A study on the swelling of a sintered nickel hydroxide electrode

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The swelling and blistering of a sintered nickel hydroxide electrode, which usually determine the life of the electrode, have been found to be dependent on the the change in the density of the active material during charge and discharge. In particular, the swelling after cycling has been related to the degree of formation of γ-NiOOH. The largest swelling, as represented by an increase in the thickness of the electrode, occurs when β-NiOOH changes to γ-NiOOH during charging rather than discharging. Addition of cadmium, zinc and magnesium is effective in preventing the formation of γ-NiOOH. In particular, the swelling can be almost completely prevented by addition of cobalt and cadmium together, even with overcharging at the 1 C rate.

1. Introduction

Currently, Ni–Cd cells are widely used as power sources for computer memory back-ups, portable videos, emergency lighting and other important applications. The sintered nickel hydroxide electrodes used in the Ni–Cd cells are required to show a stable capacity over a wide range of temperature and current density during charging or discharging, a high energy density and a long life.

The unstable capacity of a nickel electrode associated with a low capacity after charging at an elevated temperature or a high capacity after charging at a low temperature can now be improved with additives such as cobalt and cadmium to the active material. A low capacity of a nickel electrode after charging at a high temperature is attributable to a low charge acceptance resulting from the competitive reactions of the oxidation of active material and the evolution of oxygen. The charge acceptance of a nickel electrode at high temperature is generally related to the oxygen overpotential. The addition of cobalt to the nickel hydroxide crystals lowers the oxidation potential of the nickel hydroxide, while coating the electrode surface with $Cd(OH)_2$ increases the oxygen evolution potential. A low oxidation potential and a high oxygen evolution potential are essential to ensure good charge acceptance when charging at high temperature. A high capacity after charging at a low temperature is related to the formation of a higher oxide, γ-NiOOH, and the addition of cadmium to the nickel hydroxide crystals prevents the formation of the γ-NiOOH [1–3]. Therefore, the major problem that remains to be solved is the swelling and blistering of a nickel hydroxide electrode with cycling, especially of an electrode with a high active material loading for a high energy density. It has been reported that swelling and blistering are caused by a decrease in strength or volumetric expansion of the nickel plaque due to its corrosion with cycling, by a high active material loading, by a change in the active material density, or by the O_2 gas pressure [4–6]. Also, attempts to prevent swelling of a nickel electrode by applying a low active material loading, electrochemical impregnation to reduce the corrosion of the nickel plaque, addition of cadmium to the active material, or surface treatment of a nickel electrode with cobalt hydroxide have been reported [4, 7, 8, 9].

This paper deals with the mechanism of swelling and blistering of a nickel electrode with a high active material loading and a means of preventing these problems.

2. Experimental details

The test electrodes were prepared with chemical impregnation of substrates which were made of sintered nickel powder on nickel-plated perforated steel plates 40 mm wide, 40 mm long and 0.7 mm thick. The impregnation solution was of nickel nitrate containing cobalt nitrate, cadmium nitrate, zinc nitrate, magnesium nitrate and/or calcium nitrate. After vacuum impregnation with the solution, the nitrates were converted to hydroxides in alkaline solution then rinsed with water and dried. This process was repeated seven times to load the plaque with active material to approximately 1.7 g cm^{-3} of the plate volume. The test electrodes thus prepared were coupled with cadmium electrodes in KOH solution of specific gravity 1.20 and were subjected to charge/discharge tests. The potentials of the test electrodes were measured against a Hg–HgO reference electrode. The crystal structure of the active material was determined by X-ray diffraction analysis with Co$K\alpha$, Cu$K\alpha$ and Cr$K\alpha$ radiation after a test electrode wet with alkaline solution was dried in vacuum for 1 h and pulverized. The ratio of γ-NiOOH to the total of γ-NiOOH and β-NiOOH was calculated from the integrated intensities of the γ-NiOOH(0 0 3) peak and the β-NiOOH(0 0 1) peak. Change in plate thickness was determined by measurement with a micrometer at several predetermined areas with markings. A cycle life test was conducted with repeated charging at 0.5 C for 3 h and discharging at 0.2 C to 0.00 V against the Hg–HgO reference electrode using an automatic cycler with a high impedance potentiometer. The porosity of a test electrode was measured by means of a nondestructive method utilizing buoyancy in water as shown in the footnotes of Table 1.

3. Results and discussion

3.1. *Relation between active material composition and swelling of a nickel electrode with cycling*

As shown in Fig. 1, the thickness of an electrode tended to increase with cycling. The rate of increase varied with the active material composition and the electrode with addition of only cobalt showed
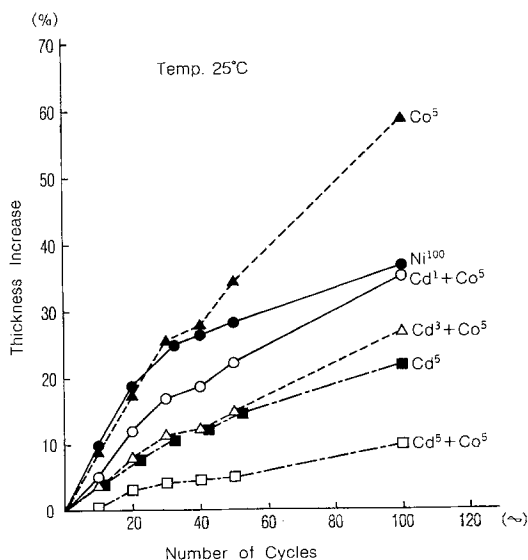

Fig. 1. Thickness change of various nickel electrodes with cycling.

Table 1. Physical properties of sintered nickel electrodes with various composition

Active material composition (mol%)		Plate porosity P* (%)	$\gamma/(\beta + \gamma)$ at the end of charge	Thickness increase (%)	$\gamma/(\beta^\dagger + \gamma)$ at the end of discharge	Thickness increase (%)
Ni(OH)$_2$	100	24.8	0.905	33.2	0.417	39.5
Ni(OH)$_2$	93.4	25.2	0.816	23.4	0.386	31.2
Co(OH)$_2$	6.6					
Ni(OH)$_2$	96.2	24.5	0.462	14.0	0.041	7.2
Cd(OH)$_2$	3.8					
Ni(OH)$_2$	90.0	26.3	0.186	1.7	0.020	3.5
Co(OH)$_2$	5.4					
Cd(OH)$_2$	4.6					
Ni(OH)$_2$	96.4	27.5	1.000	36.3	0.447	41.8
Ca(OH)$_2$	4.6					
Ni(OH)$_2$	94.5	26.4	0.461	7.7	0.125	12.2
Mg(OH)$_2$	5.5					
Ni(OH)$_2$	96.5	23.5	0.433	8.1	0.088	11.9
Zn(OH)$_2$	3.5					

$$P^* = (W_3 - W_1)/(W_3 - W_2) \times 100$$

where W_1 = weight of the dry plate; W_2 = weight of the plate in water; W_3 = weight of the wet plate wiped free of excess water.

$\beta^\dagger$: the line at $21-23°$ (CoKα radiation) is considered to be a mixture of the β-NiOOH(0 0 1) line and the β-Ni(OH)$_2$(0 0 1) line.

the largest increase in electrode thickness, resulting in blistering after 100 cycles. In this experiment, cobalt, which has long been used as an active material stabilizer, was not effective in preventing swelling. As shown in Fig. 2, addition of cadmium together with cobalt was effective in preventing swelling, the effect being proportional to the cadmium content. The effect of cadmium in this respect seems to be enhanced by the addition of cobalt.

In the nickel electrodes after 100 cycles, three types of crystals, γ-NiOOH, β-NiOOH and β-Ni(OH)$_2$, were observed. Fig. 3 shows the ratio of γ-NiOOH to the total of γ-NiOOH and β-NiOOH against the thickness increase at the end of charge after 100 cycles. The thickness increase, or swelling, was proportional to the content of γ-NiOOH, the exception being the result with the electrode containing only cobalt as an additive. This was probably due to insufficient charging owing to poor current conduction caused by blistering. These results suggest that formation of γ-NiOOH is connected with swelling.

3.2. Relation between swelling and crystal change in active material during charging and discharging

Fig. 4 shows an increase in the plate thickness and depicts crystal changes in the active material during charging and discharging of a nickel electrode without any additives. The plate thickness decreased slightly during charging (A → B) until the electrode approached the approximately 75% charged state, after which the plate thickness increased in proportion to the amount of charging. In
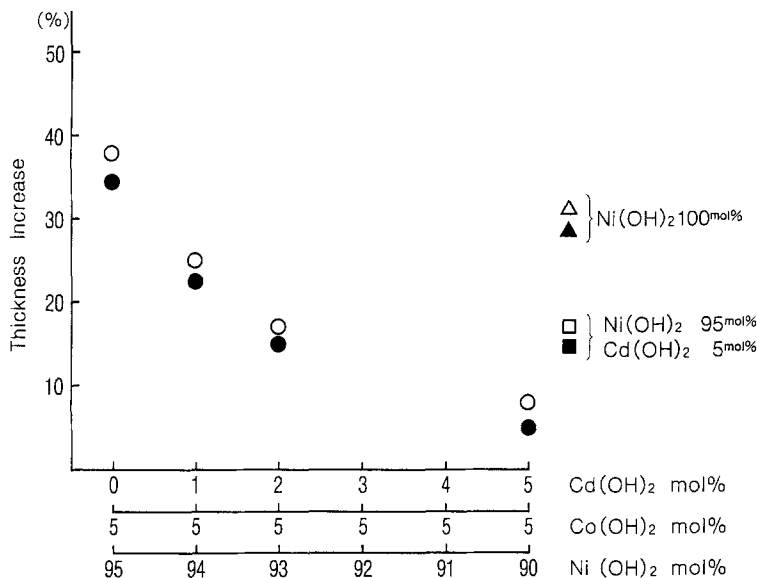
Fig. 2. Thickness change versus active material composition after 50 cycles. ○ △ □ : plate thickness at the end of discharge. ● ▲ ■ : plate thickness at the end of charge.

the overcharging region (C → D) the plate thickness increased markedly. During discharging (D → E → F) the plate thickness still increased markedly with a slight decrease at the end of discharging and during subsequent standing. In the following charging (150% charge) and discharging cycle the plate thickness showed a similar change, resulting in a higher thickness than that before charging. Thus the plate thickness increased with cycling. X-ray diffraction characteristic charts of the electrode at various stages of charging or discharging, C, D, E, F (Fig. 4) are shown in Fig. 5. These results suggest the following crystallographic changes during charging and discharging.
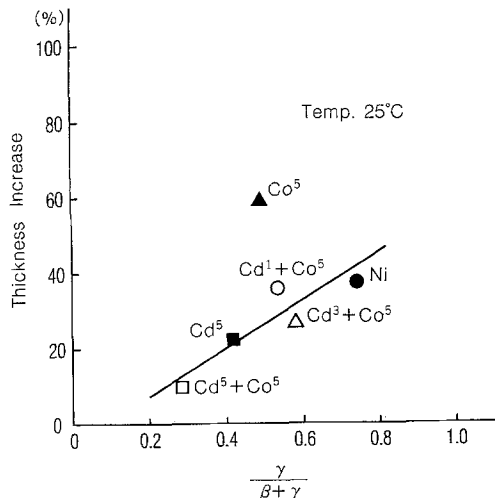

Fig. 3. Thickness change versus ratio of γ-NiOOH to the total of γ-NiOOH and β-NiOOH at the end of charge after 100 cycles.
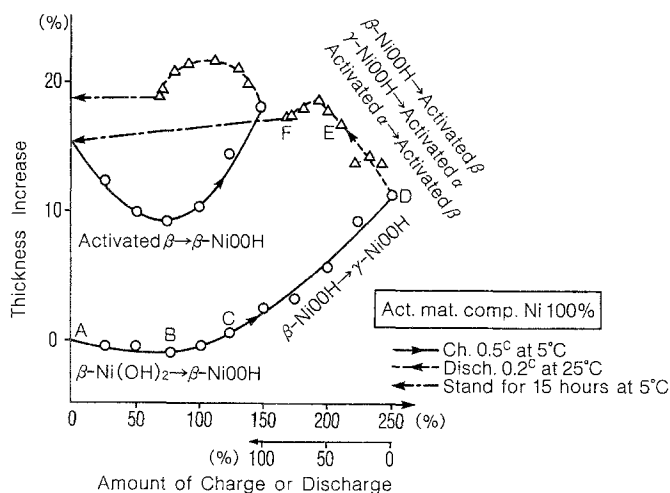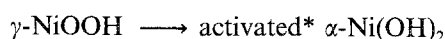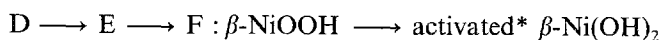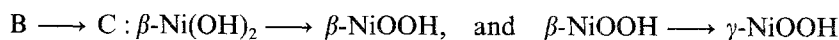
Fig. 4. Change in plate thickness during charge and discharge.

A $\longrightarrow$ B : β-Ni(OH)$_2$ $\longrightarrow$ β-NiOOH

B $\longrightarrow$ C : β-Ni(OH)$_2$ $\longrightarrow$ β-NiOOH, and β-NiOOH $\longrightarrow$ γ-NiOOH

C $\longrightarrow$ D : β-NiOOH $\longrightarrow$ γ-NiOOH

D $\longrightarrow$ E $\longrightarrow$ F : β-NiOOH $\longrightarrow$ activated* β-Ni(OH)$_2$

γ-NiOOH $\longrightarrow$ activated* α-Ni(OH)$_2$

activated* α-Ni(OH)$_2$ $\longrightarrow$ activated* β-Ni(OH)$_2$

In the X-ray diffraction analysis of the electrodes at stages E and F, however, no activated α-Ni(OH)$_2$ was observed, although the analysis was completed with the electrodes still containing electrolyte within 10 min of the end of discharge. This suggests that the chemical conversion from activated α-Ni(OH)$_2$ to activated β-Ni(OH)$_2$ proceeded very quickly.

Changes in the crystal forms of nickel hydroxide during charge and discharge together with the associated change in density, are shown in Fig. 6 [10, 11]. The reduction in plate thickness in the stage A → B is considered to be due to the 15% higher density of β-NiOOH as compared with that of β-Ni(OH)$_2$. The remarkable increase in the plate thickness in the stage C → D is considered to be due to the 23% lower density of γ-NiOOH compared to β-NiOOH. As the X-ray diffraction analysis indicated, both γ-NiOOH and β-NiOOH were contained in the electrode after overcharging (stage D). When this electrode was discharged it showed a two-step discharge curve, suggesting preferential discharge of β-NiOOH. An X-ray diffraction analysis indicted that the electrode discharged to the end of the first step discharge curve (stage E) contained a substantial amount of γ-NiOOH comparable to that before the discharge. Therefore the increase in the plate thickness in the stage D → E is considered to be primarily due to the decrease in the density from β-NiOOH to activated β-Ni(OH)$_2$. The increase in the plate thickness in the stage E → F would have been much larger if it had been due to the 34% lower density of activated α-Ni(OH)$_2$ compared to γ-NiOOH. In fact, the increase in the plate thickness was relatively small, which suggested that the conversion of α-Ni(OH)$_2$ to β-Ni(OH)$_2$ coupled with the 29% density increase also occurred at the same time. Change in the plate thickness during charge and discharge of an electrode containing active material

* When β-NiOOH was completely discharged it was found that the β-NiOOH had not been reduced to divalent, but always remained 2.20- to 2.26-valent. This was called 'Activated β-Ni(OH)$_2$,' to distinguish it from the conventional divalent β-Ni(OH)$_2$. In a similar sense, 'Activated α-Ni(OH)$_2$' was distinguished from the conventional divalent α-Ni(OH)$_2$.
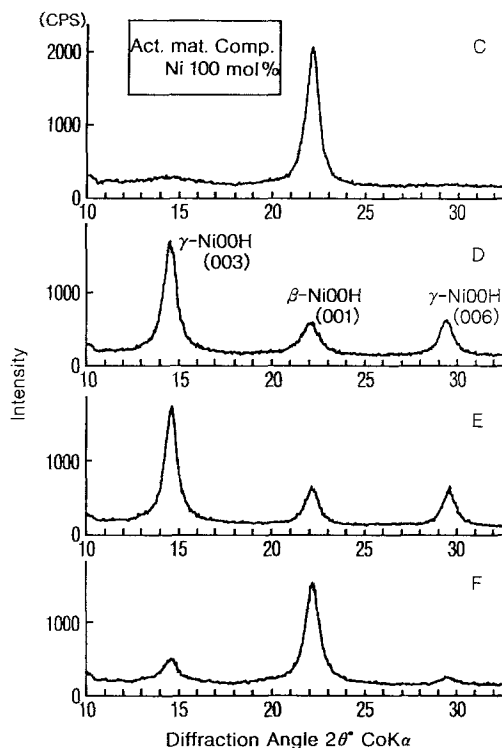
Fig. 5. X-ray diffraction patterns for nickel electrodes during charge and discharge.

composed of 90% $Ni(OH)_2$: 5% $Cd(OH)_2$: 5% $Co(OH)_2$, which showed the least swelling in cycling, is shown in Fig. 7. The plate thickness changed very little. As shown in Fig. 8 the active material after 250% overcharging consisted of almost only β-NiOOH with very little γ-NiOOH. Thus it is believed that the electrode having active material composed of nickel, cadmium and cobalt undergoes charging and discharging with the crystal change primarily between β-Ni(OH)$_2$ or activated β-Ni(OH)$_2$ and β-NiOOH with a small density change. Consequently it can be concluded that the change of active material to a dense crystal, γ-NiOOH in particular, plays an important role in causing swelling of a nickel electrode.

3.3. *Relation between the plate porosity and various nickel hydroxide crystals*

In additon to the plate thickness change, the change in plate porosity during charge and discharge was examined in order to correlate it with the change in crystal form of the active material. Fig. 9 shows a change in the plate porosity during charge and discharge at the various stages as shown in
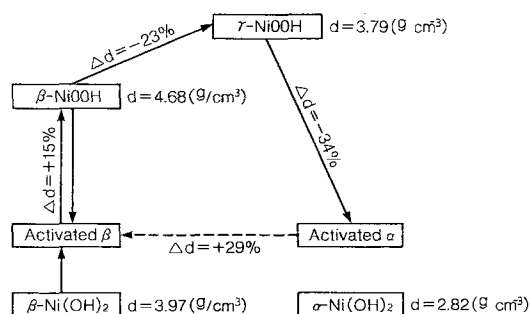

Fig. 6. Density and crystal change in nickel active material on charge and discharge.
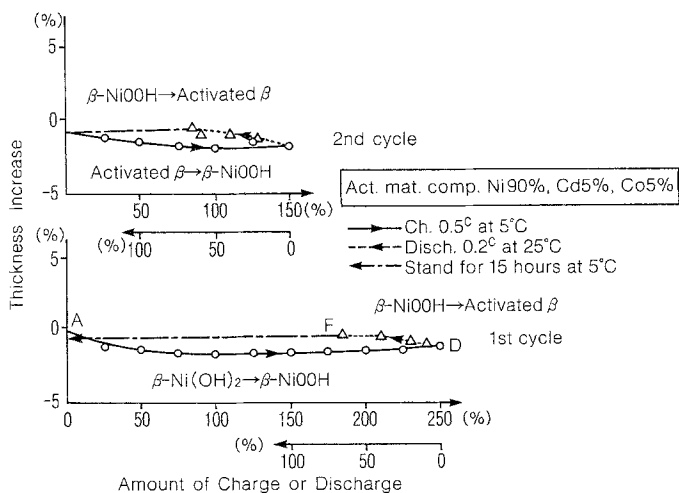
Fig. 7. Change in plate thickness during charge and discharge.

Fig. 4. During the charging period corresponding to the stage A → B, the porosity increased in agreement with the density increase of active material caused by the crystal change from β-Ni(OH)$_2$ to β-NiOOH. In the latter part of the charging period corresponding to the stage B → C the porosity decreased slightly, probably due to partial formation of low density γ-NiOOH which was confirmed by X-ray diffraction analysis. During the overcharging period corresponding to the stage C → D, however, the porosity again increased in spite of the overwhelming formation of low density γ-NiOOH. During the discharging period corresponding to the stage D → E → F the porosity change was small, resulting in a more porous state compared to that before charging. Thus the porosity increase caused by the formation of γ-NiOOH during overcharging was never offset in the subsequent discharge.
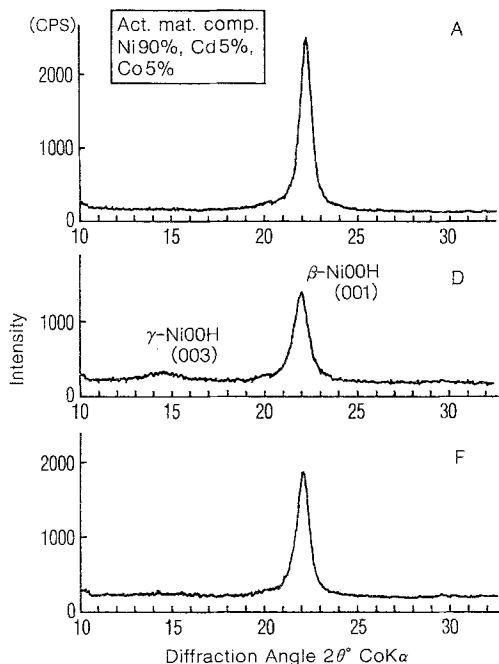

Fig. 8. X-ray diffraction patterns for nickel electrodes during charge and discharge.
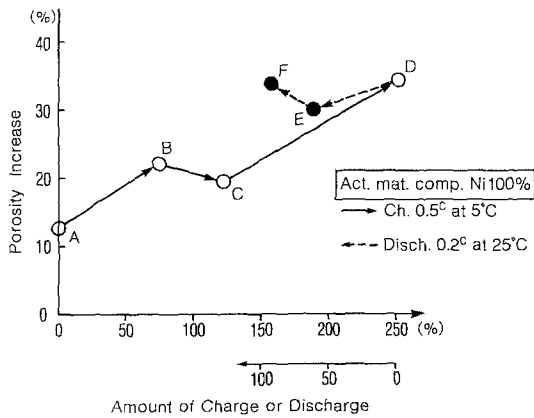
Fig. 9. Change in plate porosity during charge and discharge.

3.4. *Relation between active material composition and plate swelling*

There are reports that lithium, cobalt and cadmium are effective in preventing formation of γ-NiOOH [8, 12], but as shown in Table 1, the cobalt added in co-precipitation with nickel hydroxide was not effective in preventing formation of γ-NiOOH. It has been found [1] that the cadmium added by co-precipitation with nickel hydroxide has two functions: it causes an increase in the oxygen evolution potential and prevents the formation of γ-NiOOH. It was also found that, unlike cobalt, cadmium has no effect in lowering the oxidation potential of nickel hydroxide; rather, the oxidation potential becomes slightly higher with addition of cadmium. Hence cobalt has no effect in preventing formation of γ-NiOOH in overcharging. In this sense, elements with a fixed valence which can substitute for divalent nickel are considered to be effective in preventing formation of nickel with a higher valence. For this reason, magnesium, calcium and zinc together with cadmium were selected from the Group II elements in the periodic table, excluding barium which is only sparingly soluble in high-concentration nickel nitrate solution and mercury which was avoided from the standpoint of pollution. These samples of $Ni(OH)_2$ containing various additives were prepared by co-precipitation from nitrate solution using NaOH solution. Contents of additives in samples were determined by chemical analysis.

The test electrodes were charged at the 1 C rate for 10 h [9] to promote formation of γ-NiOOH and discharged at the 0.2 C rate to 0.00 V versus Hg–HgO for deep discharge. Table 1 summarizes the test results. As shown, no correlation was observed between the plate porosity and the plate
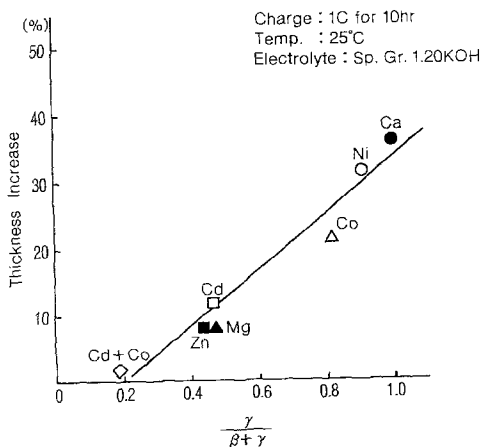

Fig. 10. Thickness change versus ratio of γ-NiOOH to the total of γ-NiOOH and β-NiOOH for various nickel electrodes when overcharged.
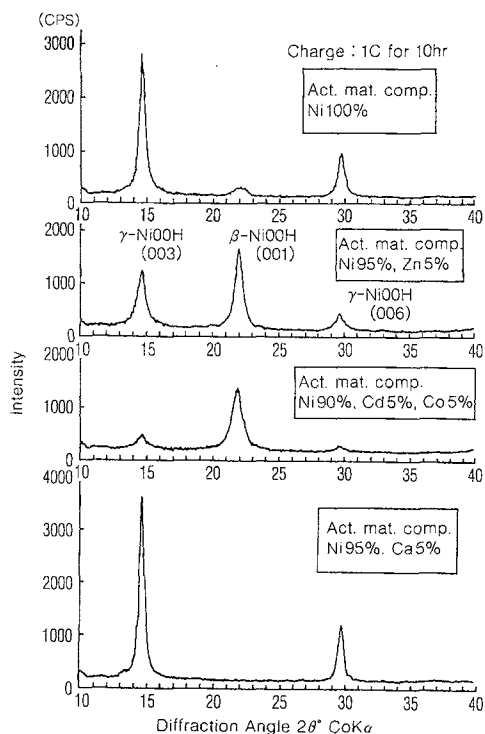
Fig. 11. X-ray diffraction patterns for nickel electrodes containing various additives when overcharged.

thickness increase. This was probably due to the fact that a porosity lower than 30% was not sufficient to absorb the expansion and contraction of active material. The plate thickness increase is proportional to the amount of γ-NiOOH formed. Fig. 10 shows the effect of the additives in the prevention of plate swelling. Zinc, magnesium and cadmium are effective, with cadmium and cobalt together being the most effective. Calcium with the largest ion radius, however, brought about an accelerated formation of γ-NiOOH as shown in the X-ray diffraction chart in Fig. 11. This could be due to the possible poor dissolution of calcium with nickel hydroxide to become a solid–solution. All the additives selected from the Group II elements showed a higher oxidation potential in charging, but the addition of cobalt and cadmium together showed a lower oxidation potential than that with no additives. This suggests that addition of cobalt and any of the Group II elements together is beneficial since they compensate for each other.

4. Conclusion

The present study has indicated that the swelling and blistering of a nickel electrode are brought about by the density change of active material from β-NiOOH to γ-NiOOH during overcharging. This suggests that the life of the electrode can be prolonged by prevention of the formation of γ-NiOOH. Cobalt itself was not effective for this purpose, but zinc, magnesium or cadmium selected from the Group II elements in the periodic table were effective. Use of cobalt and cadmium together was most effective. Further studies should be carried out on the addition of cobalt and other Group II elements together.

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