DEVELOPMENT OF A NICKEL ELECTRODE HAVING STABLE PERFORMANCE AT VARIOUS CHARGE AND DISCHARGE RATES OVER A WIDE TEMPERATURE RANGE

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Summary

Studies were made of improvements to be obtained in Ni electrodes by increasing charge acceptance and stabilising capacity at various charge and discharge rates over a wide temperature range. The charge acceptance of Ni electrodes is generally related to the oxygen evolution overvoltage· the addition of $Co(OH)_2$ to $Ni(OH)_2$ crystals has been found to lower the oxidation potential of $Ni(OH)_2$, while coating the electrode surface with $Cd(OH)_2$ has been found to increase the oxygen evolution potential. Capacity stabilization of Ni electrodes can be basically achieved by preventing the formation of a higher oxide, γ-NiOOH, and the addition of $Cd(OH)_2$ to $Ni(OH)_2$ crystals has been found to be effective for this purpose. Thus, a Ni electrode has been developed consisting of a solid-solution of $Ni(OH)_2$ and an adequate amount of $Co(OH)_2$ and $Cd(OH)_2$ and where the content of the latter is relatively high at the electrode surface This electrode exhibits a stable capacity over wide operating conditions throughout cycling.

Introduction

During widespread use of sealed Ni–Cd batteries, they are often used under a variety of conditions including charging at various rates over a wide temperature range. The Ni electrode is well known for delivering a lower capacity when charged with a low current at an elevated temperature, and delivering increased capacity when charged at high currents and relatively low temperatures The decreased capacity of a Ni electrode is a problem because the capacity of a sealed Ni–Cd battery is generally designed to be limited by the Ni electrode. On the other hand, the higher than expected capacity of the Ni electrode is also a problem because it adversely changes the predetermined positive/negative electrode capacity ratio which, in the sealed Ni–Cd battery, is vital to avoid hydrogen evolution.

Some papers [1, 2] have reported that the addition of $Co(OH)_2$ in a relatively large amount to $Ni(OH)_2$ crystals or the use of LiOH electrolyte improves the capacity of the Ni electrode when charged at a low current and

an elevated temperature The addition of $Co(OH)_2$ in relatively large amount, however, has been shown to result in a substantial decrease in discharge voltage, and the use of LiOH electrolyte impairs the capacity during charge at low temperature One of the authors of the present paper reported [3] that the addition of both $Co(OH)_2$ and $Cd(OH)_2$ to $Ni(OH)_2$ crystals improved the capacity of the Ni electrode when charged at low current and elevated temperature, but its mechanism was not clear.

It is known that the increase in capacity of the Ni electrode is associated with a change in the NiOOH crystals Several papers [4 - 6] have been published on the change in NiOOH crystals, but there are few papers [7] which discuss the influence of additives on the NiOOH crystal change

It is the purpose of this paper to discuss the mechanism and the effect of additives to the Ni electrode in improving its capacity when charged at a low current and an elevated temperature, and in preventing an increase in capacity when charged at a high current and a relatively low temperature.

Experimental

Sintered Ni-powder plaques, 40 mm wide, 40 mm long and 0 65 mm thick, were filled with active material by repeated impregnation with $Ni(NO_3)_2$ solution with/without $Co(NO_3)_2$ and/or $Cd(NO_3)_2$ followed by drying, and then conversion to hydroxides in alkaline solution, followed by drying, to obtain test electrodes For some of the electrodes prepared in this way, the so-called APM (Anti-Polar Mass) additional impregnation process [8] was applied, which included impregnation with 2 - 4 molar $Cd(NO_3)_2$ solution, followed by drying, and conversion to hydroxides in alkaline solution prior to final drying. These positive electrodes were tested in KOH solution of sp gr 1 20, their voltages being measured against an Hg/HgO reference electrode

To determine the crystalline structure, X-ray diffraction data were obtained using Cu $K\alpha$ or Co $K\alpha$ radiation In addition, C-size cells were fabricated with positive electrodes, prepared in a manner similar to that described above, coupled with regular negative electrodes and separators, and tested to confirm cell performance.

Results and discussion

1 Capacity variation of Ni electrodes when charged at various rates and temperatures

The capacity of a pure $Ni(OH)_2$ electrode varied considerably when it was charged at various rates over a relatively large temperature range, as shown in Table 1 When expressed as a ratio with capacity after charging at a 0.1 C rate at 25 °C, the capacity varies from 68 to 120%. The capacity variation, however, is 72 - 114% for the 95 mol% $Ni(OH)_2$ 5 mol% $Co(OH)_2$ composition, and 79 - 108% for the 95 mol% $Ni(OH)_2$.5 mol% $Cd(OH)_2$

TABLE 1

Positive active material compositions *vs* capacities

Act mat comp (mol%)		Charge temperature (°C)								
		25			5			45		
		Charge current (time, h)								
		0 033 C (45)	0 1 C (15)	0 5 C (3)	0 033 C (45)	0 1 C (15)	0 5 C (3)	0 033 C (45)	0 1 C (15)	0 5 C (3)
Ni(OH)$_2$	100	0 279 A h (79%)	0 352 A h (100%)	0 401 A h (114%)	0 386 A h (110%)	0 394 A h (112%)	0 424 A h (120%)	0 238 A h (68%)	0 290 A h (82%)	0 411 A h (117%)
Ni(OH)$_2$ Co(OH)$_2$	95 5	0 242 (72%)	0 337 (100%)	0 364 (108%)	0 349 (104%)	0 359 (107%)	0 377 (112%)	0 272 (81%)	0 304 (90%)	0 383 (114%)
Ni(OH)$_2$ Cd(OH)$_2$	95 5	0 361 (99%)	0 364 (100%)	0 371 (102%)	0 360 (99%)	0 366 (101%)	0 368 (101%)	0 286 (79%)	0 379 (104%)	0 394 (108%)
Ni(OH)$_2$ Cd(OH)$_2$ Co(OH)$_2$	90 5 5	0 339 (98%)	0 346 (100%)	0 345 (100%)	0 338 (98%)	0 345 (100%)	0 341 (99%)	0 367 (106%)	0 360 (104%)	0 364 (105%)

Discharge 0 2 C to 0 00 V us Hg/HgO at 25 °C

composition, which is somewhat small compared with that for the pure $Ni(OH)_2$ composition, indicating some effect of the Co or Cd addition Furthermore, the capacity variation is even smaller, 98 - 106%, for the 90 mol% $Ni(OH)_2$:5 mol% $Co(OH)_2$ 5 mol% $Cd(OH)_2$ composition, implying that the capacity variation can be minimized by the addition of an appropriate amount of $Co(OH)_2$ and/or $Cd(OH)_2$

2 Charge potential of Ni electrode

On the assumption that the poor capacities of the Ni electrodes after charging at a low rate under normal or high temperature are attributable to a low charge efficiency resulting from the competitive reactions of the oxidation of active material and the evolution of oxygen, test electrodes in a discharged state were charged at a 0 1 C rate at 25 °C to obtain their charge voltage curves, from which the median oxidation potential, Vox 1 (the median potential to oxygen evolution), the oxygen evolution potential, Vo2, and the voltage difference, η, between Vo2 and the maximum oxidation potential (the oxidation potential just before oxygen evolution starts), Vox 2, as shown in Fig 1, were obtained
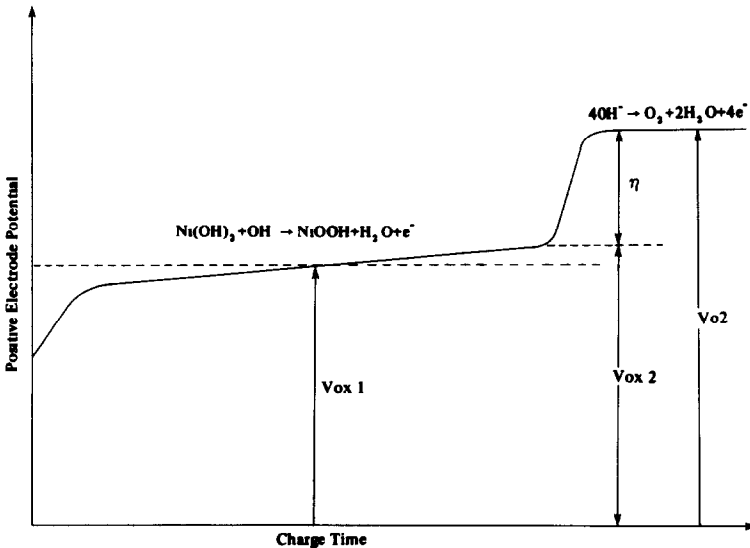
Vox 1 Charge potential after 5 hr in charging at 0.1C rate

Fig 1 Positive electrode potential change during charge

2 1 Additives affecting the median oxidation potential, Vox 1

As shown in Fig 2, the addition of 5 mol% of $Co(OH)_2$ to $Ni(OH)_2$ crystals lowered the median oxidation potential, Vox 1, considerably, but the addition of $Cd(OH)_2$ showed either no effect or even an adverse effect.
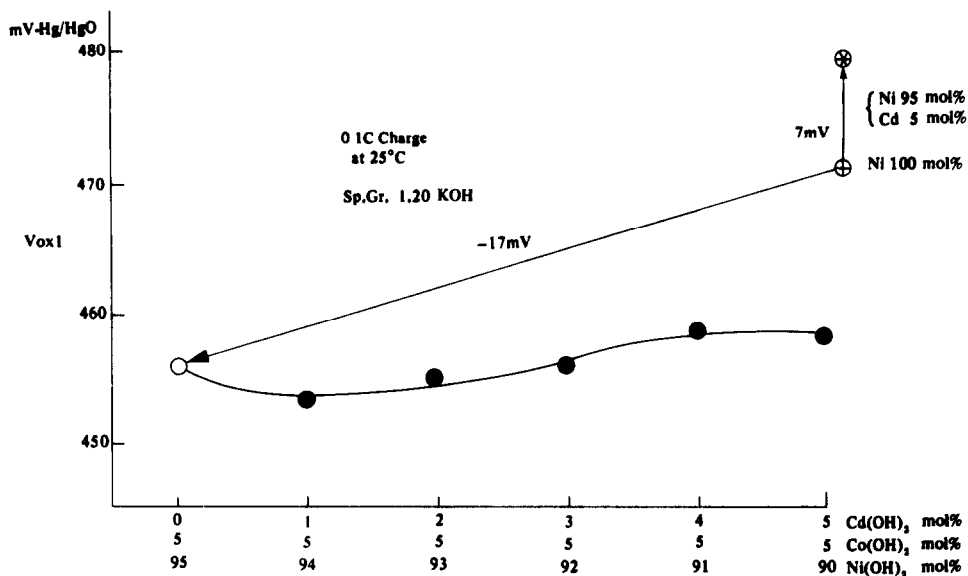
Fig 2 Positive active material composition *vs* median oxidation potential
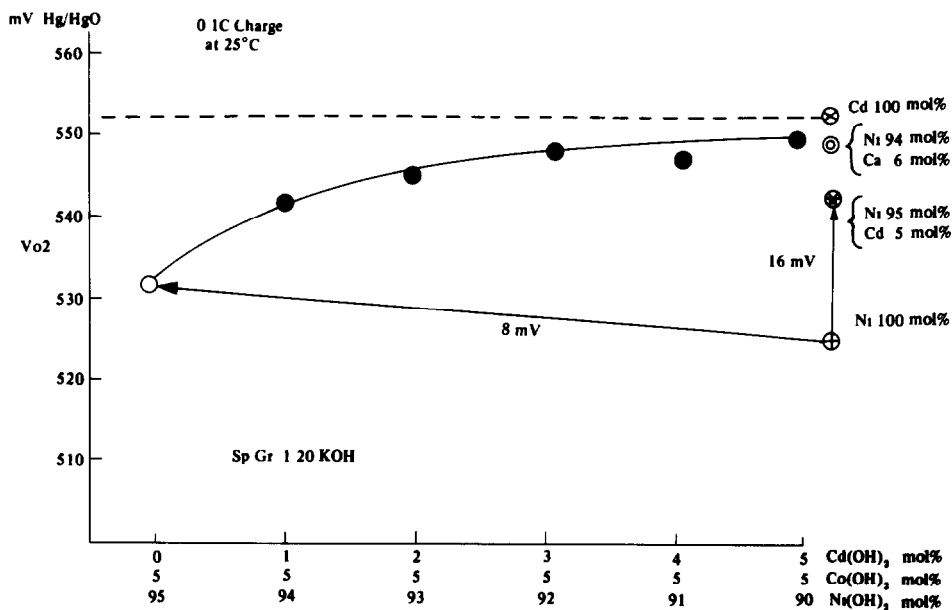

Fig 3 Positive active material composition *vs* oxygen evolution potential

2.2. *Additives affecting the oxygen evolution potential, Vo2*

As shown in Fig. 3, the addition of 5 mol% of $Co(OH)_2$ to $Ni(OH)_2$ crystals resulted in a shift of the oxygen evolution potential, Vo2, to a more noble potential, but the addition of 5 mol% of $Cd(OH)_2$ instead of $Co(OH)_2$

shifted the oxygen evolution potential to an even more noble potential The addition of up to 5 mol% of Cd(OH)₂ to the 95 mol% Ni(OH)₂ 5 mol% Co(OH)₂ composition shifted the oxygen evolution potential to an even more noble potential, suggesting a tendency that the greater the Cd(OH)₂ content, the higher the oxygen evolution potential Ca(OH)₂ showed a similar effect to Cd(OH)₂ in shifting the oxygen evolution potential to a higher potential

2 3 Combination of additives to obtain a large voltage difference, η, between the maximum oxidation potential and the oxygen evolution potential

As shown in Fig 4, the addition of either 5 mol% of Co(OH)₂ or of Cd(OH)₂ resulted in a substantial increase in η compared with pure Ni(OH)₂ Furthermore, the addition of up to 5 mol% of Cd(OH)₂ to the 95 mol% Ni(OH)₂ 5 mol% Co(OH)₂ composition further increased η, suggesting that the greater the Cd(OH)₂ content, the higher is η Also, an increase in Co(OH)₂ may also be effective in increasing η, but the known drawback of a low discharge voltage will limit the addition of Co(OH)₂ to 5 mol% in practice Since Cd(OH)₂ does not reduce the discharge voltage, the amount of its addition is not limited provided that the amount of Ni(OH)₂ is not excessively reduced

Cobalt, being an element with a variable valency, is considered to improve the proton conductivity of Ni(OH)₂, resulting in a lower Ni(OH)₂
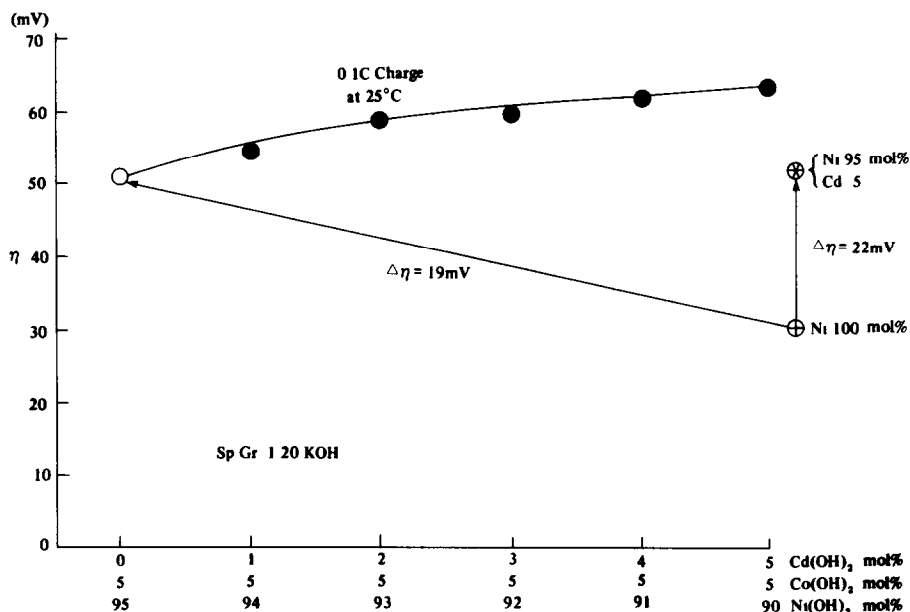

Fig 4 Positive active material composition *vs* voltage difference between maximum oxidation potential and oxygen evolution potential

oxidation potential, while cadmium, being an element of fixed valency, is not considered to be suitable for this purpose

2 4 Coating of the electrode with Cd

The reaction leading to oxygen evolution is generally believed to take place at the surface of the electrode For this reason, the charge–voltage curve of an electrode whose surface was coated with Cd by the APM additional impregnation process was compared with an electrode with no APM treatment, as shown in Fig 5 After the additional impregnation, the Cd(OH)$_2$ content was considered to have increased, on average, for the total electrode by about 1 5 mol% judging from a weight increase of approximately 2% of the total electrode weight The electrode coated with Cd, however, showed a higher oxygen evolution potential than was expected from a 1.5 mol% Cd(OH)$_2$ addition throughout the active material, indicating that the higher Cd content at the surface is more effective in obtaining higher η by shifting the oxygen evolution potential to a higher potential. Figure 6 shows a schematic representation of the process, suggesting that the change occurs at the surface of the electrode in the APM additional impregnation On immersing the electrode in Cd(NO$_3$)$_2$ solution, the surface layer of the active material would be partly dissolved and impregnated with Cd(NO$_3$)$_2$ instead After drying, on immersion in alkaline solution followed by drying, the active material would consist of a double-layered structure in which the outer layer would be of Cd-rich Ni(OH)$_2$ containing Co(OH)$_2$, which would be coated with isolated Cd(OH)$_2$
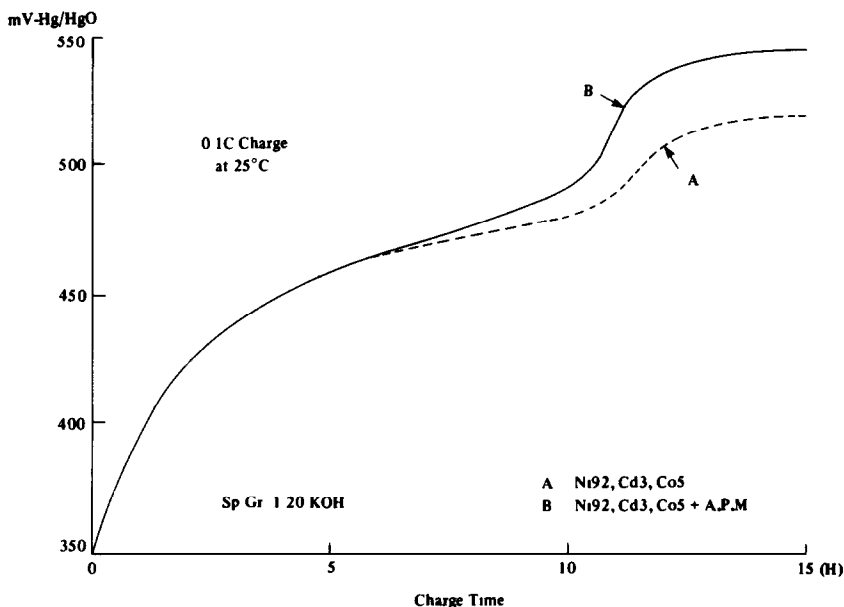

Fig 5 Surface coating with cadmium for higher oxygen evolution potential
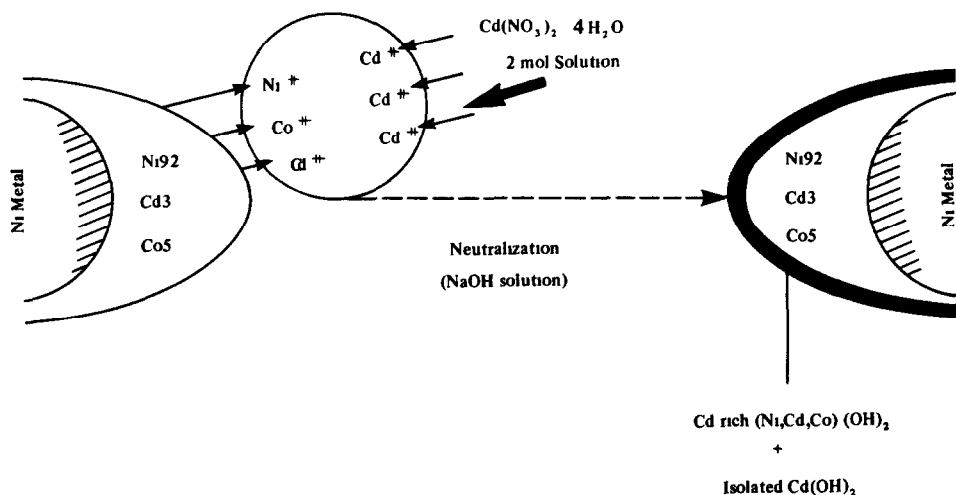
Fig. 6 Model showing surface coating with cadmium

2 5 Capacities of cells with positive electrodes of various compositions

Table 2 shows the capacities, after charging at a 1/30 C rate at 45 °C, for C-size cells with positive electrodes of various compositions considered suitable for this type of use. The cells with positive electrodes containing Co, either with or without Cd, which were processed by the APM additional impregnation technique apparently showed higher capacities. This confirms the assumption that the poor capacities of the Ni electrodes after charging at a low rate at normal or high temperatures are attributable to low charge efficiency. This is caused by the competitive reactions of the oxidation of the active material and the evolution of oxygen, which, accordingly, can be improved by increasing the voltage difference between the oxidation potential and the oxygen evolution potential

TABLE 2

Positive active material composition vs capacity after charging at a low rate at 45 °C for "C" size cell

Pos act mat comp (mol%)	Capacity (mA h)
Ni 92, Co 5, Cd 3	1412
Ni 95, Co 5 + A.P M	1555
Ni 92, Co 5, Cd 3 + A P.M	1554

Charge 1/30 C for 48 h
Discharge 1 C to 1 10 V
Temp 45 °C

3 The effect of additives on the change in NiOOH crystals

3 1 Change in NiOOH crystals by charging at a high current density

The increase in capacity after charging at a 0 5 C rate, especially for the positive electrodes not containing Cd and shown in Table 1 is considered to be related to a change in the NiOOH crystals, because in charging at a high rate the electrodes are believed to be completely charged, regardless of their compositions When positive electrodes of various compositions were charged at a 1 C rate for 10 h at 25 °C, the electrodes not containing Cd showed a lower voltage on discharge than is usually observed in the discharge of β-NiOOH. This lower voltage corresponded to what was observed in the discharge of γ-NiOOH.

Figure 7 shows the ratio of γ-NiOOH to β-NiOOH according to X-ray diffraction analysis of the electrodes. As shown here, the electrodes free from Cd were found to have formed a considerable amount of γ-NiOOH, implying that the increase in capacity was attributable to the formation of γ-NiOOH, as suspected The formation of γ-NiOOH was almost prevented by the addition of 5 mol% of $Cd(OH)_2$ alone, or 5 mol% of $Co(OH)_2$ together with at least 2 mol% of $Cd(OH)_2$

The measurement of the oxidation state of the positive active material, x, of NiO_x by iodometry, showed that the active material after impregnation and conversion to hydroxide corresponded to $NiO_{1 00}$, but once charged it never returned to this figure, but stayed as $NiO_{1.10}$ or even a higher oxide state when fully discharged X-ray diffraction analysis showed that the discharge product of γ-NiOOH was β-Ni(OH)$_2$ with the remainder γ-NiOOH,
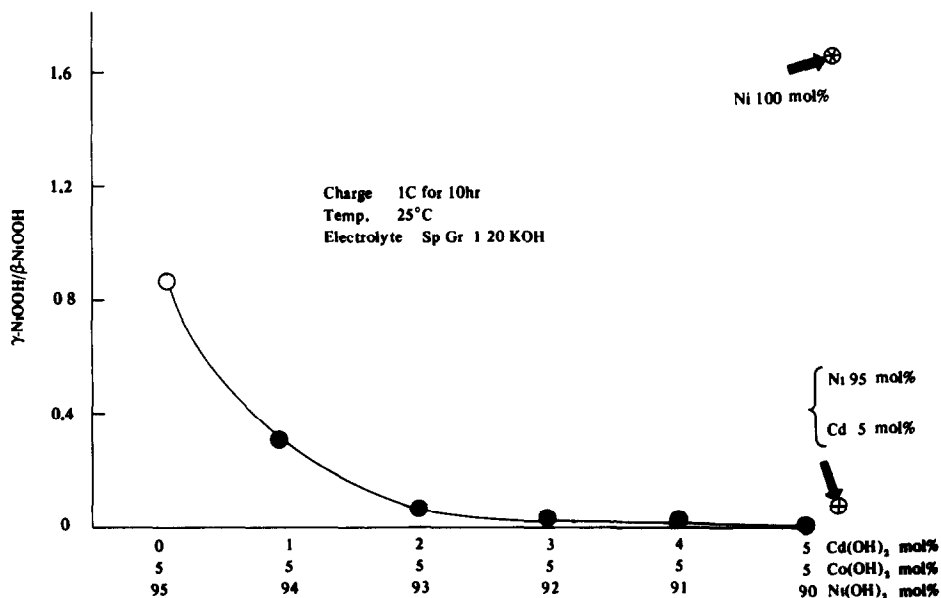

Fig 7 Positive active material composition vs ratio of γ-NiOOH to β-NiOOH when charged

though it is believed that γ-NiOOH converts to α-3Ni(OH)$_2 \cdot$ 2H$_2$O on discharge The fact that the chemically synthesized α-3Ni(OH)$_2 \cdot$ 2H$_2$O immediately converted to β-Ni(OH)$_2$ in sp gr 1 20 KOH solution suggested that α-3Ni(OH)$_2 \cdot$ 2H$_2$O formed by the discharge of γ-NiOOH immediately converted to β-Ni(OH)$_2$ also

Figure 8 summarizes these crystal changes in Ni active material on charge and discharge. For active material containing Cd in its crystals, the reaction on charge and discharge is β-Ni(OH)$_2 \rightleftarrows \beta$-NiOOH, while for material with Cd-free crystals the reaction is β-Ni(OH)$_2 \rightarrow \beta$-NiOOH $\rightarrow \gamma$-NiOOH $\rightarrow$ α-3Ni(OH)$_2 \cdot$ 2H$_2$O $\rightarrow \beta$-Ni(OH)$_2$ In contrast to the effect of improving proton conductivity in Ni(OH)$_2$, the effect of preventing the formation of γ-NiOOH by the addition of cadmium is considered to be primarily related to the fact that cadmium is an alkaline earth metal of fixed valency The
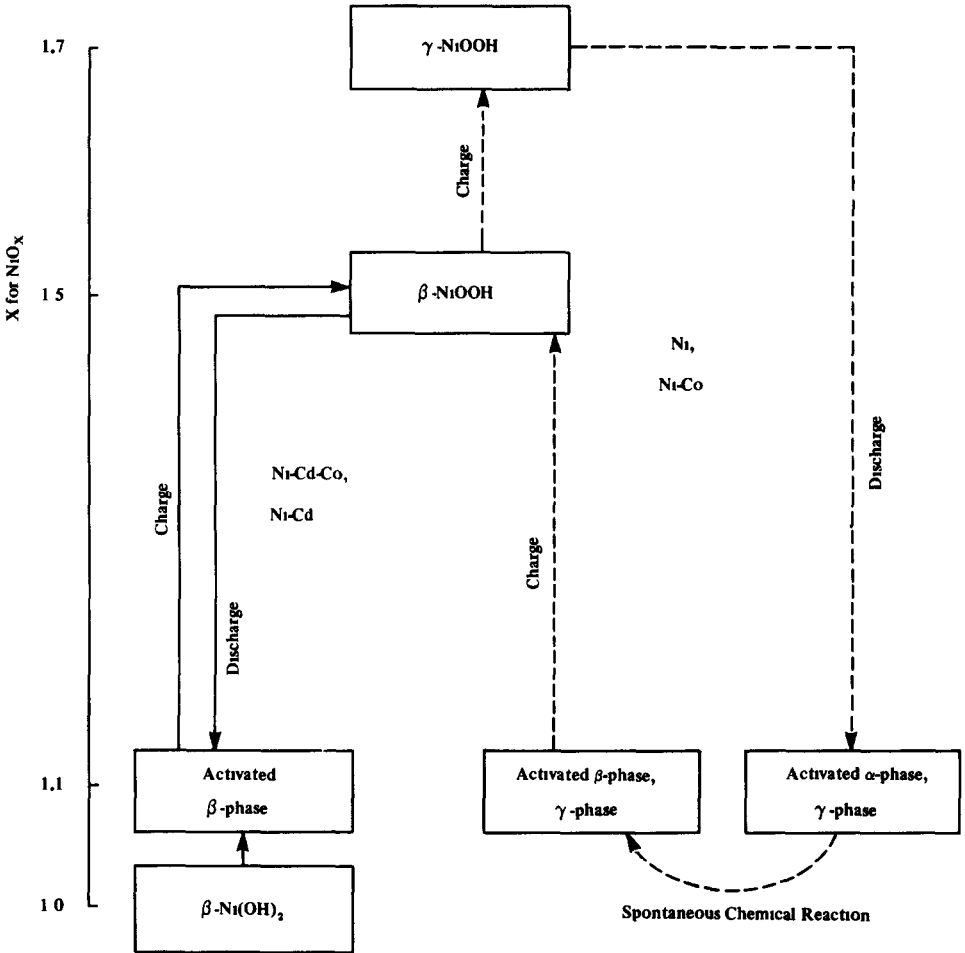

Fig 8 Positive active material composition vs crystal change in Ni active material on charge and discharge

effect of cadmium in this respect seems to be somewhat enhanced by the addition of cobalt. In this sense, magnesium and calcium are expected to show an effect similar to cadmium, while iron may behave similarly to cobalt

3 2 Increase in capacity of positive electrode with cycling

Table 3 shows the capacity increases of positive electrodes of typical composition after 400 cycles at standard charge and discharge rates The
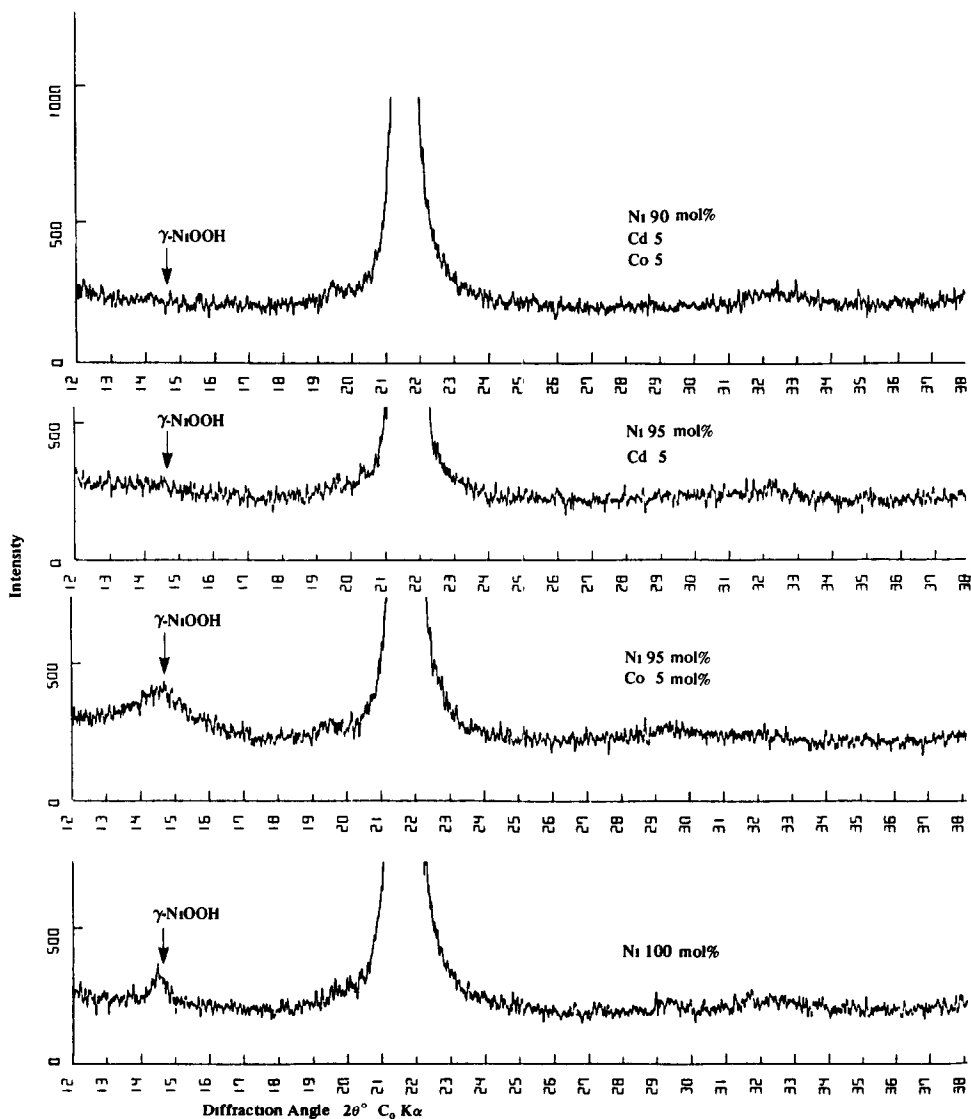

Fig 9 X-ray diffraction data for positive active materials after cycling

TABLE 3

Positive active material composition *vs* capacity increase after cycling

Capacity	Positive active material composition			
	Ni 100 mol%	Ni 95 mol% Co 5 mol%	Ni 95 mol% Cd 5 mol%	Ni 90 mol% Cd 5 mol% Co 5 mol%
Initial (mA h)	364	354	351	358
After 400 cycles (mA h)	436	433	401	400
Increase (%)	20	22	14	12

Charge 0 1 C for 15 h
Discharge 0 2 C to 0.00 V *vs* Hg/HgO.
Electrolyte sp gr. 1 20 KOH
Temperature 25 °C

increase in capacity was substantially higher for the electrodes free from Cd, suggesting the formation of γ-NiOOH in these electrodes, though they were cycled at relatively low rates Figure 9 shows X-ray diffraction patterns of the active materials of all the test electrodes in these cycling tests. In the absence of Cd the active materials clearly show the peak for γ-NiOOH in their diffraction patterns. This confirms that γ-NiOOH can be formed in the Cd-free Ni electrode after substantial cycling even when this is at relatively low rates.

Conclusions

A Ni electrode has been proposed which shows a stable capacity over wide ranges of charge and discharge rates and temperature throughout cycling. Such an electrode should contain an adequate amount of $Co(OH)_2$ and $Cd(OH)_2$ in the $Ni(OH)_2$ crystals and be coated with a $Cd(OH)_2$-rich outer layer. Cobalt has been found to lower the oxidation potential of $Ni(OH)_2$, probably by improving the proton conductivity of the electrode. Cadmium, on the other hand, has been found to have two separate effects on the electrode. Namely, the cadmium in the $Ni(OH)_2$ crystals is believed to prevent the formation of γ-NiOOH, while the cadmium on the surface of the electrode is considered to raise the oxygen evolution potential. A low oxidation potential and a high oxygen evolution potential are essential to ensure good charge acceptance when charging at a low rate under high temperature, thus providing a normal capacity after such charging; the prevention of the formation of γ-NiOOH gives a relatively constant capacity over wide operating conditions throughout cycling.

Acknowledgement

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