

The influence of calcium compounds on the behaviour of the nickel electrode

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Abstract

The nickel hydroxide electrode normally exhibits a poor charge-acceptance which results from the competitive reactions of the oxidation of active material and the evolution of oxygen. The combined addition of cobalt and a calcium compound to the nickel hydroxide can improve appreciably the utilization and discharge potential of the active material. The action of the calcium additive is to increase the oxygen evolution potential, while the cobalt imparts good conductivity to the active material for both electrons and protons. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The positive nickel electrode strongly influences the performance of nickel/cadmium and nickel/metal hydride (Ni–MH) batteries because, in these batteries, the capacity of the negative is greater than that of the positive and, hence, the cell capacity is limited by the positive electrode. For Ni–MH cells, in particular, the performance of the nickel electrode should be sufficiently high to match the superior properties of the negative, hydrogen-storage, alloy electrode.

In recent years, with the progress of research and development of Ni–MH batteries, the preparation of a high-performance nickel electrode becomes both important and urgent. It is necessary to improve the following aspects (i) discharge specific capacity; (ii) discharge potential; and (iii) charge–discharge stability (cycle life). These objectives can be reached by selecting the proper conditions to synthesize high-performance nickel hydroxide and/or by employing proper additives to modify pure nickel hydroxide. For the latter, many studies [1–11] have been reported and the majority of these are concerned either with electrodeposited [3,5,6]/coprecipitated [7–9]

thin film nickel electrodes with foreign cations such as cobalt, zinc and cadmium, or with sintered [1,2,4] nickel electrodes impregnated with cobalt, cadmium, zinc and magnesium. Oshitani et al. [10] developed a pasted nickel electrode with high active material utilization by adding CoO. This compound dissolves and precipitates on the surface of the nickel hydroxide particles as β -Co(OH)₂ during standing and is then converted to CoOOH during subsequent charging. Matsuda and Ikoma [11] investigated the effect of the addition of calcium compounds (calcium hydroxide, calcium sulfide and calcium fluoride) on the nickel electrode of a Ni–MH battery for electric vehicles. It was found that calcium could raise the oxygen evolution potential and hence increase the charge-acceptance of the nickel electrode.

It is the purpose of this paper to discuss the effect and mechanism of the simultaneous addition of metal cobalt and calcium compounds to the nickel electrode.

2. Experimental

2.1. Preparation of nickel hydroxide electrode

Pure nickel hydroxide 0.4 g, 5 wt.% metal cobalt powder, 5 wt.% calcium compound (calcium hydroxide, calcium carbonate, or calcium fluoride) and 5 wt.% graphite were mixed with 5% PTFE (containing a small amount

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(1 wt.%) of CMC) as binder. The resulting paste was filled into a foamed nickel substrate (2×2 cm). The pasted electrode was dried at 65°C and then roll pressed to 0.5 mm thick.

2.2. Cell testing

For the experimental measurements, a three-compartment glass cell containing 6 M KOH solution was used. A hydrogen-storage alloy electrode, with a capacity well in excess of the nickel electrode, was used as the counter electrode and a Hg/HgO (6 M KOH) electrode was employed as the reference electrode. The performance of the electrodes was tested using a automatic cycler (DC-5) controlled by a microcomputer at various charge–discharge rates (0.1, 0.2, 0.5 and 1C rate). The discharge cut-off potential was 0.1 V vs. Hg/HgO.

2.3. Impedance measurements

Impedance measurements were performed under potentiostatic control using a Solartron SI 1287 electrochemical interface in conjunction with a 1250 frequency response analyzer. The frequency scan was 10^4 to 10^{-2} Hz.

2.4. XRD analysis, SEM observation and EDAX measurements

Electrodes with no additive or with Co and Ca compounds were overdischarged at a low current after 45 and 220 cycles at the 1C rate, respectively. The electrodes were then washed with distilled water and dried under vacuum for XRD analysis (Rigaku D/max-3B, CuK_α), SEM observation (HITACHI S-570) and EDAX studies (PHILIPS PV9900).

3. Results and discussion

3.1. Influence of additives on activity of nickel hydroxide

The specific capacities of electrodes with no additive, with cobalt, and with simultaneous addition of cobalt and cadmium, all prepared under the same conditions, are listed in Table 1.

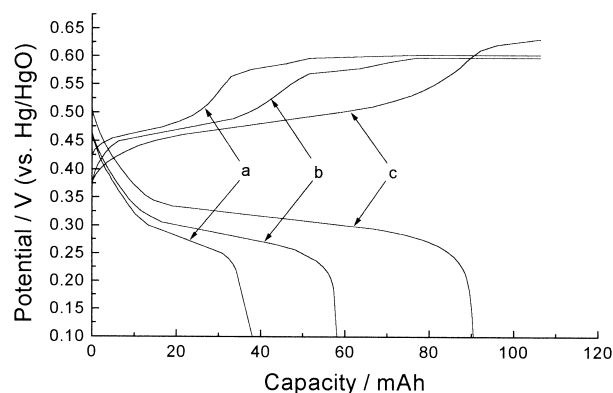
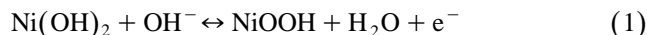


Fig. 1. Charge–discharge curves for various nickel electrodes with: (a) no additive; (b) Co; (c) Co and CaCO_3 .

The specific capacities of the active materials with simultaneous addition of Co and Ca are higher than that of active material with only the addition of Co, particularly at higher charge–discharge rates. At the 0.1C rate, the capacities of the electrodes with simultaneous addition of Co and Ca are little different from that with only the addition of Co. It is found, however, that the capacities of the nickel electrodes containing Ca increase gradually with cycling to a maximum value then decrease slowly. The data at the 0.1C rate presented in Table 1 are the second discharge (activation) capacities of newly prepared electrodes. That is to say, the capacities have not reached the maximum value. Moreover, the capacity of the electrode containing CaF_2 at the 1C rate is slightly less than that containing Ca(OH)_2 or CaCO_3 . This is probably due to the dissolution of CaF_2 during cycling.

3.2. Mechanism and effects of additives on nickel electrode

The redox reaction of the nickel electrode can be expressed as:



This is accompanied by oxygen evolution during the charge process, i.e.,



For an electrode with no additive, the oxygen evolution reaction takes place easily and this lowers the charging efficiency. With addition of a Ca compound, however, the

Table 1
Specific discharge capacity of various active materials ($\text{mA h g}^{-1} \text{Ni(OH)}_2$)

Discharge rate	No additive	Additive			
		Co	Co + Ca(OH)_2	Co + CaCO_3	Co + CaF_2
0.1C	215	234	237	234	232
0.2C	175	203	239	238	232
0.5C	152	182	221	223	211
1C	122	154	222	232	199

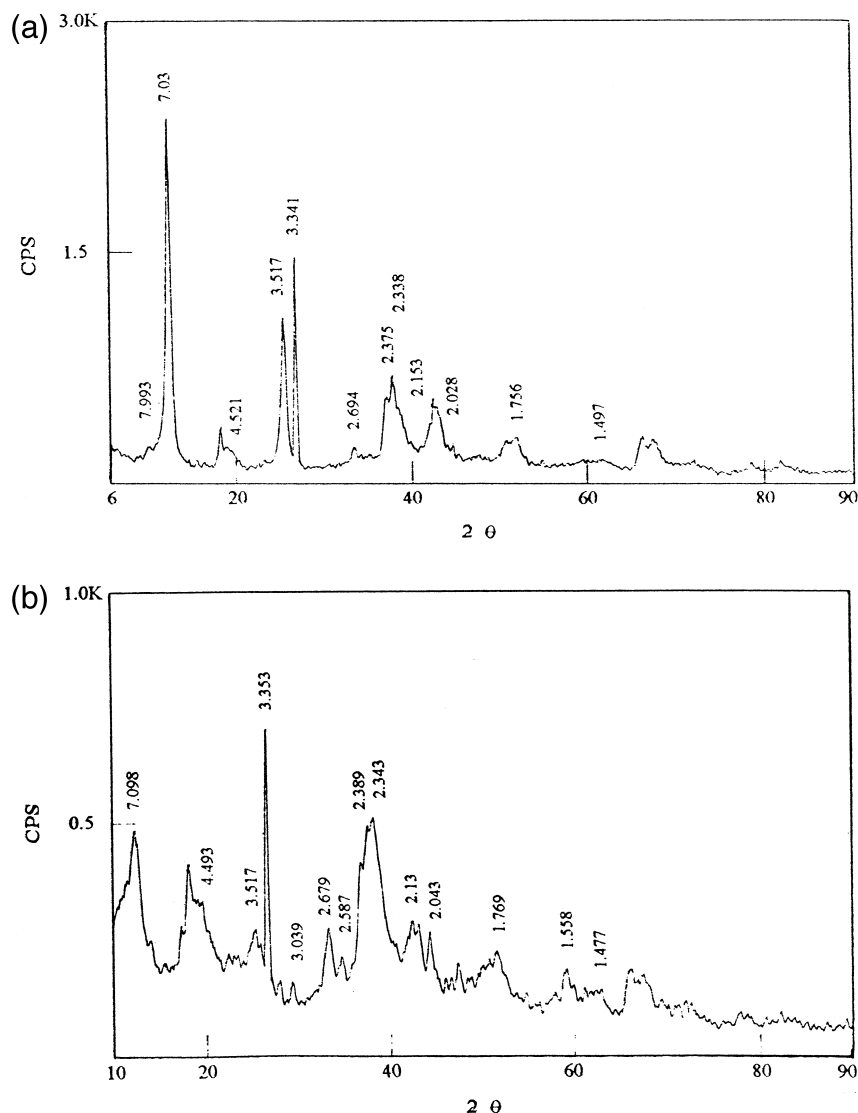


Fig. 2. XRD patterns for nickel electrodes in discharged state after 1C cycling: (a) no additive; (b) Co and CaCO_3 additives.

oxygen evolution overpotential can be increased markedly (see Fig. 1). This effect hinders reaction (2) and increases greatly the charging efficiency. The larger the charge current, the stronger the effect.

The effects of cobalt on the nickel electrode have been investigated and reported in terms of many aspects. Apart from coprecipitated Co, Co(OH)_2 , CoO and metal Co

powder have been examined. The effects of cobalt additives can be attributed to: (i) decreasing the charge-transfer resistance of the nickel electrode reaction [2,6]; (ii) improving the proton conductivity of nickel hydroxide [1,2,9]; (iii) decreasing the electric resistance and hence increasing the depth-of-discharge [5,9,10]; and (iv) raising the oxygen evolution overpotential [5,8].

Table 2
d-Values of characteristic peaks in Fig. 2 (Å)

Phase	No additive	Co + CaCO_3
β -Ni(OH) ₂	4.521, 2.694, 2.338, 1.756, 1.497	4.493, 2.679, 2.343, 1.769, 1.558, 1.477
γ -NiOOH	7.03, 3.517, 2.375	7.098, 3.517, 2.389
α -Ni(OH) ₂	7.993, 2.153	2.587, 2.13
Graphite	3.341, 2.028	3.353, 2.043

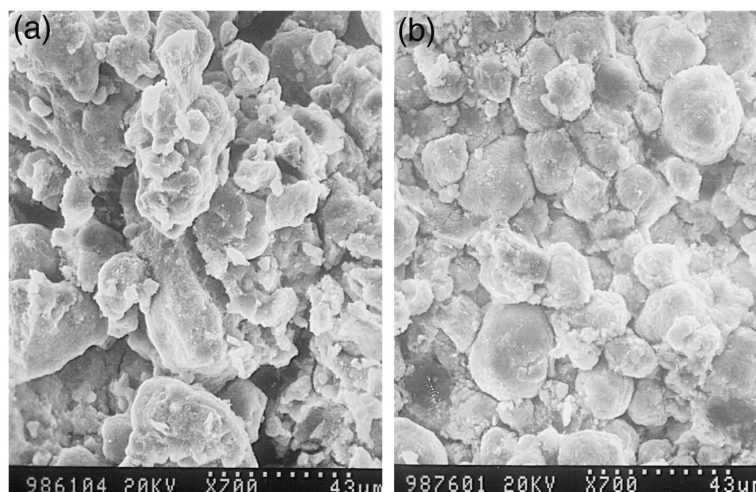


Fig. 3. Electron micrographs of nickel electrodes after cycling at the 1C rate: (a) with no additive; (b) with Co and CaCO_3 .

In this paper, metal cobalt powder was used as an additive because the authors found that addition of metal Co is superior to Co(OH)_2 . This can be related to the good conductivity of Co. The real effect of Co will be the subject of a further study.

3.3. Influence of additive on structure of active material

Fig. 2 shows the X-ray diffraction (XRD) patterns for nickel electrodes with no additive and with Co and CaCO_3 additives in the discharged state after cycling of the 1C rate for 45 and 220 cycles, respectively. The d -values of the characteristic peaks are listed in Table 2.

There are some differences between the two patterns: (i) there is no peak in Fig. 2(a) corresponding to the diffraction peak ($d = 3.039$) in Fig. 2(b) which is probably the characteristic peak for CaCO_3 ; (ii) the intensity of the peak ($d = 7.03$) for $\gamma\text{-NiOOH}$ in Fig. 2(a) is much stronger than the corresponding peak ($d = 7.098$) in Fig. 2(b) which suggests that there is more formation of $\gamma\text{-NiOOH}$ in the electrode with no additive during charging and that it cannot be fully discharged; and (iii) the crystal structure of the electrode containing additives is more disordered than that with no additive and is characterized by the breaking and broadening of some peaks. The activity of nickel hydroxide is associated with its crystal structure [1]. The more disordered the crystal, the higher the activity.

Electron micrographs of electrodes with no additive or with Co and CaCO_3 cycled at the 1C rate after 45 and 220

cycles, respectively, are shown in Fig. 3. It can be seen that the particles of active material with no additive are relatively larger and are agglomerated. By contrast, the particles of active material containing additive are nearly spherical and quite small. Accordingly, there is good contact between the particles and good electric conductivity such that the depth-of-discharge is correspondingly higher. In general, because of the higher charge-acceptance, discharge potential and depth-of-discharge, the utilization of active material in nickel electrodes containing cobalt and calcium carbonate is higher than that in an electrode with no additive. The median discharge potentials of various electrodes are listed in Table 3.

EDAX measurements show that electrodes containing Co and Ca after 220 cycles at the 1C rate still contain Co and Ca; the Co content is virtually unchanged whereas the Ca content is decreased. For Ca:Ni the electrode with Ca(OH)_2 , the atom ratio Ca:Ni before and after cycling is 0.0627 and 0.0222, respectively. With CaCO_3 , the ratio is 0.0464 and 0.0124, respectively. Although the solubility of calcium compounds in alkaline solution is small, the amount of Ca can be diminished through long-term cycling. The fact that, with 1C cycling, electrodes with Ca exhibit an increase in capacity followed by a decline can

Table 3

Median discharge potentials of various electrodes (V)

Discharge rate	No additive	Co + Ca(OH)_2	Co + CaCO_3
0.1C	0.351	0.360	0.357
0.5C	0.326	0.349	0.343
1C	0.306	0.341	0.330

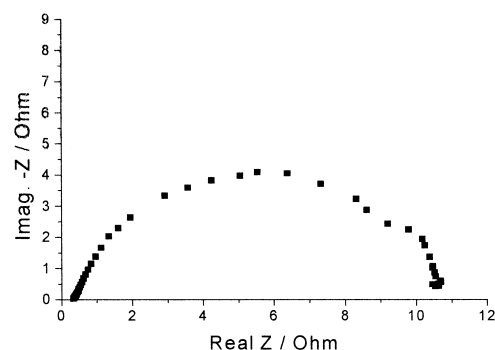


Fig. 4. Nyquist plot of nickel electrode with no additive.

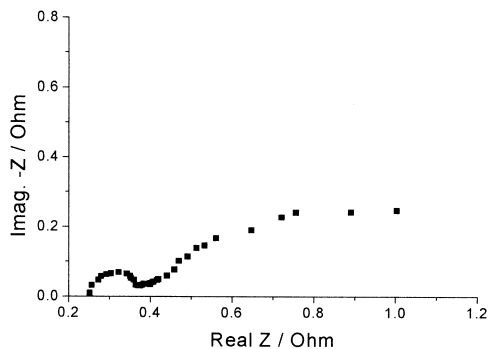


Fig. 5. Nyquist plot of nickel electrode with Co and CaCO_3 .

be interpreted as: (i) in the initial cycling stage, the Ca additive undergoes a redistribution in the active material and then gradually dissolves; and (ii) the formation of $\gamma\text{-NiOOH}$ causes plate swelling and degradation.

The impedance spectra of discharged (100% DOD) electrodes with no additive and with Co and CaCO_3 cycled for 45 and 220 cycles are presented in Figs. 4 and 5, respectively. The impedance of the electrode with no additive is large and this prevents complete discharge. By contrast, the impedance of the electrode containing Co and CaCO_3 is small and thus the discharge depth and potential are higher.

4. Conclusions

Electrochemical testing and structure analysis of nickel electrodes with and without additive show that oxygen evolution during the charging process can be inhibited by the use of a calcium additive. Thus, the charge efficiency is increased. The simultaneous addition of cobalt and a

calcium compound can improve markedly the utilization and discharge potential of the positive active material. Calcium has been found to raise the oxygen evolution overpotential. On the other hand, the effects of cobalt have been found to improve both the electronic and the protonic conductivity of the electrode. These effects increase the charge-acceptance and the discharge depth of the nickel electrode.

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