the above cases, it can be drawn that the hydrolysis rate is enhanced in the order of Mg<sup>2+</sup> < Zn<sup>2+</sup> < Cu<sup>2+</sup> < Fe<sup>3+</sup>.

To further reveal the superb improvement of MgH<sub>2</sub> hydrolysis in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, kinetic curves of hydrogen evolution from MgH<sub>2</sub> hydrolysis in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution as compared with in pure water were measured at different temperatures. As shown in Fig. 2(c), even at a low temperature of 274 K, the MgH<sub>2</sub> can release 96.1 % theoretical H<sub>2</sub> in 16 min in the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution.

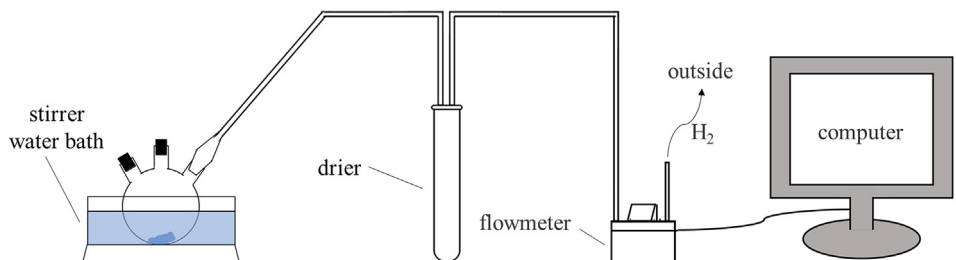
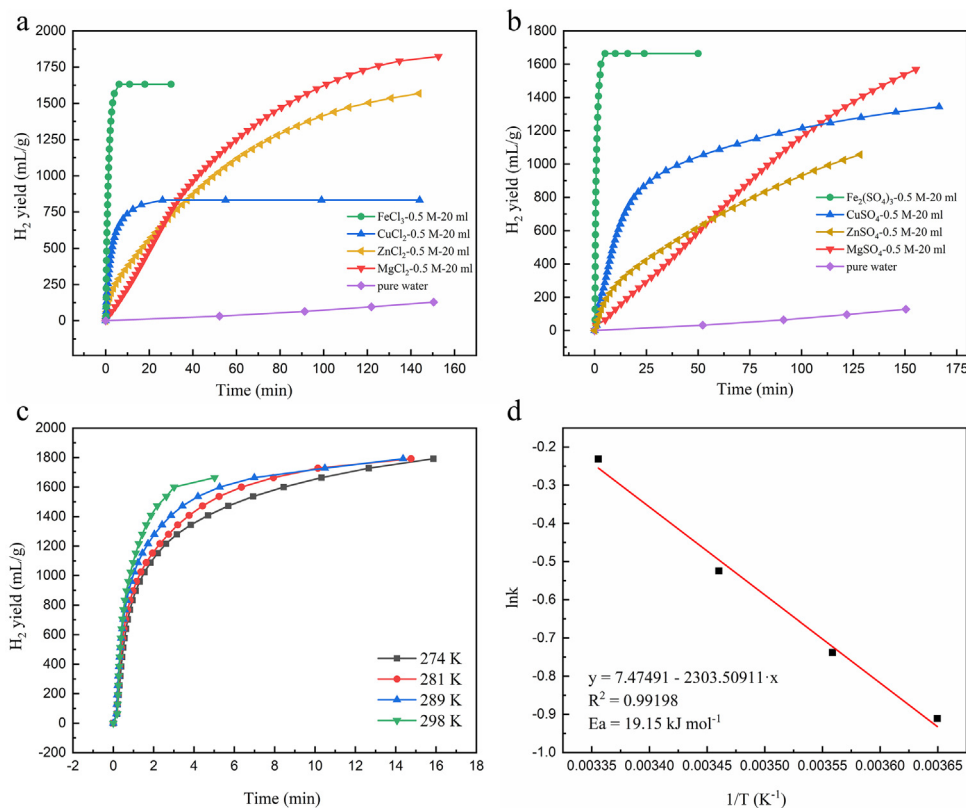


Fig. 1. Schematic diagram of hydrolysis reaction device.



**Fig. 2.** Hydrolysis kinetic curves of the  $\text{MgH}_2$  in different chloride solutions (a) and sulfate solutions (b) at 298 K. Hydrolysis kinetic curves of the  $\text{MgH}_2$  at different temperatures in  $\text{Fe}_2(\text{SO}_4)_3$  solution (c) and their Arrhenius plot (d).

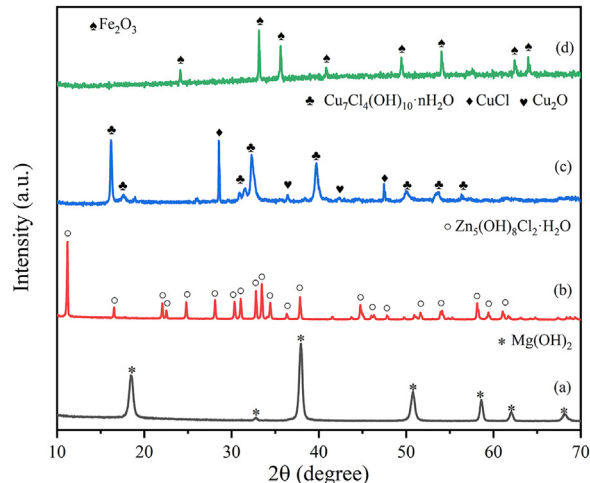
The relationship between temperature and rate of  $\text{MgH}_2$  hydrolysis can generally be expressed by the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \quad (2)$$

where  $k$  is the reaction rate constant,  $E_a$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the reaction temperature (K). Fig. 2(d) presents an Arrhenius plot for the hydrolysis of the  $\text{MgH}_2$  in  $\text{Fe}_2(\text{SO}_4)_3$  solution and the activation energy ( $E_a$ ) was calculated to be  $19.15 \text{ kJ mol}^{-1}$ , which is lower than that of previously reported hydrolysis of  $\text{MgH}_2$  in  $\text{AlCl}_3$  solution ( $21.64 \text{ kJ mol}^{-1}$ ) [25] and  $\text{NH}_4\text{Cl}$  solution ( $30.37 \text{ kJ mol}^{-1}$ ) [26]. As for the  $\text{MgH}_2$  hydrolysis in pure water, due to the inevitable formation of  $\text{Mg}(\text{OH})_2$  passivation layer on the surface of  $\text{MgH}_2$  particle, the hydrogen release rate was improved at first but quickly degraded at the high temperature, leading to a very low hydrolysis efficiency, as shown in Fig. S3.

It has been reported that cations with higher  $\text{OH}^-$  affinity are more effective for facilitating the Mg hydrolytic reaction [28]. The precipitation from the metal chloride and sulfate solutions was collected and characterized by XRD and SEM to explore the effect mechanism of cations on the  $\text{MgH}_2$  hydrolysis.

According to the XRD patterns in Fig. 3, the final  $\text{MgH}_2$  hydrolysates in different chloride solutions are the corresponding cationic hydroxides. Among them, the hydrolysate in the  $\text{FeCl}_3$  solution cannot be directly characterized by XRD due to a severe amorphization. After annealing at  $650^\circ\text{C}$  in a nitrogen atmosphere, the XRD of  $\text{Fe}_2\text{O}_3$  product indirectly confirms the presence of iron hydroxide in the hydrolysate. In addition, the XRD of hydrolysate in  $\text{CuCl}_2$  solution shows the diffraction peaks of  $\text{CuCl}$ , which may be resulted from the incomplete hydrolysis of  $\text{MgH}_2$ . During the drying process of the hydrolysate, Cu (II) was redoxed to obtain Cu (I) by  $\text{MgH}_2$ . This phenomenon also appears in the hydrolysis products of  $\text{CuSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ , and the formation of  $\text{Cu}_2\text{O}$  and  $\text{Fe}_3\text{O}_4$

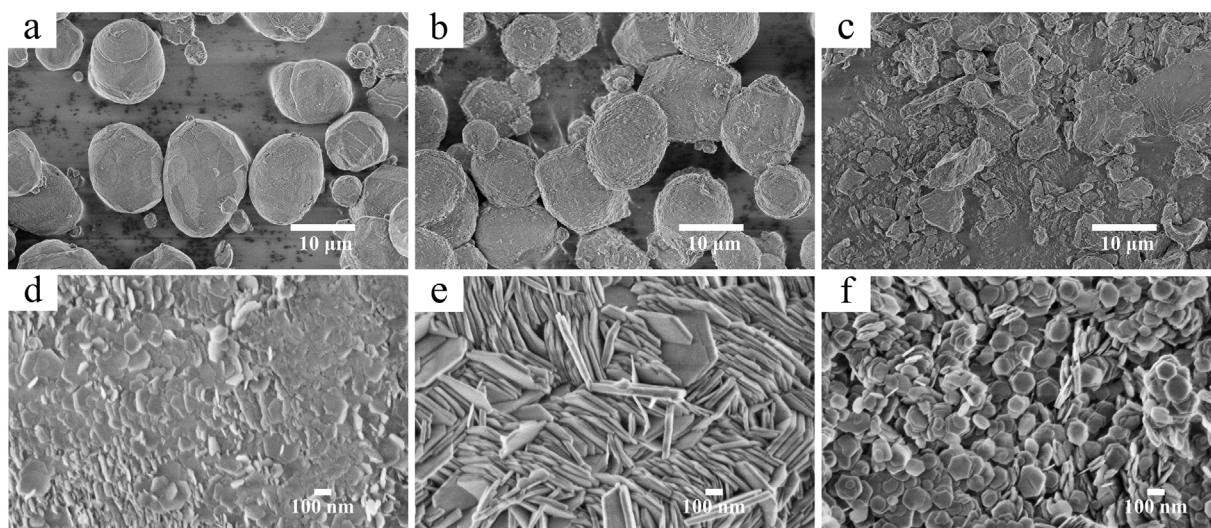


**Fig. 3.** XRD patterns of  $\text{MgH}_2$  hydrolysis products in (a)  $\text{MgCl}_2$  solution; (b)  $\text{ZnCl}_2$  solution; (c)  $\text{CuCl}_2$  solution; (d)  $\text{FeCl}_3$  solution.

phases also indicates the existence of this redox reaction (See Fig. S2 in Supplementary material).

The  $\text{H}_2$  generation rate is improved in the order of  $\text{Mg}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Fe}^{3+}$ , which is the same order as the thermodynamic tendency of hydroxide formation, i.e. the  $\text{OH}^-$  affinity of the cation.  $\text{OH}^-$  affinity is defined by the  $\text{p}K_{\text{sp}}/x$  value [28],  $\text{p}K_{\text{sp}}/x = -\lg K_{\text{sp}}/x$ ,  $K_{\text{sp}}$  is the solubility product of  $\text{M}(\text{OH})_x$ , and  $x$  is the cation valence. Apparently, the cations with higher  $\text{OH}^-$  affinity display a stronger promotion effect on the hydrogen evolution (see Table 1).

Fig. 4 shows the SEM images of the hydrolysis products, which illustrate the different induction effect of  $\text{M}^{x+}$  on the hydrolysis of  $\text{MgH}_2$ . The hydrolysis reacts violently and quickly in  $\text{FeCl}_3$  solu-



**Fig. 4.** SEM images of the integrated  $\text{MgH}_2$  particles in (a) pure water, (b)  $\text{MgCl}_2$  solution and (c)  $\text{FeCl}_3$  solution after 30 min reaction; the surface of  $\text{MgH}_2$  particles in (d) pure water, (e)  $\text{MgCl}_2$  solution and (f)  $\text{FeCl}_3$  solution after 30 min reaction.

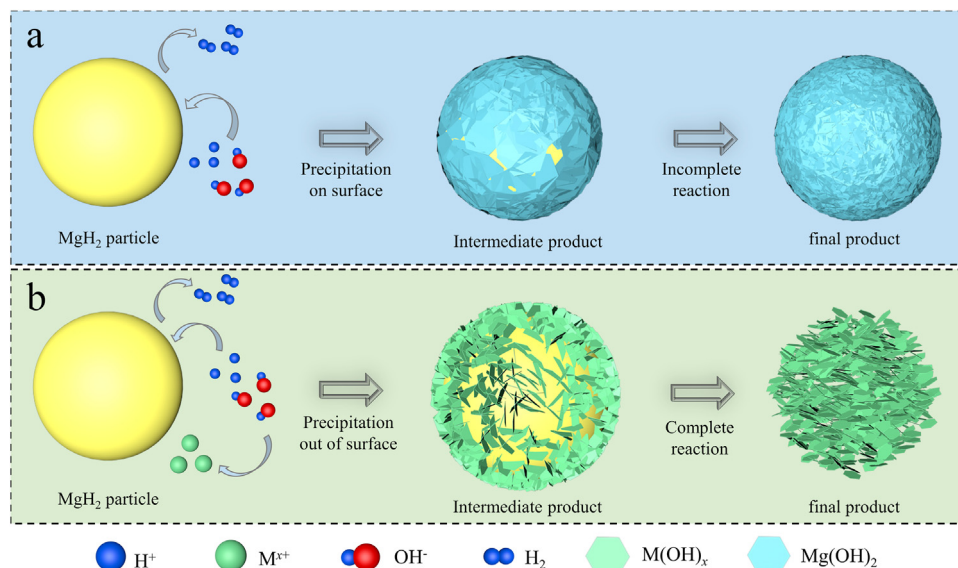
**Table 1**  
The  $\text{p}K_{\text{sp}}/x$  of cations and corresponding hydrogen evolution in different solutions.

Solution	$\text{p}K_{\text{sp}}/x$ of cation	$\text{H}_2$ yield in 10 min [ml/g]
$\text{Fe}_2(\text{SO}_4)_3$	12.85	1664.0
$\text{CuSO}_4$	9.83	558.4
$\text{ZnSO}_4$	8.83	280.0
$\text{MgSO}_4$	5.62	127.1
$\text{FeCl}_3$	12.85	1632.0
$\text{CuCl}_2$	9.83	738.6
$\text{ZnCl}_2$	8.25	373.2
$\text{MgCl}_2$	5.62	227.0

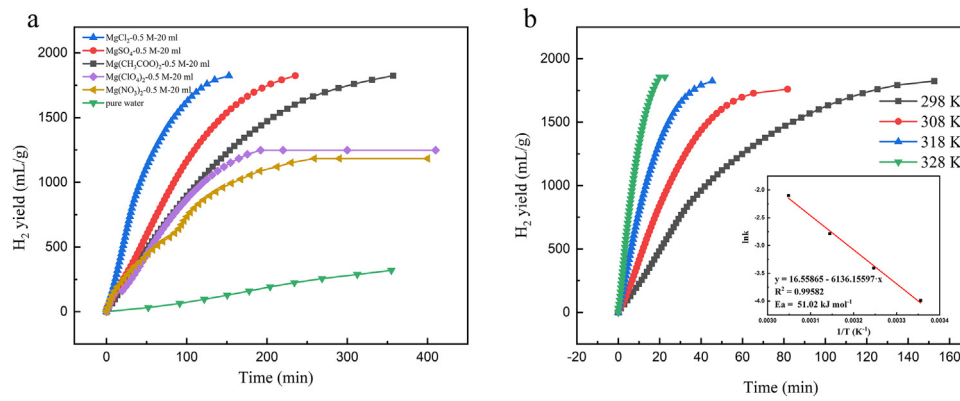
tion so that the  $\text{MgH}_2$  particles changed a lot in appearance while the overall shape of the  $\text{MgH}_2$  particles has not changed much in pure water and  $\text{MgCl}_2$  solution (Fig. 4(a)–(c)). In addition, we can see from Fig. 4(d)–(f) that there is a clear passivate  $\text{Mg}(\text{OH})_2$  layer wrapped on the surface of  $\text{MgH}_2$  particle in the pure water condition, but in the  $\text{MgCl}_2$  solution, the  $\text{Mg}(\text{OH})_2$  sheets have a tendency to extend outward, and for the  $\text{FeCl}_3$  solution, visible product particles with an average diameter  $\sim 100$  nm can be observed with

the disappearance of  $\text{MgH}_2$  particles. In the  $\text{Fe}_2(\text{SO}_4)_3$  solution, the morphology change of  $\text{MgH}_2$  particles is showed in Fig. S4b, the  $\text{MgH}_2$  particles also changed greatly in appearance and the final products are formed with lots of flakes showing a diffusion state (Fig. S4d). The change of the surface of  $\text{MgH}_2$  particles in different solutions suggests that the cations play an important role in inducing the growth of the hydrolysis products for the solution to reach the  $\text{MgH}_2$  surface. Moreover, the cations with higher affinity to  $\text{OH}^-$  will exhibit a stronger introducing effect, as the surface of  $\text{MgH}_2$  particles has a more dramatic changes in appearance in  $\text{FeCl}_3$  solution than in  $\text{MgCl}_2$  solution.

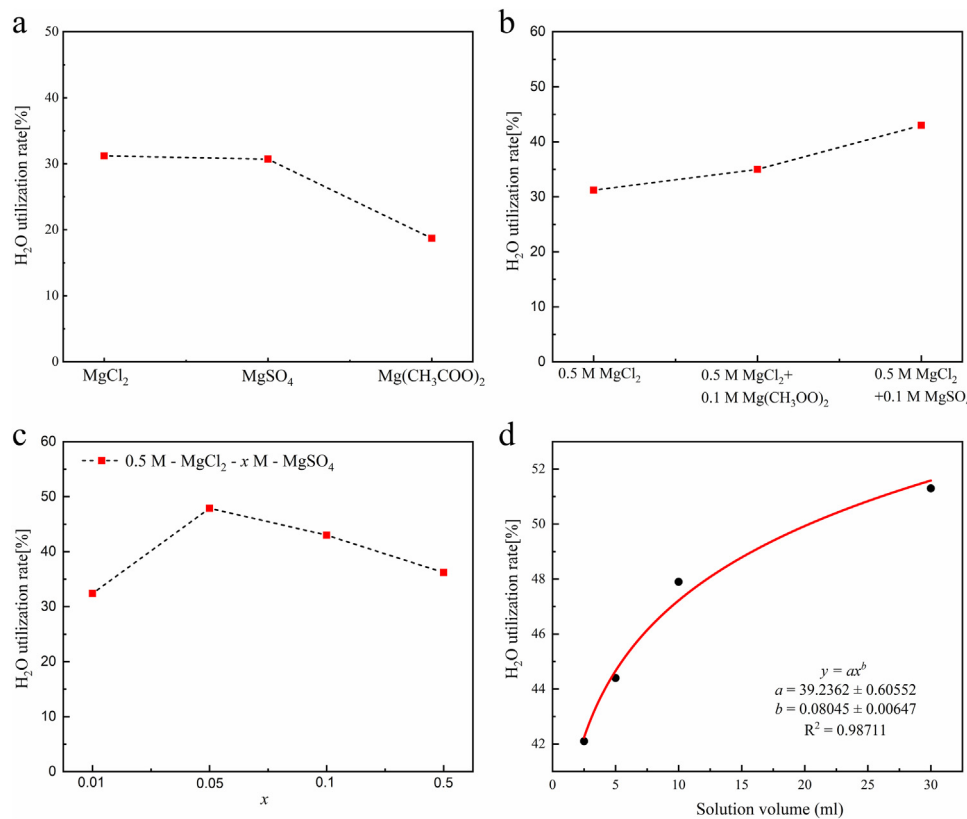
Based on the SEM results, this promotion effect of various  $M^{x+}$  can be understood as the illustration in Fig. 5. Different from the passive  $\text{Mg}(\text{OH})_2$  formed in the  $\text{MgH}_2$  surface in pure water (Fig. 5(a)), the  $M^{x+}$  existed in solution can induce the conformation of  $M(\text{OH})_x$  around the  $\text{MgH}_2$  particles (Fig. 5(b)). In this case, the cations  $M^{x+}$  with high affinity to  $\text{OH}^-$  will compete for the  $\text{OH}^-$  species and induce the growth of  $M(\text{OH})_x$  with priority, so the formation of the  $\text{Mg}(\text{OH})_2$  passivation layer in the  $\text{MgH}_2$  sur-



**Fig. 5.** Schematic illustration of the mechanism for the hydrolysis of  $\text{MgH}_2$  in (a) pure water and (b)  $M^{x+}$  solution.



**Fig. 6.** (a) Hydrolysis kinetic curves of the  $\text{MgH}_2$  in different  $\text{Mg}^{2+}$  solutions and pure water at 298 K. (b) Hydrolysis kinetic curves of the  $\text{MgH}_2$  in  $\text{MgCl}_2$  solution at different temperatures. The inset is their Arrhenius plot.



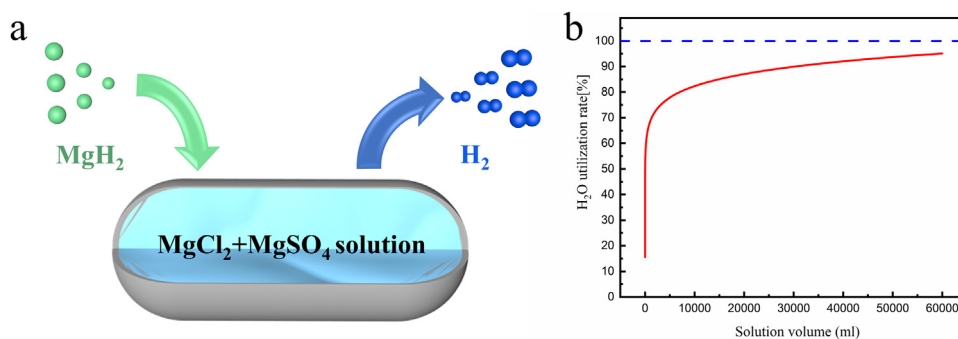
**Fig. 7.** The water utilization rate of  $\text{MgH}_2$  hydrolysis in the (a) 0.5 M  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$  solutions, and (b) the mixture solutions of 0.5 mol  $\text{L}^{-1}$   $\text{MgCl}_2$ , 0.5 M  $\text{MgCl}_2$  + 0.1 M  $\text{Mg}(\text{CH}_3\text{COO})_2$ , 0.5 M  $\text{MgCl}_2$  + 0.1 M  $\text{MgSO}_4$ , and (c) the mixed solutions of different concentration ratios for  $\text{MgCl}_2$  and  $\text{MgSO}_4$  at 298 K. The solution volume is 10 ml. (d) the power function model Eq. (3) fitting curve between  $\text{H}_2\text{O}$  utilization rate and solution volume for 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$  solution.

face is inhibited and the hydrogen generation is enhanced to a large extent. The XRD characterizations of the precipitation product also fit the statement for the induction effect of cations very well.

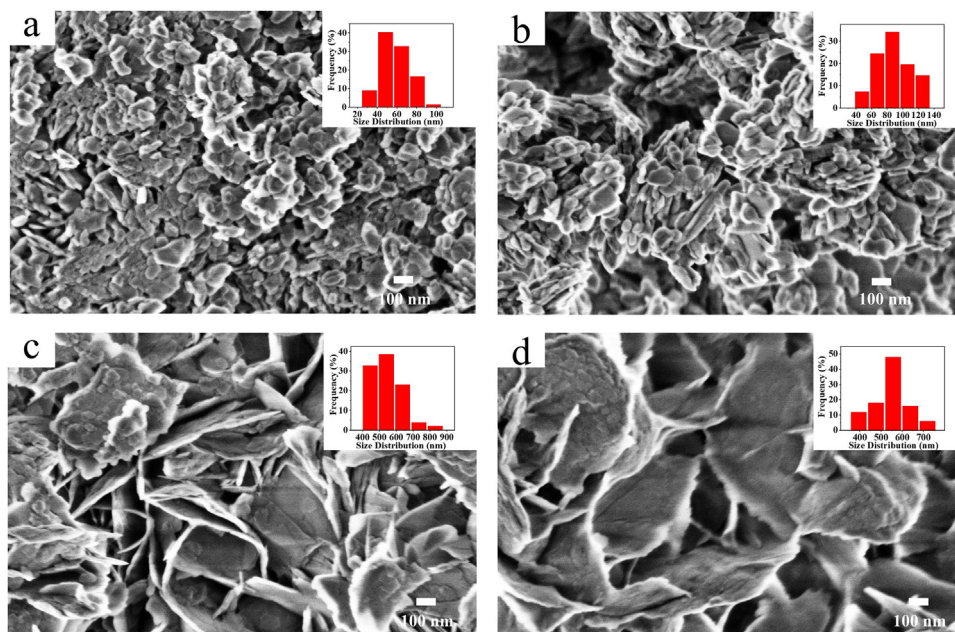
### 3.2. The influence of anions in $\text{MgH}_2$ hydrolysis

The hydrolysis kinetic curves of different magnesium salt solutions are established in Fig. 6(a). As can be seen, the presence of magnesium salts in the solution can obviously increase the hydrolysis rate compared to the pure water environment.  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$  solution can achieve a high reaction degree to near 100% (1864.0 mL/g) within 150, 235 and 357 min, respectively. Nevertheless, the hydrolysis reaction degree is 70.0% (1304.8 mL/g) for  $\text{Mg}(\text{ClO}_4)_2$  solution and 63.5% (1183.6 mL/g) for  $\text{Mg}(\text{NO}_3)_2$  solu-

tion, even though the reaction time was increased to 400 min. It is distinctly that the improvement of  $\text{MgH}_2$  hydrolysis is increased in this order of  $\text{MgCl}_2 > \text{MgSO}_4 > \text{Mg}(\text{CH}_3\text{COO})_2 > \text{Mg}(\text{ClO}_4)_2 > \text{Mg}(\text{NO}_3)_2$ . Awad et al. [22] have reported that chloride ions can replace hydroxide ions which bring the formation of soluble  $\text{MgCl}_2$  and the destruction of passive layer to promote the reaction. From our results, the various anions may have the similar function and the order of the replacement effect of anions is as follows:  $\text{Cl}^- > \text{SO}_4^{2-} > \text{CH}_3\text{COO}^- > \text{ClO}_4^- > \text{NO}_3^-$ . To further investigate the kinetics effect of  $\text{Cl}^-$ , the hydrogen generation of  $\text{MgH}_2$  hydrolysis at various temperatures in  $\text{MgCl}_2$  solution were obtained as shown in Fig. 6(b). When the system temperature increased from 298 K to 328 K, the hydrogen yield of  $\text{MgH}_2$  hydrolysis in  $\text{MgCl}_2$  solution increased from 26.1% (298 K) to 45.3% (308 K), 72.0% (318 K) and



**Fig. 8.** (a) Proposed hydrogen generation system based on the hydrolysis of  $\text{MgH}_2$  in mixed 0.5 M  $\text{MgCl}_2$  and 0.05 M  $\text{MgSO}_4$  solution with continuous feeding of  $\text{MgH}_2$ ; (b) The solid curve: simulated system  $\text{H}_2\text{O}$  utilization rate at different solution volume based on Eq. (3). The dashed line: the 100 %  $\text{H}_2\text{O}$  utilization rate.



**Fig. 9.** SEM images of hydrolysis products in the mixed solutions of (a) 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$ , (b) 0.5 M  $\text{MgCl}_2$  + 0.1 M  $\text{MgSO}_4$ , (c) 0.5 M  $\text{MgCl}_2$  + 0.5 M  $\text{MgSO}_4$ , (d) 0.5 M  $\text{MgCl}_2$  + 0.1 M  $\text{Mg}(\text{CH}_3\text{COO})_2$ .

99.6 % (328 K) in 20 min. And the apparent activation energy ( $E_a$ ) was calculated by Eq. (2) to be 51.02  $\text{kJ mol}^{-1}$ .

Besides the kinetics, it was found that the  $\text{H}_2\text{O}$  utilization rate is different in various anions solutions. Generally, the  $\text{MgH}_2$  hydrolysis is carried out in a condition that the amount of  $\text{H}_2\text{O}$  is far exceeding in order to guarantee a complete hydrolysis of  $\text{MgH}_2$ , which inevitably leads to the decreased hydrogen capacity in the whole  $\text{MgH}_2/\text{H}_2\text{O}$  system. Obviously, it is significative to enhance the  $\text{H}_2\text{O}$  utilization, so we use the  $\text{H}_2\text{O}$  utilization rate to describe the roles of anions and the results are shown in Fig. 7 (Complete and specific hydrogen release curves are shown in Figs. S5–S8). Because of the low degree of hydrolysis, the  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{Mg}(\text{NO}_3)_2$  solutions are not considered. For a single anion, the  $\text{H}_2\text{O}$  utilization rate is less than 32 % (Fig. 7(a)). However, when two anions are mixed together, the  $\text{H}_2\text{O}$  utilization rate is improved as shown in Fig. 7(b). Specially for the mixed  $\text{MgCl}_2$  and  $\text{MgSO}_4$  solution (0.5 M  $\text{MgCl}_2$  + 0.1 M  $\text{MgSO}_4$ ), the  $\text{H}_2\text{O}$  utilization rate comes to 43 %. What's more, Fig. 7(c) indicates that the concentrations of the mixed solutions also affect the water utilization, and the 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$  solution demonstrates the highest  $\text{H}_2\text{O}$  utilization rate of 47.9 %.

Except for the influence of the concentration for the mixed solution, the volume of the solution also has a certain effect on the water

utilization rate. The relationship between  $\text{H}_2\text{O}$  utilization rate and solution volume in 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$  solution can be well described by the power function of Eq. (3), as shown by the black curve in Fig. 7(d).

$$y = a \cdot x^b \quad (3)$$

This is a mathematical model to describe the trend of relationship changes, and has no actual physical and chemical meaning. However, on the grounds of this mathematical model, we designed a hydrogen evolution system as shown in Fig. 8(a). It demonstrates that if there are 60 L (normal vehicle gasoline volume) mixed 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$  solution in the system, the  $\text{H}_2\text{O}$  utilization rate will be 95.1 %. On the other hand, if the weight of water is calculated, the systematic hydrogen capacity of  $\text{MgH}_2$  hydrolysis process is 6.5 wt. %. The higher  $\text{H}_2\text{O}$  utilization rate will result in the higher systematic hydrogen capacity, and when the  $\text{H}_2\text{O}$  utilization rate comes to 100 %, deservedly the hydrogen storage capacity of the  $\text{MgH}_2/\text{H}_2\text{O}$  system is 6.5 wt. %. In this regard, with the increased volume of 0.5 M  $\text{MgCl}_2$  + 0.05 M  $\text{MgSO}_4$  solution as displayed in Fig. 8(b), which leads to an increased  $\text{H}_2\text{O}$  utilization rate, the hydrogen evolution system in Fig. 8(a) can gradually approaching 100 %  $\text{H}_2\text{O}$  utilization rate which is established as a dashed line (Fig. 8(b)). In this way, the hydrogen storage capacity

of the whole system can achieve the theoretical hydrogen storage capacity at the same time.

For the sake of exploring the mechanism of anion effect on water utilization, the morphology of the final products in various anions solutions is characterized as shown in Fig. 9. It can be seen that as the particle size of the flakes decreases, the hydrolysis efficiency increases significantly. The maximum water utilization rate obtained corresponds the smallest particle size distribution in the final products, which is mainly in the range of 40–60 nm (Fig. 9(a)). On the contrary, the minimum water utilization rate gives the largest particle size distribution of 500–600 nm (Fig. 9(d)). Furthermore, in the single anion solution, the particle size of product is even  $>1 \mu\text{m}$  (Fig. S9). These results indicate that the anion solution does affect the water utilization rate by affecting the morphology of the hydrolysate. The larger the flaky size of the hydrolysate particles, the easier it is to form a flaky cross structure (Fig. 9(c)–(d)), and the easier it is to lock in moisture, thus reducing the utilization of water.

#### 4. Conclusion

In this study, the functions of different anions and cations in solutions for  $\text{MgH}_2$  hydrolysis are demonstrated and the  $\text{H}_2$  generation from the  $\text{MgH}_2$  hydrolysis is promoted significantly by low-cost chlorides and sulfates solutions. The cations with high affinity to  $\text{OH}^-$  in the solution will induce the outward growth of hydroxide and thus inhibiting the formation of the surface  $\text{Mg}(\text{OH})_2$  passivation layer. The  $\text{H}_2$  yield of  $\text{MgH}_2$  hydrolysis in  $\text{FeCl}_3$  and  $\text{Fe}_2(\text{SO}_4)_3$  solutions, in which the  $\text{Fe}^{3+}$  has the largest affinity to  $\text{OH}^-$  among the studied metal cations, comes up to 1632.0 mL/g  $\text{H}_2$  and 1664.0 mL/g in 6.2 min and 5 min, respectively. With regard to the anions, we found it can effectively affect the morphology of hydrolysis product, thereby affecting the water utilization. Especially in the mixed 0.5 M  $\text{MgCl}_2$  and 0.05 M  $\text{MgSO}_4$  solution, the  $\text{H}_2\text{O}$  utilization rate can reach to the highest value among the various anion solutions. Furthermore, under the prediction of the mathematical model for the relationship between  $\text{H}_2\text{O}$  utilization rate and solution volume, with continuously increasing the solution volume to 60 L, the  $\text{H}_2\text{O}$  utilization rate can reach to nearly 100%. On account of the high attainable hydrogen capacity and high abundance of the raw materials, the solution promoted hydrolysis of  $\text{MgH}_2$  is highly attractive for onsite  $\text{H}_2$  generation.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jmst.2020.09.036>.

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