An overview of a long-life battery technology: Nickel–iron

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Abstract— This survey was designed following the progress of the use of solar energy. Madagascar is one of the countries that benefit enormously from this energy. As a result, many Malagasy people use photovoltaic cells for domestic and professional applications especially those who are outside the electrified areas. However, the used batteries last only 5 years or even 10 years at most, hence the idea of updating Thomas Edison's research in 1901, a nickel–iron battery technology which is distinguished by its long lifespan of more than 25 years. It is therefore a question of determining the chemical reactions involved into the battery, its aging process, its characteristics, its advantages and disadvantages compared to the lead–acid technology. Once the theoretical studies are carried out, the study proposes an application of nickel–iron technology in a photovoltaic installation in Madagascar.

I. INTRODUCTION

Photovoltaic (PV) solar energy is considered to be the most flexible of the renewable energy sources due to its use in almost all power classes ranging from *mW* to *GW* and in most places in the world. However, a PV system requires a storage unit for the energy produced during the sunny day(s) to continue to distribute it at night or on days when the cloud cover is too great for the PV cells to operate. Batteries not only ensure the appropriate response time and storage capacity to meet production and grid needs, but must also show long life and be able to withstand a large number of charge–discharge cycles: these are often the most expensive and fragile components of a solar system. [1, 2]

In this article, we will discuss an energy storage technology with a long lifespan and of which existence is little known: it is nickel–iron technology. The nickel–iron (Ni–Fe) battery is a rechargeable electrochemical power source which was created in Sweden by Waldemar Jungner around 1890. By substituting cadmium for iron, he improved cell performance and efficiency, but he abandoned its development in favor of nickel–cadmium.

While Thomas Edison believed that the Ni–Fe battery could replace the lead–acid (Pb–acid) battery, he was granted his patent in 1901. [3, 4]

The Thomas Edison battery factory in West Orange, New Jersey, USA, manufactured cells from 1903 to 1972, when it was sold to Exide Battery Company (its name at the time) which production continued until 1975, when the plant closed [3]. The Ni–Fe battery has lost its market share to the Pb–acid battery [5]. Despite this, besides Germany, companies such as Kursk Accumulator in Russia and ChangHong Battery in China still manufactured Ni–Fe cells [3, 6].

Ni–Fe batteries have been applied to almost all fields in which they are used. A list of uses [6-8] to which they are applied include electric trucks, forklifts and industrial tractors, mining locomotives and industrial, electric road vehicles, lighting and air conditioning in trains, railway signaling systems, maritime services, isolated lighting plants, clocks, the system in lighting and emergency alarm circuits, miners' capped lamps, power supplies for instruments and laboratories, communication equipment and portable lighting units. Finally, the Ni–Fe battery is

suitable for storing electrical energy derived from solar energy via photovoltaic cells [8].

II.   PRINCIPLE OF OPERATION

With regard to the active materials which constitute it, the Ni–Fe battery is composed of nickel oxyhydroxide as the positive electrode, iron as the negative electrode and a solution of potassium hydroxide, with a little lithium hydroxide added in order to exert a stabilizing effect on the capacity of the positive electrode during the charge–discharge cycle, as an electrolyte [9, 10]. These materials were originally enclosed in rectangular pockets of perforated thin sheet steel which were attached to steel frames to form the positive and negative electrodes [7]. The overall reactions that occur at the electrodes ensue from a transfer of oxygen from one electrode to another. In general, the Ni–Fe battery is represented by: $^{(-)}Fe(s)|KOH(aq)|NiOOH(s)^{(+)}$. [6]

$$2NiOOH + Fe + 2H_2O \xrightarrow[charge]{discharge} 2Ni(OH)_2 + Fe(OH)_2 \qquad (E^0 = 1.37V) \tag{1}$$
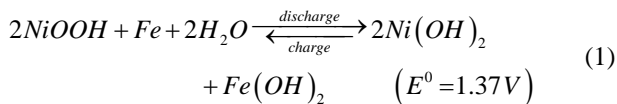
At this stage, the reactions of the cells are highly reversible. Reaction (1) proceeds under deep discharge. A Ni–Fe cell will undergo yet another discharge reaction (2), but with a lower voltage compared to the first stage: [4, 11]

$$NiOOH + Fe(OH)_2 \xrightarrow[charge]{discharge} Ni(OH)_2 + FeOOH \qquad (E^0 = 1.05V) \tag{2}$$
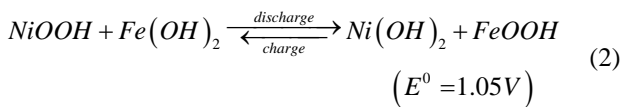
Unlike lead–acid technology, the electrolyte does not participate in chemical reactions. It is therefore not possible to determine its state of charge for any measurement of the density of the electrolyte. [5]
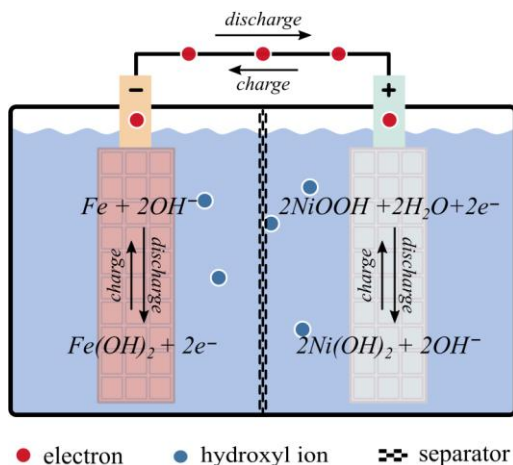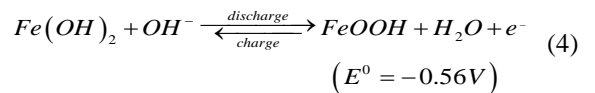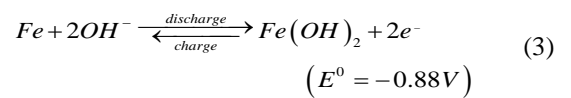

Fig. 1: Schematic representation of the operating principle of a Ni–Fe cell.

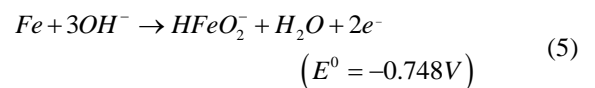## III.   AGING PROCESS

3.1 Negative electrode

Iron is an element known since prehistoric times. Unlike other battery electrode materials such as cadmium, lead, nickel and zinc, iron electrodes are quite environmentally friendly. Furthermore, iron electrodes are both mechanically and electrically robust [11]. Iron has a high theoretical capacity of around 0.97 $Ah.g^{-1}$. Depending on the design and manufacture of the electrodes, there are three different types of iron electrodes [8] namely pocket or tubular electrodes, pressed or compacted electrodes and sintered electrodes.

The charge–discharge reactions at the negative electrode of a Ni–Fe battery occur in two stages corresponding to two distinct voltage levels: [8, 11-13]
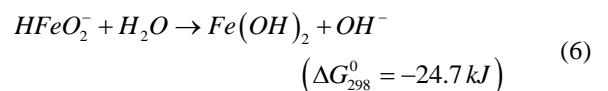
$$Fe + 2OH^- \xrightarrow[charge]{discharge} Fe(OH)_2 + 2e^- \qquad (E^0 = -0.88V) \tag{3}$$

$$Fe(OH)_2 + OH^- \xrightarrow[charge]{discharge} FeOOH + H_2O + e^- \qquad (E^0 = -0.56V) \tag{4}$$

Under strong alkaline conditions, the main process expressed by *equation* (3) manifests the reduction of ferrous ions (Fe^{2+}) to metallic iron (FeO) during charging and vice versa during discharging. In case the Ni–Fe battery is designed with excess iron, reaction (4) rarely occurs in the battery. [8, 14]

Equation (3), in its general form, reflects the initial and final states of the active material [12]. The overall mechanism of the electrode reaction (3) involves both solid (homogeneous mechanism) and liquid (heterogeneous mechanism) phases with $HFeO_2^-$ ions as dissolved intermediates which convert to iron hydroxide ($Fe(OH)_2$) during a new discharge [11, 13]: the iron is therefore oxidized into $HFeO_2^-$ ions, then into porous $Fe(OH)_2$ [12]. Accordingly, the actual course [11-13] of the reaction (3) electrodes can be expressed as follows:

$$Fe + 3OH^- \rightarrow HFeO_2^- + H_2O + 2e^- \qquad (E^0 = -0.748V) \tag{5}$$

followed by:

$$HFeO_2^- + H_2O \rightarrow Fe(OH)_2 + OH^- \qquad (\Delta G_{298}^0 = -24.7\,kJ) \tag{6}$$

During prolonged discharge, the composition of the active δ–$FeOOH$ in iron hydroxide is similar to the positive electrode in nickel. The electrode reaction involves the diffusion of protons between the solid lattices of $Fe(OH)_2$ and δ–$FeOOH$. [11]

It has been speculated that the formation of magnetite Fe_3O_4 in different oxidation states between iron hydroxides results in the reaction:

$$Fe(OH)_2 + 2\delta - FeOOH \rightarrow Fe_3O_4 + 2H_2O$$
$$\left(\Delta G^0_{298} = -74.9\,kJ \right) \quad (7)$$
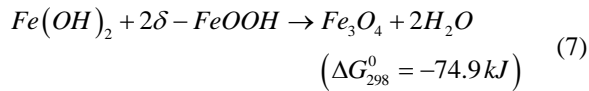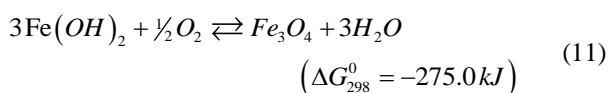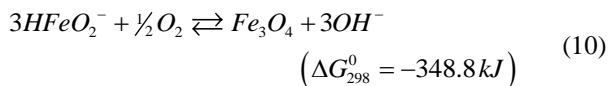
rather than by an electrochemical process [11].

X–ray phase analysis of the electrodes removed from the solutions after discharge demonstrated a decrease in the amount of iron(II) hydroxide formed in the electrodes during the first anodic process and an increase in magnetite. Therefore, the conversion of $Fe(OH)_2$ to Fe_3O_4 is described by the reaction equation: [11]

$$3Fe(OH)_2 + 2OH^- \rightarrow Fe_3O_4 + 4H_2O + 2e^-$$
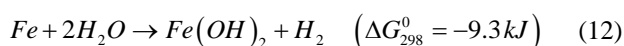$$\left(E^0 = -1.22V \right) \quad (8)$$
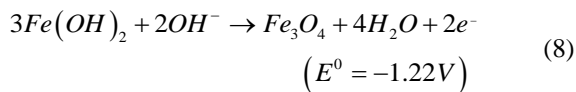
On the other hand, in the case of anodic polarization of an iron electrode in the range of the first potential plateau at 328 *K*, a considerable amount of magnetite is formed together with the main discharge product *Fe(OH)₂*. A direct electrochemical conversion of *Fe* to *Fe₃O₄* has been estimated: [11]

$$3Fe + 8OH^- \rightarrow Fe_3O_4 + 4H_2O + 8e^-$$
$$\left(E^0 = -0.913V \right) \quad (9)$$
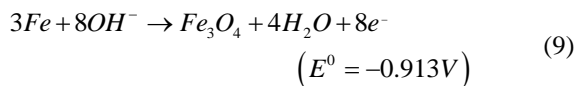
Magnetite can also be formed by the following reactions involving dissolved oxygen in the electrolyte: [12]

$$3HFeO_2^- + \tfrac{1}{2}O_2 \rightleftarrows Fe_3O_4 + 3OH^-$$
$$\left(\Delta G^0_{298} = -348.8\,kJ \right) \quad (10)$$

$$3Fe(OH)_2 + \tfrac{1}{2}O_2 \rightleftarrows Fe_3O_4 + 3H_2O$$
$$\left(\Delta G^0_{298} = -275.0\,kJ \right) \quad (11)$$

Since reaction (8) takes place in the electrolyte, it results in the formation of a black deposit of magnetite on the surface of separators and battery reservoirs. *Equation* (12) shows the reaction of iron with water and hydrogen evolution that occurs during charging: [11, 15]

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \quad \left(\Delta G^0_{298} = -9.3\,kJ \right) \quad (12)$$

$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^- \quad \left(E^0 = -0.828V \right) \quad (13)$$
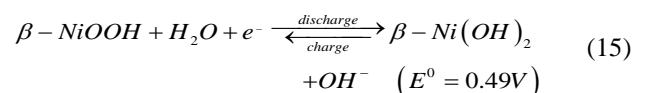
On one side, the hydrogen evolution reaction takes place since the electrode potential for this reaction is positive with respect to that of reaction (3) and on the other side, water is electrochemically decomposed into hydrogen and hydroxyl ions during charging [14, 15].

3.2 Positive electrode

Used for more than a century, nickel hydroxides (*Ni(OH)₂*) compose the active material of the positive electrodes of several alkaline cells. Understanding the reactions at these electrodes has been very slow due to the complex nature of the reactions. [16] Its maximum theoretical capacity is around 0.289 $Ah.g^{-1}$ [17]. In battery terms, the nickel electrode is often referred to the nickel oxide (*NiO₂*) and charge–discharge reactions are expressed as: [11, 13]

$$NiO_2 + 2H_2O + 2e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Ni(OH)_2 + 2OH^-$$
$$\left(E^0 = 0.49V \right) \quad (14)$$
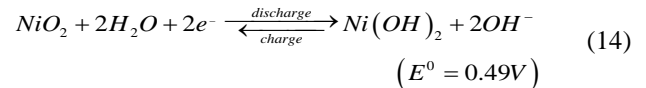
The nickel oxide forms the active material of the positive plate with nickel hydroxide as the discharged product which is recovered as nickel oxide during recharging. In practice, the discharge product, converted to beta–nickel oxyhydroxide (*β–NiOOH*) during recharging, is *β–Ni(OH)₂*. *Equation* (14) becomes: [11, 13, 17, 18]

$$\beta - NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} \beta - Ni(OH)_2$$
$$+OH^- \quad \left(E^0 = 0.49V \right) \quad (15)$$

During charging, *β–Ni(OH)₂* is therefore converted to *β–NiOOH* by a deprotonation mechanism and the reaction is reversed during discharging reducing nickel oxyhydroxide 3+ to nickel hydroxide 2+ by protonation [17]. The mechanism of reaction (15) involves an equivalent diffusion of protons through the solid state lattices of *β–Ni(OH)₂* and *β–NiOOH* so that there is a continuous change in the composition of the material active between fully charged *β–NiOOH* and fully discharged *β–Ni(OH)₂*.

Thus, *equation* (15) can also be written: [11, 13]

$$\beta - NiOOH + H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} \beta - Ni(OH)_2 \quad (16)$$
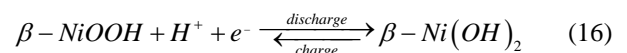
Three crystal modifications of nickel hydroxide appear as a lattice structure with alternating layers of nickel ions and hydroxide ions. The starting material for the transformation of the alkaline electrode is the α form. [11] *Fig. 2* gives an overview on the structural changes of nickel hydroxides during charging, discharging, overcharging and aging (dehydration) [11, 13, 16]
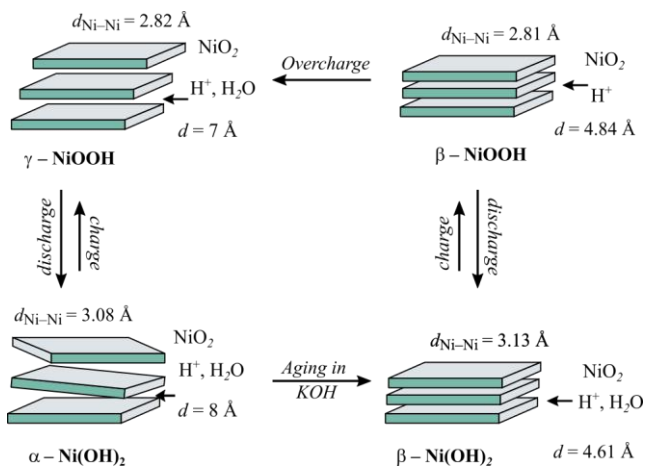
Fig. 2: Bode reaction diagram showing the various transformations of a nickel electrode. [11]

The oxidation (charge) voltage of the α and β materials, 60 mV and 100 mV respectively, is more positive than the discharge voltage. The β–$Ni(OH)_2$ is the usual electrode material. Oxidized, it is converted on charge to β–$NiOOH$ with about the same molar volume. In case of overcharge, the γ structure can form. This form also incorporates water and potassium (and lithium) into the structure. Its molar volume is about 1.5 times the β form. This shape is believed to be largely responsible for the volume expansion (swelling) which occurs during battery charging. The α form then results on discharge of the γ form. Its molar volume is about 1.8 times that of the β form and the electrode can swell further on discharge. On discharge, the α form converts to the β form in a concentrated electrolyte. Additions of cobalt (2 to 5%) improve the charge acceptance (reversibility) of the nickel electrode. [5, 13, 16]

IV. PERFORMANCE CHARACTERISTICS

The theoretical energy density of a Ni–Fe battery, lying between Ni-Cd (244 $Wh.kg^{-1}$) and Ni-MH (278 $Wh.kg^{-1}$), is 268 $Wh.kg^{-1}$. The practical energy density depends on the technology used to manufacture the electrodes. It is between 20 $Wh.kg^{-1}$ and 30 $Wh.kg^{-1}$ for tubular electrodes and can reach 40–60 $Wh.kg^{-1}$ or even up to 80 $Wh.kg^{-1}$ [19] for sintered or fiber electrodes. The open circuit voltage, discharge voltage and charge voltage of Ni–Fe cells are 1.37 V; 1.3 V at 1.0 V and 1.7 V at 1.8 V, respectively. Its nominal voltage is 1.2 V. [5, 8, 20]

Constant voltage charging of conventional Ni–Fe cells which can lead to thermal runaway and cause serious damage is not recommended. As the cell approaches full charge, gassing reactions generate heat and the cell temperature increases: a limited galvanostatic charge of

1.7 V per cell has been shown to be beneficial in controlling cell temperature. Its discharge capacity depends on the discharge rate. Indeed, when a nickel–iron system is discharged at a rate of C/1, the realized capacity is only 50% of the nominal value and the voltage varies between 1 V and 0.8 V. Batteries with tubular positive electrodes are designed for low or moderate discharge rates i.e. C/8 to C/1 while those with sintered electrodes can provide high power due to its low internal resistance. The nominal (operating or discharging) cell voltage variation is approximately 1.23 V at C/8 rate to 0.85 V at C/1 rate. The change in cell voltage on a C/8 rate is 1.32 V to about 1.15 V at 10% and 90% depth of discharge (DoD), respectively. On a rate of C/10, the voltage of the battery in the 50% charged state is 1.35 V and for low discharge currents (C/100), the voltage varies from 1.5 V (charged state) to 1.35 V (discharged state). [8, 11, 20]

Table 1: Comparison of characteristics of nickel–iron and lead–acid batteries. [6, 19, 21-23]

Main characteristics	Nickel–iron	Lead–acid
Nominal voltage (V)	1.2	2
Theoretical specific energy ($Wh.kg^{-1}$)	268	170 – 252
Specific energy ($Wh.kg^{-1}$)	20 – 80	10 – 20
Energy density ($Wh.L^{-1}$)	60 – 110	50 – 70
Life cycle (100% DoD)	> 1000	20 – 50
Calendar lifetime (years)	> 25	~5 – 10
Operating temperature ($°C$)	-10/+45	-10/+40

Its discharge capacity also depends on the surrounding temperature. When the temperature drops, the output power drops dramatically. The derived capacity is approximately 50% of nominal value at 255 K when discharged at a C/8 rate, performance is reasonably good at ~308 K. The behavior at subzero temperatures is due to passivation of the iron electrode. Self-discharge represents 0.1 to 2.5% of the nominal capacity per day below 293 K, 1 to 2% at ~298 K and 8 to 10% at ~313 K. Self-discharge of a Ni–Fe battery manifests itself more than for Ni–Cd and Ni–MH batteries. It increases significantly with temperature. As an example, self-discharge is minimal (about 10% in 1 month) at 273 K, but a cell will discharge almost completely in 15 days at +313 K. Ni–Fe batteries can be stored for long periods without any deterioration whether in a charged or discharged state. The service life is from 7 to more than 25 years. Batteries requiring high power use sintered electrodes. [8, 20]

V. ADVANTAGES AND DISADVANTAGES

The nickel–iron battery was and is almost indestructible. It has a very robust physical structure that can withstand mechanical and electrical shocks such as vibration, overcharging and over-discharging for long periods. Storage under charged or discharged conditions will not affect performance. A long service is therefore possible thanks to its long service life. Battery maintenance is quite simple. It is sufficient to top up the electrolyte by adding water or to replace it well after a considerable period of operation. [5, 8, 20]

The active materials of the battery are insoluble in alkalis. In addition, the separator does not present any particular difficulties unlike silver–zinc (Ag–Zn) and nickel–zinc (Ni–Zn) batteries. The Ni–Fe battery also does not present any toxic or corrosive effect neither for the environment nor for the working personnel. The alkaline electrolyte allows the use of mild steel in battery construction. The battery performs very well at an ambient temperature of approximately 308 *K*. [5, 8, 20]

Known for its long life, the Ni–Fe battery has a specific energy 1.5 to 2 times higher than that of a Pb–acid battery [24, 25]. It is also noted for its roughness and long life cycle under deep discharge [9, 10]. It is a promising technology in terms of safety since it does not contain toxic elements or heavy metals: it has the lowest environmental impact and risk factor during operation [8, 10, 15].

The energy efficiency of the battery is around 50%. The self-discharge is, however, quite high: 30 to 50% of its capacity is lost over a period of one month. [6] The main causes of these two aspects are the low hydrogen overpotential of the iron electrode and the close proximity of the potential of the iron electrode (in alkaline medium) and that of the hydrogen evolution reaction. As a result, hydrogen is released during charge–discharge and on the carrier. Additionally, the battery exhibits poor performance at sub-zero temperatures due to passivation of the iron electrode. [5, 8, 20, 24]The discharge capacity of a Ni–Fe battery depends on the rate of discharge and the operating temperature: which limits the operation of the battery for high discharge at low temperature [13, 23]. Compared to lead–acid technology, nickel–iron technology exhibits poor performance at low temperature, high corrosion and self-discharge rates, and low overall energy efficiency due to the low overpotential for hydrogen evolution at the iron electrode. In addition, a need for frequent maintenance due to considerable gassing which is undesirable [15] during charging is however required. [5, 9, 25]

Table 2: Summary of comparison of lead–acid and nickel–iron technologies. [5, 15, 25, 26]

Battery technology	Advantages	Disadvantages
Lead–acid	• Low manufacturing cost • High cell voltage • Available in maintenance-free mode • No memory effect	• Short lifespan • Low energy density • Presence of heavy metals • Low cycle life • Gas release
Nickel–iron	• Long life (cyclical and calendar) • Resistant to mechanical abuse (robust) • Resistant to electrical abuse (overcharging, over-discharging, shorting) • Non-toxic, non-corrosive • Does not contain heavy metals • No memory effect	• Low cell voltage • Significant self-discharge • Gas release • Poor performance at low temperature

VI. CONCLUSION

This review emphasizes nickel–iron battery technology for stationary application. It has been observed that the considerable self-discharge due to low hydrogen overvoltage is a major limitation of iron electrodes. A capacity loss of approximately 5% in 4 *h* extending to 20%

in 14 days for fully charged iron electrodes has been reported. The positive electrode made of nickel hydroxide has also been the subject of much research to study how different additives can change its properties or prevent different phases from occurring. Thus, the control of the composition of the electrolyte and the use of a combination of additives at the level of the electrodes

bring a good performance to the battery. It should be noted that the performance of a nickel–iron cell also results from the way the electrodes are manufactured. Finally, its years of existence allow us to deduce its longevity and even in the event of negligence and abuse under severe operating conditions, a long service life is possible.

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