

Effects of surface modification of Ni(OH)₂ powders on the performance of nickel cathodes

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Abstract

A porous metallic film can be fixed onto the surface of Ni(OH)₂ powders by the method of electroless plating. A nickel electrode made from modified powders exhibits better characteristics in terms of the active-material utilization, the average discharge voltage and high rate discharge. A slight amount of cobalt micro-encapsulation makes a great improvement in the utilization ratio of the active material, while micro-encapsulation of the nickel film does not merely enhance the active-material utilization but also the high rate discharge.

Keywords: Surface modification; Nickel cathode; Cobalt

1. Introduction

Many studies [1,2] concerning the role of cobalt additives in nickel electrodes have been made since Edison, in 1914 [3], patented the addition of cobalt into nickel electrode for the improvement of performance. Today, cobalt additives are widely used in nickel electrode because of their beneficial effects on the charge-storage reaction [4–8].

In previous studies, it has been established that cobalt additives exist in the electrode in the form of Co(III) during the charge/discharge processes after the initial cycle [9,10]. Olivia et al. [11] and Armstrong et al. [12] claim that the addition of cobalt species not only decreases the redox potential, but also increases the overpotential of oxygen-evolution reaction at the nickel electrode and thus gives an improvement in charge efficiency. Because of the similar lattice parameters of Co and Ni [10], cobalt incorporated into the Ni(OH)₂ crystal lattice enhances the electric conductivity of the semiconductor, Ni(OH)₂. With the absence of cobalt species, Ni(OH)₂, which accumulates at the Ni(OH)₂/electrolyte interface, prevents the crystal nuclear discharge due to the poor conductivity of Ni(OH)₂ [13,14]. The presence of Co(III), however, makes the current flow fluently, which relates to a full discharge of the crystal nucleus [9,10].

The high residual capacity of nickel hydride batteries is mainly due to the resistive layer, that is to say, Ni(OH)₂ between the active material (NiOOH) and the current-collector. Owing to its poor conductivity, as mentioned above, the layer of Ni(OH)₂ prevents the access of electrons to the

rest of the NiOOH and thus prevents the reduction of this NiOOH to Ni(OH)₂. Therefore, the nickel electrode exhibits a decline in discharge efficiency, namely, the capacity of the battery decreases. In order to reduce the residual capacity of the nickel electrode, it is necessary to enhance the conductivity between the Ni(OH)₂ and the current-collector.

Multiple research efforts have been carried out on the approaches of adding cobalt species. On the one hand, cobalt can be added into the electrode in many forms, for example, cobalt metallic powders, oxides (i.e., CoO, Co₃O₄ or Co₂O₃), hydroxides including α - and β -Co(OH)₂, carbonate, nitrate, acetate, etc. [15–21]. On the other hand, cobalt can be added in many ways. First, adding cobalt species to Ni(OH)₂-based slurry is widely adopted by most battery manufacturers owing to its simplicity and effectiveness. The quantity of cobalt can readily be adjusted by the producers according to their practical experience [22–24]. Second, nickel and cobalt hydroxides can be co-precipitated by chemical reaction of the mixed solution of nickel and cobalt salts [25] and alkaline solution, or by electrochemical reaction at a cathode in a mixed nitrate salt solution of nickel and cobalt. Additionally, a layer of active material is deposited on the substrate before it is immersed in a nitrate solution that contains cobalt [26,27]. The disadvantage of this approach lies in the fact that concentrating cobalt on the surface of electrode cannot improve the utilization ratio of active material in the depth of electrode, in other words, near the substrate. Therefore, electroplating of cobalt on the surface of substrate has been developed [28]. As a result, the utilization ratio of the active material near the

substrate is improved, but that far from it cannot increase at the same time. All the above approaches, as has been already pointed out, contribute to some improvement of the nickel cathode.

The addition of conducting agents (i.e. graphite, nickel metallic powders, or $\text{Ni}(\text{CO})_4$ powders) improves the poor conductivity between $\text{Ni}(\text{OH})_2$ powders. Nevertheless, a large amount of such additives leads to a decline in the utilization of the active material, and therefore, results in a decline in electrode capacity.

In our research, the surface of $\text{Ni}(\text{OH})_2$ -active material is uniformly micro-encapsulated with a layer of cobalt or nickel. The micro-encapsulation makes the active materials well distributed on the substrate, either on the surface of the substrate or far from it, and because of the effective catalytic effect of cobalt in the electrode in every small unit and the uniform conductivity as a result of nickel micro-encapsulation, the utilization of the active material is improved effectively and efficiently.

2. Experimental

Spherical powders of $\text{Ni}(\text{OH})_2$ were made in-house, the particle size was 5 to 20 μm . The surface of the powder was activated before being reduced, then transformed into the electroless solution. A metallic film was thus micro-encapsulated on the surface by electroless plating. Finally, a electrode using the modified powders as the active material and foamed nickel as a current-collector was produced in order to make measurements of capacity.

2.1. Surface modification of $\text{Ni}(\text{OH})_2$ powders

2.1.1. Activating

AnalaR PdCl_2 was dissolved into an appropriate amount of aqueous ammonia and the resultant solution was diluted with distilled water to 0.4 g l^{-1} . Thus, the activating solution was prepared. The $\text{Ni}(\text{OH})_2$ powders were exposed to the solution under agitation. The surfaces of the powders were activated. The activated surface was reduced by exposing it to 3 wt.% sodium hypophosphite solution. Atoms of palladium were adhered to the particle surface and used as the activating centres during electroless plating.

2.1.2. Electroless plating

2.1.2.1. The cobalt electroless solution contained AnalaR cobalt sulfate, sodium hypophosphite and potassium tartrate

The pH value was adjusted by diluted sodium hydroxide solution. Detailed information of this procedure is presented in Table 1.

When the cobalt contained in the solution was entirely deposited on the surface of $\text{Ni}(\text{OH})_2$ powders, the purple colour due to the cobalt complex vanished. The content of cobalt was determined by inductive coupled plasma (ICP).

Table 1
Technological condition in cobalt electroless solution

Component	Concentration (g/l)
$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	10
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	75
$\text{KNaC}_4\text{H}_4\text{O}_6$	60
H_3BO_3	14
pH	9 ± 0.2
Temperature ($^\circ\text{C}$)	70–75

Table 2
Technological conditions in nickel electroless solution

Component	Concentration (g/l)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	120
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	30
pH	7 ± 0.2
Temperature ($^\circ\text{C}$)	60–65

2.1.2.2. The nickel electroless solution consisted of nickel sulfate, sodium hypophosphite and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$

The pH value was adjusted by diluted sodium hydroxide solution. Details of the nickel electroless plating are given in Table 2.

When nickel contained in the electroless solution was entirely deposited on the surfaces of $\text{Ni}(\text{OH})_2$ powders, the dark green that arose from the nickel complex disappeared. The content of nickel was determined by ICP.

2.2. Determination of characteristics of nickel electrode

2.2.1. Preparation

The resulting $\text{Ni}(\text{OH})_2$ powders used as the active material were mixed with conducting agents and binders. The slurry was applied to the foamed nickel as current-collector, and then dried before being compressed. The dimensions of the resultant electrode were 4.0 cm \times 6.0 cm \times 0.7 cm. Five electrodes were prepared for each sample.

2.2.2. Determination

The test cell comprised the given nickel electrode and a cadmium anode (State Run No. 755 Factory). The electrolyte was potassium hydroxide solution to which 15 g l^{-1} lithium hydroxide was added (sp. gr. = 1.26, 25°C).

Constant-current charge/discharge experiments were performed at $25 \pm 2^\circ\text{C}$, 1 atm. The test cell was charged for 7.5 h at 0.2C mA, kept for 0.5 h at open circuit, and then discharged at the 0.2C mA rate to a cut-off voltage of 1.000 V versus a cadmium anode. The same regime was adopted in the following cycles until the discharge capacity became a constant.

When the constant capacity was obtained, the test cell was charged for 15 h at the 0.1C mA rate and then discharged at 0.2C mA to a cut-off voltage of 1.000 V versus a cadmium anode. The utilization of the active materials was calculated according to the following equation

$$\begin{aligned} \text{utilization ratio} &= \frac{\text{weight of Ni(OH)}_2 \text{ taking part in reaction}}{\text{total weight(g) of Ni(OH)}_2 \text{ in the electrode}} \times 100\% \\ &= \frac{\text{real capacity (mAh)}}{\text{theoretical capacity (mAh)}} \times 100\% \end{aligned} \quad (1)$$

After discharge at 1C mA to a cut-off voltage, the test cell was held at open circuit for 10 min, then discharged at the 0.1C mA rate to the cut-off voltage. The discharge ratio under high rate discharge was calculated according to the following equation

$$\begin{aligned} \text{discharge ratio under high rate} \\ &= \frac{\text{capacity (mAh) at 1C mA}}{\Sigma \text{ of capacity (mAh) at 1C mA } \wedge \text{ 0.1C mA}} \times 100\% \end{aligned} \quad (2)$$

3. Results and discussion

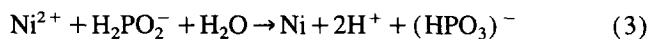
3.1. Activating the surface of Ni(OH)₂ powders

Because of the negative redox potential ($\phi_{\text{Co}^{2+}/\text{Co}}^\circ = -0.28 \text{ V}$, $\phi_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$), PdCl₂ is used as activation solution. The PdCl₂ activation solution is usually comprised of PdCl₂ and HCl. Therefore, an acid characteristic is exhibited. The dissolution reaction of Ni(OH)₂ powders occurs at pH = 5–6, however, and the usual PdCl₂ solution is inappropriate. It is found that when PdCl₂ is dissolved in ammonia and diluted with distilled water, the resulting solution can take the place of the former to activate the surface of Ni(OH)₂ powder.

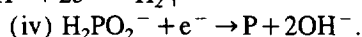
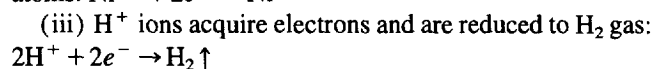
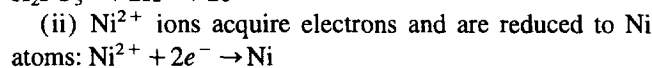
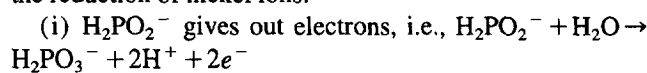
3.2. Electroless plating

At the given concentration, the pH value and the temperature of the solution as described above, activated Ni(OH)₂ powders are transformed into the electroless solution under agitation. The colour of the solution weakens and eventually vanishes. This is accompanied by the evolution of copious gas bubbles.

The overall reaction that occurs in the nickel electroless solution is



Electrons discharged from the oxidation of H₂PO₂⁻ cause the reduction of nickel ions:



The production of hydrogen gas is a parasitic reaction that accompanies the electroless process, and will contribute to the formation of a porous layer.

The thickness of the film should be adjusted to within 0.3–2 μm by controlling the amount of nickel or cobalt salt. A thinner film will increase the resistance between powders and thus fail to improve the conductivity effectively, while a thicker film will decrease the packing density of the active material.

3.3. Effect of micro-encapsulation of cobalt on the characteristics of the nickel hydroxide electrode

A nickel hydroxide electrode was made from modified powders by micro-encapsulating 1 wt.% cobalt on the surface of Ni(OH)₂ powders used as the active material. The discharge curve is shown in Fig. 1. For comparison, that of bare Ni(OH)₂ powders is also given. Since cobalt metallic powders are generally applied to the slurry of the active material that is used in battery production, the discharging curve of this kind of electrode is also shown in Fig. 1.

The curves obtained by the two approaches of adding cobalt both have a longer plateau in comparison with that obtained from the bare electrode. Furthermore, that with micro-encapsulation exhibits the longest plateau.

The effects of different adding approaches and different contents of cobalt upon the utilization of active material and the average discharge voltage of the electrode are shown in Tables 3 and 4. It can be seen that both of the adding methods can improve the utilization of the active material and increase the average discharge voltage of the nickel battery; furthermore, the effects become more remarkable with increase in cobalt content. Nevertheless, cobalt micro-encapsulation appears to be more effective than adding cobalt into the slurry. The utilization of the active materials is increased by 6.3% by adding 1 wt.% cobalt to the slurry; by contrast, an increase of 12.5% can be obtained by micro-encapsulating the same amount, which is twice the former increase and equal to that obtained by adding 5 wt.% cobalt powder to the slurry. Therefore, the required content of cobalt can be decreased by using the micro-encapsulation method. Similar effects can be found on the average discharge voltage.

As is well known, a layer of nickel and cobalt solid solution is formed on the surface of Ni(OH)₂ particles by adding cobalt, then good conductivity within the electrode is possi-

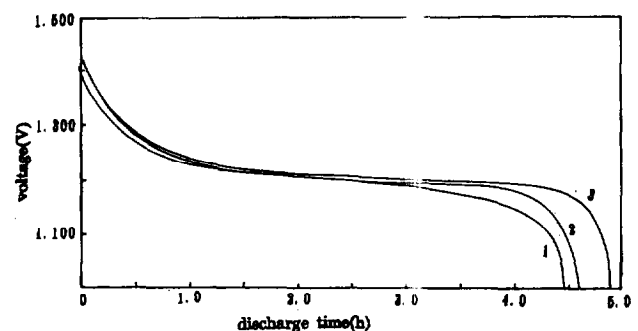


Fig. 1. Discharge curves of Ni(OH)₂ electrode for different methods of adding cobalt (1 wt.%) (discharge at 0.2C mA): (1) bare electrode; (2) adding cobalt to the slurry, and (3) micro-encapsulation of cobalt.

Table 3
Effect of different approaches of adding cobalt and different cobalt contents on utilization of the active material

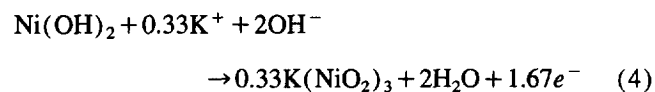
Cobalt content (wt.%)	0 (bare)	0.6	1.0	3.4	5.0	7.0	10
Added to slurry	85.5	87.0	91.8	95.6	100.4	101.0	102.9
Micro-encapsulation	85.5	94.8	98.0	99.2	105.2	106.8	108.0

Table 4
Effect of different approaches of adding cobalt and different cobalt contents on the average discharge voltage of the active material

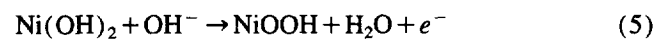
Cobalt content (wt.%)	0 (bare)	0.6	1.0	3.4	5.0	7.0	10
Added to slurry	1.202	1.210	1.215	1.219	1.223	1.224	1.225
Micro-encapsulation	1.202	1.217	1.225	1.229	1.232	1.234	1.235

ble, which leads to an improvement in utilization of the active material. Because of the dissolution of cobalt in water or electrolyte, however, it is necessary to add a large amount of cobalt metallic powder in order to achieve a significant effect. Cobalt incorporates into the Ni(OH)₂ crystal lattice by the process of dissolution/diffusion solid solution, and thus enhances the conductivity of Ni(OH)₂ to a great extent, and increases concomitantly the overpotential of the oxygen evolution potential.

It is generally thought that the charge state of Ni(OH)₂ is Ni(III) hydroxide, i.e. NiOOH, but many studies indicate that Ni(OH)₂ can be oxidized to a state above trivalence. Electrochemical and iodometric measurements made by Corrigan and Knight [29] suggest that the valence of nickel can achieve 3.6 ± 0.1 during the course of charge and return to divalence after discharge [29]. That is to say, 1.6 electrons are involved during discharge. A visible spectrum study of an Ni(OH)₂ thin film electrode also affirms the conclusion [29]. Furthermore, the authors found that K⁺ in the electrolyte incorporates into the Ni(OH)₂ thin film in the charge state, which results in a product that can be expressed by the formula K(NiO₂)₃. The reaction that occurs in the Ni(OH)₂ electrode is [29]



1.67 electrons are transformed in the process. By contrast, the generally accepted battery reaction is



there is only one electron transformed.

Armstrong and Charles [16] also claim that the nickel component may reach a maximum oxidation level of over trivalence according to data from constant capacity and linear potential scanning [6]. In practical batteries, the reason why the change of oxidation state cannot be achieved completely is because Ni(II) hydroxide of high resistance prevents the full discharge. Because of the catalytic effect of cobalt, the addition of cobalt makes it easy to achieve a nickel oxidation state of over trivalence, and thus improve the discharge capacity and active-material utilization.

In the experiments reported here, both of the methods of adding cobalt yield a utilization of Ni(OH)₂ of over 100%, which indicates that a higher valence of nickel is virtually produced during the charge processes, i.e., more than one charge is transferred during the oxidation/reduction processes.

With electroless plating, a porous cobalt metallic film can be encapsulated on the surfaces of the Ni(OH)₂ particles, and thus it becomes possible for a cobalt film to cover the surface uniformly and to form an uniform conducting film. During the process of charge, divalent cobalt turns into trivalent, then incorporates into the crystal lattice. Due to the uniformity of the film and firm adhesion to the surface of the Ni(OH)₂ particles, a conductive micro-network is constructed. By comparison, by adding cobalt powders to a slurry, a small amount of cobalt micro-encapsulation can improve markedly the conductivity and utilization of the active material.

As to micro-encapsulation, the utilization and average discharge voltage are increased with increase in cobalt content. On the other hand, a remarkable effect occurs when the content of cobalt is less than 5 wt.%. When it is beyond this value, increasing the cobalt content can only lead to a slight improvement in characteristics.

3.4. Effects of nickel micro-encapsulation on the performance of nickel hydroxide electrode

In battery manufacturing, nickel metallic powders are often added as conducting agents in order to improve the conductivity of the electrode. The micro-encapsulation of nickel on the surface of Ni(OH)₂ particles can affect the performance of nickel hydroxide electrodes. The effects are exhibited in Table 5, and Figs. 2 and 3. As can be seen from Table 5, the utilization of active material improves. Moreover, the high rate discharge characteristic is enhanced; micro-encapsulation of 30 wt.% nickel provides an outstanding effect.

By the approach of electroless plating, the surface of Ni(OH)₂ particles of poor conductivity is covered with nickel metallic film, which declines effectively the impedance between the powders of active material, or between active-

Table 5
Effect of nickel micro-encapsulation on the active-material utilization ratio

Discharge rate (C mA)	0 (bare)	20 wt. %	30 wt. %
0.2	85.4	89.6	89.6
0.5	72.6	85.6	86.9
1.0	65.8	72.6	74.9
2.0	59.8	64.5	69.8

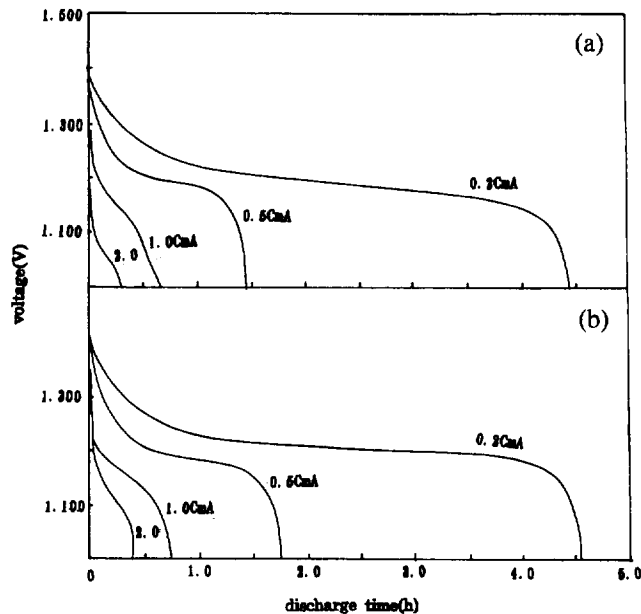


Fig. 2. Effect of micro-encapsulation of 30 wt.% nickel on discharge curves at different discharge rates: (a) bare, and (b) micro-encapsulation of 30 wt.% nickel.

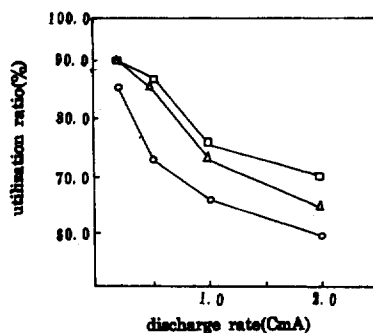


Fig. 3. Effect of micro-encapsulation of nickel on utilization of $\text{Ni}(\text{OH})_2$ electrode: (○) bare; (△) micro-encapsulation of 20 wt.% nickel, and (□) micro-encapsulation of 30 wt.% nickel.

material powders and the current-collector. This provides a direct current access. Therefore, the resultant electrode displays superior performance over a bare electrode at high rate discharge.

4. Conclusions

With electroless plating, a metallic film can be encapsulated on the surface of $\text{Ni}(\text{OH})_2$ of particle size of 5 to 20 μm . The nickel electrode uses modified powders as active materials. The characteristics, i.e., utilization ratio and high rate discharge, have been examined. Compared with adding the same content of cobalt metallic powders to a slurry, the effect is more remarkable on the characteristic above. Therefore, the required cobalt addition content is minimized.

Nickel encapsulation on the surface of $\text{Ni}(\text{OH})_2$ can also improve the utilization. In addition, the characteristic of high rate discharge is improved effectively, because the nickel lowers the impedance between the particles. A 30 wt.% nickel film gives the better result.

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