

# Analysis of stresses generated during hydrogen extraction from and injection into Ni(OH)<sub>2</sub>/NiOOH film electrode

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## Abstract

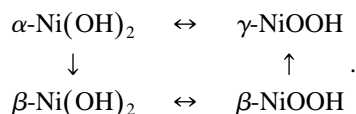
Stresses generated during the hydrogen extraction from and injection into a Ni(OH)<sub>2</sub>/NiOOH film electrode in 0.1 M KOH solution are analysed by means of a laser beam deflection technique combined with potentiostatic current transient and electrochemical quartz crystal microbalance (EQCM) techniques. From the measured values of the film thickness, the elapsed time for phase boundary movement (PBM) and the potential step given between the hydrogen extraction/injection potential and the plateau potential, the velocity and the mobility of PBM are determined to be  $2.3 \times 10^{-6}$ – $5.4 \times 10^{-6}$  cm s<sup>-1</sup> and  $3.5 \times 10^{-10}$ – $2.6 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>, respectively. From the mass change measured by means of EQCM, it is suggested that, during hydrogen extraction, the PBM continues until the insertion of K<sup>+</sup> ions begins to occur simultaneously with the desertion of such neutral species as H<sub>2</sub>O molecules or KOH molecules. During hydrogen injection, the PBM is accompanied by the extraction of K<sup>+</sup> ions, followed by the insertion of neutral species. From the mass change transient and the deflection transient, simultaneously measured with the current transient, it is suggested that the sharp rise of tensile and compressive deflections in the initial stage is traced back to the PBM. The following relaxation of tensile and compressive deflections is attributed to the extraction/insertion of neutral species. Most of the stresses developed during the hydrogen extraction and injection originate mainly from the PBM, not the extraction/insertion of K<sup>+</sup> ions and neutral species. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Stresses generation/relaxation; Ni(OH)<sub>2</sub>/NiOOH film electrode; Beam deflection technique; Quartz crystal microbalance

## 1. Introduction

Hydrogen transport through the Ni(OH)<sub>2</sub>/NiOOH electrode has been investigated extensively because of its technological application in nickel–cadmium and nickel–metal–hydride batteries [1–3]. From observation of the colour boundary movement during hydrogen extraction from and injection into the Ni(OH)<sub>2</sub>/NiOOH film electrode, it has been concluded [4] that hydrogen transport through the Ni(OH)<sub>2</sub>/NiOOH electrode proceeds via phase boundary movement (PBM).

According to Bode et al. [5], electrochemical reactions of the Ni(OH)<sub>2</sub>/NiOOH electrode are summarized as follows



In battery applications, the α-Ni(OH)<sub>2</sub>/γ-NiOOH electrode with high charge/discharge capacity has superior electrochemical properties compared with the β-Ni(OH)<sub>2</sub>/β-NiOOH electrode [6,7].

The cycle-life and the capacity of the α-Ni(OH)<sub>2</sub>/γ-NiOOH electrode are remarkably deteriorated due to the stresses generated during the hydrogen extraction from and injection into the electrode since the molar volume mismatch between α-Ni(OH)<sub>2</sub> and γ-NiOOH is larger than that between β-Ni(OH)<sub>2</sub> and β-NiOOH [6,7]. In addition, from a recent study with an electrochemical quartz crystal

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microbalance (EQCM), it has been reported [8–10] that during the hydrogen extraction/injection either alkaline cations such as  $K^+$  ions or neutral species are incorporated simultaneously into the electrode. In this respect, in order to employ the  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH electrode as positive electrode for a nickel–metal–hydride battery of high specific energy, it is necessary to analyse the stresses developed due to the PBM as well as the extraction/insertion of  $K^+$  ions and such neutral species as H<sub>2</sub>O molecules or KOH molecules. Such an analysis is reported in this paper.

## 2. Experimental

A substrate was cut from a nickel sheet (Aldrich) of thickness 100  $\mu\text{m}$  with dimensions of  $3 \times 90$  mm. The substrate surface was polished with 1  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> powder on wet cloth and then rinsed with distilled water. In order to remove residual stresses, the substrate was annealed under a vacuum of  $10^{-2}$  Pa at 750°C for 2 h, followed by furnace cooling. Since hydrogen is not soluble in gold to any measurable extent [11], a 400 nm thick layer of gold was sputtered on one side of the substrate to make that side an impermeable boundary.

The substrate was then coated on the other side with a fast-drying enamel to make that side inert. A small mirror of silvered mica was attached to the enamel-coated side, about 1.3 cm away from the end of the foil electrode, to minimize the difference between the curvature of the foil electrode that results from stresses generated during hydrogen extraction and injection and the curvature that arises from the point load used for calibration [12]. An  $\alpha$ -Ni(OH)<sub>2</sub> film was electrodeposited galvanostatically on the Au-coated side with a constant current density of 0.2 mA  $\text{cm}^{-2}$  for 1800 s in 0.5 M Ni(NO<sub>3</sub>)<sub>2</sub> solution. The thickness of the electrodeposited film was calculated to be 0.23  $\mu\text{m}$  from the mass change measured by a EQCM (SEIKO EG & G QCA 917).

The surface area of the electrode exposed to the electrolyte was  $3 \times 50$  mm = 150 mm<sup>2</sup>. The reference electrode was a mercury/mercury oxide electrode and was equipped with a Luggin capillary. A platinum wire served as the counter electrode. The 0.1 M KOH solution was deaerated by bubbling with purified nitrogen gas before the experiments.

A beam deflection technique, developed by Stoney [13] and later modified by Nelson and Oriani [12], was used to obtain the deflection generated during the hydrogen extraction and injection. The experimental apparatus and procedure have been detailed elsewhere [12,14]. Nelson and Oriani [12] calculated the stresses from the deflection of the strip specimen under a plane stress condition. The deflection obtained in the present work could not be quantitatively converted into the stresses because it did not satisfy the plane stress constraint assumed by Nelson and Oriani [12]. It should be stressed, however, that the varia-

tion of the measured deflection still corresponds to that of stresses.

The hydrogen extraction and injection have the same significance with proton extraction accompanied by the oxidation of Ni(OH)<sub>2</sub> to NiOOH, and vice versa. The Ni(OH)<sub>2</sub>/NiOOH film electrode was first polarized to a potential of 0.25, 0.30 or 0.35 V for 600 s, followed by stepping the potential to 0.55 V by means of an EG & G PARC model 263A potentiostat. Note, all potentials are reported with respect to a Hg/HgO reference electrode. The resulting decay current was recorded with time. After 600 s at this potential, the value was dropped to 0.25, 0.30 or 0.35 V. The resulting build-up of current was recorded with time. Intermittent galvanostatic charge–discharge experiments were conducted using a Solartron 1287 Electrochemical Interface (ECI). Mass change and deflection transients were measured simultaneously with a potentiostatic current transient using EQCM and laser beam deflection techniques, respectively.

## 3. Results and discussion

The typical decay current transients (in logarithmic scale,  $\log i$  vs.  $\log t$  shown in Fig. 1 were obtained during hydrogen extraction at an applied potential of 0.55 V from the Ni(OH)<sub>2</sub>/NiOOH film electrode which was previously maintained at 0.25, 0.30 or 0.35 V for 600 s in 0.1 M KOH solution. The decay current transient consists of a current plateau and a sudden fall in current with time. The duration of current plateau,  $t_p$ , is measured as the time at which the tangent line of the first-stage curve intersects

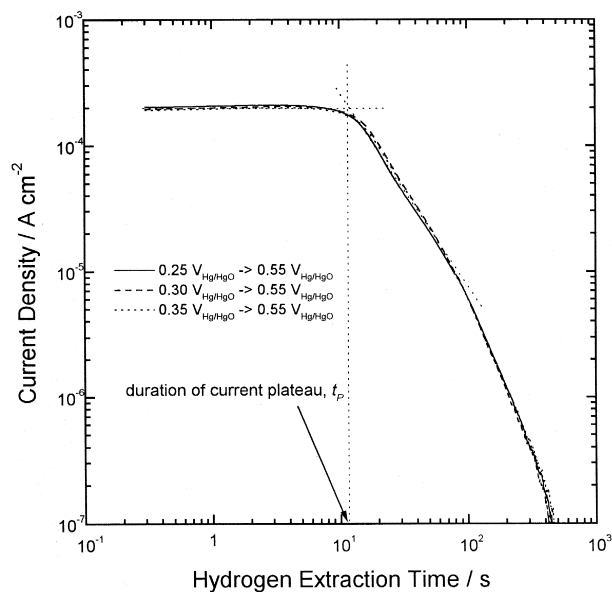


Fig. 1. Current decay transients in logarithmic scale,  $\log i$  vs.  $\log t$ . Hydrogen previously injected into Ni(OH)<sub>2</sub>/NiOOH film electrode electrodeposited on a Ni substrate in 0.1 M KOH solution for 600 s at 0.25, 0.30 and 0.35 V and then the potential stepped to 0.55 V.

that of the second-stage curve. The value of current plateau is of  $2 \times 10^{-4} \text{ A cm}^{-2}$ .

The typical build-up current transients (logarithmic scale,  $\log i$  vs.  $\log t$ ) shown in Fig. 2 were obtained during hydrogen injection at an applied potential of 0.25, 0.30 and 0.35 V into the  $\text{Ni(OH)}_2/\text{NiOOH}$  film electrode previously maintained at 0.55 V for 600 s in 0.1 M KOH solution. The three-staged build-up current transient is composed of a current plateau and a sudden fall of current with time, followed by a concave downward curve. The duration of current plateau,  $t_p$ , is also determined as the time at which the tangent line of the first-stage curve intersects that of the second-stage curve. As the hydrogen injection potential was increased,  $t_p$  was prolonged and the value of the current plateau was diminished.

Yoon and Pyun [15] have suggested that the current plateau measured during hydrogen extraction and injection corresponds to the PBM, assuming that hydrogen transport through the electrode is an interface-controlled process. Under these circumstances, it is plausible that  $t_p$  is the elapsed time for the PBM. In addition, the three-staged current transient measured during hydrogen injection indicates that hydrogen transport through the electrode is governed by hydrogen trapping [15].

Fig. 3 illustrates the galvanostatic intermittent charge–discharge curves in the potential range 0–0.5 V measured from the  $\text{H}_{1+\delta}\text{NiO}_2$  (i.e.,  $\text{Ni(OH)}_2$  ( $\delta = 1$ )/ $\text{NiOOH}$  ( $\delta = 0$ )) film electrode as a function of hydrogen content ( $1 + \delta$ ) in 0.1 M KOH solution. The electrode potential curves clearly display a potential plateau near 0.4 V during hydrogen extraction and another potential plateau near 0.37 V during hydrogen injection. The potential steps imposed in

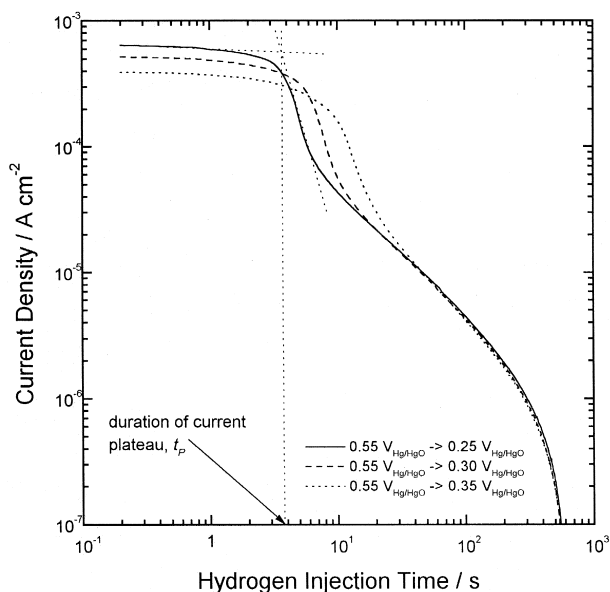


Fig. 2. Current build-up transients in logarithmic scale,  $\log i$  vs.  $\log t$ . Hydrogen previously extracted from  $\text{Ni(OH)}_2/\text{NiOOH}$  film electrode electrodeposited on a Ni substrate in 0.1 M KOH solution for 600 s at 0.55 V and then the potential stepped to 0.25, 0.30 and 0.35 V.

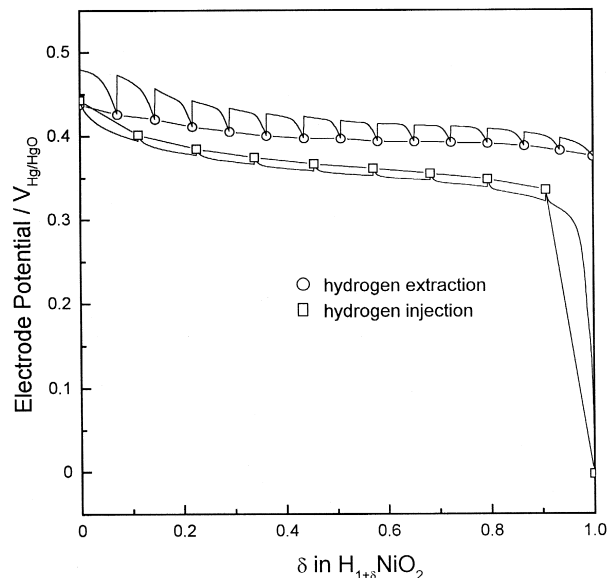


Fig. 3. Galvanostatic intermittent charge–discharge curve obtained from  $\text{Ni(OH)}_2/\text{NiOOH}$  film electrode electrodeposited on a Ni substrate. (○) and (□) represent open-circuit potentials during charging and discharging of the cell, respectively.

the decay and build-up current transients of Figs. 1 and 2, respectively, are numerically given in Fig. 4.

If the applied potential passes through the potential plateau upward during the hydrogen extraction or downward during the hydrogen injection, the hydrogen transport through the electrode proceeds in coexistence with two phases, and hence involves the PBM. Generally, it is considered [16,17] that the potential step applied from the initial potential to the plateau potential is effective as the driving force for the diffusion of alkali atoms in a single phase, and the potential step applied from the plateau potential to the applied potential is allocated to the driving

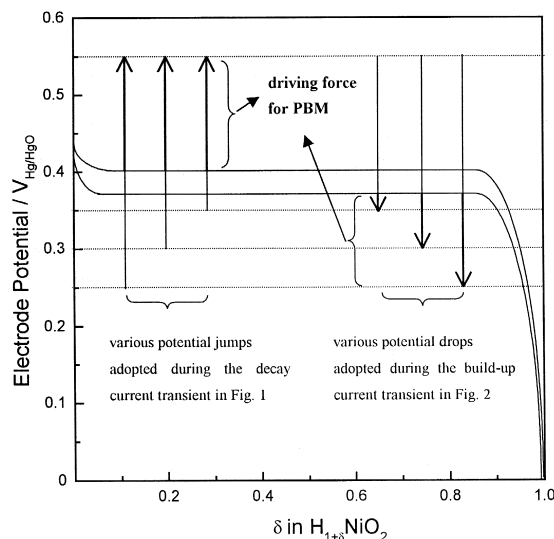


Fig. 4. Plots of potential steps employed in decay and build-up current transients of Fig. 1 and Fig. 2, respectively.

force for the PBM. Therefore, in this work, the potential step imposed between the plateau potential and the applied potential is taken as the driving force for the PBM, as shown in Fig. 4.

As a result, the decay current transients of Fig. 1 share almost one another in shape, regardless of the prior applied potential, due to the same driving force for the PBM. By contrast, the diminution of current plateau value and the extension of  $t_p$  in the build-up current transient of Fig. 2 are due to a decrease in the driving force for the PBM with increasing hydrogen injection potential.

The mass change during hydrogen extraction is plotted against the hydrogen extraction time in Fig. 5. The mass change transient first exhibits a sudden fall, then a monotonic rise, and finally saturation to a constant value. The mass change transient during the hydrogen extraction yields a transition time,  $t_T$ , at which the direction of mass change is reversed. The value of  $t_T$  was about 10 s, irrespective of the prior applied potential. This is in a good agreement with the value of  $t_p$  in the decay current transient of Fig. 1.

The mass increase was about 300 ng during hydrogen extraction. This is opposite to expectation, i.e. the mass of the film electrode should be decreased since hydrogen is removed. Therefore, an explanation must be found for the mass increase. Bernard et al. [8] showed by means of a.c. electrogravimetric measurements that the oxidation reaction of the  $\alpha$ -Ni(OH)<sub>2</sub> phase involves the hydrogen extraction process and an insertion of alkaline cations such as K<sup>+</sup> ions. Consequently, it is inferred that the mass increase after  $t_T$  is caused by the insertion of K<sup>+</sup> ions, which are 39 times heavier than hydrogen ions.

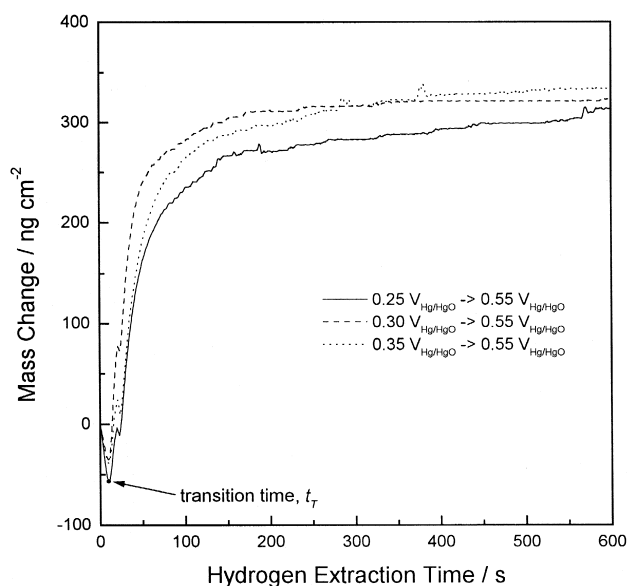


Fig. 5. Plots of mass change against hydrogen extraction time, measured on a Ni(OH)<sub>2</sub>/NiOOH film electrode in 0.1 M KOH solution by stepping to applied potentials of 0.25, 0.30 and 0.35 V to 0.55 V.

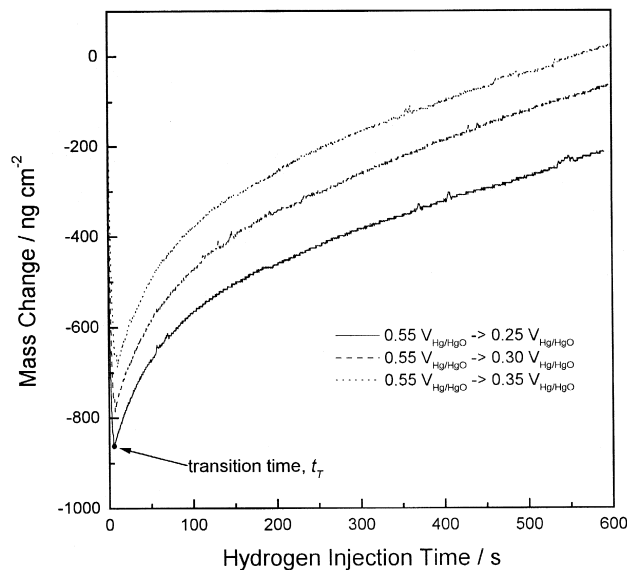


Fig. 6. Plots of mass change against hydrogen injection time, measured on a Ni(OH)<sub>2</sub>/NiOOH film electrode in 0.1 M KOH solution by dropping the applied potential of 0.55 V to 0.25, 0.30 and 0.35 V.

Let us explore why the insertion of K<sup>+</sup> ions proceeds after  $t_T$ . It is well known [18] that the growth of the  $\gamma$ -NiOOH phase begins first at the electrode/substrate interface, rather than at the electrode/electrolyte interface. From the coincidence of  $t_T$  with  $t_p$ , it is inferred that the insertion of K<sup>+</sup> ions begins after the termination of PBM, that is, after the  $\gamma$ -NiOOH phase is first formed at the electrode/electrolyte interface. Eventually, it is suggested that the insertion of K<sup>+</sup> ions into the electrode requires the presence of the  $\gamma$ -NiOOH phase at the electrode/electrolyte interface. This is born out by the fact that the exchange of K<sup>+</sup> ions for H<sup>+</sup> only occurs in the  $\gamma$ -NiOOH phase [19]. In this respect, it is asserted that  $t_T$  refers to the time at which the  $\gamma$ -NiOOH phase is first formed at the electrode/electrolyte interface.

The mass change during hydrogen injection is plotted against the hydrogen injection time in Fig. 6. The mass of the film electrode falls sharply to a minimum value and then rises slowly with time. Again, there is a transition time,  $t_T$ . The higher the hydrogen injection potential, the smaller is the mass change and the longer is  $t_T$  of the film.

Although hydrogen is injected into the film electrode, the mass falls steeply during  $t_T$ . This means that K<sup>+</sup> ions with a higher mass than hydrogen are ejected from the film electrode during the PBM. This is in contrast with the case of hydrogen extraction. Bearing in mind that the growth of the  $\alpha$ -Ni(OH)<sub>2</sub> phase begins at the electrode/electrolyte interface [18], it is quite conceivable that the removal of K<sup>+</sup> ions and the hydrogen injection occur simultaneously and hence the contribution of K<sup>+</sup> ions to mass change dominates over that of hydrogen.

The slow mass increase after  $t_T$  during hydrogen injection indicates the insertion of another species into the film

in addition to  $K^+$  ions and hydrogen. Gonsalves and Hillman [10] found that neutral species such as  $H_2O$  and  $KOH$  molecules are incorporated during hydrogen extraction from and injection into the  $Ni(OH)_2/NiOOH$  film electrode. From the difference in molar volume between hydrogen,  $K^+$  ions and neutral species, it is reasonable to consider that the large molar volume of neutral species impedes the removal/insertion of neutral species and, thereby, the desertion/insertion of neutral species proceeds more slowly, as compared with hydrogen and  $K^+$  ions. From the above consideration, it is reasonable that the slow mass increase is ascribed to the insertion of neutral species.

It should be emphasized that the values of mass change at  $t_T$  during hydrogen injection are about 680–860 ng, which are much greater than 300 ng observed during hydrogen extraction. Thus, during hydrogen extraction, the removal of neutral species and the insertion of  $K^+$  ions proceed simultaneously. By contrast, during hydrogen injection, the insertion of neutral species proceeds after the ejection of  $K^+$  ions. Hence, the mass increase due to the insertion of  $K^+$  ions during hydrogen extraction is counterbalanced by the mass decrease due to ejection of neutral species.

From the values of  $Ni(OH)_2/NiOOH$  film thickness and  $t_T$  determined from mass change transients, the velocity of PBM during hydrogen extraction and injection is calculated to be  $2.3 \times 10^{-6}$  and  $2.3 \times 10^{-6}$  to  $5.4 \times 10^{-6}$   $cm\ s^{-1}$ , respectively. The mobility of PBM during hydrogen extraction and injection is  $3.5 \times 10^{-10}$  and  $1.0 \times 10^{-9}$  to  $2.6 \times 10^{-9}$   $cm^2\ s^{-1}\ V^{-1}$ , respectively, as determined from the calculated velocity, the film thickness and the driving force for the PBM. These results are illustrated in Fig. 7. By comparing the mobility of PBM during hydro-

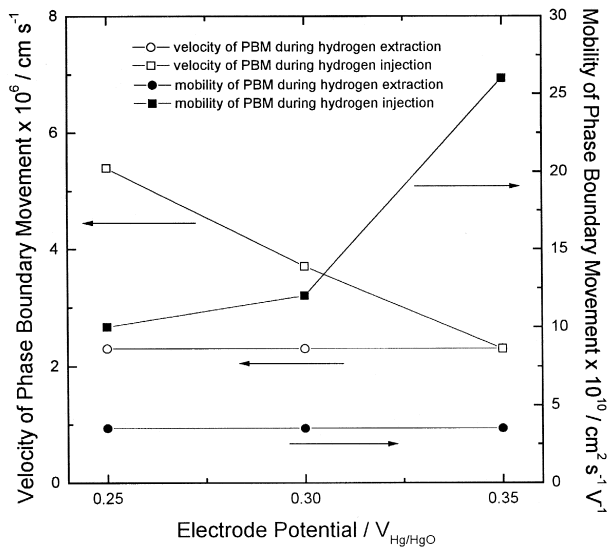


Fig. 7. Plots of velocity of PBM, determined during hydrogen extraction (○) and injection (□) and mobility of PBM, calculated during hydrogen extraction (●) and injection (■).

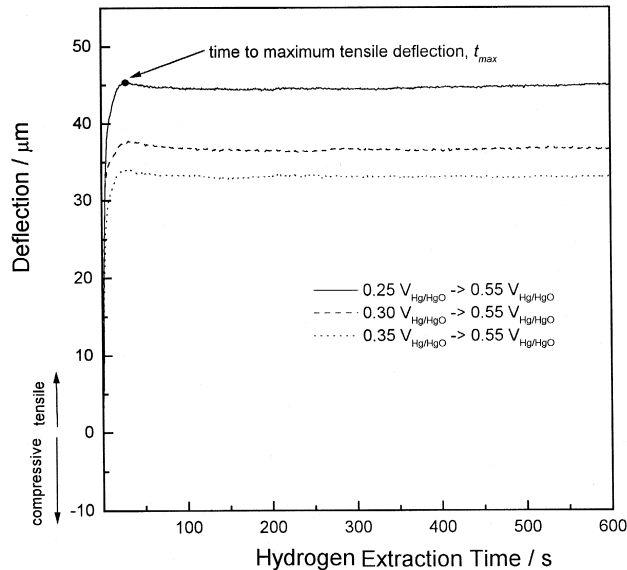


Fig. 8. Plots of tensile deflection against hydrogen extraction time, measured on a  $Ni(OH)_2/NiOOH$  film electrode in 0.1 M KOH solution by stepping the applied potentials of 0.25, 0.30 and 0.35 V to 0.55 V.

gen injection with that during hydrogen extraction, it is found that the PBM is more facile during hydrogen injection.

The deflection is plotted against the hydrogen extraction time in Fig. 8 during hydrogen extraction at 0.55 V from an electrode, which previously was maintained at 0.25, 0.30 and 0.35 V for 600 s in 0.1 M KOH solution. During hydrogen extraction, the deflection sharply increased and then slowly decreased by a small amount. The time to the maximum tensile deflection,  $t_{max}$ , was 28 s, irrespective of the prior applied potential. The hydrogen extraction in-

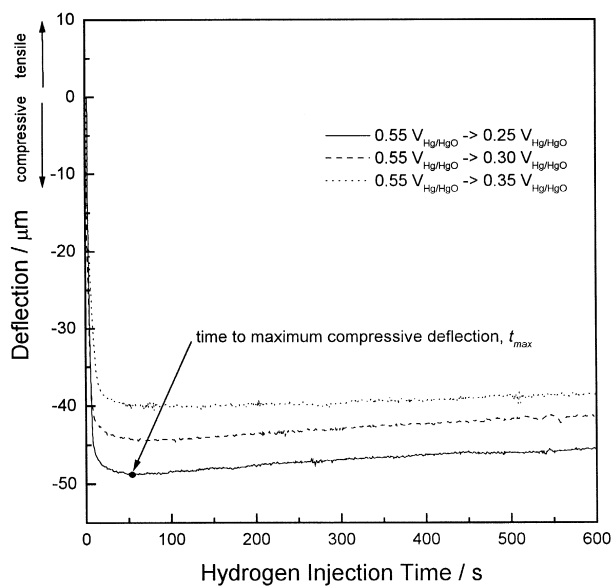


Fig. 9. Plots of compressive deflection against hydrogen injection time, measured on a  $Ni(OH)_2/NiOOH$  film electrode in 0.1 M KOH solution by dropping the applied potential of 0.55 V to 0.25, 0.30 and 0.35 V.

Table 1

Duration of current plateau,  $t_p$ , transition time of mass change transient,  $t_T$ , and time to maximum deflection transient,  $t_{max}$ , measured on a  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH film electrode in 0.1 M KOH solution at various potential steps

Potential step	Duration of current plateau, $t_p$	Transition time of mass change transient, $t_T$	Time to maximum deflection transient, $t_{max}$
0.25 → 0.55 <sup>a</sup>	11.2	10.3	27.5
0.30 → 0.55 <sup>a</sup>	11.2	10.5	28.3
0.35 → 0.55 <sup>a</sup>	11.2	10	28.7
0.55 → 0.25 <sup>b</sup>	3.6	4.3	47
0.55 → 0.30 <sup>b</sup>	5.2	6.2	52
0.55 → 0.35 <sup>b</sup>	8.4	10.5	55

<sup>a</sup>Hydrogen extraction.

<sup>b</sup>Hydrogen injection.

duced a tensile deflection over the Ni(OH)<sub>2</sub>/NiOOH film electrode, which indicated that the molar volume, on average, was contracted. As the prior applied potential was decreased, the maximum tensile deflection increased.

Undoubtedly, the phase transformation of  $\alpha$ -Ni(OH)<sub>2</sub> to  $\gamma$ -NiOOH causes the deflection of the specimen, i.e., the stresses. It is expected that the potential jump causes the specimen to move in the tensile direction since the molar volume of  $\alpha$ -Ni(OH)<sub>2</sub> is larger than that of  $\gamma$ -NiOOH [20,21].

The deflection is plotted against the hydrogen injection time in Fig. 9 for 0.25, 0.30 and 0.35 V. Again, the electrode was previously maintained at 0.55 V for 600 s in 0.1 M KOH solution. As for hydrogen extraction, the deflection transient can be separated into two steps: a rapid compressive movement and a slow relaxation to a small extent. The maximum value of the compressive deflection increases with decreasing hydrogen injection potential, which indicates that the molar volume of  $\alpha$ -Ni(OH)<sub>2</sub> increases with falling hydrogen injection potential.

Bearing in mind that the PBM always proceeds in the initial stage during the hydrogen extraction and injection, it can be seen that the accompanying steep increase in deflection is associated with the PBM. To understand the small relaxation of deflection, we should remember that the desorption/insertion of neutral species proceeds after termination of the PBM during hydrogen extraction and injection. On hydrogen injection, the relaxation of deflection appears irrespective of K<sup>+</sup> ions. This implies that K<sup>+</sup> ions do not play a role in the relaxation of deflection. As a consequence, the slight relaxation of deflection is due to the desorption/insertion of neutral species.

The values of  $t_p$ ,  $t_T$ , and  $t_{max}$  measured during hydrogen extraction and injection are summarized in Table 1. The values of  $t_p$  and  $t_T$  are similar. The value of  $t_{max}$  is however, much larger in magnitude than the values of  $t_p$  and  $t_T$ . Given that the  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH phase boundary is curved in shape [15], it is concluded that, during hydrogen extraction, a time interval exists between the first nucleation of the  $\gamma$ -NiOOH phase at the electrode/electrolyte interface and the complete phase transformation of  $\alpha$ -Ni(OH)<sub>2</sub> to  $\gamma$ -NiOOH. Furthermore,  $t_{max}$

appears when the averaged molar volume of the film electrode becomes a minimum or a maximum.

Therefore, the values of  $t_p$  and  $t_T$  during hydrogen extraction refer to the time to the first formation of the  $\gamma$ -NiOOH phase at the electrode/electrolyte interface. The  $t_p$  and  $t_T$  during the hydrogen injection correspond to the time to the first formation of  $\alpha$ -Ni(OH)<sub>2</sub> phase at the electrode/substrate interface. The  $t_{max}$  is the time to the complete phase transformation at the both interfaces during hydrogen extraction and injection.

#### 4. Conclusions

Stresses generated during the hydrogen extraction from and injection into a Ni(OH)<sub>2</sub>/NiOOH film electrode are analysed by employing a laser beam deflection technique combined with potentiostatic current transient and EQCM techniques. The experimental results led to the following conclusions.

(1) From the values of the film thickness, the elapsed time for the PBM and the potential step between the hydrogen extraction/injection potential and the plateau potential, the velocity, and the mobility of PBM during the hydrogen extraction and injection are  $2.3 \times 10^{-6}$ – $5.4 \times 10^{-6}$  cm s<sup>-1</sup> and  $3.5 \times 10^{-10}$ – $2.6 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>, respectively.

(2) During hydrogen extraction, the mass change measured suggests that the insertion of K<sup>+</sup> ions only proceeds simultaneously with the ejection of neutral species from the film electrode, after the PBM is finished towards the electrode/electrolyte interface. During hydrogen injection, as the phase boundary moves towards the electrode/substrate interface, the K<sup>+</sup> ions are extracted from the film electrode and then neutral species enter into film electrode. This difference is assigned to the fact that the  $\gamma$ -NiOOH phase grows at the electrode/substrate interface, and the  $\alpha$ -Ni(OH)<sub>2</sub> phase at the electrode/electrolyte interface.

(3) The tensile and compressive deflections measured during hydrogen extraction from injection into the film electrode, respectively, first steeply increased to maximum values and then slowly decrease by a small amount. From

the mass change, transient and the deflection transient simultaneously measured with current transient, it is suggested that the steep tensile and compressive deflections in the initial stage are due to the PBM, while the following slight decrease of the deflections is due to the desorption/insertion of neutral species. This means that the contribution of the PBM to the stresses developed during hydrogen extraction and injection mostly dominates the contribution of desorption/insertion of neutral species.

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