

# Electrolyte management considerations in modern nickel/hydrogen and nickel/cadmium cell and battery designs

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## Abstract

In the early 1980s, the battery group at the NASA Lewis Research Center (LeRC) reviewed the design issues associated with nickel/hydrogen cells for low-earth orbit applications. In 1984, these issues included gas management, liquid management, plate expansion, and the recombination of oxygen during overcharge. The design effort by that group followed principles set forth in an earlier LeRC paper that introduced the topic of pore size engineering. Also in 1984, the beneficial effect of lower electrolyte concentrations on cycle life was verified by Hughes Aircraft as part of a LeRC-funded study. Subsequent life cycle tests of these concepts have been carried out that essentially have verified all of this earlier work. During the past decade, some of the mysteries involved in the active material of the nickel electrode have been resolved by careful research done at several laboratories. While attention has been paid to understanding and modeling abnormal nickel/hydrogen cell behaviors, not enough attention has been paid to the potassium ion content in these cells, and more recently, in batteries. Examining the potassium ion content of different portions of the cell or battery is a convenient way of following the conductivity, mass transport properties, and electrolyte volume in each of the cell or battery portions under consideration. Several of the consequences of solvent and solute changes within fuel cells have been well known for some time. However, only recently have these consequences been applied to nickel/hydrogen and nickel/cadmium cell designs. As a result of these studies, several unusual cell performance signatures can now be satisfactorily explained in terms of movement of the solvent and solute components in the electrolyte. This paper will review three general areas where the potassium ion content can impact the performance and life of nickel/hydrogen and nickel/cadmium cells. Sample calculations of the concentration or volume changes that can take place within operating cells will be presented. With the aid of an accurate model of an operating cell or battery, the impact of changes of potassium ion content within a potential cell design can be estimated. All three of these areas are directly related to the volume tolerance and pore size engineering aspects of the components used in the cell or battery design. The three areas follow. (i) The gamma phase uptake of potassium ion can result in a lowering of the electrolyte concentration. This leads to a higher electrolyte resistance as well as electrolyte diffusional limitations on the discharge rate. This phenomenon also impacts the response of the cell to a reconditioning cycle. (ii) The transport of water vapor from a warmer to a cooler portion of the cell or battery under the driving force of a vapor pressure gradient has already impacted cells when water vapor condenses on a colder cell wall. This paper will explore the convective and diffusive movement of gases saturated with water vapor from a warmer plate pack to a cooler one, both with and without liquid communication. (iii) The impact of low-level shunt currents in multicell configurations results in the net movement of potassium hydroxide from one part of the battery to another. This movement impacts the electrolyte volume/vapor pressure relationships within the cell or battery.

**Keywords:** Nickel/hydrogen cells; Nickel/cadmium cells; Potassium hydroxide

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## 1. Introduction

During the development of the fuel cell technology that is now used on board the Space Shuttle, the concepts of optimum volume and volume tolerance became quantitative characteristics that were assigned to different cell designs. A previous paper details the general principles of pore size engineering as applicable to alkaline cells and batteries [1]. Briefly, optimum volume denotes the volume of electrolyte at which a particular fuel cell design has its highest perform-

ance. Volume tolerance refers to the amount of change in electrolyte volume that can take place within a cell that still leaves it operating in an acceptable manner. Alkaline fuel cells are designed to be filled with a designated amount of electrolyte, which is to remain within each cell. This situation is similar to that of nickel/hydrogen or nickel/cadmium cells. With the increased interest in more than one cell within a single container, some nickel/hydrogen devices are even more closely related to alkaline fuel cells from an electrolyte management point of view. The volume tolerance and opti-

imum volume characteristics of battery cell designs are generally not highlighted even though they are present.

Over the past two decades, there has been a gradual increase in the availability of databases developed during the life cycle testing of different cell designs. From the scatter in the longevity seen in these cycling tests, and from the results of examining internal components after disappointing cycling performances, it can be safely concluded that inappropriate cell designs or components were used to produce some of these cells. If the instances of poor quality plate and improperly prepared asbestos are eliminated, there still exists a number of reported and unreported cases of disappointing life cycle tests that can be assumed to result from inappropriate cell or battery design.

Earlier NASA reports addressed design considerations for nickel/hydrogen cells [2,3]. These considerations emphasized the management of gas movement, electrolyte volume changes, internal heat generation, and expansion of the positive plates over the life of a cell. The beneficial effects of using lower concentrations of KOH were also noted. This paper will review several other phenomena that were not included in these earlier publications. The impacts of these other phenomena, based on volume tolerance considerations, will also be outlined. Where available, appropriate literature citations will be referenced. Sample calculations will review the techniques used to estimate the changes in electrolyte volumes that result from these phenomena. The modeling studies currently in place and under development within The Aerospace Corporation will be described, as well as how these models can be used to explore the design features of candidate cell configurations, as they may be affected by volume tolerance considerations.

## 2. Phenomena impacting electrolyte quantity and concentration

### 2.1. Potassium uptake by the nickel electrode

The operation of the nickel hydroxide electrode in alkaline battery cells has been known for years to involve a number of electrochemical and chemical reactions. These reactions allow the nickel-containing active materials in this electrode to cycle between several solid-state compounds (phases). One of these phases, generally labeled as  $\gamma$ -NiOOH, has been found by a number of researchers to absorb potassium from a KOH electrolyte solution as it forms [4,5]. The quantity of potassium absorbed per mole of nickel atoms has been found to be between 0.25 and 0.33 mole. The simplest measure of this potassium uptake is illustrated by measurements of weight increase in nickel electrodes, as indicated in Fig. 1 [6]. These basic measurements indicate material being absorbed from solution to the extent of 0.30 to 0.32 mole KOH per nickel atom. It is assumed that the solid phase has a limiting nickel oxidation state of 3.67, an assumption that is consistent with thin film electrode capacity studies. This

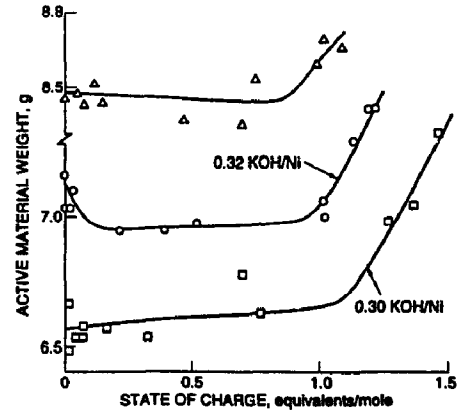


Fig. 1. Weight of active material in a nickel electrode as a function of state-of-charge.

stoichiometry suggests the compound,  $\text{Ni}_3\text{O}_6\text{H} \cdot \text{KOH}$ , as a more accurate representation of  $\gamma$ -nickel oxyhydroxide. The formation of  $\gamma$ -phase in an operating battery cell will therefore involve the uptake of 0.33 KOH units per nickel atom. As the KOH is withdrawn from the electrolyte, there is a reduction in its conductivity, diffusional limiting current, and volume.

### 2.2. Movement of water vapor under the influence of a temperature gradient

When a temperature difference is present within a cell or battery, water vapor may be transported from one part of the cell to another in order to maintain conditions of constant vapor pressure (isopiestic) within the device. The condensation of water vapor onto a cold surface from the humid air within a room is an illustration of maintaining isopiestic conditions. This situation has been experienced within operating nickel/hydrogen cells to the extent that performance was adversely affected and cycling had to be interrupted. The paper by Earl et al. [7] covers the example of a volume tolerance problem that was introduced by a temperature gradient from the plate pack to the lower cell dome. Another example of volume tolerance problems are found in a paper that mentions that early performance problems were rectified by opening the cells and submitting them to a reactivation procedure [8].

### 2.3. Redistribution of potassium hydroxide as a consequence of shunt currents

A third situation possibly present in multicell devices starts with a shunt current caused by an inadvertent electrolyte film bridging from one cell to another. In addition to causing an electrical inefficiency, this process slowly results in the net movement of solute from one cell to the next as dictated by the transference numbers of the individual ions. This situation did arise in one fuel cell, which will be described in more detail in a later section [9].

### 3. Volume tolerance characteristics of battery cells

Volume tolerance characteristics will only be treated in generalities because of the extensive nature of the topic. Briefly, the pore size character of the components is fixed by the physical properties of the electrodes. It is only the pore character of the separator and the compression of the components within the cell that can be selected by the designer. Alkaline fuel cells incorporate a separate electrolyte reservoir plate that accommodates changes in electrolyte volume without affecting the electrolyte quantities within the separator or electrodes. This is accomplished by proper selection of the pore size of this cell component. The reservoir, by virtue of its rather open pore structure relative to the separator and the wettable portions of the gas electrodes, maintains the proper amount of electrolyte in the electrode and separator portions of the cell. In battery cells, electrolyte changes over the course of a charge/discharge cycle as well as with time must be considered. The separator is generally used as the reservoir. There is an increasing degree of coarse pore character from asbestos to zircar to pellaon, which permits more electrolyte to be stored. With zircar, care must be taken not to completely fill the large pores, since in the past this has resulted in early failures due to excessive popping damage to the hydrogen electrode. As reported by Fuhr [10], overly wet zircar cells, when laid on their side, had problems during life cycle testing. It was suggested that the excess electrolyte formed a pool along the bottom of the cell and as the oxygen bubbles built up behind the electrolyte-filled separator, there were occasionally large pops due to the energetic recombination of oxygen with the hydrogen on the hydrogen electrode.

An accurate cell component model incorporating the pore size distribution of the individual cell components would be very helpful in exploring the volume tolerance aspects of candidate nickel/cadmium and nickel/hydrogen cell designs.

### 4. Sample calculations

The following sections will describe a number of examples where changes in electrolyte volume and concentration can take place within an electrode, a plate pair, or a plate pack. These changes can result from a variety of driving forces that are present in ground-based or on-orbit conditions. Temperature control and thermal gradients are very important to the maintenance of proper electrolyte distribution within a cell or battery. Also, the volume tolerance characteristics of these cells or batteries, although possibly less well understood, often make the difference between good cell performance and cell failure. In each of the following examples, the driving forces tending to disrupt the distribution of electrolyte will be described. If there are any forces that would tend to restore proper electrolyte distribution, they will also be noted. The steps involved in estimating the steady-state conditions within the cell or battery as a consequence of these disruptive forces will then be outlined. The solutions will be given in

terms of the ratio of the final volume to the initial volume ( $V/V_0$ ).

#### 4.1. Effects related to potassium uptake by nickel electrodes

In this section, various conditions of operation that are common to nickel/hydrogen battery cells are considered that can influence the performance as related to potassium uptake by the active material. While the same general issues are important in nickel/cadmium cells, the nickel/hydrogen cell environment results in more rapid potassium uptake, largely due to the more efficient nickel electrodes typically used and the reactions of hydrogen gas within the nickel electrode [11]. Clearly, any performance problems related to potassium uptake will strongly depend on the dynamics of electrolyte movement within the cell stack, as well as the temperature of the cell and many other variables. Here, we give an overview of how some of the major operating and design variables relate to potassium uptake.

A fully integrated model of the nickel hydrogen battery cell has been developed, as described in Ref. [12–14]. This model includes all electrochemical and physical processes that are known to occur in nickel/hydrogen battery cells, as well as realistic three-dimensional sintered substrate structures within the nickel electrodes. When simulating nickel/hydrogen cell performance during many cycles, it was discovered that gradual conversion of the charged  $\beta$ -NiOOH to the  $\gamma$ -phase occurred. While this conversion resulted in an increase in total stored capacity, it seemed to degrade discharge voltage performance under some conditions. This degradation resulted from an overall reduction in the concentration of the electrolyte as potassium was absorbed into the  $\gamma$ -phase during operation. The problems in cell performance resulted from two effects. First, the diminished electrolyte volume associated with the lower electrolyte concentration tended to starve the separator for electrolyte, thus increasing cell impedance. Second, at low KOH concentrations, the hydrogen electrode could become starved for hydroxide ions at high discharge rates, thus developing a large concentration polarization and forcing the cell to a very low discharge voltage. It was assumed in all these simulations that the  $\gamma$ -phase discharged to an  $\alpha$ -phase that retained the potassium until it dissolved and recrystallized as  $\beta$ -Ni(OH)<sub>2</sub> via an Ostwald ripening process.

Discharge rate is a significant factor in the potassium ion issue since this is what depletes the hydroxide at the negative electrode. Fig. 2 exhibits the electrolyte concentration profiles found between positive and negative electrodes at different discharge rates, along with the resulting discharge voltage profiles. We use a  $C/2$  discharge rate as a standard for performance comparisons, because this is a typical operational discharge rate for nickel/hydrogen battery cells. Typically, if the KOH concentration drops below about 10% in the cell, it is impossible for the normal cell transport processes to maintain adequate electrolyte in the separator and negative

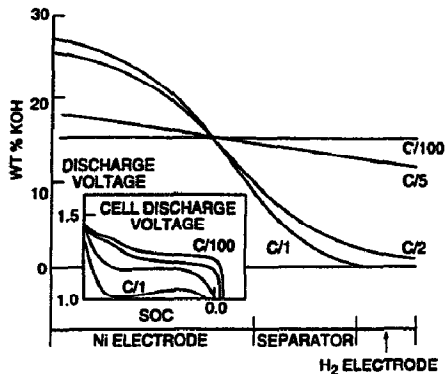


Fig. 2. Concentration profiles across a nickel/hydrogen cell during discharge at different rates.

electrode. Clearly, it is necessary to have adequate quantity and concentration of KOH electrolyte in the cell if this condition is to be avoided. Fig. 3 indicates the depletion in concentration as  $\gamma$ -phase forms with different starting volumes of electrolyte. Fig. 4 indicates the situation where a relatively dry cell that worked very well with 38% KOH would experience real performance problems with 31% KOH, or where a cell with 26% KOH would not work as well as with 31% KOH. Clearly, the selection of amount and concentration of KOH is an issue that needs to be traded off against the increased cycle life that is possible with lower electrolyte concentrations. By including sufficient KOH volume in the cell (held within appropriate reservoirs), it is also possible to realize the high cycle life capabilities of lower KOH concentration, while maintaining good performance for situations where significant  $\gamma$ -phase is formed.

The results indicated in Fig. 4 suggest a reason for the generally puzzling observation that cycle life for nickel/hydrogen cells improves as KOH concentration decreases down to 26%, but that cycle life decreases almost catastrophically if the KOH concentration drops much below 26% [15]. With sufficient electrolyte, or with alternative charge and discharge test profiles, it should be possible to operate cells containing well below 26% electrolyte. Thus, the optimum electrolyte concentration within any cell is determined by cell design and operation, as well as by electrolyte volume and the expansion of the nickel electrodes during cycle life operation.

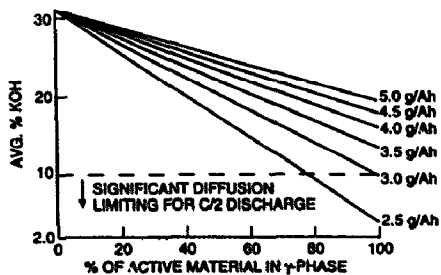


Fig. 3. Effects of potassium uptake on average KOH concentration.

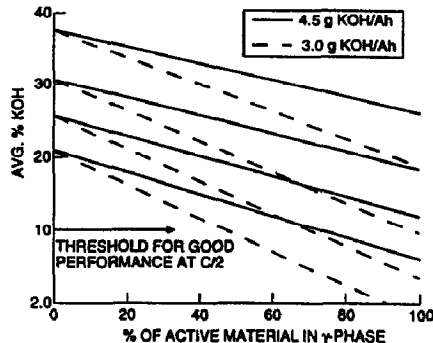


Fig. 4. Effect of initial KOH concentration on average electrolyte concentration after potassium uptake occurs.

It is clear that the effects of potassium uptake in the nickel electrode depend on the rate and extent of formation of  $\gamma$ -phase active material. The rate of  $\gamma$ -phase formation depends on the structure of the nickel electrode, cobalt additives, overcharge time and rate, temperature and thermal gradients, open-circuit stand, and the cell cycling profile. Our nickel/hydrogen cell model has been utilized here to indicate how the rate of  $\gamma$ -phase formation depends on these variables. Applying this general modeling approach to the evaluation of the performance of the nickel/hydrogen cell, it is possible to identify and develop designs that will perform reliably and with margin over a wide range of conditions.

The application of extended amounts of overcharge, particularly at higher rates, has long been known to build up significant quantities of  $\gamma$ -phase, while decreasing the KOH concentration as this phase forms. Since extended overcharge itself is generally regarded as stressful to the cell components, this condition is typically avoided in operational cells. However, since the  $\gamma$ -phase discharges at a lower voltage than does the  $\beta$ -phase, repetitive cycles with even small amounts of overcharge can build up large amounts of  $\gamma$ -phase. Fig. 5 exhibits the discharge performance for cells that have experienced differing amounts of overcharge, and which contain about 3.0 g of 31% KOH/Ah of capacity. Fig. 5 clearly indicates a marked drop in discharge voltage as the amount of overcharge and the quantity of  $\gamma$ -phase increases. As seen in the figure, greater capacity does not always guarantee better battery performance. Fig. 6 indicates the effect of extended

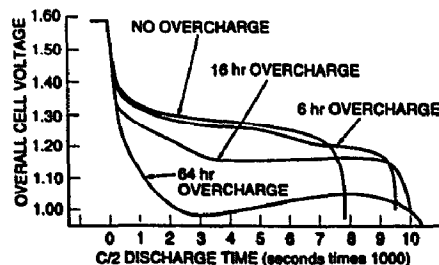


Fig. 5. Effect of extended overcharge on C/2 discharge of nickel/hydrogen cell containing 3.0 g/Ah of 31% KOH after various periods of C/10 overcharge.

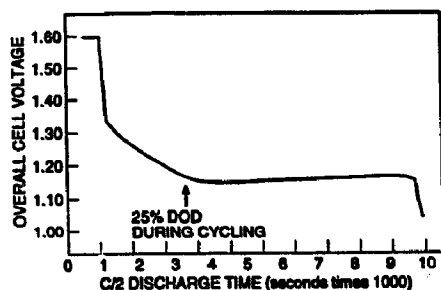


Fig. 6.  $C/2$  discharge voltage after 1500 cycles at 25% DOD in a nickel/hydrogen cell with 3.0 g/Ah of 31% KOH.

cycling on performance. As the nickel/hydrogen cell is cycled repetitively to a given depth-of-discharge (DOD), the amount of  $\gamma$ -phase present increases and finally approaches the quantity of material that is not repetitively cycled. This effect provides the 30–40 mV memory effect that is commonly seen in nickel electrodes that have not been recently reconditioned. As indicated in Fig. 6, these changes can result in a significant drop in end-of-discharge voltage, as well as a characteristic depressed discharge voltage during the final discharge of cell capacity.

Cell temperature is very important to the rate of formation of  $\gamma$ -phase, since this rate is dictated by the potential that the cell can reach before oxygen evolution commences at a high rate. At low temperatures ( $0^\circ\text{C}$ ),  $\gamma$ -phase forms very rapidly, while at higher temperatures ( $20^\circ\text{C}$ ), large amounts of  $\gamma$ -phase are difficult to form by simple overcharge of the cell. Fig. 7 indicates the effects of temperature on the  $C/2$  discharge voltage signatures for a typical nickel/hydrogen cell with about 3.0 g of 31% KOH/Ah. Depressed discharge voltage clearly is much more of a problem at the lower temperatures.

In a nickel/hydrogen cell, the catalytic reactions of the hydrogen gas with the metallic nickel in the nickel electrode initiate conversion of  $\beta$ -phase to  $\gamma$ -phase during open-circuit stand. This conversion can lead to an unusual distribution of active material phases, which is impossible to achieve through normal charge/discharge operation, as indicated in Fig. 8. These reaction and conversion processes are one major reason why large amounts of residual capacity can be completely isolated by the layers of discharged material formed during extended open-circuit stand. These processes can also

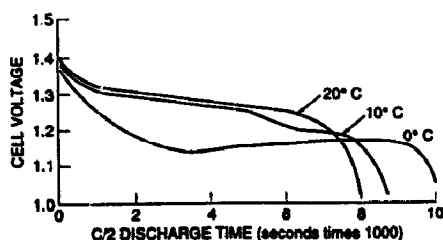


Fig. 7. Effect of temperature on discharge voltage after 16 h charge at  $C/10$  for a nickel/hydrogen cell containing 3.0 g/Ah of 31% KOH.

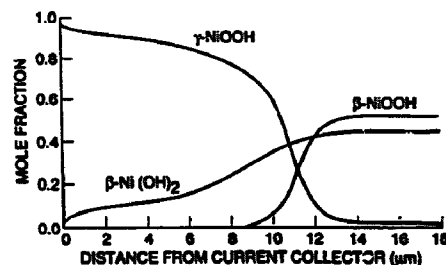


Fig. 8. Unusual distribution of phases in nickel electrodes of a nickel/hydrogen cell after 72 h of open-circuit stand in the charged state.

fully convert the stored charge in a nickel/hydrogen cell into the  $\gamma$ -phase, which, as indicated in Fig. 9, will give a quite depressed discharge voltage signature if insufficient electrolyte is present in the cell.

Cell design is critical to whether the formation of  $\gamma$ -phase constitutes a long-term performance problem. Thermal designs that produce large thermal gradients between the top and bottom of a cell (particularly in dual stack cells) can give depressed discharge voltages only during portions of the discharge. In nickel/cadmium cells, these thermal design issues are not as significant as in most nickel/hydrogen cell designs, simply because each nickel electrode has a negative electrode on each side. The equivalent nickel/hydrogen cell design (generally termed the dual anode cell) should be able to operate at much higher currents without significant voltage depression, simply because it allows twice the diffusional flux between positives and negatives. It is also important that the electrolyte concentration and volume guidelines discussed here be satisfied in each cell contained within a large multicell common pressure vessel (CPV) (single pressure vessel (SPV)). The designs used for SPV systems must also be robust enough to tolerate the changes in electrolyte distributions and any water vapor or oxygen transport between cells that can occur over life.

As discussed previously, nickel/cadmium cells are also subject to losses in discharge voltage when significant quantities of  $\gamma$ -phase are formed, generally after extended shallow DOD cycling at low temperatures (below  $10^\circ\text{C}$ ). These

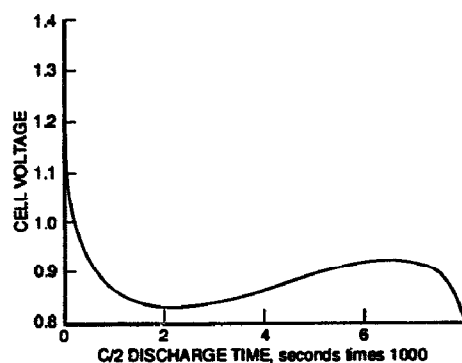


Fig. 9. Discharge voltage after 72 h open-circuit stand in the charged state at  $10^\circ\text{C}$  in a nickel/hydrogen cell with 2.8 g/Ah of 31% KOH.

losses are expected to occur primarily when KOH volume falls below about 3 g/Ah, a correlation that has been previously made in nickel/cadmium life tests. Reconditioning either a nickel/cadmium or a nickel/hydrogen cell will discharge all the  $\gamma$ -phase material, and at least temporarily will allow performance to return to normal. Since  $\gamma$ -phase can form predominantly in localized regions of cells in response to thermal gradients, it can result in high stress and accelerated degradation in these regions of the cell. Regular reconditioning provides a mechanism for eliminating this form of accelerated degradation as well as maintaining and monitoring performance in both nickel/cadmium and nickel/hydrogen cells. The mechanisms discussed here clearly suggest that regular reconditioning is most critical in battery cells that contain relatively low volumes of electrolyte. Cells containing over 4.0 g KOH/Ah are not as likely to realize major benefits from regular reconditioning, unless they are subjected to large thermal gradients.

#### 4.2. Effects caused by temperature differences

##### 4.2.1. Single plate pack with a cold dome — without wall wick

The driving force for water vapor movement is the difference in vapor pressure between the electrolyte in the plate pack and water at the cold, lower dome. There are no restoring forces in ground testing since gravity holds the condensate at this dome. In satellite applications, restoring forces will depend on the low-level gravitational forces induced by satellite movements, the surface tension characteristics of water, and the wettability characteristics of the inner cell wall. The situation of a single plate pack with a cold dome, without a wall wick, has been described in Ref. 7. This situation can be addressed using the vapor pressure relationships appearing in that reference and also in Ref. [16] (NASA Reference Publication 1314). Although the resolution of the chart in Ref. 7 is not good enough to permit accurate answers to the questions in the following examples, it does suffice to indicate the methods used in approaching these questions. Assume there is a solution of KOH in the plate pack at an overall temperature  $T_1$  (point A in Fig. 10). The solution is not in equilibrium with pure water in the cold dome of the cell. The bottom of the plate pack is radiatively looking at the cold plate such that its temperature is  $T_2$ . The general approach to

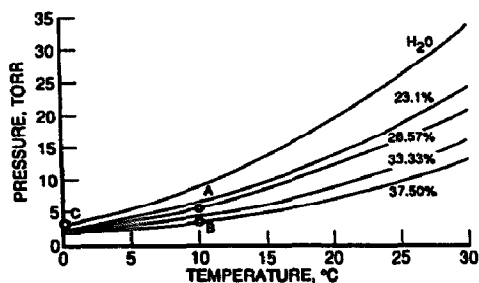


Fig. 10. Vapor pressure characteristics of KOH solutions as a function of temperature.

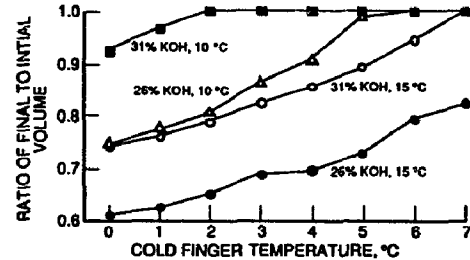


Fig. 11. Electrolyte volume changes as a result of water loss as a function of cold finger temperature, temperature difference, and electrolyte concentration.

this problem proceeds as follows. Water from the KOH solution is evaporated and condensed onto the colder dome of the cell. This proceeds until the vapor pressure of the remaining electrolyte is lowered to where it is equal to the vapor pressure of water at the temperature of the wall,  $T_2$  (B). If there is a small amount of electrolyte in the dome, it will be diluted as water vapor is condensed. In either case, horizontal straight lines on the referenced chart (Fig. 10) connect solutions of equal vapor pressure, and the amount of KOH within the cell stack remains constant. From this information, the problem can be solved. Two examples, starting with 26 and 31% KOH in the plate pack, show the differences (as identified in Ref. 7) that 26% KOH solutions are closer to their dew point than 31% KOH solutions. The 26% KOH solutions are thus more susceptible to water condensing at the cold, lower dome. Fig. 11 shows the results of the two different starting electrolyte concentrations, for two different plate pack temperatures and various cold finger temperatures. Where the ratios of final volume to initial volume are 1.0, the vapor pressure of water corresponding to the dome temperature is still above the vapor pressure of the electrolyte in the stack, and there would be no driving force to condense water vapor at the cooler portion of the cell.

Depending on the volume tolerance characteristics of the particular cell design, a lower limit to the value of  $V/V_0$  would help in suggesting a lower limit to the cold finger temperature of the cold cell dome. The volume tolerance characteristics of any cell design are not only a function of the reservoir properties of the cell design, but depend on the initial electrolyte volume, the expansion characteristics of the nickel electrodes, and possibly other factors. Because of all these factors, the thermal gradients within a cell, and the selection of the electrolyte concentration and the method of heat removal from the cells, are very important. The use of thermal skirts, as opposed to centrally located thermal flanges, results in larger temperature differences between the top and bottom of the cell. When the bottom dome of the cell is good radiative view of the cold plate, the situation can become exacerbated.

##### 4.2.2. Single plate pack with a cold dome — with wall wick

This situation is similar to the one described in the preceding section, but now the capillary forces of the cell components act as a restoring force to return the water to the plate

pack. The separators must, however, be in contact with the wetted cell wall and yet not act to block the free movement of gases within the cell. Several manufacturers offer cells that have a wettable layer of zirconia sprayed onto the interior wall of the cell case. This wall wick, as it is usually called, is also available with catalyzed strips to enable oxygen to recombine on the cell wall. Cell designs based on the Air Force or Man Tech designs employ wall wicks.

#### 4.2.3. Two or more plate packs at different temperatures — without wall wick — without shunt currents

In this situation, one plate pack is at one temperature and another is at a different temperature. Communication of the water vapor, but not of the electrolyte, is allowed between the two plate packs. An IPV cell with central girth welds fits this situation. This communication can exist in a split stack IPV cell (cells built for HST) or a two-cell or multicell CPV battery. In these cases, the amount of dissolved KOH in each stack remains constant, while the amount of water adjusts itself until the two units at the different temperatures have the same vapor pressure. At the start of the reequilibration process, solution 1, the warmer plate pack, and solution 2, the cooler plate pack, will be at the same concentration but at different temperatures (different vapor pressures). The final concentrations will drift towards the condition where the warmer stack will become more concentrated and the cooler solution will become more dilute as water vapor is transported from the warmer to the cooler portion of the cell or battery. Note that any horizontal line (e.g., 1, 2, or 3 in Fig. 12) will designate two solutions that are in equilibrium over this temperature difference. However, the weight of KOH in each of the two stacks (no electrolyte communication) remains constant. Also, the sum of the two water amounts must be equal to the initial conditions following the establishment of isopiestic conditions. There will therefore be a unique solution

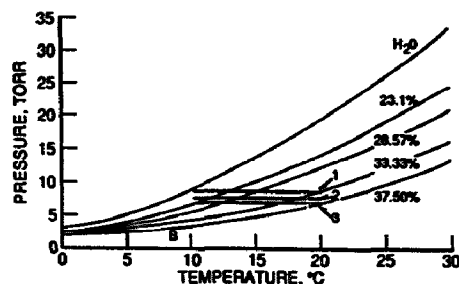


Fig. 12. Trial-and-error solution technique to two-stack water redistribution example.

to the problem of calculating the final concentration and volume of each part of the cell. Table 1 shows typical results of some sample calculations.

#### 4.2.4. Two or more plate packs at different temperatures — with wall wick — without shunt currents

This situation is similar to the preceding one, except that wall wicks or other devices permit electrolyte communication between the two stacks. However, there is no voltage difference between the two stacks. An IPV cell with a split stack that employs a wall wick to help redistribute electrolyte with the cell describes this example. The solution for this situation does not exist in closed form, but can be solved iteratively if the pore size distributions of the components are known. As in the preceding situation, it can be seen that, given a temperature gradient, water will be evaporated from the warmer stack and condense into the cooler stack. The concentration gradient that is established will attempt to equilibrate, and KOH will begin to move from the warmer to the cooler stack. Further, gravitational forces will tend to favor movement from the upper to the lower stack. The pore size character of the components will be the only restoring force in this situa-

Table 1  
Trial-and-error calculation of final volumes

Starting solution in upper and lower stack: 150 g of 31% KOH (volume:  $150/1.31 = 114.5 \text{ cm}^3$ ; KOH weight:  $150 \times 0.31 = 46.5 \text{ g}$ ) at  $15^\circ\text{C}$ .

Assume upper stack warms by  $2.5^\circ\text{C}$  and lower stack cools by  $2.5^\circ\text{C}$ . Upper stack half will concentrate, and lower stack will dilute. Sum of two solutions will still equal 300 g, and KOH weight in each substack will be 46.5 g.

From Fig. 12, lines 1, 2, 3, or any other will connect solutions of constant vapor pressure. Assuming line 2 of Fig. 12 is the answer, final concentrations of 33 and 26% are suggested.

Material balance of upper and lower solution weights:

Upper weight:  $X \times 0.33 = 46.5 \text{ g KOH}$ ,  $X = 141 \text{ g of solution}$

Lower weight:  $Y \times 0.26 = 46.5 \text{ g KOH}$ ,  $Y = 179 \text{ g of solution}$

Sum greater than 300 g, try again.

Assuming line 3 of Fig. 12, is the answer, final concentration of 35 and 28% are suggested.

Retry material balance of upper and lower solution weight:

Upper weight:  $X \times 0.35 = 46.5 \text{ g KOH}$ ,  $X = 133 \text{ g of solution}$

Lower weight:  $Y \times 0.28 = 46.5 \text{ g KOH}$ ,  $Y = 166 \text{ g of solution}$

Sum close enough to 300 g

Calculation of new volumes:

Original:  $114.5 \text{ cm}^3$  in each half

New upper =  $133/1.35 = 98.5 \text{ cm}^3$

New lower =  $166/1.28 = 129.7 \text{ cm}^3$

tion, but can be significant in terms of being able to maintain an ample electrolyte quantity in the upper stack.

#### 4.3. Consequences of shunt currents

There is a situation when two or more plate packs are at different temperatures, with electrolyte paths and shunt currents. This situation is coupled with the requirement to maintain isopiestic conditions. The situation can arise in two-cell or multicell CPV batteries that are subject to small shunt currents caused by electrolyte film bridging from one cell to another.

This phenomenon was seen during a fuel cell development effort carried out at NASA LeRC. The program was with Pratt and Whitney Aircraft (now International Fuel Cells). The fuel cell stack was to be assembled from stack elements that had six cells placed side by side that were electrically connected in series (Fig. 13(a)). The six cells were separated by elastomeric seals to preclude the communication of the electrolyte from one cell to the next. There was a common gas flow field across the backside of these six-cell plaques. This flow field permitted the equilibration of the vapor pressure of the electrolytes contained in the individual cells. The electrical connection from one cell to the next was accomplished by the screen used to support the anode catalyst of one cell and the cathode catalyst of the next (Fig. 13(b)). In less than 1000 h, it became evident that there was a problem with the performance of these six-cell units. Diagnostic evaluation was performed, based on the volume tolerance characteristics of the cells. It was deduced that one of the end cells was gradually being depleted of electrolyte and the cell at the opposite end was gaining in electrolyte volume. This can be understood in terms of the cumulative effects of a low-level shunt current, where the current is being carried partially by the potassium ions and partially by the hydroxide ions. The fraction being carried by each kind of ion is a function of the transference number of the two ion types. If we assume that the transference number for potassium ion is 0.2, then the Hittorf-type diagram in Fig. 14 would suggest that the cell at the positive end of the stack would tend to increase in concentration relative to the cell at the most negative end of the stack. Since the common gas plenum behind all six cells permitted the free movement of water vapor, the cell gaining in hydroxide tended to gain electrolyte volume as water was evaporated from the cell with the lower concentration and

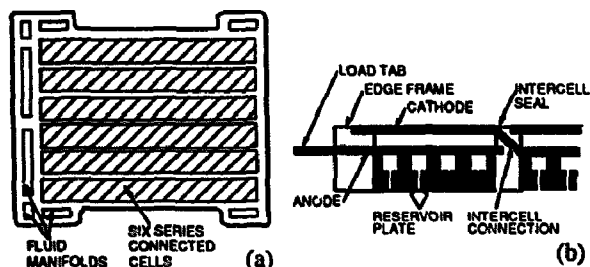


Fig. 13. (a) Platform of six fuel cells connected in series and having a common gas plenum. (b) Cross section of a single cell.

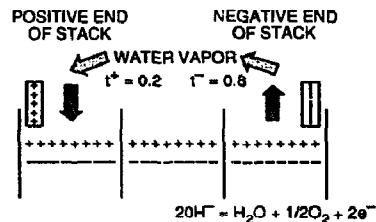


Fig. 14. Hittorf-type schematic of shunt current situation resulting in the net movement of solute from one of the strings to the other.

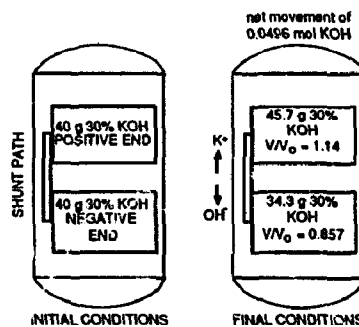


Fig. 15. Estimated redistribution of solvent and solute following 1000 h given a 1.5 kΩ shunt path between adjacent cells with KOH electrolyte.

condensed into the one with the higher concentration (Fig. 13(a)). Since the cells were all at the same temperature, the final concentration within each of the cells was constant. Only the volume changed as a consequence of the movement of water vapor. In this type of problem, it is not the magnitude of the shunt path that is important, but the cumulative effect of the passage of ionic species when the transference numbers are not 0.50.

There are two examples of contemporary nickel/hydrogen devices that may be subject to this type of problem: the two-cell CPV and the multicell CPV. Multicell CPV designers are fully aware of this problem, and use plastic encasements fitted with hydrophobic plugs to preclude the establishment of shunt paths between adjacent cells. In two-cell CPV batteries, different schemes are used to isolate the electrolyte from electrolyte communication between the two series-connected cells. KOH films are very difficult to completely eliminate. For this situation, it is assumed that there is a connecting film 0.5 cm wide, 3 cm long, and 0.01 cm thick between the two stacks of a two-cell CPV battery. Fig. 15 shows the results of this calculation when 0.2 is the transference number for potassium ion, 2.5 Ω cm is the resistivity for KOH, and 1000 h is the time allotted.

#### 4.4. Other situations

It can be seen that a number of other situations could be mentioned. The same general approach used in the previous situations described could be used to investigate the volume tolerance aspects of those particular cell and battery designs. These other situations would be combinations of those already described, and their solutions are left to the reader. From the material presented here, it is seen that the following



features of any cell and battery design must be understood before a cell design can be considered appropriate for the application for which it is being designed.

1. The pore size characteristics of each component and how they change over the cycle life of the application.
2. The physical dimensions of each component and how they change over the cycle life of the application.
3. The temperature profile within the cell over the range of performance of the battery.
4. The volume tolerance characteristics of the plate pack, cell, or battery.

## 5. Summary

A mechanism for degradation in nickel/cadmium and nickel/hydrogen cells has been identified that involves the depletion of KOH electrolyte in the separator and negative electrodes during high rate discharge. This mechanism, which has been simulated in a nickel/hydrogen cell model, is initiated by the uptake of potassium by the nickel electrode when large amounts of  $\gamma$ -phase formation occur in the active material. Guidelines for choosing electrolyte volume and concentration combinations to avoid this problem were presented. These battery and cell performance problems are accentuated by extended overcharge, low temperature operation, extended cycling at low to moderate DOD, thermal gradients, extended open-circuit stand, and cell designs that limit KOH volume or transport below critical levels. However, regular reconditioning provides an effective means to prevent these processes from causing permanent degradation to the cell components in both nickel/cadmium and nickel/hydrogen cells.

Other related phenomena, which were already known in principle, were examined as they pertain to volume tolerance considerations. The movement of water vapor and KOH under the influences of temperature gradients and shunt currents was examined for selected situations. The principles involved will permit the reader to explore other, more complicated, situations.

## 6. Conclusions

Several factors that affect electrolyte volume, concentration, distribution, and transport properties in alkaline cells have been reviewed. Reasonable estimates of which changes can take place as a consequence of these factors, and the importance of incorporating these considerations into modern cell and battery designs, have been established. In most cases, battery and cell designers have these general principles and concepts in mind, but lack an accurate way of factoring all of them into their designs. The resulting trial-and-error approach is both time consuming and expensive. However, a different approach, using mathematical cell models developed from first principles, represents an attractive alternative. The mod-

els, however, must be validated by real cell data and must be able to replicate a growing number of signatures from cells that have experienced life cycling difficulties due to inappropriate cell designs. At The Aerospace Corporation, cell and battery modeling studies are being carried out under the direction of one of the authors to examine how these considerations impact modern power system designs. The modeling studies have already been able to explain cell and battery signatures that, at the time they first appeared, were not fully or logically explainable. As the results from these cell modeling studies become more accepted through validation, they could be used to predict the performance of existing cell designs under a variety of cycling and thermal situations. More important, cell and battery designers may be able to take advantage of the predictive nature of the studies. Thus, some of the extensive performance and life cycle testing could be eliminated that is currently required to validate an existing design under a new set of mission requirements or to suggest a new design for an upcoming mission.

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