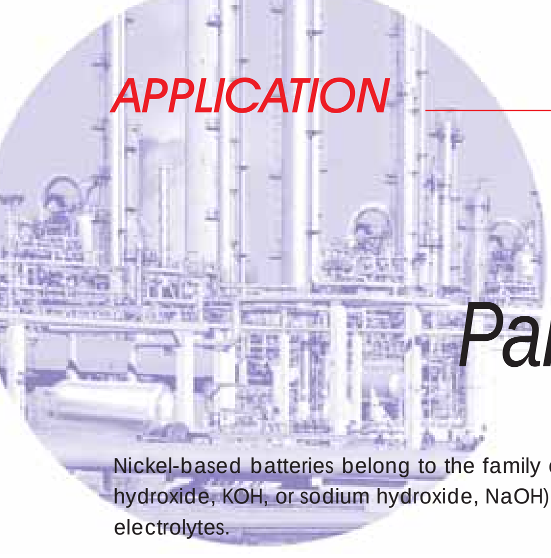

Rechargeable batteries – Part 2: Nickel based batteries

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Nickel-based batteries belong to the family of alkaline rechargeable batteries due to their use of an aqueous alkaline solution (potassium hydroxide, KOH, or sodium hydroxide, NaOH) as the electrolyte. Electrode materials are less reactive with alkaline electrolytes than with acid electrolytes.

In addition, the charge-discharge mechanism in the alkaline electrolyte involves only the transport of oxygen or hydroxyl ions from one electrode to the other; hence the composition or concentration of the electrolyte does not change during charge and discharge. Nickel-iron (NiFe), nickel-cadmium (NiCad) and nickel metal hydride (NiMH) batteries are the foremost examples of nickel-based batteries.

Nickel-iron batteries

The nickel-iron battery was important from its introduction in 1908 until the 1970s, when it lost its market share to the industrial lead-acid battery. It was used in materials-handling trucks, mining and underground vehicles, railroad and rapid-transit cars, and in stationary applications[10].

Designed by Edison, the nickel-iron battery was and is physically almost indestructible. It has a very rugged physical structure and can withstand electrical abuse such as overcharge, over-discharge, standing discharged for extended periods, and short circuiting. The battery is best applied where high cycle life at repeated deep discharges is required (such as traction applications) and as a standby power source with a 10 to 20 year life. Its limitations, namely, low specific energy, poor charge retention, and poor low-temperature performance, and its high cost of manufacture compared with the lead-acid battery led to a decline in usage [10].

Fig. 4: Nickel-iron battery [BeUtilityFree Inc].

The active materials of the nickel-iron battery are metallic iron for the negative electrode, nickel oxide for the positive, and a potassium hydroxide solution with lithium hydroxide for the electrolyte. The active materials are held in nickel-plated steel tubes or perforated pockets (Fig. 4). The nickel-iron battery has a nominal cell voltage of 1,2 V.

The overall electrode reactions result in the transfer of oxygen from one electrode to the other. The exact details of the reaction can be very complex and include many species of transitory existence. The electrolyte apparently plays no part in the overall reaction, as noted in the following reactions:

$3Fe + 8N_iOOH + 4H_2O \leftrightarrow 8N_i(OH)_2 + Fe_3O_4$ (4)

The discharge reaction is from left to right while the charge reaction is from right to left in Equation (4). As the electrolyte remains essentially unchanged during charge and discharge, it is not possible to use the specific gravity of the electrolyte to determine the state of charge, unlike the lead-acid battery.

Advanced nickel-iron batteries

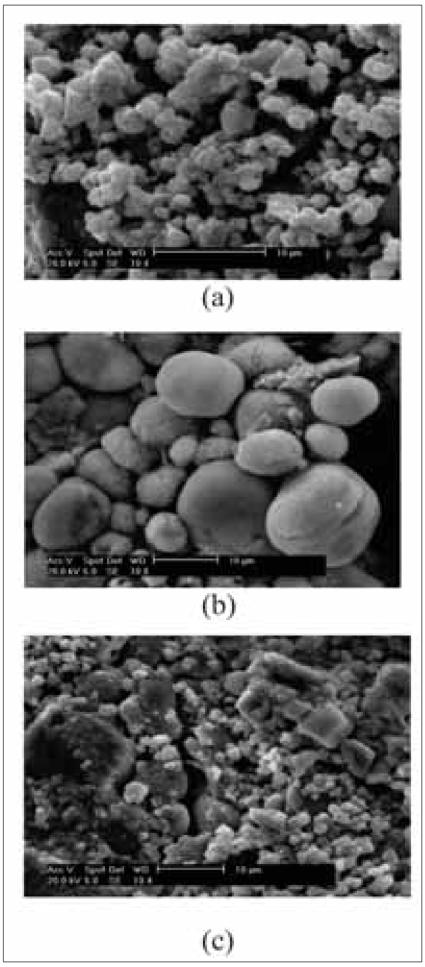
In the past, the desire to use the attractive features of the nickel-iron couple, such as ruggedness and long life, in applications requiring high-rate performance and low manufacturing costs has led to the development of advanced nickel-iron batteries with performance characteristics suitable for electric vehicles and other mobile traction applications. The capability of these batteries did allow an electric vehicle to have a range of at least 150 km between charges, acceleration rapid enough to merge into motorway traffic, and a cycling life equivalent to 10 or more years of on-the-road service. The advanced battery utilises sintered-fibre metal (steel wool) plaques, impregnated with active material, for both the positive and negative electrodes. Non-woven polypropylene sheets were used as separators between electrodes. The techniques for making plaques, impregnation and activation, stacking, and assembly are all amenable to high-volume production methods similar to those used in lead-acid battery manufacture. [10]

Fig. 5: Sintered plate nickel cadmium (a) Cell and, (b) Battery [HBL Power systems Ltd].

Nickel-cadmium batteries

The nickel-cadmium (NiCad) battery is the most popular alkaline rechargeable battery and is available in several cell designs and in a wide range of sizes. The original cell design used the pocket-plate construction. The vented pocket-type cells are very rugged and can withstand both electrical and mechanical abuse. They have very long lives and require little maintenance beyond occasional topping with water. This type of battery is used in heavy-duty industrial applications, such as materials-handling trucks, mining vehicles, railway signalling, emergency or standby power, and diesel engine starting. The sintered-plate construction (Fig. 5) is a more recent development, having a higher energy density. It gives better performance than the pocket-plate type at high discharge rates and low temperatures, but is more expensive [10].

It is used in applications, such as aircraft engine starting and communications, and electronic equipment, where lighter weight and superior performance are required. Higher energy and power densities can be obtained by using nickel foam, nickel



(a)

(b)

(c)

Fig. 6: SEM photographs captured at 10 μm of the positive plates of (a) a good battery, (b) an aged battery, and (c) a restored battery.

fibre, or plastic-bonded (pressed-plate) electrodes. A third design is the sealed cell. It uses an oxygen-recombination feature similar to the one used in sealed lead-acid batteries to prevent the build-up of pressure caused by gassing during charge. Sealed cells are available in prismatic, button, and cylindrical configurations and are used in consumer and small industrial applications [10].

The "Memory effect" and cell ageing

A major weakness exhibited by some NiCad batteries is a phenomenon known as the "memory effect". The purported "memory effect" observed in NiCad batteries can be described as an apparent reduction in cell capacity to a predetermined cut-off voltage resulting from highly repetitive patterns of use. If a NiCad battery has been cycled to a certain shallow depth of discharge for a large number of cycles, for example, the battery will not produce a capacity as large as the one corresponding to full discharge-charge cycles. The temporary capacity loss i.e. "memory effect", can be caused by two factors associated with the cadmium electrode.

Cadmium crystals

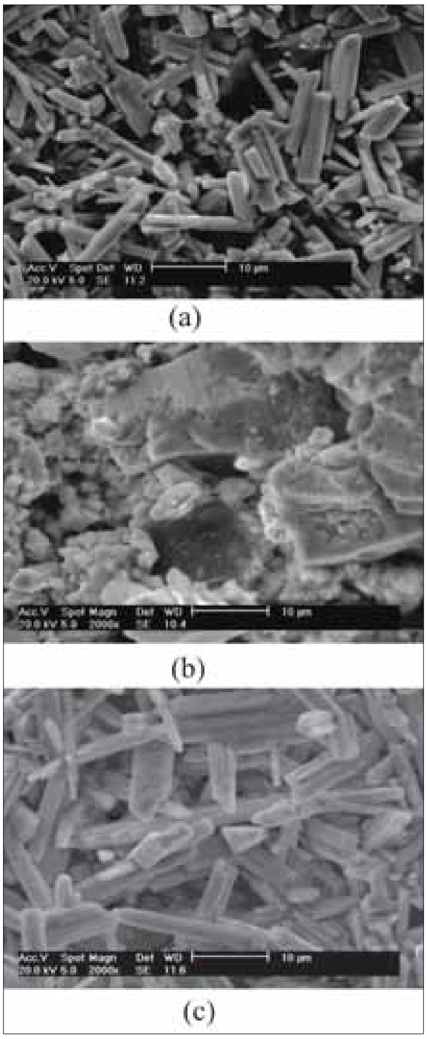
Cadmium crystals of growing size are observed when the battery is recharged at a low current rate. This crystal growth can be enhanced when the battery is subjected to repeated partial discharge and recharge, and the recharge occurs at a moderate current rate. But increased crystal size means reduced surface area of the active material which causes an additional voltage drop during discharge. Consequently, the voltage level of the whole discharge curve is reduced and the end-of-discharge voltage is reached earlier, which results in a reduced capacity. This effect can be eliminated by complete discharge and subsequent recharge with not too-low current densities [5].

Nickel content of the cadmium in the negative electrode

Another reason for the "memory effect" is connected with a certain nickel content of the cadmium in the negative electrode. This is the "memory effect" observed in NiCad batteries with sintered electrodes. The nickel may have been added to the active material deliberately as a conducting aid and as an expander. The presence of nickel in the active material can also be due to corrosion reactions of the substrate during precipitation of the cadmium hydroxide into the sintered substrate. Nickel and cadmium form inter-metallic compounds like Ni2Cd5 or Ni5Cd. The proportion of these compounds can grow during the repeated partial discharges and recharges in the unaffected part of the active material. If subsequently a complete discharge is carried out, the cadmium bound in the inter-metallic phases or at least a part of it has to be used as well. However, the inter-metallic phases are discharged at a more positive potential than the cadmium electrode and this causes a reduction of about 150 mV of the battery voltage during discharge. This "memory effect" diminishes when the electrode is deeply discharged and recharged repeatedly because the inter-metallic compounds are eventually destroyed [5].

Another possible cause of the "memory effect" has been attributed to the nickel electrode as reported by Sato et al.[11] The X-ray diffraction (XRD) analysis carried out revealed the formation of Oxy-nickel hydroxide (NiOOH) on the nickel electrode in the charged state after repetitive shallow (charge/discharge) cycling of the cells or overcharging of the cells. This *NiOOH* is initially formed at the collector side of the electrode and it then grows into the electrolyte. However, it was observed that *NiOOH* disappeared within a few cycles of the normal charge-discharge cycling.

The stages of crystalline formation on the positive and negative plates of a NiCad cell are illustrated in Figs. 6 and 7 respectively. The enlargements by SEM at 10 μm show the battery plates in a proper functioning crystal structure (figures 6a and 7a), crystalline formation after several partial charge/discharge cycles (Figs. 6b and 7b), and after restorative charge/discharge cycling (Figs. 6c and 7c.)



(a)

(b)

(c)

Fig. 7: SEM photographs captured at 10 m, of the negative plates of (a) a good battery, (b) an aged battery, and (c) a restored battery.

Fig. 7b shows clearly the presence of $Ni(OH)_2$ powder, a crystalline growth (shown as the larger particles in the diagram), in the discharged positive electrode of an aged battery. This crystalline growth has a high density compared to the normal $Ni(OH)_2$ powder observed in the case of a healthy battery as shown in figure 6a. After a series of partial charge and discharge cycles, the crystals grow and conceal the active material from the electrolyte. In advanced stages, the crystals can penetrate the separator, causing high self-discharge or electrical short. A similar trend can be observed in the case of negative electrodes as illustrated in Fig. 7. Fine crystals of $Cd(OH)_2$ are normally formed in the negative electrode of a good battery, Fig. 7a. These crystals later grow in size to high density crystals due to ageing and exacerbated by partial charge and discharge, as shown in Fig. 7b.

Restoration of aged batteries i.e. batteries affected by the "memory effect", is usually carried out by subjecting the batteries to

Fig. 8: Nickel-metal hydride batteries [Panasonic].

a number of full charge and discharge cycles to decompose the large crystal formation. The effect of restoration on aged batteries is illustrated in Figs. 6c and 7c. The SEM photographs show that the crystal size within an aged battery has reduced considerably through a sequence of full charge and discharge cycles. It has also been confirmed by the University of Leicester that the size of the crystal growth can be controlled to some degree by the current density. So after a complete discharge, a high magnitude pulsed current is beneficial in the restoration of aged batteries. The magnitude of the pulses should not be greater than a C0.5 [1] charging current. Any greater then I^2R heating of the battery may become significant. When using this pulsed technique, it is also advisable to monitor the battery temperature: a sudden rise will indicate the end of charging has been reached as the charging of this battery is an endothermic process.

Nickel-metal hydride batteries

The rechargeable sealed nickel-metal hydride battery (Fig. 8) is a relatively new technology with characteristics similar to those of the sealed nickel-cadmium battery. The principal difference is that the nickel-metal hydride battery uses hydrogen, absorbed in a metal alloy, for the active negative material in place of the cadmium used in the nickel-cadmium battery. The replacement of cadmium not only increases the energy density, but also produces a more environmentally friendly power source with less severe disposal problems. The nickel-metal hydride battery, owing to its higher energy density and other comparable characteristics, has been able to replace the nickel-cadmium battery in computers, mobile phones and other consumer electronic applications (before Lithium-ion became readily available) with the possible exception of high-drain power tools and applications where low battery cost is the major consideration. Nonetheless, the nickel-metal hydride battery has almost been replaced by the lithium-ion battery which has a higher specific energy density. Furthermore, the nickel-metal hydride battery has a lower charge/discharge rate capability, poorer charge retention and is less tolerant to overcharge than the nickel-cadmium battery. In addition, a nickel-metal hydride battery is less durable than a nickel-cadmium battery. Cycling under heavy load and storage at high temperature reduces the service life. A nickel-metal hydride battery suffers from high self-discharge, which is higher than a nickel-cadmium battery. However, battery experts agree that the nickel-metal hydride battery has greatly improved over the years, but limitations remain. Most shortcomings are native to the nickel-based technology and are shared with nickel-cadmium.

Nickel-zinc batteries

As the automotive industry moves forward with the development of electric and hybrid vehicles and other alternatives to the conventional petrol/diesel-powered car, existing battery technologies are being stretched to their limits in terms of weight, size, cell balance issues, environmental concerns and cost reduction. Less than ten years ago the nickel-zinc battery (Fig. 9) was considered by many battery researchers as the most promising solution to the problem of the power supply for electric vehicle propulsion because of its light weight, high power capability, deep cycle ability, low cost and environmentally acceptable chemistry (free from cadmium, mercury and lead). [6,10] Furthermore, Nickel-zinc has an energy density that is about twice that of the nickel-cadmium battery, but the cycle life has been limited due to the tendency of the zinc electrode changing shape over time. This reduces the battery capacity and dendritic formations will eventually cause internal short-circuiting. However, later development work extended the cycle life of nickel-zinc batteries through the use of additives in the negative electrode (zinc / zinc oxide) in conjunction with the use of a reduced concentration of KOH to suppress zinc solubility in the electrolyte. Both of these modifications extended the cycle life of this system, and so it became popular in the market for use in electric bicycles, scooters and trolling motors in the United States and Asia. Nickel-zinc batteries have also been found in a number of other commercial applications including electric lawn and garden equipment, and deep cycle marine applications [10].

Fig. 9: Nickel-zinc batteries [Xellerion Ltd].

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