Hydrogen Generation for Fuel Cells from an Alkaline NaBH₄ Solution using Co-Ni-P Catalysts Electrodeposited on TiO₂ Nanotube Substrate

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We investigated the effects of a TiO₂ nanotube substrate on the electrodeposition of Co-Ni-P catalysts and the catalytic generation of hydrogen from an alkaline NaBH₄ solution. In addition, the performance of the catalysts formed on the TiO₂ nanotube substrate was compared with that on a Cu substrate. The nucleation rate of the Co-Ni-P catalysts on the TiO₂ nanotube substrate was much faster than that on the Cu substrate, indicating that the TiO₂ nanotube substrate supplies more nucleation sites than the Cu substrate. Furthermore, the surface area of the Co-Ni-P catalysts formed on the TiO₂ nanotube substrate was larger than that on the Cu substrate; this larger surface area improved the efficiency of the catalytic generation of hydrogen from the alkaline NaBH₄ solution.

Keywords: TiO₂ Nanotube, NaBH₄, electrodeposition, Co-Ni-P catalyst, hydrogen generation

1. INTRODUCTION

Sodium borohydride (NaBH₄) is one of the most attractive hydrogen storage materials because of its high potential hydrogen storage capacity of up to 10.8 wt. %, its convenient handling characteristics, and its safety. NaBH₄ generates hydrogen by the following hydrolysis reaction:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 \qquad (1)$$
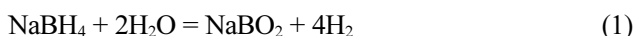
Nevertheless, the hydrolysis of NaBH₄ is restricted in an alkaline solution.[1] Thus, the use of an alkaline NaBH₄ solution enables safe, stable, and high-density hydrogen storage. Noble metal catalysts such as Ru and Pt have been used to accelerate the hydrolysis of a NaBH₄ solution to generate hydrogen.[2-4] However, due to the high price of noble metal catalysts, alternative catalysts based on cheaper transition metals need to be developed.[5-7]

The lower catalytic activity of such transition metals as Co and Ni alloys compared to that of the noble catalysts can be compensated by their high specific surface area. Recently, we successfully fabricated a three dimensional (3-D) Co-Ni-P catalyst layer on a Cu substrate by electrodeposition.[8,9] The catalysts exhibited excellent hydrogen generation efficiency from an alkaline NaBH₄ solution. Nevertheless, they still exhibited low nucleation density during the electrodeposition process and further improvement is desirable. The use of a TiO₂ nanotube substrate may offer such an improvement

because of its high nucleation density during electrodeposition, as Ryu *et al*. previously reported in Cu electrodeposition.[10]

In this study, we fabricated Co-Ni-P catalysts on a TiO₂ nanotube substrate using electrodeposition and examined the characteristics of the catalytic hydrogen generation from an alkaline NaBH₄ solution. In addition, the performance of the Co-Ni-P catalysts formed on the TiO₂ nanotube substrate was compared with that on the Cu substrate.

2. EXPERIMENTAL

Pure Cu and TiO₂ nanotube substrates as shown in Fig. 1 were used for the electrodeposition of the Co-Ni-P catalysts. The TiO₂ nanotube substrate was prepared by anodizing pure Ti for 6 h at 20 V in a solution of 0.5 wt. % NH₄F and 1 M malonic acid.[10,11] The average diameter of the highly ordered TiO₂ nanotube was approximately 90 nm.

The Co-Ni-P catalysts were electrodeposited on the Cu and TiO₂ nanotube substrates at 25°C using a three-electrode system consisting of the substrates as a working electrode, a saturated calomel electrode (SCE) as a working electrode, and a Pt wire as a counter electrode. The electrodeposition bath was composed of 0.1 M CoCl₂·6H₂O, 0.04 M NiCl₂·6H₂O, 0.8 M NaH₂PO₄·H₂O, and 0.6 M NH₂CH₂COOH.[8] The applied cathodic current density was 0.1 A·cm⁻² and the electrodeposition time varied from 10 to 600 s. The surface morphologies and chemical compositions of the electrodeposited catalysts were analyzed using scanning electron microscopy (SEM) and attached energy disper-
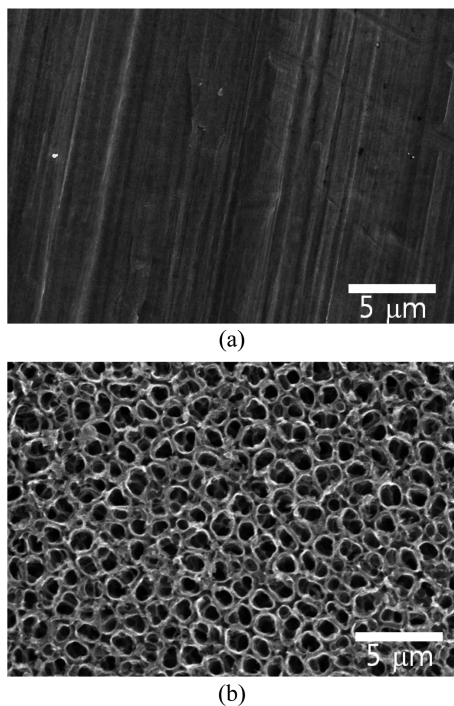
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(a)

(b)

Fig. 1. Surface morphologies of (a) pure Cu and (b) TiO₂ nanotube substrates.

sive spectroscopy (EDS).

The catalytic hydrogen generation rate was analyzed in a 70 ml solution of 10 wt. % NaBH₄ and 10 wt % NaOH at 30°C using water displacement method.
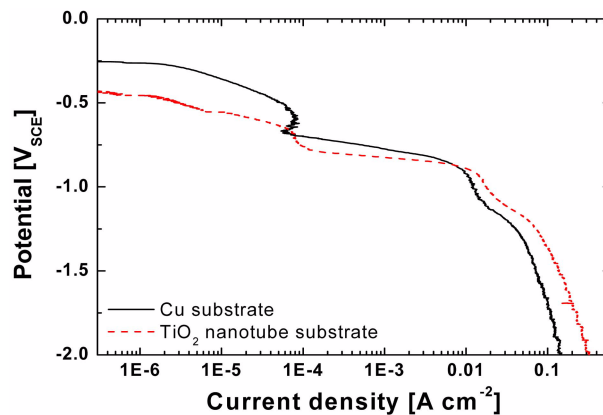

Fig. 2. Cathodic polarization curves for the pure Cu and TiO₂ nanotube substrates.

3. RESULTS AND DISCUSSION

Figure 2 shows the cathodic polarization curves for the electrodeposition of Co-Ni-P on the Cu and TiO₂ substrates. The electrodeposition of Co-Ni-P was started at -690 mV$_{SCE}$ for pure Cu and at -780 mV$_{SCE}$ for the TiO₂ nanotube substrate. The cathodic current density close to a limiting current density of 0.1 A·cm^{-2} was selected as the applied current density to induce three-dimensional (3-D) growth of the catalysts. At this cathodic current density, the deposition potential for the TiO₂ nanotube substrate was nobler than that for the pure Cu substrate.
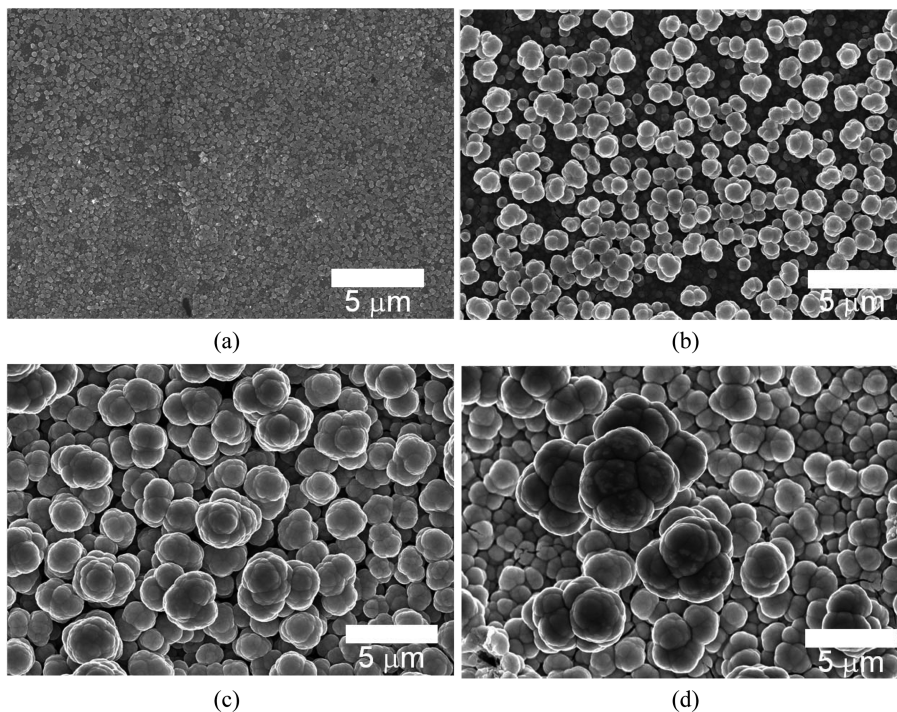
Figures 3 and 4 show the effect of the electrodeposition

(a)

(b)

(c)

(d)

Fig. 3. Surface morphologies of Co-Ni-P catalysts electrodeposited for (a) 10 s, (b) 30 s, (c) 120 s and (d) 300 s on TiO₂ nanotube substrates.
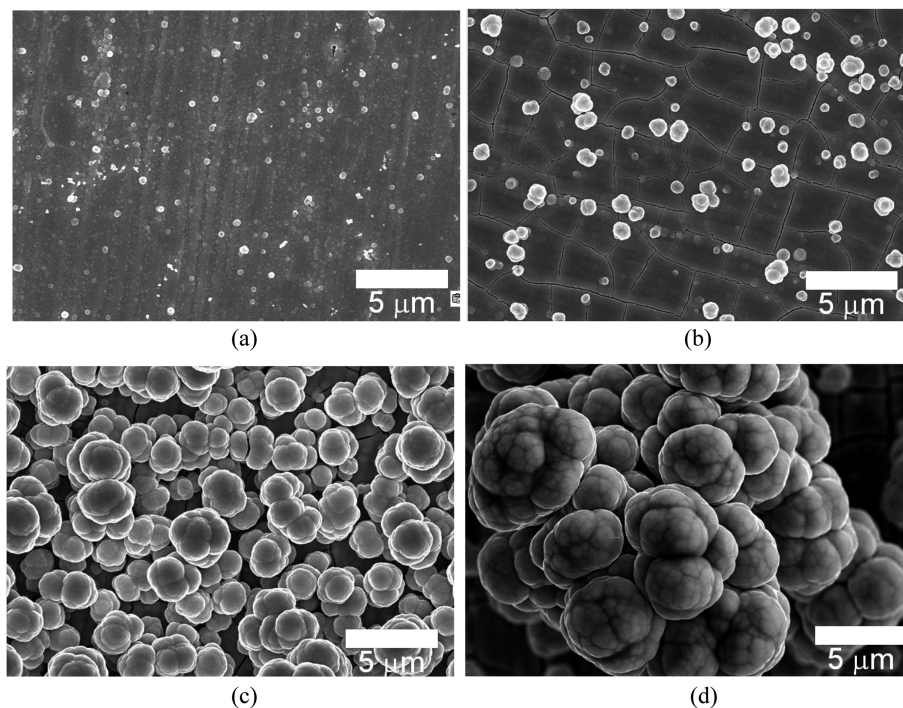
Fig. 4. Surface morphologies of Co-Ni-P catalysts electrodeposited for (a) 10 s, (b) 30 s, (c) 120 s and (d) 300 s on pure Cu substrates.

time on the surface morphologies of the Co-Ni-P catalysts electrodeposited at a cathodic current density of 0.1 A·cm^{-2} on the TiO$_2$ nanotube and Cu substrates, respectively. The average chemical composition of the catalysts was 81 at. % Co – 10 at. % Ni – 9 at. % P. In the initial stage of electrodeposition, the Co-Ni-P catalysts nucleated and grew uniformly and two-dimensionally. After 30 s, 3-D growth of the catalysts occurred because of the localized preferential nucleation. With an increasing electrodeposition time, the catalyst that had previously nucleated three-dimensionally grew continuously while the growth of the catalyst in other areas was relatively suppressed, resulting in the localized protuberance of the catalyst clusters.

Comparing the electrodeposition of the Co-Ni-P catalysts on the two substrates in the early stage of electrodeposition, the nucleation density of the catalyst appeared to be higher on the TiO$_2$ nanotube substrate than on the Cu substrate, suggesting that the former supplied more nucleation sites than the latter. Ryu *et al.* previously reported that the mouth of the TiO$_2$ nanotube acts as a preferential site for the nucleation of Cu electrodeposits and thereby facilitates the high nucleation density of Cu during the electrodeposition.[10] This explanation was also confirmed in the electrodeposition of the Co-Ni-P catalysts.

In addition, the size of the Co-Ni-P catalyst cluster electrodeposited for 300 s on the Cu substrate was much larger than that on the TiO$_2$ nanotube substrate. The surface area of the Co-Ni-P catalyst generally increased with the 3-D

growth of the catalysts. However, the excessive growth of a catalyst cluster is unfavorable since the total surface area of these catalysts was relatively lower than that of the uniformly distributed catalysts formed on the TiO$_2$ nanotube substrate.

The hydrogen generation kinetics by the fabricated catalysts from a 70 ml solution of 10 wt. % NaBH$_4$ and 10 wt. % NaOH are presented in Fig. 5. The catalytic hydrogen generation rate generally increased with an increasing electrodeposition time for the fabrication of the catalysts. In addition, the hydrogen generation rate by the Co-Ni-P catalysts formed on the TiO$_2$ nanotube substrate was much higher than that on the Cu substrate. The TiO$_2$ nanotube substrate supplied numerous nucleation sites for electrodeposition of the Co-Ni-P catalysts. Furthermore, the catalysts nucleated and grew uniformly and three-dimensionally, thereby exhibiting a high surface area and catalytic efficiency for the hydrolysis of NaBH$_4$.

4. CONCLUSIONS

The nucleation rate of the Co-Ni-P catalyst on the TiO$_2$ nanotube substrate was much higher than that on the pure Cu substrate since the mouth of the TiO$_2$ nanotube acts as a preferential nucleation site. Accordingly, the Co-Ni-P catalysts three-dimensionally grown on the TiO$_2$ nanotube substrate exhibited a higher surface area and greater catalytic efficiency for the hydrolysis of NaBH$_4$.
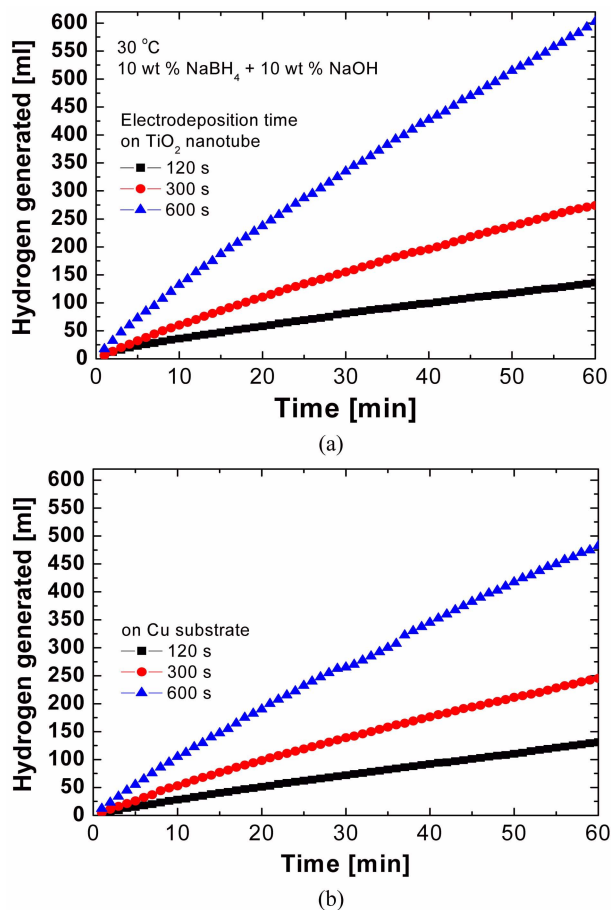
Fig. 5. Effect of electrodeposition time for Co-Ni-P catalysts formed on (a) TiO₂ nanotube and (b) Cu substrates on the catalytic hydrogen generation kinetics in a 70 ml solution of 10 wt. % NaBH4 and 10 wt. % NaOH at 30°C.

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