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Enhanced Hydrogen Generation by $LiBH_4$ Hydrolysis in MOH/water Solutions (MOH: C_2H_5OH, C_4H_8O, C_4H_9OH, CH_3COOH) for Micro Proton Exchange Membrane Fuel Cell Application

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Abstract: *$LiBH_4$ has high hydrogen storage capacity, and its high gravimetric hydrogen density reaches 18.36%. However, $LiBH_4$ 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 $LiBH_4$ was evaluated. Results show that agglomeration can be avoided and that $LiBH_4$ 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 $LiBH_4$ 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 $LiBH_4$. MOH acts as not only a carrier for water and $LiBH_4$ but also as a reactant to form intermediate $LiBH_4\cdot[MOH(H_2O)_x]_y$, which slows the hydrolysis kinetics of $LiBH_4$. Hydrolysis conditions were optimized, and high hydrogen amount was achieved correspondingly. The experimental data presents the potential application of $LiBH_4$ 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 H_2 storage or portable hydrogen production system with high H_2 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 $LiBH_4$ and $NaBH_4$ 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 $NaBH_4$ alkali solution and relative catalysts [10, 11]. At present, hydrogen generation from $NaBH_4$ is becoming widely applied to fuel cells and is gradually decreasing the cost of $NaBH_4$.

$LiBH_4$ 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 $LiBH_4$. The practical application of $LiBH_4$ in reversible hydrogen storage materials presents many challenges. Hydrolysis of $LiBH_4$ may be a feasible method for the dissociation of H atoms from $LiBH_4$ under moderate conditions [12]. Compared with 10.8 wt% for $NaBH_4$ hydrolysis, the theoretical hydrogen capacity of $LiBH_4$ hydrolysis reaches 13.9% (based

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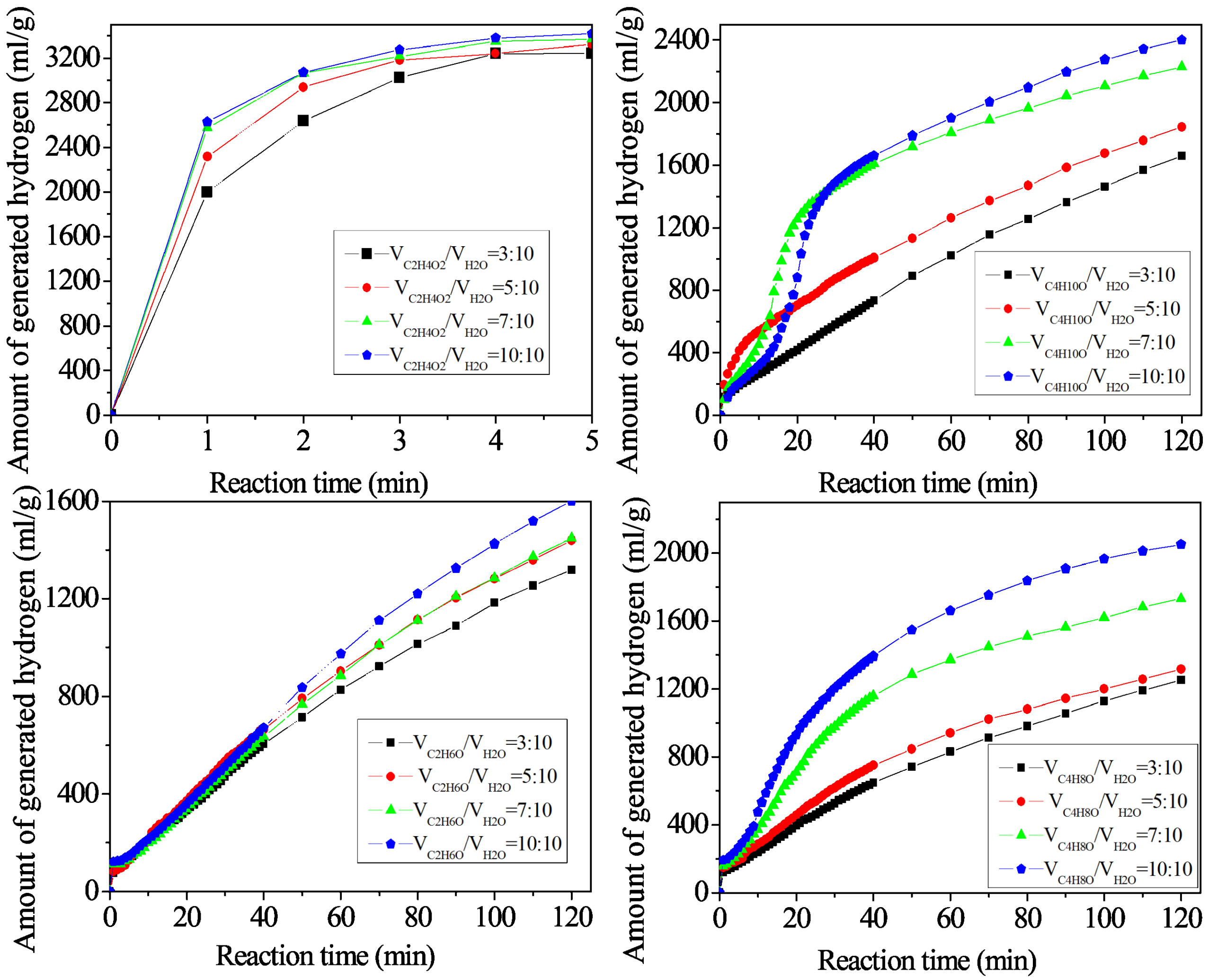

Figure 1. Hydrogen generation from $LiBH_4$ hydrolysis in MOH/water solutions at 323 K

on the weight of hydrides and the stoichiometric amount of water required). The hydrolysis of $LiBH_4$ is initially fast, but low hydrogen yield occurs because of the formation and deposition of a solid and impermeable mass on $LiBH_4$ surface. Kojima [13] used nano Pt loaded on $LCoO_2$ and the Pt- $LCoO_2$ had high catalytic activity on $LiBH_4$ hydrolysis. Nano materials could disperse $LiBH_4$ to avoid the agglomeration effect. Weng [2] found that diethyl ether could enhance the hydrolysis performance of $LiBH_4$. The formation of a new phase of $LiBH_4$ $[Et_2O]_x$ releases a theoretical amount of hydrogen from $LiBH_4$ hydrolysis. The solvent effect may be a method to avoid the agglomeration preventing $LiBH_4$ hydrolysis. Potential highly-efficient organic solutions are worth exploring.

In this work, some organics mixed with pure water were used as solutions, on which $LiBH_4$ hydrolysis was performed. The effects of organic species, organic/water volume ratio, and hydrolysis temperature on the hydrolysis of $LiBH_4$ were evaluated. This work aims to elaborate on the potential mechanism of $LiBH_4$ hydrolysis in organic solution and design the optimized organic/water solution.

2. EXPERIMENTAL

The materials, including $LiBH_4$, ethanol, tetrahydrofuran, butanol, and acetic acid, were bought from China Chemical Company, Ltd. and their purity reached AR, except for $LiBH_4$ (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 $LiBH_4$ was pressed into a tablet in a 10 mm diameter stainless steel molded 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.

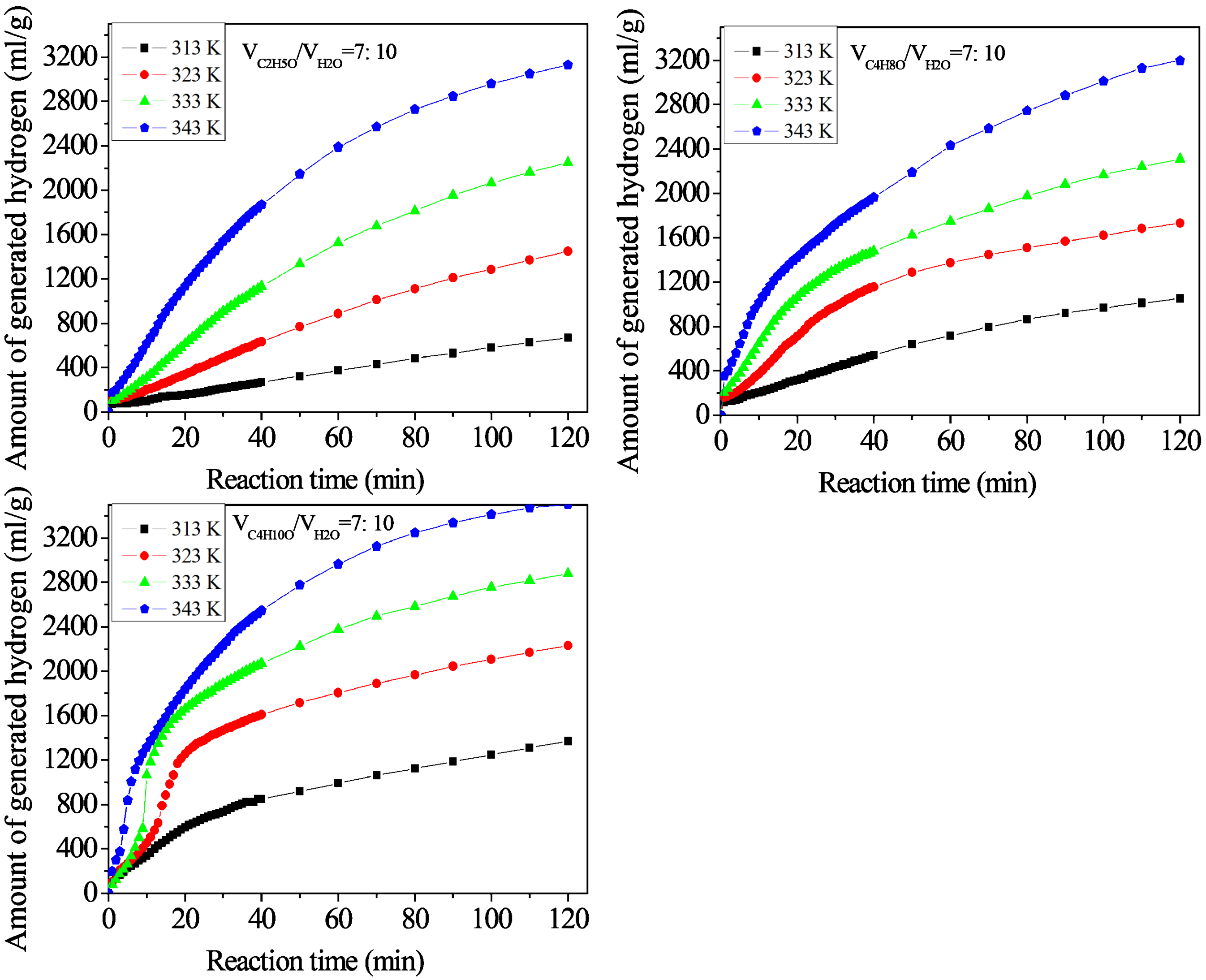

Figure 2. Hydrogen generation from $LiBH_4$ hydrolysis in MOH/water solutions at different temperatures

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 $LiBH_4$ in MOH/water solutions

Fig. 1 compares the hydrogen generation profiles of $LiBH_4$ in MOH/water solutions at 323 K. In the relative hydrolysis of neat $LiBH_4$, 200 mL/g hydrogen was generated, and the reaction was ended immediately. Meanwhile, hydrogen generation rates from hydrolysis of $LiBH_4$ 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 192mL/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 $LiBH_4$. The best hydrolysis performance of $LiBH_4$ 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,

$LiBH_4$ 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 $LiBH_4$ hydrolysis than those in other MOH/water solutions at the same conditions.

3.2. Apparent activation energy of the hydrolysis of $LiBH_4$ and MOH/water solutions

To understand the effect of MOH species and obtain better hydrolysis performance of $LiBH_4$, $LiBH_4$ hydrolysis at different temperatures was investigated. Hydrolysis performance of $LiBH_4$ 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 $LiBH_4$ in the above three MOH/water solutions are evidently controllable even at 343 K. The apparent activation energy of $LiBH_4$ 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 In $[H_2]$ and 1/T was shown in Fig. 3, and the slope was considered to be -E/R.

$$k=k0\exp(-E/RgT) \tag{1}$$

$$In[k]=Ink0-E/RgT \tag{2}$$

The apparent activation energies of $LiBH_4$ 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 $LiBH_4$ 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 $LiBH_4$ 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 $LiBH_4$ in MOH/water solutions

The hydrolysis performance improvement of $LiBH_4$ in MOH/water solutions can be attributed to the solvent effect. Laversenne [16] confirmed that $LiBO_2.2H_2O$ and H_2 are the hydrolysis products of $LiBH_4$ below 120 °C, and the real reaction process can be expressed in the following reaction:

$$LiBH_4 + 2H_2O \rightarrow LiBO_2.2H_2O + 4H_2 \tag{3}$$

The hydrolysis product $LiBO_2 \cdot 2H_2O$ has low solubility in water and deposits on $LiBH_4$ to hinder the contact of $LiBH_4$ 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 $LiBH_4$ in water. Thus, the clogging effect prevents $LiBH_4$ 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 $LiBH_4$ and water by diluting both water and $LiBH_4$. However, this condition may not be a unique effect. Weng [2] found that organic Et_2O could combine

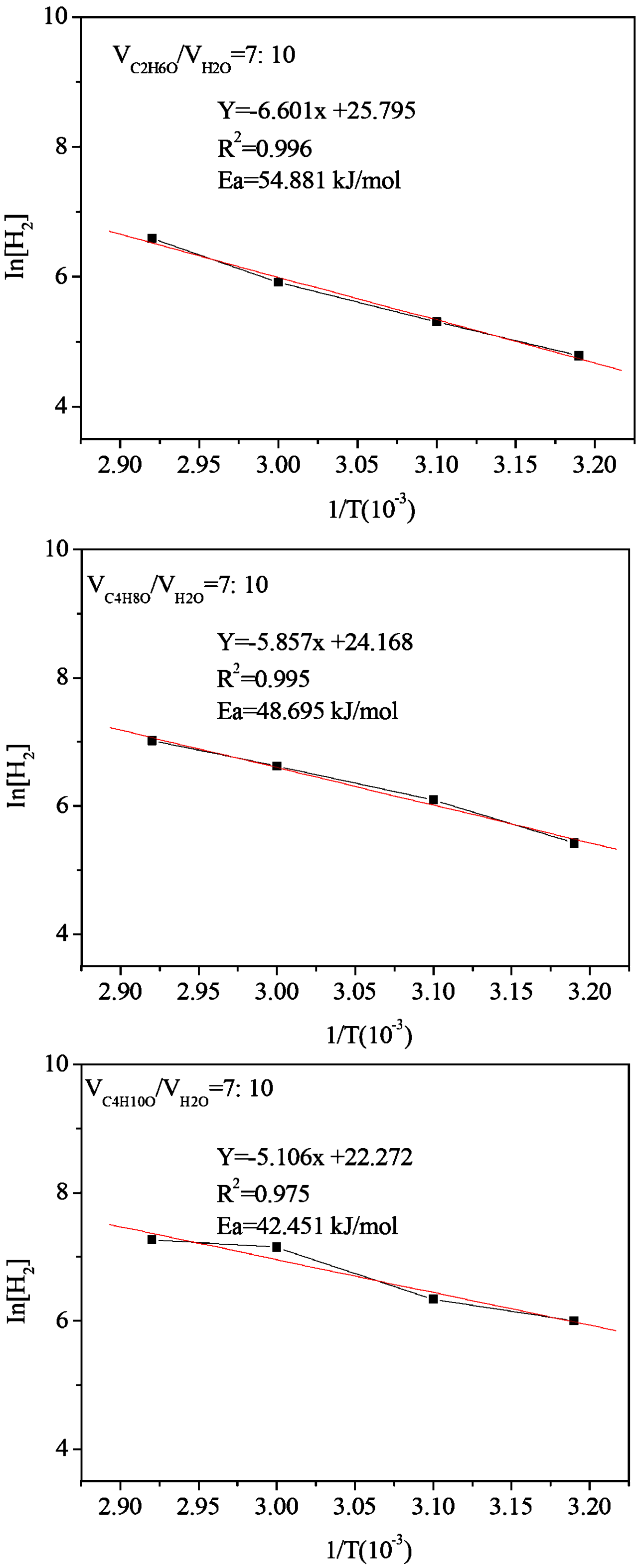

Figure 3. Relationship between ln $[H_2]$ and 1,000/T based on $LiBH_4$ hydrolysis in Fig. 2

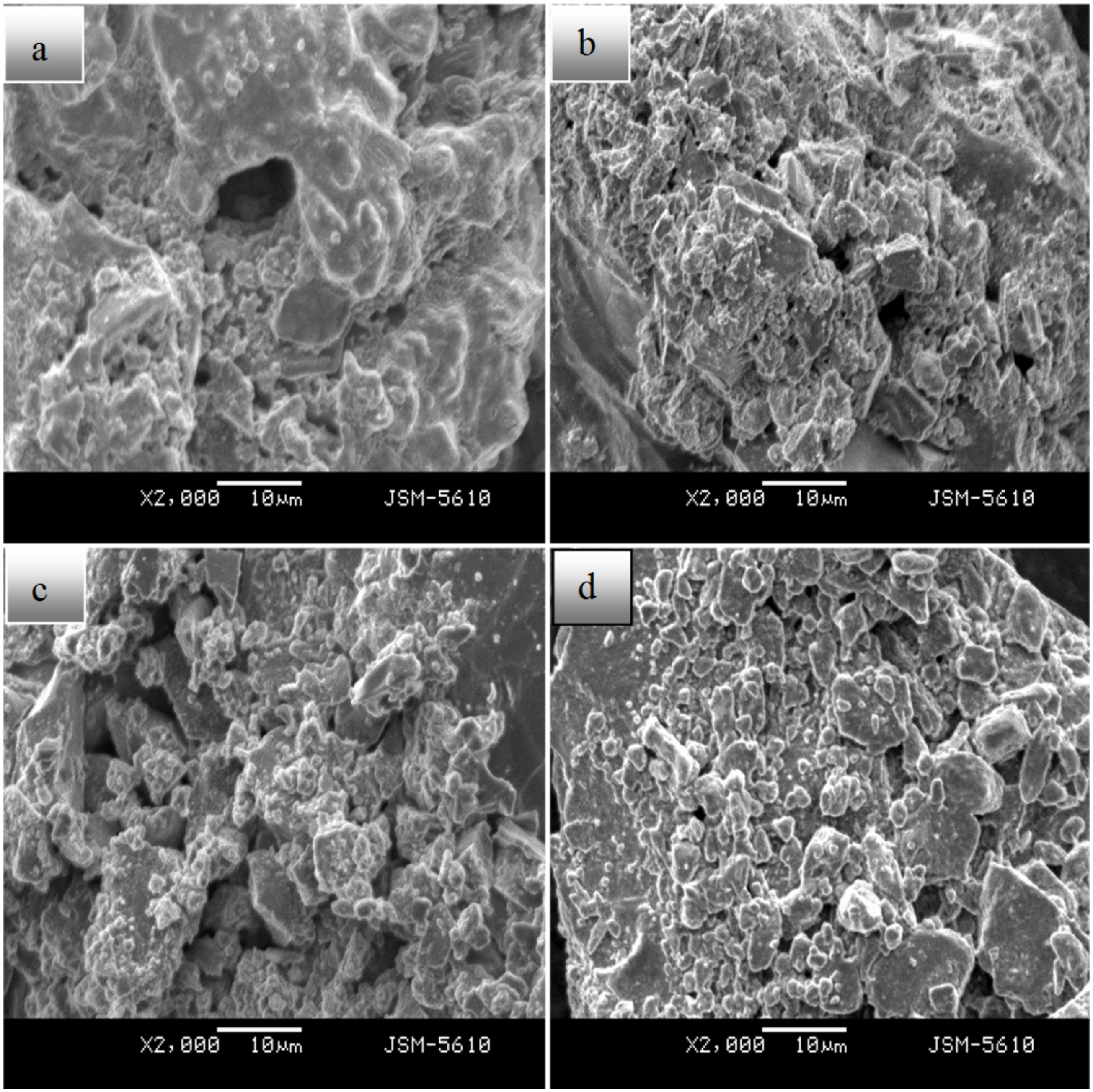

Figure 4. SEM images of the hydrolysis byproducts of $LiBH_4$ in MOH solutions: a, ethanol/water solution; b, tetrahydrofuran/water solution; c, butanol/water; and d, acetic acid/water solution.

with $LiBH_4$ to form new $LiBH_4(Et_2O)_x$, which significantly restrains effective contact between $LiBH_4$ and water. Some additional effects are observed from acetic acid, ethanol, tetrahydrofuran, and butanol. Djamali [17] found that $LiBO_2$ had good solubility in an acetic acid solution at room temperature according to the following reaction:

$$LiBO_2 + H_2O + CH_3COOH \rightarrow CH_3COOLi + H_3BO_3 \quad (4)$$

$LiBH_4$ 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 $LiBH_4$ 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, tetra hydrofuran, 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 $LiBH_4$ and $LiBO_2$ compared with pure water. Numerous combined

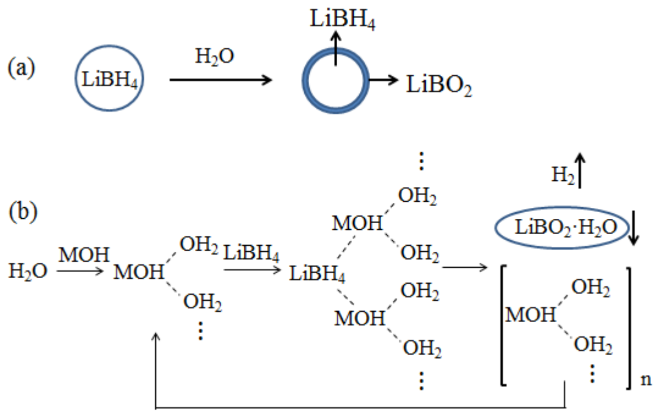

Figure 5. Schematic hydrolysis mechanism of LiBH4 in water and MOH/water solutions.

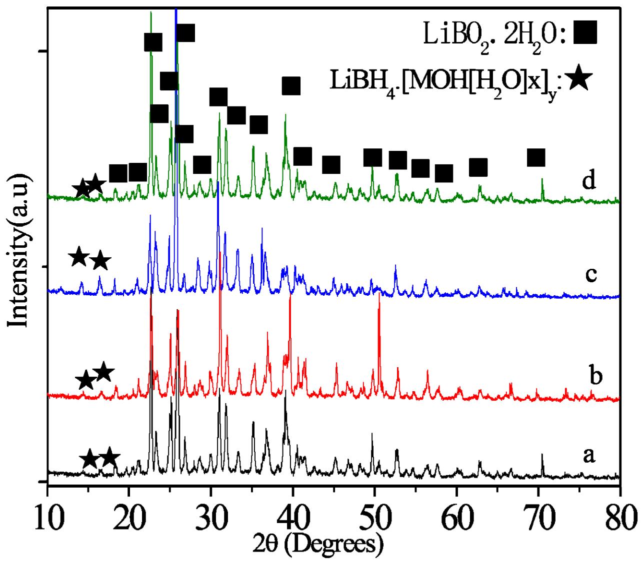

Figure 6. XRD patterns of the hydrolysis byproducts of LiBH4 hydrolysis in different MOH solutions: a, ethanol/water solution; b, tetrahydrofuran/water solution; c, butanol/water; and d, acetic acid/water solution.

MOH/water molecul es are present in the solutions. When $LiBH_4$ was added to the solution, $LiBH_4$ 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 $LiBH_4$ and H_2O.

$$LiBH_4 + MOH\ (H_2O)_x \rightarrow LiBO_2.2H_2O{+}MOH\ {+}4H_2 \qquad (5)$$
$$MOH:\ C_2H_5OH,\ CH_3COOH,\ C_4H_9OH,\ C_4H_8O,\ \text{etc.}$$

Lithium metaborate is insoluble in MOH solution and breaks away from the $LiBH_4$ surface. Thus, the hydrolysis of $LiBH_4$ can be conducted until the $LiBH_4$ 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 $LiBH_4$ in pure water and MOH/water solutions are further described in Fig. 5. $LiBH_4$ hydrolysis produces H_2 and $LiBO_2{\cdot}2H_2O$, which deposits on unreacted $LiBH_4$ surface and hinders the contact of $LiBH_4$ and water. Hydrogen atoms in $LiBH_4$ are known to be electron-deficient and easily combined with electron abundant oxygen atom of $MOH(H_2O)x$ in MOH/water solution. Evidence is available to confirm the formation of $LiBH_4$ hydrate [24]. A similar phenomenon is observed in the XRD results of hydrolysis byproducts of $LiBH_4$ in MOH/water solution, as shown in Fig. 6. Most peaks are identified as those of $LiBO_2.2H_2O$, except peaks at 14.4 and 16.5, which do not correspond to those of pure $LiBH_4$ but to those of $LiBH_4.[MOH(H_2O)_x]_y$. Considering the similar phenomena observed in hydrolysis products of $LiBH_4$ and different MOH/water solutions, the explanation is reasonable. Thus, we propose the following hydrolysis process of $LiBH_4$ and MOH/water solutions: Before reaction, MOH and water molecules combine to form organic hydrate via hydrogen bond. When $LiBH_4$ is added to MOH/water solutions, a new combination of $LiBH_4$ and $MOH(H_2O)_x$ is formed because of the existence of electron-efficient hydrogen atoms in $LiBH_4$ and electron-abundant oxygen atoms in $MOH(H_2O)_x$. The intermediate of $LiBH_4{\cdot}[MOH(H_2O)_x]_y$ is formed and facilitates hydrolysis reaction. The stability of $LiBH_4{\cdot}[MOH(H_2O)_x]_y$ is linked to the bonding capability between $LiBH_4$ and $MOH(H_2O)_x$. Higher polarity indicates better stability of $LiBH_4{\cdot}[MOH(H_2O)_x]_y$. $LiBH_4{\cdot}[MOH(H_2O)_x]_y$ reduces the kinetic activity of $LiBH_4$ hydrolysis. $LiBH_4$ 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 $LiBH_4$ and H_2O but also as a reactant to form $LiBH_4{\cdot}[MOH(H_2O)_x]_y$.

4. CONCLUSIONS

Lithium borohydride presented high hydrogen production amount and rate in organic solutions at 323 K. The hydrolysis of $LiBH_4$ 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 $LiBH_4$ and water by diluting water and $LiBH_4$, as well as resolves the clogging problem caused by $LiBO_2{\cdot}2H_2O$ via the solution effect. Moreover, the addition of MOH alters the hydrolysis route. The organic acts as a carrier for water and $LiBH_4$ and as a reactant to form intermediate $LiBH_4{\cdot}[MOH(H_2O)_x]_y$. Our results show that $LiBH_4$ in MOH/water solutions has good hydrolysis performance and has potential application in proton exchange membrane fuel cells.

5. ACKNOWLEDGMENTS

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