DESIGN PRINCIPLES FOR NICKEL HYDROGEN CELLS AND BATTERIES

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ABSTRACT

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 Lewis Research Center (LeRC) of the NASA 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 LeRC and their contractors. These principles are rather straightforward 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) application where the cycle life requirements are much more severe than the geosynchronous orbit (GEO) application. Nickel hydrogen cells have already been successfully flown in an increasing number of GEO missions.

INTRODUCTION

Reviews of the history, status, progress, and projections related to nickel hydrogen have appeared in a variety of meetings and publications. The IECEC proceedings over the last few years probably contain the best selection of formal papers. The nickel hydrogen technology group at the Lewis Research Center of the NASA has contributed about a dozen or so papers over the last three years on various aspects of nickel hydrogen technology. The intent of this short paper is to briefly describe the underlying principles upon which all of the aforementioned papers are based. The relatively recent entry into this technology area by NASA was precipitated by a desire to modify existing cell designs to increase their cycle life for low earth orbit (LEO) applications. Contemporary IPV designs may roughly be divided into those based on back-to-back designs (Comsat) and those based on recirculating designs (Air Force/Hughes). Several different types of electrode impregnation procedures are currently in use, as well as several types of separator materials. It was not the intent of the LeRC effort to develop completely new IPV designs but rather to first try to understand the operating characteristics of these cells and then to formulate design guidelines or component requirements or constructional philosophies that would result in increased cycle life at deep depths of discharge. The cycle life history of nickel hydrogen devices in simulated LEO orbits at deep DOD's can best be described as widely dispersed. The gradual accumulation of post test analysis has been very important in formulating our design principles and, in fact, cells made to our specifications by a commercial supplier which incorporate these principles are currently under test. These design (Ref. 1) modifications have already been fully described in the most current IECEC proceedings and will not be repeated here. Instead, a summary of our design principles is presented for comment, criticism, and review. Besides the growing amount of post test analysis that has been helpful in formulating corrective design strategies, the nearly twenty year background in the alkaline fuel cell area has also been a contributing factor. The background in the alkaline fuel cell area has been responsible for being able to lay out a number of principles that are based on the constructive use of capillary forces to perform some very delicate electrolyte and gas management tasks.

THE BASIC CELL

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 conductive 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 to LEO regimes at deep depths of discharge indicates that not all of the variables are fully under control. Since at the single cell level nickel hydrogen and nickel cadmium device weigh about the same, (a 40 to 50 Ahr cell at 100% DOD has an energy density of about 40 Whr/Kg), then nickel hydrogen cells only display significant improvements in energy density when they can be cycled at depths of discharge that are well beyond 25% DOD. The types of shortcomings that are currently associated with nickel hydrogen devices can be divided into two categories: 1) those that are obvious based on the results of post test analysis:

a) unaccommodated for cathode expansion

b) uncontrolled recombination of hydrogen and oxygen

c) unreplenished loss of electrolyte within the cell components

and 2) those decay processes that have gone undetected due to the rapid loss of performance of the device due to the first type of decay processes. It is this second class of cell decay processes that are of particular interest since the ones in the first group will eventually recede as proper design principles are applied. The work of Lim (ref. 2), as well as others, is slowly culminating in a non phenomenological decay model for nickel electrodes. Fuel cell experience can shed some light on the long term sintering (with the resultant loss of catalyst activity) of highly dispersed catalyst surfaces, and the very gradual loss of the hydrophobic nature of the gas electrode. The design principles to be outlined here are meant to address both classes of cell decay modes. By their very nature then, they are based on preconceived assumptions relative to how these devices work and how they might be designed so that they will display long cycle lives at deep DOD's.

CONCEPTS AND PHENOMENOM

For a clearer understanding of the terminology to be used to explain the basis for these principles, a series of concepts and phenomenon that are closely related to this subject will be presented. A minimum of mathematics will be used so as to make the conversion from battery terminology to fuel cell terminology as simply as possible.

OPTIMUM VOLUME

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 there is too much electrolyte (flooded), then the catalyst sites are covered over with a thick liquid film and poor performance results. On the other hand, if there is too little electrolyte (starved), then there are not enough catalyst sites connected to the electrolyte network. The matrix resistance will not go through a minimum, but as the amount of electrolyte is reduced the resistance of the cell will increase. In like manner the nickel electrode performance will be effected more by being starved than flooded. How the electrolyte distributes itself between the three or more components that make up 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 amounts of electrolyte that is added to a cell. In general, the smallest, most wettable pores are filled first followed by successively larger pores. It should be obvious that each particular grouping of components which is intended to be identical may have slight variations in its optimum volume. In a typical IPV cell, there are many groups of components connected together in parallel. One cannot individually place the optimum amount of electrolyte volume into each one of these groupings. Some groupings will therefore be on the wet side of the optimum volume, while others will be on the dry side. What is desired then is a cell design that is said to have "volume tolerance." That is to say, the performance should not be too highly dependent upon the amount of electrolyte volume contained within the grouping of components.

VOLUME TOLERANCE

Figure 1 illustrates how volume tolerance is incorporated into the fuel cells of the type used on the Shuttle Orbiter. It consists of a thin cathode that incorporates a certain degree of wet proofing (hydrophobicity), a fully wettable, high bubble pressure, electrolyte matrix, a thin anode similar to the cathode and an electrolyte reservoir. The pore size and pore size distribution is engineered such that the electrolyte reservoir will have the largest pores and as such will have the "last call" on electrolyte. The cell is initially filled with electrolyte in such a manner that the reservoir will be only partially filled. As conditions arise that result in an excess or a deficiency in electrolyte, the reservoir either empties or fills. In effect, volume tolerance has been incorporated into the cell. The virtues of volume tolerance go well beyond being able to accommodate "wet" or "dry" conditions. It also permits a number of groupings of components that possess a certain degree of stochastic variability to be assembled together and filled in some average manner and still have proper performance of the device as a whole.

RESERVOIRING

Reservoiring is the technique of providing for a certain amount of extra electrolyte at the beginning of life for use at some later time when either more electrolyte is required or some of the original electrolyte has been displaced for one reason or another. In current nickel hydrogen designs a variety of schemes have been used to provide a reservoir of extra electrolyte. Besides the electrolyte plate as used in hydrogen oxygen fuel cells, wall wicks used with excess free electrolyte, specially constructed pore sizing in the nickel electrode and separators containing bimodel pore size distributions have been proposed and or used to perform this reservoiring function. Reservoiring must work very closely with volume tolerance in terms of employing capillary forces to maintain proper electrolyte quantities in the individual cells and components.

OXYGEN MANAGEMENT

One of the most important aspects of cell design deals with oxygen management. The nickel electrode evolves oxygen during recharge and this gas must be directed out of the nickel electrode and chemically recombined with hydrogen. This requires a certain degree of care so as to not ruin the hydrogen electrode. Based on our knowledge of the sintering tendencies of noble metal based catalysts, we have made the decision to employ a separate catalyst surface for the recombination procedure. The LeRC technology group has devised and brought into practice several novel concepts to this end. The catalyzed wall wick is felt to be of special interest for modified IPV designs since it helps in the heat dissipation process.

ISOPIESTIC REDISTRIBUTION

One of the fundamental physical chemical principles taking place within nickel hydrogen devices is the tendency for the vapor pressure in all parts of the device to be equal. When temperature and or concentration differences are set up, then water vapor will move from place to place in an attempt to bring about the equilibrium of the vapor pressure. This is helpful for returning the water resulting from the recombination of oxygen and hydrogen back into the cell electrolyte. It can also be a source of difficulty when a hot spot occurs and water vapor leaves for a cooler or a more concentrated portion of the electrolyte within the cell. The resulting localized "wet" or "dry" conditions may result in an undesired flooding of the anode in the former case or an undesired increase in the cell internal resistance in the latter case. The thermal management scheme used has as one objective the elimination of any large thermal gradients within a cell that might result in local dry out or flooding.

VAPOR/LIQUID DISENGAGEMENT

As hydrogen gas is generated within the anode during the charging process, it can dislodge and carry away small amounts of electrolyte. One technique used to correct this situation is to place a microporous, hydrophobic film on the back side of the electrode. This will permit the free passsage of hydrogen through the small pores, while at the same time prohibit the small droplets of electrolyte form passing through. For monopolar cell designs this scheme is a viable option, whereas teflon's electrical insulating characteristics precludes its use in bipolar configurations.

AGING EFFECTS

If it were not for changes that take place within the individual cell components, one would be ready to draw up the specifications for the design of an IPV cell or a bipolar battery. The results of post test analysis are very important in supplying the required information on this matter. There are three types of changes that must be followed if one is to begin with a proper cell design.

Wettability

Since the entire electrolyte management philosophy is built upon the capillarity characteristics of the individual cell components, then some knowledge is needed as to how the wettability of the components change during the course of cell testing. For instance, so called "wettable" material used as the separator can very quickly lose this wettable character. This will disrupt the entire "pecking order" as to where the electrolyte will be. The internal resistance in a cell containing a wettable matrix that goes non-wettable increases rather abruptly. The more gradual loss of hydrophobicity of the hydrogen electrode caused by constituents within the matrix, perhaps, that are deposited onto the anode by electrophoritic processes can be another problem. In the fuel cell area it is felt that asbestos contains some constituents that migrate or are electrophoretically deposited within the anode and ultimately lead to a loss in the hydrophobic nature of the electrode. Since in a fuel cell the operating temperatures are much higher 90° C vs 20° C and the ionic flow is only in one direction (due to the primary character of the fuel cell), it is not apparent that properly reformulated asbestos is an unsuitable separater material for nickel hydrogen devices.

Pore size/Poresize Distribution

Due to the morphological changes brought about by cycling the active material between two valence states, there is a gradual change in not only the average pore size, but the pore size distribution. With nickel electrodes there is a tendency to develop more small pores as the electrode is cycled. The reader is referred to the post test analysis work of Lim (Ref. 2) and others on this matter. The properties at the end of the required service life must be known and accounted for in the proper design of a nickel hydrogen cell or stack.

Electrode Growth

Probably the most bothersome change that takes place during the course of cycling is the increase in thickness of the nickel electrode. The reasons for this vary depending on the investigator and there have been a variety of claims for ways to reduce this expansion by using certain impregnation procedures. The growth management schemes are of utmost importance because the cycling of a nickel hydrogen cell can be prematurely terminated due to this phenomenon. This problem can be attacked using several different approaches.

In fuel cell terminology a "locked up" stack is the term used to describe an assembly of cells or components that is of fixed dimensions (see figure 2(a)). The only way the stack could expand in length would be via the stretching of the tie bolts. Thermal expansions in thickness of the metallic and plastic stack parts are accommodated by the slight amount of elastic stretching of the tie bolts in flight weight hardware or the use of compression springs along with the oversize tie bolts in laboratory hardware. From what is known about the expansion characteristics of cycled nickel electrodes, a "locked up" stack can lead to certain difficulties that have been documented over the years; most recently by Mackowski and Mueller, (Ref. 3). One solution to this problem as proposed by Smithrick, et al (Ref. 1) is to employ a "floating" stack that is designed to accommodate a certain degree of stack expansion. The spring constant is set once the compression characteristics of the separator material and the expansion characteristics of the nickel electrode structure are known. In the design of a floating stack the resevoiring and electrolyte volume management schemes become very important so as to be able to make up for the extra electrolyte required by the expanding cathode. A collapsible reservoir would represent another alternative for maintaining a proper quantity of electrolyte within each cell grouping. A set of compression strength/conductivity plots (Fig. 3) are required to fully assess the effects on cell performance that results from a certain amount of compression on the cell components. It can be seen that a highly compressible matrix material would make the design of a "floating" stack very difficult. Further, there is some evidence that the expansion characteristics of an electrode are somewhat related to the degree of compression it is under in the stack assembly.

CELL AND BATTERY DESIGN PRINCIPLES

The foregoing list of topics form the basis of developing the required design principles for a nickel hydrogen device. It should be noted that the actual electrochemistry that goes on inside the device was never mentioned. Only as the electrochemistry effects the electrolyte volume, the component pore size/pore size distribution, or the expansion characteristics, is it important. Measurement of the pore size and the distribution of that pore size for each one of the cell components as a function of cycle life and degree of compression is the essential starting point for this procedure. This permits one (with the help of some wettability information) to calculate the distribution among cell components of the electrolyte as a function of electrolyte content. The pore size characteristics of the matrix material used as the separator is subject to a certain amount of adjustment depending on the particle size and physical nature of the ingredients used in their formulation. This is followed by a series of measurements whereby the ionic/electrical conductivity is measured as a function of the compressive forces placed on the component. This is usually done in a fully saturated condition but can also be done as a function of electrolyte content.

There is probably not any one best way to design a cell or battery but there is a certain degree of formalism required to adequately account for all the changes that take place over the course of the useful life of a cell or battery. Once the oxygen management, electrolyte reservoiring, thermal management, and the component growth management techniques are all decided upon, then a series of rather straight forward calculations based on pore size engineering principles (Ref. 4) can be applied to insure proper cell and stack performance over the expected cycle life of the cell. The overall output of these principles have resulted in the cell and stack designs that have been produced by the nickel hydrogen technology group at the Lewis Research Center. These designs have been fully documented at earlier conferences and current cycle life results will be reported at this current workshop session. It is the current philosophy of the group to:

1) Use a separate recombination catalyst (rather than the hydrogen electrode) to recombine the oxygen coming from the nickel electrode. This then dictates the use of a separator matrix that will have a sufficiently small pore size to preclude the passage of oxygen through open pores within the separator.

2) Use a "floating" stack rather than a "locked up" stack to circumvent the problems associated with positive plate growth. The modified IPV designs use springs which permit actual stack expansion, whereas the bipolar designs employ collapsible components.

3) Provide electrolyte management schemes which will maintain proper electrolyte content within the cell components. These are all based on pore size engineering principles in conjunction with the knowledge of matrix fabrication techniques.

By applying these principles, cells and stacks have already been made and are being tested with results that have led us to believe that much of the mystique that currently enshrouds contemporary electrochemical device technology should be able to be replaced with a rather simple set of straight forward formalisms based on elementary principles of physical chemistry.

CONCLUDING REMARKS

Nickel hydrogen cells have been made by a number of groups over the past fifteen years or so. These devices are intended to replace nickel cadmium cells and batteries in aerospace applications. They have already been successfully introduced in 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 in large disappointing in terms of being able to consistently display 10's of thousands of cycles at deep DOD's. The nickel hydrogen technology group at the Lewis Research Center of the NASA 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 to GEO applications as well. Over the past two years these designs have been translated to working hardware. This short 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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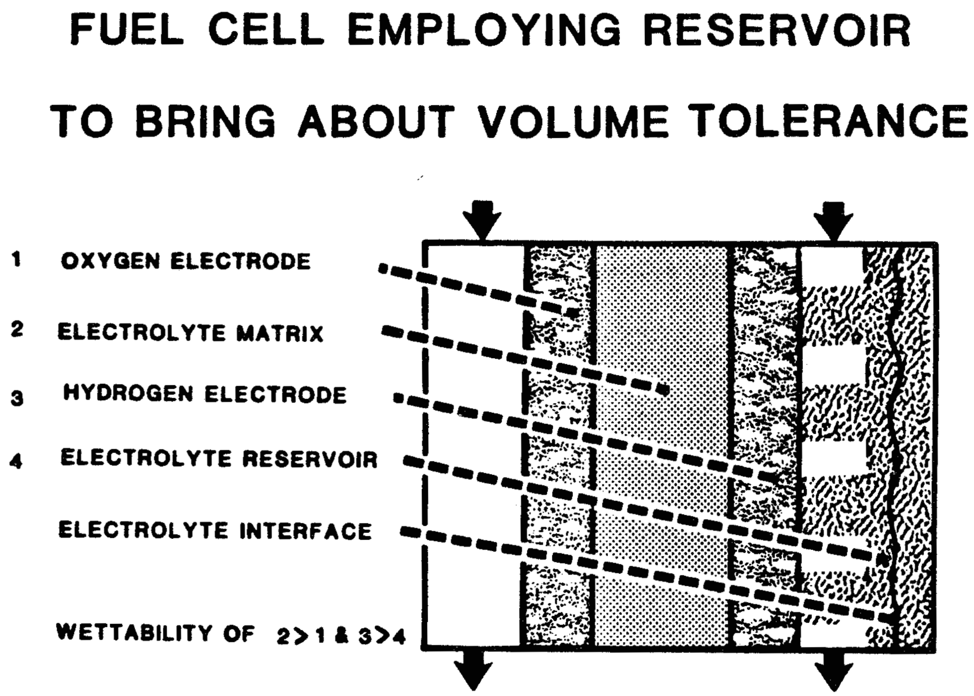

Figure 1. Fuel Cell Employing Reservoir to Bring About Volume Tolerance

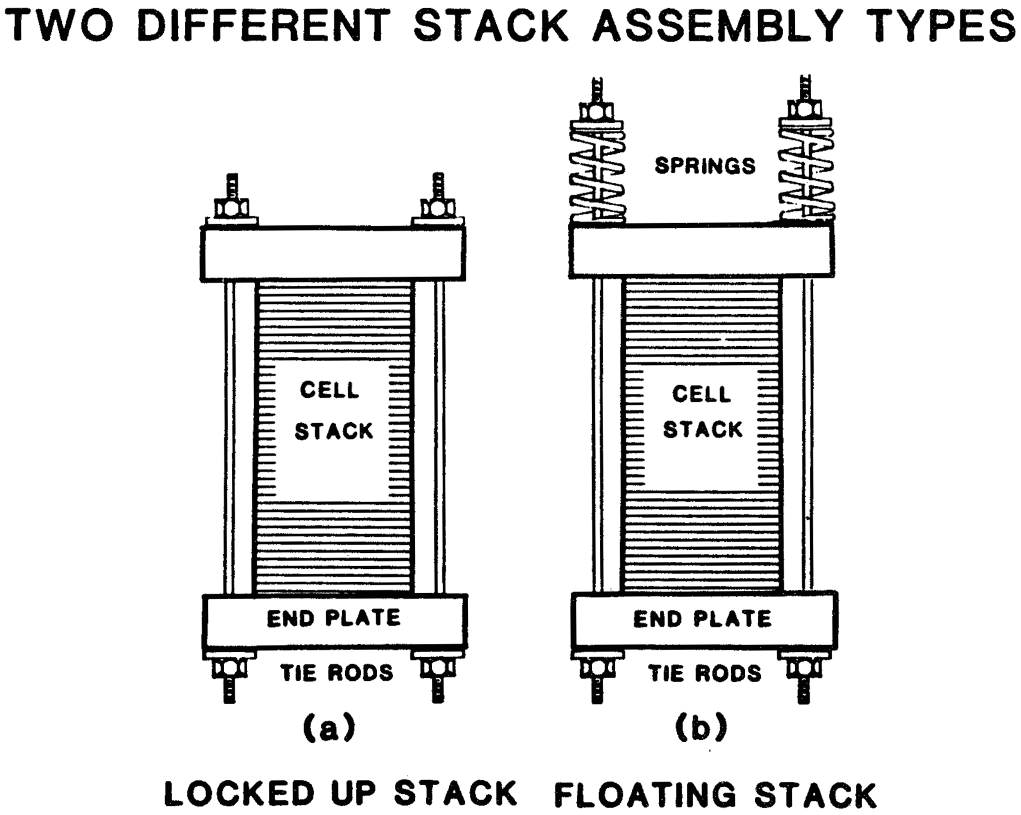

Figure 2. Two Different Stack Assembly Types

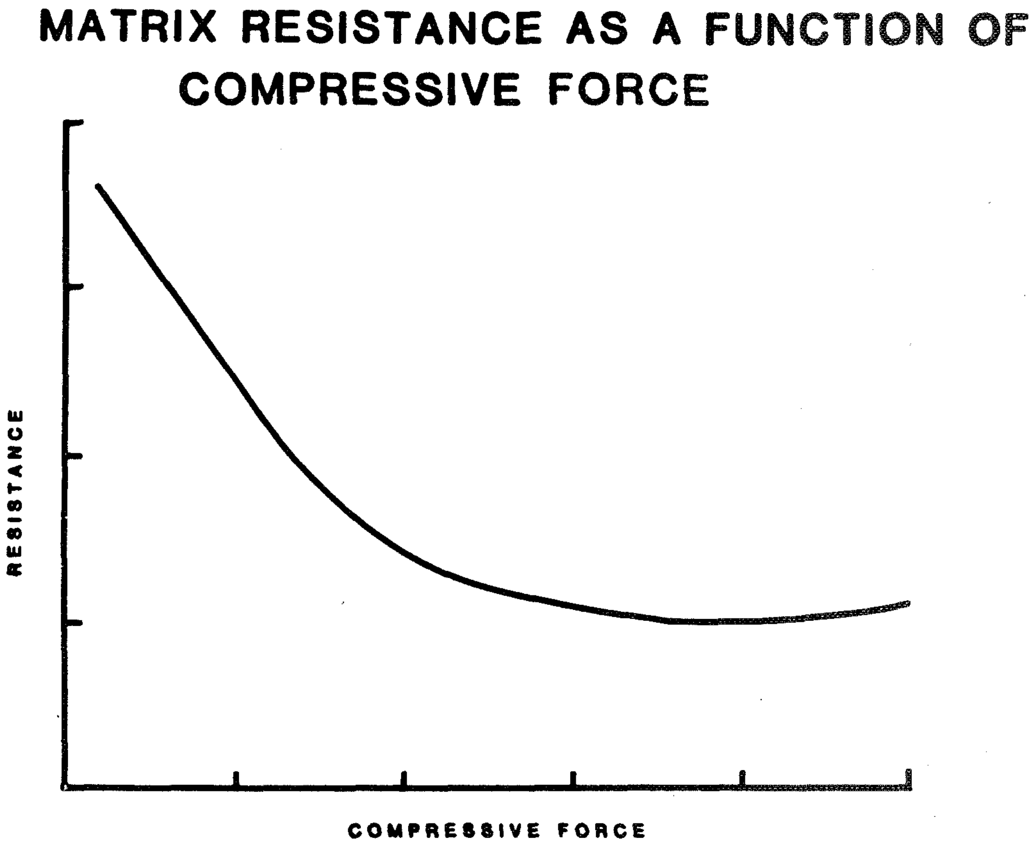

Figure 3. Matrix Resistance as a Function of Compressive Force