### Transformation Characterization of Ni(OH)<sub>2</sub>/NiOOH in Ni-Pt Films Using an Electrochemical Quartz Crystal Microbalance for Ethanol Sensors

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The transformation characterization of Ni(OH)<sub>2</sub>/NiOOH in Ni-Pt films was investigated using an electrochemical quartz crystal microbalance (EQCM) in an alkaline electrolyte under various experiment conditions. The Ni-Pt films were prepared by electro-deposition on gold-coated quartz crystal chips. When cyclic voltammetry (CV) was performed continually, the OH<sup>-</sup> ions diffused into the Ni-Pt film to form Ni(OH)<sub>2</sub>. The transformation from mixed type Ni(OH)<sub>2</sub>/NiOOH to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH occurred gradually. The phase transformation of Ni(OH)<sub>2</sub>/NiOOH was strongly affected by the composition, deposited weight, and aging conditions of the Ni-Pt films. The results show that high Pt content or high deposited weight of Ni-Pt films postponed the transformation to the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phase.  $\beta$ -Ni(OH)<sub>2</sub> was directly formed by dipping fresh Ni-Pt films in KOH solution while mixed type Ni(OH)<sub>2</sub> was obtained after aging fresh Ni-Pt films in humid O<sub>2</sub> atmosphere. These two pre-aging conditions accelerate the phase transformation of Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH into  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH. After 1050 and 2100 cycles of the electro-oxidation process of ethanol, the Ni(OH)<sub>2</sub> phase in Ni-Pt films still remained in a  $\beta$ -Ni(OH)<sub>2</sub>-like phase with some  $\alpha$ -Ni(OH)<sub>2</sub>. The well-defined  $\beta$ -Ni(OH)<sub>2</sub> phase that formed in the Ni-Pt film after 1050 cycles of CV was more stable in a KOH solution than in a humid O<sub>2</sub> atmosphere at room temperature. Ni-Pt films were also evaluated as a sensing element for an ethanol sensor. [doi:10.2320/matertrans.M2010079]

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#### 1. Introduction

The nickel hydroxide/nickel oxyhydroxide couple is a redox pair that is widely used as a catalyst in the electrooxidation of organic compounds. Since nickel is cheap and the redox pair of Ni(OH)<sub>2</sub>/NiOOH can be easily formed on a nickel electrode, a series of electrochemical ethanol sensors based on nickel electrocatalysts was designed in our previous studies.<sup>1–4)</sup> However, the unstable sensitivity of nickel-based electrodes in the reproducibility test may result from the phase transformation of the redox pair Ni(OH)<sub>2</sub>/NiOOH.

The existence of the two forms of Ni(OH)<sub>2</sub> ( $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>) was first discovered by Bode *et al.*<sup>5)</sup> in 1966.  $\alpha$ -Ni(OH)<sub>2</sub> has a hydrated structure and its crystalline is disordered. The lattice parameters  $a_0$  (Ni-Ni) and  $c_0$  (the intersheet of the NiO layer) of  $\alpha$ -Ni(OH)<sub>2</sub> have been reported to be 0.542 nm and 0.806 nm, respectively.<sup>6)</sup>  $\beta$ -Ni(OH)<sub>2</sub> has a well-defined crystalline structure, and its lattice parameters  $a_0$  and  $c_0$  are 0.307 nm and 0.461 nm, respectively.<sup>7)</sup> The oxidation of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> produces  $\gamma$ -NiOOH and  $\beta$ -NiOOH, respectively. Figure 1 shows the phase transformation of Ni(OH)<sub>2</sub> in an alkaline solution during electrochemical processes. According to this diagram,  $\gamma$ -NiOOH is the oxidation product of  $\alpha$ -Ni(OH)<sub>2</sub>; however, it can also be produced by overcharging  $\beta$ -NiOOH. According to reference,<sup>8)</sup> the oxidation state of Ni changes from +2to +3 when  $\beta$ -Ni(OH)<sub>2</sub> is oxidized to  $\beta$ -NiOOH. However, the oxidation state of Ni changes from +2 to  $+3 \sim +3.75$ when  $\alpha$ -Ni(OH)<sub>2</sub> is oxidized to  $\gamma$ -NiOOH.  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> have different electron-exchange numbers during



Fig. 1 Diagram of phase transformation for nickel hydroxides.<sup>5)</sup>

oxidation. More electrons are transported in the  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH reaction because the oxidation state of  $\gamma$ -NiOOH is higher than that of  $\beta$ -NiOOH. This suggests that the unstable phase of Ni(OH)<sub>2</sub> is responsible for the unsteady electronic signal during ethanol sensing.

An electrochemical quartz crystal microbalance (EQCM) is used to simultaneously measure the electrochemical response and frequency/mass changes of electrodes. The behavior of ion exchange in Ni(OH)<sub>2</sub>/NiOOH was carefully studied in references.<sup>9–12)</sup> The mechanisms of ion exchange for  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH and  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH, which were investigated using a electrochemical quartz crystal microbalance (EQCM), are as follows: (1)  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH:

$$Ni(OH)_{2} + yM^{+} (H_{2}O)$$

$$\longleftrightarrow x/y(M_{y}H_{z}(NiO_{2})_{x}) + (2 - z)H^{+} + (2 - z - y)e^{-}$$
(H<sup>+</sup> transport model) (1)
$$Ni_{1-x}H_{x}(OH)_{2}0.64H_{2}O + xK^{+} + (x + y)OH^{-}$$

$$\longleftrightarrow Ni_{1-x}K_{x}OOH_{2-y}0.64H_{2}O + (x + y)H_{2}O + ye^{-}$$

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#### (2) $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH:

$$Ni(OH)_{2} \longleftrightarrow NiOOH + H^{+} + e^{-}$$

$$(H^{+} \text{ transport model}) (3)$$

$$Ni(OH)_{2} + OH^{-} \longleftrightarrow NiOOH + H_{2}O + e^{-}$$

$$(OH^{-} \text{ transport model}) (4)$$

According to the mechanisms, the mass change which was caused by the ion exchange of H<sup>+</sup>, OH<sup>-</sup>, H<sub>2</sub>O, and K<sup>+</sup> can be measured by EQCM. The results show that  $\alpha$ -Ni(OH)<sub>2</sub>/  $\gamma$ -NiOOH and  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH have distinct masschange behavior. Cations or water molecules participate in the exchange of H<sup>+</sup> or OH<sup>-</sup> ions during the redox reaction of  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH, resulting in an increase in the mass of the films during the oxidation of  $\alpha$ -Ni(OH)<sub>2</sub> and a decrease in the mass during the reduction of  $\gamma$ -NiOOH. In contrast, the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH redox reaction is believed to take place with the transport of  $H^+$  or  $OH^-$  ions without any contribution of cations or water molecules, resulting in a decrease in the mass of the films during the oxidation of  $\beta$ -Ni(OH)<sub>2</sub> and an increase in the mass during the reduction of  $\beta$ -NiOOH.<sup>8,9,11–18)</sup> Thus, the mass change behavior of the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH redox pair during the oxidation and reduction processes is opposite to that of  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH. Kim et al.9) demonstrated that the mass change behavior of  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH is related to the intercalation and deintercalation involving K<sup>+</sup> and H<sup>+</sup>, and that the intercalation and deintercalation of H<sup>+</sup> is responsible for the mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH during the redox reaction. In reaction (2),<sup>9)</sup> the valence states of Ni for  $\gamma$ -NiOOH which were calculated from reference<sup>9)</sup> lie within  $3 \sim 3.68$ .

Ni-Pt electrocatalysts have been shown to be promising candidates for the electro-oxidation of organic molecules.<sup>3,19–21)</sup> Thus, it is important to examine the phase transformation of Ni(OH)<sub>2</sub>/NiOOH in Ni-Pt films during cyclic voltammetry (CV). In this work, Ni-Pt films were prepared using the electro-deposition method on Au-coated quartz crystal chips to investigate the behavior of phase transformation of Ni(OH)<sub>2</sub>/NiOOH using EQCM. Ni/Pt composition, deposited weight, and aging conditions, which affect the phase transformation of Ni(OH)<sub>2</sub>/NiOOH in Ni-Pt film, were investigated.

#### 2. Experimental Method

#### 2.1 Preparation and characterization of Ni-Pt films

In the EQCM experiment, gold-coated quartz crystal was used as a substrate for preparing the working electrode. The diameters of the quartz crystal and gold disk were 13.7 and 5.11 mm, respectively. Ni and Ni-Pt alloy layers were prepared using an electroplating method on the gold film in solutions containing NiCl<sub>2</sub>·6H<sub>2</sub>O and H<sub>2</sub>PtCl<sub>6</sub>. All electrodeposition processes were conducted using the potential step in the electroplating solution without stirring at 25°C. After electro-deposition, the electrodes were rinsed with double deionized water. All chemicals utilized were of reagent grade without purification, and the solution was prepared with double de-ionized water. The chemical composition of the Ni-Pt films was characterized using a field emission electron



Fig. 2 Experiment instruments; (a) EQCM setup and (b) working electrode.

probe microanalyzer equipped with a wavelength-dispersive X-ray spectrometer (FE-EPMA, JXA-8500F). The depth profile of the films was analyzed with Auger electron spectroscopy (AES, PHI 700).

#### 2.2 EQCM measurements

The experiments were carried out in an EQCM cell which consisted of three round Teflon pieces. The cell had a height of 37 mm and a diameter of 35 mm. The top piece was the cell top, which had two holes to hold reference and counter electrodes, respectively. The center piece was the cell body, which was filled with electrolyte solution. The bottom piece was used for mounting the quartz crystal in the cell. Four screws were used to tighten the bottom piece and center piece together. The quartz crystal was placed between the center and bottom pieces. The seal consisted of two O-rings pressed together by the four screws.

Ag/AgCl (in saturated aqueous KCl) and the Pt plate were the reference and counter electrodes, respectively. The area of the working electrode was fixed at  $0.205 \text{ cm}^2$ . The electrolyte (0.4 M KOH<sub>(aq)</sub>) was prepared from analytical grade potassium hydroxide. The CV and frequency change were recorded using an EQCM analysis system (containing a CHI 405 potentiostat and an external box with oscillator circuitry) and CHI 405 electrochemical analysis system software in 0.4 M KOH<sub>(aq)</sub> solution, as shown in Fig. 2. All procedures and measurements were conducted at 25°C.

#### 3. Results and Discussion

### 3.1 Phase transformation of Ni(OH)<sub>2</sub>/NiOOH in Ni-Pt films during cyclic voltammetry

Figure 3 shows the CV and mass change results of the electro-deposited Ni-Pt film during 1050 cycles of CV in 0.4 M KOH solution. The scan rate was  $20 \text{ mV} \cdot \text{s}^{-1}$  and the temperature was  $25^{\circ}$ C. The chemical composition of the



Fig. 3 Cyclic voltammetry and mass change results of electro-deposited Ni-Pt (31 at% Ni and 69 at% Pt) film during 1050 cycles of cyclic voltammetry in 0.4 M KOH solution. Scan rate  $= 20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

electro-deposited Ni-Pt film was 31 at% nickel and 69 at% platinum. The deposited weight of the Ni-Pt film was 5 µg. The oxidation peak of Ni(OH)<sub>2</sub> shifted to higher positive potential with increasing number of cycles of CV, as shown in Fig. 3(a). The shift of the oxidation peak during the transformation of  $\alpha$ -Ni(OH)<sub>2</sub> into  $\beta$ -Ni(OH)<sub>2</sub> in the Ni-Pt films was smaller than that in the pure  $\alpha$ -Ni(OH)<sub>2</sub> films reported in the literature.<sup>10)</sup> The redox potential of Ni(OH)<sub>2</sub>/ NiOOH depends on the intersheet distance and charge capacity of Ni(OH)<sub>2</sub>/NiOOH.  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH has larger intersheet distance and charge capacity than  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH, resulting in smaller redox potential.<sup>8)</sup> Moreover, Kim<sup>10)</sup> concluded that the addition of Co changes the charge capacity of Ni(OH)2, reducing the shift of the redox potential to make it more positive. Therefore, the smaller shift of the oxidation peak could be due to the structure and phase transformation of Ni(OH)2 in the Ni-Pt films being influenced by the addition of platinum in the alloy

lattice. The oxidation peak of  $Ni(OH)_2$  became significantly larger with increasing number of cycles of CV. This implies that the formation of  $Ni(OH)_2$  in the Ni-Pt layer may not only occur in the beginning but also throughout the 1050 cycles of CV. This caused the amount of  $Ni(OH)_2$  in the Ni-Pt layer to continue to increase during CV. The generation rate of  $Ni(OH)_2$  gradually declined and eventually became stable after a large number of cycles of CV.

The mass change behavior of the Ni-Pt films during 1050 cycles of CV in 0.4 M KOH solution is shown in Fig. 3(b). The mass change behavior was not distinct enough for identifying the phase of Ni(OH)<sub>2</sub> in the Ni-Pt film at the 5th cycle of CV. The data suggest that the formation of Ni(OH)<sub>2</sub> from Ni and OH<sup>-</sup> in the Ni-Pt film and the oxidation of Ni(OH)<sub>2</sub> occurred simultaneously. This process involved the transport of H<sup>+</sup>, K<sup>+</sup>, and water molecules between the lattice and the solution at the 5th cycle of CV. This complicated the mass change behavior so the standard type of Ni(OH)<sub>2</sub> could not be definitely recognized. From the 50th to the 450th cycles, more Ni(OH)<sub>2</sub> continuously formed in the Ni-Pt film and the mass of the Ni-Pt film decreased during the oxidation of Ni(OH)<sub>2</sub> and increased during the reduction of NiOOH. This is associated with the mass change behavior of the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phase. H<sup>+</sup> ions were released into the electrolyte during the oxidation of  $\beta$ -Ni(OH)<sub>2</sub>, resulting in a decrease of the mass of the film; H<sup>+</sup> ions moved into the lattice of the film during the reduction of  $\beta$ -NiOOH, resulting in an increase of the mass of the film. The mass change results show that the phase of Ni(OH)<sub>2</sub> in the Ni-Pt film gradually transformed into the  $\beta$ -Ni(OH)<sub>2</sub>-like phase during the 50th to 450th cycles of CV. In addition, the film contained increasingly more  $\beta$ -Ni(OH)<sub>2</sub> with increasing number of cycles of CV. The mass change behavior exhibited the phase transformation of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH from the 600th to the 1050th cycle of CV. It can be concluded that well-defined  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH formed in the Ni-Pt films after a long period of CV. According to the results, the signal of sensing ethanol would be variable due to the phase transformation from  $\alpha$ -Ni(OH)<sub>2</sub> to  $\beta$ -Ni(OH)<sub>2</sub> on the Ni-Pt film in the beginning of sensing ethanol. With the time of sensing increasing,  $\alpha$ -Ni(OH)<sub>2</sub> converting to  $\beta$ -Ni(OH)<sub>2</sub> completely and stayed in  $\beta$ -Ni(OH)<sub>2</sub>. The stability of sensing would become better.

According to reference,<sup>9)</sup> the theoretical mass change of  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH can be calculated using the following equations:

 $Ni_{1-x}H_x(OH)_20.64H_2O + xK^+ + (x + y)OH^-$ 

$$\leftrightarrow \operatorname{Ni}_{1-x} K_x \operatorname{OOH}_{2-y} 0.64 \operatorname{H}_2 \operatorname{O} + (x+y) \operatorname{H}_2 \operatorname{O} + y \operatorname{e}^- (5)$$

$$Q = ynF \tag{6}$$

$$n = m_{\rm film} / M W_{\rm film} \tag{7}$$

$$\Delta m_{\rm e}/(Q/F) = \Delta m_{\rm t}/ny \tag{8}$$

$$\Delta m_{\rm t} = n[xAW_{\rm K^+} - (x+y)AW_{\rm H^+}]$$
(9)

where Q is the anodic charge; F is Faraday's constant;  $m_{\text{film}}$  is the mass of the film;  $MW_{\text{film}}$  is the molecular weight of  $\alpha$ -Ni(OH)<sub>2</sub>;  $\Delta m_{\text{e}}$  is the measured mass change;  $\Delta m_{\text{t}}$  is the theoretical mass change; and  $AW_{\text{K}^+}$  and  $AW_{\text{H}^+}$  are the atomic weights of K<sup>+</sup> and H<sup>+</sup>, respectively. According to reference,<sup>9)</sup> it suggests that current efficiency can be calculated

by the equation  $\Delta m_e/(Q/F) = \Delta m_t/ny$  (or  $\Delta m_e/\Delta m_t = Q/nFy$ ). However, the theoretical anodic charge and y are related by the equation  $Q = ynF = y(m_{\text{film}}/MW_{\text{film}})F$ . For pure  $\alpha$ -Ni(OH)<sub>2</sub> film, the mass of the film;  $m_{\text{film}}$ , is equal to the mass of  $\alpha$ -Ni(OH)<sub>2</sub> film and theoretical anodic charge can be obtained. In this research, the film contains the mixture of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> during CV. Unlike the system in the literature,<sup>9)</sup> the deposited film is consisted of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> which is generated during CV. Therefore,

$$Q = ynF$$
  
=  $y \left[ \left( \frac{m_{\text{film}-\alpha-\text{Ni(OH)}_2}}{MW_{\text{film}-\alpha-\text{Ni(OH)}_2}} \right) + \left( \frac{m_{\text{film}-\beta-\text{Ni(OH)}_2}}{MW_{\text{film}-\beta-\text{Ni(OH)}_2}} \right) \right] F$  (10)

However, the actual ratio of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> is unknown at each stage of CV and it is very difficult to quantify the real mass of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> in the film. At present, it may be considered that the relationship between the measured mass change and the theoretical mass change is a function of the rate of Ni(OH)<sub>2</sub> production and the ratio of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>.

#### 3.2 Depth profile of Ni-Pt films during cyclic voltammetry

Figure 4 shows the depth profile obtained using AES for electrodeposited Ni-Pt film (31 at% Ni and 69 at% Pt) before and after CV. The sputtering rate was 2.2 nm per minute. The relative thickness of the Ni-Pt layer was estimated to be about 24 nm. As shown in Fig. 4(a), except for the most exterior surface of Ni-Pt film and the interface between Ni-Pt film and the Au substrate, the intensity of oxygen in the Ni-Pt film was very low before CV. This implies that no Ni(OH)<sub>2</sub> was obtained in the fresh Ni-Pt films. Oxygen was present on the exterior surface of the Ni-Pt film and in the interface between the Ni-Pt film and the Au substrate due to a tiny amount of oxygen absorption after and before the electro-deposition of the Ni-Pt film in the atmosphere, respectively. After 150 and 1050 cycles of CV, the oxygen intensity markedly increased, as shown in Fig. 4(b). The Ni-Pt film had the highest content of oxygen after 1050 cycles of CV. The AES results also show that the quantity of Ni(OH)<sub>2</sub> increased in the Ni-Pt layer during CV sweeps.

## 3.3 Effect of Ni-Pt film chemical composition on the phase transformation of Ni(OH)<sub>2</sub>/NiOOH during cyclic voltammetry

Various compositions of Ni-Pt film were prepared using the electroplating method. The composition effect on the transformation of Ni(OH)<sub>2</sub>/NiOOH in the Ni-Pt films is discussed below. Figure 5 shows CV and mass change results of electro-deposited Ni-Pt films with various compositions for 150 cycles of CV in 0.4 M KOH solution. Figure 5(a) shows that the films had different values of peak potential and peak current at the 5th cycle of CV, which was due to the different chemical compositions of the thin films. The anodic peaks shifted to more positive potential with increasing platinum content in the films. It has been reported that Pt favors pulling electrons;<sup>2)</sup> therefore, it is reasonable that the oxidation potential of Ni(OH)<sub>2</sub> shifted to more



Fig. 4 Depth profile obtained using AES of electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) before and after cyclic voltammetry; (a) fresh Ni-Pt film and (b) after 150 and 1050 cycles of cyclic voltammetry. Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

positive potential with increasing Pt content. The magnitude of the peak current became larger with higher content of nickel due to more Ni(OH)2 being formed and electrooxidized to NiOOH during CV. Of note, the mass change behaviors of the Ni-Pt films with nickel content levels of 31 at%, 36 at%, and 73 at% were slightly different, as shown in Fig. 5(a). They do not have the standard mass changing pattern of  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH or  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH due to the complicated exchange of H<sup>+</sup>, K<sup>+</sup>, and water molecules between the Ni-Pt film and electrolyte at the 5th cycle of CV. This implies that the films contained a small amount of  $\beta$ -Ni(OH)<sub>2</sub> and a large amount of  $\alpha$ -Ni(OH)<sub>2</sub>. In contrast, the mass change behavior of pure nickel film exhibited a clear redox behavior of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH at the 5th cycle of CV. This shows that a large amount of  $\beta$ -Ni(OH)<sub>2</sub> formed in pure Ni film at the beginning of the CV sweep.

Since OH<sup>-</sup> ions continued to react with Ni to form new Ni(OH)<sub>2</sub> in the film, the anodic and cathodic peak currents of all Ni-Pt films increased after 150 cycles of CV, as shown



Fig. 5 Cyclic voltammetry and mass change results of the electro-deposited Ni-Pt film with various compositions after 150 cycles of cyclic voltammetry in 0.4 M KOH solution; (a) 5th cycle and (b) 150th cycle. Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

in Fig. 5(b). Except for the films with 31% Ni content, all anodic peaks of the films shifted very slightly to less positive potential. In Fig. 5(b), all mass change behaviors of the Ni-Pt films correspond to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH. Films with a high content of nickel (i.e., 73 at% Ni) had better and clearer mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH than that of films with low nickel content (i.e., 31 at% Ni). According to previous research,<sup>19)</sup> the addition of Pt into films may deform the FCC lattice of Ni.<sup>19)</sup> In addition,  $\alpha$ -Ni(OH)<sub>2</sub> has a disordered structure and a large intersheet distance which is caused by the intercalation of  $H_2O^{.5,8)}$  The results (Fig. 5(a)) show that the redox reaction of Ni(OH)<sub>2</sub>/NiOOH is involved in the intercalation and deintercalation of K<sup>+</sup> and H<sub>2</sub>O in alloy films. Therefore, it is reasonable to consider that a disordered lattice allows more K<sup>+</sup> ions and H<sub>2</sub>O molecules to pass in and out of the Ni-Pt films than the amount in pure Ni films during CV. This suggests that higher platinum content postpones the transformation from  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH in Ni-Pt films; however, the phase of Ni(OH)<sub>2</sub>/NiOOH eventually transforms into  $\beta$ -Ni(OH)<sub>2</sub>/  $\beta$ -NiOOH after 150 cycles of CV. This also implies the signal of sensing ethanol on the Ni-Pt films would be more fluctuant during sensing ethanol than that on the Ni films due to platinum postponing the transformation from  $\alpha$ -Ni(OH)<sub>2</sub>/

 $\gamma$ -NiOOH to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH in Ni-Pt films. It could make the signal of sensing ethanol of Ni-Pt films decay much more slowly than Ni films during a long period of sensing time.

# 3.4 Effect of deposited weight of Ni-Pt films on the phase transformation of Ni(OH)<sub>2</sub>/NiOOH during cyclic voltammetry

The Ni-Pt films were prepared using the electroplating method. The deposited weight of the films was controlled to be from 5 to 20 µg in order to investigate the effect of deposited weight on the phase transformation of Ni(OH)<sub>2</sub> in the Ni-Pt films. Figure 6 shows mass change results of the electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) with various deposited weights during CV in 0.4 M KOH solution. The scan rate was  $20 \text{ mV} \cdot \text{s}^{-1}$  and the temperature was  $25^{\circ}\text{C}$ . The deposited weights of the Ni-Pt films were fixed at 5, 10, 15, and  $20 \,\mu g$  respectively. Figure 6(a) shows that Ni-Pt films with weights of 15 and 20 µg had a higher mass increase in the oxidation reaction and a higher mass drop in the reduction reaction than those of films with weights of 5 and  $10 \,\mu g$  at the 5th cycle of CV. This can be attributed to the redox reaction of Ni(OH)<sub>2</sub> being accompanied by a large exchange of H<sub>2</sub>O, and  $K^+$  in 15 and 20 µg Ni-Pt films. This suggests that more



Fig. 6 Mass change of the electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) with deposited weights of 5, 10, 15, and 20 µg during cyclic voltammetry in 0.4 M KOH solution; (a) 5th cycle and (b) 150th cycle. Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}\text{C}$ .

 $\alpha$ -Ni(OH)<sub>2</sub> developed in films with weights of 15 and 20 µg than in films with weights of 5 and  $10 \mu g$ . In Fig. 6(b), the exchange of K<sup>+</sup> or H<sub>2</sub>O can be found during the redox reaction of Ni(OH)<sub>2</sub> in 15 and 20 µg films after 150 cycles of CV. It can be clearly seen that the 15 and  $20 \,\mu g$  films show mass change behavior of the intermediate phase or  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH type, which is different from the mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH. After 150 cycles of CV, the mass change behavior of Ni-Pt films with weights of 5 and 10  $\mu$ g shows that the phase transformation rate from  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH was faster than that for films with weights of 15 and  $20 \,\mu g$ . The term "rate" in this paper means "how fast the mass change behavior of Ni(OH)<sub>2</sub> in the films completely transforms to the mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub>". Therefore, the rate of mass change behavior of Ni(OH)2 transforming to mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub> is associated with the rate of Ni(OH)<sub>2</sub> transforming to  $\beta$ -Ni(OH)<sub>2</sub> in this paper. Ni-Pt films with 15 and 20 µg deposited weights exhibited phase transformation which led to a small amount of  $\beta$ -Ni(OH)<sub>2</sub> combined with a large amount of  $\alpha$ -Ni(OH)<sub>2</sub> in the redox reaction. Figure 7 shows the depth profile of oxygen content



Fig. 7 Depth profile of oxygen content in Ni-Pt films (31 at% Ni and 69 at% Pt) with deposited weights of 5, 10, and 20  $\mu$ g after 150 cycles of CV in KOH solution. Scan rate = 20 mV·s<sup>-1</sup>,  $T = 25^{\circ}$ C.

in the Ni-Pt films (31 at% Ni and 69 at% Pt) with various deposited weights after 150 cycles of CV in KOH solution. The film thicknesses of the Ni-Pt films with 5, 10, and  $20 \mu g$ deposited weights were about 26, 48, and 90 nm, respectively. It can be seen that film thickness increased proportionally with deposited weight of Ni-Pt films. In addition, oxygen content of the Ni-Pt films after 150 cycles of CV markedly increased with increasing deposited weight. These results show that Ni-Pt layers with higher deposited weight were thicker and may form more  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH during CV. These thicker layers were involved in the exchange of K<sup>+</sup> or H<sub>2</sub>O during the redox reaction and exhibited the mass change behavior of the intermediate phase or  $\alpha$ -Ni(OH)<sub>2</sub>/  $\gamma$ -NiOOH type, as shown in Fig. 6(b). It can be concluded that increasing the weight of deposited films led to more disordered  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH in the Ni-Pt films in the redox reaction during CV experiments. These thick films did not rapidly transform from  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH to  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH like thin films did after 150 cycles of CV. This suggests that thick films would have better stability on sensing ethanol than thin films. The signal of sensing ethanol on thick films would decline slightly with time.

# 3.5 Effect of aging conditions of Ni-Pt films on the phase transformation of Ni(OH)<sub>2</sub>/NiOOH during cyclic voltammetry

Aging experiments were conducted on Ni-Pt films in order to examine the aging effects on the phase transformation of Ni(OH)<sub>2</sub>. Figure 8 shows CV and mass change results of the electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) after being dipped in 0.4 M KOH solution for 0, 12, 24, and 48 h. The scan rate was 20 mV·s<sup>-1</sup> and the temperature was 25°C. Figure 8(a) shows that the anodic peaks of Ni(OH)<sub>2</sub> in the Ni-Pt films with aging pretreatment moved to more positive potential and that their current became larger compared to Ni-Pt film that was not dipped in KOH solution. In addition, Ni-Pt films with aging pretreatment tended to exhibit more obvious mass change behavior of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH compared to that of fresh film. The degree of welldefined  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH redox behavior of the Ni-Pt



Fig. 8 Cyclic voltammetry and mass change of electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) after being dipped in 0.4 M KOH solution for various periods of time; (a) fresh Ni-Pt film, (b) 12 h, (c) 24 h, and (d) 48 h. Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

films is proportional to the KOH aging time. This is due to the OH<sup>-</sup> ions diffusing into Ni-Pt films and forming  $\beta$ -Ni(OH)<sub>2</sub> during dipping in KOH solution. It can be concluded that  $\beta$ -Ni(OH)<sub>2</sub> can be created in Ni-Pt film by dipping the film in KOH solution at room temperature. The highest quantity of  $\beta$ -Ni(OH)<sub>2</sub> in Ni-Pt films was obtained after 48 h of aging. This suggests that dipping Ni-Pt films in KOH solution for a period of time before sensing ethanol can help the Ni(OH)<sub>2</sub> stabilize into the  $\beta$ -Ni(OH)<sub>2</sub> phase and improve the signal stability of sensing ethanol on the Ni-Pt film.

The CV and mass change results of Ni-Pt film (31 at% Ni and 69 at% Pt) after aging in O<sub>2</sub> atmosphere in a humidity range of 60 to 70% RH for various periods of aging are shown in Fig. 9. The scan rate was  $20 \text{ mV} \cdot \text{s}^{-1}$  and the deposited weight of the Ni-Pt film was  $5 \mu \text{g}$  at  $25^{\circ}$ C. All of Ni-Pt films had larger anodic and cathodic currents than those of fresh film at the 5th cycle of CV. Furthermore, increasing the aging time in O<sub>2</sub> atmosphere from 12 to 48 h increased the amount of mass change of redox reaction at the 5th cycle of CV. This indicates that when the Ni-Pt films were placed in a humid O<sub>2</sub> atmosphere, some O<sub>2</sub> and water molecules became absorbed into the film to produce more Ni(OH)<sub>2</sub> in the layer.

From Fig. 9(b), the fresh Ni-Pt film without aging in a humid O<sub>2</sub> atmosphere had larger anodic and cathodic peak currents with increasing number of cycles (up to 150) of CV. The Ni-Pt films aged in a humid O<sub>2</sub> atmosphere had no change in the peak current with increasing number of cycles. However, the peak shape and over-potential changed after 150 cycles of CV. The mass change behavior of all aged Ni-Pt films tended to turn into the mass change behavior of the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phase. In addition, the films aged for 24 and 48 h had a larger mass change in the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH redox reaction than those of fresh films and the films aged for a period of 12 h. The Ni-Pt films thus had more Ni(OH)<sub>2</sub> in the Ni-Pt layer after aging in a humid O<sub>2</sub> atmosphere at room temperature. The phase of  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH formed after 150 cycles of CV.

Figure 10(a) shows CV results of Ni-Pt films dipped in 0.4 M KOH solution after the films were aged by CV for 300, 1050, and 2100 cycles in 0.4 M KOH solution containing 0.1 M ethanol. The deposited weight of the Ni-Pt film was 5 µg. A higher peak current and a more positive shift of peak potential were observed for Ni-Pt films pretreated with 300, 1050, and 2100 cycles of CV in 0.1 M ethanol solution compared to those of films without pretreatment (see Fig. 3(a) and Fig. 10(a)). The extra cathodic current at 0.2 V as shown in Fig. 10(a) can be considered to be due to a few NiOOH being reduced to Ni(OH)2 or some impurities adsorbed to the surface being reduced during the reverse scanning of CV. From Fig. 10(b), the films aged using CV in ethanol solution exhibited mass change behavior of the  $\beta$ - $Ni(OH)_2/\beta$ -NiOOH phase. This indicates that the phases of Ni(OH)<sub>2</sub>/NiOOH in the films remained mostly in the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phases after many cycles of the electrooxidation process of ethanol. However, the aged Ni-Pt films (after many cycles of the electro-oxidation process of ethanol) contained some hydrated nickel hydroxide, as shown in Fig. 10(b). The redox of Ni(OH)<sub>2</sub>/NiOOH, which accompanies the electro-oxidation reaction of ethanol, complicated the ion exchange between the Ni-Pt film and the electrolyte. This suggests that the structure transformations of Ni(OH)<sub>2</sub> and Ni-Pt films were influenced by the adsorption, diffusion, and reaction of ethanol molecules in the solution. Moreover, the adsorption and reaction of ethanol molecules with electrode materials could accelerate the aging action and worsened the stability of sensing ethanol. The few ng difference in mass change at the beginning and the end of 1050 cycle and 2100 cycle CV (Fig. 10(b)) can be attributed to some extra reactants or products adsorbed or desorbed during CV, especially after many cycles of CV involving ethanol oxidation. This is due to ethanol, the intermediate product, and the final product possibly adsorbed into the films after ethanol oxidation.

The CV results of Ni-Pt films which were continuously aged in KOH solution or  $O_2$  atmosphere in a humidity range of 60 to 70% RH for 48 h after 1050 cycles of CV are shown



Fig. 9 Cyclic voltammetry and mass change results of electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) after aging in O<sub>2</sub> atmosphere in a humidity range of 60 to 70% RH for various periods of time; (a) 5th cycle and (b) 150th cycle. Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

in Fig. 11(a). The peak current of the aged Ni-Pt films was reduced and the peak potential shifted to higher positive potential compared to that of the film treated with only 1050 cycles of CV. According to Fig. 11(b), the mass change of the film already processed with 1050 cycles of CV had no change in shape and magnitude after the film was additionally aged in KOH solution for 48 h. This indicates that the phase of Ni(OH)<sub>2</sub> remained in the  $\beta$ -Ni(OH)<sub>2</sub> phase when Ni-Pt films were stored in KOH solution for 48 h after 1050 cycles of CV. However, the magnitude of mass change of the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phases decreased for the film stored in an  $O_2$  atmosphere (60 to 70% RH) for 48 h after 1050 cycles of CV. This suggests that the original structure of  $\beta$ -Ni(OH)<sub>2</sub> produced after 1050 cycles of CV was broken by the exterior oxygen and water molecules. The results indicate that  $\beta$ -Ni(OH)<sub>2</sub> generated in Ni-Pt films after many cycles of CV can be preserved in KOH solution for 48 h. On the other hand,  $\beta$ -Ni(OH)<sub>2</sub> formed after 1050 cycles of CV may be destroyed if the film is stored in a humid  $O_2$ atmosphere for 48 h, which is different from the result for fresh film which was aged directly in a humid O<sub>2</sub> atmosphere. For fresh Ni-Pt films, there was initially no Ni(OH)<sub>2</sub>. Ni(OH)<sub>2</sub> was created in the films after the films were placed in an  $O_2$  atmosphere with  $60 \sim 70\%$  RH for 48 h (see Fig. 9). Consequently, the  $\beta$ -Ni(OH)<sub>2</sub> phase formed in Ni-Pt films after 1050 cycles was more stable in alkaline solutions than in damp atmospheres at room temperature.

### **3.6** Evaluation of the practical utility of Ni-Pt films for an ethanol sensor

According to the results in this work, the working electrode of an ethanol sensor obtained by electroplating Ni-Pt films would have an unstable sensitivity in the initial stage of the sensing processes due to the formation of mixed type Ni(OH)<sub>2</sub>. The electrodes (31 at% Ni and 69 at% Pt) can be activated and stabilized by sweeping cyclic voltammetry for 1050 cycles before use as sensors. After performing many ethanol sensing tests, the phase of Ni(OH)<sub>2</sub> in Ni-Pt films remained in the  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phase and contained little  $\alpha$ -Ni(OH)<sub>2</sub>. Ni(OH)<sub>2</sub> can be generated in the electrodes by aging fresh electrodes in a humid O<sub>2</sub> atmosphere. The well-defined  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH phase can be created in Ni-Pt film by dipping fresh film in KOH solution at room temperature. It is important to ensure that the electrodes are stored appropriately before and after use to avoid significant aging, which would result in fluctuating sensitivity of the ethanol sensor for long term stability tests. It is also necessary to precisely control the preparation conditions (i.e., the composition and film thickness) to ensure that electrodes have good reproducibility.



Fig. 10 Cyclic voltammetry (in 0.4 M KOH without ethanol) and mass change results of electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) after aging for 300, 1050, 2100 cycles of cyclic voltammetry in 0.4 M KOH solution containing 0.1 M ethanol. Scan rate  $= 20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}$ C, and the deposited weight of the Ni-Pt film was 5 µg.

#### 4. Conclusion

Ni-Pt thin films were prepared using electroplating. The phase transformation of Ni(OH)<sub>2</sub>/NiOOH formed in the film was studied using EQCM technology in an alkaline electrolyte (0.4 M KOH<sub>(aq)</sub>) under various experiment conditions. Ni(OH)<sub>2</sub> was continually generated by OH<sup>-</sup> ions moving into the film and bonding with Ni atoms in Ni-Pt films during a long period of CV. Increasing the platinum content increased the inhibition for the formation of the  $\beta$ -Ni(OH)<sub>2</sub> phase in the Ni-Pt film. However, the phase of Ni(OH)<sub>2</sub> in Ni-Pt films (31 at% Ni and 69 at% Pt) transformed into a  $\beta$ -Ni(OH)<sub>2</sub>-like phase after 150 cycles of CV and finally settled in a welldefined  $\beta$ -Ni(OH)<sub>2</sub> phase after 1050 cycles of CV. Ni-Pt films with a higher deposited weight were thicker and formed more  $\alpha$ -Ni(OH)<sub>2</sub> during CV. The results showed that well-defined  $\beta$ -Ni(OH)<sub>2</sub> was created in the films when fresh Ni-Pt films were dipped in KOH solution at room temperature. When fresh Ni-Pt films were place in a humid O<sub>2</sub> atmosphere, some  $O_2$  and water molecules entered the films to form  $\beta$ -Ni(OH)<sub>2</sub>, which then mixed with some  $\alpha$ -Ni(OH)<sub>2</sub>. After many cycles of the electro-oxidation process of ethanol, the phase of Ni(OH)<sub>2</sub> in Ni-Pt films still remained in a  $\beta$ -Ni(OH)<sub>2</sub>-like



Fig. 11 Cyclic voltammetry and mass change results of electro-deposited Ni-Pt film (31 at% Ni and 69 at% Pt) after 1050 cycles of cyclic voltammetry and aging in KOH solution or O<sub>2</sub> atmosphere in a humidity range of 60 to 70% RH for 48 h; Scan rate =  $20 \text{ mV} \cdot \text{s}^{-1}$ ,  $T = 25^{\circ}\text{C}$ , and the deposited weight of the Ni-Pt film was 5 µg.

phase with some  $\alpha$ -Ni(OH)<sub>2</sub>. After sweeping 1050 cycles of CV, the well-defined  $\beta$ -Ni(OH)<sub>2</sub> phase that formed in the Ni-Pt film was more stable in KOH solution than in a humid O<sub>2</sub> atmosphere at room temperature.

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