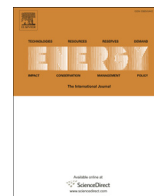




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A study of hydrogen generation by reaction of an activated Mg–CoCl₂ (magnesium–cobalt chloride) composite with pure water for portable applications

Qian Sun, Meishuai Zou^{*}, Xiaoyan Guo, Rongjie Yang, Haitao Huang, Peng Huang, Xiangdong He

School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

Hydrogen production based in the corrosion of light metals in water solutions is an interesting alternative. Among all of them, Mg is probably the most adequate metal for energetic purposes due to its high electron density and oxidation potential. A safe and environmental-friendly method of hydrogen production from milled Mg–CoCl₂ composites in water was proposed in this paper. An improved mechanism for the reactivity was developed. The experimental results indicated that the activated Mg–CoCl₂ composites are very promising materials for hydrogen generation upon reaction with pure water. When immersed in pure water (50 °C), the hydrolysis reaction of the Mg-6 wt% CoCl₂ composite began immediately, and the reaction rate reached 558.6 mL(min g)⁻¹ in the first minute; the evolution of hydrogen reached 98.6% of the theoretical yield.

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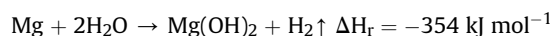
1. Introduction

The combustion of traditional fossil fuels is causing severe environmental pollution and energy crisis [1,2]. Hydrogen is considered “the green energy for the twenty-first century” due to its unique features, and many countries are deploying hydrogen-based energy strategies [3].

And first of all a proper hydrogen source is required. Hydrogen does not typically exist by itself in nature and must be obtained from some compounds. Traditional methods which produce hydrogen from fossil fuel, natural gas, and methanol [4]. However, there are some limiting factors deter their applications, such as low conversion, high cost and environmental pollution. In order to resolve these problems, many new hydrogen generation methods are proposed by researchers. Among these methods, hydrogen generation by the reaction of metal, metal alloy or metal compounds with water is becoming the research focus [5–7].

Recently, on-board hydrogen generation via the hydrolysis of electrochemically active light metal such as magnesium has

attracted much attention [8–10]. Magnesium is a very promising hydrolysing material due to its low density, high capacity, good activity and abundance in the earth. Water is considered the most promising hydrogen source due to its high hydrogen content. Therefore, the reaction between magnesium and water is a favourable hydrogen production method, and the hydrogen can be produced by the following reaction:



The most challenging issue for the direct reaction between water and magnesium is the native thin oxide layer on the magnesium surface, which prevents water from penetrating into the core and thus prevents oxidation and corrosion reactions [11]. However, many studies [12–16] have shown that the yield and kinetics of this hydrolysis reaction can be improved using Mg-based materials prepared by ball milling. Grosjean et al. [17] found that the hydrolysis reactions of Mg and the Mg–Ni composite exhibited a higher reaction rate and yield in 1 M KCl than in pure water because the chloride ions accelerated the corrosion of Mg in the conductive aqueous media. Jun-Yen Uan [18] studied the hydrolysis of alloy scraps catalysed by a platinum-coated titanium net in an aqueous NaCl solution. Y.G. Liu et al. [7] reported that the

^{*} Corresponding author. Tel.: +86 010 68913456; fax: +86 010 68914862.
E-mail address: zoumeishuai@gmail.com (M. Zou).

effect of AlCl_3 addition and ball milling on the hydrolysis performance of Mg powder, 6 h-milled Mg-3mol% AlCl_3 shows the best performance with a hydrogen yield of 93.86% and initial hydrogen generation rate of $455.9 \text{ mL min}^{-1} (\text{g Mg})^{-1}$ within 1 h. We also studied the hydrolysis reaction between ball-milled Mg–Co and Mg–Ni composites with seawater [19]. In these studies, complete hydrolysis reactions primarily depend on the use of an aqueous solution with a high concentration of chloride ions. However, for many applications, where aqueous solutions with a high concentration of chloride ions cannot be directly used, especially for emergency power supply applications, a new type of hydrogen production material with an excellent hydrolysis property in pure water is required.

Several recent studies [20,21] have reported that Mg–metal chlorides composites exhibit excellent hydrolysis properties in pure water. There have been no detailed investigations of the hydrolysis properties of Mg– CoCl_2 materials. We demonstrated in a previous study that the intense hydrolysis reaction of Mg–Co composite was due to the formation of a micro-galvanic cell reaction between Mg and Co. Therefore, we have prepared activated Mg– CoCl_2 materials using high-energy milling and studied the hydrolysis reaction of Mg– CoCl_2 materials in pure water. In addition, the influence of several reaction parameters was investigated.

2. Experimental

The starting materials included magnesium powder (Mg, >99 wt%, 60–300 mesh), cobalt chloride (CoCl_2 , analytically pure) and pure water.

The milling experiments were performed using a Simoloyer CM01 instrument with a chamber volume of 1 L. The magnesium powder and cobalt chloride were weighed according to different ratios (Table 1), mixed, and placed in the Simoloyer CM01 chamber. An inert argon atmosphere was used to prevent oxidation during the milling process. The milling process parameters are provided in Table 2. After the milling experiment, the activated Mg– CoCl_2 composites were prepared.

The hydrolysis reactions of the activated Mg– CoCl_2 composites with pure water were performed in a 250 mL flask reactor with two openings (i.e., a water inlet and a gas outlet). Prior to adding the pure water to the reactor, it was preheated to the desired temperature. Then, the flask reactor was placed in a thermostatic circulator to study the process under isothermal conditions. The produced gas was passed through a condenser and drierite to remove all of the water vapour prior to passing through a digital hydrogen mass flow meter (Sevenstar2000, China). The flow meter was connected to a computer recording the gas flow and volume as a function of time. Each test was repeated at least two times. The amount of magnesium used in each experiment was 1 g. All of the experiments were performed without stirring.

The samples were characterised by powder XRD (X-ray diffraction) using an X' Pert PRO MPD diffractometer with $\text{Cu K}\alpha$ radiation.

SEM (scanning electron microscopy) observations were performed using a FE-SEM S4800 microscope.

Table 1
Composition of Mg– CoCl_2 composites.

Sample	Mg/g	CoCl_2/g	Milling time/h
Mg-2 wt% CoCl_2	98	2	1
Mg-4 wt% CoCl_2	96	4	1
Mg-6 wt% CoCl_2	94	6	1
Mg-8 wt% CoCl_2	92	8	1
Mg-10 wt% CoCl_2	90	10	1

Table 2
Milling equipment and parameters.

Ball miller	Simoloyer CM01-21
Milling balls	Material: steel (100Cr6) Diameter: 5.1 mm
Powder/ball mass ratio	1:10
Milling atmosphere	Argon
Milling time	1 h
Rotary speed	1300 rpm/48 s, 1000 rpm/12 s
Operating model	Cycle
Cooling-grinding unit	Water

The specific surface areas of the powders were measured by N_2 adsorption (BET) using a NOVA4200e system.

3. Results and discussion

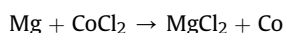
3.1. Characterisation of Mg– CoCl_2 composites

The activated Mg– CoCl_2 composites were prepared using high-energy milling. Fig. 1 shows the SEM images of the blended Mg/ CoCl_2 and the activated Mg-6 wt% CoCl_2 composite. The original material was a spherical powder, which after 1 h of milling, became irregular and exhibited exit grain boundaries and dislocations in the powder surface.

The specific surface areas of the blended Mg/ CoCl_2 and the activated Mg-6 wt% CoCl_2 were measured, and the results indicated that the blended Mg/ CoCl_2 possessed a small specific surface area of $0.482 \text{ m}^2/\text{g}$. However, the specific surface area of the activated Mg-6 wt% CoCl_2 was $4.072 \text{ m}^2/\text{g}$. It is generally known that the repeated cold welding and fracturing process of ball-milling change the samples' microstructure, redistribute the constituents and induce severe plastic deformation and defects which combine to promote the corrosion of metals.

The microstructures of the blended Mg/ CoCl_2 and the activated Mg– CoCl_2 powders were determined using X-ray diffraction. The X-ray diffraction patterns are shown in Fig. 2.

The blended Mg/ CoCl_2 material exhibited a well-defined set of Mg and CoCl_2 peaks. For the activated Mg– CoCl_2 powders, there is no CoCl_2 peak, and the magnesium peak is noticeably broadened, reflecting a decrease in the Mg crystallite size during milling due to the repeated breaking up of the grains, cold welding and re-welding [22]. A replacement reaction between Mg and CoCl_2 may occur during the milling process due to the effect of mechano-chemistry [23] via the following reaction:



In the XRD curve of activated Mg– CoCl_2 , characteristic peaks of MgCl_2 and metal Co were not clearly observed, which is most likely due to the peaks corresponding to magnesium chloride overlapping with those of magnesium [24]. In addition, metallic Co was not observed due to its low content and the strong absorption of the $\text{Cu K}\alpha$ radiation by Co [25].

3.2. Hydrolysis reactions of the activated Mg– CoCl_2 composite

3.2.1. Effect of CoCl_2 content

The hydrogen generation curves from the experiments conducted at the same water temperature (i.e., 30°C) for activated Mg– CoCl_2 composites with different CoCl_2 contents (2, 4, 6, 8 and 10 wt%) are shown in Fig. 3. The conversion yields and hydrogen generation rates at different stages of the hydrolysis reaction for the various activated Mg– CoCl_2 powders are presented in Table 3.

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