Development of lightweight nickel electrodes for zinc/nickel oxide cells

Waltraud Taucher *, Thomas C. Adler, Frank R. McLarnon, Elton J. Cairns

Energy and Environment Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94 720, USA

Abstract

A method for fabricating lightweight nickel electrodes has been developed by electrochemical impregnation of two different nickel fiber substrates. The electrochemical impregnation technique was applied galvanostatically at 35–50 mA/cm^2 in acidic solutions of nickel and cobalt nitrates (pH = 3). The nickel and cobalt contents of impregnated and formed electrodes was analyzed with atomic absorption spectrometry (AAS) and the amount of active nickel hydroxide was calculated. NiOOH electrode cycle-life performance testing was carried out in alkaline electrolyte (4.2–6.9 M KOH, 1 M LiOH) at a ~ C/5 rate during charge and discharge. Electrodes based on substrate materials of high porosity (90%, FN 090 Nickel Felt, Sorapec) deliver excellent specific capacities of 133–145 mAh/g in moderately alkaline electrolyte (4.2 M KOH) with an active material utilization of 67–95% depending on the quantity of co-precipitated cobalt (1.3–8.3%). NiOOH electrodes using substrates with lower porosity (81%, Fibrex 50/50 = fiber/Ni powder, National Standard) obtain very stable specific capacities (400 cycles) of 91–93 mAh/g with a utilization rate of 110% in highly alkaline electrolytes (6.9 M KOH).

Keywords: Nickel; Electrodes; Zinc; Nickel oxide

1. Introduction

Rechargeable alkaline Zn/NiOOH cells can be designed to deliver high specific energy (55–85 Wh/kg) and excellent specific power (> 200 W/kg), but their short lifetimes are a serious obstacle for commercial application [1–6]. Secondary cells that use zinc electrodes typically have problems with zinc material redistribution during charge and discharge [7,8]. However, recent investigations of low-zinc-solubility electrolytes (KOH–KF–K$_2$CO$_3$) exhibit a beneficial effect on the rate of zinc-active material redistribution (shape change), thereby extending lifetime of 1.35 Ah Zn/NiOOH cells to more than 500 cycles (> 60% initial capacity) on deep discharge [9–11]. The better performance of the zinc electrode consequently leads to the situation that now the NiOOH electrode limits the cycle life of Zn/NiOOH cells and investigations focus on the improvement of the nickel electrode.

Several methods of electrochemical impregnation of porous substrates with nickel hydroxide have been described for the preparation of nickel electrodes [12–16]. These techniques differ in substrate materials (sintered, non-sintered), composition of the bath (0.2–4 M Ni(NO$_3$)$_2$, aqueous or ethanolic solution), temperature (20–105 °C) and current density (50–150 mA/cm^2).

Electrochemically impregnated electrodes show better cycling behavior and exhibit reduced swelling and blistering during their cycle life compared to chemically impregnated electrodes [17]. Stagnant impregnation techniques are preferred to flow-through processes that suffer from removal of freshly precipitated Ni(OH)$_2$ by a convection mechanism [18].

The development of lightweight nickel electrodes with non-sintered substrate materials is a main goal for increasing the specific energy of Zn/NiOOH cells and to replace the heavier, more costly sintered nickel plaques. For non-sintered substrate materials the current collector grid is eliminated and a 12% weight saving over the sintered nickel plaques is achieved [19]. A further advantage of lightweight nickel fiber mats is the higher porosity, active material loading and specific capacity [20]. In this paper, a method to fabricate lightweight NiOOH electrodes delivering excellent capacities over hundreds of deep discharge cycles is described.

2. Experimental

2.1. Materials and equipment

Electrochemical impregnation solutions were prepared by dissolving nitrate salts of nickel and cobalt (Mallinckrodt,

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* Present address: Institute of Inorganic Chemical Technology, Technical University of Graz, Stremayrgasse 16/III, 8010 Graz, Austria.

chemical grade) in distilled water. The pH of the solution was measured with a Corning 220 pH meter and adjusted to 3.0 by adding ammonium hydroxide and/or nitric acid. After each impregnation the pH of the electrolyte is re-adjusted. Approximately 10 impregnations can be done with the same solution exhibiting no adverse effect on the loading efficiency of the electrode.

Lightweight nickel fiber mats from Sorapec, France (90% porosity, 56 mg/cm^2, 40 mil (1.016 mm)) and from National-Standard, Nonwoven Metal Products, Indiana (81% porosity, 107 mg/cm^2, 25 mil (0.635 mm)) were investigated as the substrates. The current collector tab for the nickel electrode consisted of a 5 mil ((0.127 mm) thick nickel foil that was also used as the anode material.

The electrochemical impregnation and formation experiments were carried out with a potentiostat/galvanostat from EG&G Princeton Applied Research, Model 371.

Impregnated/formed electrodes and fiber substrates were analyzed with atomic absorption spectroscopy (AAS) using a 2380 Perkin-Elmer atomic absorption spectrophotometer to determine the actual contents of nickel and cobalt. Nickel electrodes and fiber substrate samples (1 cm^2) were completely dissolved in a small portion of concentrated HNO$_3$ and further diluted with a 15% HNO$_3$ solution to an estimated concentration 2–5 ppm range.

## 2.2. Electrochemical impregnation and formation procedure

All experiments were carried out in a rectangular poly(vinyl chloride) (PVC) container (450 cm^3) with side grooves providing support for the electrodes. In order to assure a uniform impregnation pattern throughout the fiber substrate a simultaneous two-side electrode impregnation arrangement was used. Fig. 1 shows the experimental cell for electrochemical impregnation and formation.

The fiber substrate was cut into rectangules of 5.4 cm × 5 cm. Finally the effective substrate dimension measured 5 cm × 5 cm because the electrode was inserted on both sides in the grooves of the PVC container. The current collector tab was spotwelded to one edge of the nickel fiber substrate. Two nickel foils (5.4 cm × 10 cm) were used as the anodes and placed 2.5 cm from the cathodic fiber substrate. The unimpregnated fiber electrodes were cleaned in hot alkaline

Fig. 1. Experimental cell used for electrochemical impregnation and formation; cathode: nickel fiber substrate, anodes: nickel foils.

solution (10 w/o Alconox) and carefully rinsed with distilled water. After drying their weight was determined prior to impregnation.

The lightweight nickel fiber substrates were impregnated galvanostatically at current densities of 35–50 mA/cm^2 for about 2 h until a maximum loading of active Ni(OH)$_2$ was obtained. Higher current densities ($\geq$ 100 mA/cm^2) result in a non-uniform precipitation mainly on the surface of the electrode that can be seen by visual examination and leads to pore plugging and non-uniform distribution of impregnated material inside the pores [21]. Stagnant aqueous impregnation solutions containing 1.5 M Ni(NO$_3$)$_2$, 0.035–0.175 M Co(NO$_3$)$_2$ and 0.1 M NaNO$_3$ were used at 20 °C.

During the cathodic reaction of the impregnation process nitrate ions are reduced to ammonium hydroxide and hydroxide ions are generated:

$$NO^{3-} + 7H_2O + 8e^- \rightarrow NH_4OH + 9OH^- \qquad (1)$$
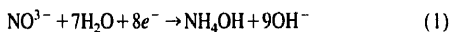
involving a pH change which leads to precipitation of active nickel hydroxide inside the nickel fiber substrate pores [22]:

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2\downarrow \qquad (2)$$

The impregnated electrodes were washed with distilled water and ethanol, dried at 105 °C for 20–30 min and weighed.

For cleaning purposes, e.g. removal of nitrate ions from the pores and to wash out loose nickel hydroxide, the impregnated electrodes were submitted to a formation procedure. A few formation cycles (3 1/2 and 5 1/2) were carried out in alkaline solution (4.2 M KOH, 1 M LiOH) establishing the electrode capacity during this simplified oxidation/reduction process [23]:

$$\beta\text{-Ni(OH)}_2 + OH^- \leftrightarrow \beta\text{-NiOOH} + H_2O + e^- \qquad (3)$$

Typical current densities of 10–50 mA/cm^2 are applied for 20–30 min per half cycle. The formation process was started and finished with a cathodic cycle.

Thereafter, the above-mentioned washing and drying procedure was repeated and the final weight of the formed nickel electrodes was determined.

2.3. Testing of nickel electrodes

Each formed nickel electrode was wrapped with a layer of Pellon 2524 non-woven nylon wick (Freudenberg Nonwoven, Chelmsford, MA). Two electrodes were placed in a 1.35 Ah Zn/NiOOH cell case described in Ref. [24]. The electrolyte level was kept about 1 cm above the top edge of the electrodes and an Hg/HgO reference electrode was used. Nickel electrode testing was carried out for the most part in moderately alkaline electrolyte (4.2 M KOH, 1 M LiOH), as higher alkalinity causes problems with zinc material redistribution in Zn/NiOOH cells during cycling [4]. Prior to regular electrode testing a few formation cycles at low current (C/10 rate) are necessary to characterize the electrode with regard to Ah capacity (0.50–0.70 Ah). Electrode cycling was
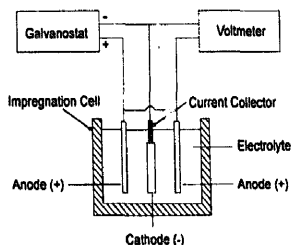
carried out with a ~C/5 rate during charge and discharge using the same computer-controlled system as for Zn/NiOOH cell cycling [25]. During a half-cycle one NiOOH electrode was charged and the second one was discharged simultaneously. An overcharge factor of 10% was applied and the NiOOH electrodes were kept at open circuit for 30 min after each half-cycle.

3. Results and discussion

3.1. Atomic absorption spectrometry

The nickel and cobalt content of impregnated (i) and formed (f) electrodes and the nickel amount of the fiber substrates was determined by AAS. In Table 1, the results of AAS analyses of nickel and cobalt are summarized. For electrodes 18f and 19i a Fibrex substrate was used and the impregnation solution contained 0.175 M $Co(NO_3)_2$. Electrode 26f was made of a Sorapec substrate and the cobalt content of the former impregnation solution was diminished to one fifth (0.035 M $Co(NO_3)_2$).

From AAS analysis it can be seen that the amount of nickel and cobalt is higher for the impregnated than for the formed electrode (Table 1). This effect may be due to an extraction of loose material and to a change of active material composition during the formation process. The amount of nickel hydroxide in formed electrodes is only 65%, independent of the selected fiber substrate. Portemer et al. [17] report that the active material contains different amounts of NO^{3-} and Co^{3-} ions and crystal water, but a complete structural characterization of the active material of the NiOOH in the electrodes [26] was not the intention of this work.

Table 1
Atomic absorption spectroscopy analyses of impregnated (i) and formed (f) nickel electrodes and their fiber substrates

Sample	Ni (%)	Ni(OH)₂ (%)	Co (%)	Co(OH)₂ (%)
Fibrex [a]	95.1		1.1	
18f	41.3	65.2	8.3	13.0
19i	45.8	72.3	9.1	14.4
Sorapec [b]	80.9		0.01	
26f	40.7	64.3	1.3	2.1

[a] Fibrex 50/50: 81% porosity, 25 mil (0.635 mm), 107 mg/cm². National Standard, Nonwoven Metal Products, IN. Substrate for 18f, 19i.
[b] FN 090 Nickel felt: 90% porosity, 40 mil (1.016 mm), 56 mg/cm². Sorapec, France. Substrate for 26f.

Table 2
Mole ratio, m_r, of cobalt to nickel

Electrode	m_r (impregnation solution)	m_r (electrode)
18f	0.120	0.200
19i	0.120	0.200
26f	0.023	0.032

After the impregnation and formation procedures it is found that the Co:Ni ratio in the electrodes is greater than that in the impregnation solution. The electrochemical impregnation process causes an increase of cobalt hydroxide content in the electrode. In Table 2 the mole ratio, m_r, of cobalt to nickel is determined for the impregnation solution and for the corresponding electrodes. In the case of higher-cobalt impregnation solution the Co:Ni mole ratio of the electrodes 18f and 19i increased remarkably to 67%. For the lower-cobalt solution it increased less (39%) as can be seen for electrode 26f. A definite percentage of cobalt in the final electrode can thus be obtained even with an impregnation solution of much lower Co:Ni ratio.

3.2. Electrode cycle-life performance

In Fig. 2–4 the capacities of NiOOH electrodes are shown as a function of cycle number. The first three cycles refer to capacities of formation cycling with low current (C/10 rate). Electrodes 16 and 17 (Fig. 2) were made from a Fibrex substrate and for all other electrodes (Fig. 3 and Fig. 4) a Sorapec substrate was used. Impregnation of the electrodes was carried out at 35–50 mA/cm² for about 2 h. The formation process of the electrodes was applied for 5 1/2 cycles except for electrode 29 (3 1/2 cycles).

Table 3 summarizes the weight gain, loading level and theoretical capacities of the two different substrate materials.
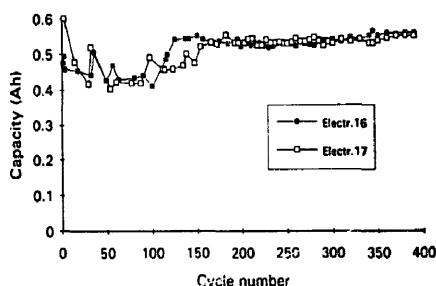
Fig. 2. Capacity of NiOOH electrodes using a Fibrex fiber substrate vs. cycle number. ~C/5 rate on charge and discharge; cobalt: 8.3%; electrolyte: 4.2 M KOH; 1 M LiOH (cycle: 1–116); 6.9 M KOH, 1 M LiOH (>116 cycles).
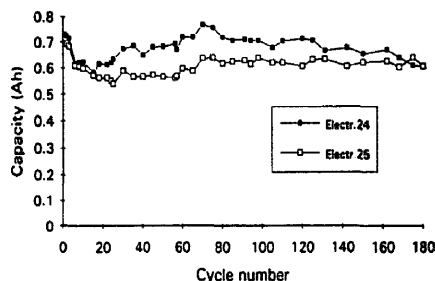
Fig. 3. Capacity of NiOOH electrodes using a Sorapec fiber substrate vs. cycle number. ~C/5 rate on charge and discharge; cobalt: 8.3%; electrolyte: 4.2 M KOH, 1 M LiOH.

Table 3
Theoretical capacity of nickel fiber electrodes using different substrates and loading levels

Electrode no.	Substrate material	Weight gain (g)	Loading level [a] (g/cm³ void)	Electrode capacity [b] (Ah)	Specific capacity [c] (mAh/g)
16	Fibrex	2.59	1.3	0.49	93
17	Fibrex	2.49	1.2	0.47	91
24	Sorapec	3.98	1.2	0.73	136
25	Sorapec	3.98	1.2	0.73	136
27	Sorapec	4.76	1.4	0.89	145
29	Sorepec	3.39	1.0	0.64	133

[a] Weight gain per void volume.
[b] Calculated from the weight gain after impregnation/formation process based on 65% active $Ni(OH)_2$ from atomic absorption spectroscopy analysis, using the electrochemical equivalent of 0.289 Ah/g: $Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$.
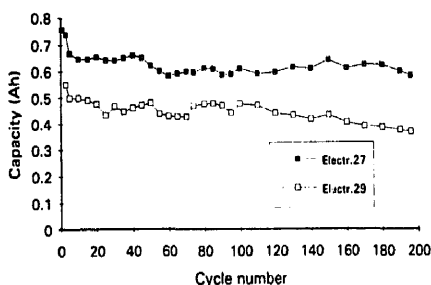[c] Based on electrode weight without tab.

Fig. 4. Capacity of NiOOH electrodes using a Sorapec fiber substrate vs. cycle number. ~ $C/5$ rate on charge and discharge; cobalt: 1.3%; electrolyte: 4.2 M KOH, 1 M LiOH.

Fig. 5. Utilization of NiOOH fiber electrodes using a Fibrex substrate (electrode 16, Co: 8.3%) and Sorapec substrates (electrode 24, Co: 8.3%; electrode 27, Co: 1.3%) vs. cycle number. ~ $C/5$ rate on charge and discharge.

The high porosity of the Sorapec substrate (90%) yields a better weight gain and capacity compared to the lower porosity Fibrex substrate (81%). The theoretical capacities of the electrodes are calculated from the weight gain after the impregnation/formation process based on 65% of $Ni(OH)_2$ from AAS analysis (Table 1).

The capacities of electrodes 24 and 25 (Fig. 3) are about 0.15-0.25 Ah higher compared to electrodes 16 and 17 (Fig. 2) up to cycle 120. These results can be regarded as a consequence of the much higher loading with active $Ni(OH)_2$ (49-55%) of electrodes 24 and 25 as shown in Table 3. Differences in capacity between electrode 24 and 25 result from a slightly different formation process.

Electrodes 27 and 29 (Fig. 4) also exhibit higher capacities in comparison to electrodes 16 and 17 (Fig. 2). The capacity of electrode 29 is 0.15-0.20 Ah lower than that of electrode 27. Due to a different formation process (3 1/2 cycles) the loss of active material of electrode 29 was extremely high (23%) after the cleaning procedure and consequently yields a much lower capacity.

3.3. Effect of electrolyte concentration

After 116 cycles the electrolyte of electrodes 16 and 17 was exchanged to higher alkalinity (4.2 M KOH, 1 M LiOH → 6.9 M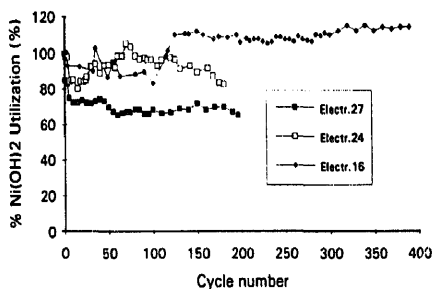 KOH, 1 M LiOH). The capacities of the following cycles increased from about 0.43 to 0.53 Ah. Some fluctuations in capacity observed during earlier cycles are due to changes of the cycling regimen. The $Ni(OH)_2$ utilization of electrodes 16 (Fig. 5) and 17 increases remarkable up to 110% for cycle numbers higher than 116 and the capacity is very stable over a wide cycle range (400 cycles). This behavior can be attributed to the fact that NiOOH electrodes show a better performance in highly alkaline electrolyte and the ionic conductivity of the electrolyte improves with increasing OH^- concentration with an optimum at 6.4 M.

The utilization of electrode 24 (Fig. 5) after 100 cycles is 95% and much higher than that of electrode 16 in moderately alkaline electrolyte (4.2 M). This electrode would probably operate at a utilization rate of at least 120% in higher alkaline electrolyte.

3.4. Effect of cobalt amount

Electrodes 27 (Fig. 5) and 29 exhibit relatively poor utilization (67-75%) of the theoretical capacity (Table 3) due to the low amount of cobalt hydroxide (2.1%). The addition of cobalt hydroxide that is co-precipitated with nickel hydroxide from the impregnation bath raises the oxygen overpotential of the nickel electrode and favors the charging efficiency [27]. Another beneficial effect is the better reversibility of the $Ni(II)/Ni(III)$ redox reaction of electrode cycling if

some amounts of cobalt are present in the nickel electrode [28,29].

4. Conclusions

Lightweight nickel fiber electrodes exhibiting excellent capacities and good cycle-life performance have been developed by electrochemical impregnation of various nickel fiber substrates. The electrochemical impregnation was carried out at 35–50 mA/ t^2 in acidic solutions (pH = 3) of nickel and cobalt nitrates (1.5 M, 0.035–0.175 M) leading to precipitation of active nickel hydroxide. Depending on the fiber substrate (FN 090 Nickel Felt, Sorapec/Fibrex 50/50, National Standard) the electrodes show different weight gains and capacities.

From AAS analysis of formed electrodes it can be seen that only 65% of the loaded material consists of active $Ni(OH)_2$. The data further show that the electrochemical impregnation process causes an increase of cobalt hydroxide content in the electrode. The Co:Ni mole ratio is definitely higher in the electrodes (39–67%) than in the original impregnation solution.

Electrode testing was carried out in alkaline electrolyte (4.2–6.9 M KOH, 1 M LiOH) with a $\sim C/5$ rate during charge and discharge using an Hg/HgO reference electrode. Nickel fiber electrodes prepared by this electrochemical impregnation technique exhibit a very stable cycling performance (at least 400 cycles) and extremely high specific capacities (91–145 mAh/g). Increasing the cobalt amount of the electrodes (1.3% to 8.3%) yields better utilization of active material (67% to 95%) in 4.2 M KOH. Highly alkaline electrolytes (6.9 M KOH, 1 M LiOH) increase the $Ni(OH)_2$ utilization of less-porous electrodes up to 110% of the theoretical capacity.

Acknowledgements

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