ELSEVIER

Journal of Power Sources 56 (1995) 115–119

JOURNAL OF POWER SOURCES

Short Communication

# Effects of dopants on electrochemical performance of nickel cathodes

Ding Yunchang, Li Hui, Yuan Jiongliang, Chang Zhaorong

*Department of Chemistry, Henan Normal University, Xingxiang, 453002, Henan, People's Republic of China*

Received 20 March 1995; accepted 18 April 1995

**Abstract**

A paste-type electrode using spherical nickel hydroxide powder as the main active material and a foamed nickel grid as a current collector has been prepared. The effects of dopants such as cobalt, cadmium, zinc, copper and H-absorbing alloy on the electrode performance are examined. The most effective dopant and its optimum content is identified.

*Keywords:* Cathodes; Nickel; Dopants

## 1. Introduction

Compared with the conventional sintered nickel electrode, the paste-type has many advantages. Nevertheless, there are still some problems with its use. Since the nickel hydroxide active material is a semi-conductor and the binder in the electrode raises the internal resistance, the performance of the paste-type cathode (e.g., super high-rate discharge, cycle life) is inferior to that of the sintered type. Numerous investigations [1–13] indicate that the addition of certain dopants is beneficial.

It is reported that spherical nickel hydroxide is superior to the non-spherical variety in terms of tap density and charge/discharge efficiency [14,15], thus the spherical is used in the experiments reported here. The latter examines the influence of various dopants, such as cobalt, cadmium, zinc, copper and H-absorbing alloy, upon initial capacity, high-rate discharge and electrode potential, as well as the relationship between the level of dopant and these characteristics.

## 2. Experimental

### 2.1. Preparation of spherical nickel hydroxide

Given amounts of nickel salt solution and alkaline aqueous solution were fed to a reaction tank and held for a given residence time at a temperature of $60 \pm 1$ °C and a fixed pH with vigorous stirring. This produced primary particles of 0.1 $\mu$m or less that served as nuclei for the continuous preparation of nickel hydroxide with spherical or nearly spherical particles. Electron micrographs of the resulting nickel hydroxide powders are shown in Fig. 1. The powders have a particle size of about 2–50 $\mu$m.

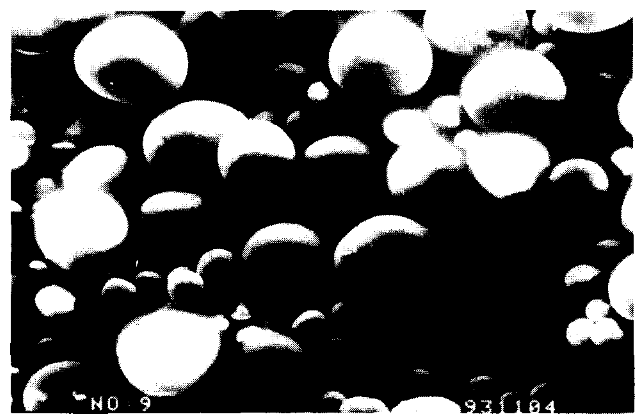

Fig. 1. Scanning electron micrograph of spherical nickel hydroxide powder (×300).

### 2.2. Preparation of paste-type electrodes

The nickel hydroxide-based active materials were blended with scaly graphite, acetylene black and binder. The mixture was filled into a foamed nickel grid, dried at 70–80 °C for 20–30 min, and then pressed under 40–50 MPa pressure. The electrode dimensions were 6.2 cm × 4.2 cm × 0.08 cm.

### 2.3. Electrolytic solution composition

The electrolyte was an aqueous solution of potassium hydroxide that contained 15 g/l lithium hydroxide.

0378-7753/95/$09.50 
*SSDI* 0378-7753(95)02213-Z

### 2.4. Measurement of capacity

The test cell comprised the sample electrode as a cathode, a sintered cadmium anode (State-run No. 755 Factory), a separator of unwoven nylon cloth, and an alkaline electrolytic solution. The capacity was measured under constant-current conditions.

### 2.5. Cyclic voltammetric measurement of CoO-containing electrode

A CoO-containing electrode of 1 $cm^2$ area was used. The sweep rate was 1 mV $s^{-1}$, and the sweep range 0 to 0.7 V (versus Hg/HgO reference electrode).

## 3. Results

### 3.1. $Co(CH_3COO)_2$ dopant

The effects of adding 1, 3 and 5 wt.% $Co(CH_3COO)_2$ (based on the weight of $Ni(OH)_2$) to the nickel electrodes are shown in Table 1. The data show that the addition of $Co(CH_3COO)_2$ enhances the utilization of active material. Furthermore, the higher the content of $Co(CH_3COO)_2$, the higher the utilization. When the addition is 5 wt.%, the utilization at a 0.2*C* discharge rate increases from 83.5 to 92.2%.

### 3.2. CdO dopant

1, 3 and 5 wt.% CdO was added. The effects are shown in Table 2. CdO also increases the coefficient of utilization, but the effect is less than that with $Co(CH_3COO)_2$.

### 3.3. CoO dopant

The effect of adding 3, 5 and 7 wt.% CoO on the electrode performance is presented in Table 3. It can be seen that the addition of CoO improves the electrode performance to a great extent. The coefficient of utilization of the active material with 7 wt.% CoO increases by 11.6% up to more than 95%, and the average voltage of the battery system is higher.

Table 1
Effect of $Co(Ac)_2$ on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (Ah) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | 0 | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | 1 | 1.225 | 0.320 | 4.59 | 0.276 | 86.1 | 0.250 | +2.6 |
| | 3 | 1.233 | 0.300 | 4.46 | 0.268 | 89.3 | 0.258 | +5.8 |
| | 5 | 1.224 | 0.303 | 4.66 | 0.279 | 92.2 | 0.267 | +8.7 |
| 0.3*C* | 1 | 1.201 | 0.320 | 3.12 | 0.272 | 84.9 | 0.245 | |
| | 3 | 1.210 | 0.300 | 3.06 | 0.266 | 88.7 | 0.256 | |
| | 5 | 1.213 | 0.303 | 3.12 | 0.271 | 89.6 | 0.259 | |
| 0.5*C* | 1 | 1.130 | 0.320 | 1.76 | 0.264 | 82.5 | 0.239 | |
| | 3 | 1.190 | 0.300 | 1.74 | 0.260 | 86.8 | 0.251 | |
| | 5 | 1.159 | 0.303 | 1.77 | 0.265 | 87.2 | 0.253 | |
| 1*C* | 1 | 1.120 | 0.320 | 0.92 | 0.257 | 80.3 | 0.232 | |
| | 3 | 1.174 | 0.300 | 0.90 | 0.253 | 84.2 | 0.243 | |
| | 5 | 1.131 | 0.303 | 0.94 | 0.264 | 86.9 | 0.251 | |

Table 2
Effect of CdO on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (Ah) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | 0 | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | 1 | 1.222 | 0.303 | 4.30 | 0.250 | 85.2 | 0.246 | +1.7 |
| | 3 | 1.228 | 0.333 | 4.83 | 0.290 | 87.1 | 0.252 | +3.6 |
| | 5 | 1.225 | 0.287 | 4.29 | 0.257 | 89.6 | 0.259 | +6.1 |
| 0.3*C* | 1 | 1.190 | 0.303 | 2.80 | 0.252 | 83.3 | 0.241 | |
| | 3 | 1.216 | 0.333 | 3.18 | 0.286 | 85.9 | 0.248 | |
| | 5 | 1.224 | 0.287 | 2.80 | 0.252 | 87.8 | 0.254 | |
| 0.5*C* | 1 | 1.164 | 0.303 | 1.64 | 0.246 | 81.3 | 0.235 | |
| | 3 | 1.167 | 0.333 | 1.86 | 0.279 | 83.8 | 0.242 | |
| | 5 | 1.165 | 0.287 | 1.66 | 0.248 | 86.5 | 0.250 | |
| 1*C* | 1 | 1.156 | 0.303 | 0.82 | 0.237 | 78.2 | 0.226 | |
| | 3 | 1.156 | 0.333 | 0.92 | 0.267 | 80.1 | 0.232 | |
| | 5 | 1.151 | 0.287 | 0.84 | 0.243 | 84.8 | 0.245 | |

Table 3
Effect of CoO dopant on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (Ah) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | 0 | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | 3 | 1.245 | 0.318 | 5.19 | 0.286 | 89.8 | 0.260 | +6.3 |
| | 5 | 1.241 | 0.291 | 4.94 | 0.272 | 93.4 | 0.270 | +9.9 |
| | 7 | 1.256 | 0.294 | 5.08 | 0.280 | 95.1 | 0.275 | +11.6 |
| 0.3*C* | 3 | 1.226 | 0.318 | 3.33 | 0.283 | 88.9 | 0.257 | |
| | 5 | 1.220 | 0.291 | 3.13 | 0.266 | 91.5 | 0.265 | |
| | 7 | 1.235 | 0.294 | 3.22 | 0.273 | 93.0 | 0.269 | |
| 0.5*C* | 3 | 1.164 | 0.318 | 1.99 | 0.279 | 87.6 | 0.253 | |
| | 5 | 1.160 | 0.291 | 1.84 | 0.257 | 88.7 | 0.256 | |
| | 7 | 1.200 | 0.294 | 1.92 | 0.268 | 91.2 | 0.264 | |
| 1*C* | 3 | 1.132 | 0.318 | 0.97 | 0.271 | 85.1 | 0.246 | |
| | 5 | 1.150 | 0.291 | 0.91 | 0.255 | 87.6 | 0.253 | |
| | 7 | 1.167 | 0.294 | 0.94 | 0.264 | 89.7 | 0.295 | |

Table 4
Effect of addition of H-absorbing alloy on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (Ah) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | 0 | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | 2 | 1.230 | 0.332 | 5.09 | 0.280 | 84.4 | 0.244 | +0.9 |
| 0.3*C* | 2 | 1.229 | 0.332 | 3.45 | 0.276 | 83.2 | 0.241 | |
| 0.5*C* | 2 | 1.186 | 0.332 | 2.04 | 0.275 | 82.9 | 0.240 | |
| 1*C* | 2 | 1.160 | 0.332 | 1.01 | 0.268 | 80.7 | 0.233 | |

Table 5
Effect of addition of Cu additive on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (Ah) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | 0 | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | 4 | 1.238 | 0.324 | 5.10 | 0.281 | 86.6 | 0.250 | +3.1 |
| 0.3*C* | 4 | 1.221 | 0.324 | 3.48 | 0.272 | 83.8 | 0.242 | |
| 0.5*C* | 4 | 1.195 | 0.324 | 2.05 | 0.266 | 82.1 | 0.237 | |
| 1*C* | 4 | 1.183 | 0.324 | 1.00 | 0.260 | 80.2 | 0.232 | |

Table 6
Additive content in electrodes in %

| | None | a | b | c | d | e |
|---|---|---|---|---|---|---|
| CoO | 0 | 7 | 7 | 7 | 5 | 5 |
| ZnO | 0 | 2 | 5 | 7 | 5 | 0 |
| CdO | 0 | 0 | 0 | 0 | 5 | 2 |
| $Ba(OH)_2$ | 0 | 0 | 0 | 0 | 0 | 1 |

### *3.4. H-absorbing alloy*

Adding 2 wt.% H-absorbing alloy to the electrodes yields the results presented in Table 4. Unfortunately, the dopant has little influence on the utilization which increases by only 0.9%. On the other hand, the battery voltage is raised and there is less of a decline in capacity at high-rate discharge.

### *3.5. Copper dopant*

The addition of 4 wt.% copper enhances both the utilization ratio and working voltage of the battery to some extent (Table 5).

### *3.6. Mixed dopants*

The influence of mixed additions of CoO, ZnO, CdO and $Ba(OH)_2$ was examined. The content of each additive is given in Table 6, and the results are listed in Table 7.

As shown above, all dopants increase the utilization of the active material. Nevertheless, the effect occurs to different extents, and the influence of dopant content is important, as shown in Fig. 2. The results suggest that CoO gives the best results.

Table 7
Influence of mixed dopants on electrode performance

| Discharge current | Content (wt.%) | Average voltage (V) | Theoretical capacity (Ah) | Discharge time (h) | Real capacity (AH) | Utilization ratio (%) | Average specific capacity (Ah $g^{-1}$) | Percentage improvement (%) |
|---|---|---|---|---|---|---|---|---|
| 0.2*C* | none | 1.221 | 0.317 | 4.41 | 0.265 | 83.5 | 0.241 | |
| | a | 1.259 | 0.382 | 6.10 | 0.366 | 95.8 | 0.277 | +12.3 |
| | b | 1.251 | 0.322 | 5.24 | 0.314 | 94.7 | 0.274 | +11.2 |
| | c | 1.239 | 0.321 | 5.00 | 0.300 | 93.5 | 0.270 | +10.0 |
| | d | 1.232 | 0.298 | 5.14 | 0.283 | 94.9 | 0.274 | +11.4 |
| | e | 1.242 | 0.332 | 5.92 | 0.325 | 98.0 | 0.283 | +14.5 |
| 0.3*C* | a | 1.246 | 0.382 | 4.75 | 0.361 | 92.6 | 0.268 | |
| | b | 1.234 | 0.332 | 3.66 | 0.311 | 93.8 | 0.271 | |
| | c | 1.223 | 0.321 | 3.44 | 0.293 | 91.2 | 0.264 | |
| | d | 1.231 | 0.298 | 3.48 | 0.279 | 93.5 | 0.270 | |
| | e | 1.222 | 0.332 | 3.96 | 0.317 | 95.4 | 0.276 | |
| 0.5*C* | a | 1.213 | 0.382 | 2.35 | 0.347 | 90.8 | 0.263 | |
| | b | 1.208 | 0.332 | 2.05 | 0.308 | 92.8 | 0.268 | |
| | c | 1.173 | 0.321 | 1.91 | 0.286 | 89.1 | 0.258 | |
| | d | 1.202 | 0.298 | 2.10 | 0.272 | 91.4 | 0.264 | |
| | e | 1.203 | 0.332 | 2.38 | 0.310 | 93.5 | 0.270 | |
| 1*C* | a | 1.148 | 0.382 | 1.18 | 0.343 | 89.8 | 0.260 | |
| | b | 1.179 | 0.332 | 1.03 | 0.299 | 90.1 | 0.261 | |
| | c | 1.109 | 0.321 | 0.98 | 0.283 | 88.2 | 0.255 | |
| | d | 1.163 | 0.298 | 1.02 | 0.266 | 89.3 | 0.258 | |
| | e | 1.169 | 0.332 | 1.16 | 0.302 | 91.0 | 0.263 | |

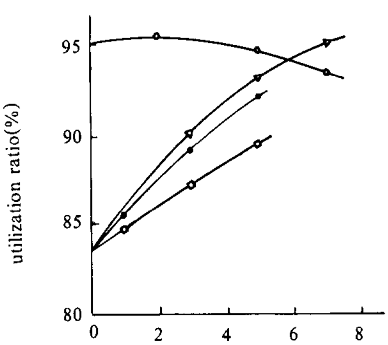


Fig. 2. Effect of dopants at different levels on electrode performance: (□) CdO; (●) $Co(Ac)_2$; (Δ) CoO; (○) ZnO (7 wt.% CoO).

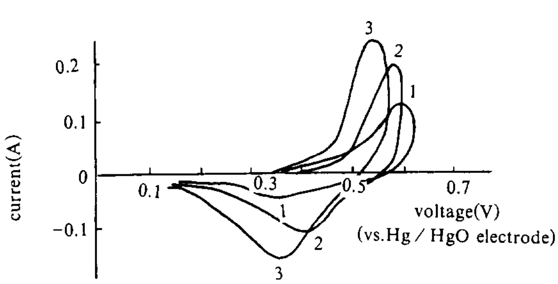


Fig. 3. Cyclic voltammograms for CoO-containing nickel electrodes: (1) no dopants; (2) 3 wt.% CoO; (3) 5 wt.% CoO.

### *3.7. Cyclic voltammetry of CoO-containing electrodes*

Fig. 3 presents the voltammogram for electrodes containing 0, 3 and 5 wt.% CoO. As the CoO content increases, both the oxidation and the reduction peak currents increase, with a corresponding decrease of separation in potential between the peaks. This suggests that the addition of CoO causes a marked improvement in capacity, as well as the reversibility between the oxidation and reduction states. Furthermore, the reduction potential at the CoO-containing electrodes is lower at the same current density, i.e., the addition of CoO suppresses the polarization. Thus, the electrodes are more suitable for high current discharge.

## 4. Discussion

Utilization of the active material of nickel electrodes is modified appreciably by doping with cobaltous compounds, especially CoO. The reason lies in the fact that CoO dissolves in the alkaline solution and precipitates into $\beta$-$Co(OH)_2$ which attaches to the surfaces of the $Ni(OH)_2$ particles during charging. Also, $\beta$-$Co(OH)_2$ is irreversibly oxidized to CoOOH. Since CoOOH has a good conductivity, it decreases the resistance between the $Ni(OH)_2$ particles and the grid and, therefore, the utilization is improved.

Because $Cd^{2+}$ connects each layer of $NiO_2$, and improves the conductivity of $Ni(OH)_2$, the addition of CoO also enhances the electrode capacity and utilization. The presence of $Cd^{2+}$ decreases the formation of $\gamma$-NiOOH with low density, so expansion of the electrode is prevented. For practical use, the oxides of Co and Cd are applied at the same time.

## 5. Conclusions

1. The addition of dopants improves the performance of paste-type nickel electrodes.

2. Cobalt compounds are particularly potent dopants, but various cobalt compounds exert beneficial effects to different extents; CoO is the most effective.

3. In addition to cobalt compounds, H-absorbing alloy, copper powders, ZnO, etc., are also advantageous in terms of higher voltage and higher discharge current.

4. The level of dopant has a great effect on the electrode performance.

## References


[1] K. Micka, Z. Zábransky and M. Svata, *J. Power Sources, 8* (1982) 9.

[2] M. Oshitani, H. Yufu, K. Takashiwa, S. Tsuji and Y. Matsumaru, *J. Electrochem. Soc., 136* (1989) 1590.

[3] K. Nishiyama, K. Nakamitsu, H. Yasuda and M. Mori, *GS New Tech. Rep., 48* (1) (1989) 23–29.

[4] *Jpn. Patent No. JP 03 147 258 [91 147 258].*

[5] *Jpn. Patent No. JP 0377 272 [91 77 272].*

[6] *Jpn. Patent No. JP 03 274 666 [91 274 666].*

[7] R.D. Armstrong and E.A. Charles, *J. Power Sources, 25* (1989) 89.

[8] *Eur. Patent No. EP 523 284.*

[9] *Jpn. Patent No. JP 03 149 752 [91 149 752].*

[10] *Jpn. Patent No. JP 01 289 067 [89 289 067].*

[11] *Jpn. Patent No. JP 05 47 379 [93 47 379].*

[12] *Jpn. Patent No. JP 63 45 754 [88 45 754].*

[13] *Jpn. Patent No. JP 04 342 957 [92 342 957].*

[14] *Jpn. Patent No. JP 63 187 765 [88 187 765].*

[15] *Jpn. Patent No. JP 0421 061 [92 21 061].*