Enhanced Hydrogen Generation by LiBH₄ Hydrolysis in MOH/water Solutions (MOH: C₂H₅OH, C₄H₈O, C₄H₉OH, CH₃COOH) for Micro Proton Exchange Membrane Fuel Cell Application

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Abstract: LiBH₄ has high hydrogen storage capacity, and its high gravimetric hydrogen density reaches 18.36%. However, LiBH₄ exhibits poor hydrolysis performance in water because the abrupt ending caused by the agglomeration of its hydrolysis products limits its full utilization [1, 2]. In this paper, four kinds of organics, namely, ethanol, tetrahydrofuran, acetic acid, and butanol (referred to MOH) were added to water, and the effect of MOH species and amount on the hydrolysis performances of LiBH₄ was evaluated. Results show that agglomeration can be avoided and that LiBH₄ has a controllable hydrogen generation rate and high hydrogen generation amount in MOH/water solutions compared with that in pure water. The order in terms of the hydrolysis performance of LiBH₄ in MOH/water solutions is as follows: acetic acid > butanol > tetrahydrofuran > ethanol. From XRD, SEM, and other analyses, the enhancement performance is explained by the diluting and solvent effects. Moreover, the addition of MOH alters the hydrolysis route of LiBH₄, MOH acts as not only a carrier for water and LiBH₄ but also as a reactant to form intermediate LiBH₄·[MOH(H₂O)ₓ]ₙ, which slows the hydrolysis kinetics of LiBH₄. Hydrolysis conditions were optimized, and high hydrogen amount was achieved correspondingly. The experimental data presents the potential application of LiBH₄ as a highly efficiency and stable hydrogen source for fuel cells.

Keywords: Hydrogen generation, organic/water solution, hydrolysis mechanism, Lithium borohydride

1. INTRODUCTION

Hydrogen is a clean energy source for electrical devices and vehicles because its chemical energy can be easily converted into electric energy by polymer electrolyte membrane (PEM) fuel cells [1–3]. A convenient and safe H₂ storage or portable hydrogen production system with high H₂ storage density should be developed to ensure that PEM fuel cells function successfully using hydrogen [4–6]. In the past 20 decades, various attempts have been made to develop a hydrogen storage technology with high capacity, such as liquid hydrogen vessels, metal hydrides, borohydride, and carbon nanotubes [7–9]. However, no satisfactory material can be used for commercial applications because of numerous limitations, including high decomposition temperature, low efficiency, or low hydrogen storage density. Examples such as LiBH₄ and NaBH₄ have to decompose at a temperature higher than 673 K. Chemical hydrides that directly generate hydrogen on board have received considerable attention. These hydrides can support hydrogen directly into PEMFC when and where hydrogen is needed. A number of previous studies conducted in the last 10 years focused on hydrogen generation from the hydrolysis of NaBH₄ alkali solution and relative catalysts [10, 11]. At present, hydrogen generation from NaBH₄ is becoming widely applied to fuel cells and is gradually decreasing the cost of NaBH₄.

LiBH₄ has a high hydrogen storage capacity (18.36 wt.%) and could potentially serve as a superior hydrogen storage material. However, strong covalent and ionic bonds result in poor thermodynamic and kinetic properties of LiBH₄. The practical application of LiBH₄ in reversible hydrogen storage materials presents many challenges. Hydrolysis of LiBH₄ may be a feasible method for the dissociation of H atoms from LiBH₄ under moderate conditions [12]. Compared with 10.8 wt% for NaBH₄ hydrolysis, the theoretical hydrogen capacity of LiBH₄ hydrolysis reaches 13.9% (based
on the weight of hydrides and the stoichiometric amount of water required). The hydrolysis of LiBH₄ is initially fast, but low hydrogen yield occurs because of the formation and deposition of a solid and impermeable mass on LiBH₄ surface. Kojima [13] used nano Pt loaded on LCoO₂ and the Pt-LCoO₂ had high catalytic activity on LiBH₄ hydrolysis. Nano materials could disperse LiBH₄ to avoid the agglomeration effect. Weng [2] found that diethyl ether could enhance the hydrolysis performance of LiBH₄. The formation of a new phase of LiBH₄[Et₂O] releases a theoretical amount of hydrogen from LiBH₄ hydrolysis. The solvent effect may be a method to avoid the agglomeration preventing LiBH₄ hydrolysis. Potential highly-efficient organic solutions are worth exploring.

In this work, some organics mixed with pure water were used as solutions, on which LiBH₄ hydrolysis was performed. The effects of organic species, organic/water volume ratio, and hydrolysis temperature on the hydrolysis of LiBH₄ were evaluated. This work aims to elaborate on the potential mechanism of LiBH₄ hydrolysis in organic solution and design the optimized organic/water solution.

2. EXPERIMENTAL

The materials, including LiBH₄, ethanol, tetrahydrofuran, butanol, and acetic acid, were bought from China Chemical Company, Ltd. and their purity reached AR, except for LiBH₄ (98%). The materials were used without any further processing. Hydrolysis experiments were conducted with a sealed 50 mL hydrogen reactor placed in a thermostatic bath at 323 K and attached to a condenser and a hydrogen generation collector in our previous works [14]. Hydrogen was collected at 298 K and 1 atm, after which it was measured based on water level change in the cylinder, that is, the water displaced. Then, 0.3 g LiBH₄ was pressed into a tablet in a 10 mm diameter stainless steel mold under 1 ton pressure before hydrolysis if no special treatment was conducted. The operation was conducted in an argon-filled glove box. Organic and water were mixed before hydrolysis. The volume ratio was set as 3:10, 5:10, 7:10, and 10:10. The reaction time began with the first bubble, and the final volume of the produced hydrogen was collected after 1 h. Hydrogen generation rate was calculated from the first bubble that evolved from the start of the test.

Figure 1. Hydrogen generation from LiBH₄ hydrolysis in MOH/water solutions at 323 K
Powder X-ray diffraction (XRD) patterns of the as-prepared samples were characterized using an X-ray diffractometer (Thermo ARL, Switzerland, model ARL X’TRA) over a range of diffraction angles (θ) from 2θ = 10° to 2θ = 80°, with Cu Kα radiation filtered by a monochromator. Scanning electron microscopy (SEM) observations were performed using the JSM-5610LV model (JEOL Company) equipped with INCA energy dispersive X-ray spectroscopy (EDS) measurements. The solid hydrolysis byproduct in the reactor was filtered using a vacuum pump and then dried in an oven at 313 K for 5 h.

**3. RESULTS AND DISCUSSION**

**3.1. Hydrolysis performance of LiBH₄ in MOH/water solutions**

Fig. 1 compares the hydrogen generation profiles of LiBH₄ in MOH/water solutions at 323 K. In the relative hydrolysis of neat LiBH₄, 200 mL/g hydrogen was generated, and the reaction was ended immediately. Meanwhile, hydrogen generation rates from hydrolysis of LiBH₄ in MOH/water solutions become significantly slower. Hydrogen generation rates can be controlled by MOH/water volume ratio and MOH species. The value of hydrogen generation rate increases with increasing MOH/water volume ratio. For example, the value of hydrogen generation rates in tetrahydrofuran/water solution with their ratios of 3:10, 5:10, 7:10, and 10:10 are 122, 144, 154, and 192 mL/g·min at 323 K, respectively. Similar results can be obtained in other MOH/water solutions. In addition, MOH species significantly affect the hydrolysis of LiBH₄. The best hydrolysis performance of LiBH₄ is achieved in an acetic acid/water solution. Approximately 3000 mL/g hydrogen can be collected within 5 min at 323 K. The hydrogen generation rate in acetic acid/water solution is significantly higher than those in other MOH/water solutions. Among the other three MOH solutions,
LiBH₄ has better performance in butanol/water solution than those in tetrahydrofuran/water and ethanol/water solution under the same conditions. Among the four organics, ethanol/water solution exhibited worse LiBH₄ hydrolysis than those in other MOH/water solutions at the same conditions.

3.2. Apparent activation energy of the hydrolysis of LiBH₄ and MOH/water solutions

To understand the effect of MOH species and obtain better hydrolysis performance of LiBH₄, LiBH₄ hydrolysis at different temperatures was investigated. Hydrolysis performance of LiBH₄ improved with temperature increasing from 313 K to 343 K. The amount of hydrogen generation within 120 min at 343 K respectively reached up to 3126, 3198, and 3504 mL/g in ethanol/water, tetrahydrofuran/water, and butanol/water solutions with MOH/water volume ratio of 7:10. The hydrolysis rates of LiBH₄ in the above three MOH/water solutions are evidently controllable even at 343 K. The apparent activation energy of LiBH₄ hydrolysis can be calculated according to Arrhenius equations (reactions 1 and 2). The temperature dependence of the rate constant, k, could be obtained as the maximum hydrogen generation rate in Fig. 2. The linear relationship between ln [H₂] and 1/T was shown in Fig. 3, and the slope was considered to be -E/R.

\[ k = k_0 \exp(-E/RgT) \]  
\[ \ln[k] = \ln k_0 - E/RgT \]  

The apparent activation energies of LiBH₄ hydrolysis were collected in butanol/water, tetrahydrofuran/water and ethanol/water solutions with MOH/water volume ratio of 7:10; the results were found to be 42.451, 48.695, and 54.881 kJ/mol, respectively. The hydrolysis process of LiBH₄ is controlled by a chemical step rather than by a mass transfer because of the value of the activation energy higher than 40 kJ/mol [15]. With the strengthened MOH effect on LiBH₄ hydrolysis, hydrolysis performance is improved significantly, which suggests that the MOH solution can alter the hydrolysis route.

3.3. Hydrolysis mechanism of the hydrolysis of LiBH₄ in MOH/water solutions

The hydrolysis performance improvement of LiBH₄ in MOH/water solutions can be attributed to the solvent effect. Laververne [16] confirmed that LiBO₂·2H₂O and H₂ are the hydrolysis products of LiBH₄ below 120 °C, and the real reaction process can be expressed in the following reaction:

\[ \text{LiBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{LiBO}_2\cdot2\text{H}_2\text{O} + 4\text{H}_2 \]  

The hydrolysis product LiBO₂·2H₂O has low solubility in water and deposit on LiBH₄ to hinder the contact of LiBH₄ and water. The agglomeration preserves the generated hydrogen and forms a pressure below products. The pressure builds up to a threshold and breaks the external impermeable mass. A sudden gas eruption is commonly detected in the hydrolysis of LiBH₄ in water. Thus, the clogging effect prevents LiBH₄ in the solid mass from reacting with the water outside. The addition of MOH effectively resolves clogging problems, as confirmed by the results in Fig. 1. The addition of MOH reduced the contact rate of LiBH₄ and water by diluting both water and LiBH₄. However, this condition may not be a unique effect. Weng [2] found that organic Et₂O could combine...
with LiBH₄ to form new LiBH₄(Et₂O)ₓ, which significantly restrains effective contact between LiBH₄ and water. Some additional effects are observed from acetic acid, ethanol, tetrahydrofuran, and butanol. Djamali [17] found that LiBO₂ had good solubility in an acetic acid solution at room temperature according to the following reaction:

LiBO₂ + H₂O + CH₃COOH → CH₃COOLi + H₃BO₃  (4)

LiBH₄ is soluble in alcohols and ethers [18–20], and water is also soluble in the above solutions. The MOH solutions can act as a carrier for water and LiBH₄ and reduces their contact, which may be considered as the solvent effect. In the hydrolysis process, MOH solution was uniformly distributed in water. Acetic acid, ethanol, tetrahydrofuran, and butanol belong to polar molecules and have hydroxyl bonds, such that water can combine with acetic acid, ethanol, tetrahydrofuran, and butanol through hydrogen bonds [21–23]. Therefore, MOH/water solution has lower capability to absorb LiBH₄ and LiBO₂ compared with pure water. Numerous combined

Figure 4. SEM images of the hydrolysis byproducts of LiBH₄ in MOH solutions: a, ethanol/water solution; b, tetrahydrofuran/water solution; c, butanol/water; and d, acetic acid/water solution.
MOH/water molecules are present in the solutions. When LiBH\textsubscript{4} was added to the solution, LiBH\textsubscript{4} came in contact with MOH/water molecules and reacted with water to produce hydrogen and lithium metaborate. The hydrolysis process can be elaborated as reaction 5, which is different from the hydrolysis of LiBH\textsubscript{4} and H\textsubscript{2}O.

\[
\text{LiBH}_4 + \text{MOH}(\text{H}_2\text{O})_k \rightarrow \text{LiBO}_2\cdot2\text{H}_2\text{O}+\text{MOH} + 4\text{H}_2
\]

Lithium metaborate is insoluble in MOH solution and breaks away from the LiBH\textsubscript{4} surface. Thus, the hydrolysis of LiBH\textsubscript{4} can be conducted until the LiBH\textsubscript{4} was completely consumed. Therefore, lithium metaborate separated from MOH/water solutions and formed loose and porous solids, as shown in Fig. 4. The different hydrolysis routes of LiBH\textsubscript{4} in pure water and MOH/water solutions are further described in Fig. 5. LiBH\textsubscript{4} hydrolysis produces H\textsubscript{2} and LiBO\textsubscript{2}·2H\textsubscript{2}O, which deposits on unreacted LiBH\textsubscript{4} surface and hinders the contact of LiBH\textsubscript{4} and water. Hydrogen atoms in LiBH\textsubscript{4} are known to be electron-deficient and easily combined with electron abundant oxygen atom of MOH(H\textsubscript{2}O)x in MOH/water solution. Evidence is available to confirm the formation of LiBH\textsubscript{4} hydrate [24]. A similar phenomenon is observed in the XRD results of hydrolysis byproducts of LiBH\textsubscript{4} in MOH/water solution, as shown in Fig. 6. Most peaks are identified as those of LiBO\textsubscript{2}·2H\textsubscript{2}O, except peaks at 14.4 and 16.5, which do not correspond to those of pure LiBH\textsubscript{4} but to those of LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x]. Considering the similar phenomena observed in hydrolysis products of LiBH\textsubscript{4} and different MOH/water solutions, the explanation is reasonable. Thus, we propose the following hydrolysis process of LiBH\textsubscript{4} and MOH/water solutions: Before reaction, MOH and water molecules combine to form organic hydrate via hydrogen bond. When LiBH\textsubscript{4} is added to MOH/water solutions, a new combination of LiBH\textsubscript{4} and MOH(H\textsubscript{2}O)x is formed because of the existence of electron-efficient hydrogen atoms in LiBH\textsubscript{4} and electron-abundant oxygen atoms in MOH(H\textsubscript{2}O)x. The intermediate of LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x] is formed and facilitates hydrolysis reaction. The stability of LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x] is linked to the bonding capability between LiBH\textsubscript{4} and MOH(H\textsubscript{2}O)x. Higher polarity indicates better stability of LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x]. LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x] reduces the kinetic activity of LiBH\textsubscript{4} hydrolysis. LiBH\textsubscript{4} was observed to have lower kinetic activity in ethanol/water solution than in tetrahydrofuran/water and butanol/water solutions because ethanol has higher polarity than tetrahydrofuran and butanol. In the hydrolysis process, MOH acts as not only a carrier for LiBH\textsubscript{4} and H\textsubscript{2}O but also as a reactant to form LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x].

**4. CONCLUSIONS**

Lithium borohydride presented high hydrogen production amount and rate in organic solutions at 323 K. The hydrolysis of LiBH\textsubscript{4} is experimentally proven to be moderate and sustainable in MOH/water solution compared with the sudden ending of such reaction in pure water. The improvement is attributed to the effects of MOH. The addition of MOH decreases the contact of LiBH\textsubscript{4} and water by diluting water and LiBH\textsubscript{4}, as well as resolves the clogging problem caused by LiBO\textsubscript{2}·2H\textsubscript{2}O via the solution effect. Moreover, the addition of MOH alters the hydrolysis route. The organic acts as a carrier for water and LiBH\textsubscript{4} and as a reactant to form intermediate LiBH\textsubscript{4}[MOH(H\textsubscript{2}O)x]. Our results show that LiBH\textsubscript{4} in MOH/water solutions has good hydrolysis performance and has potential application in proton exchange membrane fuel cells.

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