Short Communication

Study of the electrochemical performance of nickel hydroxide

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Abstract

The tap density and activity of nickel hydroxide prepared under various conditions is determined. The influence of the preparation conditions on the electrochemical properties of nickel hydroxide is undertaken in order to provide reliable information on the preparation of nickel hydroxide with excellent performance.

Keywords: Nickel hydroxide; Tap density; Activity

1. Introduction

The electrochemical performance of nickel hydroxide is related to its crystal structure and the quantity of crystal water. These are determined by the method and conditions of preparation [1].

The reaction taking place in the preparation nickel hydroxide is:

$$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2 \qquad (1)$$
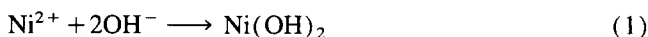
where the nickel salt refers to $NiSO_4$, $Ni(NO_3)_2$ or $NiCl_2$, and the alkali is $NaOH$ or KOH. Conditions such as the feeding rate, the feeding method, the reaction temperature, pH value and drying temperature must be controlled in order to obtain nickel hydroxide with high activity [1–5].

The work reported here describes the influence of preparation conditions on the final products, e.g. feeding method, pH, deposition temperature, drying temperature and various nickel salt and alkaline solutions. This information is required to provide reliable information on the preparation of nickel hydroxide with excellent performance.

2. Experimental

2.1. Preparation of nickel hydroxide

Given amounts of nickel salt solution and alkaline solution were fed to a reaction tank at a fixed temperature with vigorous stirring. The product was filtered, dried, and washed with distilled water in order to remove any residual SO_4^{2-} ions in the $Ni(OH)_2$. The product was dried again, pulverized and sieved.

2.2. Determination of tap density of Ni(OH)$_2$

Nickel hydroxide powders were packed into a 20 ml measuring cylinder (weight $= A$ g) and then tapped for 200 times. The weight (B g) of the measuring cylinder and powder and the volume (D ml) of the nickel hydroxide were then measured. The tap density was calculated from the formula: $(B - A)/D$.

2.3. 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. Finally, the electrode was immersed in the electrolyte solution.

2.4. Measurement of capacity

The test cell comprised the sample nickel electrode as a cathode, a sintered cadmium anode (State-run No. 755 factory), a separator of unwoven cloth, and an alkaline electrolyte solution. The capacity was measured under constant-current conditions. Charge/discharge cycles were performed at 20 ± 2 °C. One cycle comprised carrying out charging at $0.3C$ mA and discharging to 1.0 V at $0.2C$ mA.

The activity (namely, the utilization factor, η, of active material) was calculated by the following formula:

$$\eta = \frac{itM}{26.8W} \times 100\%$$

where i is the discharge current (A), t the discharge time (h), M the gram equivalent of $Ni(OH)_2$ (g), and W the weight of $Ni(OH)_2$ (g).

3. Results and discussion

3.1. Effect of feeding methods

The results of different feeding methods, for example, nickel salt added to alkaline solution (A), alkali added to nickel salt solution (B), or nickel salt and alkaline solutions fed together to the reaction tank (C), are shown in Table 1. (The utilization factor in Table 1, and other Tables, is for a 0.2C discharge rate.)

Nickel hydroxide precipitation takes place under alkaline conditions when nickel salt solution is added to alkaline solution, the pH of solution is from high to low. Alternatively, nickel hydroxide can be produced under nearly neutral conditions, the pH of solution changes from low to high. When nickel salt and alkaline solution are fed at the same time, the precipitate is formed instantaneously and the solution is kept at a fixed pH. Thus, the precipitate is homogeneous and has a good performance.

3.2. Effects of reaction pH

The reaction can be performed at various pH values by controlling the feeding rates of the nickel salt and the alkaline solutions. Table 2 shows the effects. It can be seen that both the tap density and the activity of $Ni(OH)_2$ are excellent when the reaction pH is high. When the pH is low, the concentration of the OH^- ion is low, so it is impossible for the nickel salt and alkali to form basic salt. This not only makes the precipitate difficult to wash, but also the nickel salt cannot be used fully.

As is well known, the electrochemical behaviour of the nickel hydroxide system is very complicated because of the variety of crystal types. The hydroxide is composed mainly of a α-$Ni(OH)_2$ and β-$Ni(OH)_2$. The anode oxidation of α-$Ni(OH)_2$ and β-$Ni(OH)_2$ commences at the solid phase boundary of Ni/α-$Ni(OH)_2$ in alkaline medium and at the boundary of β-$Ni(OH)_2$/solution, respectively. Because of the difference in the mechanism of anode oxidation, the activity of β-$Ni(OH)_2$ is higher than that of α-$Ni(OH)_2$. It is beneficial to produce β-$Ni(OH)_2$ in strong alkaline medium [1].

3.3. Effects of drying temperature

Nickel hydroxide, produced by simultaneous feeding and at a reaction pH of 12.9–12.2, was dried at various temperatures. The results are given in Table 3. The electrochemical activity of $Ni(OH)_2$ is excellent at a drying temperature of 50 and 110 °C. It has been reported [7–9] that the electrochemical activity increases with increase in the content of

Table 1
Effect of feeding method

Feeding method	Theoretical capacity (Ah)	Real capacity (Ah)	Utilization factor (%)	Specific capacity (Ah g^{-1})	Tap density (g cm^{-3})
A	0.361	0.284	78.7	0.228	1.60
B	0.303	0.234	76.2	0.220	1.54
C	0.867	0.740	85.3	0.247	1.71

Table 2
Effect of reaction pH

pH	Theoretical capacity (Ah)	Real capacity (Ah)	Utilization factor (%)	Specific capacity (Ah g^{-1})	Tap density (g cm^{-3})
11.0–11.2	0.690	0.490	71.0	0.205	1.46
11.2–11.4	0.750	0.572	76.3	0.221	1.55
11.4–11.6	0.760	0.588	77.4	0.224	1.58
11.6–11.8	0.760	0.584	76.9	0.222	1.58
11.8–12.0	0.510	0.372	73.0	0.211	1.55
12.0–12.2	0.867	0.740	85.3	0.247	1.71
12.2–12.4	1.300	1.079	83.0	0.240	1.65
12.6–12.8	0.950	0.803	84.6	0.245	1.68
12.8–13.0	0.780	0.625	80.1	0.232	1.67

Table 3
Effect of drying temperature

Drying temperature (°C)	Theoretical capacity (Ah)	Real capacity (Ah)	Utilization factor (%)	Specific capacity (Ah g^{-1})	Tap density (g cm^{-3})
50	0.350	0.284	81.0	0.234	1.68
70	0.347	0.257	74.2	0.215	1.52
90	0.760	0.561	73.8	0.213	1.49
110	0.310	0.268	86.5	0.250	1.70
120	0.310	0.252	81.3	0.235	1.67
130	0.320	0.265	82.7	0.239	1.66

Table 4
Effect of deposition temperature

Deposition temperature (°C)	Theoretical capacity (Ah)	Real capacity (Ah)	Utilization factor (%)	Specific capacity (Ah g^{-1})	Tap density (g cm^{-3})
40	0.350	0.266	76.1	0.220	1.50
60	0.290	0.251	86.5	0.250	1.70
70	0.347	0.303	87.2	0.252	1.77
80	0.318	0.271	85.3	0.247	1.71
90	0.351	0.283	78.3	0.226	1.63

Table 5
Effect of type of nickel salt and alkali

Nickel salt	Alkali	Theoretical capacity (Ah)	Real capacity (Ah)	Utilization factor (%)	Specific capacity (Ah g^{-1})	Tap density (g cm^{-3})
NiSO$_4$	NaOH	0.347	0.303	87.2	0.252	1.77
Ni(NO$_3$)$_2$	NaOH	0.303	0.253	83.4	0.241	1.70
NiCl$_2$	NaOH	0.321	0.246	76.5	0.221	1.59
NiSO$_4$	KOH	0.329	0.286	86.8	0.251	1.75

water in the crystalline phase. The crystal water is present by virtue of hydrogen bonding. When the drying temperature is below 50 °C, the hydrogen bond in Ni(OH)$_2$ is destroyed only slightly so that the content of crystal water is high and stable. Thus, the performance of Ni(OH)$_2$ is good. The content of crystal water decreases with increase in the drying temperature. When the drying temperature is higher than 100 °C, the hydrogen bond is destroyed violently. Nevertheless, the activity of Ni(OH)$_2$ rises. This is because the crystal water is no longer the main determinant of the activity of Ni(OH)$_2$. The latter is influenced more by the crystal structure. The greater the content of β-Ni(OH)$_2$, the higher the activity of Ni(OH)$_2$. The content of β-Ni(OH)$_2$ is determined by the drying temperature [3]; the content increases with increase in drying temperature. On the other hand, decomposition can occur when the drying temperature is greater than 150 °C. Accordingly, the activity decreases sharply.

3.4. Effects of deposition temperature

The nickel hydroxide precipitate was produced at various reaction temperatures by controlling the reaction

pH in the range 12.0–12.2 by using simultaneous feeding method.

The data given in Table 4 suggest that the performance of nickel hydroxide is excellent when the reaction temperature is 60–80 °C. This is because α-Ni(OH)$_2$ can transform into highly active β-Ni(OH)$_2$ when it is heated in a strong alkali medium [4]. Moreover, the precipitate formed at high temperatures is easy to wash [3]. When the temperature is too high, however, the precipitation speed increases, as does the solubility of Ni(OH)$_2$. It is therefore difficult to filter the product.

3.5. Effect of various nickel salts and alkalines

The experimental conditions were controlled as follows: reaction pH 12.0–12.2; deposition temperature 70 °C; drying temperature 110 °C; Ni(NO$_3$)$_2$ and NiCl$_2$ used instead of NiSO$_4$, and NaOH used instead of KOH.

The results presented in Table 5 show that the performance of nickel hydroxide produced by NiSO$_4$ and NaOH is excellent. The reason for this behaviour is that SO$_4^{2-}$ ions can easily adhere to the surface of precipitate by adsorption, and,

therefore, lower the amounts of impurities. The volume of the Cl^- ion is small and it closely combines with $Ni(OH)_2$. Thus, it is difficult to remove. The type of alkali (KOH or NaOH) has little influence on the performance of $Ni(OH)_2$. This observation has been made previously.

4. Conclusions

Nickel hydroxide with tap density of 1.77 g cm^{-3} and a specific capacity of 0.252 Ah g^{-1} is obtained by controlling appropriate experimental conditions, namely, $NiSO_4$ and NaOH fed to the reaction tank at the same time; a temperature of 70 °C, a fixed pH of 12.0–12.2, and a drying temperature of 110 °C. The initial capacity of the resulting $Ni(OH)_2$ is superior to that of $Ni(OH)_2$ produced by adding $NiSO_4$ solution to the alkali.

The reaction pH exerts a significant effect on the performance of $Ni(OH)_2$. A high reaction pH can improve the activity of $Ni(OH)_2$.

The activity of $Ni(OH)_2$ is enhanced by increasing the reaction temperature.

The performance of $Ni(OH)_2$ from various nickel salts is different under the same reaction conditions.

References

[1] C. Junqiang, Dianchi, 4 (1991) 12.
[2] Jpn. Patent No. 04 284 360.
[3] K. Micka, Z. Zábranský and M. Svatá, J. Power Sources, 8 (1982) 9.
[4] Jpn. Patent No. 63 16 556.
[5] Jpn. Patent No. 01 24 362.
[6] Eur. Patent No. EP 524 284.
[7] H. Bode and K. Vehelt, Electrochim. Acta, 11 (1966) 1079.
[8] W. Dennsted and W. Loser, Elektrochim. Acta, 16 (1971) 429.
[9] Y. Sasaki, T. Vamaskita, Hyomen Gijutsu, 40 (1989) 86–88.