ULTRA LOW MAINTENANCE NICKEL CADMIUM BATTERIES: WHAT IS THIS ALL ABOUT?

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ABSTRACT

There are a number of ultra low maintenance type nickel cadmium batteries available on the market today. These range from standard vented flooded types to those using catalyst recombination technology, vented partial internal recombination, and valve regulated partial internal recombination.

The growing trend to try to provide the customer with a "maintenance free" battery has extended itself into the area of development of nickel cadmium battery systems. These "ultra low maintenance" NiCd's can be found today in applications from UPS, utility switchgear, power generation and process control to telecom outside plant.

How do these technologies differ from valve regulated lead acid products (VRLA)? And what are the differences among the various product types available? What benefit, if any, do these different technologies provide the user?

This paper will discuss the basic design concepts concerning many of these technologies and explore the advantages and disadvantages of the various "ultra low maintenance" nickel cadmium battery technologies available today.

INTRODUCTION

Battery users have, for a long time, been on a search for the perfect "maintenance free battery." For the technical purist among the battery manufacturers, the best of all worlds is the flooded or vented battery system, so any deviation from this concept becomes a compromise in some fashion in the battery system. Valve regulated lead acid batteries are a good example of this compromise. The design life of the plates of many of these VRLA batteries may clearly indicate an expected life of the battery of either 10 or 20 years; however, other effects come into play, such as dry out, loss of polarization of the negative electrode, corrosion of the positive electrode at elevated temperatures, etc., which can limit the life of many of these designs to less than expected. Work continues to address many of these effects, and efforts in some areas have been successful.

Valve regulated lead acid batteries (VRLA) are quite common in stationary applications. The basic concept is quite well known, where under pressure and in the absence of oxygen from an outside source, oxygen generated at the positive plate recombines at the negative plate. This oxygen cycle under ideal conditions produces a battery that should provide the user with a battery system that requires relatively little maintenance. These advantages are:

- Reduced maintenance due to no water addition.
- Lower charge voltage.
- The battery can be installed in various configurations such as vertical or horizontal.

Some disadvantages are:

- Heat is generated internally to the cell due to the heat of the oxygen cycle. This heat has to be dissipated from the cell to reduce increased corrosion of the positive electrode.
- VRLA batteries are of the "starved" electrolyte design and, typically, water cannot be added to the cells if water is lost due to overcharge or loss by permeation through the cell container wall.
- Boost or equalize charge is normally not used, so full recharge time for a complete discharged battery can be several days.

The Stationary nickel cadmium (NiCd) battery compromise to the “maintenance free” battery resulted in the ultra low maintenance concept. This has evolved to provide similar advantages as the VRLA type batteries, with the added reliability and robustness of the nickel cadmium electrode couple. There are various ultra low maintenance NiCd battery types produced for stationary applications, and these utilize different design concepts.

CHEMISTRY OF NiCd BATTERIES

The electrochemistry of NiCd cells is based on the sum of the single electrodes. During charge and discharge, the following simplified reactions occur:

Figure 1

Nickel Cadmium Half Cell Reactions

Positive Electrode:

$$2Ni(OH)_2 + 2OH^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 2NiOOH + 2H_2O + 2e^-$$

Negative Electrode:

$$Cd(OH)_2 + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Cd + 2OH^-$$

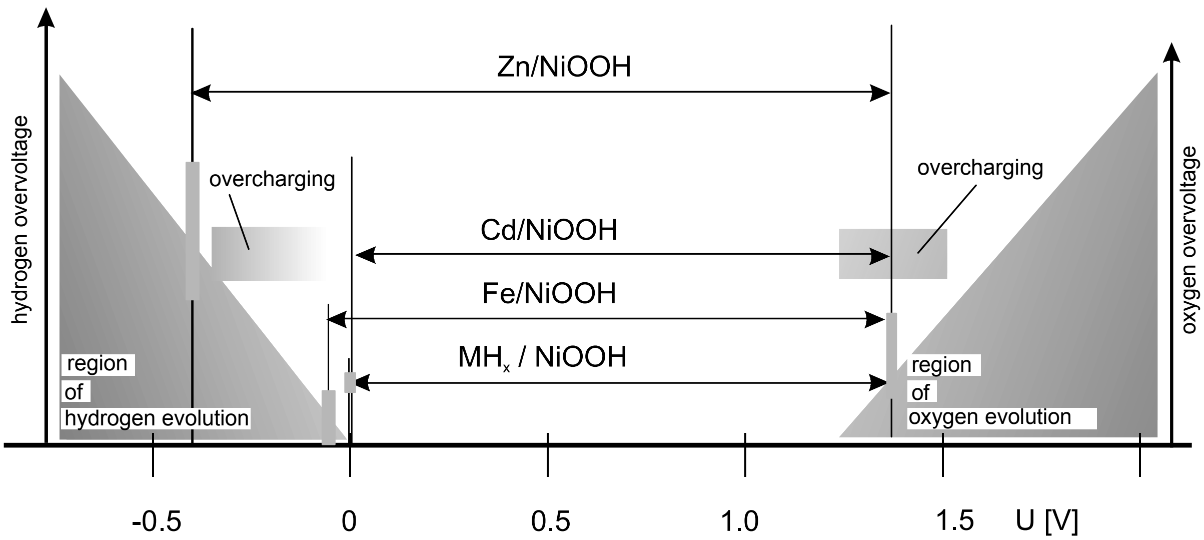
Overall Reaction:

$$2Ni(OH)_2 + Cd(OH)_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 2NiOOH + Cd + 2H_2O$$

The electrolyte is alkaline and consists of potassium hydroxide (KOH) in water and is not directly involved in the cell reaction. (Only the solvent water takes part in the reaction.) Thus, the freezing point of the electrolyte is not affected by the charging state, and the specific gravity does not appreciably change with the state of charge as it does with a lead acid cell. There are no side reactions at the electrodes that can lead to corrosion products, as seen at the positive electrode of LA systems. In addition, the cells are not sensitive to storage at low states of charge for long periods of time.

Unlike the lead-acid system, the NiCd system is thermodynamically stable, as its cell voltage is lower than the decomposition voltage of the electrolyte. During the charging process, there is practically no hydrogen evolution at the negative electrode as long as there is excess $Cd(OH)_2$ available during charging. At the positive electrode, there will be oxygen evolution before the electrode becomes fully charged (Figure 2).

Figure 2: Electrode Potentials in Alkaline Batteries



On extended overcharging, water from the electrolyte is decomposed, and there is hydrogen and oxygen evolution in faraday equivalent quantities. The water decomposition reactions seen at each individual electrode is shown in Figure 3.

Figure 3: Water decomposition equations for each electrode in a nickel cadmium battery

Nickel Cadmium Overcharge Reactions

Positive Electrode:

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

(oxygen evolution)

Negative Electrode:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

(hydrogen evolution)

The cell voltage during overcharging is determined by the negative electrode, as the hydrogen evolution at a Cd electrode displays a considerable hydrogen overvoltage. The hydrogen overvoltage is also responsible for the current limitation if the cells are charged at constant voltage.

CONVENTIONAL NICKEL CADMIUM CELL DESIGNS

Depending on the construction of the cell, there is a certain portion of oxygen that may reach the surface of the negative electrode. In normal flooded cells, this quantity depends mainly upon the oxygen solubility in the electrolyte and the distance between both electrodes.

In flooded cells, there is only a small amount of oxygen that crosses the gap between electrodes during overcharging. This oxygen will become reduced due to the electric potential of the negative electrode. As a consequence, the production of hydrogen in flooded cells is slightly decreased. The oxygen evolution starts before the positive electrode is completely charged. Therefore, the charging efficiency of the negative is slightly higher than that of the positive electrode. If the cell is charged with limited voltage, this difference in the charging efficiency may cause the charging process of the cell to remain incomplete, as the charging current will decline when the potential of the negative electrode drops at the point of hydrogen evolution.

Figure 4
Comparison of various nickel cadmium cell designs
showing the gas transfer mechanism

Figure 4A

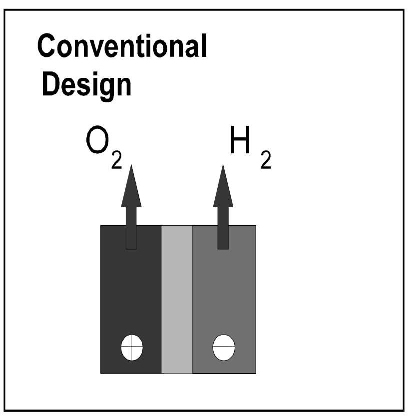


Figure 4B

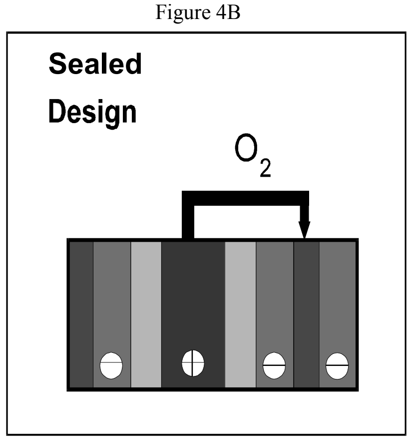
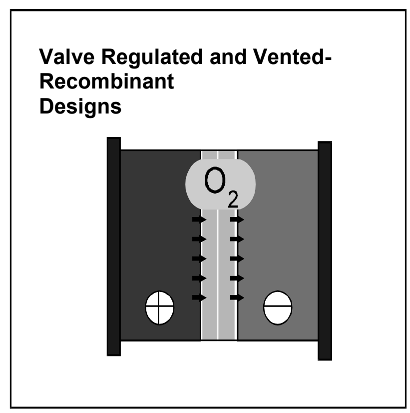


Figure 4C



ULTRA LOW MAINTENANCE NI-CD CELL DESIGNS

The concept of creating an ultra low maintenance cell involves enhancing the recombination of the oxygen produced at the positive electrode. This can be done either in a partial recombinant valve regulated cell, in a partial recombinant vented cell without valve regulation or by utilizing precious metal catalysts external to the cell or alternately inside the cell with the use of a low-pressure valve to enhance gas contact with the catalyst.

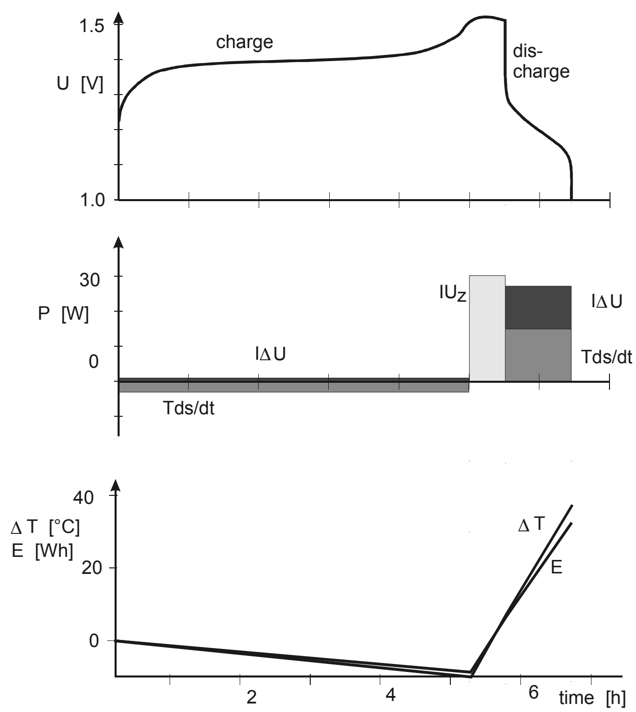
Sealed NiCd Cell Designs

In true sealed cells used for aerospace and electric vehicle applications, the elements are sealed under vacuum with or without the use of an overpressure valve. In this design, the oxygen transfer can be enhanced by the use of special separators and by limiting the amount of electrolyte in the separator, creating unfilled pores to allow the diffusion of oxygen (Figure 4B). By restricting the amount of electrolyte in a way that the separator is permeable to oxygen, the oxygen cycle can be enhanced to such an extent that 100% of the gas formed is transferred from the positive to the negative electrode. An example of such a design is shown in Figure 5.

Figure 5

A consequence of such a strong oxygen cycle in a cell is the formation of heat during overcharging. This is illustrated in Figure 6, which shows the charge / discharge thermal characteristics of a NiCd couple.

Figure 6: Thermodynamic characteristics of a nickel cadmium cell during charge and discharge



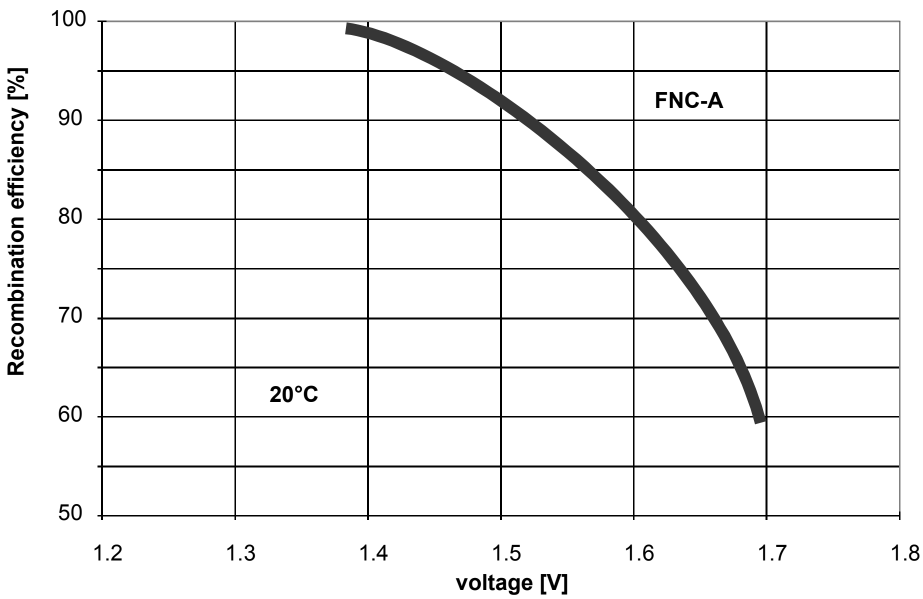
During charging, the reaction is endothermic and the cell cools. When the overcharge phase is reached, the temperature begins to rise due to the oxygen cycle. The stronger the oxygen cycle, the steeper and faster the rise in temperature. During overcharge, the charge current that follows the oxygen cycle will contribute very little to electrochemical energy storage and will simply be converted to heat. Because of the efficiency of recombination in a sealed cell design and the limited amount of electrolyte resulting in a small, specific heat capacity, the temperature will rise very rapidly as an indication of the state of complete charge. Because of this, it is necessary to closely control the end of charge of this type of very efficient recombining NiCd cell. For this reason, these types of sealed cell designs are not suitable for standby applications.

Valve Regulated Partial Recombinant NiCd Cell Designs

Using cells with the ability of oxygen recombination in stationary batteries requires special precautions in the design to prevent overheating. Typically, this is accomplished by limiting the oxygen transfer to the negative plate as well as increasing the amount of electrolyte in the cell, resulting in a higher specific heat capacity. In valve regulated NiCd cells, a low-pressure valve is incorporated to enhance the oxygen cycle and, at the same time, special separators are chosen to limit the oxygen transfer as the cell potential increases (Figure 8).

Since the current of oxygen reduction generated at the negative plate reduces the hydrogen evolution in a completely charged cell, and since the negative electrode tends to charge at a higher efficiency than the positive plate, this hydrogen reduction at the negative reduces the cell potential and allows the positive plate to become more fully charged. This allows the cell to be charged to a higher state of charge with a lower cell potential, thus reducing the amount of gas loss from the cell.

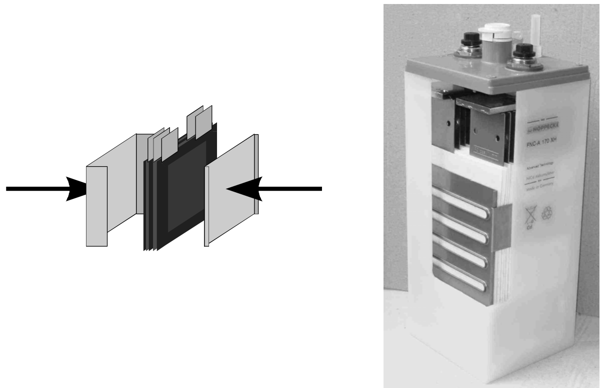
Figure 8: Cell Recombination efficiency vs voltage



Vented-Partial Recombinant NiCd Cell Designs

Flooded cells generally will display only small tendencies toward oxygen recombination, as the separators are normally kept filled with electrolyte. If the charge voltage is limited to low values, the charging of the positive electrode will be blocked by the potential change at the negative electrode. In the case, where a partial transfer of oxygen to the negative plate is allowed, this will slow the recharge of the negative electrode and enhance the recharge of the positive electrode. As a consequence, the cell will display a higher rest current, and such a cell will exhibit a better charge retention at lower voltages, compared to conventional cells. The ability to efficiently charge at this lower voltage minimizes the requirement for water addition. The cells may be operated at lower charging voltages and will have longer intervals of water topping-up.

Figure 7: Special vented – recombinant battery design with internal steel pressure plates.



The design is based on the principle of a standard vented NiCd cell, with standard positive and negative electrodes. The plates are placed close together, and the electrode package is compressed between special plates to force oxygen between the electrodes. In addition, the design makes use of special non-woven separators that have been optimized to limit transfer of oxygen between the plates.

There is no difference in the cell behavior as long as the cell has not reached the overcharge phase. But, during overcharge, the standard vented cell shows a high rise in the cell voltage due to the polarization of the negative electrode (hydrogen over-voltage). With the vented-recombinant concept, an optimum compromise is achieved between properties of recombinant valve regulated and vented flooded designs. In the overcharge phase, the cell achieves the same performance as that in a valve regulated recombinant NiCd design. Due to the internal oxygen recombination, the required charging voltage is reduced and, in turn, topping-up intervals are prolonged.

Ultra Low Maintenance Designs with Catalysts

Other concepts used to create ultra low maintenance NiCd designs utilize standard vented, flooded cell in conjunction with a precious metal catalyst device to recombine the oxygen and hydrogen produced during the overcharge phase. This can be done either by the use of a catalyst mounted external to the cell or internal (inserted into to the cell head space) to the cell.

Figure 9: External catalyst used with a vented flooded cell. Hydrogen and oxygen combine at the central catalyst and form water vapor. The water vapor condenses on the inside surface of the vent and is directed back into the cell.

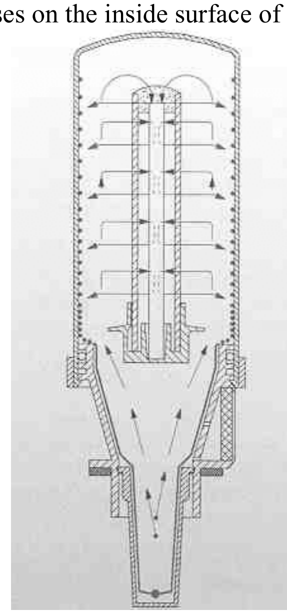


Figure 10:
Internal catalyst design utilizing a low pressure vent with a catalyst and flame arrestor inserted into headspace of the cell. Hydrogen and oxygen gas escaping from the plates recombines at the catalyst surface to form water vapor. The condensed water falls back into the cell.

The most commonly used catalyst material is palladium. In this design, the voltage of the negative electrode is allowed to rise due to polarization, and the cell functions very much as a flooded cell. When an external catalyst is applied (Figure 9), the gases are recombined at the surface of the catalyst. Water is given off in the form of vapor and condenses on the inner surface of the vent "bulb." This water is then directed back into the cell by the shape of the vent design.

In the internal catalyst design (Figure 10), the headspace of the cell above the plates is used as the condensation surface for the water vapor. Additionally, a low-pressure valve is used to close the cell and increase the residence time for the gasses on the surface of the catalyst to maximize recombination efficiency.

It is also important for both designs that there be a flame arrestor built into the vent to prevent back flash into the cell from an external ignition source.

The principal advantage of these designs is that the cell functions as a normal vented NiCd cell. Cell potentials are generally higher than those seen in recombinant cell designs. This is due to the fact that hydrogen is not evolved from the negative electrode until a capacity of 95% to 100% is reached.

CONCLUSIONS

Although the approach to ultra low maintenance NiCd systems is, in some instances, similar to that of the VRLA design, there are obvious differences in the technology that result in significant advantages.

- Resistance to mechanical abuse – able to withstand severe shock and vibration due to the mechanical construction of the electrodes and cell.
- Resistance to electrical abuse
    - overcharge
    - deep discharge
    - short circuits
    - not affected on charge by high ripple currents
- Wide operating range from –40 deg C to +60 deg C (-40 deg F to +140 deg F)
- Excellent reliability - sudden death failure due to internal corrosion is not possible
- Twenty plus years battery life
- These cells are designed for ultra low maintenance, and water addition is possible when operated in severe environments (high temperature, high charge voltages) or if needed due to an overcharge condition of the charger
- The cell designs are generally flooded with reserve electrolyte that provides a higher specific heat capacity and results in a lower heat rise during charging.
- Those types utilizing catalysts generally operate as flooded cells, and heat build up in the cell due to recombination as well as thermal runaway are not issues.

As seen by the variation in design concepts, there are a number of ways that NiCd battery systems can be designed to provide ultra low maintenance to the end user. In the end, a failure or breakdown of the valve, recombination system, catalyst, etc. of the cell will not lead to a failure of the battery system as a whole, as with a VRLA. As long as the cell is not damaged in any way, the NiCd cell can continue to operate at a higher cell voltage and water consumption.

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