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Hydrogen generation from LiBH_4 solution catalyzed by multiwalled carbon nanotubes supported Co–B nanocatalysts for a portable micro proton exchange membrane fuel cell application

Baicheng Weng ^{a,*}, Fenghua Xu ^{a,1}, Zhu Wu ^b, Zhilin Li ^b

^a Yancheng Institute of Technology, No. 9, Xiangwang Avenue, Yancheng, China

^b Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, 865, Changning Road, Shanghai, China

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ABSTRACT

LiBH_4 has high hydrogen storage capacities, and could potentially serve as a superior hydrogen storage material. In the hydrolytic process, however, incomplete hydrolysis caused by the agglomeration of its hydrolytic product and un-reacted LiBH_4 limits its full utilization. Furthermore, application of hydrogen generated from LiBH_4 aqueous solution for proton exchange membrane fuel cell (PEMFC) has not been reported yet. In this paper, CNTs-supported Co–B nanocatalyst was used for hydrogen generation from LiBH_4 solution. 22 wt% LiBH_4 alkaline solution can fully release its stoichiometric amount of hydrogen and supply a 2.3 W portable PEMFC stack to run stably. The overall power density of the PEMFC/ LiBH_4 solution system with Co–B/CNTs addition is 1020 Wh L^{-1} . Due to the high gravimetric and volumetric hydrogen capacities, the LiBH_4 solution could be used as a promising liquid hydrogen storage material for hydrogen fuel cells-based devices.

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Introduction

Micro proton exchange membrane fuel cell (PEMFC) has attracted much attention as a promising electrochemical power source in portable and miniature electronic devices [1,2]. To fuel the PEMFC, a hydrogen source is required. In order to meet the requirement of high power density, chemical hydride with at least 10.0 wt% hydrogen storage capacity appears to be an attractive hydrogen source.

Lithium borohydride (LiBH_4) has high gravimetric (18.5 wt%) and volumetric (121.0 kg m^{-3}) capacities of hydrogen, so it can potentially serve as a good hydrogen storage material [3–5]. However, thermodynamic and kinetic limitations caused by strong covalent and ionic bonds greatly restrain the practical application of LiBH_4 as a reversible hydrogen storage material. Hydrolysis of LiBH_4 is of interest for hydrogen generation, because its hydrogen generation capacity is 8.6 wt% [6], which is higher than 5.8 wt% for NH_3BH_3 [7] and 7.2 wt% for NaBH_4 [16] (taking anhydrides into account).

* Corresponding author. Tel.: +86 956 802 7828; fax: +86 956 665 3527.

E-mail address: baichengweng@gmail.com (B. Weng).

¹ These authors contribute equally to this work.

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Previous results have demonstrated that hydrolysis of LiBH_4 never generates more than 50.0 wt% of its theoretical amount of hydrogen. Kojima et al. [6] found that the gravimetric and volumetric hydrogen densities increased with increasing $\text{H}_2\text{O}/\text{LiBH}_4$ ratio, and reached the maximum values of 7.4 wt% and 60.0 kg m^{-3} at $\text{H}_2\text{O}/\text{LiBH}_4$ ratio of 3:1 (mol/mol), respectively. And the maximum hydrogen yield was only 50.0 wt%. Zhu et al. [8] also found the similar results and they believed the insufficiency was attributed to LiBH_4 and its products forming a single solid and impermeable mass clogged the reaction vessel, thus limiting the full utilization of LiBH_4 . In addition, their results revealed that LiBH_4 hydrolysis could release 30.0% of stoichiometric amount of hydrogen within 3 h (corresponding to $6.8 \text{ mL min}^{-1} \text{ g}^{-1}$) at slow water injection rate of $10 \mu\text{L h}^{-1}$. And the hydrogen generation kinetics was faster than that of NaBH_4 . Through investigation on reaction of LiBH_4 with water steam, Matthews et al. [9] demonstrated that hydrolysis of LiBH_4 never produced more than 60.0% of its theoretical yield, because the products and un-reacted LiBH_4 formed a single solid mass inside the reactor that was difficult to be removed at the end of the experiment.

These studies have demonstrated that the insufficiency of hydrogen generation is caused by the agglomeration of hydrolytic products with un-reacted LiBH_4 . Therefore, high hydrogen yield would be achieved if the agglomeration could be avoided. However, researches on this issue are still insufficient.

Metal borohydrides including NaBH_4 and LiBH_4 react violently with neutral water ($\text{pH} = 6\text{--}8$) resulting rapid hydrogen release which makes them inapplicable for micro PEMFC usage. But at higher pH solution ($\text{pH} = 11\text{--}14$) [10], BH_4^- ions essentially are inert and could be stored for a longer period of time, which decreases the safety requirements for long-distance transportation. Researches on PEMFC supplied by the hydrogen from hydrolysis of LiBH_4 solution, however, are still insufficient as well.

Recently, cobalt boride (Co–B) catalyst with good catalytic activity and low cost as an attractive candidate for sodium borohydride hydrolysis has been intensively investigated [11–31]. However, agglomeration of Co–B catalysts and sticking of fine powders during exothermic reaction restrict the hydrogen generation kinetics due to the reduction of surface area. In order to overcome agglomeration, the effective method is supporting particles into/onto porous matrix [16,17] or incorporating Co–B with other transition elements such as chromium, phosphorus or nickel [18–22]. The widely used supporting materials are metal oxides, nickel foam, activated carbon and clay minerals [16–31]. Porous structure and surface area of the catalyst affect its catalytic efficiency. Supporting materials with high surface area favor the distribution on surface, resulting in better catalytic activity. Interestingly, in some researches mesoporous materials could enhance mass transport on the surface and contribute catalytic activity [19,23,26,29]. Carbon nanotubes (CNTs) is one of the important porous materials that been widely used as the supporting materials of catalysts, due to its porous nature and its high thermal and electrical conductivity. So far, the using of CNTs supported Co–B nanocatalyst for LiBH_4 hydrolysis is rarely reported.

In this paper, we present a novel strategy for completely hydrolyzing LiBH_4 to provide hydrogen for PEMFC by CNTs supported Co–B nanocatalyst (Co–B/CNTs). Our recent findings that CNTs can create gas channels among the hydrolytic products avoiding gas eruption caused by agglomeration. The performance of a micro PEMFC supplied by the hydrogen generated from LiBH_4 solution was evaluated in this work.

Experimental

Materials and methods

Lithium borohydride (LiBH_4 , 50–100 μm), cobalt chloride (CoCl_2 , ~50 μm), sodium borohydride (NaBH_4 , ~30 μm), sodium hydroxide (NaOH), ammonia water (NH_4OH) and boric acid (HBO_3) were purchased from Sigma–Aldrich. All sample handlings were performed in an MBraun Labmaster 130 glovebox maintained under argon atmosphere with <1 ppm O_2 and H_2O vapor. Mutliwalled carbon nanotubes (CNTs, >95 wt %) were purchased from Cheap Tubes Inc.

4 wt% CNTs were dispersed in water by sonication. Then CoCl_2 and HBO_3 were added, followed by adjusting pH with ammonia water to 9. The concentration of Co and B was 70 mM and 35 mM, respectively. Excess NaBH_4 solution was added, followed by stirring vigorously for 1 min in the ice bath. The resulted catalysts were separated by centrifugation, washed with distilled water (DI water) and dried at 70°C in a vacuum overnight.

For testing the cyclic performance, the catalyst was regenerated by washing with 0.1 M NaOH and DI water and then, centrifugation. The regenerated catalyst was dried at 70°C in a vacuum overnight.

Characterizations

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2400 diffractometer using $\text{Cu}/\text{K}\alpha$ radiation. Samples were mounted onto a 1 mm depth glass board and sealed with a polyvinylchloride membrane to avoid oxidation during the XRD measurements. Morphology of hydrolytic products was characterized using a field emission scanning electron microscopy (FESEM, Sigma VP, Zeiss, Germany) with an acceleration voltage of 5 kV. Raman measurements were performed using a Bruker Senterra Raman spectrometer with a 785 nm excitation laser. Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker IFS 55 Equinox FTIR spectrophotometer using KBr pellets. Inductively coupled plasma – optical emission spectrometry (ICP-OES) assay was carried out using an ICP-OES instrument (Optima 7300DV, PerkinElmer, USA).

Apparatus and procedures

A schematic diagram of the experimental setup used to measure hydrogen generation is shown in our previous paper [10]. Briefly, the apparatus consisting of a 100 mL glass reaction vessel, a syringe pump, and a water trap was designed for the reaction of LiBH_4 with liquid water. The syringe pump was used to deliver water into the vessel to react with the hydrides.

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