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Effect of carbons (G and CFs), TM (Ni, Fe and Al) and oxides (Nb_2O_5 and V_2O_5) on hydrogen generation from ball milled Mg-based hydrolysis reaction for fuel cell

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ABSTRACT

This paper dedicated to investigation the effect of carbons (graphite and carbon fibers), transition metals (TM = Ni, Fe and Al) and oxides (Nb_2O_5 and V_2O_5) on Mg–H hydrolysis reaction in aqueous media (3.5 wt% NaCl). Mg – 10 wt% X (X = C, TM and oxides) mixtures were prepared by mechanical milling (1, 3 and 5 h). Mg – 10 wt% G mixtures show the best hydrolysis performance (95% of theoretical hydrogen generation yield in almost 3 min) in comparison to Mg – oxide and Mg – TM mixtures. In addition to the presence of micro-galvanic cells, particle size, MgH_2 content, density defects, fractures and cracking have an important influence on the hydrolysis reaction. Synergetic effect of carbons and transition metals has been studied for Mg – 5 wt% G – 5 wt% Ni mixture. Activation energies were calculated using Avrami–Erofeev model. An activation energy of 14.34 kJ/mol was found for Mg/G/Ni mixture which demonstrates the best hydrolysis behavior (95% of theoretical hydrogen generation yield within 2 min). Hydrogen generated from Mg–H hydrolysis reaction was fed directly to a single Proton Exchange Membrane Fuel Cell (PEMFC). At 0.15 A, the cell voltage exhibited a stable value of approximately 0.52 V for roughly 35 min.

1. Introduction

Hydrogen production is one of the main challenges on the way to replace fossil fuel for green and sustainable one. Hydrogen (H_2) is a very good alternative fuel because of the (i) high power density, (ii) non-polluted reaction product and (iii) possible abundant nature source. The combustion of hydrogen is sustainable and environmental friendly because it does not generate green-house gases [1,2].

In the last few decades, a lot of effort to produce hydrogen in large quantity has been focused on catalytic reforming of fossil fuel [3]; also electrolysis and dark fermentation have been envisaged as possible alternatives [4,5]. Hydrogen production based on hydrolysis reaction of various materials has been recognized. This method is promising because no additional energy is required (low temperature operation) and it offers the possibility to produce delocalized and rather pure hydrogen. Many kind of materials such as complex hydrides [6,7], metal [8], metal hydride [9] and intermetallics [10,11] have been tried in the literature. Among these materials, magnesium metal has attracted much attention for hydrogen production via hydrolysis reaction due to its electrochemical activity, low density, low cost, abundance and non-toxicity. Magnesium and magnesium hydride react with water according to the following equations (Eqs. (1) and (2) respectively):

$$Mg + 2H_2O = Mg(OH)_2 + H_2 \quad (1)$$

$$MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2 \quad (2)$$

The theoretical hydrogen yield is 8.2 wt% and 15.2 wt% (no water included in the calculation) for Mg and its hydride respectively. The Mg hydrolysis reaction is always blocked by the formation of a passive hydroxide layer $Mg(OH)_2$ and cannot be carried out completely. In order to improve the hydrolysis performance of Mg powder, different solutions have been investigated.

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S.D. Kushch *et al.* have demonstrated that hydrogen generation is improved *via* the interaction of magnesium with organic acids [12]. Ultrasonic irradiation was also considerably effective in improving the hydrolysis of MgH_2 [13].

Grosjean *et al.* [14–16] showed that ball milling of pure magnesium has no effect on the Mg reactivity for hydrolysis in pure water. Ball milling effect is assumed to be masked by the significant Mg passivation in pure water. Nevertheless, our previous work showed that ball milling enhances the hydrogen yield in case of magnesium hydride [17]. Otherwise, ball milling of Mg in presence of additives can improve the hydrolysis performance. Wang *et al.* [18] found that the Mg–metal chlorides (*i.e.* 0.5 h milled Mg-10 wt% $FeCl_3$) composites are very promising for hydrogen generation by hydrolysis reaction. The micro-galvanic cell formed between Mg and the other metal which are produced by replacement reaction during the ball-milling process is very beneficial for the hydrolysis. The addition of chloride can also prevent the cold welding process (and act as anti-sticking agent) of the mixture during the ball milling process to produce more defects and fresh surfaces, which will improve the hydrolysis kinetics effectively.

The activated Mg–$CoCl_2$ composites are very promising materials for hydrogen generation upon reaction with pure water [19,20]. When immersed in pure water (50 °C), the hydrolysis reaction of the Mg-6 wt% $CoCl_2$ 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.

Liu *et al.* [21] have found that Mg-3 mol% $AlCl_3$ (*i.e.* Mg − 16.5 wt % $AlCl_3$), ball milled during 6 h, shows better kinetics compared with pure Mg. 6 h-milled Mg-3 mol% $AlCl_3$ shows the best performance with a hydrogen yield of 93.86% and initial hydrogen generation rate of 455.9 mL/min (g Mg)$^{-1}$ within 1 h. A new Mg–$LiBH_4$–$AlCl_3$ system was also established by Y.G. Liu *et al.* [22], a synergistic effect between Mg and $LiBH_4$ has been found for the first time when hydrolysis is performed with ball milled Mg–$LiBH_4$ composites, and the addition of $AlCl_3$ further optimizes the overall hydrogen generation performances. In addition to the chloride role mentioned previously, the dissolution of aluminum chloride generates chloric acid which promotes the oxidation of Mg powder. Indeed, the positive role of chloric acid and other acids was also reported in our previous work on the hydrolysis reaction of magnesium hydride [17]. The reason may be the degradation (neutralization) of $Mg(OH)_2$ on the particles surface by H_3O^+ ions.

Furthermore, the presence of transition metals was considered as key factor to accelerate and achieve the hydrolysis reaction. In this context, Grosjean *et al.* [15] showed that Mg-10 at% Ni composite milled for 30 min could release all its theoretical hydrogen in 1 h in the presence of chloride ions due to the creation of micro galvanic cells between Mg and dispersed Ni elements. The conductor solvent (salt solution) is necessary for the establishment of these micro-galvanic cells. For this reason, the addition of transition metals in pure water has no effect. It is also important to note that the reactive materials must be a good electronic conductor which is not the case of magnesium hydride (band gap of 5 eV). Accordingly, the galvanization process and corrosion of this latter is rapidly interrupted. Kravchenko *et al.* [23] noticed that a notable increase in the Mg oxidation rate can be achieved through mechanical activation (*e.g.* milling), using Mg alloys with Co, Ni, Cu and mechanically alloyed compounds (*e.g.* Mg–$MgCo_2$, Mg–$MgNi_2$ and Mg–$MgCu_2$). When alloys are oxidized (*i.e.* hydrolyzed), the rate of reaction depends on the nature of the chloride solution were NaCl was found to be the best one.

A lot of metal oxides have been tried as catalyst of Mg and its hydride in hydrogen sorption reaction [24,25] but only MgO was studied in hydrolysis reaction [26]. The creation of numerous defects and clean surfaces combined with the decrease in the particle size in the milled MgH_2 + 5%MgO powder are considered to be responsible for the increase in the reactivity of the MgH_2 particles with water, leading to the increase in the yield and hydrogen generation rate.

After we showed in our previous work [17], the positive role of carbon additives (graphite and carbon fibers) on MgH_2 hydrolysis reaction, we report in the present paper its role on Mg hydrolysis reaction. The synergetic effect of graphite and transition metals, like Ni, was also investigated. Additionally, two metal oxides (Nb_2O_5 and V_2O_5) were co-milled with Mg and the hydrolysis reaction was studied. It is imported to be noted that we are the first team who investigate the effect of carbon and metals oxide on hydrolysis reaction of Mg-based materials. The mixture of Mg–C can be considered as a very promising material for *in situ* hydrogen generation for mobile application. Several recent studies [15,18,23,26] have reported the hydrolysis properties of magnesium in chloride solution. There have been no detailed investigations of the hydrolysis reaction mechanism. We wonder to investigate in this present study a detailed hydrolysis mechanism. After that, the activation energies of best mixtures were calculated using Avrami–Erofeev model. Finally, the feasibility of the onboard hydrogen production, from the hydrolysis of MgH_2, to supply PEMFC has also been investigated.

2. Experimental part

Mg powder (Stream Chemicals, 99.9%) was used as starting material. Mg hydride was produced from this powder by heating it at 350 °C under 50 bars of H_2 gas. From XRD characterization, the powder appears to be composed of 96% of MgH_2. The mixtures MgH_2–10 wt% X (X = graphite, carbon fibers, Ni, Fe, Al, Nb_2O_5 and V_2O_5) were prepared by ball milling (using a Fritsch P5 ball miller) in stainless steel vial under 10 bar of H_2 for 1, 3 and 5 h with 15 min of continuous milling followed by 2 min of rest (in order to allow the system to cool down). The vial was recharged with hydrogen every 30 min to ensure a constant pressure in the system. The ball to powder weight ratio was 17:1 corresponding to 8 g of powder and 34 stainless steel balls (10 mm of diameter) and the rotation speed was fixed to 250 rpm. The milling vial was handled in a glove box filled with purified argon. The hydrolysis reaction was carried out in NaCl 3.5 wt% solution. The samples were characterized by XRD (X-ray diffraction) using a Philips PANalytical X'Pert (PW1820) diffractometer with Cu $K_{\alpha 1}$ radiation. The amount of hydride and metallic phases (*e.g.* hydrogen content) were estimated from XRD refinement using EVA software. SEM (Scanning electron microscopy) observations were made using a TESCAN VEGA3 SB and SERON TECHNOLOGY microscopes. Auger spectroscopy was used to study the formation of $Mg(OH)_2$ and $MgCl_2$ on the surface of reactive material. Particle size was measured using Laser Granulometry (Mastersizer 2000S). Experimental set-up developed to follow the hydrolysis reaction [17] was completed by a set-up allowing the control of the power generation (using a fuel cell). To investigate the feasibility of on board hydrogen production from hydrolysis of Mg/MgH_2 alloy to power a PEMFC, a single cell was connected directly to the hydrogen production reactor. The polarization curve of a single PEM was measured using a potentiostat (AUTOLAB PGSTAT302N).

3. Results and discussion

3.1. Effect of carbons and transition metals

Fig. 1 shows the XRD patterns of Mg − 10 wt% X (X = carbon, Ni, Fe and Al) after 5 h of ball milling. The diffraction patterns of both Mg − 10 wt% Al and Mg − 10 wt% carbon are similar (patterns (a)