

Progress Towards Computer Simulation of NiH₂ Battery Performance Over Life

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The long-term performance of rechargeable battery cells has traditionally been verified through life-testing, a procedure that generally requires significant commitments of funding and test resources. In the situation of nickel hydrogen battery cells, which have the capability of providing extremely long cycle life, the time and cost required to conduct even accelerated testing has become a serious impediment to transitioning technology improvements into spacecraft applications. The utilization of computer simulations to indicate the changes in performance to be expected in response to design or operating changes in nickel hydrogen cells is therefore a particularly attractive tool in advanced battery development, as well as for verifying performance in different applications.

Computer-based simulations of the long-term performance of rechargeable battery cells have typically have very limited success in the past. There are a number of reasons for the lack in progress in this area. First, and probably most important, all battery cells are relatively complex electrochemical systems, in which performance is dictated by a large number of interacting physical and chemical processes. While the complexity alone is a significant part of the problem, in many instances the fundamental chemical and physical processes underlying long-term degradation and its effects on performance have not even been understood. Second, while specific chemical and physical changes within cell components have been associated with degradation, there has been no generalized simulation architecture that enables the chemical and physical structure (and changes therein) to be translated into cell performance. For the nickel hydrogen battery cell, our knowledge of the underlying reactions that control the performance of this cell has progressed to where it clearly is possible to model them. The recent development of a relatively generalized cell modeling approach¹ provides a framework for translating the chemical and physical structure of the components inside a cell into its performance characteristics over its entire cycle life. This report describes our approach to this task in terms of defining those processes deemed critical in controlling performance over life, and the model architecture required to translate the fundamental cell processes into performance profiles.

Model Architecture

The general architecture for the modeling method employed here has been described in detail in Refs. 1 and 2. This modeling approach breaks a nickel hydrogen cell into a number of finite elements that encompass all internal cell components and materials.² These include gas spaces, wall wicks, nickel electrodes, separators, and hydrogen electrodes. The reagents that move through these components are electrolyte, hydrogen gas, and oxygen gas. These materials move throughout the cell under the combined forces of migration, convection, capillary pressure, and diffusion.

The performance of the nickel electrode, which typically limits cell life, is critical in defining

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performance over life. The nickel electrode model used here is based on the finite element model described in Ref. 1. This model describes the active material in the nickel electrode as a porous deposit within pores of a given diameter in a nickel metal substrate. Charge transport is allowed by movement of holes and protons in the solid active material grains, and movement of ions in the electrolyte. The charge transfer processes considered at the interface between the active material grains and the electrolyte include oxidation of β -Ni(OH)₂, oxidation and reduction of β -NiOOH, reduction of γ -NiOOH, oxidation and thermal decomposition of α -Ni(OH)₂, oxygen evolution from both β -NiOOH and γ -NiOOH, and the reaction of hydrogen gas with the charged materials. At the interface between the sintered nickel substrate and the active material, corrosion of nickel is allowed, as well as catalytic oxidation of hydrogen gas and catalytic reduction of oxygen gas.

Models that have been previously utilized to describe the nickel electrode^{1,3} are based on a one dimensional layer of active material placed in contact with a substrate surface. While this is clearly an excellent local description of the physical structure of the nickel electrode, as indicated in Fig. 1 there is a wide distribution of layer thicknesses and substrate structures occurring in real nickel electrodes. We have found that there are significant performance differences between the results from model simulations for the realistic structure of Fig. 1 and the simplistic one-dimensional approach that has been used in the past. As indicated in Fig. 2, a model based on the 3-dimensional structure cross-sectioned in Fig. 1 provides much more realistic charge behavior, particularly charge efficiency as the fully charged state is approached, than does the idealized one-dimensional model. Thus, a key aspect of simulating performance over life is to include in the simulation the real structure of the sinter substrate, as well as all other cell components. It is not realistic to expect a model to be capable of predicting performance over life without also providing that model a complete description of the internal structure of all cell components. Thus, a three-dimensional model of the pores within the nickel electrode will be used in this study. The structure of these pores will be measured from actual nickel electrodes of the same type as those being simulated in the operating cells.

Degradation Modes

The model described in the above paragraphs has been demonstrated^{1,2,4} to be capable of accurately predicting cell performance for any specific structures within the nickel electrodes or the nickel hydrogen cell. Thus, the remaining task in simulating performance over life is to predict how the chemical and physical structure of the internal cell components change over life. The degradation modes that will be focussed on in this study involve the nickel electrode and are: (1) substrate corrosion, (2) active material phase changes, (3) substrate swelling, (4) active material extrusion, (5) electrode cracking, and (6) short-circuiting through the separator. The rate of each of these degradation processes will be based on the underlying driving forces for the processes, such as voltage, density changes, pressure differentials, and chemical gradients.

Substrate corrosion is assumed to be occurring on a passivated nickel surface, on which the rate of corrosion is linearly dependent on the voltage. In addition it is assumed that the volume changes from oxidation and reduction of the oxides on the nickel surface will periodically fracture the passivation layer. Thus, corrosion will occur over the surface area of the sintered substrate at a rate proportional to the active material voltage at the interface with the substrate, and also at an additional rate proportional to the changes in density of the active material immediately adjacent to the metal surface. In this model, the layer of active material immediately adjacent to the sinter is about 100

Angstroms thick. Sinter corrosion will decrease substrate area, increase active material density near the substrate, decrease cobalt additive levels near the substrate, increase electrolyte concentration, and increase cell hydrogen pressure. The increase in active material from corrosion can, in some instances, cause increased capacity to be available in the nickel electrode. The model described above will be used to determine the combined effect of all these changes on performance when a realistic three-dimensional sintered structure is used.

Phase changes in the nickel electrode active material will occur during the simulation process in response to gradients that develop in electrolyte concentration, temperature, and potential through the cell. The electrochemical reactions discussed above and programmed into the nickel electrode simulation module will assure that the different phases will interconvert during cycling in the manner expected in a real battery cell.

Nickel electrode swelling will be allowed to occur at a rate based on the difference between the positive and negative forces normal to the electrode surface. Forces that drive swelling are expansion of active material during discharge or phase changes, and electrolyte hydrodynamic forces, and gas pressure differentials. The swelling of the electrode structure will be based on the magnitude of these forces that are calculated by the model, along with the mechanical strength properties of the electrode itself. Swelling within each element of the electrode will be assumed to occur via a homogenous expansion of the three-dimensional structure of the sinter.

Active material extrusion will be driven by essentially the same forces as nickel electrode swelling, but is based on the elasticity of the active material. Additionally, the active material will be allowed to extrude not only from one element into another within the nickel electrode, but into the separator as well. Extrusion of active material into and through the separator can produce short circuit paths, with the short circuit current being dependent on the resistivity of the active material. In a properly constructed nickel hydrogen cell, such short circuits are probably the ultimate failure mode, since they can cause the cell state of charge to drop below that needed to sustain cycling. The physical extrusion of active material from the sintered substrate will result in a decrease in available active material for charge discharge cycling.

Cracking of nickel electrodes can occur as a result of swelling if the sintered structure is forced past its yield point, or if corrosion etches away interconnecting metal. For this approach to effectively model cell capacity loss due to cracking of the sinter structure, the cumulative deformation forces in the sinter structure relative to the force needed to cause separation of the sinter must be modeled. The plan at present is to track these forces as the sinter structure is allowed to swell, and to adjust the conductivity paths to reflect separation of the conductive matrix. Cracking of the conductive matrix will force more current to be carried through the active material, thus will result in earlier depletion and lower utilization.

Present Degradation Model Status

The present life cycle degradation model consists first of a three dimensional cell model, that includes a three dimensional microscopic model of the nickel electrode. The nickel electrode model, which is most critical to modeling the performance of the nickel hydrogen cell, can track the formation of different active material phases through the cell stack (or stacks), the charge efficiency, the self-discharge, and the voltage vs. capacity behavior during cycling if it has the physical and chemical state of the internal cell components well defined. The second part of this life cycle model

defines how the physical and chemical state of the internal cell components are to be adjusted as the cells cycle. This portion of the model is now under development, with the adjustments in sinter structure due to corrosion having been put into a preliminary simulation model. This preliminary model is consistent with about 40% corrosion of a typical sinter structure after 40,000 LEO cycles at 80% depth of discharge. The various degradation modes discussed above are each being developed as individual modules that are capable of making small adjustments to the state of the cell components after each cyclic interval.

The computational approach used here for simulating a nickel hydrogen cell life test is to utilize two work-stations. These networked work-stations will be programmed to run a cell model through a life test, periodically calculating updated cell performance and stress forces. The stress forces are used to adjust the physical and chemical state of the cell components, with these adjustments being typically 0.1 to 1% over a cyclic interval. Cyclic intervals would vary according to the rate of change of cell performance parameters. Early in the cycling the computers will update cell performance every few cycles, while after thousands of cycles, 10-100 cycles may be allowed to elapse between computational updates. When the cell begins to fail after extensive cycling, computational updates will again be performed relatively frequently. This approach is expected to give a full life test in about 1 month of time using a two-processor approach, assuming that individual cycles can be run at about a real time rate (as suggested in preliminary calculations).

Conclusions

An approach to simulating a life test of a nickel hydrogen battery cell in a computer system has been outlined. This approach is based on two key elements. The first of these is a model of the nickel hydrogen cell that can very accurately predict performance from a detailed knowledge of the physical and chemical states of the internal cell components. This first element is now largely developed and ready to integrate into a life test simulation. The second key element is a degradation model that utilizes internal stresses and forces that are obtained from the dynamic cycling of the cell model, to periodically adjust the physical and chemical state of the cell components to reflect the key degradation processes. While at present the second part of this effort is not fully developed, we are confident that this general simulation approach can successfully be used to follow and predict the performance of battery cells during their operational life. We anticipate applications of this approach to the characterization and validation of design advances, the design of power systems, and the operational management of nickel hydrogen batteries in spacecraft power systems.

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**Figure 1. Cross Section of Nickel Sinter
Showing Metal As White Regions**





