



An electrochemically impregnated sintered-nickel electrode

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Abstract

An electrochemically impregnated sintered-nickel porous electrode with a capacity of 225 ± 10 mAh per g of active material has been developed. This capacity is comparable with any state-of-the-art nickel hydroxide electrode reported in the literature, such as the stabilized α -nickel hydroxides that contain aluminium, iron and other trivalent cations. A technical update on various types of nickel positive electrodes is given.

Keywords: Nickel hydroxide; Electrochemical impregnation; Cells; Batteries; Electrodes

1. Introduction and technical update

Nickel hydroxide is the positive-electrode material for a number of nickel-based alkaline secondary cells such as Ni/Cd, Ni/Fe, Ni/Zn and Ni/MH cells. Since nickel hydroxide is an electronic semiconductor, the positive electrodes have to include a conductive support. The latter adds considerably to the weight of the electrode and, therefore, the specific capacity is lowered. Consequently, continuous efforts are being made to fabricate high-performance nickel hydroxide electrodes for a range of storage batteries. In general, these efforts encompass three critical aspects: (i) synthesis and stabilization of novel nickel hydroxide phases [1–4] that are capable of delivering more than $1 e^-$ charge per nickel atom during reversible cycling and, hence, will result in an increased specific capacity, i.e. Ah per g of active material (SCAM); (ii) development of ultra-light conductive supports [5–8] with a high surface area and a high porosity that are capable of accepting high loads of active material and will therefore lead to a high specific capacity in terms of the total electrode weight (SCEW), inclusive of the weight of the support; (iii) development of suitable methods to load the active material onto different supports [9–12] with a view to achieving maximum material utilization at high loading levels, good mechanical and morphological characteristics under prolonged cycling, and high cycle life.

Of the many novel nickel hydroxide phases [13–15], those modelled on the layered double hydroxides that contain 20

to 25 mol% of trivalent ions such as Co [1], Fe [2] or Al [3,4] have been the most successful. Although thin films of nickel hydroxide are known to exchange $1.67 e^-$ per Ni atom [16] (corresponding to a SCAM of 482 mAh g^{-1}), nickel hydroxide doped with cobalt [1] is reported to deliver the highest known SCAM in bulk electrodes, viz., 345 to 375 mAh g^{-1} that corresponds to 1.2 to $1.3 e^-$ exchange per metal (Ni, Co) atom. Further improvements in the SCAM of these materials, which are now known to be isostructural with α -nickel hydroxide [17], will be the subject of a forthcoming publication by the authors.

The sintered-nickel porous plaques [18] that are conventionally used as conductive supports are heavy and constitute nearly 60% of the weight of the positive electrode. These are being replaced by lighter supports, such as sintered-nickel fibrous plaques [19] that are known to reduce the electrode weight by about half. Using these lightweight supports, Oshitani et al. [7] have achieved a record SCEW of 170 mAh g^{-1} at a SCAM of 250 mAh g^{-1} . Zhu et al. [20] report an SCEW of 141 mAh g^{-1} at 85–90% utilization of active material (SCAM: 245–260 mAh g^{-1}) by electrochemical impregnation of sintered-nickel plaques that contain both nickel fibres and particles (Fibrex/P supports) [21]. The fibrous plaques have porosity of up to 90% (as against the 80% porosity of porous plaques), but they have a much smaller surface area so that the utilization of material is lower in fibrous than in conventional porous plaques. This situation is somewhat improved in Fibrex/P supports. The use of alternative supports drastically reduces the material utilization to

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38–58% (SCAM: 110–170 mAh g⁻¹) [6]. As a result, the sintered-nickel porous plaques are still the best supports as they have a much higher surface area compared with the lighter plaques and, therefore, provide better electrical contact and material utilization at higher loads. In fact, Oshitani et al. [22] have used sintered-nickel porous plaques to realise 100% material utilization (SCAM: 289 mAh g⁻¹) in a dip-loaded electrode.

There are many methods by which the active material can be bonded to the conductive support [23]. Many loading techniques, especially dip loading, expose the support to aggressive corrosion by the nickel nitrate solution. As a result, the possibility of over-estimating the specific capacity is very real [24]. Of all these techniques, electrochemical impregnation (ECI) is considered to be the best. Cathodic polarization of the plaques creates a hydrogen gas blanket that protects the plaques from corrosion. ECI is a one-step process that takes place by nitrate reduction [25]. ECI is the only technique that is effective in filling the cavities of the support without blocking the pore outlets. In all other loading techniques, pore closure due to surface deposition is inevitable.

A survey of the literature reveals that the sintered-nickel porous plaques loaded by the ECI route are still the preferred nickel hydroxide positive electrodes and are being employed extensively in commercial batteries. Since the technical details of ECI techniques are protected, a vast majority of researchers in this area are deprived of valuable data. Ho [25] and Ho and Jorne [25] have studied the ECI route in detail, both experimentally and theoretically, to optimize the various experimental parameters, but they do not report any capacity measurements. Law and Sapjeta [26] have optimized the ECI process for Fibrex/P supports but, again, do not report either the SCAM or SCEW values for the electrodes.

Two factors affect the performance of nickel hydroxide as an electrode material. First, the conductivity varies with the state-of-charge and the discharged phase has poor conductivity; during the discharge cycle, the material close to the conductive support discharges first and forms an insulating layer that prevents discharge of the active material away from the support. Second, the charged and discharged phases have different unit cell volumes, especially on overcharge; the electrode swells due to γ -NiO(OH) formation and this causes mechanical strain, shedding of the active material and morphological changes that adversely affect electrode performance.

Additives are invariably added to nickel hydroxide to improve its conductivity and prevent swelling. These additives include Zn(OH)₂, Co(OH)₂ and CoO at levels in the 5–10 mol% range. In this composition range, such additives do not affect the phase or the structural chemistry of nickel hydroxide. Inclusion of additives further complicates the ECI procedure. Zimmerman [27] has studied the effect of different ECI parameters on the cobalt content of the active material deposited from a mixed metal nitrate bath.

Pickett and Maloy [28] have used a 40–50 vol.% ethanol-water mixture as the solvent for a mixed metal nitrate bath. Later, Earl and Noble [29] studied the ageing of the bath used for the ECI procedure. Neither of these (or other) studies have investigated the role of ethanol on the structural and spectral properties of the active material or its role in enhancing electrode performance.

Electrodes made up of β -nickel hydroxide exhibit stabilized capacities (SCAM) of only 188 mAh g⁻¹ [30] in the absence of any additives. Except for Oshitani et al. [22] who report 100% material utilization (SCAM 289 mAh g⁻¹), all other studies report a lower material utilization in the 70–85% range (SCAM 202–245 mAh g⁻¹) in the presence of a variety of additives. Of late, nickel foam substrates pasted with nickel hydroxide have shown promise. Watanabe et al. [31] report a SCAM of 200 ± 10 mAh g⁻¹, while Hui et al. [32] report 210–250 mAh g⁻¹. The values correspond to 70 and 72–86% material utilization, respectively. The specific capacity values realised by different authors are summarized in Table 1.

It is noteworthy that in view of the experimental results of Delmas and co-workers [1,2], Corrigan and Knight [16] and the model of Ismail et al. [33], the potential theoretical capacity of nickel hydroxide has to be reevaluated on the basis of a 1.67 e⁻ change per Ni atom during reversible cycling, which amounts to a SCAM of 480 mAh g⁻¹. Thus, a new target has been set for high-performance electrodes. Nevertheless, since this value has not been widely accepted, the reported percentage utilization has been converted into SCAM values, in this study, by using the more widely accepted theoretical capacity of 289 mAh g⁻¹ for the nickel hydroxide electrode.

Although sintered-nickel porous plaques loaded by the ECI procedure are widely used, an examination of Table 1 reveals that there are no adequate data in the literature on the SCAM values of such electrodes. This communication reports SCAM values of nickel hydroxide electrodes that are obtained by ECI of sintered-nickel porous plaques.

2. Experimental

Sintered-nickel porous plaques (porosity 80%) were rinsed in double-distilled water and degreased in 6 M KOH at 30 mA cm⁻². The plaques were washed and dried to constant weight at 90 °C. The degreased plaques were then immersed in nickel nitrate solution (0.2 M mixed with absolute alcohol in a 70:30 volume ratio) and allowed to stand for 2 to 3 min. Nickel hydroxide was then deposited galvanostatically into the plaque under constant stirring by cathodically polarizing the plaque with respect to a cylindrical nickel mesh anode. The pH of the bath solution was between 5 and 6 and the deposition current density was varied between 8 and 30 mA per cm² geometric area of the plaque. The time of deposition was 10 to 30 min. Subsequent to deposition, the plaque was washed in double-distilled water and dried to constant weight at 90 °C to estimate the weight gain. At times,

Table 1
Summary of the performance of various nickel positive electrodes from literature

No.	Support	Loading method	Phase	SCAM (mAh g ⁻¹)	SCEW (mAh g ⁻¹)	Ref.
1	Ni-fibrex	CI			115	[8]
2	Propylene fibre	CI, ECI	β	109-168 ^a		[6]
3	Ni-fibre	ECI	β		141	[20]
4	Plexiglass	CI	β	170 ^b		[30]
5	Ni-foam	Pasted	β	210		[31]
6	Ni-porous plaque	ECI	β	220		[24b]
7	Ni-foam	Pasted	α (Fe-doped)	232		[2]
8	Ni-grid	Pasted	α (Al-doped)	240		[4]
9	Ni-foam	Pasted	β	221-241		[32]
10	Ni-gauze	Pasted	α (Fe-doped)	237-241		[3b]
11	Ni-gauze	Pasted	α (Al-doped)	250		[3a]
				193		[3a]
12	Ni-fibre	Pasted	β	250-255	120	[7]
13	Ni-fibre	CI	β	222-239 ^a		[12]
14	Ni-porous plaque	CI	β	> 289 ^a		[22]
15	Ni-porous plaque	CI	β	240-300 ^c		[24a]
16	Ni-foam	Pasted	α (Co-doped)	345 ^d		[1]

CI: chemical impregnation; ECI electrochemical impregnation.

^a Based upon percent utilization of active material.

^b Based upon specific capacity data of Ni.

^c Over estimated due to plaque corrosion.

^d Based upon number of electrons exchanged in the redox reaction.

the weight gain was marginal, and under such circumstances the plaque was re-soaked and deposition was repeated. During the second deposition, a rapid weight gain was observed. In the event of surface deposition the deposit was brushed off with a stiff polypropylene brush and the plaque was re-weighed. Plaques loaded with 0.5 to 0.75 g of nickel hydroxide were used for capacity studies. Control experiments of nickel hydroxide deposited from pure aqueous baths were carried out for comparison. The deposition setup was similar to that employed previously [9]. The final deposition conditions were:

bath temperature	70 °C
pH	5.8-6
bath medium	30% ethanol:70% 0.2 M Ni(NO ₃) ₂ aqueous solution
impregnation current	8 mA cm ⁻²
nature of counter electrode	soluble electrode, Ni mesh
plaque drying temperature	90 °C

The impregnated plaques were then soaked overnight in 6 M KOH for wetting and galvanostatically charged to 120-200% overcharge of the expected theoretical absolute capacity of the plaque. The potential of the plaque was measured against a Hg/HgO(MMO) reference electrode and two sintered-nickel plates (geometric area four times the plaque) were used as the counter electrodes. Galvanostatic discharge was carried out at C/4 to C rates to a cutoff potential of 0.25 V. A Spectrum Engineers (India) d.c. power supply coupled with a MECO (India) milliammeter was employed for the charge/discharge studies. The potential of the working electrode was measured using a high-impedance millivoltmeter. The measurements were restricted only to SCAM values.

Each electrode was cycled through 15 to 20 cycles to determine the stabilized capacity. At least two electrodes corresponding to each deposition condition were investigated for establishing reproducibility of the electrode behaviour. All the experiments were conducted at 30 °C.

The active material brushed off from overdeposited plaques was characterized by powder X-ray diffraction (JEOL JDX8P diffractometer) and infrared spectroscopy (Nicolet Impact 400D FT-IR spectrometer, KBr pellets, 4 cm⁻¹ resolution).

3. Results

The powder XRD pattern for nickel hydroxide deposited from an ethanolic bath is shown in Fig. 1 and is compared with the sample obtained from an aqueous bath. It is at once evident that the sample obtained from an aqueous bath has characteristics closer to that of β -Ni(OH)₂, while the sample

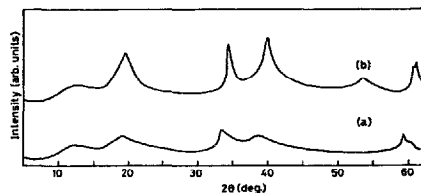


Fig. 1. XRD patterns of nickel hydroxide deposited from: (a) ethanolic bath, and (b) aqueous bath.

Table 2
XRD data of nickel hydroxide electro synthesized from aqueous and ethanolic baths

<i>hkl</i> ^a	<i>d</i> (Å)	
	Aqueous bath	Ethanolic bath
003 ^b		7.370
001 ^c	4.667	4.667
100 ^{bc}	2.696	2.704
011 ^c	2.336	2.342
012 ^c	1.757	
110 ^c	1.564	1.559
112 ^b		1.541

^a The *d*-spacings were indexed according to these *hkl* indices on a hexagonal cell.

^b α -phase: $a = 3.12$ Å and $c = 22.11$ Å.

^c β -phase: $a = 3.12$ Å and $c = 4.66$ Å.

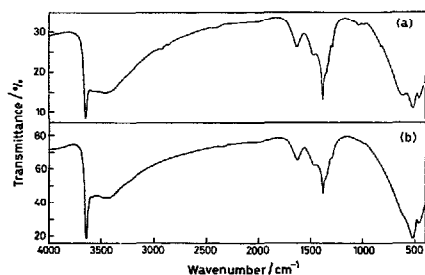


Fig. 2. Infrared spectra of nickel hydroxide deposited from: (a) ethanolic bath, and (b) aqueous bath.

obtained from an ethanolic bath is much more disordered with poor intensities and shows some characteristics reminiscent of α -nickel hydroxide. The prominent *d*-spacings together with their assignments are given in Table 2. Similar observations can also be made from the IR spectra (Fig. 2). The latter show signature vibrations that correspond to both the α - and β -phases in the sample obtained from an ethanolic bath, while the sample obtained from aqueous bath is similar to β -nickel hydroxide.

The variation in specific capacity as a function of cycle life for the electrodes prepared under different conditions is presented in Fig. 3. It is at once evident that plaques impregnated from pure aqueous baths yield lower capacity (195 mAh g^{-1} SCAM) than plaques impregnated from ethanolic baths which show $\sim 15\%$ improvements to give a SCAM of 225 mAh g^{-1} . A typical discharge curve for an electrode impregnated from an ethanolic bath is shown in Fig. 4. In general, plaques loaded at low current densities (8 mA cm^{-2}) perform better than those loaded at high current densities (up to 30 mA cm^{-2}). The addition of 10 mol% Co to the bath does not improve the electrode performance. All the electrodes prepared by ECI are found to exhibit their stabilized capacities within 5 to 8 formation cycles.

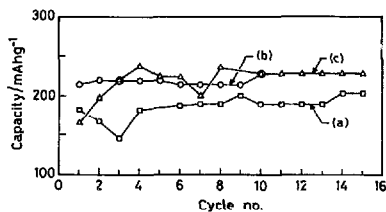


Fig. 3. Cycle-life data of nickel hydroxide electrodes obtained from: (a) aqueous bath; (b) ethanolic bath with 10 mol% Co, and (c) ethanolic bath.

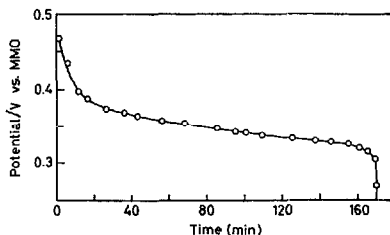


Fig. 4. Typical discharge (after 15 cycles) data for a nickel hydroxide electrode obtained from an ethanolic bath.

4. Discussion

Nickel hydroxide exists in two polymorphic forms, namely α and β [34], of which the former is known to exhibit a higher capacity. The ECI procedure is known to yield the α -form, but the α -form is unstable and rapidly ages to the β -form by a dissolution/reprecipitation mechanism [35]. The transformation is complete when impregnation is performed in a pure aqueous bath during work-up of the plaque. The β -form, obtained by the ageing of the α -form has been characterized as β_{bc} by Faure et al. [36] where 'bc' stands for 'badly crystallized'. The pattern obtained in Fig. 1 corresponds to the β_{bc} form. The presence of ethanol appears to retard the α - β transformation kinetics. Organic additives in the precipitation bath have been shown to stabilize the α -form [13]. While the exact mechanism is not clear, it is likely that the additives adsorb on the freshly formed α -particles and retard their dissolution/reprecipitation kinetics. In the present instance, the product is a mixture of α - and β -forms and is poorly ordered. Poorly-ordered phases exhibit higher electrochemical activity by virtue of a large number of defects.

The requirement of a high bath temperature and the ethanol in the bath have the secondary effect of increased wetting of the plaque which enables intimate penetration of the electrolyte into the pores. Both these effects promote electrode performance. The electrodes impregnated at room temperature from pure aqueous baths perform very poorly. Lower deposition currents also improve plaque performance by ensuring

more uniform filling of the pores. The inclusion of cobalt does not improve the electrode performance.

It is noteworthy to observe that the ECI nickel hydroxide electrode reported here performs much better than the nickel hydroxide pasted electrode [30] and as good as the foam electrodes reported by Watanabe et al. [31]. The performance is comparable with the performance of pasted electrodes made out of 'improved' stabilized- α double hydroxide materials [2,3]. Only the electrodes of Oshitani et al. [22] and Faure et al. [1] are superior to those reported here.

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