Principles for System Level Electrochemistry

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PRINCIPLES FOR SYSTEM LEVEL ELECTROCHEMISTRY

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SUMMARY

The higher power and higher voltage levels anticipated for future space missions have required a careful review of the techniques currently in use to preclude battery problems that are related to the dispersion characteristics of the individual cells. Not only are the out-of-balance problems accentuated in these larger systems, but the thermal management considerations also require a greater degree of accurate design. Newer concepts which employ active cooling techniques are being developed which permit much higher rates of discharge and tighter packing densities for the electrochemical components. A group of system level electrochemical principles are presented which can be applied to these newer concepts as a guide to their development.

INTRODUCTION

As cell electrochemistries are developed that are based on more highly energetic materials, the resultant devices are progressively more difficult to operate together in the form of a multi-cell battery. Fortunately most applications for electrochemical storage of energy require only a single cell, or at most, two cells connected in series and these cells are for the most part primaries. Applications requiring a number of secondary cells connected in series to form 12, 30, or 100 V batteries are rather rare but these have brought out a number of difficulties related to the relative states of charge of the reactive materials in each one of the many cells used within the battery. The older batteries, made from strings of Edison, Plante, or vented Junger cells were very forgiving relative to their electrochemistries and therefore capacity imbalance did not result in severe battery problems. Occasional additions of water made up for the electrolysis of the water portion of the electrolyte. Unfortunately the aforementioned cell types are not very high in energy density nor are vented cells useful for aerospace applications. Although much of the remainder of this paper will be addressing batteries for space applications, most of the principles are applicable to nonaerospace service. The main intent here is to describe the importance of thinking about all of the electrochemical reactions that take place within all of the cells that make up the battery. When the electrochemistry is viewed from the system standpoint, it will become more evident how one has to alter the design of the individual cells so as to allow them to operate more harmoniously when connected together as a battery.

There have surfaced a number of important applications for large battery systems. These applications (utility load leveling, electric vehicle, advanced aerospace missions) are of a nature such that newer, more energetic electrochemistries are required. A rather large number of electrochemical storage concepts have undergone various degrees of exploratory research, advanced development, or system demonstration over the course of the last several
decades. Several battery systems for terrestrial applications are currently undergoing serious economic examination to determine whether their already demonstrated electrochemical performance will result in a profitable item of commerce. In the aerospace field, nickel-hydrogen batteries based on the individual pressure vessel configuration of this electrochemistry are gradually displacing the market once held almost exclusively by nickel-cadmium batteries. In part, these newer electrochemical concepts have risen to a higher degree of interest because of what is referred to here as good system level electrochemistry.

This paper will put forward six semi-independent principles relating to battery systems. These principles will progressively address cell, battery and finally system related aspects of large electrochemical storage systems. They are intended to be guides towards the objective of minimizing the problems that are associated with the grouping together of a large number of individual electrochemical cells.

CELL ELECTROCHEMISTRY

A wide variety of rechargeable single cell types have been or are currently under development. The reader is referred to comprehensive texts on the subject (Linden, Editor, 1984) for a more in-depth treatment of the electrochemical and physical chemical processes taking place within these cells. The characteristics of interest in this treatment are related to the phenomenon that cause the gradual divergence in the relative states of charge of the reactive materials which act as the positive and negative electrodes. If for any reason the ampere hour efficiency of the desirable electrochemical reactions of the positive and negative electrodes are not the same, there will be a gradual divergence in the relative states of charge of the two electroactive materials. In like manner, morphological changes caused by repeated cycling as well as the solubility characteristics of the reactive material can also result in a gradual divergence within a single cell. At the battery level where the stochastic characteristics of the cell population become a part of the overall problem with repeated cycling, a gradual dispersion of net cell capacities develops. The power supply used to recharge large high voltage cell strings requires a certain degree of logic built into it so as to preclude possible damage to any one cell of the string due to inadvertent abuse of one of the cells. In the more sophisticated battery systems, not only is the charging process controlled but the discharging process and the temperature as well. Depending on the degree of sophistication required, each cell has its terminal voltage monitored and the total charge coulombs are closely controlled as is the ratio of charge to discharge coulombs. Engineering-type texts, symposium proceedings, and manufacturers' manuals provide an ample variety of circuits, protocols, and rebalancing techniques depending on the type of electrochemistry involved.

The first principle or general rule in the area of system level electrochemistry is to select a set of electrochemical couples that is forgiving in terms of being tolerant to being overcharged and overdischarged. Figure 1 illustrates this characteristic. The small circles at the end of charge and the end of discharge are meant to indicate that a noncatastrophic set of reactions take place at both ends of the curve following a well-developed signal voltage used to detect a desirable end of charge or end of discharge condition.
A positive-limited nickel-hydrogen cell is a good example of this. At the end of charge, the oxygen given off at the nickel electrode reacts chemically with the hydrogen to reform water. One needs to take care so as to not overheat the hydrogen electrode in the process. Suggested design modifications presented by Smithr1ck et al. (1984) would improve this situation. The overdischarge reaction is simply the evolution and consumption of hydrogen at the positive and negative electrodes, respectively. Even with the well-known nickel cadmium system, overdischarge can result in permanent damage due to the very slow recombination of the hydrogen evolved at the positive with the cadmium hydroxide. These cells are purposely designed to accept overcharge very readily. The evolved oxygen reacts with the metallic cadmium. Where aqueous systems are not used, then a greater degree of sophistication is required by the charging/discharging logic to preclude potentially undesirable situations. Otzinger (1984) describes a scheme whereby a string of five rechargeable lithium cells can be charged and discharged without adverse effects.

CELL PHYSICAL CHEMISTRY

Within any group of nominally like cells (Thaller 1981), it was shown that the closer they are together in terms of certain critical cell parameters, i.e., capacity, internal resistance, electrolyte content, etc., the more closely they will track together as a battery. Selection processes are carried out at the plaque, plate, and cell level by various manufacturers to help insure a properly operating battery pack. A recent paper (Kita et al. 1984) describes such a process as it relates to a population of sodium-sulfur cells.

A second principle thus refers to the matching or selection of cells so as to minimize these effects. It should go without saying that as the battery becomes larger and larger in terms of cells in series and strings in parallel, the problems related to population characteristics become more significant. Besides the processes of component and cell matching that are currently in common practice, a more concerted effort needs to be applied to the basic cell design so as to obviate as much as possible the compounding effects of placing cells together in the form of batteries.

The second principle then is to use existing post test analysis and component and cell population characteristics to first of all design a cell to operate properly within a multi-cell battery and secondly to use proper screening and selection processes in preparing a battery so as to preclude battery level problems. A brief discussion of this subject was presented at the 1985 Goddard Battery Workshop (Thaller, 1985).

BATTERY SYSTEMS

The attention thus far has been on what might be called traditional batteries wherein single cells are wired together to form a battery of the desired voltage level. More and more battery systems have been receiving attention, particularly for terrestrial applications. One of the first was the zinc-chlorine battery (Chi et al. 1979). This was followed by concepts based on zinc-bromine, hydrogen-chlorine, hydrogen-bromine, iron-chromium redox, and
hydrogen-oxygen. Figure 2 is one way of classifying these different battery concepts. The upper portion of the figure depicts the traditional secondary battery, along with a subsystem to carry away the waste heat. Certain battery systems are designed to operate at one particular temperature and since the round trip dc-to-dc energy efficiency is about 75 percent, a certain amount of waste heat must be disposed of. As battery packs become larger and the packing density is increased, the peaking power requirements are more important and the thermal management becomes much more of a critical issue. Whereas most older terrestrial batteries use only natural convection to carry away waste heat, aerospace applications require the use of passive cold plates. More advanced active cold plates are now in the design stage as well. The large lead acid battery systems used in the BEST test facility have been designed that use what may be called active cooling schemes (Delaney et al. 1984) using water-cooled terminals as a way of increasing the rate of heat dissipation.

The battery systems depicted in the center and lower portion of this figure have shown the potential for using active cooling within the cell stack. The battery systems that would be examples of the center type would be Zn-Cl₂, Zn-Br₂, bipolar Ni-H₂, etc. These storage concepts are typically complete packaged units with their own thermal control and monitoring subsystem. The cells are usually but not always connected together in a bipolar manner. What is common to this class of device is the flow of a reactant fluid and/or electrolyte through an assembly of cells. When the reactant fluids are pumped to a stack of cells, then the type of dispersion problems associated with the traditional battery is eliminated because the reactant is shared among all the cells. The states of charge of the positive electrodes where a circulating bromine solution is circulated among a group of perhaps 80 cells which are electrically in series and hydraulically in parallel are all the same providing the rates of flow to all the cells is about the same. The cell-to-cell type problems in these flowing reactant batteries become hydraulics problems rather than morphology problems. A side benefit of batteries with flowing electrolytes or reactants that is not too well appreciated is related to the excellent heat transfer and thermal control characteristics of this configuration. The cell stack resembles a well-characterized heat exchanger. Very high rates of heat transfer can take place in this configuration in comparison to traditional cells where pure conduction must take place from the cell plates to the cooling edge of a standard nickel-cadmum cell.Besides the high rates of heat transfer from this type of configuration, the scaling in cell size from one size or dimension to another becomes much more simple in comparison to a traditional cell.

The third principle relating to system level electrochemistry would suggest the use of electrochemical couples that lend themselves to being shared among all the cells of the battery system.

The fourth principle suggests the use of cells arranged in a bipolar manner wherein active cooling can be used. This principle relates to the ability of using the battery system over a wide range of power outputs and also to be able to scale up or down the size of the basic elements (cells) used in the battery stack. The work on the Zn-Br₂ system carried out in particular by the group at Exxon (Bellows et al. 1985) where versions for mobile applications were of interest brings out an appreciation for this fourth principle. The work of
that group also points up the fact that these more sophisticated electrochemical systems have their own peculiar set of problems.

Shunt currents are present in these types of systems and result not only in efficiency losses but can result in a gradual systematic redistribution of the zinc component of the battery. This same reference describes how the Exxon group has solved that problem by using their own version of system-level electrochemistry.

The third class of battery system depicted in the lower portion of Figure 2 is one where the electrochemical portion and storage portion of the overall system are independent of one another. In this class of electrochemical system, both reactants are common to all of the individual cells so there will be no difference in the state of charge of each individual cell because the state of charge is a function of the reactant material and not necessarily the cell. The cells that make up the electrochemical portion of the overall system must of course be designed and individual cells selected based on the physical chemical considerations as discussed earlier.

The Redox flow battery and the regenerative hydrogen-oxygen fuel cell are examples of this class of device. In the case of the Redox battery (Hagedorn et al. 1982), two tanks contain the two redox couples and they are pumped through an assembly of cells that are assembled together in a bipolar manner. The system power output is determined by the number of cells placed in series and the active areas of these cells. The storage capacity is of course determined by the volume and concentration of the reactant solutions. Here again electrical shunt currents are present due to the parallel flow of ionically conductive liquids within a high voltage stack of cells. Studies from this same reference have shown that this parasitic loss need not be more than several percentage points of the overall system output.

Another system of this class that has received a good deal of attention for the large storage system that will be required by the U.S. Space Station project is the hydrogen-oxygen regenerative fuel cell. In this concept as described by Hoberecht et al. (1984) a fuel cell stack and a water electrolysis stack work alternately to electrolyze water and electrochemically combine the resultant hydrogen and oxygen. Conceptually, one stack of cells could be used to perform the electrolysis as well as the fuel cell function of the system, but the current situation with the performance and life characteristic of the electrocatalyst is such that it is actually more desirable to use two separate stacks. The flexibility available to the storage subsystem design engineer is considerable. He is at liberty to independently select the current density and the capacity. With the more traditional type of cell wherein there are practical limits associated with plate thickness, long duration discharges are coupled with low current densities for charging and discharging. Low current densities do result in highly efficient discharges, but for certain electrode types where the coevolution of oxygen is present, efficient recharging does not take place at low current densities.

The alkaline fuel cell as described in a U.S. Patent (Bushnell and Stedman, 1973) overcomes much of the influence of the stochastic aspects of the cell populations that go into making nominally 32-cell stacks as used aboard the Space Shuttle.
A fifth principle would state that the most conceptually flexible electrochemical concept will permit the highest degree-of-freedom for the design engineer. Concepts with independent storage and actively cooled electrochemical stacks that are arranged in a bipolar manner represent this high degree of freedom. The energy density value that is associated with, for example, regenerative fuel cell is very much a function of the specific application under consideration. The energy density value is made up of the storage as well as the power producing portion of the overall system. For a high power, low energy application the overall weight would be dominated by the stack related portion of the overall system, whereas for a low power (small stack), high energy (large tanks) application the overall weight would be dominated by the storage portion of the system.

A case in point is the primary fuel cell system and associated tankage and plumbing used aboard the Space Shuttle. The electricity is generated by three power plants, each of which has three substacks of about 30 cells. The total weight of these three power plants is about 750 lb. The weight for the empty tanks is about 1325 lb and the plumbing between the tanks and the fuel cells about 1300 lb. The weight of the reactants is 2600 lb. The electrical energy that can be delivered by this power system is about 2.5x10^6 Wh. The sum of the weights is about 6000 lb. This would result in an energy density of the system of 420 Wh/lb or 925 Wh/kg. An actual energy density value over the first 8 flights averaged 300 Wh/lb (660 Wh/kg) due to the fact that the mission ended prior to the usage of all of the hydrogen and oxygen.

In essence then, this electrochemical system functions as a very high energy density primary battery. The energy density values for these types of systems can vary well over an order of magnitude depending on the specific application.

**ACTUAL APPLICATION CONSIDERATIONS**

Figure 3 is meant to depict an overall power system as would be used for an aerospace application. Here the battery (energy storage subsystem) is just one portion of the overall power system. The solar array, power processing, and heat rejection functions make up the remainder of the system. The dashed lines associated with the solar array and the radiator imply that they must be sized according to the characteristics of the specific system under consideration. A typical operating temperature for a nickel-cadmium battery is 0 °C to 10 °C and its electrical efficiency is about 80 percent. The weight of the power processing portion of the system that can be assigned to the storage portion depends on the degree of complexity associated with it. Early charge control circuits were very crude and grossly abused the battery resulting in reduced life. Highly sophisticated circuits exist whereby individual cells can be switched out of the circuit if they develop a shorted condition. Regenerative fuel cells based on state-of-the-art hardware have a lower efficiency compared to nickel-cadmium or nickel-hydrogen cells (larger solar array) but would have a smaller radiator due to the higher heat rejection temperature. The orbit (dark-light durations) to be used for the space station would result in about 36 min of darkness and 59 min of light. A module size in the range of 20 to 50 kW is currently under consideration. All of these specifics permit what is referred to as a point design to be made. For any particular application a point design permits a proper comparison to be made between different competing technologies.
The sixth principle would state that in order for a proper comparison to be made, the complete power system must be designed based on the specific application (capacity, power, and duration) under consideration. The objective of the complete power system may or may not be minimum weight. The drag considerations associated with large solar arrays are such that battery system efficiency may well be more important than subsystem energy density. Figure 4 shows some preliminary results generated several years ago to illustrate some of these last points. The weights associated with the individual components were estimated to see which technology (if any) appeared most desirable for a Space Station type application. The general conclusion of this unpublished study was that nickel-cadmium batteries are too heavy. Most of the other technologies which are at various stages of development are not significantly different from one another to make any accurate projections as to ultimate, overall best system from an energy density point of view.

SUMMARY

It is seen that when an actual application for electrochemical energy storage is considered, a variety of principles comes under consideration. These principles cover a disjointed spectrum of scientific disciplines so that, although separately each one of these six principles is rather elementary, very few people have occasion to view all of them at the same time. They are not intended to represent a complete listing but represents a set of considerations the author has found to be important based on his experience in the field. These principles involve at least in part the electrochemistry and physical chemistry of the battery of interest. Beyond that, they involve considerations relative to system concepts and configurations, design flexibility, and the feasibility of active cooling to be incorporated with the electrochemical stack. The final and most important consideration is related to a suggested method of accurately and fairly comparing one candidate to another.

These principles as they relate to electrochemical systems in reality are attempts to consider all parts (cells) of the system at the same time and yet also in an ongoing sequencing of time. The term system level electrochemistry comes as close to capturing the essence of these thoughts as is necessary.

A summary then of these principles is as follows:

1. Select a set of reactants that result in a forgiving electrochemical situation when considering the possible overcharge and overdischarge that will take place in a large battery system over the course of its expected useful life. In cases where this is not possible, as with most of the higher energy density couples, a more sophisticated charge and discharge controller must be traded off against this increase in cell level energy density.

2. Use existing post test analysis and cell population characteristics to design a single cell that will be tolerant toward slight variations from cell to cell. This is primarily a physical chemical task related to plate and separator design, screening, and selection.

3. Use electrochemical couples that lend themselves to being shared among the entire grouping of cells in the electrochemical stack. This trades the
morphological for the hydraulic problems of an electrochemical system and dis-
persion problems of a battery pack. It is felt that the hydraulic problems are
the more tractable than the other two.

4. Use the bipolar arrangement of cells that are amenable to active cooling
to increase the voltage efficiency and the peaking capability of the device.
This arrangement also facilitates the scaling of the basic cell size to ones
that are larger or smaller without significantly affecting the overall thermal
characteristics.

5. Select a system that permits the independent sizing of the storage por-
tion and the power producing portion of the overall system. This, coupled with
active cooling between cells arranged in a bipolar manner, results in the most
versatile, flexible storage system.

6. Carry out a point design of the complete power system including (for the
case of a space application) the solar array, power processor, and space rad-
lator for each one of the competing systems to get a more accurate idea of the
overall system weights and areas. It is this final overall system which will
eventually be used.

In this entire discussion, no mention was made of the energy density that
results from using these different design principles. It is left to the reader
to start with the suggested energy densities as proposed by the cell manufac-
turers and then successively apply these principles to see what a practical
energy density for an energy storage system might be. For example, a typical
50 Ah nickel-cadmium single cell has an energy density of about 40 Wh/Kg. When
used in a battery this number is reduced to about 6 Wh/Kg to account for the
fact that deep depths of discharge do not result in long life, cells must be
firmly held together with end plates and tie bolts to preclude bulging due to
the oxygen pressure with the cells, cold plate, and battery charge control
features must be accounted to the battery. The more advanced concepts which
can take advantage of the potential offered using systems which comply with
the more sophisticated principles (3, 4, and 5) should not only have high
energy densities, but should be more versatile and capable in meeting high
peak load requirements.

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8


Figure 1. - Schematic of desirable single cell charge/discharge characteristics.

Figure 2. - Three different classes of electrochemical storage systems.
Figure 3: Components of a large space power system.

Figure 4: Power system mass breakdown by major subsystem.
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