

Nickel/iron batteries

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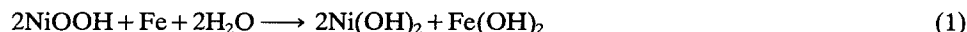
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Abstract

Nickel/iron batteries have been developed and tested extensively in the USA, Japan, Europe and the former Soviet Union with good results. The major factor that limits the commercial impact of this battery is that it cannot be made sealed, that is, maintenance-free. This review examines the performance characteristics of the nickel/iron battery under varying operational conditions.

Introduction

The nickel/iron battery was developed by Edison in the USA and Jünger in Sweden in 1901. Between 1910 and 1960, it was used widely for traction applications. The interest in this battery decreased from 1960 but revived again around 1975, particularly for electric vehicle applications. The battery is based on the use of nickel oxyhydroxide (NiOOH) at the positive electrode and iron at the negative electrode, which react galvanically during cell discharge according to the reaction:



Under deep discharge, a nickel/iron cell with a negative-limited configuration will undergo a further discharge reaction at a potential that is lower than the first step, i.e.:



The cell reactions are highly reversible in the alkaline electrolyte, particularly if the discharge is limited to the first step. The reversibility at the two electrodes confers a long charge/discharge cycle life on the battery. The two sets of electrodes are arranged alternatively and interlaced with porous separators usually of polyvinyl chloride (PVC), nylon, polyethylene, polyamide or polypropylene. The whole electrode-separator stack is kept immersed in a solution of alkaline electrolyte (30 wt.% KOH). Cell terminals and links are usually made from nickel-plated mild steel. The cells are provided with vents, which may be of different designs, to prevent spillage and carbonation while permitting the escape of gases produced in the cell. Positive-limited nickel/iron cells yield the best cycle life [1].

Even under abusive usage that involves mechanical shocks and vibrations, overcharge/over-discharge and storage in a charged or discharged state, the cycle life of the nickel/

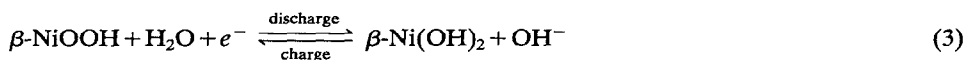
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iron battery, with deep discharge between cycles, is of the order of 3000 cycles and the calendar life is about twenty years [2–8].

Operating principles

Electrochemistry of the positive electrode

The charge/discharge reactions at the positive electrode of the nickel/iron battery can be represented as:



The standard potential of eqn. (3) is 0.49 V versus SHE. (Note, all potentials are reported with respect to the standard hydrogen electrode (SHE).) On prolonged charging, $\beta\text{-NiOOH}$ is converted to $\gamma\text{-NiOOH}$ and causes an irreversible damage to the electrode due to the accompanied mechanical deformation. Therefore, there have been attempts to synthesize the alkali-stable $\alpha\text{-Ni(OH)}_2$ [9] that has a higher interlayer spacing of 23.5 Å as compared with 4.6 Å for $\beta\text{-Ni(OH)}_2$, and that can be cycled to $\gamma\text{-NiOOH}$ without any mechanical deformation [10–12]. Also, since a larger number of electrons are exchanged per nickel atom during the $\alpha \rightleftharpoons \gamma$ (oxidative) phase transition, a higher theoretical capacity is expected for a nickel-positive electrode that comprises $\alpha\text{-Ni(OH)}_2$ than an electrode of $\beta\text{-Ni(OH)}_2$.

Although H_2O and OH^- are shown in the equilibrium of eqn. (3), the mechanism of the reaction involves, in fact, an equivalent diffusion of hydrogen ions (protons) through the solid-state lattices of $\beta\text{-Ni(OH)}_2$ and $\beta\text{-NiOOH}$ so that there is a continuous change in the composition in the active material between the fully charged ($\beta\text{-NiOOH}$) and fully discharged ($\beta\text{-Ni(OH)}_2$) forms (homogeneous mechanism). Thus, the actual course of eqn. (3) may be represented as:



Practice has shown that the addition of Co(OH)_2 at 2 to 10 wt.% in $\beta\text{-Ni(OH)}_2$ improves remarkably the performance of the electrode, especially with respect to charge acceptance and cycle life under deep-discharge conditions [6]. The effects are attributed partly to an increase in the overpotential for the anodic oxygen evolution, and partly to an isomorphous dispersion of the active material that prevents the natural tendency for crystal growth and reduction in active area and, thereby, the onset of passivation.

It is noteworthy that the capacity stabilization of the positive electrode is adversely affected due to the presence of Fe(OH)_3 . This species arises from the migration of Fe(OH)_2 in the negative electrode through the dissolved ion intermediate (HFeO_2^-). The adverse effect, however, may be minimized by the addition of a small quantity of LiOH to the electrolyte. This becomes adsorbed on the electrode and counteracts the effects of Fe(OH)_3 .

A freshly charged positive electrode undergoes fairly fast self-discharge due to the instability of the higher oxidation state of nickel (NiO_2) formed towards the end of charge. After a few days of charge stand, however, any self-discharge that takes place is due to a relatively slow reaction:

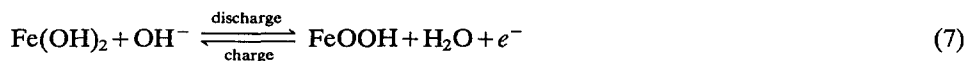


It has been possible to decrease the rate of this self-discharge reaction by incorporating certain inhibitors of the oxygen-evolution reaction, such as CdO , in the active material.

The degree of utilization (faradaic efficiency) of nickel-positive electrodes varies from 60% for the pocket or pressed plate to 90% for the sintered plate. The superior performance of the latter is due to the property of the sintered nickel support which acts as a porous electrode as well as a current collector.

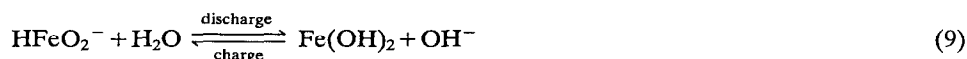
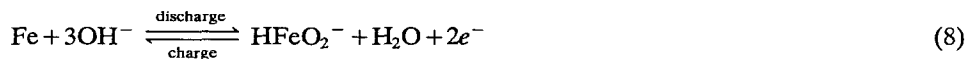
Electrochemistry of the negative electrode

The charge/discharge reactions at the negative electrode of the nickel/iron cell occur in two steps [3, 5, 6, 13, 14]. These may be represented as:



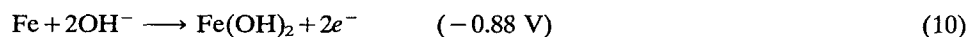
The standard potential for the eqns. (6) and (7) are -0.88 and -0.56 V, respectively.

The mechanism of electrode reaction (6) is generally considered to be one that involves both solid and liquid phases (heterogeneous mechanism) with a dissolved ion intermediate, HFeO_2^- [14–16]. Thus the actual course of the electrode reaction (6) is:

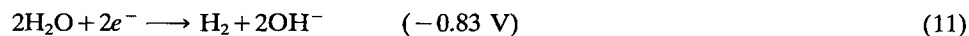


In other words, the iron-electrode discharge results first in the formation of ferrite ion which dissolves in the solution. The anion then hydrolyzes to precipitate as ferrous hydroxide. Although the solubility of ferrite ion anion in alkali is only of the order of 10^{-4} M [17], this concentration is adequate to sustain operational current conditions at the iron electrode due to the finely-divided state of the active material. Similar to the nickel-positive electrode, the mechanism of the electrode reaction involves diffusion of protons through the solid-state lattices of $\text{Fe}(\text{OH})_2$ and $\delta\text{-FeOOH}$, so that there is a continuous change in the composition of the active material between $\text{Fe}(\text{OH})_2$ and $\delta\text{-FeOOH}$. As the transformation of $\text{Fe}(\text{OH})_2$ to $\delta\text{-FeOOH}$ is a bulk feature, the mechanism involved during the second discharge step is homogeneous in nature [18].

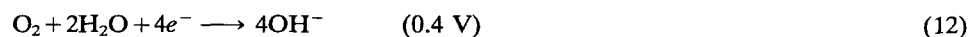
The open-circuit potential of the charged alkaline iron electrode is always more negative than the hydrogen electrode in the same solution [19]. Consequently, iron is thermodynamically unstable and suffers corrosion through local cells with hydrogen evolution as the conjugate reaction. These reactions are:



and



Furthermore, the dissolved oxygen in alkaline solution can be a conjugate reaction, i.e.:



Reaction (12) facilitates the corrosion of iron. Owing to the corrosion reactions, the alkaline iron electrodes undergo a self-discharge of about 1 to 2% of the nominal capacity per day at 25°C . Hydrogen evolution also occurs concomitantly while charging

the alkaline iron electrodes and brings about a decrease in the charge acceptance. The degree of utilization (or the faradaic efficiency) of iron electrode, based on the 2-electron reaction (6), varies from about 30% for electrodes of commercially pure iron to 60% for electrodes that comprise high-purity iron.

Performance characteristics of nickel/iron battery or cell

A typical charge/discharge curve of a commercial nickel/iron cell is shown in Fig. 1, while discharge curves at different rates at 25 °C are given in Fig. 2. The data show that the nominal (operating or discharge) voltage of nickel/iron cells could vary from about 1.23 V at the $C/8$ rate to 0.85 V at the $C/1$ rate. The open-circuit voltage, as well as the nominal voltage at discharge rates between $C/10$ and $C/100$, lie in the range 1.3 to 1.4 V. The discharge curves are fairly flat with the change in the cell voltage at the $C/8$ rate, i.e., 1.32 V at 10% depth-of-discharge to about 1.15 V at 90% depth-of-discharge. The discharge capacity of the nickel/iron battery or cell is not only dependent on its discharge rate but also on the operational temperature, as shown in Fig. 3. This limits the application of nickel/iron batteries for high discharge applications at low temperatures. At most commonly used charging rates, the maximum voltage of the cell is between 1.6 and 1.65 V.

The self-discharge profile of a nickel/iron cell (shown in Fig. 4) indicates that the rate of self-discharge could be as high as 8 to 10% of the nominal capacity per day at an operational temperature of about 40 °C. Therefore, at high ambient

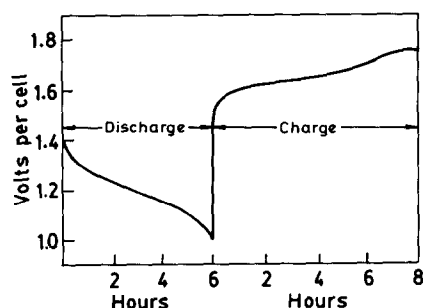


Fig. 1. Typical voltage characteristics for a nickel/iron cell during constant-rate discharge and recharge.

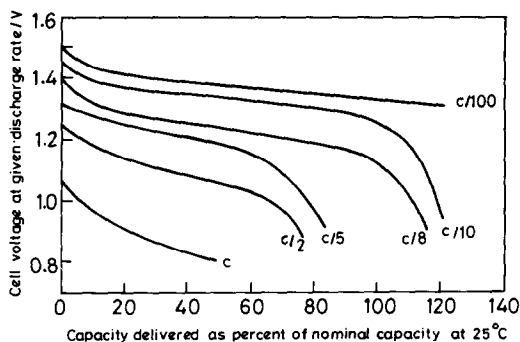


Fig. 2. Typical discharge curve for a nickel/iron cell at 25 °C. Numbers on curves are discharge rates with C as the current in A numerically equal to the nominal Ah capacity of the cell.

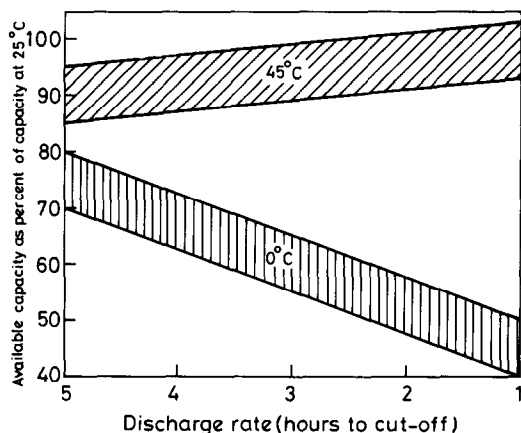


Fig. 3. Discharge capacity at high and low temperature for a nickel/iron cell vs. rate of discharge. The band spread shown is due to differences in size, type and number of cells in the battery packs.

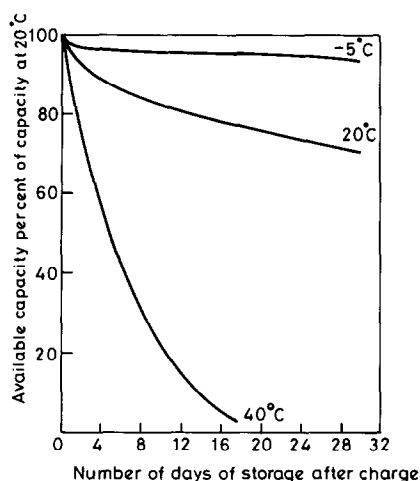


Fig. 4. Discharge capacity of a nickel/iron cell at end of different periods of storage.

temperatures, the nickel/iron battery is useful only for applications where the duty schedule permits a recharge at least on every alternate day or so, in order that a minimum of 80% of the nominal capacity be available during discharge. At 20 °C and below, the self-discharge rate of the nickel/iron cell is, however, considerably less. At these operational temperatures, the interval between recharges could be a month or more in order that the battery may be able to deliver at least 80% of its nominal capacity at any point of time.

At operational temperatures within 30 °C, the charge/discharge cycle life of nickel/iron batteries is of the order of 3000 cycles under normal conditions of use in industrial traction vehicles and railway-carriage service that involve deep discharge between cycles, moderate vibrations, and shocks with fairly regular duty schedules. Under similar

conditions of usage, a calendar life of about twenty years has also been realized for the nickel/iron batteries. But at operational temperatures of about 45 °C, the service life of the nickel/iron battery is nearly 1500 charge/discharge cycles over about eight years of calendar life. The wet shelf life of nickel/iron batteries in the discharged state exceeds two years. The battery provides the normal charge/discharge cycle life even after a continuous period of wet storage in its discharged state. The wet shelf life can be extended to ten years or more with a reconditioning cycle every six months or so. Therefore, even with irregular duty schedules or periods of neglect under field conditions, the actual service life of nickel/iron batteries remains unaffected. The only routine maintenance operation for batteries in service is the addition of water to make up for that lost during overcharge.

The nickel/iron batteries are usually charged galvanostatically. Charging is usually performed at the $C/5$ rate for 7 h and could go up to $C/3$ rate for 4 h. The higher charging rates are permissible provided the temperature of the electrolyte at the end-of-charge does not exceed 45 °C. Typical charging for a nickel/iron cell at 25 °C is shown in Fig. 5. The average voltage at the normal rate is in the range 1.6 to 1.65 V up to about 50% state-of-charge. The charging voltage gradually rises between 1.8 and 1.85 V at the end of full charge.

The internal resistance of a 100 Ah nickel/iron cell under static conditions is of the order of 1 to 2 m Ω . The internal resistance decreases for higher capacity cells, and vice versa.

Current status

In the USA, research and development on nickel/iron batteries has been mainly conducted by Eagle-Picher Industries (EPI) under a cost-shared contract with the US Department of Energy (DOE). Since 1978, EPI has concentrated on the development of high-performance batteries using sintered nickel and iron electrodes. During this time, significant advances in the performance, life and cost of nickel/iron batteries have been achieved. The capacity of the EPI battery, even after powering an electric vehicle for over 28 000 miles of operation, was reported to exceed its original rated capacity.

SAFT, in France, has been pursuing the development of improved nickel/iron batteries for electric vehicles. SAFT considers the nickel/iron battery to be more

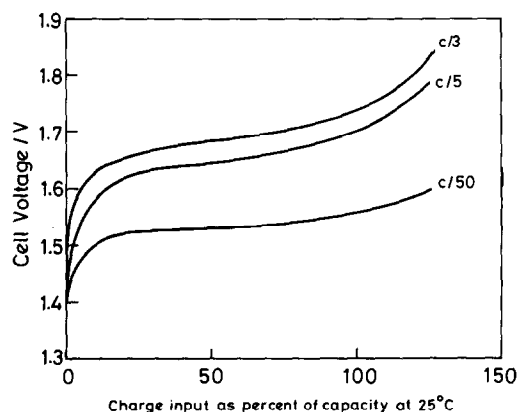


Fig. 5. Typical charging curves for a nickel/iron cell at 25 °C. Numbers on curves are charging rates with C as current in A numerically equal to the nominal capacity of the cell.

suitable than nickel/cadmium counterparts for electric vehicles because of its higher specific energy and greater cycle life under deep discharge. Intensive development work and testing was carried out in Europe by SAFT and Peugeot, but was discontinued about three years ago.

In Germany, nickel/iron batteries for electric vehicles were tested in 1977 by converting an AUDI to use units manufactured by VARTA. Since then, however, VARTA has discontinued fabrication of nickel/iron batteries. Subsequent development of nickel/iron batteries was taken up by DAUG in a programme to develop and evaluate a version for electric vehicles. The battery used fibre-type nickel electrodes and achieved a specific energy of 45 Wh kg^{-1} at the C/5 rate and a 30 s specific power of 80 W kg^{-1} at 50% depth-of-discharge.

In Sweden, SAB-NIFE has been a major manufacturer of nickel/iron batteries for stand-by power, diesel locomotive starting and other power electronics equipment. SAB-NIFE has provided several batteries to various European organizations for test and demonstration. A 120 V, 300 Ah nickel/iron battery was installed in a Mercedes-Benz service van and operated by the Swedish Telephone Company. This vehicle has been in service since January 1981 in parallel with other diesel versions. Results have been quite satisfactory; the vehicle has proved to be reliable over a 30 to 70 km range. SAB-NIFE has also focused on the applicability of its nickel/iron batteries for the European market for fork-lift trucks.

In Japan, Matsushita Electric Co., with a subsidy from the Ministry of International Trade and Industry (MITI), has been an active developer of both iron/air and nickel/iron batteries. In association with Daihatsu Motors Co., Matsushita conducted vehicle-track tests of its nickel/iron battery. These test results indicated a maximum speed of 110 km h^{-1} over a 100 km range schedule under an urban driving pattern. Nevertheless, research and development in Japan on nickel/iron batteries for electric vehicles closed down some years ago.

The former Soviet Union has maintained a constant interest in the nickel/iron battery. The production has been directed mainly towards fork-lift truck and other electric traction applications such as open-pit mining vehicles. The Russian Federation produces about 2.5 million 400 Ah size nickel/iron cells per year.

Technical challenges and commercial impact

The key problem in the development of nickel/iron batteries is the poisoning of the iron electrode [20]. As explained above, the iron electrode undergoes self-discharge as a result of the corrosion reactions. Recent studies [21, 22] have demonstrated that a substantial improvement in the overall performance of nickel/iron cells is possible by the electrocatalysis of the iron-electrode reaction. But a complete suppression of the hydrogen-evolution reaction appears to be difficult.

Electric vehicle producers are looking for a sealed and maintenance-free battery. In this context, it would be difficult for the nickel/iron battery to emerge as a competitor to nickel/cadmium and nickel/metal-hydride batteries. On the other hand, nickel/iron batteries will remain attractive for powering fork-lift trucks and open-pit mining vehicles.

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