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# Design Principles for Nickel-Hydrogen Cells and Batteries

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# DESIGN PRINCIPLES FOR NICKEL-HYDROGEN CELLS AND BATTERIES

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## SUMMARY

Nickel-hydrogen cells and, more recently, bipolar batteries have been
built by a variety of organizations. The design principles that have been
used by the technology group at the NASA Lewis Research Center draw upon their
extensive background in separator technology, alkaline fuel cell technology,
and several alkaline cell technology areas. These design principles have been
incorporated into both the more contemporary individual pressure vessel (IPV)
designs that were pioneered by other groups, as well as the more recent bipolar
battery designs using active cooling that are being developed at NASA Lewis
Research Center and under contract. These principles are rather straight-
forward applications of capillary force formalisms, coupled with the slowly
developing data base resulting from careful post test analyses. The objective
of this overall effort is directed towards the low-earth-orbit (LEO) applica-
tion where the cycle life requirements are much more severe than the geosync-
hronous-orbit (GEO) application.

A summary of the design principles employed is presented along with a
discussion of the recommendations for component pore sizes and pore size dis-
tributions, as well as suggested materials of construction. These will be
made based on our experience in these areas to show how these design princi-
ples have been translated into operating hardware.

## INTRODUCTION

The basic nickel-hydrogen cell consists of a gas electrode for the anode,
a separator to form an ionic bridge to the cathode, and the cathode consisting
of nickel hydroxide that is contained within the pores of an electrically con-
ductive substrate. Beyond these basic components there is a wide variety of
options for other components, depending on the methods or techniques used to
assist in electrolyte management and oxygen management. The fact that nickel-
hydrogen devices do not consistently display attractive cycle lives when tested
in LEO regimes at deep depths of discharge indicates that not all of the vari-
ables are fully under control.

The types of shortcomings that are currently associated with nickel-
hydrogen devices can be divided into two categories: (1) those that are obvi-
ous based on the results of post test analysis, in cases where cell failure
had occurred:

(a) unaccommodated for cathode expansion
(b) uncontrolled recombination of hydrogen and oxygen
(c) unreplenished loss of electrolyte within the components
(d) component performance degradation

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and, (2) those decay processes that have not yet been identified as failure modes due to the rapid loss of performance of the device due to the first type of decay processes.

The design principles to be outlined here are meant to address both classes of decay modes. They are based on preconceived assumptions relative to how these devices work and how they might be designed so that they will display longer cycle lives at deep depths of discharge.

There are two approaches to addressing the above shortcomings. The first is to try to attack the problem itself - for example, try to redesign the nickel electrode to eliminate or limit expansion to the point where it is no longer a problem. The second is to accommodate the problem or situations that exist so they no longer become a source of failure. In the case of the nickel electrode, allowance for electrode expansion can be made in the design of the cell. Our approach has generally followed the latter example.

By applying design principles to nickel-hydrogen cells and batteries in the areas of oxygen management, electrolyte management and reservoiring, thermal management and component growth management techniques, designs have been proposed for both IPV and bipolar cells and batteries that should serve to improve cell performance and extend cycle life.

## ELECTROLYTE MANAGEMENT

Electrolyte management can have a significant effect on the cycle life and performance of a nickel-hydrogen device and should be a prime consideration in the overall design of an IPV cell or a bipolar battery. The objective of electrolyte management is to establish and maintain an optimum distribution of electrolyte throughout the components over the life of the device. How the electrolyte distributes itself between the three or more components in a single cell is a very important topic and deserves the utmost consideration. The combination of pore size, pore size distribution and wettability will dictate how the electrolyte is partitioned between the components as a function of the amount of electrolyte that is added to a cell. The approach taken here has been to achieve this objective through pore size engineering of the components so that each can operate within an optimum range (ref. 1).

Nickel-hydrogen cells are assumed to have an optimum volume. That is, there is a volume of electrolyte that when placed within the basic anode/ separator/cathode grouping will result in the highest performance. This is due mainly to the properties of the gas electrode. If the gas electrode is flooded (there is too much electrolyte), then the catalyst sites become blocked with electrolyte and poor performance results. If on the other hand, if the electrode is starved, (there is too little electrolyte) then there are not enough catalyst sites connected to the electrolyte network and again, poor performance results. What is desired then is a cell design that is said to have "volume tolerance;" that is, a cell were electrolyte can be drawn from or stored in a reservoir while within the other cell components the amount of electrolyte remains close to the optimum amount. This is accomplished by the incorporation of a reservoir into the cells, wherein pore size and pore size distributions are engineered such that the electrolyte reservoir will have the largest average pore size, and thus the "last call" on the electrolyte. The reservoir serves to hold extra electrolyte at the beginning of life for use

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later when either more electrolyte is required or some of the original electrolyte has been displaced for some reason.

Electrolyte management depends mostly on component pore sizes and the interrelationships of the pore size distributions. Measurement of these properties as a function of cycle life for the particular nickel and hydrogen electrodes should be performed to serve as the basis for the pore size relationships. The next step is then engineering the pore size, and pore size distribution into the separators and/or reservoirs to accommodate these standard components. Figure 1 shows the progression of pore size distribution with cycling for the nickel electrode used in our bipolar stack, (this is also representative of the distribution in IPV nickel electrodes). There is a definite shift in the average pore size and pore size distribution toward smaller pores. The peaks at 0.7, 2, and in the range greater than 7 μm decrease while the peak at 0.01 μm shifts slightly to the right and increases in size. This shift in pore size and distribution must be accommodated in the design of the pore size ranges for the separator and/or reservoir. With the shift to smaller pores and the increase in the volume requirements of the nickel electrode resulting from the increase in electrode thickness, the nickel electrode will have a greater affinity for the electrolyte which can lead to a dry separator if a reservoir is not present and/or the separator has no reservoiring capabilities. The pore size distribution for the hydrogen electrode used in our bipolar battery is shown in figure 2. This shows a somewhat broader distribution than the nickel electrode with some rather large pores (30μm) which are the normal hydrophobic passages through which the hydrogen gas diffuses into and out of gas electrode.

For electrolyte management to work effectively, the separator must contain small pores in ranges similar to those of the electrodes in order to maintain an optimum conductive path of electrolyte. It should also contain a volume of larger pores to act as an electrolyte reservoir that can readily provide or absorb electrolyte as needed. In order to prevent flooding, the hydrogen electrode contains large hydrophobic pores. Overlapping of the pore size distributions should facilitate the transfer of electrolyte within a cell and prevent flooding and drying of the individual components. A graph showing the desired overlapping of pore size distributions is presented in figure 3.

Figure 4 shows the pore size distributions for the baseline separators used in our nickel-hydrogen cells, beater-treated asbestos (BTA) and zircar cloth, ZYK15H. Asbestos has a near ideal pore size distribution for a nickel-hydrogen cell. Its distribution effectively overlaps those of the nickel and hydrogen electrodes and contains larger pores which provide a reservoiring function, but are not too large. The pore size should not be so large as to permit free movement of gas across the separator. That is to say a certain minimum bubble pressure is required by the design principle described in this paper. The zircar cloth does not meet all of our design criteria for effective electrolyte management and distribution. Although it has some of the small pores that are required to maintain a conductive path, its distribution does not effectively overlap those of the electrodes. Another of the drawbacks of the zircar cloth is its low bubble pressure. In our designs, a high bubble pressure separator is required to direct the oxygen produced on charge away from the hydrogen electrode toward alternate recombination sites.

The pore size distribution for a separator prepared from 80 percent potassium titanate fibers and 20 percent zirconium oxide fibers is shown in

figure 5. It has a distribution similar to asbestos with the greatest number of pores in the region that overlaps the peaks for the electrodes, however, the peak that overlaps the electrodes is much narrower for the 80:20 PKT:ZrO$_2$ than it is for asbestors. The 80:20 PKT:ZrO$_2$ has the advantage of being fabricated from readily available materials.

The volume tolerance of nickel-hydrogen devices can be greatly increased by incorporation of a reservoir into cell designs. In IPV cells designed by the Air Force, reservoiring is accomplished by allowing the separators to contact the vessel wall which has been coated with zirconium-oxide to serve as a wick to transfer electrolyte from the vessel to the stack. This becomes critical when the zircar cloth is used as the separator. Without a wall wick launch forces could expel electrolyte from the large pores in the separator and there would be no mechanism for its return to the stack. In the bipolar configuration, reservoiring is engineered into the design by the introduction of an electrolyte reservoir plate (ERP) adjacent to the nickel electrode. The reservoir size and storage capability must be tailored to the nickel electrode end-of-life electrolyte requirements. It must also be optimized for volume and weight and still be electrically conductive. Based on data out to 4700 LEO cycles, the ERP must be able to provide 0.12 g/cc volume of the nickel electrode. Without a reservoir present the electrolyte would have to come from the separator. The loss of this volume of electrolyte from a BTA separator would reduce its electrolyte content to 60 percent of its original content which would lead to a doubling of separator resistance (ref. 2).

Our calculations have shown that an ERP with pores in the range of 35 to 40 μm would effectively retain electrolyte through the g-loads associated with launch and also provide electrolyte to the other components as needed.

Effective electrolyte management can reflect itself in improved cell performance and longer cycle life. Maintenance of optimum levels of electrolyte through pore size engineering and reservoiring directly addresses some of the failure mechanisms that have been found in IPV nickel-hydrogen cells.

## OXYGEN MANAGEMENT

One of the most important aspects of cell design deals with oxygen management. The nickel electrode evolves oxygen during the latter part of charge and on overcharge. This gas must be directed out of the nickel electrode and chemically recombined with hydrogen in order to maintain a proper electrolyte balance. In current IPV nickel-hydrogen cells the oxygen is allowed to recombine on the hydrogen electrode either by directly crossing a low bubble pressure separator like zircar or by being forced off of the back of the nickel electrode and over to the hydrogen electrode of the adjacent electrode pair by a high bubble pressure asbestos separator. These recombination methods have the following disadvantages: (1) localized hot spots resulting from rapid recombination of a concentrated bubble of oxygen that can lead to burning of the hydrogen electrode, (2) possible flooding of the hydrogen electrode, particularly on overcharge when the rate of oxygen generation and recombination is the highest, (3) maldistribution of electrolyte-since oxygen generated at one pair of electrodes can be recombined on an adjacent pair (recirculating design), and (4) possible sintering and agglomeration of the catalyst on the hydrogen electrode. As a consequence of these factors it was decided that both our IPV cells and bipolar batteries should employ a separate catalyst

surface for oxygen recombination. In NASA developed IPV designs (ref. 3), a high bubble pressure separator is used to direct the oxygen generated during the latter portions of charge and on overcharge either to an alternate catalytic surface that is between two back-to-back nickel electrodes or toward the wall of the vessel that has been treated with catalyst. This latter method provides the additional advantage of producing the heat of recombination outside the stack and on the wall of the vessel from where it is more easily removed. In both of these cases reliance is made upon the relative pore size distributions of the individual components and the isopiestic driving forces to return the water to the proper component.

In the bipolar nickel-hydrogen system the ERP at the back of the nickel electrode is modified to contain recombination surfaces. Here a high bubble pressure separator is used to force the oxygen off the nickel electrode into the ERP. The recombination sites are catalyzed with platinum which is encapsulated within a vapor permeable casing to allow passage of gases in and water vapor out. The casing also electrically isolates the catalyst from the nickel electrode and the bipolar plate to prevent any parasitic reactions. This method also benefits the overall electrolyte management scheme as the oxygen formed during electrolysis is kept and recombined within the cell where it was generated. This helps maintain the electrolyte balance which becomes more critical in a bipolar stack where the cells are more or less isolated from one another. Again, wicking mechanisms and isopiestic gradients are used to return the product water to the proper components in the cell.

The recombination strips are located adjacent to the bipolar plate which also aids in thermal management as heat is removed through the bipolar plates. Studies are presently underway that should allow us to determine the amount of catalyst required to accommodate recombination of the oxygen produced in both IPV and bipolar cells.

As oxygen management involves water electrolysis and hydrogen and oxygen recombination, it is very closely interrelated with electrolyte management. The wicking mechanisms and pore size distributions that serve to keep the electrolyte properly distributed also serve to redistribute the water generated from recombination.


THERMAL MANAGEMENT

Thermal management is of particular concern because it will effect system performance and ultimately life if not considered as an intergral part of the overall design. The performance of the nickel electrode in regards to its discharge capacity, self discharge characteristics, and life is a function of the operating temperature. Charge acceptance of the nickel electrode is a function of temperature and state-of-charge thus, to maintain a set of cells that constitute a battery in balance from an electrochemical point of view, only small temperature variations from cell to cell are allowable. Temperature limits must be maintained to maximize life. These limits are set forth based on the desired operating temperature, electrolyte concentration, and equilibrium vapor pressure established under these conditions. When temperature and/or concentration differences exist, the vapor pressure will seek a new equilibrium condition, forcing water vapor to transfer from place to place.

Under the conditions where nickel-hydrogen systems perform, the maximum temperature gradients will range from 7 to 10 °C. When the maximum temperature gradient is exceeded, an undesirably large amount of water vapor will redistribute itself to different locations in the cell, from one cell to another, or to the pressure vessel wall. If the gradients are established within a cell, localized conditions result where undesired flooding of the anode or an increase in cell resistance might occur. When the temperature gradients exist from cell to cell, cells will be displaced from their optimum volumes towards either a wet or a dry condition. And if water is condensed outside the stack, an eventual dry out can be experienced. Any kind of temperature gradient resulting in water maldistribution will ultimately effect performance and life.

Since the recombination reaction is highly exothermic it is desirable to locate recombination sites as close to the heat removal mechanism as possible. Its location will be highly dependent on the kind of heat removal system utilized. In IPV cells, where a passive cooling system is used, the heat is removed from the pressure vessel wall and temperature gradients between the stack and vessel are automatically established. When the stack gradients are considered, a limit to the maximum cell capacity and allowable heat removal rate is established. The pressure vessel wall is therefore the ideal location for the recombination sites. With the heat of recombination deposited on the cell wall rather than in the stack, lower temperature gradients will exist between the stack and the cell. This was the idea behind the newly proposed catalyzed wall wick design for IPV cells. The recombination reaction is removed from the gas electrode and transferred to the cell wall. A back to back configuration is employed with a gas screen between the nickel electrodes. A high bubble pressure separator is employed to force the oxygen generated on overcharge off the back side of the nickel electrode facing the gas screen. An oxygen seal prevents the oxygen from entering the core of the stack, as a result, the oxygen is forced out of the stack towards the wall of the vessel which has been treated with catalyst. The oxygen then recombines with hydrogen on the wall of the vessel. The water is returned to the stack via a combination of isopiestic forces and wicking mechanisms as the separator contacts the wall of the vessel. This scheme for recombination aids both thermal and electrolyte management in addition to protecting the hydrogen electrode from damage (ref. 3).

The bipolar systems are designed for high power, high voltage applications. These imply active areas so large that a completely passive cooling system can not be used because of the extreme temperature gradients that would be necessary for effective heat dissipation. Therefore an active cooling system has been incorporated into the overall system design. Heat is removed form the bipolar plates into a heat sink. This cooling mechanism keeps the cell and stack temperatures uniform to prevent water transport within the cells. Different cooling designs are being studied both in-house and by contractors in an effort to determine and optimum design. In both designs recombination occurs on catalyzed surfaces located directly behind the bipolar plates which facilitates not only heat transfer but also aids in electrolyte management.

Overall, in a bipolar system where isolation of the cells is necessary, thermal management is extremely important to prolong life. IPV cells have the advantage of a common reservoir and wicking mechanism to redistribute water when temperature gradients cease to exist, this allows them to return to their

normal operating conditions. Bipolar systems will be more adversely and permanently affected when extreme gradients are allowed to exist.

## GROWTH MANAGEMENT

Probably the most bothersome change that takes place during the course of cycling is the increase in thickness of the nickel electrode. The growth management schemes are of utmost importance because the cycling of a nickel-hydrogen cell can be prematurely terminated due to this phenomenon. If not accommodated, the expansion of the nickel electrode can contribute to cell failure in various ways. In a "locked up" stack, excessive pressures can build up as the cathode expands. The increased compression on the components can effect the ability of the separator to readsorb electrolyte and thereby contribute to cell dryout and high resistance. In extreme cases the increased compression can lead to shorting (ref. 4).

The solution that has been employed in our IPV cells is to employ a "floating stack," one that is designed to accommodate a certain amount of nickel electrode expansion, as described by Smithrick et al. in reference 3. Here a series of Belleville washers is used to accommodate the expansion. The spring constant can be set once the compression characteristics of the components, particularly the separator, and the expansion characteristics of the nickel electrode are known.

A compressible reservoir is incorporated into our bipolar cells to accommodate the nickel electrode expansion. The plot of compression versus force shown in figure 6 shows the compression of the total stack, the separator alone and the ERP grouped with the electrodes. Since plots of compression versus force for the nickel and hydrogen electrodes show very little compression with force, figure 6 shows that the separator and ERP work together to accommodate the initial compressive force, but once the separator reaches its maximum compression the ERP continues compressing to accommodate the nickel electrode expansion. The ionic resistance of the separator fully saturated with electrolyte reaches a minimum as it is compressed then remains essentially constant as more force is applied as shown in figure 7. The expanding nickel electrode will require additional electrolyte which is available from the ERP. Here again the interrelationships of the design principles employed to accomplish both electrolyte management and growth management in nickel-hydrogen cells and batteries are evident.

## SUMMARY AND CONCLUSIONS

Nickel-hydrogen cells have been made by a number of groups over the past 15 yr or so. These devices are intended to replace nickel-cadmium cells and batteries in aerospace applications. They have already been successfully introduced into GEO applications where the cycle life requirements are rather limited. In simulated LEO applications, the cycle life history of nickel-hydrogen cells has been somewhat erratic but by and large disappointing in terms of being able to consistently display tens of thousand of cycles at deep DOD's. The nickel-hydrogen technology group at the NASA Lewis Research Center has been developing both IPV cells that are modifications of the basic back to back and recirculating designs, as well as large bipolar battery systems. These designs are intended primarily for LEO applications but will be extended

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to GEO applications as well. Over the past 2 yr these designs have been translated to working hardware. This paper is a discussion of the design principles that have been used in developing these new designs. They are based on a combination of the existing data base coming from post test analyses of several cell types, as well as the use of capillary forces to provide the required electrolyte volume management. A number of novel schemes have also been factored into these designs in an attempt to rectify some of the documented failure mechanisms. An active program to address other anticipated decay and failure mechanisms is also underway both on contract, as well as via inhouse projects. Cell hardware incorporating these design concepts are currently under test. As newer information becomes available on factors that will effect cell cycle life, it will be factored into upgraded cell designs.

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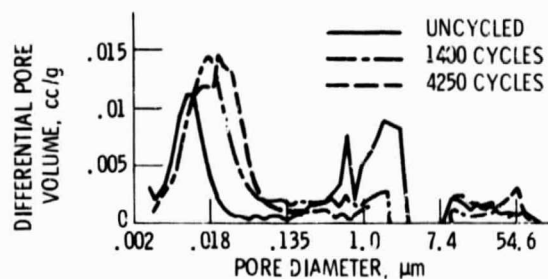
Figure 1. - Differential pore volume vs pore diameter-nickel electrode.
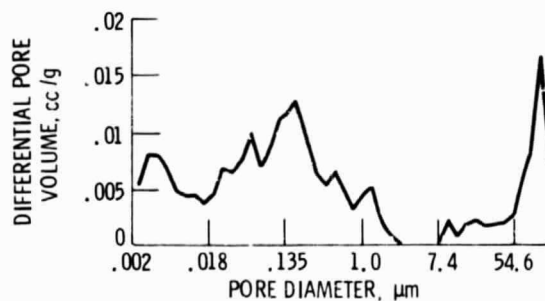


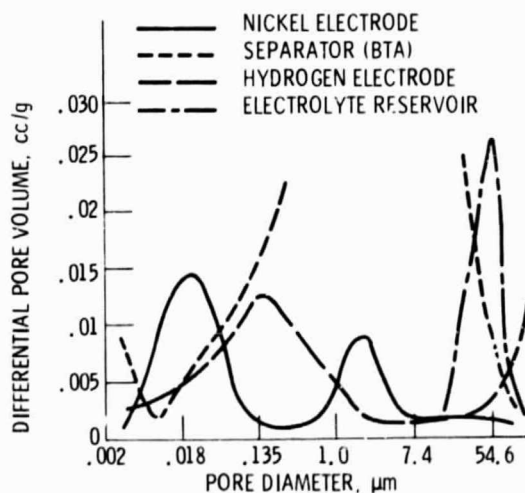Figure 2. - Differential pore volume vs pore diameter-hydrogen electrode.



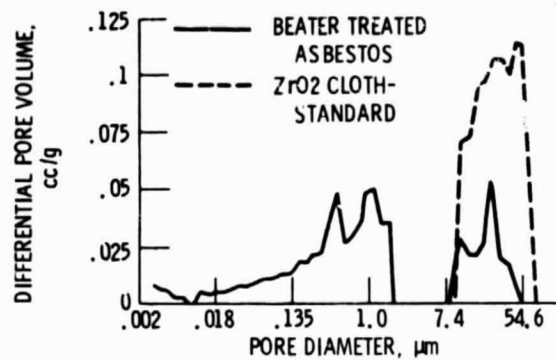Figure 3. - Differential pore volume vs pore diameter.

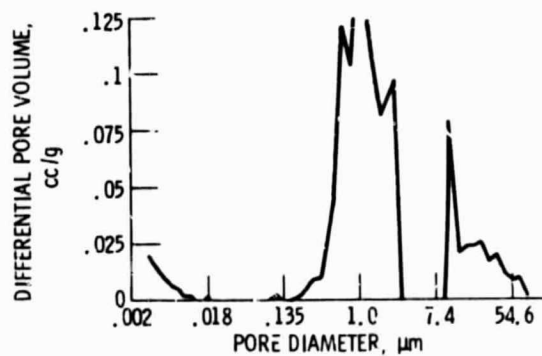Figure 4. - Differential pore volume vs pore diameter.



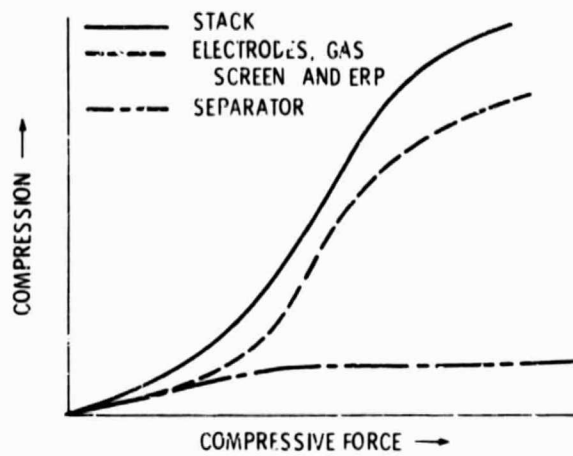Figure 5. - Differential pore volume vs pore diameter 80:20 PKT: ZrO2.
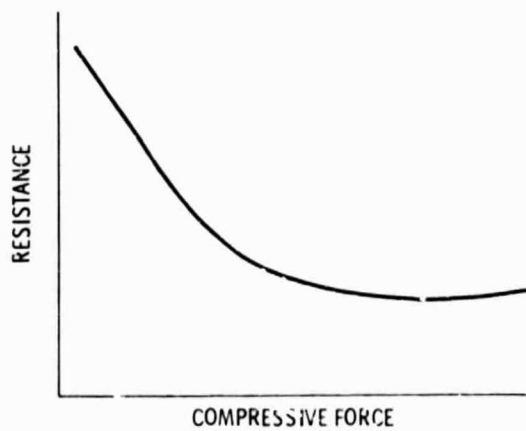
Figure 6. - Compression vs force.



Figure 7. - Matrix resistance as a function of compressive force.

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16. Abstract

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