

Quantitative estimation of reversibility of the discharge process undergone by nickel hydroxide film cathodically deposited on pure nickel as a positive supercapacitor electrode using cyclic voltammetry and potential drop method

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Abstract

This work presents the way how to evaluate the degree of reversibility of the discharging process undergone by the nickel hydroxide film cathodically deposited on pure nickel as a positive electrode for electrochemical capacitor using the combined cyclic voltammetry and potential drop method, supplemented by galvanostatic discharge and open-circuit potential transient methods. The time interval necessary just to establish the current reversal of anodic to cathodic direction from the moment just after applying the potential inversion of anodic to cathodic direction, was obtained on cyclic voltammogram. The cathodic charge density passed upon dropping the applied potential, was calculated on potentiostatic current density-time curve. Both the time interval and the cathodic charge density in magnitude can be regarded as being measures of the degree of reversibility of the discharging process undergone by the positive active material for supercapacitor, *i.e.*, the longer the time interval is, the lower is the degree of reversibility and the greater the cathodic charge density is, the higher is the degree of reversibility. From the applied potential dependences of the time interval and cathodic charge density, discharge at 0.42 V_{sc} was determined to be the most reversible.

Key words : Reversibility, Supercapacitor discharge, Nickel hydroxide, Cyclic voltammogram, Potentiostatic current transient

1. Introduction

The capacitor has been used to store information in computer memories, to regulate voltages in power supplies, to establish electric fields or to store electric energy. Interest in electrochemical capacitor for energy-storage, also called supercapacitor, has arisen in recent years on account of the possibility of utilizing it in hybrid electric vehicle power systems.¹⁻⁷⁾ Supercapacitor which can store electric energy much more than the conventional type of physical dielectric capacitor, can be classified into two groups: one is electric double layer capacitor (EDLC) based on a charge separation at the electrode/electrolyte interface; the other is pseudocapacitor associated with various electrochemical reactions on the electrode surface. It was reported that the best electrode material, at which pseudocapacitance is developed, is ruthenium oxide RuO₂, and other materials of IrO₂, Co₃O₄, MoO₂ and WO₃ exhibit pseudocapacitive behaviour.^{2,5)}

In general, the discharge rate of capacitor is faster than that of battery, and the term of power output of capacitor is shorter than that of battery. It was reported¹⁾ that transitional behaviour between battery and supercapacitor characteristics

can arise, depending upon the discharge rate. Nickel hydroxide is a typical active material used for a positive electrode in battery systems,^{8,9)} and its discharge rate is crucially determined by diffusion rate of protons in the films.¹⁰⁻¹³⁾ Several investigators^{12,13)} suggested that the diffusion coefficient of protons in nickel hydroxide films is a function of the state of electric charge of the active material, which is dependent upon the applied potential. Therefore, it is expected that the discharge rate of the nickel hydroxide films would be significantly influenced by the applied potential.

Many studies¹⁻⁷⁾ have been made on the supercapacitive behaviour of the active materials, which results from reversibility of their discharging processes. Conway²⁾ suggested that ideal supercapacitive behaviour of the active materials is manifested by "mirror-image" anodic and cathodic voltammograms, *i.e.*, reversal of the direction of potential sweep immediately leads to an opposite discharging current, provided the process is kinetically reversible. However, the degree of reversibility of the supercapacitor discharging process has not been quantitatively considered even in his work.²⁾ Moreover, since most of other investigators³⁻⁷⁾ have concentrated just on finding new active materials that exhibit supercapacitive behaviour, at present little is known about the way how to evaluate the degree of reversibility of the

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supercapacitor discharging process.

The present work was undertaken to propose the way how to quantitatively estimate the degree of reversibility of the discharging process undergone by the nickel hydroxide film cathodically deposited on pure nickel electrode as a positive electrode for supercapacitor as a function of applied potential in 0.01 M NaOH solution. For this purpose, cyclic voltammetry and potential drop method were mainly employed. In addition, galvanostatic discharge experiment and open-circuit potential transient measurement were supplemented.

2. Experimental

2.1. Preparation of Ni(OH)₂ film

The pure nickel rod electrode of 5.56 mm diameter was set in a block of polyethylene and the upper surface of the block was ground with silicon carbide papers up to 2000 grit to expose the cross section of the electrode to the solution. The electrode surface was finally polished with 1 μm Al₂O₃ powder on wet cloth and then rinsed with distilled water. Thin film of nickel hydroxide Ni(OH)₂ was cathodically deposited on the pure nickel substrate at room temperature for 2, 4 and 8 min at an applied cathodic current density of 0.5 mA cm⁻² in 0.05 M Ni(NO₃)₂ solution, as detailed elsewhere.^{8,9} After deposition of Ni(OH)₂ on pure nickel electrode, the nickel hydroxide film electrode was washed in distilled water and then used as a positive electrode* for electrochemical measurements.

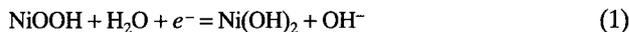
2.2. Electrochemical measurements

A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte used for electrochemical experiments was 0.01 M NaOH solution. In this work, four kinds of electrochemical measurements were carried out at ambient temperature by using an EG&G Model 263A Potentiostat/Galvanostat.

Galvanostatic discharge experiment was conducted on the cathodically deposited Ni(OH)₂ film at an applied cathodic current density of 0.1 mA cm⁻². The discharge data were collected on the fully charged film*. Cyclic voltammetry was performed on the Ni(OH)₂ film in the potential range of -0.5 to 1.0 V_{SCE} with a scan rate of 20 mV s⁻¹. Cyclic voltammetry was conducted to 5 cycles and the voltammogram of the fifth cycle was presented. The Ni(OH)₂ film electrode was first polarized to the potential ranging from 0.32 V_{SCE} to 0.46 V_{SCE} for 200s, and then the potential was dropped by 10 mV of a small potential step. From the moment just after dropping the applied potential, the resulting current was recorded with time. The cathodic current density transient was numerically integrated over time from t=0 to t=1s to obtain the cathodic charge density passed for 1s. Open-circuit potential was measured with time on the Ni(OH)₂ film from the moment just after interrupting the applied potential. The film electrode was previously polarized to the potential 0.34 to 0.46 V_{SCE} for 200s.

3. Results and Discussion

Fig. 1 gives galvanostatic discharge curves obtained from the completely charged nickel hydroxide films** in 0.01 M NaOH solution. The discharge curves are characterized by a potential plateau around 0.38 V_{SCE} followed by an abrupt decrease in potential. The potential plateau around 0.38 V_{SCE} arises from the reduction reaction of NiOOH to Ni(OH)₂^{13,14)}



It is well known¹⁵⁻¹⁷⁾ that the normal cycling reaction of the electrode involves back and forth conversion between NiOOH and Ni(OH)₂ phases, which are separate phases rather than end members of a continuous solid solution.

The abrupt decrease in potential in Fig. 1 is due to the complete discharge of the film**. Assuming that NiOOH is reduced fully to Ni(OH)₂ just after the potential decreases abruptly and the surface area of the active material is constant, irrespective of the film thickness, the thickness of the film (*d*) can be calculated from the charge passed until the time at which the potential decreases abruptly in Fig. 1

$$d = \frac{QM}{|z|F\rho A} \quad (2)$$

where *Q* is the charge passed during galvanostatic discharge; *M*, the molar mass of Ni(OH)₂; |*z*|, the number of electrons transferred (|*z*|=1) according to reaction (1); *F*, the Faraday constant; ρ, the density of Ni(OH)₂ and *A* represents the

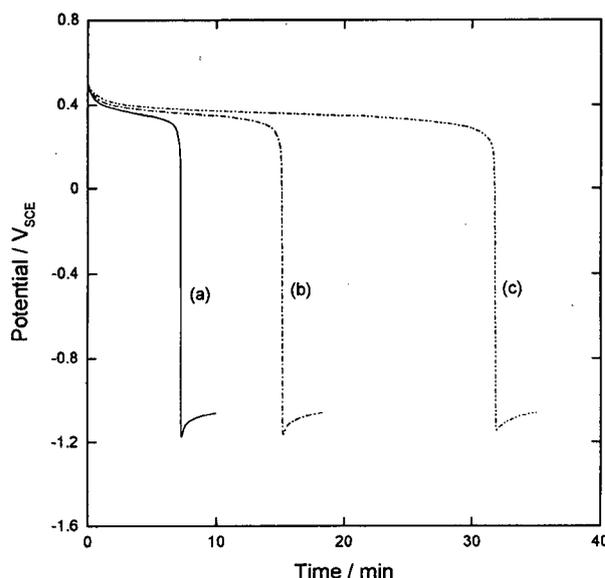


Fig. 1. Galvanostatic discharging curves of nickel hydroxide films at an applied cathodic current density of 0.1 mA cm⁻² in 0.01 M NaOH solution. The films were previously deposited at an applied cathodic current density of 0.5 mA cm⁻² for : (a) 2 min, (b) 4 min, (c) 8 min.

* Discharged state of the nickel hydroxide film as a positive electrode of supercapacitor means reduced state of the NiOOH/Ni(OH)₂ redox-couple, *i.e.*, hydrogen is injected into the film. Conversely, charged state means just the opposite.

**Hydrogen is injected into the film.

exposed area of the specimen ($A=0.242 \text{ cm}^2$). If ρ is assumed as 3.5 g cm^{-3} ,^{12,13} a charge density of 1 mC cm^{-2} corresponds to the film thickness of about 2.74 nm . The film thickness was calculated to be proportional to deposition time as summarized in Table 1, indicating cathodic deposition of Ni(OH)_2 with a constant rate. It is well known that the Ni(OH)_2 film is precipitated by the chemical reaction of nickel ions with hydroxide ions (OH^-) formed by reductions of the nitrate ion and water during cathodic polarization.^{8,9}

Fig. 2 demonstrates a plot of $-dQ/dV$ against applied potential, obtained from galvanostatic discharge curve (Fig. 1). The occurrence of a peak around $0.38 \text{ V}_{\text{SCE}}$ on $-dQ/dV$ versus potential curve, which is characteristic of the phase transition during charge/discharge,^{18,19} manifests the transition between NiOOH and Ni(OH)_2 phases around $0.38 \text{ V}_{\text{SCE}}$ according to reaction (1).

Fig. 3 shows a cyclic voltammogram for the nickel hydroxide film cathodically deposited for 2 min. The anodic and cathodic current density peaks, corresponding to oxidation and reduction of the nickel hydroxide film,⁹ were observed. A constant current density (current plateau) region was observed during charge*** in the potential range of about 0.30 to $0.44 \text{ V}_{\text{SCE}}$. A constant current density (i) under a constant rate of potential sweep (dV/dt), implies a constant value of capacitance (C), independent of potential. This is called pure capacitive behaviour of the active material.

$$C = i / (dV/dt) \quad (3)$$

Table 1. The thickness of Ni(OH)_2 film cathodically deposited for various deposition times at 0.5 mA cm^{-2} in $0.05 \text{ M Ni(NO}_3)_2$ solution

deposition time	2 min	4 min	8 min
film thickness (μm)	0.12	0.25	0.53

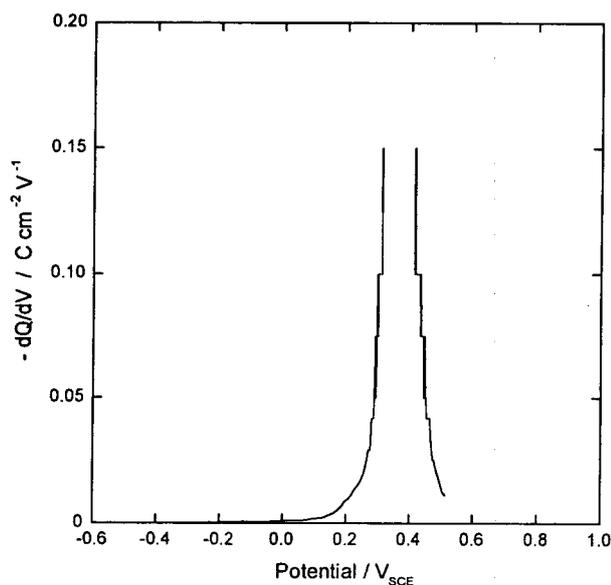


Fig. 2. Typical plot of derivative of $-dQ/dV$ against applied potential obtained from Fig. 1. The film was previously deposited at an applied cathodic current density of 0.5 mA cm^{-2} for 2 min.

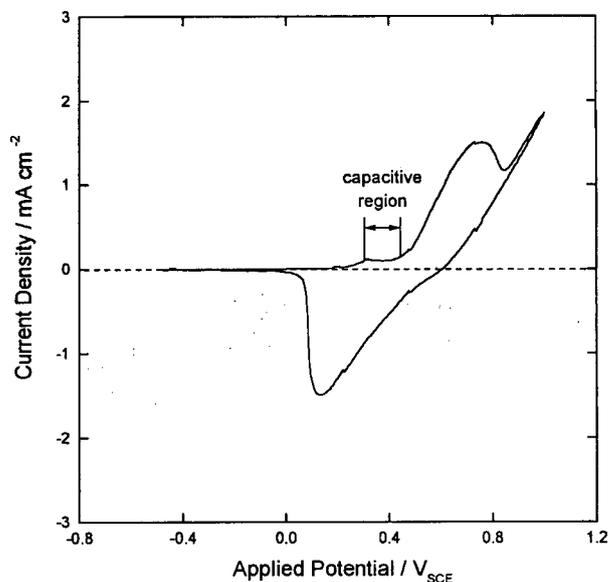


Fig. 3. Cyclic voltammogram of nickel hydroxide film in the potential range between $-0.5 \text{ V}_{\text{SCE}}$ and $1.0 \text{ V}_{\text{SCE}}$ at a constant scan rate of 20 mV s^{-1} in 0.01 M NaOH solution. The film was previously deposited at an applied cathodic current density of 0.5 mA cm^{-2} for 2 min.

From a constant value of i on a voltammogram and a given potential scan rate, pseudocapacitance can be calculated according to equation (3). The pseudocapacitance of the nickel hydroxide film, which arises from reaction (1), was calculated to be about 5 mF cm^{-2} . This value is much higher than pseudocapacitance of about 0.6 mF cm^{-2} at heavily electrochemically hydrogen-adsorbed noble metals and double-layer capacitance of about 0.03 mF cm^{-2} at carbon, reported by Conway.²

Pseudocapacitance is not a true electrostatic capacitance. In fact it arises from faradaic reactions in one direction and/or another, which are reversible. In order to define a quantitative scale of reversibility of the discharging process undergone by the film as a positive electrode for supercapacitor at a given potential, we measured cyclic voltammograms with various anodic potential limits and the results are demonstrated in Fig. 4. The opposite discharging current density (cathodic current density) was observed at a certain time interval after the direction of potential sweep was reversed at various anodic potential limits ranging from 0.36 to $0.50 \text{ V}_{\text{SCE}}$. In a supercapacitor, energy should be withdrawable on discharge by changing the direction of potential sweep. This behaviour stems from reversibility of the discharging process undergone by the active materials, which is manifested by "mirror-image" anodic and cathodic voltammograms, *i.e.*, reversal of the direction of potential sweep immediately leads to an opposite discharging current, provided the process is kinetically reversible.² This behaviour was shown in cyclic voltammograms of RuO_2 .^{2,20} However, the Ni(OH)_2 film requires a certain period of time between two moments of the potential inversion and current reversal of anodic to

***This means hydrogen is extracted from the Ni(OH)_2 film.

cathodic direction on potential sweep. This implies that the $\text{Ni}(\text{OH})_2$ film exhibits a slower discharge rate than ideal supercapacitor material like RuO_2 . In some cases an active material with high energy density and medium discharge rate like the $\text{Ni}(\text{OH})_2$ film, which is between ideal capacitor and battery, can be utilized practically.

We define a certain period of time as the time interval t_{int} needed just to establish the current reversal of anodic to cathodic direction in response to a change in the direction of potential sweep from the moment just after applying the potential inversion of anodic to cathodic direction on cyclic voltammogram. Thus, we can regard the value of t_{int} as being a measure of the degree of reversibility of the discharging process undergone by the nickel hydroxide film as a positive electrode for supercapacitor at a given potential, *i.e.*, the shorter the value of t_{int} is, the more is reversibility of the discharging process improved. Fig. 5 displays the value of t_{int} obtained from Fig. 4 as a function of anodic potential limit. The value of t_{int} decreased slowly with increasing anodic potential limit up to $0.42 \text{ V}_{\text{SCE}}$ and then increased rapidly, indicating that discharge is the most reversible at $0.42 \text{ V}_{\text{SCE}}$, but less reversible at other applied potentials 0.36 to $0.50 \text{ V}_{\text{SCE}}$ than $0.42 \text{ V}_{\text{SCE}}$.

Fig. 6 presents typical cathodic current density transients on semilogarithmic scale obtained from the nickel hydroxide film in 0.01 M NaOH solution from the moment just after dropping the respective applied potential 0.32 to $0.46 \text{ V}_{\text{SCE}}$ by the amount of 10 mV . The discharging current density showed a constant value (current plateau) in the initial stage and then decreased with time. The occurrence of the initial current plateau indicates that the hydrogen transport in the initial stage proceeds via an interface controlled phase boundary movement rather than a diffusion controlled phase bound-

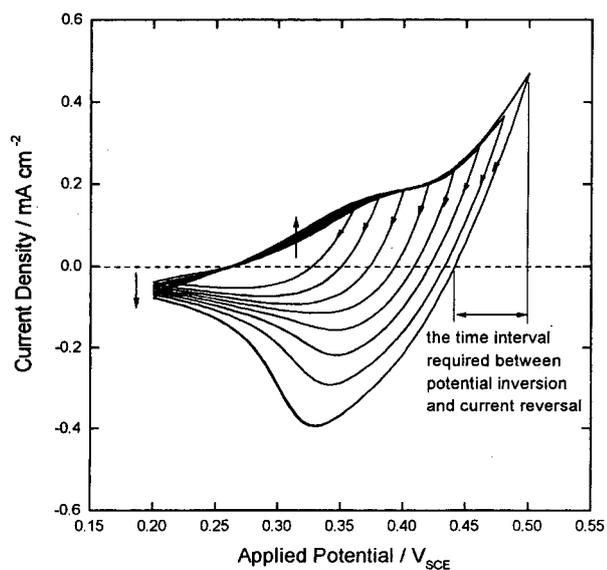


Fig. 4. Cyclic voltammograms of nickel hydroxide film with various anodic potential limits at a given cathodic potential limit of $0.2 \text{ V}_{\text{SCE}}$ and a constant scan rate of 20 mV s^{-1} in 0.01 M NaOH solution. The film was previously deposited at an applied cathodic current density of 0.5 mA cm^{-2} for 2 min.

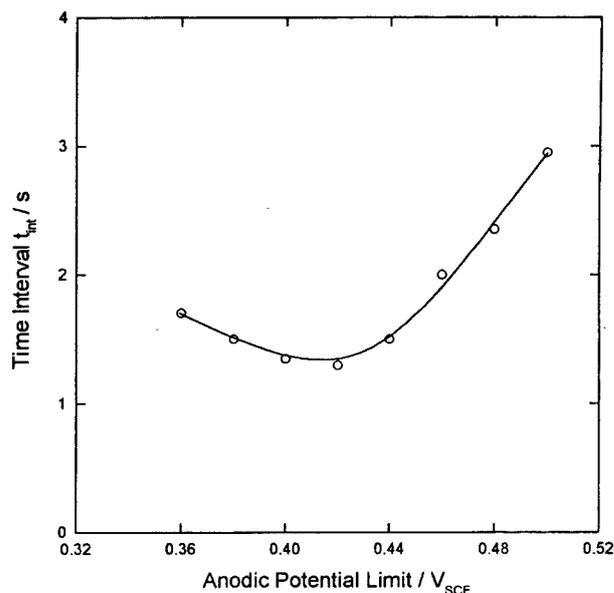


Fig. 5. Plot of the time interval t_{int} necessary between two moments of the potential inversion and current reversal of anodic to cathodic direction on potential sweep versus anodic potential limit obtained from Fig. 4.

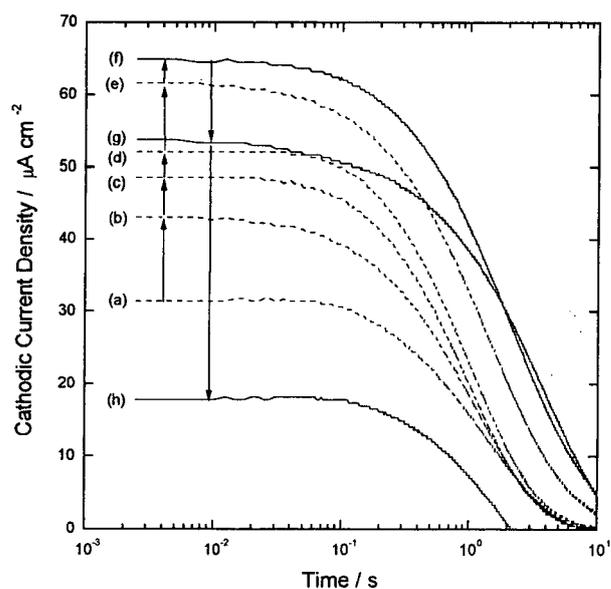


Fig. 6. Typical cathodic current density-time curves obtained from nickel hydroxide film in 0.01 M NaOH solution from the moment just after dropping the applied potential of (a) 0.32 , (b) 0.34 , (c) 0.36 , (d) 0.38 , (e) 0.40 , (f) 0.42 , (g) 0.44 , (h) $0.46 \text{ V}_{\text{SCE}}$ by the amount of 10 mV . The film was previously deposited at an applied cathodic current density of 0.5 mA cm^{-2} for 2 min and then subjected to the respective applied potential ranging between 0.32 and $0.46 \text{ V}_{\text{SCE}}$ for 200s.

dary movement, as suggested in a previous paper.²¹⁾

The cathodic charge density Q_{cath} passed for 1s during dropping the applied potential was obtained by integrating the potentiostatic cathodic current density-time curve (Fig. 6) over time from $t=0$ to $t=1\text{s}$. The value of Q_{cath} is illustrated as a function of applied potential in Fig. 7. The value of Q_{cath} increased slowly with increasing applied potential up to

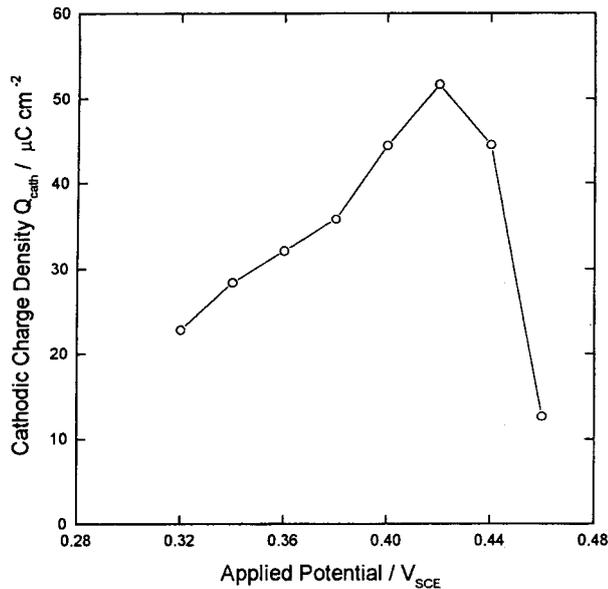


Fig. 7. Plot of the amount of cathodic charge density Q_{cath} passed for 1s against applied potential, obtained by integrating cathodic current density transient over time from $t=0$ to $t=1s$ in Fig. 6.

0.42 V_{SCE} and then decreased rapidly. Finally the cathodic charge density Q_{cath} disappeared above 0.46 V_{SCE} , indicating that the reversible behaviour of the discharge process appears only below 0.46 V_{SCE} if the nickel hydroxide film undergoes the discharge process as a positive electrode of supercapacitor. The attainment of a minimum value of t_{int} coincides with the quantity of Q_{cath} reaching a maximum value. As the applied potential increases, reversibility of the discharge process is slowly improved up to a maximum at 0.42 V_{SCE} and then is rapidly degraded. From the maximum value of Q_{cath} of 50 $\mu C cm^{-2}$ passed for 1s (Fig. 7), the pseudocapacitance of the nickel hydroxide film was obtained to be 5 $mF cm^{-2}$.

Fig. 8 exhibits potentiostatic cathodic current density transients on logarithmic scale obtained from the nickel hydroxide films in 0.01 M NaOH solution from the moment just after dropping the applied potential 0.42 V_{SCE} to 0.41 V_{SCE} . It is noted that the duration of the initial current plateau increased with increasing film thickness. Assuming that the duration of the initial current plateau approximately corresponds to the time required for the NiOOH/Ni(OH)₂ phase boundary to move from the film surface to the substrate/film interface, one can calculate the velocity for the phase boundary movement as suggested by Yoon and Pyun.²¹⁾ From the values of the duration of the initial current plateau and film thickness, the velocity of the phase boundary movement was calculated as about 3.2×10^{-4} , 3.0×10^{-4} and 2.0×10^{-4} $cm s^{-1}$ for the films of 0.12 μm , 0.24 μm and 0.50 μm thickness, respectively. These values are much higher as compared to the value in order of 10^{-6} $cm s^{-1}$ estimated for the 0.5 μm thickness film by Yoon and Pyun.²¹⁾

Recognizing that in the present work we employed a small potential step of 10 mV rather than large potential steps of 180 to 400 mV used by Yoon and Pyun,²¹⁾ it seems reasonable that it is not sufficient for the NiOOH/Ni(OH)₂

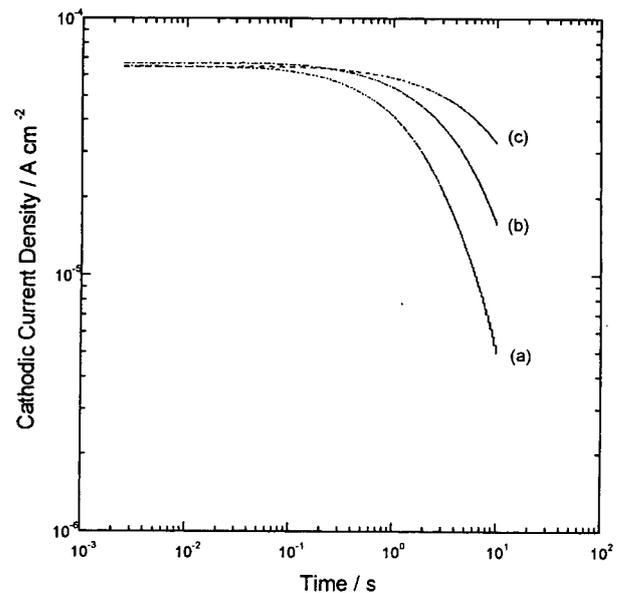


Fig. 8. Plots of cathodic current density against time obtained from nickel hydroxide films in 0.01 M NaOH solution from the moment just after dropping the applied potential 0.42 V_{SCE} to 0.41 V_{SCE} . The films were previously deposited at an applied cathodic current density of 0.5 $mA cm^{-2}$ for (a) 2 min, (b) 4 min and (c) 8 min, and then subjected to the applied potential of 0.42 V_{SCE} for 200s.

phase boundary to move through the whole film in thickness under the application of such a small potential drop of 10 mV which is regarded as a driving force for the phase boundary movement. In other words one should take the real distance of the phase boundary movement as much

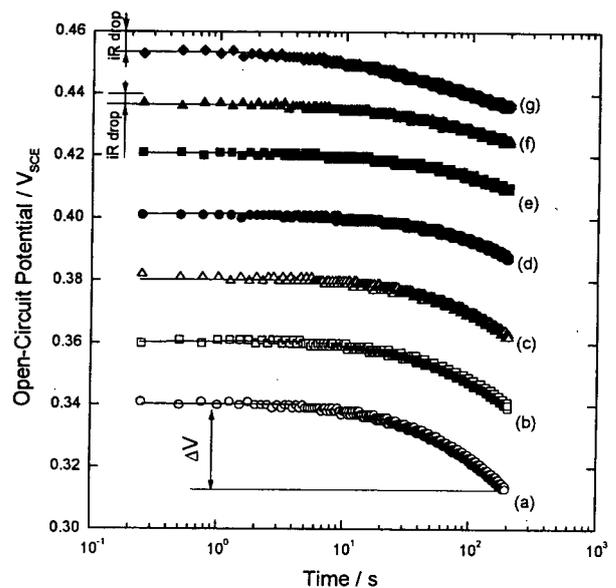


Fig. 9. Open-circuit potential transients obtained from nickel hydroxide film in 0.01 M NaOH solution from the moment just after interrupting the applied potential of : (a) 0.34, (b) 0.36, (c) 0.38, (d) 0.40, (e) 0.42, (f) 0.44, (g) 0.46 V_{SCE} . The film was previously deposited at an applied cathodic current density of 0.5 $mA cm^{-2}$ for 2 min, and then subjected to the respective applied potential ranging between 0.34 and 0.46 V_{SCE} for 200s.

thinner than each of the film thickness. By considering that the amount of potential step employed by Yoon and Pyun²¹⁾ is several ten times larger than that used in this work, the real velocity of the phase boundary movement obtained in this work may be reduced to a value in order of 10^{-6} cm s⁻¹, which is consistent with the value reported by Yoon and Pyun.²¹⁾ The effect of large and small potential steps on the potentiostatic current transients has been discussed in detail elsewhere.²²⁻²⁴⁾

Fig. 9 depicts open-circuit potential transients on semi-logarithmic scale obtained from the nickel hydroxide film from the moment immediately after interrupting the respective applied potential 0.34 to 0.46 V_{SCE} in 0.01 M NaOH solution. The open-circuit potential showed a constant value (potential plateau) in the initial stage and then decreased with time. It is noted that above 0.42 V_{SCE} iR drop appeared and the extent of change in open-circuit potential during the lapse of time 200s (ΔV) showed a minimum value at 0.42 V_{SCE}, indicating that the corresponding equilibrium composition of the film is attained the most rapidly at 0.42 V_{SCE}.

4. Conclusions

The degree of reversibility of the discharging process undergone by the nickel hydroxide film cathodically deposited on pure nickel electrode as a positive electrode for supercapacitor, was evaluated as a function of applied potential in 0.01 M NaOH solution by analyzing the combined cyclic voltammogram and cathodic current transient, supplemented by galvanostatic discharge curve and open-circuit potential transient. The time interval t_{int} required between two moments of the potential inversion and current reversal of anodic to cathodic direction on potential sweep, was determined on cyclic voltammogram. The value of t_{int} decreased slowly with increasing applied potential up to 0.42 V_{SCE} and then increased rapidly. In addition, the cathodic charge density Q_{cath} passed upon dropping the applied potential was calculated by integrating the cathodic current transient with respect to time. The value of Q_{cath} increased slowly up to 0.42 V_{SCE} and then decreased rapidly. Hence we can take both the quantity of t_{int} and Q_{cath} as being a quantitative scale of reversibility of the discharging process. From the applied potential dependences of t_{int} and Q_{cath} , the discharging process at 0.42 V_{SCE} was obtained to be the most reversible.

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