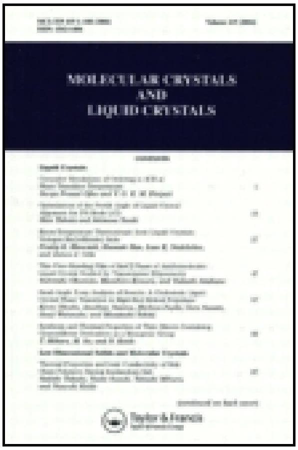

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# Effect of Cobalt Additive on the NiOOH/Ni$(OH)_2$ Phase Boundary Movement

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# Effect of Cobalt Additive on the NiOOH/Ni$(OH)_2$ Phase Boundary Movement

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Effect of cobalt additive on the NiOOH/Ni$(OH)_2$ phase boundary movement has been investigated by analysing build-up and decay current transients under the application of various voltage steps(70 to 400 mV). The occurrence of current plateau upon hydrogen extraction from the completely hydrogen-injected films indicated that the hydrogen transport through the film proceeds by the movement of NiOOH/Ni$(OH)_2$ phase boundary. The velocity and mobility of the phase boundary movement upon hydrogen extraction were determined to be orders of $10^{-6}$ cm $s^{-1}$ and $10^{-5}$ cm $s^{-1}$ $V^{-1}$ in magnitude, respectively. It is concluded that β-Ni$(OH)_2$ phase is stabilised by the Co$(OH)_2$ incorporation into the Ni$(OH)_2$ film and hence both the velocity and mobility of the NiOOH/Ni$(OH)_2$ phase boundary movement is raised by the Co$(OH)_2$ incorporation.

Keywords: hydrogen transport; phase boundary movement, nickel hydroxide film, cobalt hydroxide incorporation, current transient

## INTRODUCTION

Hydrogen transport in the nickel hydroxide[Ni$(OH)_2$] and nickel oxyhydroxide(NiOOH) electrodes has been studied by many researchers with various techniques such as cyclic voltammetry[1,2], current transient method[3,4], and ac-impedance spectroscopy[5]. Apparent hydrogen diffusion coefficient determined at room temperature ranges between $10^{-8}$ and $10^{-12}$ $cm^2$ $s^{-1}$, depending on the crystal structure and measuring techniques.

Simple hydrogen diffusion model in the homogeneous phase was criticised by Glarum and Marshall[6]. They argued from ac-impedance study that a rapid bulk response with no indications of limitation by proton diffusion within the film is attributable to the phase boundary propagation within individual grains. It has for long been known[7-9] from the observation of colour boundary motion that the hydrogen transport in the Ni$(OH)_2$ proceeds by the movement of NiOOH/Ni$(OH)_2$ phase boundary.

Electrosynthesized nickel hydroxide(ESN) designated as α-Ni$(OH)_2$ has been found to have superior electrochemical properties compared to chemically prepared β-Ni$(OH)_2$ [10].

The electrochemical properties of ESN are found to improve on the addition of Co and several studies are reported in the literature concerning the effect of cobalt on the mechanical[11,12], chemical [13] and electrochemical [14-16] properties of ESN.

This work is aimed at better understanding the movement of two kinds of phase boundaries and dependence of hydrogen diffusivity on the hydrogen content in pure and cobalt hydroxide-incorporated electro-deposited nickel hydroxide films. For this purpose, potentiostatic current transient experiments with various voltage steps were carried out. From the results, the phase boundary movement determined from pure and cobalt hydroxide-doped nickel hydroxide film specimens was discussed in terms of the incorporated $Co(OH)_2$.

## EXPERIMENTAL

Nickel hydroxide($Ni(OH)_2$) films containing various mole fractions of cobalt hydroxide($Co(OH)_2$) were electro-deposited onto a nickel substrate galvanostatically with a current density of 0.5 mA $cm^{-2}$ for 830 s in 0.05 M nickel nitrate solution containing various amounts(0, 10, 20, 30 and 50 Vol. %) of 0.05 M cobalt nitrate solution.

The aqueous solution of 1 M KOH was deaerated by bubbling purified nitrogen gas before and during the experiments. The surface area of the electrode exposed to electrolyte was 1 $cm^2$. A platinum wire and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively.

Build-up and decay current transients (chronoamperograms) under the application of various voltage steps were measured on pure and $Co(OH)_2$-incorporated nickel hydroxide films. The film specimens were first polarised to the potential of 0.40 V(SCE) for 1400 s to obtain a low steady-state current density. Then, the potential was abruptly dropped to values ranging from -0.02 to 0.34 V(SCE). From this moment the build-up current transients were recorded. After the currents reached steady-states, the electrode potential was jumped to 0.40 V(SCE). From this moment the resulting current decay transients were measured.

All electrochemical experiments were performed at room temperature.

## RESULTS AND DISCUSSION

In order to analyse the measured current transient curves in detail, the reduced currents were calculated as the measured current divided by total charge transferred into or from the $H_{1+\delta}NiO_2$ film at a given voltage step during the hydrogen injection or extraction. The results are plotted against time($i/Q_m$ vs. time) in Fig. 1 in logarithmic scale. Figure 1 presents typical decay transients(reduced current vs. time) for electro-deposited $H_{1+\delta}NiO_2$ films containing various fractions of $Co(OH)_2$ after jumping the applied potential 0 - 0.1 $V_{SCE}$ (completely hydrogen injected states, $\delta=1$) to 0.40 $V_{SCE}$. All the films show current plateaus in the early stage, followed by steep decays.

The occurrence of plateaus in the current transients at $\delta=1.0$ means that hydrogen concentration gradient is constant just beneath the electrode surface and therefore the hydrogen transport in the initial stage is not a diffusion-controlled process but an interface-controlled process. The appearance of the current plateau seems to be related with the phase boundary movement. Briggs and Fleischmann[7] and Barnard et al.[8] have observed the motion of the colour boundary during the hydrogen extraction from and injection into the active material. The Ni(OH)$_2$(bleached state) and NiOOH(coloured state) are green and black in colour, respectively. Huggins et al.[9] attributed this moving colour boundary to the movement of NiOOH/Ni(OH)$_2$ phase boundary. According to the authors[9], the hydrogen extraction/injection reaction takes place at the NiOOH/Ni(OH)$_2$ boundary and this boundary moves from the film/electrolyte interface toward the conducting substrate/film interface during the hydrogen injection and vice versa during the hydrogen extraction.

Considering the phase boundary movement previously reported, it seems that during the hydrogen extraction from the Ni(OH)$_2$ film, the hydrogen flux from the film surface remains constant until the outer Ni(OH)$_2$ layer becomes discontinuous patches as the inner NiOOH layer grows to the film surface.

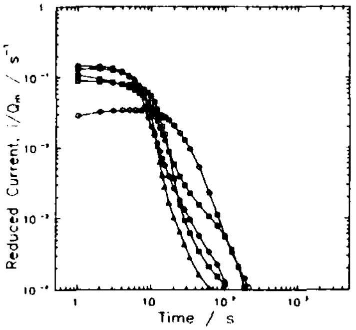


FIGURE 1 Typical decay transient(reduced current vs. time) for electro-deposited $H_{1+\delta}NiO_2$ films containing various fractions of Co(OH)$_2$ : O, 0 mole %; □, 10 mole %; Δ, 20 mole %; ●, 30 mole %; ■, 50 mole %. The applied potential of 0 - 0.10 V$_{SCE}$(completely hydrogen injected state, $\delta = 1$) was jumped to 0.40 V$_{SCE}$.

The phase boundary movement is believed to be greatly retarded by the strain field generated around phase boundary. Yang and Pyun[17] and Yang et al.[18] reported from the ac-impedance study as well as current transient analysis on the Pd electrode that the formation and decomposition of the β-PdH from and into the α-PdH are inevitably accompanied by the large change of strain field around the β-PdH, impeding the hydrogen transport from the β-PdH region toward the α-PdH region and vice versa, respectively.

It is known that Ni(OH)$_2$ exists as two structural modifications called α and β forms[19]. The α form of Ni(OH)$_2$ is comprised of interslab spaces containing water and anions in addition to hydrogen. The α-Ni(OH)$_2$ stabilises by dehydrating to the more stable β form on cycling or on standing in alkaline solution with a resultant decrease in lattice spacing. The β-Ni(OH)$_2$ can be oxidised to β-NiOOH on hydrogen extraction and to γ-NiOOH on severe extraction. In the cycling between β-NiOOH and β-Ni(OH)$_2$ there is no water and K$^+$ ions involved, contrary to that between γ-NiOOH and α-Ni(OH)$_2$[20,21]. Also, it is generally known[11,21] that the lattice parameter change is larger in the case of phase transformation of γ-NiOOH to α-Ni(OH)$_2$ than for transition of β-NiOOH to β-Ni(OH)$_2$. Therefore, the strain generated at the α-Ni(OH)$_2$/γ-NiOOH phase boundary is considered to be larger than that at the β-Ni(OH)$_2$/β-NiOOH phase boundary.

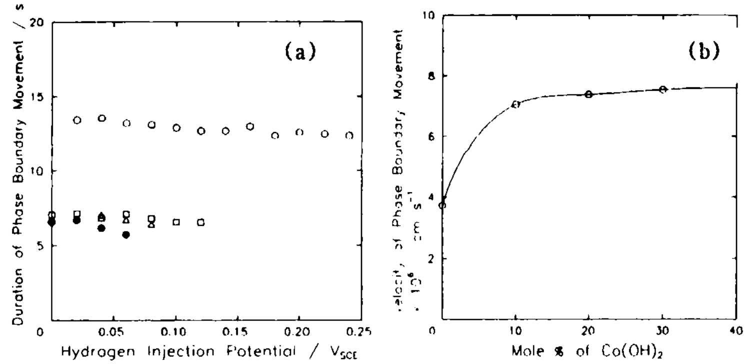
It can be conjectured that the interface-controlled hydrogen transport dominates over the diffusion-controlled hydrogen transport as the strain generated at the phase boundary increases. The higher level and shorter duration of current plateau for the $H_{1+\delta}NiO_2$ containing higher fraction of $Co(OH)_2$ indicate that the velocity of the phase boundary movement of pure film is slower than those of the films containing $Co(OH)_2$. The slow velocity of pure film boundary seems to originate from the larger strain generated at the phase boundary of pure film than those at the phase boundary of $Co(OH)_2$ incorporated films. Thus, it is suggested that β-$Ni(OH)_2$ and β-NiOOH phases are stabilised by the $Co(OH)_2$ incorporation. This argument is consistent with the reports[15,16] that the $Co(OH)_2$ incorporated into the $Ni(OH)_2$ acts as a stabiliser of both the β-NiOOH and β-$Ni(OH)_2$ phases. Considering the effect of strain generated on the phase boundary movement, the hydrogen transport is expected to proceed considerably slower via γ-NiOOH/α-$Ni(OH)_2$ phase boundary movement than that via β-NiOOH/β-$Ni(OH)_2$ phase boundary movement. This expectation is born out by the results of decay transients that the current plateau level required for the γ-NiOOH/α-$Ni(OH)_2$ phase boundary movement is lower than that needed for the β-NiOOH/β-$Ni(OH)_2$ phase boundary movement.

Assuming that duration of the current plateau approximately corresponds to the time required for NiOOH/$Ni(OH)_2$ phase boundary to reach the film surface, one can calculate the velocity for the phase boundary movement. Fig. 2(a) represents duration of phase boundary movement for film thickness of 0.5 μm as a function of hydrogen injection potential. The current plateau duration required for γ-NiOOH/α-$Ni(OH)_2$ phase boundary of pure film is about two times longer than that for β-NiOOH/β-$Ni(OH)_2$ phase boundary of the $Co(OH)_2$-incorporated films. From the current plateau length and film thickness measured from the completely hydrogen injected film, the velocity for the phase boundary movement during the hydrogen extraction was calculated. The results are plotted against $Co(OH)_2$ fraction incorporated into the $Ni(OH)_2$ film in Fig. 2(b). The velocities were calculated to be about $3.7\times10^{-6}$ cm $s^{-1}$ for the γ-NiOOH/α-$Ni(OH)_2$ phase boundary movement and a nearly constant value of about $7.3\times10^{-6}$ cm $s^{-1}$ for the β-NiOOH/β-$Ni(OH)_2$ phase boundary movement, regardless of $Co(OH)_2$ fraction, indicating that the $Co(OH)_2$ incorporation into the $Ni(OH)_2$ film enhances the phase boundary movement.

The mobility for the phase boundary movement can be calculated from the velocity and driving force, which is the difference between the hydrogen extraction potential and the potential at which phase boundary movement occurs throughout the entire film thickness. The potentials for phase boundary movement corresponding to the redox reaction of NiOOH/$Ni(OH)_2$ were determined to be −0.02 to 0.34V(SCE) from the current plateaus of the charge/discharge curves. The mobilities were calculated to be $2.3\times10^{-5}$ cm $s^{-1}$ $V^{-1}$ for the γ-NiOOH/α-$Ni(OH)_2$ phase boundary movement and a nearly constant value of about $2.0\times10^{-5}$ cm $s^{-1}$ $V^{-1}$ for the β-NiOOH/β-$Ni(OH)_2$ phase boundary movement, irrespective of $Co(OH)_2$ fraction.

The reduced charge passed during the phase boundary movement was determined as the charge due to the hydrogen transferred by the phase boundary movement, Q, divided by total charge passed during the hydrogen extraction, $Q_{H}$. The reduced charge is determined by the values of the level and duration of the current plateau. The result is plotted against hydrogen injection potential in Fig. 2(c). The reduced charge required is about 50 % for the γ-

NiOOH/α-Ni(OH)$_2$ phase boundary movement and higher values ranging from 65 to 84 % for the β-NiOOH/β-Ni(OH)$_2$ phase boundary movement.



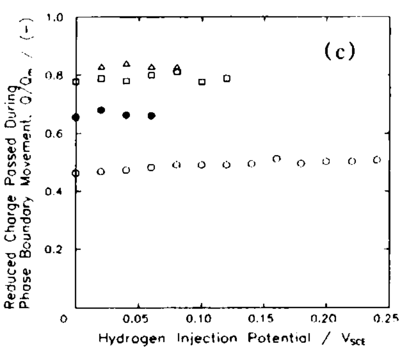


FIGURE 2(a) Duration of phase boundary movement versus hydrogen injection potential for films containing various fractions of Co(OH)$_2$ : ○, 0 mole %; □, 10 mole %; Δ, 20 mole %; ●, 30 mole %. (b) Velocity of phase boundary movement during hydrogen extraction versus mole % of Co(OH)$_2$ incorporated into the films. (c) Reduced charge passed during phase boundary movement, Q/Q$_m$, versus hydrogen injection potential for films containing various fractions of Co(OH)$_2$ : ○, 0 mole %; □, 10 mole %; Δ, 20 mole %; ●, 30 mole %.

Let us consider the reduced charge with respect to the two kinds of phase boundaries γ-NiOOH/α-Ni(OH)$_2$ and β-NiOOH/β-Ni(OH)$_2$. The current plateau during the hydrogen extraction continues until the front of the moving NiOOH/Ni(OH)$_2$ phase boundary reaches the film surface. : The flatter the shape of the boundary, the more reduced the material when the boundary has stopped moving. In this respect, the higher reduced charge values for the β-NiOOH/β-Ni(OH)$_2$ phase boundary movement than that for γ-NiOOH/α-Ni(OH)$_2$ phase boundary movement suggests that the curved β/β phase boundary is flatter in shape than the curved γ/α phase boundary. The non-planar phase boundary is already suggested by Huggins et al.[9]. This result implies that dispersed Ni(OH)$_2$ phase appears as small patches in the NiOOH phase as a result of the phase boundary movement. Considering the degree in flatness of the curved phase boundary, we believe that the calculated values of velocity and mobility of the γ/α phase boundary movement are more overestimated as compared to the β/β phase boundary movement. Thus, both the real velocity and mobility of the γ/α phase boundary movement are considered to be lower than those of the β/β boundary movement. It can be concluded that the Co(OH)$_2$ incorporation into the Ni(OH)$_2$ film increases both the velocity and mobility of the NiOOH/Ni(OH)$_2$ phase boundary movement.

## CONCLUSIONS

It is suggested that the hydrogen transport through the film proceeds by the movement of $NiOOH/Ni(OH)_2$ phase boundary. From the higher level and shorter duration of current plateau for the $H_{1+\delta}NiO_2$ containing higher fraction of $Co(OH)_2$, it is indicated that both the $\beta$-$Ni(OH)_2$ and $\beta$-NiOOH phases are stabilised by the $Co(OH)_2$ incorporation. The velocity and mobility of the phase boundary movement upon hydrogen extraction were determined to be orders of $10^{-6}$ cm $s^{-1}$ and $10^{-5}$ cm $s^{-1}$ $V^{-1}$ in magnitude, respectively. From the reduced charge during the hydrogen extraction, we infer that the $\beta$-NiOOH/$\beta$-$Ni(OH)_2$ phase boundary of the $Co(OH)_2$-incorporated films is flatter in geometrical shape than the $\gamma$-NiOOH/$\alpha$-$Ni(OH)_2$ phase boundary of pure film. Considering the phase boundary flatness, it is concluded that both the velocity and mobility of the $\beta$-NiOOH/$\beta$-$Ni(OH)_2$ phase boundary movement are larger than those of the $\gamma$-NiOOH/$\alpha$-$Ni(OH)_2$ phase boundary movement.

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