Short communication

Hydrogen generation utilizing alkaline sodium borohydride solution and supported cobalt catalyst

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Abstract

Supported Co catalysts with different supports were prepared for hydrogen generation (HG) from catalytic hydrolysis of alkaline sodium borohydride solution. As a result, we found that a γ-Al$_2$O$_3$ supported Co catalyst was very effective because of its special structure. A maximum HG rate of 220 mL min^{-1} g^{-1} catalyst and approximately 100% efficiency at 303 K were achieved using a Co/γ-Al$_2$O$_3$ catalyst containing 9 wt.% Co. The catalyst has quick response and good durability to the hydrolysis of alkaline NaBH$_4$ solution. It is feasible to use this catalyst in hydrogen generators with stabilized NaBH$_4$ solutions to provide on-site hydrogen with desired rate for mobile applications, such as proton exchange membrane fuel cell (PEMFC) systems.
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1. Introduction

It is well known that during the process of commercialization of proton exchange membrane fuel cell (PEMFC), besides the remaining challenges for itself [1], the lack of efficient, safe, onboard supply technologies of pure hydrogen also makes the steps slower than expected.

Hydrogen, the preferred fuel source for PEMFCs, may be produced from the reformation of nature gas and petroleum using technologies such as steam-methane reforming (SMR), steam/oxygen reforming (SMR/O$_2$R), and auto-thermal reforming (ATR) [2]. However, the performance of PEMFC is deteriorated in the presence of even a small amount of carbon monoxide (CO) [3], which is the by-product of those processes. On the other hand, those processes are ideal for large-scale, centralized production but not easily scaled down for distributed production. Nevertheless, for portable devices, efficient with quick response on-site hydrogen supply technology is required.

Recently, much attention has been given to hydrogen generation (HG) from hydrolysis of chemical hydrides [4–6] because

the hydrogen generated is pure and controllable. Among the hydrides, NaBH$_4$ is much more attractive due to its various advantages: relatively high hydrogen content (10.7 wt.%); stable and nonflammable alkaline solution; controllable hydrolysis reaction; environmentally friendly and renewable. When contacting with a given catalyst, its alkaline solutions (the alkali usually acts as a stabilizer to restrain the self-hydrolysis of NaBH$_4$ in aqueous solution [7]) can release hydrogen rapidly in the following way:

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_4 + 4H_2 + 217\,kJ \quad (1)$$
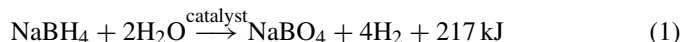
In the early of 1950s, Schlesinger et al. [8] extensively and qualitatively studied the accelerating effects of acids and transition metal salts on the rate of NaBH$_4$ hydrolysis. Ever-since then, various catalysts such as Ru-based catalyst [9,10], Pt-based catalyst [11,13,14], Ni-based catalyst [12,15], Co-based catalyst [15–17], PtRu alloy catalyst [18], etc. have been developed for HG based on Eq. (1). Although supported catalysts of noble metals have perfect performance, their exiguity and relatively high price compel us to look for low-cost catalyst. Ni–B, Co–B catalysts have high performance, yet their powder structures make it difficult for them to application in successive hydrogen generators directly due to great propensity for drifting with the fluid,

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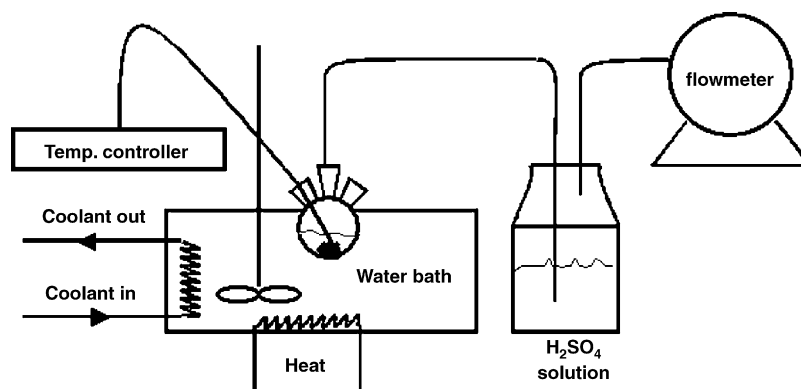 *E-mail address:* zhanghm@dicp.ac.cn (H. Zhang).

Fig. 1. Intermittent HG test apparatus.

even clogging the reactor. To solve this problem, supported Co or Ni catalyst is a viable choice. However, few studies have been reported on the application of supported cobalt or nickel catalysts for the hydrolysis of $NaBH_4$ from its alkaline solutions.

In this work, several kinds of supported Co catalysts were studied. As a result, we have developed a γ-Al_2O_3 supported Co catalyst with a good performance and investigated its characteristics for HG from alkaline sodium borohydride solution in an intermittent and a successive way, respectively.

2. Experimental

2.1. Catalyst preparation

Cobalt(II) nitrate (Tianjin Kermel Chemical Reagent, Tianjin) was adopted as precursor. Active carbon and different structured Al_2O_3 were used as supports. All supports were ground and separated with 16–50 mesh sieve before use. All the catalysts were prepared by impregnation-reduction method. As a representative, to make a Co/active carbon catalyst, the active carbon support was first impregnated in the precursor solution for 12 h, and then held at 403 K in vacuum for 10 h. After that, it was calcined in N_2 atmosphere for 2 h at 673 K. Finally, the as-prepared precursor was held at 623 K for 4 h in reductive atmosphere. Thus a supported Co catalyst was obtained. The Co loadings in catalysts used in this paper were all 9 wt.%.

2.2. Catalyst testing

In typical intermittent HG experiments, the hydrolysis reactions were carried out in a thermostated (303–323 ± 0.2 K) round-bottomed flask (Fig. 1). The reagent solutions ($\sim$30 ml of 1–25% $NaBH_4$ and 1–15% NaOH) were placed in the flask prior to the HG reaction. About 50 mg catalyst (support + Co) was dropped into the solution to begin H_2 generation. The evolved hydrogen was imported into a bottle to wash out the residual alkali, as well as cool down to the ambient temperature. Subsequently the hydrogen was introduced into the flowmeter. The cumulative volumes of the hydrogen were measured as a function of time.

For a successive HG experiment, a special designed tubular reactor was adopted. A certain amount of catalyst was placed in the reactor prior to the HG reaction. The system was sealed, and then 5% $NaBH_4$–5% NaOH solution was pumped from a storage tank into the reactor with a certain flow rate (1–5 mL min^{-1}). $NaBH_4$ hydrolyzed on catalyst bed successively. The generated hydrogen, the by-product and the residual reactant solution were imported into a gas–liquid separator. The rest processes were similar to the intermittent reactions. The pump was stopped after running for 40 min at each flow rate. The system was not preheated, and no attempt was made to control the temperature of the experimental system during testing, as we were looking for relative differences in reaction rates with different flow rates of $NaBH_4$ solutions.

For the convenience of preparing the reactant solutions, all the solution concentrations used in our study were expressed as the ratio of weight of $NaBH_4$ or NaOH to solution volume. The values of hydrogen volumes were those of standard temperature and pressure (STP).

Nitrogen adsorptions of the catalysts were measured at 77 K with an ASAP 2010 surface area analyzer (Micromeritics Instrument). Prior to the measurements, the samples were dried in vacuum at 383 K for 12 h. The specific surfaces of the supports and catalysts were determined from the N_2 adsorption–desorption isotherms by the BET method and pore size distributions (PSDs) of the catalysts were obtained by means of density functional theory (DFT) method. X-ray diffraction (XRD) measurements were taken on a Philips X'pert pro diffractometer (Philips, Holland), operated at 40 kV, 40 mA, using Cu Kα radiation.

3. Results and discussion

3.1. Support screening

For a supported catalyst, mechanical strength is first of all characteristics that it should have. During our researches on Eq. (1) with different kinds of supported cobalt catalysts, similarly to the result of Ref. [19], several kinds of Al_2O_3 supported catalysts were broken up. Co/active carbon and Co/γ-Al_2O_3 were specially studied because they were steady in NaOH solutions and not break up during the hydrolysis reactions. Fig. 2 shows the generated hydrogen volumes as a function of time using 50 mg of catalysts with different supports. It can be seen that those
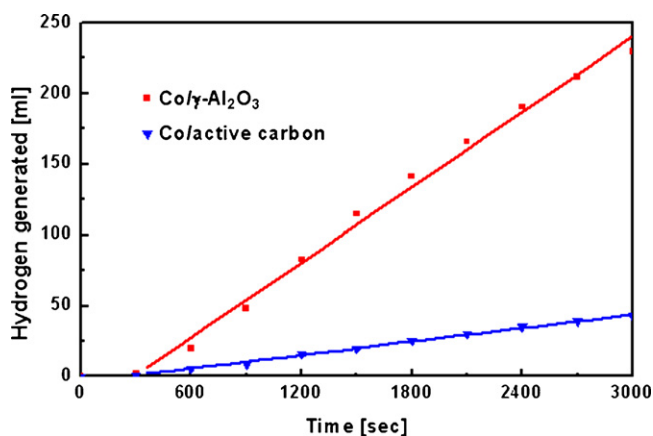
Fig. 2. Volume of hydrogen generated as a function of time from 15 ml 1% NaBH$_4$–5% NaOH solution at 303 K using 50 mg of catalysts with different supports.

Table 1
BET specific surfaces and pore structure parameters of the supports and the catalysts

Sample	S_{BET} (m^2/g)	Average pore diameter (nm)
γ-Al$_2$O$_3$	208	6.0
Active carbon	1017	2.1
Co/γ-Al$_2$O$_3$	184	6.2
Co/Active carbon	827	2.1

two catalysts exhibited significantly different catalytic activity. The HG rate on the γ-Al$_2$O$_3$ supported catalyst is much higher than that on the active carbon supported catalyst. Further more, the Co/γ-Al$_2$O$_3$ catalyst has comparable HG performance with some reported precious metal catalysts [9–11], being a promising alternative non-precious catalyst for HG from the NaBH$_4$ alkaline solution.

The data in Table 1 and Fig. 3 indicate the difference in textural characteristics of the supports and the catalysts. It is shown that the γ-Al$_2$O$_3$ or Co/γ-Al$_2$O$_3$ have smaller BET specific surfaces but larger pore diameters than those of active carbon or Co/active carbon. PSDs of the supports and catalysts were obtained from the analysis of the nitrogen isotherm using DFT method, according to IUPAC convention, almost a half of
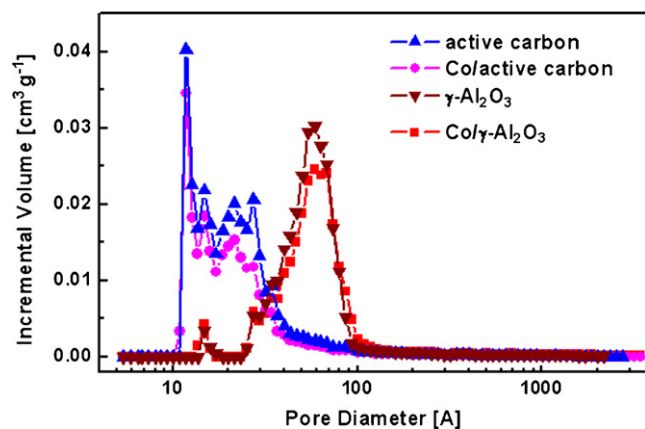

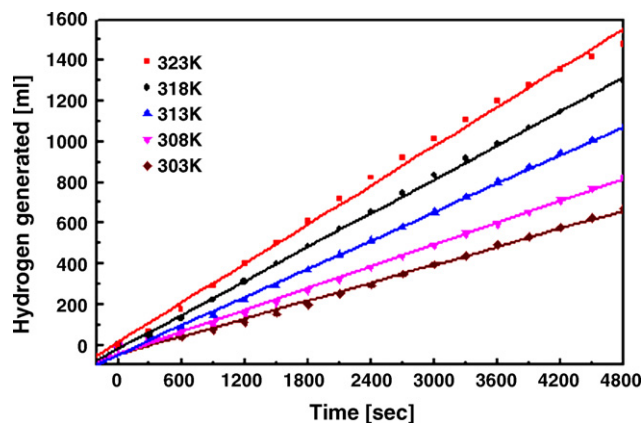Fig. 3. DFT pore size distribution of supports and catalysts.

Fig. 4. Effects of solution temperature on the HG rate using 50 mg Co/γ-Al$_2$O$_3$ catalyst in 15 ml 5% NaBH$_4$–5% NaOH solution.

the pores of active carbon or Co/active carbon are micropores (<20 Å), while those of Co/γ-Al$_2$O$_3$ are mesopores (between 20 and 500 Å). Co/γ-Al$_2$O$_3$ catalyst shows superior catalytic performance to Co/active carbon catalyst, maybe because of its larger pore diameter so that NaBH$_4$ can reach the active sites easily and the products can leave the active sites smoothly. No evident Co metal peaks were seen from their XRD patterns possibly due to their high dispersion and/or their overlap with those of supports. Characteristics of the Co/γ-Al$_2$O$_3$ made under various conditions will be studied in detail in a preparing article.

Based on the above results, Co/γ-Al$_2$O$_3$ catalyst was selected and its characteristics for HG from alkaline NaBH$_4$ solution were researched more detailed as follows.

3.2. Intermittent HG test

Fig. 4 shows effects of reaction temperature on the HG rate using 50 mg Co/γ-Al$_2$O$_3$ catalyst in 15 ml 5% NaBH$_4$–5% NaOH solution. As expected, the HG rates rose with the increase of temperature. It is shown in Fig. 4 that the hydrogen volumes nearly increase linearly with reaction time, which suggests that the reaction rates were unchanged as the hydrolysis reaction carrying on and can be considered as zero order reaction. According to the function between ln r_{NaBH_4} and $1/T$ plotted in Fig. 5, ln r_{NaBH_4} changes linearly with $1/T$, the reaction rate equation can be written as follows:

$$r_{NaBH_4} = k_{NaBH_4} = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where ln r_{NaBH_4} is the reaction rate (mol min^{-1} g^{-1}) of NaBH$_4$, k_0 the pre-exponential parameter (mol min^{-1} g^{-1}), E_a the activation energy for the reaction, R the gas constant and T is the reaction temperature. From the slope of ln r_{NaBH_4} versus $1/T$, activation energies of Co/γ-Al$_2$O$_3$ and Co/active carbon for the HG reaction are calculated to be 32.63, and 45.64 kJ mol^{-1}, respectively, which are much smaller than the value of 64.87 kJ mol^{-1} obtained by Jeong et al. [16] in higher NaBH$_4$ and same NaOH concentration with Co–B catalyst, and the values of metal catalyzed NaBH$_4$ hydrolysis (Co,
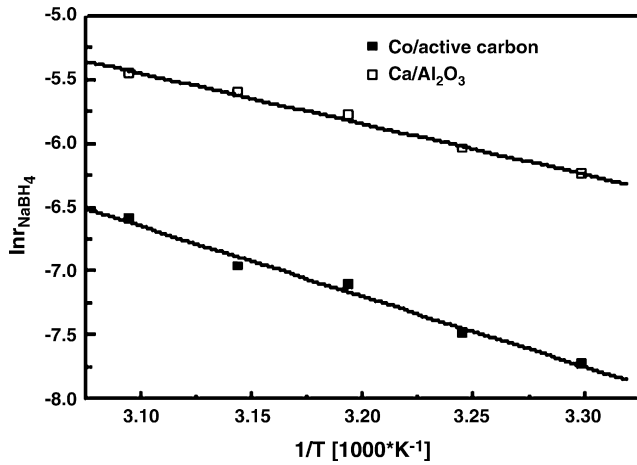
Fig. 5. ln r_{NaBH_4} vs. 1/T following Eq. (1) with Co/γ-Al$_2$O$_3$ and Co/active carbon catalysts.

75 kJ mol^{-1}; Ni, 71 kJ mol^{-1}; Raney Ni, 63 kJ mol^{-1}) reported by Kaufman and Sen [20].

The effect of NaBH$_4$ concentration on the HG rate in x% NaBH$_4$ + 5% NaOH solutions (x = 5, 10, 15, 20, 25) at 303 K using 50 mg of Co/γ-Al$_2$O$_3$ catalyst was studied and shown in Fig. 6. With increasing NaBH$_4$ concentration in solutions from 5% to 25%, the HG rates decrease from 209 to 90 mL min^{-1} g^{-1} catalyst. These results are consistent with those of the previous researches [16] on this aspect of the hydrolysis reaction. It was observed that the higher beginning concentration of NaBH$_4$ ended with more viscous solution. So it is reasonable to attribute these results to the increase of the solution viscosity. In the viewpoint of practical application, to keep the byproduct (NaBO$_2$) a solution state and get relatively high hydrogen storage efficiency, a concentration of 15% NaBH$_4$ is suggested.

The effect of NaOH concentrations on the HG rate was further studied from 5% NaBH$_4$ + x% NaOH solutions (x = 1, 5, 10, 15) at 303 K using 50 mg of Co/γ-Al$_2$O$_3$ catalyst by measuring the cumulative volumes of hydrogen periodically. The results are shown in Fig. 7. With increasing NaOH concentration from 1% to 10%, the HG rates increase from 85 to a maximum value of 220 mL min^{-1} g^{-1} catalyst. While at higher concentration of

NaOH (x = 15), the HG rate decreases to 150 mL min^{-1} g^{-1} catalyst. There is a little difference from the results of Hua et al. [12] and Jeong et al. [16], who reported that using a NaBH$_4$ solution containing a higher concentration of NaOH produced hydrogen at a higher rate with Ni or Co–B catalysts. Those results demonstrate that the effect of NaOH concentration on the NaBH$_4$ hydrolysis is greatly dependent on catalysts and is different for Co/γ-Al$_2$O$_3$ catalyst from Co–B or Ni catalysts and Ru catalyst. Further researches are necessary to elucidate the reaction mechanism of this hydrolysis reaction.

3.3. Successive HG test

To estimate whether the Co/γ-Al$_2$O$_3$ catalyst is suitable for application in a hydrogen generator, its successive HG performance was also investigated. Fig. 8 shows the successive HG performances of Co/γ-Al$_2$O$_3$ for a 5% NaBH$_4$–5% NaOH solution and constant catalyst loading. When the pump started for the first time at 1 mL min^{-1}, the HG rate increased slowly in the first few minutes due to the activation of the catalyst and then reached a maximum steady value, which is 91.2% of the theoretically expected HG rate value based on Eq. (1) at this operating condition. When the feeding pump stopped at the end of 40 min,
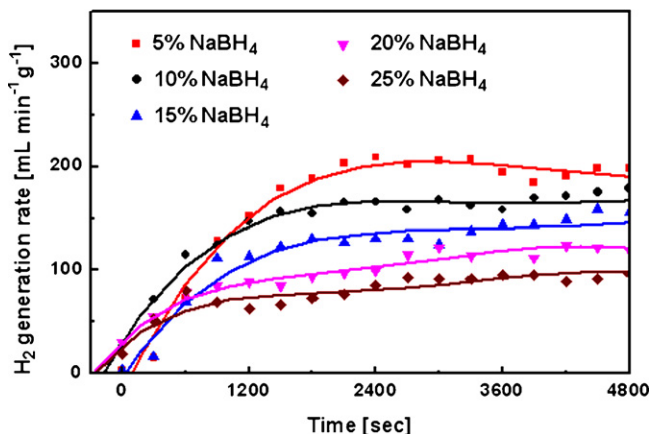

Fig. 7. Effects of NaOH concentration on the HG rate in 5 wt.% NaBH$_4$ + x wt.% NaOH solutions at 303 K using 50 mg catalyst.

Fig. 6. Effects of NaBH$_4$ concentration on the HG rate in x wt.% NaBH$_4$ + 5 wt.% NaOH solutions at 303 K using 50 mg catalyst.
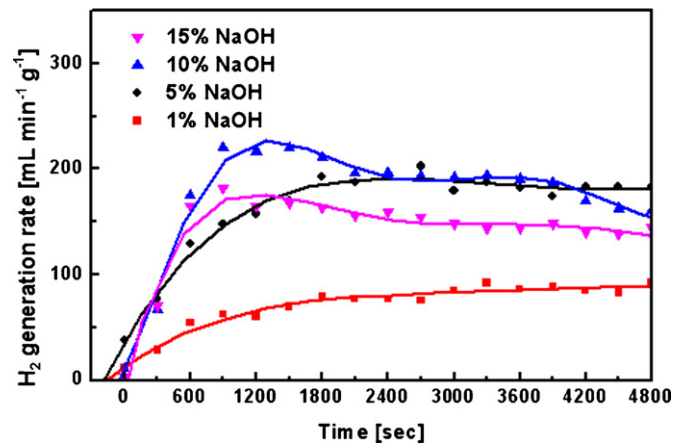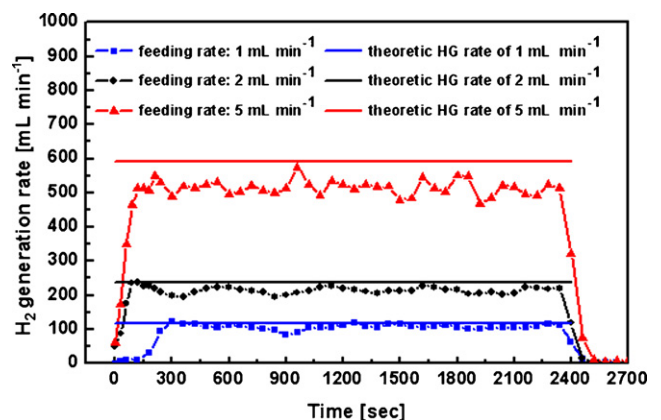

Fig. 8. Successive HG rate as a function of time using 5 g of Co/γ-Al$_2$O$_3$ catalyst. The reactant is 5% NaBH$_4$–5%NaOH solution. Changing the feeding flow rate.
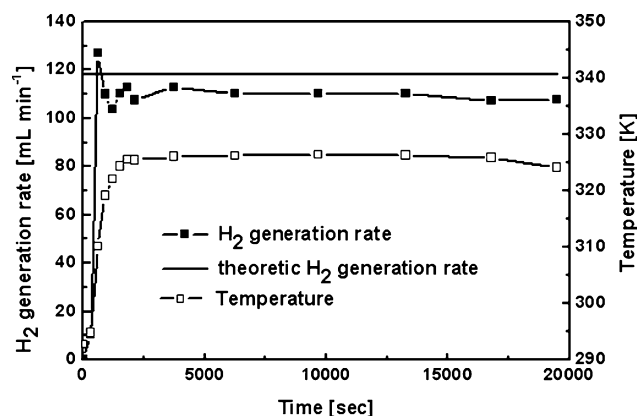
Fig. 9. Durability testing of the catalyst applied 5% NaBH$_4$–5% NaOH solution with feeding flow rate of 1 mL min^{-1} using the catalyst used in experiments of Fig. 8.

the HG ceases in 150 s. While the feeding flow rate was changed to 2 and 5 mL min^{-1}, the HG rate reached its steady value soon after the pump was switched on. This occurs because the catalyst has already been activated during the reaction of 1 mL min^{-1}. However, the efficiency of the catalysts decrease to 90.4% and 87.3% respectively, the reason is a lack of sufficient NaBH$_4$ diffuse to the active sites of the catalyst owing to a reduced residence time.

It is known that durability is one of the major criteria for a catalyst. After the experiments of Fig. 8 were finished, the catalyst was washed with deionized water and dried in vacuum for the durability test. Fig. 9 shows the temperature of catalyst bed and the HG rate as a function of time. There is no decrease in catalytic activity and the temperature of catalyst bed keeps constant during 5.5 h at 1 mL min^{-1} of solution flow rate. It shows that the catalyst has good durability to the hydrolysis of stabilized NaBH$_4$ solution.

4. Conclusions

An effective non-noble metal catalyst, Co/γ-Al$_2$O$_3$, has been developed for hydrolysis of sodium borohydride from its alkaline solution, which was prepared by dispersing Co on γ-Al$_2$O$_3$ support using impregnation-reduction method. With a Co/γ-Al$_2$O$_3$ catalyst containing 9 wt.% Co, a maximum HG rate of 220 mL min^{-1} g^{-1} catalyst was achieved. The catalyst has quick response and good durability. It is feasible to apply in a hydrogen generator with NaBH$_4$ alkaline solutions to provide hydrogen on-site with desired rate for mobile applications, such as proton exchange membrane fuel cell systems. Further researches on coupling the hydrogen generator with PEMFC system are in process.

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