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Electrochemical Properties of Nickel Hydroxide/Oxyhydroxide Film Prepared Electrochemically

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Abstract: - Nickel hydroxide and oxyhydroxide films were prepared electrochemically and its electrochemical properties were examined using cyclic voltammetry and a.c. impedance method in solution and air environments. In both the solution and air environments, nickel oxyhydroxide film was observed to be much more conductive than nickel hydroxide film. The conduction through nickel oxyhydroxide film seems to be largely due to the film itself, not by free water in the film. The detailed conduction mechanism through nickel oxyhydroxide film, including protonic and electronic conductivity, will be further examined.

Key-Words: - Nickel hydroxide, cathodic deposition, CV, AC impedance, battery, supercapacitor, fuel cell.

1 Introduction

Nickel hydroxide has been widely used as a positive electrode material for alkaline rechargeable batteries [1-3], supercapacitor [4] or molten carbonate fuel cell [5]. Nickel hydroxide is normally prepared as powders to increase its activity. Nickel hydroxide is known as a semi-conductor and shows poor electric conductivity [2]. Thus, it should be bonded to a suitable porous conducting support to be used as an electrode.

Nickel hydroxide can be formed as a film using a cathodic deposition method in nickel nitrate solution [4,6]. nickel oxyhydroxide film can be obtained by oxidation of the cathodically deposited nickel hydroxide film. If the nickel hydroxide film or nickel oxyhydroxide film show a good protonic conductivity and poor electronic conductivity, it may be used as an electrolyte material for fuel cells. However,, at present, little has been known about electrochemical properties of the films of nickel hydroxide and nickel oxyhydroxide especially in gaseous environments.

In this work, nickel hydroxide film was prepared cathodically from nickel nitration solution and its electrochemical properties were investigated in 1M NaOH solution and in air using cyclic voltammogram and AC impedance method.

2 Experimental

Nickel hydroxide film was deposited cathodically on the Ni foil at a constant current density of 10 mA/cm^2 and 20 ^oC for 300 s in 1M $Ni(NO_3)_2$ solution. The Ni foil with an exposed area of 1 cm^2 was degreased in acetone, etched in concentrated nitric acid for 60 s, and then used for the deposition.

Cyclic voltammetry of the deposited nickel hydroxide film was carried out in 1M NaOH to stabilize the deposited $Ni(OH)_2$ film at 20 mV/s and 20 ^oC with various upper potential limits from 0.35 V_{SCE} up to 0.43 V_{SCE}.

AC impedance measurement was conducted on the deposited $Ni(OH)_2$ film in 1M NaOH at various applied potentials using three-electrode cell arrangement, and in air at various temperatures from 20 ^oC to 100 ^oC, as shown in Table 1, using two-electrode cell arrangement. The two electrode cell consists of Ni disc/film/Ni foil prepared simply by placing a Ni disc onto the deposited film.

Cyclic voltammetry and AC impedance measurement were performed with an Autolab potentiostat/galvanostat by Echochemie. A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

3 Results and Discussion

$Ni(OH)_2$ films deposited cathodically were tested by cyclic voltammetry and a.c. impedance method in both the solution and air environments. Figure 1 shows cyclic voltammograms of the $Ni(OH)_2$ film at 20 mV/s in 1M NaOH with different upper potential limits. During the positive going scan of potential, the anodic current begins to increase around 0.3 V_{SCE} and at the same time the color of the film changes from green to black. In the negative going scan of potential, the current changes from anodic to cathodic around 0.33 V_{SCE}. The anodic current above 0.3 V_{SCE} during the positive potential scan and cathodic

current below 0.33 V_{SCE} during the negative potential scan are attributed to the oxidation of nickel hydroxide and reduction of nickel oxyhydroxide, respectively.

$$Ni(OH)_2 = NiOOH + H^+ + e^- \quad (1)$$

The color of the film turns back to green around 0 V_{SCE} during the negative potential scan between 0 V_{SCE} and 0.35 V_{SCE}. However, when the upper potential limit is increased to 0.37 V_{SCE}, the color did not back to green during the potential cycling between 0 V_{SCE} and 0.37 V_{SCE} at 20 mV/s, implying that the nickel oxyhydroxide remains in the film.

When the upper potential limit is not higher than 0.4 V_{SCE}, the anodic and cathodic current densities slightly increase with increasing number of cycle, as indicated by the arrows in Fig. 1 (a) and (b). In contrast, if the upper potential limit is higher than 0.4 V_{SCE}, the anodic and cathodic current densities decrease with increasing number of cycle, as indicated by the arrows in Fig. 1 (c). The film was observed to be broken into particles in part after CV experiment in the case of Fig. 1(c). These suggest that the decreased anodic and cathodic current densities with the number of cycle result from the reduced volume of the film. Thus, in order to obtain a stable film of NiOOH, the applied potential should not exceed 0.4 V_{SCE} in 1M NaOH solution.

Figure 2 presents AC impedance spectra obtained from the $Ni(OH)_2$ film at various applied potentials in 1M NaOH solution. Straight lines on the Nyquist plot were observed below 0.3 V_{SCE}, suggesting a diffusion limited process. The magnitude of impedance of the film at 10 Hz drops markedly from 100 ohms at 0.3 V_{SCE} to 5.2 ohms at 0.35 V_{SCE}, indicating that nickel oxyhydroxide is much more conductive than nickel hydroxide in 1M NaOH solution.

AC impedance of the films were measured on the nickel hydroxide film and nickel oxyhydroxide using two-electrode cell arrangement of Ni/film/Ni in air. The nickel hydroxide film showed straight lines on the Nyquist plot in air as well as in the solution. On the other hand, nickel oxyhydroxide film in air showed a semicircle on the Nyquist plot, as demonstrated in Fig. 3.

The impedance spectra of nickel oxyhydroxide in air showed only one semicircle with zero real impedance at high frequency, suggesting that the film impedance does not arise from the Ni/film interface but only from the film itself. As can be seen in Fig. 3, the resistance of nickel oxyhydroxide film increased slightly from 93 ohms to 143 ohms by drying of the film, but the film capacitance is markedly lowered two orders from 3.8 μF to 0.015 μF by the drying process.

The large decrease of the film capacitance is ascribed to the removal of free water in the film by the drying process.

Table 1. AC impedance measurements on $Ni(OH)_2$ film at various conditions.

	Applied potential	Temperature
(a) in 1M NaOH	0.25 V_{SCE}	25 °C
	0.3 V_{SCE}	
	0.35 V_{SCE}	
(b) in air	0 V_{SCE}	20 °C
		40 °C
		60 °C
		80 °C
		100 °C

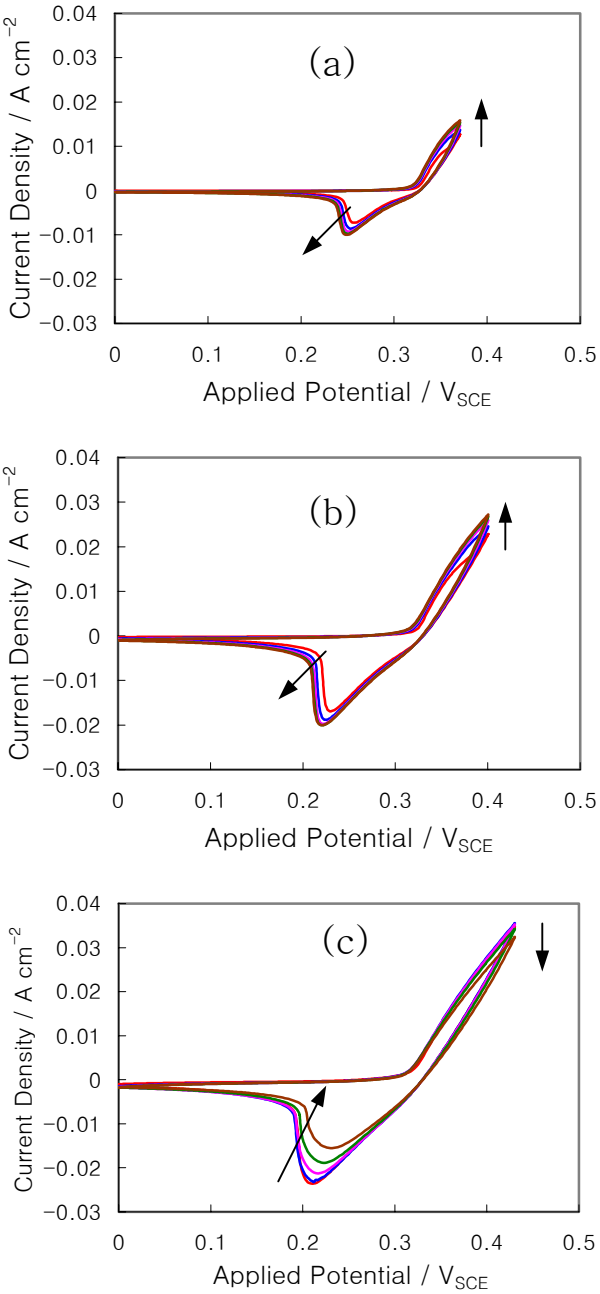

Fig. 1 Cyclic voltammograms of $Ni(OH)_2$ film at 20 °C and 20 mV/s in 1M NaOH with different upper potential limits of : (a), 0.35 V_{SCE}; (b), 0.4 V_{SCE}; (c) .43 V_{SCE}.

On the other hand, the film resistance is just increased about 50 % after drying even though free water is removed from the film. This suggests that conduction through the film is largely due to the nickel oxyhydroxide film itself, not by free water in the film.

AC impedance of nickel oxyhydroxide film was measured with temperature during the cooling process after heating, and typical spectra were presented in Fig. 4. The magnitude of semicircle increased with cooling the cell. This suggests that the conduction through the nickel oxyhydroxide film is an activation process. The detailed conduction mechanism of the nickel hydroxide/nickel oxyhydroxide film, including protonic and electronic conduction, will be further studied in the following paper.

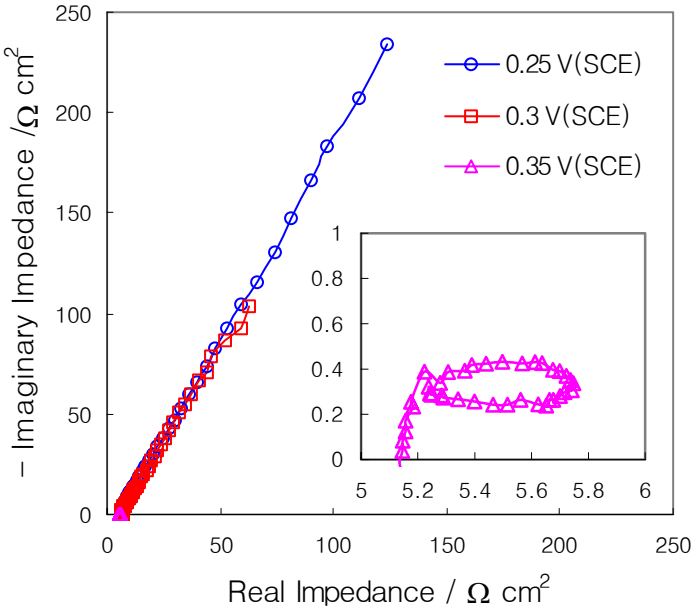

Fig. 2 AC impedance spectra for $Ni(OH)_2$ film in 1M NaOH at applied potentials of : (a), 0.3 V_{SCE} (b),35V_{SCE}.

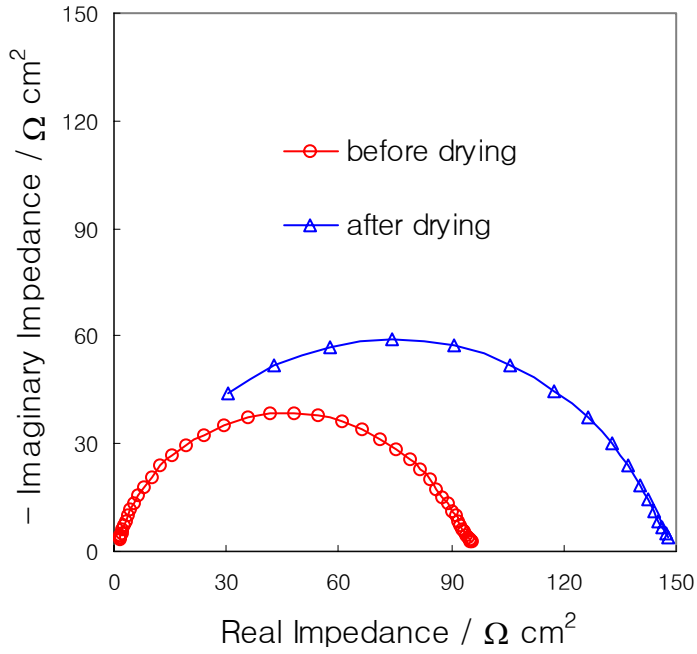

Fig. 3 AC impedance spectra for NiOOH film in air at 0 V and 20 °C (a) before and (b) after drying of the film.

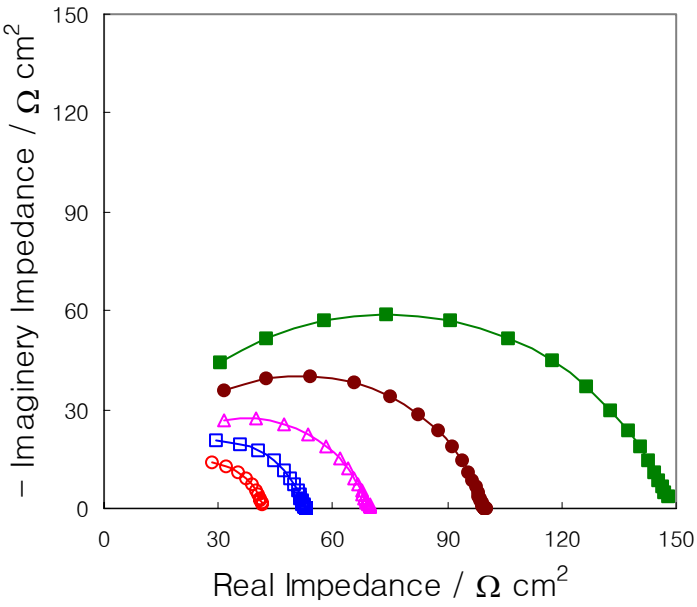

Fig. 4 AC impedance spectra for NiOOH film in air at 0 V with temperature : ○, 100 °C; □, 80 °C; Δ, 60 °C; ●, 40 ; ■, 20 °C.

4 Conclusions

1. Nickel oxyhydroxide film obtained electrochemically was observed to be much more conductive than nickel hydroxide film in both the 1M NaOH solution and air environments.

2. The impedance spectra of nickel oxyhydroxide in air showed only one semicircle with zero real impedance at high frequency, suggesting that the film impedance arises only from the film itself.
3. The conduction through nickel oxyhydroxide film seems to be largely due to the film itself, not by free water in the film. The detailed conduction mechanism through nickel oxyhydroxide film, including protonic and electronic conductivity, is necessary to be further examined.

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