



## Short Communication

On the performance of stabilized  $\alpha$ -nickel hydroxide as a nickel-positive electrode in alkaline storage batteriesV. Ganesh Kumar <sup>a</sup>, N. Munichandraiah <sup>b</sup>, P. Vishnu Kamath <sup>c</sup>, A.K. Shukla <sup>a</sup><sup>a</sup> Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India<sup>b</sup> Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India<sup>c</sup> Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

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**Abstract**

The internal resistance of a stabilized  $\alpha$ -nickel hydroxide electrode is found to be lower than that of a  $\beta$ -nickel hydroxide electrode as shown from studies of the open-circuit potential–time transients at all states-of-charge. Nevertheless, the self-discharge rates of the former is higher. Gasometric studies reveal that the charging efficiency of the  $\alpha$ -nickel hydroxide electrode is higher than that of the  $\beta$ -nickel hydroxide electrode.

**Keywords:** Alkaline storage batteries; Nickel hydroxide; Positive electrodes

**1. Introduction**

Conventional  $\beta$ -nickel hydroxide electrodes used in nickel/cadmium batteries usually contain a cadmium additive to enhance performance. Nevertheless, many present-day battery manufacturers have been studying a cadmium-free nickel electrode that will be suitable for nickel metal–hydride batteries that are environmental friendly. In a recent publication [1], the authors demonstrated that stabilized  $\alpha$ -nickel hydroxide is an attractive material for high-performance nickel-positive electrodes. It is noteworthy that  $\beta$ -nickel hydroxide is converted to  $\gamma$ -NiOOH on prolonged charging and causes an irreversible damage to the electrode due to the accompanied mechanical deformation. By contrast,  $\alpha$ -nickel hydroxide can be cycled to the  $\gamma$ -NiOOH phase reversibly without any mechanical deformation. Additionally, a larger number of electrons are exchanged per nickel atom during the  $\alpha \rightleftharpoons \gamma$  phase transformation since the oxidation state of nickel in  $\gamma$ -NiOOH is close to 3.5. As a result, a higher theoretical capacity is expected for a nickel-positive electrode that comprises  $\alpha$ -nickel hydroxide as opposed to  $\beta$ -nickel hydroxide.

This communication reports a study of certain parameters (namely, internal resistance and self-discharge) of stabilized  $\alpha$ -nickel hydroxide electrodes and compares them with those of  $\beta$ -nickel hydroxide electrodes. Such data are central to the performance of  $\alpha$ -nickel hydroxide electrodes for application in storage batteries.

**2. Experimental***2.1. Synthesis of  $\alpha$ - and  $\beta$ -nickel hydroxides*

Both  $\alpha$ - and  $\beta$ -nickel hydroxides were synthesized as described Ref. [1]. In brief,  $\beta$ -nickel hydroxide was prepared by precipitation from  $\text{Ni}(\text{NO}_3)_2$  solution at a pH of about 10, followed by repeated washing to  $\text{pH} \approx 7$  and drying at  $100^\circ\text{C}$ . Stabilized  $\alpha$ -nickel hydroxide of the formula  $\text{Ni}_{0.8}\text{Al}_{0.2}(\text{OH})_2(\text{CO}_3)_{0.1} \cdot n\text{H}_2\text{O}$  was prepared by dropwise addition of a mixed metal nitrate solution of nickel and aluminum in the required stoichiometric ratio to 1 M NaOH solution containing three times the stoichiometric requirement of sodium carbonate at  $35^\circ\text{C}$ . The final pH of the solution was maintained between 9 and 11. The blue-green gel thus obtained was aged for 12 h at  $65^\circ\text{C}$ , filtered, and washed copiously to  $\text{pH} \approx 7$ . It was then dried to a constant weight at  $65^\circ\text{C}$ . The resulting  $\alpha$ - and  $\beta$ -nickel hydroxides were characterized by their X-ray diffraction patterns and infrared spectra.

*2.2. Preparation of nickel-positive electrodes*

Nickel-base grids with a geometrical area of  $6.5\text{ cm}^2$  ( $2.8\text{ cm} \times 2.3\text{ cm}$ ) were subjected to degreasing in 30% KOH at  $25^\circ\text{C}$  at a current density of  $60\text{ mA cm}^{-2}$ , followed by chemical etching in 10% HCl for 2 min. The etched nickel-base grids were washed copiously with distilled water.

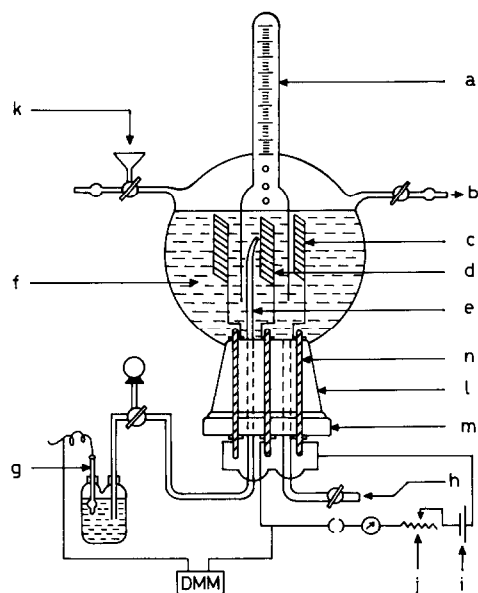


Fig. 1. Schematic representation of the setup for gasometric studies: (a) graduated glass-tubing; (b) opening to air; (c) counter electrodes; (d) working electrode; (e) Luggin capillary; (f) electrolyte; (g) reference electrode; (h) drain tube; (i) d.c. power supply; (j) rheostat; (k) funnel; (l) glass joint; (m) Teflon cone, and (n) stainless-steel connectors.

Nickel-positive electrodes were fabricated by sandwiching the etched nickel-base grids between the layers of the active material (70 wt.%) mixed with powdered graphite (15 wt.%) and polyethylene powder (15 wt.%), and subsequently hot-compacted at a temperature and pressure of 130 °C and 120 kg cm<sup>-2</sup>, respectively. The geometrical area of the electrode was 13 cm<sup>2</sup>.

### 2.3. Electrochemical studies

The electrodes were soaked in 6 M KOH for 24 h before coupling them with counter electrodes on either side. The electrodes were subjected to formation cycles until these attained their stabilized capacity values. Studies of the transients of open-circuit potential for both types of formed electrodes were carried out by charging the electrode at a constant current of 10 mA for a certain duration to reach a precalculated state-of-charge (SOC)<sup>1</sup> value, followed by opening the circuit. The electrode potential was measured in the open-circuit condition using a digital multimeter (DMM) with  $\pm 0.01$  mV sensitivity. The data were collected at several SOC values.

Gasometric studies during the charging of both  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes were carried out with the setup shown in Fig. 1. The volumes of oxygen evolved were estimated at normal temperature and pressure (NTP). The concomitant changes in potential were also monitored for both the electrodes.

<sup>1</sup> State-of-charge is the ratio of available capacity to maximum attainable capacity.

All the experiments were performed at room temperature ( $23 \pm 2$  °C) and the electrode potentials were recorded against a precalibrated Hg/HgO, OH<sup>-</sup> (6 M KOH) reference electrode (MMO).

### 3. Results and discussion

The composition of an alkaline nickel electrode changes from Ni(OH)<sub>2</sub> in its completely discharged state (SOC = 0) to NiOOH in its fully charged state (SOC = 1) [2]. In a partially charged electrode, the ratio of Ni(OH)<sub>2</sub>/NiOOH depends on its SOC. Since the electronic conductivity of  $\beta$ -NiOOH is higher than  $\beta$ -nickel hydroxide [3], the ohmic drop across Ni(OH)<sub>2</sub>/NiOOH phase transformation decreases with an increase in the SOC of the electrode. This phenomenon is reflected in the open-circuit potential transients recorded at SOC = 1 and 0 of the  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes, see Fig. 2.

As the electrolyte (6 M KOH) is highly conducting, the ohmic drop due to electrolyte resistance could be considered to be negligibly small and the measured potential drop for all practical purposes can be attributed solely to the electrode resistance. With this presumption, the resistance values for both types of nickel-positive electrodes, as well as their self-discharge rates, have been obtained at several SOC values from the open-circuit potential decay data. The potential ( $E$ ) versus time ( $t$ ) data over a duration of 150 min following the termination of charging current for  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes are shown in Fig. 3 at several SOC values. Initially, the potential drops rapidly followed by an exponential decay. Beyond this region, the potential decreases almost linearly.

In order to measure the initial voltage drop following the termination of charging current ( $I$ ), the potential–time data have been fitted analytically to obtain the potential at zero time ( $E_{t=0}$ ). From this analysis, the initial potential drop for the  $\alpha$ -nickel hydroxide electrode (Fig. 2(a)) at SOC = 1 is

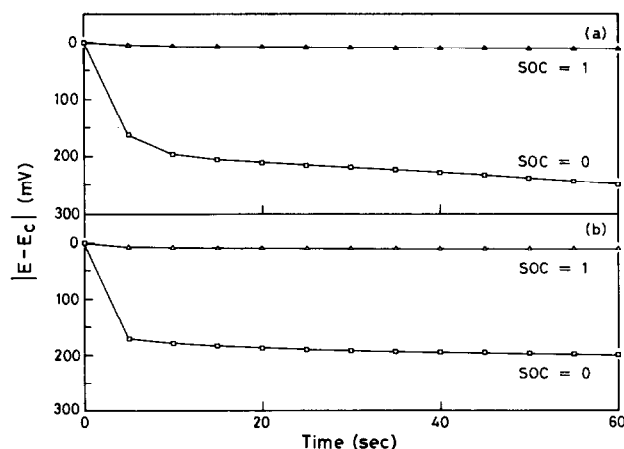


Fig. 2. Open-circuit potential drop,  $|E - E_c|$ , during the first minute of the transient for (a)  $\alpha$ - and (b)  $\beta$ -nickel hydroxide electrodes.  $E$  refers to the potential at time  $t$  after opening the charging circuit, while  $E_c$  is the potential just before opening the circuit.

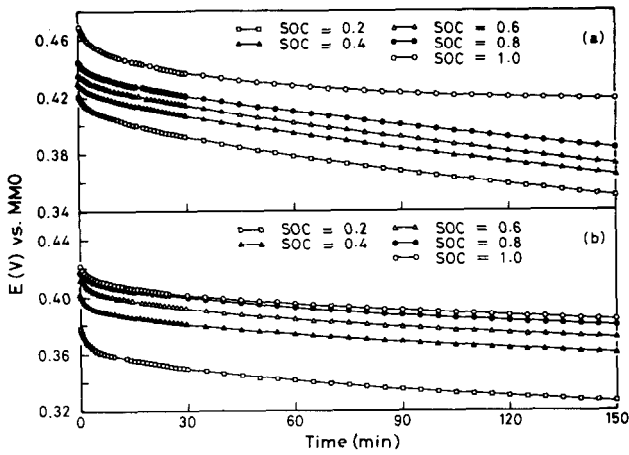


Fig. 3. Open-circuit potential ( $E$ ) decay at various states-of-charge for (a)  $\alpha$ - and (b)  $\beta$ -nickel hydroxide electrodes.

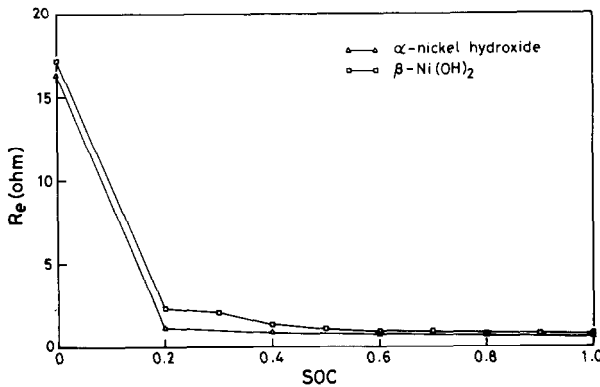


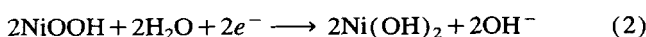
Fig. 4. Electrode resistance ( $R_e$ ) across ( $\Delta$ )  $\alpha$ - and ( $\square$ )  $\beta$ -nickel hydroxide electrodes at various states-of-charge.

found to be 6 mV, while it is as large as 163 mV for the electrode at SOC=0; the respective values for  $\beta$ -Ni(OH)<sub>2</sub> electrode are 8 and 172 mV (Fig. 2(b)). Interestingly, these values were found to be identical to those obtained by the current-interrupter method. This facilitates the estimation of the initial potential drop,  $\Delta E (= E_{t=0} - E_c)$ , where  $E_c$  is the potential prior to cutting off the charging current. Subsequently, the electrode resistance ( $R_e$ ) is obtained by:

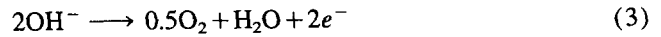
$$R_e \approx \Delta E / I \quad (1)$$

Fig. 4 shows  $R_e$  as a function of SOC for both types of electrodes. It is seen that initially up to a SOC = 0.2,  $R_e$  decreases rapidly for both types of electrodes. It is noteworthy, however, that the  $R_e$  values for the  $\alpha$ -nickel hydroxide electrode are smaller than those for the  $\beta$ -Ni(OH)<sub>2</sub> electrode at all SOC's.

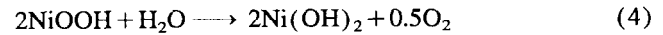
Generally, on cessation of current, the electrode potential attains a steady value subsequent to an exponential decay. The potential of both types of nickel-positive electrodes is found to decrease linearly with time (Fig. 3). Such a phenomenon could only be attributed to self-discharge of the electrode as a consequence of the reaction [4,5]:



which is accompanied by the oxygen-evolution reaction (OER), i.e.:



In the present study, since the linear region of the potential-time decay plots at all the SOC's of the nickel-positive electrodes is always positive to 0.3 V (versus MMO), only the oxygen-evolution reaction (OER) is considered to be feasible [6]. Therefore, the overall self-discharge reaction of the nickel-positive electrode under open-circuit conditions is given by:



Reactions (2) and (3) occur at the same rate at open-circuit condition on the nickel-positive electrodes. In order to estimate the self-discharge rates of  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes, the rates of OER on the electrodes have been obtained experimentally. At open circuit, the rate of OER on a nickel-positive electrode according to the Butler-Volmer equation is given by:

$$|i_{\text{OER}}| = i_0 \exp(\beta n F \eta / RT) \quad (5)$$

where  $i_0$  is the exchange current,  $2.3RT/\beta n F$  the Tafel slope for OER,  $\eta$  the overpotential, and the other symbols have their usual meaning. In the present situation,  $i_{\text{OER}}$  could be considered to be the self-discharge current ( $i_{\text{sd}}$ ) of the electrode at open circuit. Accordingly,  $\eta = E_{\text{OCC}} - E_{\text{OER}}^r$ , where  $E_{\text{OCC}}$  is the potential at open circuit, and  $E_{\text{OER}}^r$  is the reversible value of the potential for OER. The exchange currents and the Tafel slope values for the associated OER have been estimated from the steady-state polarization data obtained with fully-charged  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes. The  $i_0$  values are found to be 1.9 and 0.94  $\mu\text{A}$ , and the Tafel slopes are estimated to be 54 and 51 mV/decade for  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes, respectively. The higher value of  $i_0$  for the  $\alpha$ -nickel hydroxide electrode suggests that OER occurs more readily on this electrode.

Using the above values of exchange currents and Tafel slopes,  $i_{\text{sd}}$  values for the respective electrodes have been esti-

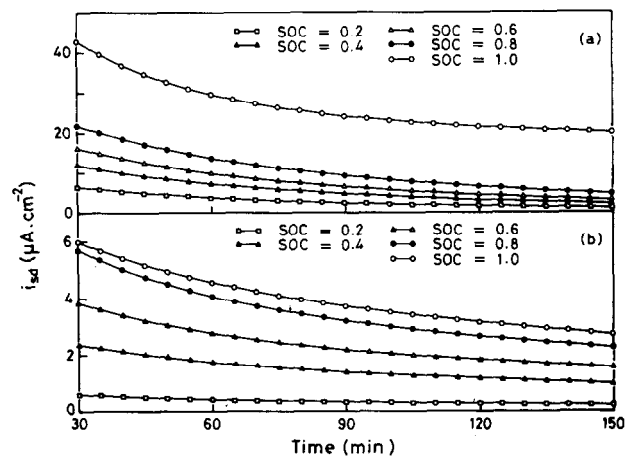


Fig. 5. Variation of self-discharge current ( $i_{\text{sd}}$ ) with time at various states-of-charge for (a)  $\alpha$ - and (b)  $\beta$ -nickel hydroxide electrodes.

mated from Eq. (5) and compiled as a function of time at several SOCs for both types of electrode in Fig. 5. It is seen that  $i_{sd}$  is higher at higher SOCs. Furthermore,  $i_{sd}$  tends to decrease slowly with the storage time at open circuit. A comparison of the data for  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes in Fig. 5 indicates  $i_{sd}$  to be substantially higher for the  $\alpha$ -nickel hydroxide electrode in comparison with the  $\beta$ -nickel hydroxide electrode. This suggests that, under open circuit, oxygen evolution occurs at a faster rate on  $\alpha$ -nickel hydroxide. Although the performance of the  $\alpha$ -nickel hydroxide electrode is found to be superior to that of the  $\beta$ -nickel hydroxide electrode in terms of its delivered capacity [1], a higher rate of oxygen evolution at the former under open circuit is undesirable in terms of shelf-life.

In order to study oxygen-evolution behaviour during charging, the rates of oxygen evolution at both  $\alpha$ - and  $\beta$ -nickel hydroxide electrodes, in terms of the volume of oxygen evolved ( $V_{O_2}$ ), have been measured. The data are summarized in Fig. 6 with the accompanying variation in the respective electrode potentials. For both types of electrode, oxygen evolution occurs only after the electrode is completely charged. Moreover, the volume of oxygen evolved at any instant during the charging process is higher for the  $\beta$ -nickel hydroxide electrode. It is also noteworthy that the potential of the  $\alpha$ -nickel hydroxide electrode remains less positive than that of the  $\beta$ -nickel hydroxide electrode in the region prior to the initiation of OER. Thus, the former electrode accepts charge more amenably.

It is conjectured that during the charging of a  $\alpha$ -nickel hydroxide positive electrode, the rate of the accompanying OER is much slower than that observed at  $\beta$ -nickel hydroxide. As a result, both the faradaic efficiency and capacity of

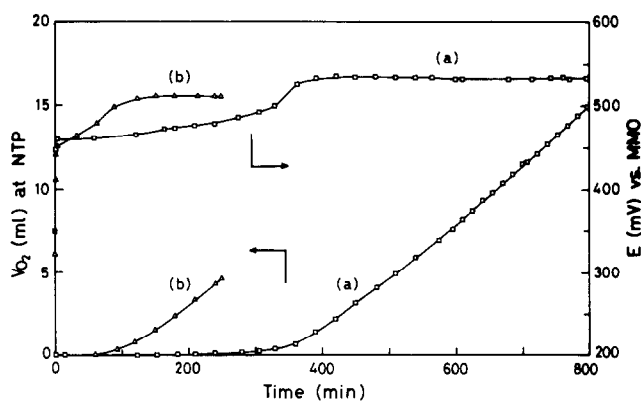


Fig. 6. Volume of oxygen evolved ( $V_{O_2}$ ) and the monitored electrode potential ( $E$ ) as a function of charging time for (a)  $\alpha$ - and (b)  $\beta$ -nickel hydroxide electrodes (charging current = 10 mA).

the  $\alpha$ -nickel hydroxide electrode will be higher for the  $\beta$ -nickel hydroxide electrode. On the other hand, the self-discharge rate for the  $\alpha$ -nickel hydroxide electrode is faster than that for the  $\beta$ -nickel hydroxide electrode and, therefore, the shelf-life is shorter.

## References

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