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Short Communication

A study of the performance of a paste-type nickel cathode

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Abstract

A nickel cathode that uses spherical nickel hydroxide as the active material is prepared by paste-type technology. An examination is made of the effects of conductive materials, binders, active material, and dopants (and their ratios) on the initial discharge capacity. The most favourable formulae is selected.

Keywords: Nickel cathode; Paste-type cathodes

1. Introduction

Nickel cathodes are widely used in nickel–cadmium and nickel–metal hydride batteries. The performance of the nickel electrode greatly affects that of the overall cell, and thus numerous investigations have been conducted on this electrode. Given the resulting reliable characteristics during high-rate charging/discharging and cycle life, nickel electrodes are mostly produced by sinter-type technology. Nevertheless, recent attention has been focused on the paste-type counterpart that uses a bulk foamed porous nickel body or a porous fibrous nickel body of a high porosity (90% or more) as the current collector. This is because such electrodes have simpler technological conditions, lower cost and higher energy density.

In order to increase further the electrode performance, it is necessary to improve the structure of the particles and crystals so as to get spherical (or nearly spherical) nickel hydroxide aggregates with high packing densities and charging/discharging efficiencies. This can be achieved controlling the reaction conditions [1–3].

This study examines the effects of the active material, conductive materials, binders and some dopants (and their ratios) on the initial capacity of nickel electrodes prepared with he paste-type technology in which spherical nickel hydroxide is used as the active material.

2. Experimental

The preparation of spherical nickel hydroxide and the test electrodes, as well as the measurement of electrode capacity have been reported previously [4].

3. Results and discussions

3.1. Effect of electrolyte concentration

The test electrodes were charged and discharged in KOH electrolyte solution of different concentrations into which 15 g/l lithium hydroxide was added. The results are shown in Table 1.

Because the electrolyte solution merely provides the conductive ions, but does not take part in the electrode reaction, its conductivity must be first considered; about 30 wt.% KOH solution has the best conductivity, and thus it is used here.

3.2. Effect of ratio of conductive materials to active material

For a weight ratio of graphite to acetylene black of 15:1 and with the binder content unchanged, the content of the conductive materials (including graphite and acetylene black) was varied for 22, 25, 28 and 33 wt.% of $Ni(OH)_2$. The results are listed in Table 2.

Because of the poor electric conductivity of the $Ni(OH)_2$ solution, certain conductive materials, e.g. scaly graphite and acetylene black, are added to the electrode. The content of these conductive materials, however, has an effect on the electrode capacity. When their content is too high, although the electric conductivity of the electrode is improved, the $Ni(OH)_2$ weight must decrease, and therefore the capacity will be decreased. On the other hand, when the $Ni(OH)_2$ content is too high, the electrode resistance becomes excessive and thus the utilization goes down.

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Table 1
Effect of concentration of electrolytic solution

Concentration (wt.%)	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity (Ah g^{-1})
22	0.2	5.37	0.285	85.8	0.248
27	0.2	5.95	0.315	95.8	0.277
31	0.2	6.03	0.319	95.2	0.278
40	0.2	5.75	0.305	91.8	0.265

Table 2
Effect of content of conductive material

Conductive material content (%)	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity (Ah g^{-1})
22	0.2	5.42	0.352	85.9	0.248
25	0.2	4.54	0.295	88.9	0.257
28	0.2	4.79	0.311	85.5	0.247
33	0.2	4.41	0.265	83.5	0.241

Table 3
Effect of ratio of scaly graphite to acetylene black

Ratio	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity (Ah g^{-1})
24:1	0.2	5.35	0.294	85.6	0.246
15:1	0.2	4.54	0.295	88.9	0.257
9:1	0.2	5.41	0.297	90.4	0.261
4:1	0.2	5.91	0.325	96.3	0.278
3:1	0.2	5.56	0.306	92.9	0.269
2:1	0.2	5.72	0.297	91.8	0.265

3.3. Effect of different ratios of scaly graphite acetylene black

For a total amount of conductive materials that was 25% that of $Ni(OH)_2$, and with the binder content unchanged, the ratio of scaly graphite to acetylene back was varied as follows: 24:1; 15:1; 9:1; 4:1; 3:1; 2:1. The results are presented in Table 3.

Because of its chain structure, low density and good water absorption characteristics, acetylene black can increase the void and electrode surface per unit volume, and thus improve the contact of the active material with the electrolyte solution. Therefore, increasing the content of acetylene black will improve the utilization. The latter begins to decrease, however, when the acetylene black content amounts to 33%, i.e., the ratio of scaly graphite to acetylene black is 2:1.

Acetylene black is superior to graphite in specific surface area, but has poorer conductivity. Therefore, a high content of acetylene black results in a decrease in the electrical conductivity of the electrode and a low utilization of active material. Moreover, because of its low density and good water absorption, increasing the acetylene black content will decrease the binding force between the active material particles and thus, will increase the internal resistance of the electrode. According to this study, the utilization is highest for a ratio of scaly graphite to acetylene black of 4:1.

3.4. Effect of ratio of total binders to active material

Using the above recommended ratios of conductive materials to active material, and graphite to acetylene black, test electrodes were made with different contents of binders, in which the weight ratio of 3% carboxymethyl cellulose (CMC) aqueous solution to 60% polytetrafluoroethylene (PTFE) solution was 1.5:1.

The results for binder contents of 76, 43, 35 and 29% of $Ni(OH)_2$ weight are presented in Table 4. It is seen that the utilization of active material decreases with an increase in binder content. This is due to the high internal resistance at high binder content. Nevertheless, a certain amount of binder is necessary to bind the particles effectively.

3.5. Effect of different ratios of CMC solution to PTFE solution

For an electrode that contains binders at a content of 29% of the $Ni(OH)_2$ weight, the ratio of CMC solution to PTFE solution was varied as follows: 3.5:1; 1.4:1; 0.75:1; 100:0;

Table 4
Effect of ratio of total binders to active material

Binder content (%)	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity ($Ah\ g^{-1}$)
76	0.2	5.42	0.298	85.1	0.246
35	0.2	5.56	0.306	92.9	0.269
43	0.2	6.07	0.334	94.1	0.274
29	0.2	5.91	0.325	96.3	0.278

Table 5
Effect of ratio of CMC solution to PTFE solution

Ratio	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity ($Ah\ g^{-1}$)
100:0					
3.5:1	0.2	5.56	0.306	86.7	0.251
1.5:1	0.2	5.91	0.325	96.3	0.278
0.75:1	0.2	5.69	0.313	94.2	0.275
0:100	0.2	5.50	0.303	93.4	0.270

Table 6
Effect of $Ni(OH)_2$ of different tap densities

Packing density ($g\ cm^{-3}$)	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity ($Ah\ g^{-1}$)
1.38	0.2	5.13	0.256	78.4	0.227
1.59	0.2	4.85	0.267	81.6	0.236
1.75	0.2	5.05	0.278	85.0	0.246
1.80	0.2	5.50	0.286	87.5	0.253

Table 7
Effect of active material content

$Ni(OH)_2$ content (%)	Discharge rate (C)	Discharge time (h)	Real capacity (Ah)	Utilization (%)	Average specific capacity ($Ah\ g^{-1}$)
60	0.2	5.76	0.288	86.8	0.251
65	0.2	5.96	0.328	94.3	0.273
70	0.2	5.50	0.286	87.5	0.253
75	0.2	4.83	0.266	81.5	0.236

0:100. The results are given in Table 5 and show that it is impossible to prepare electrodes without PTFE solution. Moreover, increasing the PTFE solution content can enhance the utilization. Although PTFE can increase the electrode intensity, an unsuitable increase will decrease the capacity because the increase in internal resistance results in greater ohmic polarization. A suitable ratio of CMC solution to PTFE solution produces a fibrous structure that holds the active material powders [5]. Evaporation of water from the CMC solution increases the electrode void, and thus increases the specific surface area of the electrode and decreases the concentration polarization. The highest utilization was obtained when the ratio of CMC solution to PTFE solution is 1.5:1.

3.6. Effect of $Ni(OH)_2$ tap density

Using a suitable CMC to PTFE ratio, electrodes were made with $Ni(OH)_2$ of different density, namely, 1.38, 1.59, 1.75 and 1.80 $g\ cm^{-3}$. The results are given in Table 6. The data show that $Ni(OH)_2$ powder of high density can provide higher utilization and besides, since at high density more $Ni(OH)_2$ powder can be filled in the electrode, the electrode capacity is enhanced.

3.7. Effect of $Ni(OH)_2$ content

The $Ni(OH)_2$ weight was changed as follows: 60, 65, 70 and 75% of the total slurry weight. The results are listed in Table 7.

The utilization of active material is not improved by increasing the $Ni(OH)_2$ content. Indeed, when the electrode contains more than 60% $Ni(OH)_2$ powder, the utilization decreases by virtue of the concomitant decrease in the void ratio. Furthermore, conductive materials decrease with increase in the $Ni(OH)_2$ content, which hinders the electron

Table 8
Performance of test electrode

Discharge rate (C)	Average voltage (V)	Discharge time (h)	Real capacity (Ah)	Utilization ratio (%)	Average specific capacity (Ah g^{-1})
0.2	1.236	5.91	0.325	99.4	0.288
0.3	1.215	3.99	0.319	97.7	0.283
0.5	1.201	2.38	0.309	94.5	0.273
1.0	1.188	1.17	0.303	92.8	0.268

transfer between $Ni(OH)_2$ particles, i.e., the internal resistance becomes more, and thus the capacity decreases.

3.8. Study of dopants

The effect of dopants, such as cobalt, cadmium, zinc, copper and an H-absorbing alloy on electrode performance has been reported previously [4]. It was concluded that the addition of cobalt compounds is effective in terms of the electrode capacity, and adding other dopants can also improve the performance of paste-type nickel cathodes.

3.9. Favourable formulae

The test electrode contained 25 wt.% conductive materials, in which the ratio of scaly graphite to acetylene black was 4:1 and 29 wt.% binders was used, in which the ratio of CMC solution to PTFE solution was 1.5:1. At the same time, 5 wt.% CoO, 2 wt.% CdO, 2 wt.% ZnO and 1 wt.% $Ba(OH)_2$ were added to the electrode. The electrode performance is shown in Table 8. Clearly, the test electrode can give high average voltage, a good utilization ratio, and an average specific capacity.

4. Conclusions

1. The concentration of the electrolyte has a remarkable effect on the utilization of active material. A 30 wt.% KOH solution gives the highest active-material utilization.
2. The content of active material affects markedly the electrode capacity. A content of 25 wt.% conductive materials, in which the ratio of scaly graphite to acetylene black is 4:1, is the most effective.
3. Adding binders improves the electrode intensity. When the electrode contains 29 wt.% binders with respect to the weight of $Ni(OH)_2$, in which the ratio of CMC to PTFE solution is 1.5:1, good performance is obtained.
4. The effects of packing density and content on electrode capacity should not be neglected. $Ni(OH)_2$ of higher tap density and at a high content can provide high capacity. Nevertheless, an excessive content of $Ni(OH)_2$ results in low utilization.

References

[1] *Jpn. Patent No. JP63 187 765[88 187 765].*
[2] *Jpn. Patent No. JP4 21 061[92 21 061].*
[3] *Eur. Patent No. EP 523 284.*
[4] D. Yunchang, L. Hui, Y. Jiongliang and C. Zhaorong, *J. Power Sources, 56* (1995) 115–119.
[5] S.S. Kulcsar, J. Agh, A. Fazekas, J. Vigh and Z. Bujdoso, *J Power Sources, 8* (1982) 55.