

A FLOODED-STARVED DESIGN FOR NICKEL-CADMIUM CELLS

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Summary

It is suggested that some of the design technology used in alkaline fuel cells be applied to the design of nickel-cadmium aerospace cells. In particular, the use of an electrolyte reservoir coupled with appropriate pore size engineering of the electrodes and separator should result in cells of superior performance as well as increased tolerance to manufacturing variations

Introduction

Sealed nickel-cadmium cells for aerospace applications have been made for several decades by a number of manufacturers. Although each manufacturer has his own set of processes, procedures, and design techniques, these cells owe much of their long cycle life to the electrochemical couples employed and the physical properties of the separator material used. The separator has the combination of pore size distribution and wetting characteristics which permits the oxygen evolved at the positive electrode during the latter stages of charge to have access to the metallic cadmium on the negative electrode, while at the same time holding enough electrolyte to maintain good ionic conductivity between the electrode pairs. This condition is usually referred to as being "starved" in terms of the amount of electrolyte. Depending on the particular separator type and number of layers, the characteristics of the electrodes, and the compression on the plate pack, a particular electrolyte loading value ($X \text{ cm}^3/\text{A h}$) will yield the proper balance in terms of gas permeability and electrolyte conductivity. A particular manufacturer will adjust the electrolyte loading value to obtain a certain cell pressure on overcharge based on the experience gained from past performance. There are possible difficulties associated with this procedure which may well result in substandard performance of the cell. This results, in part, from the statistical aspects among groupings of plate packs and/or cell sets and, in part, from the growth with cycling characteristics of the electrodes used in these cells.

It is the purpose of this paper to describe in detail a somewhat analogous situation among groupings of alkaline fuel cells where the stochastic aspects have been much more accurately documented, and then to illustrate

how this problem was eliminated using straightforward principles of pore size engineering [1]. This is followed by a suggested method of adapting these same design principles to nickel-cadmium cells. It must be kept in mind that when cells are cycled to typically twenty percent depth of discharge, eighty percent of the capacity is unused and its associated weight is simply dead weight. Some of this dead weight might be put to better use by trading it for a scheme that would increase the time during which the cell would be working more closely to its optimum set of operating parameters

Background

In the early stages of the development of alkaline fuel cell technology at what is now called International Fuel Cells, a cell was made up as shown in Fig. 1. These cells employed a fixed, trapped amount of electrolyte within each cell. The oxygen electrode was a thin screen onto which was placed a mixture of catalyst powder and Teflon. The Teflon content was such as to render the electrode wet proof. The separator was an asbestos mat fully filled with electrolyte and the hydrogen electrode was a thick (~ 0.060 in.) sheet of sintered nickel which was catalyzed more or less uniformly throughout. The pore sizes of the individual components were selected so that the separator would at all times be filled with electrolyte. The electrolyte-gas interface would be set up somewhere within the thick nickel sinter. As conditions arose that resulted in temporary changes in the volume of the electrolyte, this interface simply moved slightly to the right or left.

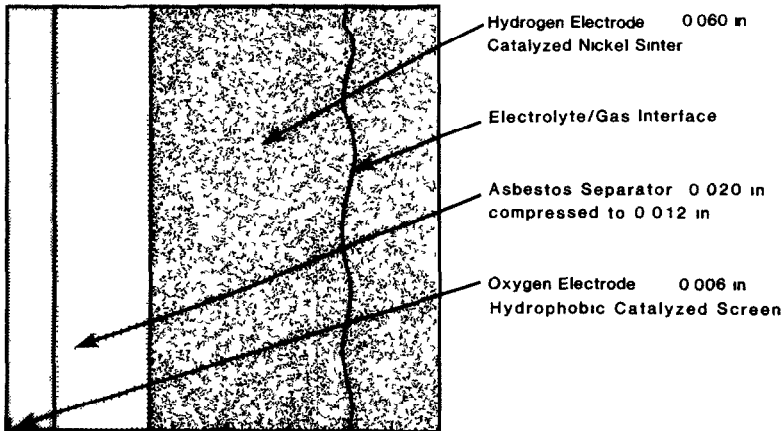


Fig 1 Schematic of a sinter-screen fuel cell

Optimum volume

Optimum volume is a term that is used to describe the effect of electrolyte volume on cell performance and, in particular, that volume which

results in the peak performance of the cell. The reason for a change in performance with cell electrolyte volume (interface position) and an optimum volume can be readily seen with the help of Fig. 1. If the electrolyte-gas interface is very close to the gas cavity (right hand edge of the hydrogen electrode) then most of the catalytic surface is covered with electrolyte. The slow diffusion of hydrogen through the bulk electrolyte, along with the relatively high ionic IR drop across this thick electrode will result in poor cell performance. As the interface recedes into the sintered electrode, there will be a greater degree of electrolyte film-catalyst surface-gas interface, and performance will increase. As this interface approaches the matrix, the diffusion of gas into, and water vapor out of, this sinter becomes the controlling factor, and again performance falls off. This discussion is not meant to imply any similarity between a nickel-cadmium cell and a hydrogen-oxygen fuel cell. It is only meant to illustrate how a cell can have a preferred amount of electrolyte for optimum operation.

An interesting series of experiments was carried out on a group of 36 individual cells of this type which illustrates several characteristics of groupings. Using a technique which is peculiar to the fuel cell industry and is not particularly germane to the discussion at hand, the optimum volumes of each one of these cells was determined.

Figure 2 shows the histogram of these results. The results, of course, show a considerable standard deviation or spread in the values of the optimum volume. These results are particularly significant in that fuel cells are filled as a group that are stacked together in a manner that results in each cell receiving approximately the same volume. This, of course, would result in some cells receiving more than their optimum amount and some cells receiving less than their optimum amount.

Before being able to discern whether this would result in acceptable or unacceptable performance of this particular grouping of cells, a second

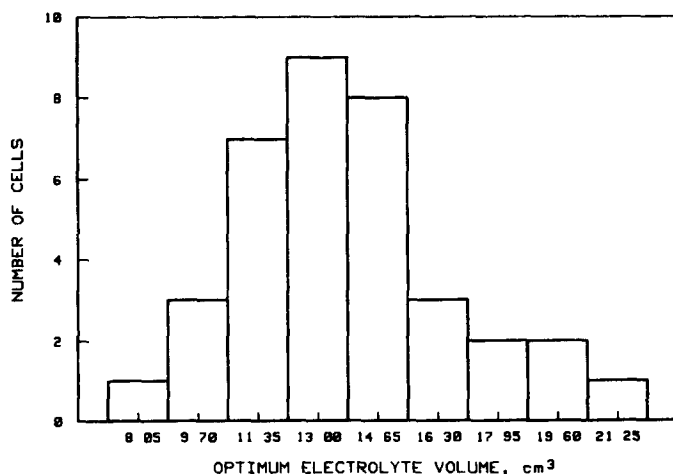


Fig 2 Distribution of optimum electrolyte volumes

characteristic called volume tolerance, must be known. As the name implies, volume tolerance describes the cell performance as a function of the electrolyte volume. In essence, the shape of the electrolyte volume *versus* cell performance curve is a measure of the volume tolerance of the cell. Without going into the details of the matter, it can be stated (and it should be obvious) that if the grouping of cells as shown in Fig. 2 were all filled with 13 cm³ of electrolyte, then three of the cells would be over filled whereas eight cells would be under filled.

The answer to this problem in the fuel cell industry was the invention of what was called the electrolyte reservoir [2]. The thick, nickel sinter electrode was replaced with a thin screen Teflon-catalyst type gas electrode similar to the oxygen electrode (Fig. 3). Placed behind the hydrogen electrode was a porous nickel sinter with a waffled pattern on it so that reactant gas could flow on the back side of the electrode while the sinter would also be in contact with it. Here again, the pore size and pore size distribution of each component is carefully selected so as to maintain proper electrolyte placement. The electrolyte reservoir has the largest pore size of wettable material so that it will freely accept and give up electrolyte as the cell undergoes temporary wetting or drying conditions. The electrodes themselves under normal conditions do not undergo any changes in their electrolyte volume; only changes in the electrolyte concentration as the water content temporarily is in excess of, or is less than, that value about which the control point is fixed.

Figure 4 is a plot of the volume tolerance characteristics of three different cell constructions that have been used over the years by IFC. The slanted straight line depicts the characteristics of the cells that employ the electrolyte reservoir behind the screen hydrogen electrode. The curve showing the intermediate degree of volume tolerance was the configuration described earlier with the thick sintered electrode. The cell construction showing a very minimal amount of volume tolerance was of yet an earlier level of technology. Cells with the widest degree of volume tolerance are the type used aboard the Space Shuttle. Groupings of these cells are much less affected by the stochastic aspects associated with groupings of individual cells.

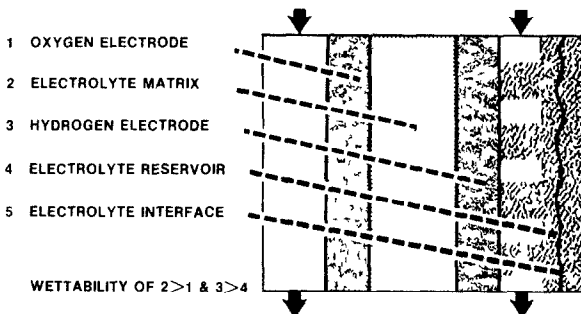


Fig 3 Fuel cell employing electrolyte reservoir

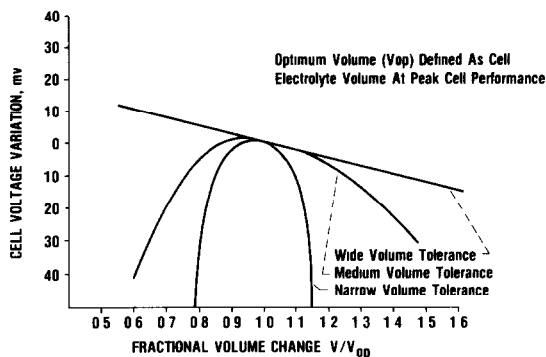


Fig 4 Cells constructed with different degrees of volume tolerance

Flooded-starved design for nickel-cadmium cells

It is likely that a nickel-cadmium cell has an optimum electrolyte volume associated with it. The optimum electrolyte volume in this case is related to the balance required between the cell ionic resistance and the gas recombination characteristics. Probably, among a grouping of cells there would be a certain distribution associated with the optimum volume values. When a group of cells is filled, some cells are probably overly filled while others are under filled. The growth characteristics of the nickel electrode, coupled with the chemical degradation of the nylon separator material in the KOH and oxidative environment, may result in a change in the cell optimum volume. What is suggested is to adopt, where feasible, some of the techniques used in the alkaline fuel cell field into the nickel-cadmium technology

Figure 5 shows a simplistic diagram of a nickel-cadmium cell that employs an electrolyte reservoir consisting of a wettable material with a pore size intermediate between the large, gas-filled pores and the small, electrolyte-filled pores of the separator. Even in well behaved nickel electrodes, there is an increase in the fine pore structure of the active material which would tend to draw electrolyte out of the separator [1]. If a reservoir were present it could yield up electrolyte as needed to replace the amount lost to the electrodes. The placement of the reservoir at the bottom is just meant to be illustrative. Depending on the pore size characteristics of the separator, the reservoir function could be performed by the separator itself. It should be noted here that there are driving forces other than capillary pressure (pore size) that come into play in these cells which need to be taken into account when doing an overall cell design. They include diffusional forces and migrational forces, and possibly some electro-osmotic effects. In nickel-cadmium cells in contrast to nickel-hydrogen cells, there is a greater amount of electrolyte volume change due to the water associated with the electrochemical reaction.

The steps involved in designing a flooded-starved cell might proceed as follows:

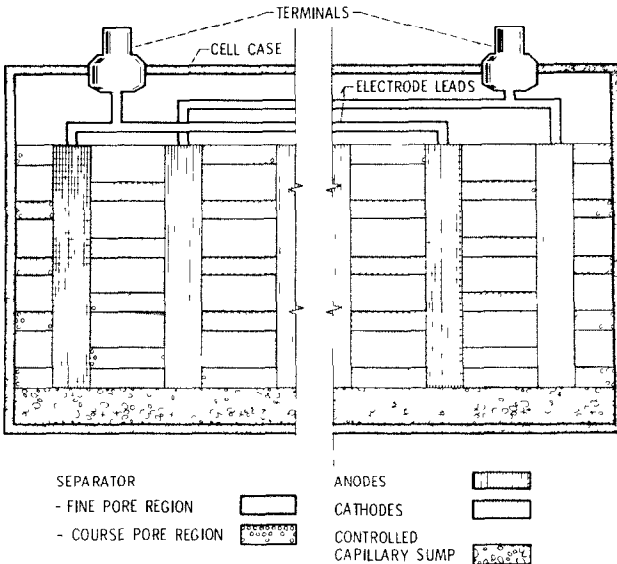


Fig 5 A flooded-starved design for nickel-cadmium cells

(i) Investigate the electrolyte volume tolerance characteristics of nickel-cadmium cells. This should be done both from an optimum volume point of view as well as a volume tolerance point of view

(ii) Investigate the stochastic aspects of the optimum volume characteristics so the degree of variance within a cell population can be estimated

(iii) Establish the net plate expansion characteristics (while under the pack compression) of both the nickel and cadmium electrodes

(iv) Establish the pore size and pore size distribution characteristics of the cell plates as a function of cycling, electrolyte composition, plate additive, etc

(v) Establish the pertinent physical characteristics of chemically stable, oxidation-resistant separator materials. These would include their compressibility-pore size distribution characteristics

(vi) Calculate the reservoir requirements so as to keep the cell(s) within proper electrolyte tolerance bounds over the expected lifetime of the cell(s)

Conclusion

A methodology for increasing or extending the useful lives of nickel-cadmium cells and batteries is suggested based on a somewhat analogous situation that was present in early technology, trapped electrolyte, alkaline fuel cells. The fuel cell industry was able to document and quantize the

problem. The solution came when the volume tolerance characteristics of the cells were widened. This same approach is suggested for first quantifying the problem and then gathering the required data to develop a modified nickel-cadmium cell design.

References

- 1 K M Abbey and L H Thaller, *Proc 17th IECEC, 1982, Vol 2, AIAA, New York, pp 757 - 764*
- 2 J. K. Stedman and C L Bushnell, Matrix-type fuel cell, *US Pat #3779811* (1973)