A study of the electrochemistry of nickel hydroxide electrodes with various additives

Wen-Hua Zhu [a], Jia-Jun Ke [a], Hong-Mei Yu [b], Deng-Jun Zhang [a]

[a] Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080, China
[b] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116012, China

Abstract

Nickel composite electrodes (NCE) with various additives are prepared by a chemical impregnation method from nitrate solutions on sintered porous plaques. The electrochemical properties, such as utilization of active material, swelling and the discharge potential of the nickel oxide electrode (NOE) are determined mainly through the composition of the active material and the characteristics of nickel plaques. Most additives (Mg, Ca, Sr, Ba, Zn, Cd, Co, Li and Al hydroxide) exert effects on the discharge potential and swelling of the NOE. Chemical co-precipitation with the addition of calcium, zinc, magnesium and barium hydroxide increases the discharge potential by more than 20 mV, but that with zinc hydroxide results in an obvious decrease of active-material utilization and that with calcium and magnesium hydroxide produces a larger increase of electrode thickness. The effects of anion additives are also examined. Less than 1% mol of NiS in the active material increases the discharge potential. Cadmium, cobalt and zinc hydroxide are excellent additives for preventing swelling of the NCE. Slow voltammetry (0.2 mV s^{-1}) in 6 M KOH is applied to characterize the oxygen-evolving potential of the NCE. The difference between the oxygen-evolution potential and the potential of the oxidation peak for the NCE with additives of calcium, lithium, barium and aluminium hydroxide is at least $+60$ mV.

1. Introduction

The secondary nickel/hydrogen (Ni/H$_2$) battery was developed originally for space power [1,2]. Currently, the nickel/metal hydride (Ni/MH) battery is being used successfully for terrestrial applications. The energy density and power density of available batteries utilizing the nickel oxide electrode (NOE) are often limited because they must be designed with large void volumes to avoid excessive swelling of the nickel electrodes and to provide pathways of mass transfer [3].

The use of additives in the NOE, termed nickel composite electrodes (NCE) in this paper, has been shown [4–9] to modify the electrochemical performance of the NOE. The addition of Co(OH)$_2$ in relatively large amounts is found [4,10] to decrease the discharge voltage but to improve the capacity of the NCE when it is charged at a low current and an elevated temperature. Coating the electrode surface with Cd(OH)$_2$ decreases the oxygen-evolving potential, while the addition of Co(OH)$_2$ to Ni(OH)$_2$ lowers the oxidation potential of Ni(OH)$_2$ [5]. The swelling of the NOE is related to the formation of γ-NiOOH [8]. Electrochemical measure-

ments on thin films of nickel hydroxide with chemically co-precipitated cobalt, iron and manganese have also been conducted [11,12]. The electrochemistry of the NOE with metal hydroxide additives has been examined by using cyclic voltammetry in 1 M KOH [13]. Iron and zinc ions in the electrolyte decrease the charge-storage ability [7]. The effects of lithium, zinc and iron ions on the NOE have been investigated by slow voltammetry (0.1 mV s^{-1}) [9]. A study of the electrochemistry of the NCE is essential in order to understand battery properties and to provide avenues to improve the quality of products.

This work deals with the effects of additives on the properties of the NOE, i.e., utilization of active material, discharge potential, swelling and oxygen-evolving potential. Anion additives are also discussed. Where possible, industrial parameters are used.

2. Experimental

A fibrous sintered support was produced by using small hollow nickel fibres, nickel powder and cellulose. The nickel

Table 1
Utilization of active material, capacity, average discharge potential [a] and swelling of the nickel composite electrodes with metal hydroxide additives

No.	Hydroxide additive	Utilization of active material (%)	Capacity (mAh)	E (mV, vs. Hg/HgO)	ΔE (mV)	Swelling (% $\Delta d/d$)
261	Ca(OH)₂	98.1	103.0	354	24	6.0
262	Mg(OH)₂	89.0	91.7	350	20	8.0
265	Ba(OH)₂	87.6	103.4	357	27	1.0
267	Zn(OH)₂	73.2	84.2	360	30	1.0
268	Sr(OH)₂	88.2	97.0	320	−10	6.0
269	Co(OH)₂	77.0	81.6	311	−19	2.9
270	LiOH	90.8	91.7	327	−3	4.3
271	Cd(OH)₂	88.0	92.4	339	9	2.2
272	Al(OH)₃	100.0	55.2	328	−2	0
276		98.6	93.7	330	0	4.3

[a] $E = \Sigma E(t_i)/n$, $i = 1, 2, ..., n$, $t_1 = 0.5$ h, $t_n = 2.0$ h).

Table 2
Solubility product constant, K_{sp}, of metal hydroxides

Hydroxide	Ca(OH)₂	Mg(OH)₂	Cd(OH)₂	Co(OH)₂	Ni(OH)₂	Zn(OH)₂
K_{sp}	5.5×10^{-6}	1.8×10^{-11}	2.5×10^{-14}	1.6×10^{-15}	2.0×10^{-15}	1.2×10^{-17}

fibres had outer diameters of ~20 μm, an inner diameter of ~15 μm, and a length of 0.5–5 mm. These materials were fabricated by a traditional slurry-scraping method on nickel-plated perforated steel plates. The plaque was sintered at 1273 K for about 30 min under the reduction atmosphere.

The NCE was prepared by chemical co-precipitation of nickel hydroxide on fibrous sintered plaque from aqueous nickel nitrate that contained an additive of metal nitrate. The addition of anions was performed by adding AlO_2^- or Na_2S to the alkaline solution of impregnation.

The test electrodes (Nos. 261–276) for examination of the utilization of active material, and the discharge potential and swelling of the NCEs were 20 mm long, 17 mm wide and 0.9 mm thick. The impregnation process was repeated for six times and the loading level of the active material was approximately 1.6–1.7 g cm⁻³ void. Nickel foil was used for the counter electrode. These were placed on both sides of the working NCE. A Hg/HgO reference electrode was employed to measure the potential of the working electrode. The formation was carried out with repeated (three cycles) charging at 0.5C for 150% theoretical capacity and discharging at 0.3C to 0.0 V. The effects of additives on the NOEs can be determined approximately through the utilization of active material, and the discharge potential and swelling of the NCE at 0.3C.

The test electrodes (Nos. 225–234, 10 mm × 8 mm × 0.7 mm) in 6 M KOH were prepared using the procedure described above. After three-cycle formation, the electrode was placed in a three-compartment unit. A generator HB-104 (Hokuto Denko Ltd.) and a dual potentio-galvanostat DPGS-1 (Nikko Keisoku) were used to conduct linear-sweep voltammetry. The sweep began negatively from 550 to 220 mV, and was backed to the starting potential. The resulting

voltammetric curves provided the potential of oxygen evolution, as well as the difference in potential between the oxidation peak and oxygen evolution.

X-ray diffraction analysis with Fe Kα radiation was performed on several drying and pulverizing NCEs (selected from Nos. 261–276, charging at 0.5C for 10 h).

3. Results and discussion

3.1. Utilization of active material and capacity of nickel composite electrodes

Ten electrodes (Nos. 261–276) with different additives were studied. All of these NCEs were prepared by the chemical co-precipitation method. The content of each metal nitrate additive was 6 mol%. The utilization of active material and the capacity of the NCEs varied considerably with different additives, as shown in Table 1. The utilization of Ni(OH)₂ was determined from the capacity at 0.3C, and the theoretical capacity was determined by 94% Ni(OH)₂ in total co-precipitation. Not considering aluminium addition [1], the NCE of calcium hydroxide addition reached 103 mAh with 98% utilization of active material. That of zinc hydroxide addition was not less than 85 mAh with 73% utilization of active material. The results can be explained by considering the solubility product (K_{sp}) of the metal hydroxide. When K_{sp} is less than 10^{-6}, the sequence of K_{sp} values is shown in Table 2. The sequence of Ni(OH)₂ utilization (see Table 1)

[1] Al(OH)₃ is difficult to dissolve, and obstructs the tiny pores. Consequently, the co-precipitation of aluminium nitrate by the chemical method failed to form metal hydroxide in the porous plaques.
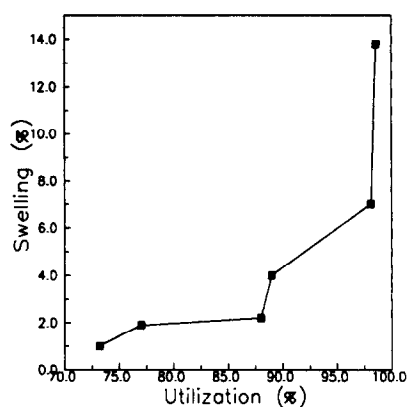
Fig. 1. Electrode swelling vs. utilization of active material. Charging at 0.5C for 10 h, 6 M KOH.
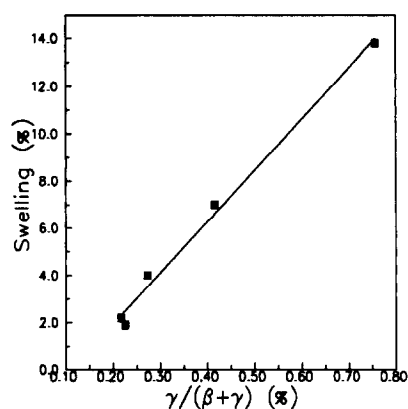

Fig. 2. Relationship between the degree of swelling and ratio of γ-NiOOH to total γ-NiOOH and β-NiOOH. Charging at 0.5C for 10 h, 6 M KOH.
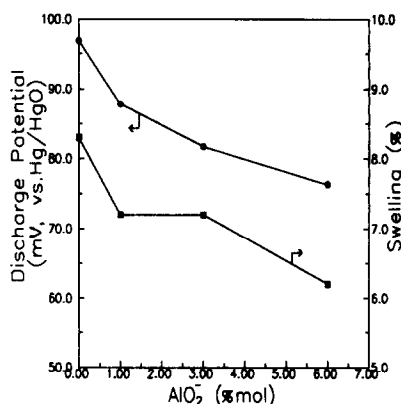

Fig. 3. Utilization of active material and electrode swelling as a function of AlO_2^- content.

is the same as that in Table 2, i.e., calcium > magnesium > cadmium > cobalt > zinc hydroxide. Utilization of nickel hydroxide in the NCEs with lithium, magnesium, strontium, barium and cadmium hydroxide additives is approximately 88–91%. The relationship between utilization of active material and the solubility product of the metal hydroxide additive suggests that it is necessary to consider the effects of K_{sp} in battery manufacturing.

3.2. Discharge potential and swelling of nickel composite electrodes

As shown in Table 1, the addition of zinc, barium, calcium and magnesium hydroxide resulted in a substantial increase in the discharge potential compared with a pure nickel hydroxide. The difference, ΔE, between the potentials of the composite and pure $Ni(OH)_2$ electrodes was more than +20 mV. In terms of improvement in the discharge potential and capacity of the NCEs, the preferred additives of chemical co-precipitation are: calcium, magnesium or barium hydroxide.

The swelling of NCEs increases with utilization of the active material, see Fig. 1. The NCE swelling with calcium, magnesium and strontium hydroxide additives was more than 6% after the third discharge operation, while that with cobalt, cadmium, zinc and barium hydroxide additives was less than 3%. Considering utilization of active material, capacity, discharge potential and swelling of the NCEs, the barium and cadmium hydroxide are used as one component additives.

The degree of swelling is related to the formation of γ-$Ni(OH)_2$ [8]. The integrated intensities of the γ-NiOOH (003) and β-NiOOH (001) peaks were used to calculate the ratio of γ-NiOOH to the total amount of β-NiOOH and γ-NiOOH. The rapid formation of γ-NiOOH by overcharging at 0.5C for 10 h is shown in Fig. 2. It is concluded that changes in the thickness can be used to evaluate the amount of γ-NiOOH that is formed.

3.3. Anion additives of AlO_2^- and S^{2-}

Replacement of nickel by aluminium in the brucite-type $Ni(OH)_2$ layers leads to double hydroxides. These can be used as active material for nickel hydroxide electrodes. The above tests showed that it was difficult to fill the tiny pores of active material directly with aluminium hydroxide by the co-precipitation method because the solubility product of aluminium hydroxide is 1.3×10^{-33}. Consequently, $Al(OH)_3$ was transformed to AlO_2^- with 6 M NaOH solution, which was used to form the NCE in a 6-cycle impregnation. Utilization of active material and swelling of the NCEs with addition of AlO_2^- (Fig. 3) were unsatisfactory compared with metal hydroxide. When the amount of AlO_2^- in the alkaline solution was 6 mol%, the utilization of active material was 76.3%. This is similar to that of zinc hydroxide addition. On the other hand, stability of α-type $Ni(OH)_2$ in alkaline solutions is better with Al-substituted materials than with Ni-/Co-active materials [14].

Nickel oxide (NiO) is a non-conductor, but NiS, NiSe, and NiTe are all good conductors [15]. In the case of NiS oxidation, the electrode was charged to 100% theoretical capacity at 0.1C. The discharge potential is shown in Fig. 4; it increases more than +10 mV in comparison with pure $Ni(OH)_2$ electrodes. Because the K_{sp} of NiS is less than 3.2×10^{-19}, it is preferred to dissolve NiS in 6 M NaOH rather than to add Na_2S to alkaline solution.
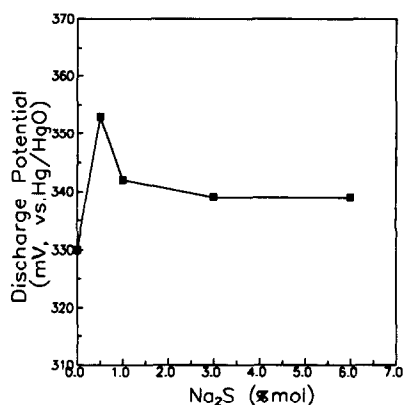
Fig. 4. Discharge potential as a function of mole ratio of Na$_2$S to alkaline impregnation solution.
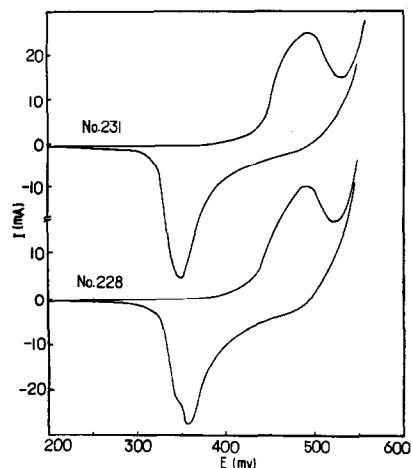

Fig. 5. Voltammograms for two nickel hydroxide electrodes in 6 M KOH. Scan rate = 0.2 mV s^{-1}.

3.4. Potential of oxygen evolution for nickel oxide electrodes with additives

Cobalt hydroxide additive has been investigated by many authors [2,5,8,9]. The addition of cobalt to the active material lowers the oxidation of nickel hydroxide. To study the effects

of aluminium, cadmium, zinc, lithium and some cluster IIA metal hydroxides, co-precipitated electrodes by chemical impregnation were prepared in nickel nitrate solution (sp. gr. 1.75 g cm^{-3}, 80 °C) and additives of 6 mol% metal nitrate. Two voltammograms obtained from individual test electrodes in fresh 6 M KOH solution are shown in Fig. 5, and the experimental results describing the features of the voltammograms are given in detail in Table 3. The average peak potential was used as a measure of the reversible potential and the peak potential separation was taken as a measure of reversibility [7,9]. The difference between the oxygen-evolving potential and the oxidation peak potential (DOP) is beneficial for the nickel electrode in secondary batteries. The pure Ni(OH)$_2$ electrode (No. 234) has the largest DOP value, but with the greatest degree of swelling during charge/discharge cycling, as mentioned above. Addition of calcium ions in the impregnation solutions results in a +10 mV change of oxidation potential and a decrease in the oxygen-evolution potential by about 10 mV, in comparison with a pure Ni(OH)$_2$ electrode. The DOP of calcium shifted negatively by 20 mV, but its discharge potential increased by about 20 mV (Table 1). Addition of cadmium hydroxide in the Ni(OH)$_2$ lattice did not increase the DOP value. This differs from the increase in DOP given by coating the electrode surface with cadmium hydroxide [5]. Addition of aluminium hydroxide caused the NCE to reach a higher potential (570 mV) for oxygen evolution, but with a typical discharge potential and a moderate degree of swelling. Interestingly, a small addition of aluminium compound accelerates the chemical impregnation rate.

4. Conclusions

This study has examined the utilization of active material, discharge potential, capacity, swelling, and oxygen-evolution potential of nickel oxide electrodes with various additives. The utilization of active material with additives decreases in

Table 3
Potential values of voltammetric features for nickel electrodes with various additives. (The chemical impregnation composition of additives in a solution of nitrate was 6 mol% and the scan rate was 0.2 mV s^{-1}.)

	Electrode No.								
	225	226	227	228	229	230	231	233	234
Additive of metal hydroxide	Ca	Zn	Mg	Sr	Al	Cd	Ba	Li	
Potential of oxidation peak (mV)	337	335	336	357	335	332	349	355	351
Potential of reduction peak (mV)	490	502	498	490	488	490	494	492	479
Average peak potential (mV)	414	419	417	424	412	411	422	424	415
Separation of oxidation/reduction peak potential (mV)	153	176	162	133	153	158	145	137	128
Oxygen-evolving potential (mV)	555	542	540	543	570	535	554	554	563
Difference in potential between oxidation and oxygen-evolution peaks (mV)	65	40	42	53	82	45	60	62	84

the order: calcium > magnesium > cadmium > zinc hydroxide. This is related to the solubility product of the respective metal hydroxide. The degree of swelling of the NOE with calcium, magnesium and strontium hydroxide additives is increased, but that of cadmium and zinc hydroxide additives does not change at the end of overcharging to 500% of the theoretical capacity. Additives of calcium, magnesium, zinc, barium hydroxide and NiS are beneficial for increasing the discharge potential of the nickel oxide electrode. The addition of an aluminium compound increases the chemical impregnation rate.

Acknowledgements

References

[1] D.L. Britton, NASA-TM-100958, 1988.
[2] H.S. Lim, Proc. 27th Intersociety Energy Conversion Engineering Conf., AIAA, New York, NY, USA, Vol. 1, 1992, pp. 1.239–244.
[3] B.A. Johnson, R.E. Ferro, G.M. Swain and B.T. Tatarchuk, J. Power Sources, 47 (1994) 251–259.
[4] E.J. Rubin and B. Baboian, J. Electrochem. Soc., 118 (1971) 428.
[5] M. Oshitani, Y. Sakaki and K. Takashima, J. Power Sources, 12 (1984) 219–231.
[6] B. Klapste, K. Micka, J. Mrha and J. Vondrak, J. Power Sources, 8 (1982) 351–357.
[7] D.A. Corrigan and R.M. Bendert, J. Electrochem. Soc., 136 (1989) 723–728.
[8] M. Oshitani, T. Takayama, K. Takashima and S. Tsuji, J. Appl. Electrochem., 16 (1986) 403–411.
[9] I. Krejci and P. Vanysek, J. Power Sources, 47 (1994) 79–88.
[10] S. Januszkiewicz, Proc. 13th Annu. Power Sources Conf., Fort Monmouth, NJ, USA, 1959, p. 75.
[11] S.I. Cordoba, R.E. Carbonio, M.L. Teijelo and V.A. Macagno, Electrochim. Acta, 31 (1986) 1326–1332.
[12] M.E. Folquer, J.R. Vilche and A.J. Ariva, J. Electroanal. Chem., 172 (1984) 235–253.
[13] D.A. Corrigan, J. Electrochem. Soc., 134 (1987) 377–384.
[14] K.T. Ehlsissen, A. Delahaye-Vidal, P. Genin, M. Figlarz and P. Willmann, J. Mater. Chem., 3 (1993) 883–888.
[15] A.R. West, Solid State Chemistry and its Applications, Wiley, New York, 1984, Ch. 14.