High Charge And Discharge Cycle Durability Of The Sodium Sulfur (NAS) Battery

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Abstract

The Tokyo Electric Power Company (TEPCO) and NGK Insulators, Ltd. (NGK) have made the decision to launch commercialization of sodium sulfur (NAS) batteries in April 2002. This decision stems from their extensive joint development, testing and demonstration programs. At this time, superior performance characteristics have been confirmed, including durability in cyclic applications and the predictability of important degradation mechanisms. This paper reports on the observed durability of NAS performance, with emphasis on the bases for NGK's confidence in the ability to predict capacity and efficiency degradation.

1. Introduction

Since 1984, TEPCO and NGK have been jointly engaged in developing the NAS battery energy storage system for peak-shaving and electricity supply stabilization applications in Japan. The NAS battery uses a beta-alumina ceramic tube as the solid electrolyte and separator between sulfur and sodium electrodes, and it operates at about 300C to maintain the electrodes in a liquid state. The Open Circuit Voltage (OCV) of NAS cells is about 2V, and cells are configured in series/parallel arrays within a stainless steel, vacuum insulated enclosure to form a battery module. Our current product is rated at 50kW and 360kWh.

NGK's NAS battery development program advanced in three major stages: 1) Improvement of beta-alumina tube strength, resistivity, and manufacturability; 2) Development of the NAS cell and battery module designs, and 3) Optimization of energy density, performance, and life parameters. A critical aspect at arriving at an optimal design was understanding the mechanisms of degradation and acquiring the ability to predict changes in performance over the life of the battery. Such knowledge permits unncessary material margins to be eliminated, which improves both electrical performance and energy density. Combined with nearly 30MW of commercial-scale field tests, it fortifies the decision to proceed with commercialization. At this time, we have evolved a design capable of high pulse power that can be cost effectively adapted to combined short-term power quality and peak shaving applications, as well as to the original peak shaving application.

2. NAS Battery Requirements

The data in Table 1 illustrate the evolution of NGK's NAS cell designs. Cell size is limited by the capability to manufacture the beta-alumina tube. A decade of work has brought forth a factor of almost 4 improvement in cell capacity and a 45% increase in energy density. These achievements have led to lower costs and better space utilization for NAS battery users.

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Table 1. Evolution of NAS Cell Capacity and Energy Density

Year		1992-	1995-	1999-
Cell	Cell Design	T3-T4.1 Cells	T4.2 Cell	**Commercial T5 Cell**
	Size [mm]	62(dia.) 376(H)	68(dia.) 391(H)	**91(dia.) 521(H)**
	Capacity [Ah]	To 160	248	**632**
Battery Module	Power [kW]	12.5	25	**50**
	Cells /Module	336	480	**320**
	Size [m]	1.0 (W) 1.9(D) 0.5(H)	1.4(W) 1.9(D) 0.5(H)	**2.2(W) 1.7(D) 0.6(H)**
	Energy Density [kWh/m^3]	110	145	**160**

The specifications of NGK's 50kW NAS battery are listed in Table 2. It is designed to deliver 360kWh per cycle at 81% DC efficiency after 15 years and 2500 charge/discharge cycles.

Table 2. 50kW NAS Battery Module Specifications

Energy Capacity	360kWh (After 2500cycles)
DC efficiency / initial	87% (without rectifier,inverter & heater)
/ after 2500cyc	81% (without rectifier,inverter & heater)
Operating temperature	300degree C
Shelf Life	15years
Cycle life	2500 (100%DOD)

3. NAS Battery Degradation
3.1 Degradation Mechanisms

Figure 1 illustrates changes of cell performance. The increase in charge, and decrease in discharge, voltage caused by increased resistance after 2500 cycles (solid lines) may be compared with initial values (dashed lines). Increases in cell resistance degrade both cell capacity and efficiency. As shown in the figure, efficiency loss is caused by the increase in cell ohmic resistance, while capacity loss is caused by the increase of charge end resistance.

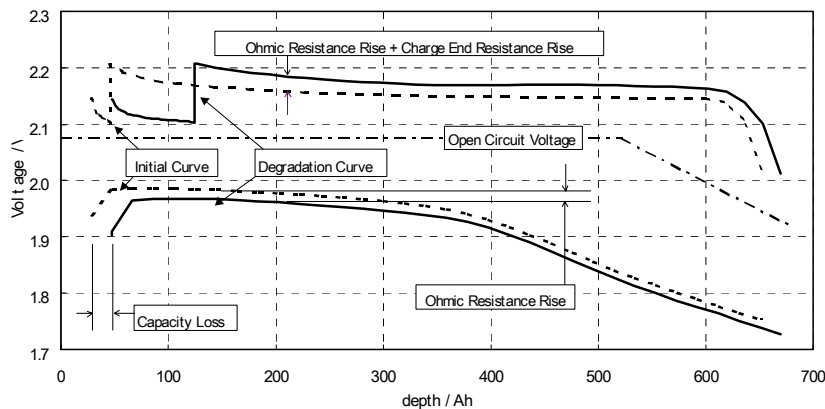**Figure 1. Changes in the Resistance and Capacity of NAS Cells**

Figure 2 shows details of cell construction as well as the electron flow path through the sulfur container to the electrode. Note that a protection layer is deposited on the inner surface of the sulfur container to inhibit corrosion.

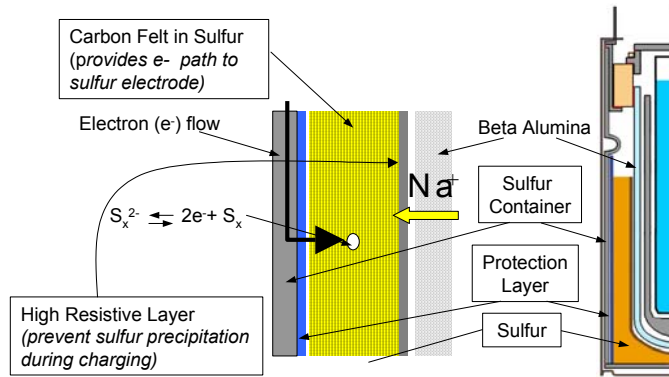**Figure 2. Details of NAS Cell Construction**

Figure 3 illustrates the relationship between the materials selected for the protectioin layer and the corresponding increase in cell resistance. These results led to the selction of Fe70Cr for the protection layer.

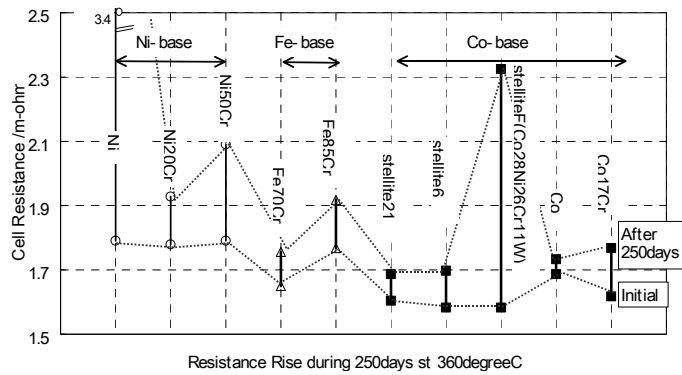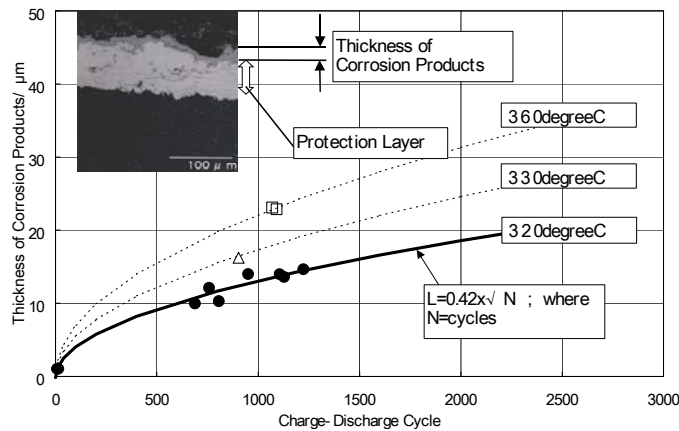**Figure 3. Protection Layer Materials vs Resistance Increase**

Figure 4 shows the relationship between the change in thickness of corrosion products versus operating cycles. As expected, the rate of corrosion product growth decreases with time (i.e., in accordance with the parabolic law for diffusion.)

Figure 4. Corrosion Growth vs Operating Cycles

The mathematical relationship between corrosion thickness, L, and the number of cycles may be written as $L=0.42 \times \sqrt{N}$; where N equals the number of cycles. This data also allows the coefficient of resistance

formation, ρ, to be derived from the relationship, $R = \rho \times L/S$, where:

R = cell resistance rise

S = surface area (determined by the cell design)

L = thickness of corrosion products (post test measurement)

The foregoing analysis yields ρ equal to 130 ohm-cm. Using this relationshp, the calculated curve for corrosion thickness versus cycles shown in Figure 5 is obtained. The strong correlation between measured and calculated values confirms that resistance increase is determined by corrosion products.

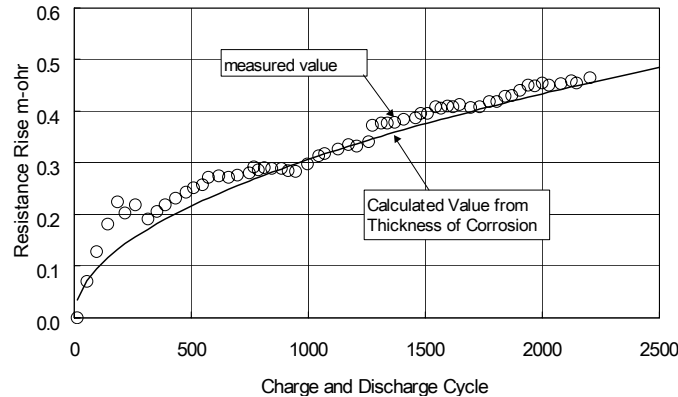**Figure 5. Measured and Calculated Resistance Increase with Operating Cycles**

Figure 6 shows an X-ray CT image of a NAS cell cross section. This figure shows that dissolved corrosion products have collected at the highly resistive layer placed on the outer surface of the beta alumina tube to prevent sulfur deposition at the end of the charge cycle. The presence of the corrosion products increases the conductivity of the highly resistive layer (i.e., degrades its performance) enough to cause sulfur deposits to form. These deposits affect charge end resistance; hence, cell capacity.

**Figure 6. X-ray CT Image of NAS Cell Cross Section**
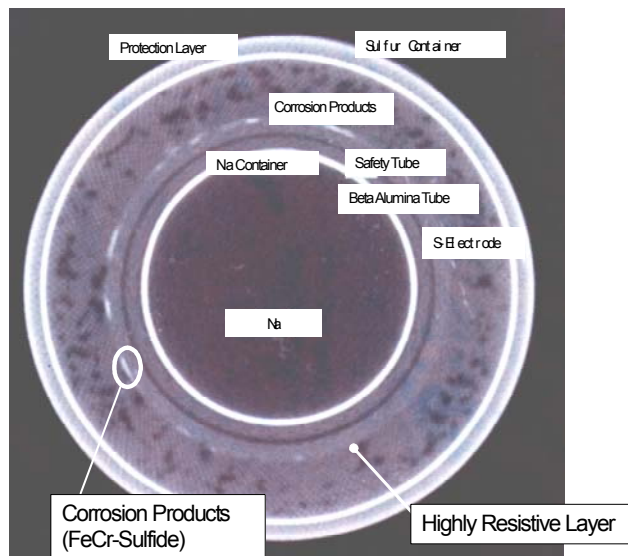
3.2 Accelerated Cyclic Durability Tests

Figure 7 shows the results of accelerated cyclic durability tests in which the energy of each cycle is kept the

same (e.g., 160Ah discharge per cycle) and the frequency is increased (e.g., 8-hr per cycle instead the standard 16-hr per cycle). Accelerated cyclic testing conducted in this manner requires that the electric current (i.e., the power) be increased in proportion to the increase in frequency. As shown in Figure 7, after 7000 charge/discharge cycles, capacity loss is only 7%, and efficiency loss is only 1%.

**Figure 7.** **Degradation Under Accelerated Cyclic Testing Conditions**
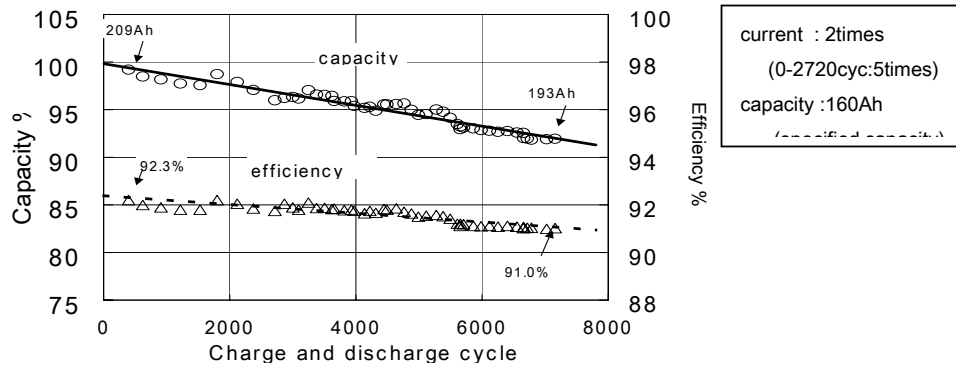
Figures 8 and 9 show the comparison between the standard cyclic rate, corresponding to 20A for 8 hours and the accelerated rates corresponding to 40A and 100A for 4 and 1.6 hours, respectively. In Figure 8, data are plotted with respect to the number of charge/discharge cycles that have been imposed. In Figure 9, data are plotted with respect to the charge/discharge time interval in which time spent in standby mode is excluded. The close correlation between standard and accelerated rate data in Figure 9 confirm that degradation is determined by the duration of charge and discharge intervals, and not by the number of charge/discharge cycles.

Figure 8. **Degradation vs Charge/Discharge Cycles**
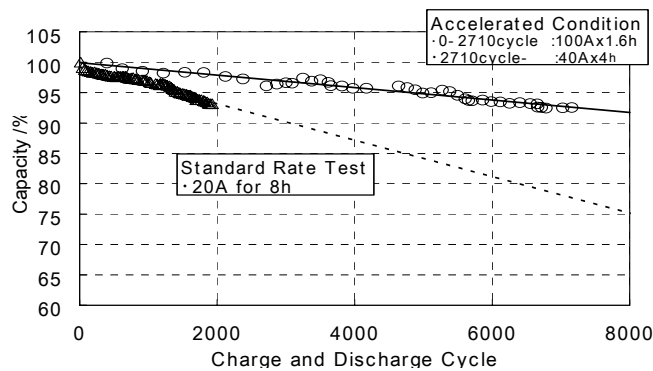
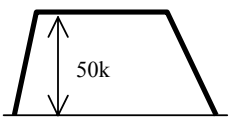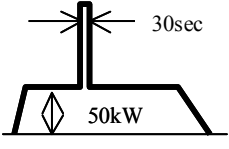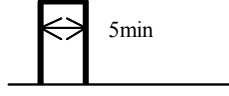**Figure 9. Degradation vs Charge/Discharge Time Interval(Standby Time Excluded)**
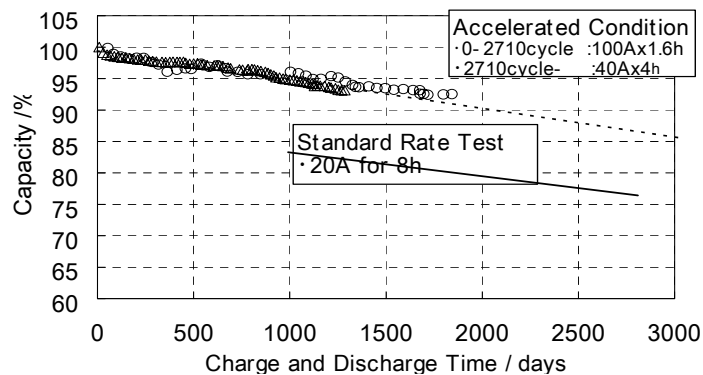
4. Summary & Conclusions

Tests of NAS cells and batteries have shown that degradation of both capacity and efficiency are determined by corrosion mechanisms at the sulfur electrode. Specifically, corrosion products formed on the protection layer on the sulfur container cause cell resistance to increase, effecting efficiency, and corrosion products dissolved into the highly resistive layer on the beta-alumina tube cause an increase in end of charge resistance; hence, capacity loss. These corrosion mechanisms are dependent on the duration of exposure to current, e.g., the total time in charge and discharge operating modes, and the normal operating temperature. These corrosion mechanisms are NOT dependent on the magnitude of current (power level) or the cumulative number of charge-discharge cycles. This makes the battery well suited for power quality applications requiring 3 to 5 times nominal power in combination with peak shaving.

Further, the rate of degradation does not change dramatically with time or after 2500 cycles. Using NGK empirical methods and extensive test data, degradation is predictable for a variety of application duty cycles, including those in Table 3.

Table 3. NAS Battery Application Duty Cycles

Application	Duty Cycle Profile	Max Power [kW]	Capacity [kWh/PS cycle]	PS Cycle Life
Peak Shaving (PS)	50k	50	360	2500
Peak Saving + Power Quality	30sec 50kW	150	360	2500
		180	150	5000
		250	150	2500
Standby Power Quality	5min	250	NA	NA

The knowledge of degradation mechanisms has enabled NGK to optimize the battery design and to reduce unnecessary material margins. This leads to the enchanced performance, better space utilization and lower costs. In addition, such knowledge gives us confidence in our products.