

# A structured Co–B catalyst for hydrogen extraction from NaBH<sub>4</sub> solution

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## Abstract

A structured Co–B catalyst has been developed to produce hydrogen from an alkaline NaBH<sub>4</sub> solution. The catalyst was prepared by chemical reduction of Co precursors coated on a Ni foam support. The effects of catalyst preparation conditions on activity of the catalyst were investigated. The active catalyst was amorphous in structure and contains boron with a Co/B molar ratio of 1.5–2.8. With increasing the heat treatment temperature, the catalyst showed a maximum activity to hydrogen generation at approximately 250 °C. Adhesion of the catalyst to the support was also enhanced by heat treatment at 300–400 °C. The catalysts were successfully applied in both a batch reactor and a flow reactor for continuous generation of hydrogen.

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**Keywords:** Hydrogen generation; NaBH<sub>4</sub>; Co–B catalyst; Structured catalyst; Ni foam support

## 1. Introduction

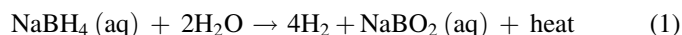
In response to the ever increasing demands of power in portable electronic devices as more enhanced features and complexity are introduced to the devices, the fuel cells have attracted much attention as replacements for lithium batteries. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) have emerged as a strong candidate due in large part to the advantages of using a liquid fuel. Even though hydrogen-powered polymer electrolyte membrane fuel cells (PEMFCs) operate more efficiently with higher power densities than DMFCs, hydrogen supply has been an obstacle to the application of PEMFC to portable power sources.

Hydrogen has been stored in tanks of compressed or liquefied H<sub>2</sub>, in hydrogen-storing alloys, and on activated carbon or nanoscale materials such as carbon nanotubes. However, none of these methods are suitable for portable applications due to the low volumetric and gravimetric efficiency of hydrogen storage as well as their associated safety issues. Instead of those hydrogen storage methods, liquid fuels (methanol, ethanol, gasoline, etc.) and chemical hydrides

(NaBH<sub>4</sub>, KBH<sub>4</sub>, LiH, NaH, etc.) could be employed as hydrogen sources for portable PEMFC. However, in the case of the liquid fuels, high-temperature reforming processes are too complex to satisfy the requirements of portable PEMFC operation.

Among the chemical hydrides, sodium borohydride (NaBH<sub>4</sub>) has been intensively studied as a hydrogen storage material because of its advantages of: nonflammability and stability in air, easily controlled hydrogen generation rate, side product recyclability, and high H<sub>2</sub> storage efficiency. Previous studies on hydrogen production from NaBH<sub>4</sub> are summarized in a recent review [1].

Base-stabilized NaBH<sub>4</sub> solution hydrolyzes to hydrogen and sodium metaborate (NaBO<sub>2</sub>) only when being in contact with specific catalysts:



The catalysts based on Ru and Pt have been mostly employed for the hydrolysis of NaBH<sub>4</sub> [2–13]. However, non-noble catalysts such as Ni- or Co-based catalysts have also been investigated [14–20]. According to the results, metallic Ni or Co catalysts exhibited considerably lower activity to the hydrogen generation reaction compared with the noble metal catalysts.

Catalysts in the form of very fine powders have been mainly used in previous studies to investigate the catalytic activity

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toward the hydrogen generation reaction. It is preferred, however, to support or coat the active catalysts on suitable substrates for practical operation of the hydrogen generation reactor. To this end, Ru catalysts have been prepared on ion-exchange resin beads [2–4],  $\text{Al}_2\text{O}_3$  pellets [5] or carbon substrates [6] to be applied in various types of hydrogen generators. As for the Pt-based catalysts, layers of Pt–LiCoO<sub>2</sub> were coated on a honeycomb monolith and the structured catalysts were successfully employed in a 10 kW<sub>e</sub>-scale hydrogen generator [10]. Other than noble metal catalysts, metallic Ni or Co catalyst has been coated on Ni foam substrates and used in batch reactors [16,17].

Since the hydrolysis of  $\text{NaBH}_4$  is highly exothermic with heat of reaction of ca. 210 kJ/mol [21], the reactor temperature often increases over 100 °C, especially when the reactor is operated in a continuous flow mode. Considering that catalyst in the hydrolysis of  $\text{NaBH}_4$  is exposed to a hot caustic environment, catalyst durability is crucial for practical application [22].

In this study, we prepared a structured Co–B catalyst on the Ni foam substrate. The Ni foam was adopted as a substrate due to its high thermal and chemical stability in the reaction environment. Co–B catalyst was employed in this study since Co–B catalysts showed much higher activity to hydrogen generation than metallic Co catalyst, while exhibited comparable activity to noble metal catalysts [20]. The Co–B catalysts were prepared by chemical reduction method on Ni foam substrates, and the effects of the preparation conditions on the resulting catalysts' activities were examined.

## 2. Experimental

### 2.1. Catalyst preparation on a Ni support

The structured Co–B catalysts were prepared by chemical reduction.  $\text{CoCl}_2$  (DAEJUNG) and  $\text{NaBH}_4$  (DAEJUNG) were used as a Co precursor and a reducing agent, respectively. The aqueous precursor solutions were prepared with various Co concentrations from 5 to 40 wt%, while the solution containing 20 wt%  $\text{NaBH}_4$  and 1 wt% NaOH was employed as the reducing solution. Nickel foam (INCO-FOAM<sup>TM</sup>) was used as the support for the catalyst. The 2 mm thick nickel foam had an open pore structure with density of about 600 g/m<sup>2</sup> and cell size of 0.55–0.70 mm. Cleaned nickel foam was first immersed into the precursor solution for 10 s and then reduced in the reducing solution for another 10 s. Then, the structured catalyst was washed with distilled water for 30 s. This dip-coating process was repeated until a desired amount of Co–B catalyst was coated on the nickel foam.

Heat treatment of the structured catalyst might enhance the adhesion between the coated catalysts and the substrate. In order to investigate the effect of calcination on the adhesion and the catalytic activity for hydrogen production, the prepared structured catalysts were calcined in an argon environment. The structured catalysts were heated up at a

ramp rate of 2 °C/min to the desired temperature between 100 and 500 °C. The structured catalysts were then held at the desired temperature for 2 h before being cooled to room temperature.

### 2.2. Catalyst characterization

The morphology, physical properties, and phase structure of the prepared catalysts were characterized by several analytical methods. Phase structures of the prepared catalyst were characterized by X-ray diffraction (XRD, Rigaku D/MAX-III A). The morphologies of the prepared catalysts were examined by a scanning electron microscope (SEM, JEOL JSM 5200). BET surface areas of the prepared catalyst were measured by a nitrogen adsorption–desorption instrument (Micromeritics ASAP 2010). The Co and B contents of the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, ELAN 6100).

### 2.3. Hydrogen generation test

Activities of the synthesized catalysts to hydrogen production were examined in a batch reactor. The reactor was made of stainless steel with an internal volume of 150 mL. Fig. 1 depicts the experimental apparatus devised to measure the hydrogen generation rate from base-stabilized aqueous  $\text{NaBH}_4$  solution. The catalyst plate with the size of 1 cm<sup>2</sup> (1 cm × 1 cm) was loaded into the reactor and the hydrogen production test was started by introducing 80 mL of the aqueous solution containing 25 wt%  $\text{NaBH}_4$  and 3 wt% NaOH into the reactor. The solution temperature was maintained within 2 °C of its set point using an external water jacket. The hydrogen production rate at 25 °C and 1 atmospheric pressure was measured using a mass flow meter.

For continuous production of hydrogen using a batch or a flow reactor, the catalyst plate with area of 6 cm<sup>2</sup> (2 cm × 3 cm) was employed. In the batch reactor, only one catalyst plate was used, while, in the continuous flow reactor, six catalyst plates were arranged in a plate-type reactor.

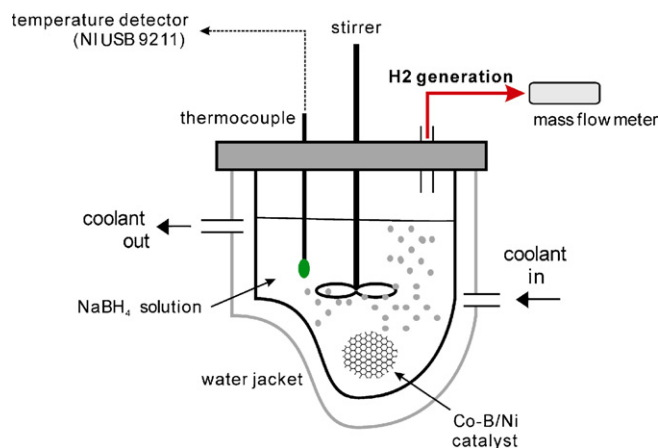


Fig. 1. Configuration of a reactor for measuring the hydrogen generation rate from  $\text{NaBH}_4$  solution.

### 3. Results and discussion

#### 3.1. Effect of catalyst preparation condition

Structured Co–B catalysts were prepared under various conditions and the effects of the preparation conditions on the resulting catalysts' activities were examined. First of all, the relationship between number of dip-coating cycles and catalyst loading was examined.  $\text{CoCl}_2$  concentration in the precursor solution was fixed at 30 wt%. The amounts of Co–B catalyst coated on the unit area of substrate ( $1 \text{ cm}^2$ ), measured by weight gain, are plotted with the number of dip-coating cycles in Fig. 2. As expected, the amount of Co–B catalyst coated on the support increased linearly with number of dip-coating cycles. The average amount of Co–B catalyst coated on the nickel foam by one dip-coating cycle was about  $2.9 \text{ mg/cm}^2$ . Using the prepared structured catalysts without any heat treatment, hydrogen production rate from an aqueous solution containing 25 wt%  $\text{NaBH}_4$  and 3 wt%  $\text{NaOH}$  was measured while maintaining the solution temperature at  $20^\circ\text{C}$ . The measured hydrogen production rates per unit area of structured catalyst are also presented in Fig. 2. The hydrogen production rate also increased with the number of dip-coating cycles, and a hydrogen production rate of  $374 \text{ mL/min cm}^2$  was obtained with the structured catalyst prepared by 20 dip-coating cycles.

Structured catalysts were prepared using the precursor solutions with different Co concentrations at a fixed number of dip-coating cycles of 15. The measured catalyst loading and hydrogen production rate were plotted with the concentrations of the precursor solutions in Fig. 3. As shown in the figure, the amount of Co–B catalysts coated on the nickel foam substrate increased with the concentration of the precursor solution. For the solutions with Co concentrations lower than 20 wt%, loading of the catalyst increased steeply and then increased slowly for the solutions with Co concentrations higher than 20 wt%. The hydrogen production rate also increased with increasing  $\text{CoCl}_2$  concentration in the precursor solution. Similar to the case of catalyst loading, the hydrogen production rate increased steeply in the low concentration range and

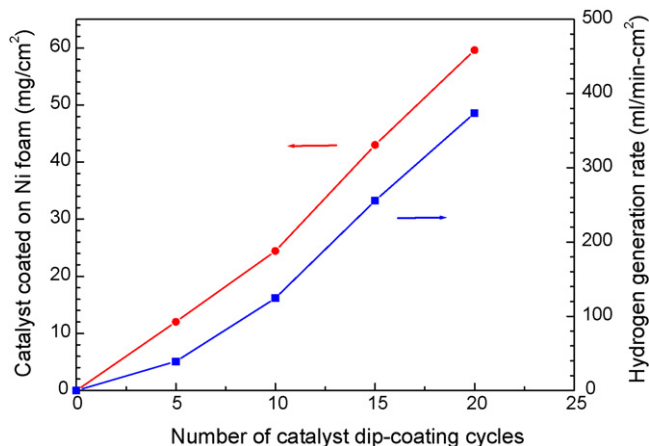


Fig. 2. Variation of the amount of catalyst coated on the substrates and their hydrogen production rates with number of dip-coating cycles.

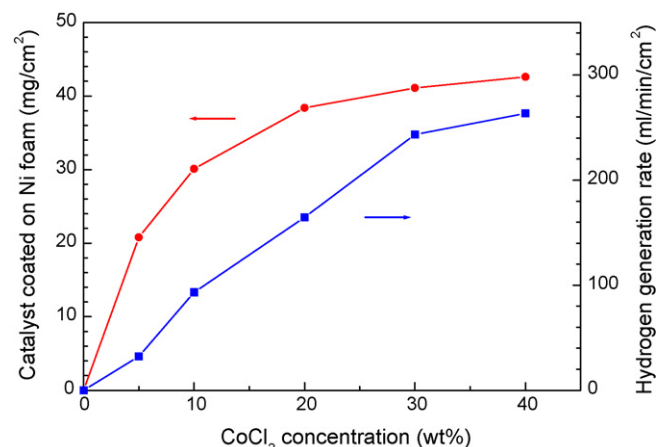


Fig. 3. Variation of the amount of catalysts coated on the substrates and their hydrogen production rates with  $\text{CoCl}_2$  concentrations in the precursor solution.

increased slowly in the high concentration range. Thus, the results clearly demonstrated that the hydrogen production rates strongly depended on the amount of the catalysts coated on the nickel foam substrates. In the subsequent experiments, catalysts were prepared through 15 dip-coating cycles using a precursor solution containing 30 wt%  $\text{CoCl}_2$ .

Previous work on chemical reduction of metal salts by  $\text{NaBH}_4$  indicates that the composition and morphology of the synthesized particles are influenced by the molar ratio of  $\text{NaBH}_4$  to metal cation in the precursor solution [23]. In order to investigate the influence of the precursor concentrations on the morphology and the composition of the catalyst, SEM and ICP analysis were carried out. Within the range of  $\text{CoCl}_2$  concentration employed to prepare the catalysts in this study, the SEM analysis did not clearly show the differences in the morphology and size of the as-made catalyst particles. A representative SEM image is shown in Fig. 6(a) below. The molar ratios of Co/B were analyzed by ICP and the results are presented in Table 1. The molar ratios of Co/B were obtained between 1.5 and 2.8 and no relationship between the molar ratio and the  $\text{CoCl}_2$  concentration in the precursor solutions was found in the present study.

#### 3.2. Effect of heat treatment

The heat treatment of the prepared structured catalysts might improve the adhesion between the Co–B catalysts and the substrates. In order to examine the effect of heat treatment on the catalytic activity, the prepared catalysts were calcined at temperatures between 100 and  $500^\circ\text{C}$  in pure argon environment. After calcination, the catalysts were placed in

Table 1

Variation of the molar ratio of Co/B in the catalyst with  $\text{CoCl}_2$  concentration in the precursor solution

Concentration of $\text{CoCl}_2$ (wt%)	Molar ratio of Co/B
10	2.01
20	2.30
30	2.77
40	1.48

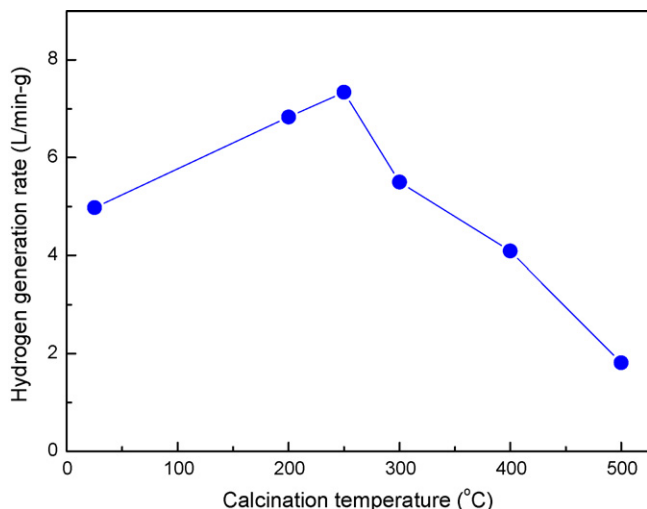


Fig. 4. Variation of hydrogen production rates with calcination temperatures of structured catalysts.

a batch reactor maintained at 20 °C and rates of hydrogen production from 25 wt% NaBH<sub>4</sub> solution containing 3 wt% NaOH were measured. As presented in Fig. 4, the hydrogen production rates increased with increasing the calcination temperature up to 250 °C, while the rates decreased with calcinations temperature above 300 °C. The reduction in the activity of the catalysts calcined at temperatures above 300 °C might be caused by phase transformation and/or the sintering of the catalysts. XRD, SEM and BET analyses were carried out for the catalysts calcined at different temperatures in order to examine the phase structure and the surface area change of the catalysts.

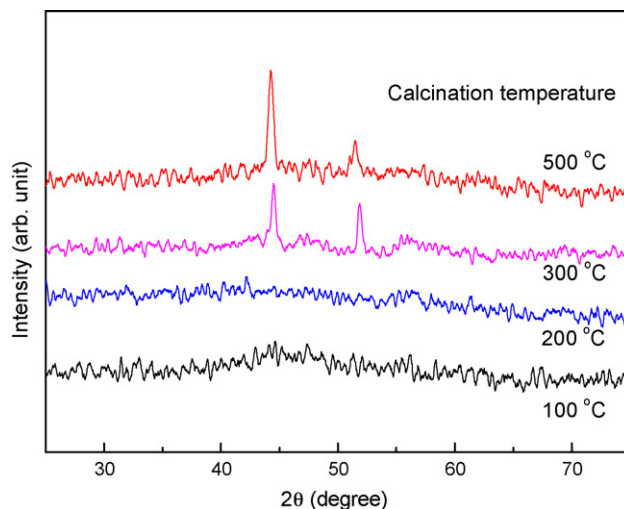


Fig. 5. XRD patterns of catalysts heat treated at different temperatures.

Fig. 5 shows XRD patterns of the structured catalysts calcined at different temperatures. The catalysts calcined at 100 and 200 °C had amorphous structures, while small peaks corresponding to metallic Co were found in the catalysts calcined above 300 °C. It was reported that as-made Co–B catalysts were amorphous in structure, while crystallization and decomposition of the Co–B amorphous alloy occurred with heat treatment above 300 °C [19,24]. The result shown in Fig. 5 indicates that some of amorphous Co–B catalyst coated on Ni foam underwent decomposition at calcination temperatures above 300 °C.

Fig. 6 shows SEM images of the structured catalysts. The catalysts calcined at temperatures below 200 °C exhibited

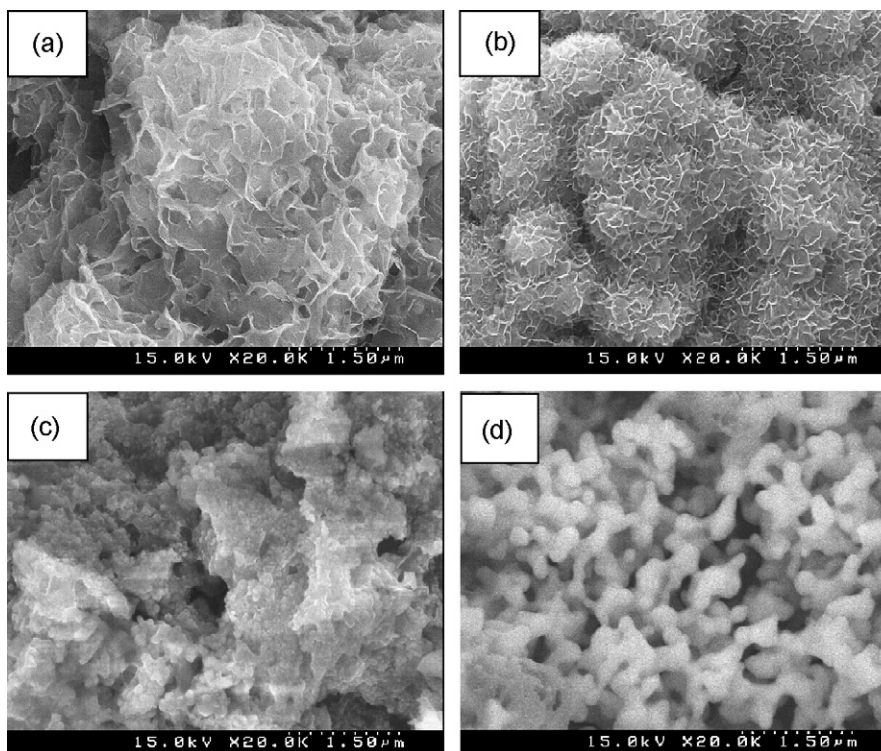


Fig. 6. SEM images of (a) the as-made catalyst and the catalyst after heat treatment at (b) 200 °C, (c) 300 °C, and (d) 500 °C.



Table 2  
Effect of heat treatment on BET surface area of the catalyst

Heat treatment temperature	BET surface area (m <sup>2</sup> /g)
As made	30.3
200 °C	40.7
300 °C	16.2
500 °C	1.6

different morphology from those calcined at temperatures above 300 °C. This was in good accordance with the XDR results that the former and the latter ones had different structures. Fig. 6(c) and (d) reveals that the catalyst calcined at the higher temperature had the larger particle size.

The BET surface areas for the catalysts calcined at different temperatures were measured by N<sub>2</sub> adsorption and the results are presented in Table 2. The BET surface area of the catalysts increased with increasing the calcination temperatures up to 200 °C, and then decreased at higher calcination temperatures. Overall results of hydrogen production rates, XRDs, and BET surface areas, indicate that amorphous Co–B catalyst had higher activity for hydrogen production. Also, in the catalysts calcined at temperatures above 300 °C, metallic Co was obtained and the surface area decreased with increasing the calcination temperature. This caused the reduction of hydrogen production rates of the catalysts calcined at temperatures above 300 °C.

On the other hand, it was observed in the as-made catalysts that the Co–B particles fell apart from the nickel foam substrates easily during the hydrogen production experiment. Thus, adhesion between the Co–B catalyst particles and the nickel foam substrate was enhanced by the calcination. In order to quantify the enhancement of the adhesion by the calcination, several structured catalysts calcined at different temperatures were prepared and the weight loss was observed after one and 2 h of catalyst immersion in an ultrasonic bath. The weight of catalyst remaining in the structured catalyst was measured and is presented in Fig. 7. As shown in the figure, the structured

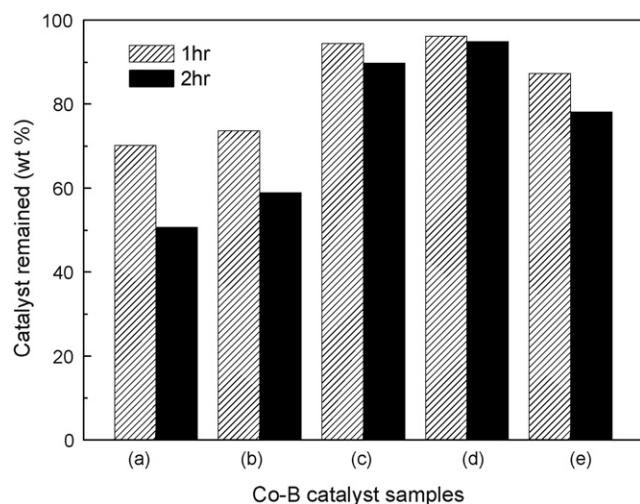


Fig. 7. Weight loss of the catalysts in an ultrasonic reactor: (a) the as-made sample and catalysts heat treated at (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C.

catalysts calcined at 200 °C lost 40–50% of their coated catalyst after 2 h of ultrasonic treatment. However, the structured catalysts calcined at 300 °C and 400 °C lost less than 10% of their coated catalyst after 2 h of ultrasonic treatment. Consequently, the adhesion between the Co–B catalysts and the nickel foam substrates was enhanced by the calcinations at 300 °C and above.

### 3.3. Hydrogen production using the structured catalyst

Using the structured catalyst calcined at 300 °C, hydrogen production experiments were performed in a batch reactor and a continuous flow reactor. For the batch reactor, a catalyst plate of 6 cm<sup>2</sup> (2 cm × 3 cm) in area was used and the reaction temperature was controlled by an external water jacket, as shown in Fig. 1. The hydrogen production rates from 25 wt% NaBH<sub>4</sub> solution containing 3 wt% NaOH were measured at solution temperatures of 20, 30 and 40 °C, and the results are presented in Fig. 8. As expected, a hydrogen production rate increased with increasing reactor temperature. The hydrogen production rates remained almost constant for about an hour after an initial transient period of a few minutes. Activation energy of 45 kJ/mol was obtained for the hydrogen production reaction using the structured catalysts prepared in the present study. This value is lower than the value of 65–69 kJ/mol published for the Co–B powder catalysts [19,20].

The continuous flow reactor was designed for the operation of a 300–400 W<sub>e</sub> PEMFC stack with a hydrogen production requirement of about 6 L/min. In the continuous flow reactor, six pieces of the structured catalyst were installed in the plate-type reactor. The reactant solution containing 20 wt% NaBH<sub>4</sub> and 0.2 wt% NaOH was introduced into the structured catalyst at a constant flow rate using a liquid pump. Fig. 9 shows the evolution of hydrogen production rate and temperature of the reactor when reactant solution was introduced to the reactor at a rate of 16.6 cm<sup>3</sup>/min. As shown in the figure, the reactor continuously produced hydrogen for 2 h at a steady reactor temperature of approximately 100 °C. In the initial stage, the

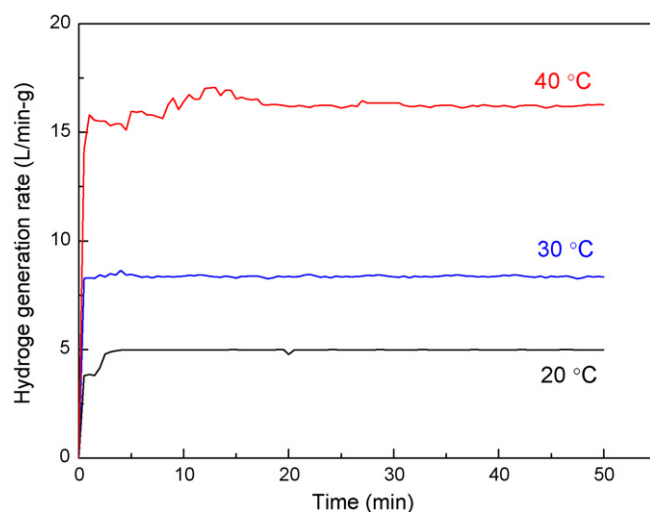


Fig. 8. Evolution of hydrogen production rates in the batch reactor employed with the structured catalyst.

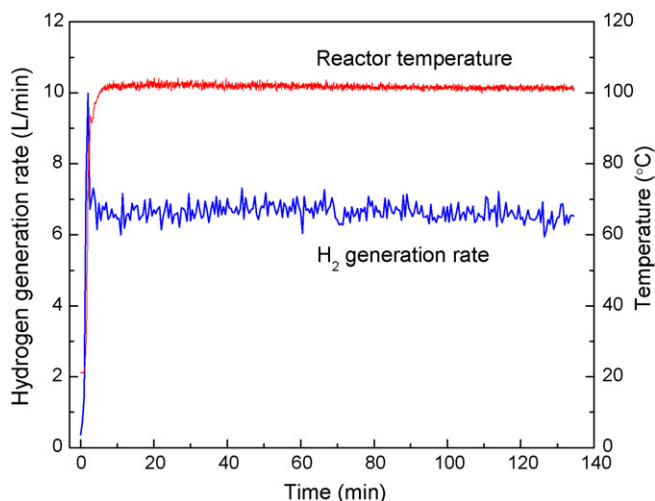


Fig. 9. Performance of the continuous flow reactor employed with the structured catalysts for hydrogen generation.

temperature of the reactor jumped up to 100 °C abruptly and it was stable at 100 °C during the operation. Thus, the continuous flow reactor is an autothermal reactor, which does not need external heating or cooling source to control the reaction temperature. The conversion of  $\text{NaBH}_4$  calculated from flow rates of the reactant and hydrogen was about 75%. The configuration of the reactor was not optimized in the present study and it might be reason of the low conversion of  $\text{NaBH}_4$ . Thus, the modification and optimization of the reactor is necessary to improve the conversion of  $\text{NaBH}_4$  into hydrogen.

#### 4. Conclusions

Structured Co–B catalysts were prepared on nickel foam substrates using a chemical reduction method. The amount of the Co–B catalysts coated on the substrates increased with increasing the number of dip-coating cycles and the concentration of  $\text{CoCl}_2$  in the precursor solution. Hydrogen production rate increased with increasing the amount of the catalysts coated on the substrate. Calcination of the structured catalysts enhanced the adhesion between the catalysts and the substrate. Calcination at temperatures above 300 °C, however, led to decomposition and sintering of the Co–B catalyst, reducing the catalytic activity to hydrogen generation reaction.

The catalysts were successfully applied in both a batch reactor and a flow reactor for continuous generation of hydrogen.

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