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Effects of electrodeposited Co and Co–P catalysts on the hydrogen generation properties from hydrolysis of alkaline sodium borohydride solution

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Abstract

Co and Co–P catalysts electroplated on Cu in sulfate based solution without or with an addition of $H_2PO_2^-$ ions were developed for hydrogen generation from alkaline $NaBH_4$ solution. The microstructures of the Co and Co–P catalysts and their hydrogen generation properties were analyzed as a function of cathodic current density and plating time during the electrodeposition. An amorphous Co–P electrodeposit with micro-cracks was formed by electroplating in the sulfate based solution containing $H_2PO_2^-$ ions. It was found that the amorphous Co–P catalyst formed at 0.01 A/cm^2 exhibited 18 times higher catalytic activity for hydrolysis of $NaBH_4$ than did the polycrystalline Co catalyst. The catalytic activity of the electrodeposited Co–P catalyst for hydrolysis of $NaBH_4$ was found to be a function of both cathodic current density and plating time, that is, parameters determining the concentration of P in the Co–P catalyst. Especially, Co–13 at.% P catalyst electroplated on Cu in the Co–P bath at a cathodic current density of 0.01 A/cm^2 for 1080 s showed the best hydrogen generation rate of 954 ml/min g-catalyst in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

Keywords: Sodium borohydride; Hydrogen storage and production; Hydrolysis; Co–P catalyst; Electroplating

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) using hydrogen as a fuel are attractive alternative power sources for vehicles and portable electronic devices because of their high efficiency, high power density and zero emission of environment pollutants. In order to operate PEMFC successfully, a safe and convenient hydrogen storage and production system with high hydrogen storage density needs to be developed. In the past few decades, many efforts have been made to explore high capacity hydrogen storage systems using high pressure vessels [1], metal hydrides [2,3] and carbon nanotubes [4]. However, their hydrogen storage capability in terms of specific energy density is still not sufficient for commercial applications. Recently, chemical hydrides such as $NaBH_4$, $LiBH_4$, NaH and $NaAlH_4$ have received considerable attentions as excellent hydrogen storage materials. Among them, sodium borohydride ($NaBH_4$) provides a safe and practical mean of hydrogen storage and production at an economical cost compared with other chemical hydrides [5–11].

$NaBH_4$ provides the high hydrogen storage density up to 10.8 wt.%, and it can produce double amount of its stored hydrogen by a hydrolysis reaction as follows:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2, \quad \Delta H = 300\,\mathrm{kJ}$$

In addition, it stores hydrogen safely in an alkaline solution at room temperature. For generation of hydrogen from alkaline $NaBH_4$ solution, suitable catalysts such as Ru and Pt are needed to promote the hydrolysis reaction of $NaBH_4$ [5,6]. Since the cost of such noble metal catalysts are very expensive, it is necessary to develop an economical alternative catalyst with an excellent efficiency of hydrogen generation.

In the 1950s, Schlesinger et al. found that cobalt chlorides and nickel chlorides could accelerate the hydrogen generation from alkaline $NaBH_4$ solution [7]. It is notable that cobalt chlorides react with $NaBH_4$, release H_2 gas and produce cobalt boride (Co–B) compounds as by-products, and Co–B, acting as a catalyst, contributes to the hydrogen generation spontaneously.

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There have been many researches on the hydrogen generation properties of Co–B and Ni–B catalysts [8–11], and they commonly reported that metallic borides showed much higher catalytic activities for hydrolysis of $NaBH_4$ than original metals, and Co–B catalysts were more effective for hydrogen generation from alkaline $NaBH_4$ solution than Ni–B. However, because most of them used Co–B catalysts prepared by chemical reduction method without support or substrate, it was very difficult to use the catalysts repeatedly. On the other hand, Burchardt examined the hydrogen generation properties of electrodeposited Ni–P catalysts on Ni in 1 M KOH solution [12], and found that electroplating conditions affected the concentration of P in the Ni–P layer, resulting in the variations of catalytic activities. However, hydrogen generation properties of electroplated Co–P catalysts in alkaline $NaBH_4$ solution have not yet been reported.

In the present paper, we synthesized Co and Co–P catalysts by an electroplating method, and examined their hydrogen generation properties in alkaline $NaBH_4$ solution. The effects of electroplating conditions such as cathodic current density and electroplating time on the microstructures of the Co–P catalysts and their catalytic activities on the hydrolysis of $NaBH_4$ are also investigated in order to develop high performance catalysts for hydrogen generation from hydrolysis of $NaBH_4$.

2. Experimental

2.1. Preparation of catalysts

A commercially pure copper sheet with an exposed surface area of 3 cm × 3 cm was used as a substrate for Co and Co–P electroplating. A pure cobalt plate was used as an anode. The cathode sheet was successively degreased with acetone, washed with distilled water, and activated for 1 min in 10 wt.% H_2SO_4 solution prior to the plating. The Co and Co–P catalysts were electrodeposited on Cu substrate using two electrode systems.

Electroplating of the Co and Co–P catalysts was conducted using dc current in sulfate based solution agitated by a magnetic stirrer at 100 rpm. The solution for Co electroplating was prepared by mixing 0.05 M $CoSO_4{\cdot}7H_2O$, 0.2 M $C_6H_5Na_3O_7{\cdot}2H_2O$ and 0.5 M $(NH_4)_2SO_4$. The composition of the solution for Co–P electroplating was 0.05 M $CoSO_4{\cdot}7H_2O$, 0.2 M $C_6H_5Na_3O_7{\cdot}2H_2O$ and 0.5 M $(NH_4)_2SO_4$ with 0.2 M $NaH_2PO_2{\cdot}H_2O$. Details in the electroplating conditions are presented in Table 1. The Co catalyst was electroplated for 12 min at a cathodic current density of 0.01 A/cm^2. The Co–P catalysts were deposited for 40–3600 s at 0.001–1 A/cm^2. All the experiments were performed at an ambient temperature (22 ± 2 °C).

The surface morphology and composition of the Co and Co–P catalysts were analyzed using scanning electron microscope (SEM), X-ray diffraction (XRD), and Auger electron spectroscope (AES).

Table 1
Bath composition and plating conditions for the electrodeposited Co and Co–P catalysts

Chemicals	Concentration (M)	
	Co bath	Co–P bath
$CoSO_4{\cdot}7H_2O$	0.05	0.05
$NaH_2PO_2{\cdot}H_2O$	–	0.2
$C_6H_5Na_3O_7{\cdot}2H_2O$	0.2	0.2
$(NH_4)_2SO_4$	0.5	0.5
Bath temperature (°C)	22 ± 2	
Substrate	Cu (20 μm)	

2.2. Measurement of hydrogen generation rate

Hydrogen generation tests of the Co and Co–P catalysts were performed in 50 ml 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C. The volume of generated hydrogen gas was measured by a gas flow meter. The reactor was immersed in a water bath to stabilize the temperature, and no stirring was carried out in the reactor.

3. Results and discussion

3.1. Electrodeposited Co and Co–P catalysts

Fig. 1 shows the surface morphologies of Co and Co–P catalysts electroplated on Cu respectively in the Co bath and the Co–P bath, containing 0.2 M of $H_2PO_2^-$ ions, at same

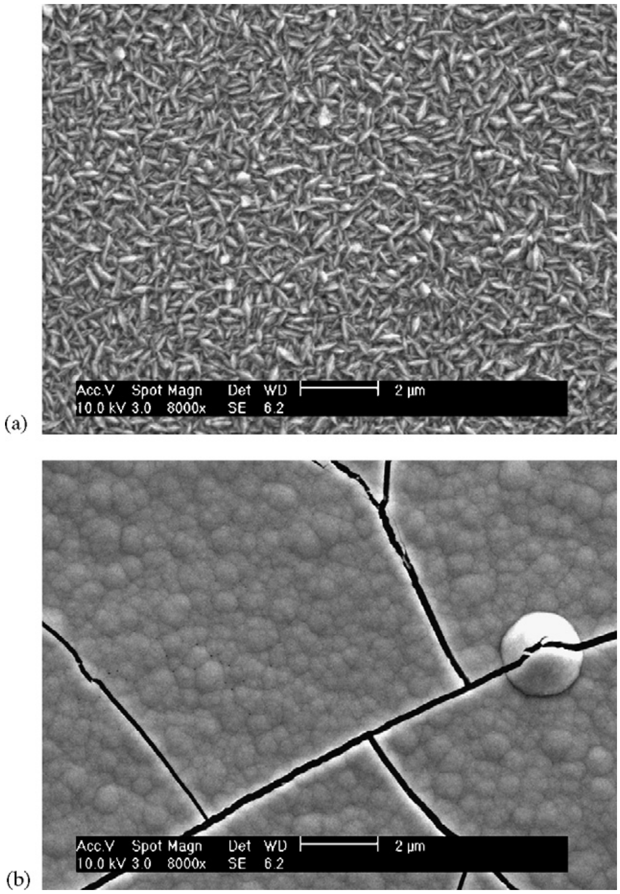

Fig. 1. SEM micrographs on the surface morphologies of (a) Co and (b) Co–P catalysts electroplated on Cu respectively, in the Co bath and the Co–P bath at a cathodic current density of 0.01 A/cm^2 (deposited electrodeposit weight: 1 mg/cm^2 for both cases).

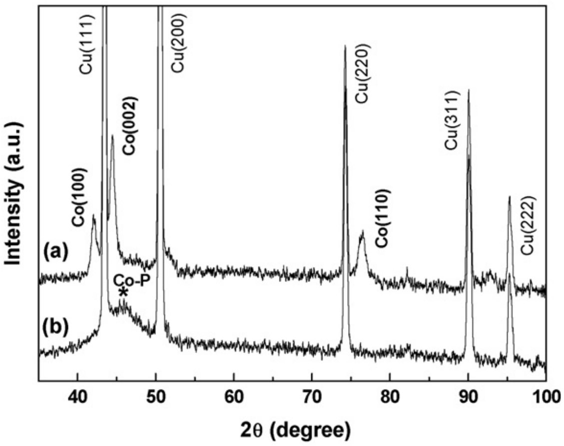

Fig. 2. XRD spectra of (a) Co and (b) Co–P catalysts electroplated on Cu in the Co bath and the Co–P bath respectively at a cathodic current density of 0.01 A/cm^2.

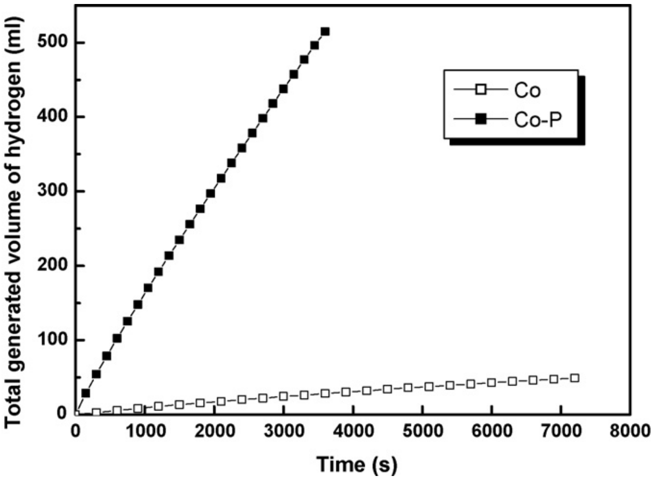

Fig. 3. Hydrogen generation kinetics of Co and Co–P catalysts, electroplated on Cu respectively, in the Co bath and the Co–P bath at a cathodic current density of 0.01 A/cm^2, in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

cathodic current density of 0.01 A/cm^2 (deposited weight of electrodeposit: 1 mg/cm^2). In the case of the Co catalyst, ridge shaped crystals of Co were arranged randomly. However, the microstructure of the Co–P catalyst looks round and very smooth. It is notable that micro-cracks are only observed on the Co–P catalyst, indicating that there exist high residual stresses in the Co–P catalyst layer. The occurrence of cracks on Co–P electrodeposits was previously reported by Lucas et al. [13]. They suggested that hydrogen evolution during the Co–P electroplating caused the residual stresses in the coating, and thereby resulting in the cracks. However, it appears that the differences in structure and brittleness between the Co and Co–P electrodeposits may contribute to the occurrence of micro-cracks. Especially, fine grain boundaries in the Co electrodeposit may reduce the residual stress caused by hydrogen evolution during the electrodeposition, thereby forming poly crystal structure without the micro-cracks. From EDS analysis, it was found that the composition of the Co–P catalyst was about Co–13 at.% P.

Fig. 2 shows XRD patterns of the electrodeposited Co and Co–P catalysts. For the Co catalyst, the (1 0 0), (0 0 2) and (1 1 0) planes of the hexagonal close packed (HCP) Co phase were detected, and the sharp peaks explained that Co electrodeposit was crystalline structure. However, for the Co–P catalyst, the only broad peak except for the peaks of Cu substrate was detected, demonstrating that the electrodeposited Co–P catalyst is an amorphous structure. XRD analysis revealed that as $H_2PO_2^-$ ions were added to the Co bath, the microstructure of electrodeposit was changed from polycrystalline structure to amorphous structure due to the reduction of P.

Fig. 3 shows the hydrogen generation properties of electrodeposited Co and Co–P catalysts in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C. Hydrogen generation rates of the Co and Co–P catalysts were determined to be 52 and 954 ml/min g-catalyst, respectively. It clearly showed that the Co–P catalyst exhibited much higher hydrogen generation rate than did the Co catalyst. It was confirmed from AFM analysis that the difference in surface area between the Co and Co–P catalysts was negligible. Moreover, when Cu substrate without Co or Co–P catalysts was immersed in alkaline $NaBH_4$ solution, the hydrogen generation rate was almost zero. This result indicated that Cu showed a very low catalytic efficiency for hydrolysis of $NaBH_4$ in alkaline solution and the effect of Cu substrate on hydrogen generation in alkaline $NaBH_4$ solution was also negligible. Thus, for hydrolysis reaction of $NaBH_4$ in an alkaline solution, the catalytic activity of the Co–P electrodeposit is much higher than that of the Co electrodeposit.

In order to optimize electroplating conditions for the Co–P catalysts with the best hydrogen generation rate, the effects of a cathodic current density and electroplating time on the microstructure and hydrogen generation rate of Co–P electrodeposits were investigated.

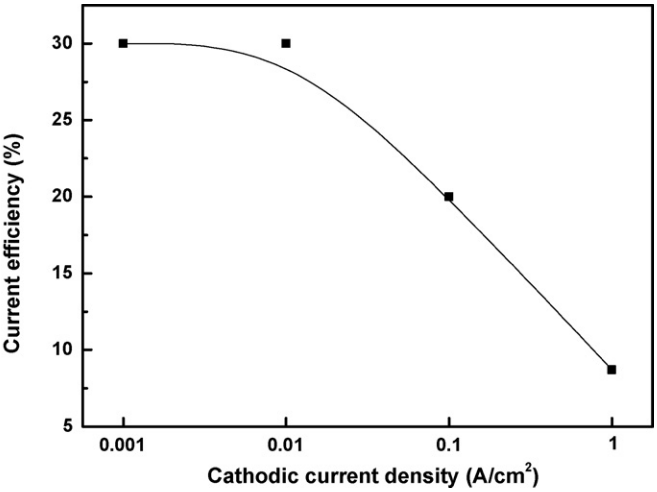

Fig. 4. Current efficiency of Co–P electroplating as a function of a cathodic current density in which Co–P was deposited on Cu from 0.05 M $CoSO_4{\cdot}7H_2O$, 0.2 M $C_6H_5Na_3O_7{\cdot}2H_2O$, 0.5 M $(NH_4)_2SO_4$, and 0.2 M $NaH_2PO_2{\cdot}H_2O$ solution at 22 ± 2 °C.

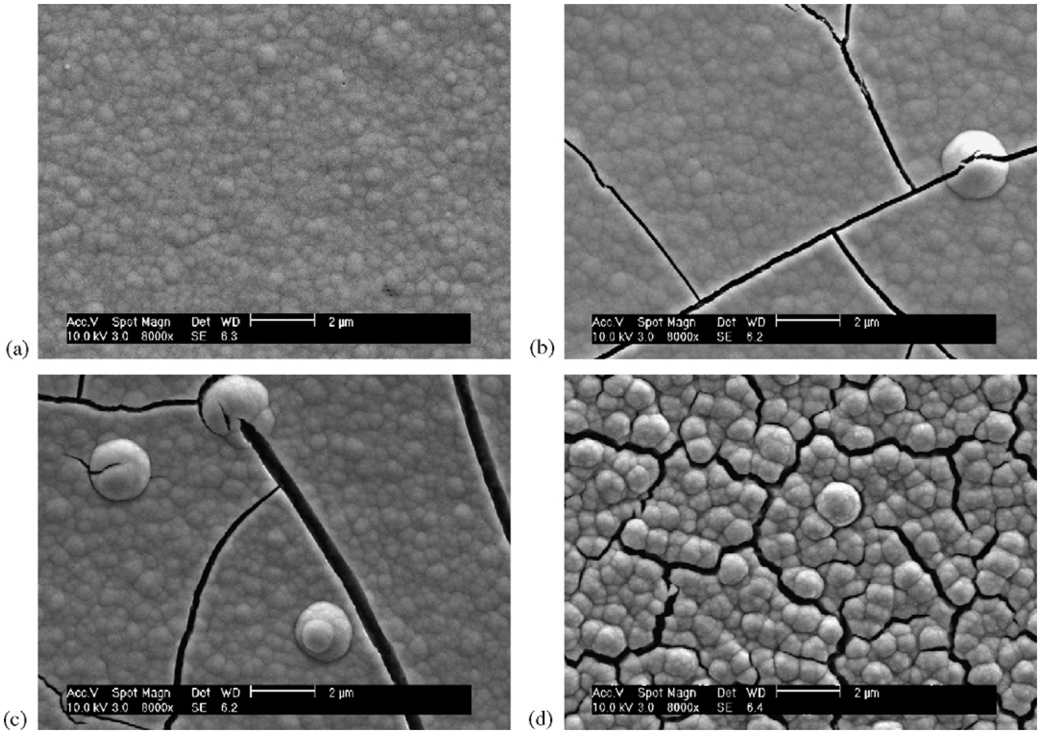

Fig. 5. SEM micrographs on the surface morphologies of Co–P catalysts electroplated on Cu in the Co–P bath at a cathodic current density of (a) 0.001 A/cm^2, (b) 0.01 A/cm^2, (c) 0.1 A/cm^2, and (d) 1 A/cm^2 (deposited electrodeposit weight: 1 mg/cm^2).

3.2. *Effects of cathodic current density*

In order to control the deposited weight of the Co–P catalysts, we examined a current efficiency from the Co–P bath at ambient temperature (22 ± 2 °C) as a function of a cathodic current density, and the results were presented in Fig. 4. The current efficiency was measured by comparing the total charge (from integrating the current–time curves) with the weight gain of deposited Co–P. At a low cathodic current density between 0.001 and 0.01 A/cm^2, the current efficiency was about 30%. However, with an increase in a cathodic current density more than 0.01 A/cm^2, the current efficiency decreased rapidly, demonstrating that hydrogen evolution reaction occurred more severely at a higher cathodic current density during Co–P electroplating.

Fig. 5 shows that the surface morphology of Co–P electrodeposits looks significantly different depending on the applied cathodic current density (deposited electrodeposit weight: 1 mg/cm^2). At a low cathodic current density of 0.001 A/cm^2, round shaped crystals of Co–P were formed

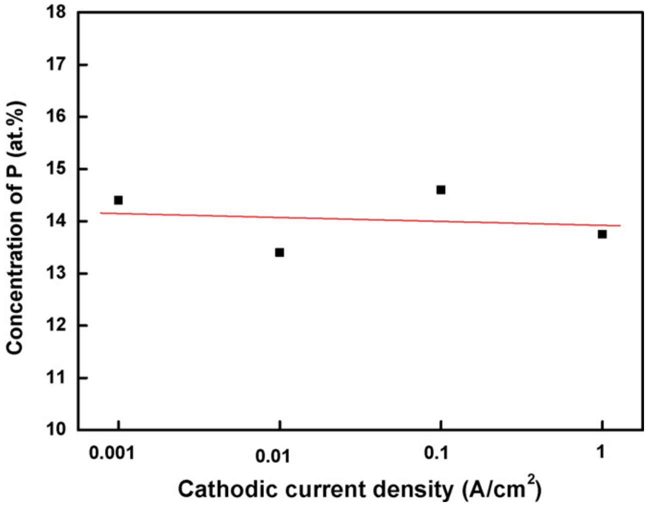

Fig. 6. Chemical composition of the electrodeposited Co–P catalysts as a function of a cathodic current density in which Co–P was deposited on Cu from 0.05 M $CoSO_4 \cdot 7H_2O$, 0.2 M $C_6H_5Na_3O_7 \cdot 2H_2O$, 0.5 M $(NH_4)_2SO_4$, and 0.2 M $NaH_2PO_2 \cdot H_2O$ solution at 22 ± 2 °C.

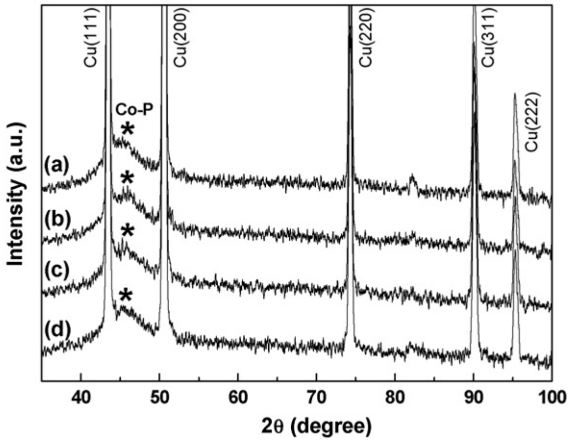

Fig. 7. XRD spectra for Co–P catalysts electroplated on Cu in the Co–P bath at a cathodic current density of (a) 0.001 A/cm^2, (b) 0.01 A/cm^2, (c) 0.1 A/cm^2, and (d) 1 A/cm^2.

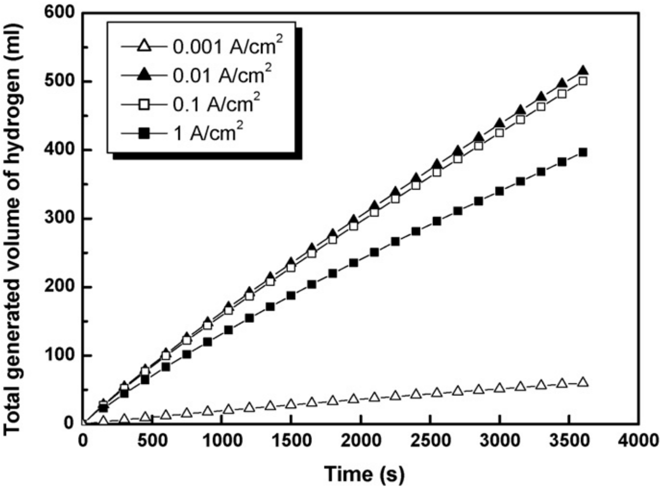

Fig. 8. Effects of a cathodic current density on the hydrogen generation kinetics of the Co–P catalysts, electroplated on Cu from the Co–P bath, in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

smoothly, and then micro-cracks were initiated on the smooth Co–P layer at a higher cathodic current density of 0.01 A/cm^2. When the cathodic current density increased more, the micro-crack density on the Co–P layer also increased due primarily to the increase in residual stress by the hydrogen evolution reaction. This is consistent with the previous report by Lucas et al. [13].

Fig. 6 shows that chemical composition of the Co–P catalysts is almost insensitive to the cathodic current density. The concentration of P in the Co–P layer was measured to be about 14 at.% for all Co–P electroplated at a different cathodic current density with a same deposited weight of 1 mg/cm^2.

In order to investigate the effects of a cathodic current density on the structure of the Co–P catalysts, XRD analysis were performed, and the results were presented in Fig. 7. Except the sharp peaks for Cu substrate, only the broad peak, as described in Fig. 2, was detected for all the Co–P catalysts, indicating that the electrodeposited Co–P catalysts were amorphous structure irrespective of the applied cathodic current density.

Fig. 8 shows the effects of a cathodic current density on the hydrogen generation properties of the electrodeposited Co–P catalysts in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C. The Co–P catalyst electroplated at 0.001 A/cm^2 showed low hydrogen generation rate of 110 ml/min g-catalyst, but with an increase in a cathodic current density between 0.01 A/cm^2 and 0.1 A/cm^2, the hydrogen generation rate of the Co–P catalyst increased up to 954 ml/min g-catalyst very rapidly. However, with further increase in the cathodic current density to 1 A/cm^2, hydrogen generation rate decreased gradually. Because Cu has very low catalytic activity for hydrolysis of $NaBH_4$, the effects of Cu substrate on hydrogen generation rate in alkaline $NaBH_4$ solution were negligible. It is notable that the catalytic activities of the Co–P catalysts largely depend on the cathodic current density, and the Co–P catalysts electroplated at 0.01 A/cm^2 shows the highest hydrogen generation rate.

3.3. Effects of electroplating time

The effects of electroplating time on the surface morphologies of the Co–P catalysts, formed on Cu in the Co–P bath at a

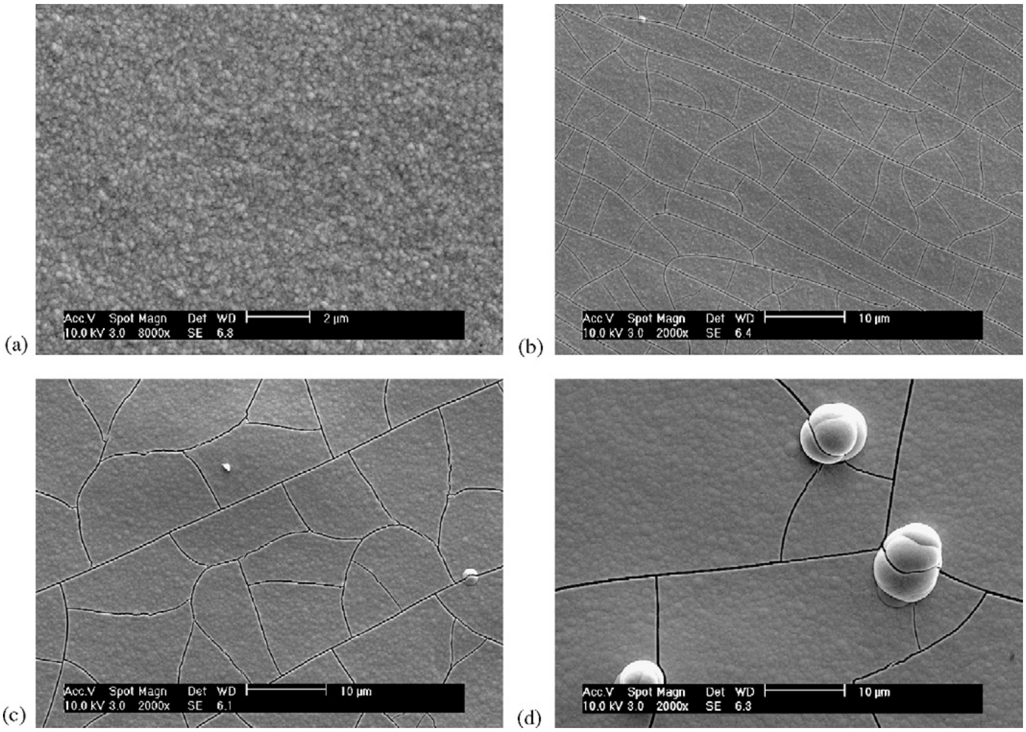

Fig. 9. SEM micrographs on the surface morphologies of Co–P catalysts electroplated on Cu in the Co–P bath at a cathodic current density of 0.01 A/cm^2 for (a) 120 s, (b) 360 s, (c) 1080 s, and (d) 3600 s.

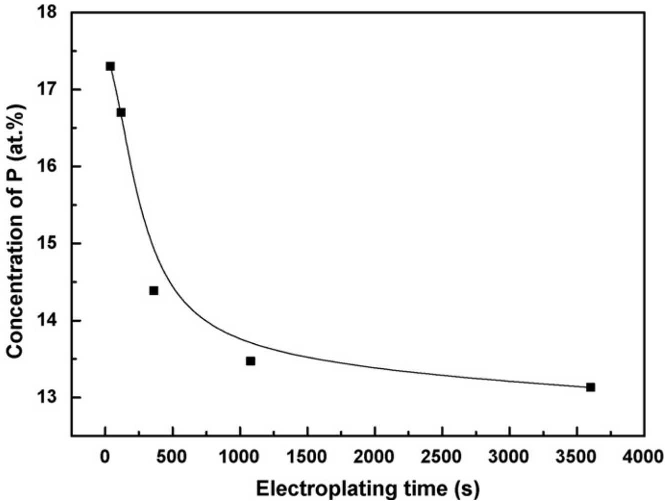

Fig. 10. Chemical composition of the electrodeposited Co–P catalysts as a function of electroplating time in which Co–P was deposited on Cu from 0.05 M $CoSO_4·7H_2O$, 0.2 M $C_6H_5Na_3O_7·2H_2O$, 0.5 M $(NH_4)_2SO_4$, and 0.2 M $NaH_2PO_2·H_2O$ solution at 22 ± 2 °C.

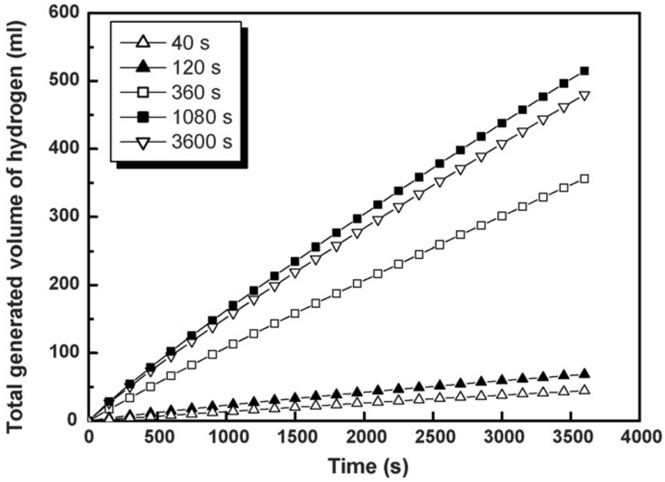

Fig. 12. Effects of electroplating time on the hydrogen generation kinetics of the Co–P catalysts, electroplated on Cu from the Co–P bath at a cathodic current density of 0.01 A/cm^2, in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

cathodic current density of 0.01 A/cm^2, are shown in Fig. 9. Co–P catalyst electroplated on Cu sheet for 40 and 120 s showed a smooth surface with tiny round shaped crystals of Co–P. As electroplating time increased from 120 to 360 s, micro-cracks were formed on the Co–P layer. However, with increasing the electroplating time from 360 to 3600 s, the micro-crack density on the Co–P layer decreased, demonstrating that the micro-cracks provided new nucleation sites and the deposition of Co–P were conducted on the micro-cracks, and finally the micro-cracks were annihilated. Fig. 9(d) clearly shows that new granular particles of Co–P were formed on the micro-cracks, which is the evidence that the micro-cracks acted as nucleation sites of the Co–P layer with an increase in the electroplating time. EDS analysis in Fig. 10 revealed that the chemical composition of the Co–P catalysts depended on the electroplating time. When the electroplating time increased from 40 to 1080 s, the concentration of P in the Co–P layer decreased from 17.3 to 13.5 at.%. However, the composition of the Co–P layer electroplated for 3600 s did not change significantly compared with that for 1080 s.

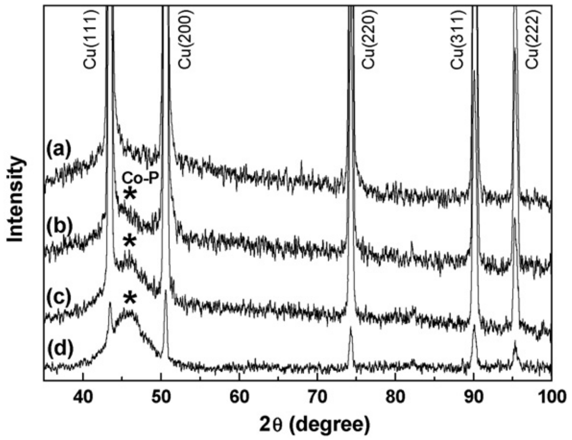

Fig. 11. XRD spectra for Co–P catalysts electroplated on Cu in the Co–P bath at a cathodic current density of 0.01 A/cm^2 for (a) 120 s, (b) 360 s, (c) 1080 s, and (d) 3600 s.

Fig. 11 shows the X-ray diffraction patterns of the electrodeposited Co–P catalysts as a function of electroplating time. When the electroplating time increased, the intensity of the broad peak for the electrodeposited Co–P catalysts also increased, indicating an increase in the thickness of the amorphous Co–P layer.

Fig. 12 shows the effects of electroplating time on the hydrogen volume generated on the electrodeposited Co–P catalysts in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C. The Co–P catalysts electroplated at 0.01 A/cm^2 for 40 s showed very low volume of generated hydrogen, but with increasing electroplating time up to 1080 s, the volume of generated hydrogen increased drastically. However, with further increasing electroplating time to 3600 s, the volume of generated hydrogen decreased slightly. When the hydrogen generation properties in Fig. 12 are compared with the EDS analysis on the chemical composition of the Co–P layer, it appears that the hydrogen generation properties of the Co–P catalysts are largely affected by the concentration of P in the Co–P catalysts; the catalytic activity of the Co–P catalyst for hydrolysis of $NaBH_4$ decreased with increasing P content in the Co–P catalyst.

From these experiments, it was found that the Co–P catalyst electroplated on Cu in the Co–P bath at a cathodic current density of 0.01 A/cm^2 for 1080 s showed the best hydrogen generation rate of 954 ml/min g-catalyst in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

4. Conclusions

The effects of cathodic current density and electroplating time on the microstructures of electrodeposited Co and Co–P catalysts and their hydrogen generation properties in alkaline

$NaBH_4$ solution were investigated to develop high performance catalysts for hydrogen generation from hydrolysis of $NaBH_4$. The findings of this work are as follows:

1. An amorphous Co–P electrodeposit with micro-cracks was formed by electroplating in the sulfate based Co bath containing $H_2PO_2^-$ ions. Chemical concentration of P in Co–P electrodeposit was measured to be about 14 at.% that is almost insensitive to the cathodic current density, but was sensitive to the deposition time, during the electrodeposition. Concentration of P in Co–P layer decreased from 17.3 to 13.1 at.% with an increase in plating time from 40 to 3600 s.
2. The Co–P catalyst exhibited much higher catalytic activity for hydrolysis of $NaBH_4$ than did the Co catalyst; the Co–P catalyst formed at 0.01 A/cm^2 showed 954 ml/min g-catalyst that is 18 times higher than that of the Co catalyst.
3. The catalytic activity of the electrodeposited Co–P catalyst for hydrolysis of $NaBH_4$ was found to be a function of both cathodic current density and plating time. Especially, the Co–13 at.% P catalyst electroplated on Cu in the Co–P bath at a cathodic current density of 0.01 A/cm^2 for 1080 s showed the best hydrogen generation rate of 954 ml/min g-catalyst in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30 °C.

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