Component Variations and Their Effects on Bipolar Nickel-Hydrogen Cell Performance

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Abstract

A 50 cell bipolar nickel-hydrogen battery was assembled to demonstrate the feasibility of constructing a high voltage stack of cells. Various component variations were tested in this battery. The battery had approximately 1 ampere-hour of capacity and was constructed from components with an active area of 2" x 2". The components were parametrically varied to give a comparison of nickel electrodes, hydrogen electrodes, separators, fill procedures and electrolyte reservoir plate thicknesses. Groups of five cells were constructed using the same components; ten combinations were tested in all. The battery was thoroughly characterized at various change and discharge rates as well as with various pulse patterns and rates. Over a period of 1400 40% DOD LEO cycles some of the groups began to exhibit performance differences. In general, only separator variations had a significant effect on cell performance. It also appears that shunt currents may have been operating within the stack, resulting in electrolyte transfer from one cell to another, thus contributing to cell performance variations.

Introduction

A 50 cell nickel-hydrogen battery that employs the bipolar design and assembly techniques pioneered at the Lewis Research Center has been built, characterized, and tested under a pulse regime and a 40% DOD LEO cycle regime. This high voltage battery, 65 volts, was built of subscale size cell components having an active area of 2" x 2", and a capacity of approximately one ampere-hour. This battery was assembled to demonstrate the feasibility of constructing and testing a high voltage stack of cells without experiencing unacceptably high shunt current losses.

Since the bipolar technology is a relatively new one when applied to the nickel-hydrogen system there are many unanswered questions concerning component variations and construction techniques. We therefore took this opportunity to evaluate the effects of component and constructional variations on cell performance in a stack of cells that would be subjected to the same cycle conditions. The components were parametrically varied to give a comparison of nickel electrodes, separators, hydrogen electrodes, fill procedures, and electrolyte reservoir plate thicknesses. No attempts were made to limit electrolyte paths and subsequent shunt currents. Groups of five cells were constructed using the same components, ten combinations were tested in all. The battery was thoroughly characterized at various charge and

discharge rates. Pulse discharge characteristics were also evaluated varying from one second on and one second off to five seconds on and twenty seconds off. The pulse currents ranged from 5 amperes to 10 amperes (5C to 10C). The battery was cycled on a low-earth-orbit regime at 40% depth of discharge. During the testing, groups of five cells began to exhibit variations in performance. After 1500 cycles the battery was disassembled. It is presently undergoing extensive post test analyses in an attempt to identify reasons for the variations observed in cell performance.

Component Variations and Construction Details

The 50 cell stack was constructed with subscale size hardware. The general construction techniques and design details are similar to those used for the larger capacity stacks (6.5 and 40 AH, 10 cell stacks) constructed earlier [1,2,3]. A sample of the cell components is shown in figure 1. The components used in the stack were those available from previous purchases from several vendors. None of the components was made
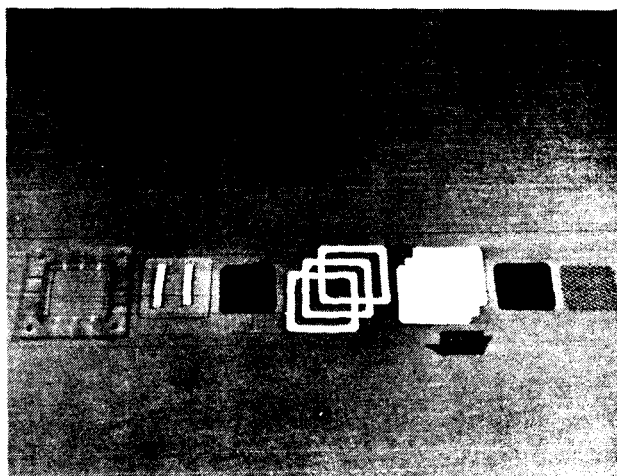

FIGURE 1
CELL COMPONENT LAYOUT

specifically for this application. The frames used for this battery had been intended for use in the screening of components and design features for bipolar stacks. The following is a summary of the components and procedures evaluated in the

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50 cell stack:

Nickel electrodes- 40 mil electrochemically impregnated nickel electrodes from Yardney Battery Division and Eagle Picher Industries were evaluated in the test matrix.

Hydrogen electrodes - Two types of hydrogen electrodes were evaluated. Both were bipolar type electrodes in that they consisted of a mixture of platinum and teflon applied to a screen, with no Goretex layer on the backside of the electrode. Electrodes from Life Systems Incorporated (LSI) and Yardney Battery Division were tested. Those from LSI had a gold plated nickel screen as the current collector and those from Yardney used a fine mesh nickel screen.

Separators - Two layers of zircar cloth, three layers of beater treated asbestos (BTA) and a combination consisting of one layer of beater treated asbestos and one layer of zircar cloth were the variations of separators tested. In the cells with the combination separator the zircar was towards the nickel electrode to aid in gas management.

Electrolyte reservoir plates - This stack was built with available frames from another project. As a result the frame thickness varied from 150 to 245 mils. The ERP's were individually sized to accommodate the variations in frame thickness. The ERP thickness varied from 50 to 140 mils. Foammetal from Astromet was used as the ERP. The original material was approximately 120 mils thick, for most cells one layer was compressed to the thickness that would result in the desired compression in the cell. In one group of five cells two layers were required to give the desired thickness. ERP thickness was not expected to have a noticeable effect on cell performance but the experiment was designed to allow evaluation of this variable.

Fill procedure - The separators either were vacuum-filled prior to incorporation into the stack or filled with a predetermined amount of electrolyte, based on tests of their retention capabilities, during construction. Similarly, at the time of their insertion into the stack, the electrolyte reservoir plates were filled with a predetermined amount of electrolyte based on studies of their retention characteristics. The electrodes were all vacuum filled and allowed to drain before assembly into the stack. The group of five cells with BTA separators that were to be vacuum filled was constructed dry, then immersed in electrolyte and vacuum backfilled because the BTA does not have enough strength to be handled and incorporated into a cell once wet with KOH. This allowed a comparison between vacuum filling the separators and the addition of a metered amount which is referred to simply as 'fill'.

Gas screen - The gas screen used in all 50 cells was Exmet 5 Ni 35 1/0, with a 60 mil nominal thickness. This material was compressed to 40 mils before stack construction.

Frames - The frames from the 2" x 2" bipolar component evaluation program were used for this test. The frames were made of polysulfone. Frame thickness varied from 150 mils to 245 mils total. In all cases the hydrogen cavity was 50 mils deep.

The differences in the frame thicknesses were accommodated by varying the thickness of the ERP's.

Stack compression - The scheme for determining stack compression varied with separator. In cells with asbestos, three layers, nominally 21 mils thick, were compressed to 15 mils, the total component thickenesses were set to give the desired final separator thickness. For cells with zircar, it was determined that 12 mils excess total component unloaded thickness was required to obtain the desired loading on the cells. Table I summarizes the above component and fill procedure variations.

GROUP	NICKEL ELECTRODE	HYDROGEN ELECTRODE	SEPARATOR	FILL PROCEDURE	ERP THICKNESS	
1	YARDNEY	LSI	ZIRCAR	VACUUM	70	B
2	YARDNEY	LSI	ZIRCAR	VACUUM	140	G
3	YARDNEY	LSI	ZIRCAR	FILL	50	A
4	YARDNEY	LSI	ZIRCAR	FILL	110	E
5	YARDNEY	LSI	ZIRCAR/BTA	FILL	100	D
6	YARDNEY	LSI	BTA	VACUUM	85	C
7	YARDNEY	LSI	BTA	FILL	85	C
8	YARDNEY	YEC	ZIRCAR	FILL	110	E
9	EAGLE PICHER	LSI	ZIRCAR	FILL	115	F
10	EAGLE PICHER	LSI	BTA	FILL	90	C

TABLE 1

COMPONENT VARIATIONS IN THE 50 CELL BIPOLAR NICKEL-HYDROGEN BATTERY STACK

The experiment was designed to make component and procedural variations in such a way that direct comparisons of the desired features could be made. For example, the comparison of hydrogen electrodes was made between two groups of cells that had all other components and fill procedures the same. The only exception to this scheme was with ERP thickness. The available frames differed in thicknesses and these differences were accommodated by varying the thickness of the ERP so, in some cases, the ERP thickness was varied along desired parameter. In order to evaluate this variation, ERP thickness comparisons were included in the test matrix.

Test Regime Summary

The battery was characterized at various charge and discharge rates, ranging from C/10 to C for the charge and C/4 to 10C for the discharge. The first 60 cycles were a mixture of constant current discharges and pulse discharges. Cycles 64-119 were 40% DOD LEO cycles. Cycles 124-150 were pulse LEO cycles in which the charge was .47 A for 1 hour, constant current and the discharge was run at the 40% DOD LEO rate of 0.8 amps on a pulse regime of 1 second on 4 seconds off for a total discharge load time of 30 minutes or a total discharge period of 2.5 hours. The LEO cycles were interrupted at cycle 150 by several extended open circuit periods ranging from two to six weeks and some pulse discharges. In addition to the constant current discharges, pulse discharges, and LEO cycles, open circuit stands ranging from 65 to 250 hours were performed at frequent intervals over the life of the battery.

Stack Teardown

After cycling a total of 1500 cycles the stack was disassembled. Components were visually inspected for damage and anomalies that may have occurred

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during cycling. All components were weighed upon removal from the stack. During construction, wet and dry weights were recorded for each component as it was incorporated into the stack. Electrolyte distributions, based on the actual weight data taken at the times of construction and teardown for the new and cycled cells, were calculated and compared. Thicknesses of all components were also measured upon removal and compared to the new component thicknesses. Further analyses are presently underway. These include electrolyte extractions from the separators and rings and flooded capacity tests on the nickel electrodes.

Results and Discussion

Battery Cycle Data - A general discussion of the battery performance during the characterization, pulse testing and LEO cycling can be found in reference 4. The data and discussions reported here will center on performance variations between the groups of five cells. There were no data available on individual cells or groups of five for any of the pulse tests run. This results from the fact that the data system scans the battery cell voltages in 18 second intervals and the pulse rates varied from 1 second on and 1 second off to 5 seconds on and 20 seconds off: there was no way of identifying where in a pulse the data were taken. The performance variation discussions will thus be limited to the constant current discharges, the open circuit stands and the 40% DOD LEO cycles.

The same general performance trends can be seen by comparing voltage performance and capacity to a 1.0 volt cut-off for the constant current characterization data cycles, and the end-of-discharge (eod) voltage vs cycles and the general discharge voltage performance for the LEO cycles. In all cases it can be seen that in general the component variations tested here, with the exception of separators, had little or no effect on cell performance. There were essentially no performance var-
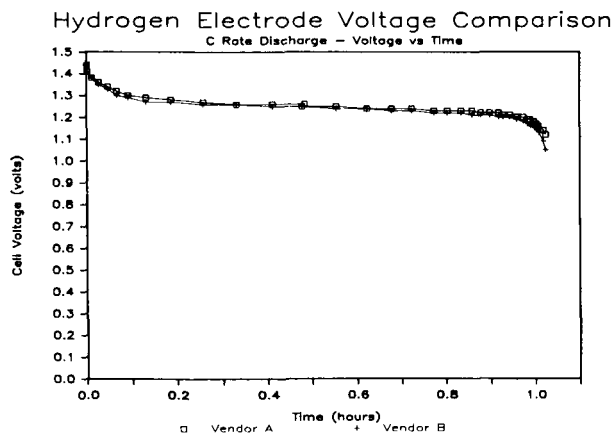
Hydrogen Electrode Voltage Comparison

FIGURE 2

iations that could be attributed to ERP thickness, hydrogen electrode, nickel electrode, or fill procedure differences. Since ERP thickness did not affect performance, groups with different ERP thicknesses were compared for subsequent evaluations. Figure 2 shows curves comparing the voltage vs time performance for a C rate discharge on a representative cell from each of two groups (groups 4 and 8) that are identical except for the hydrogen electrodes. There is essentially no dif-

ference in the curves. Average end-of-discharge voltages are plotted against cycle number for two groups that vary only in nickel electrode manufacturer in figure 3. The group average end-of-discharge voltages vary by only 3 to 5 millivolts.

As with the previous comparison, there is essentially no difference in cell performance. Similar results were found when comparing cells that varied only in electrolyte fill procedure.

Separator variations, on the other hand, led to varied performance differences between the groups of five cells. In general the groups with beater treated asbestos separators had poorer voltage performance and lower capacity than the groups with zircar separators. This is as expected since the asbestos has a higher resistance than the zircar[5]. The group of cells with the combination zircar/BTA separator performed more like those with zircar than those with asbestos.
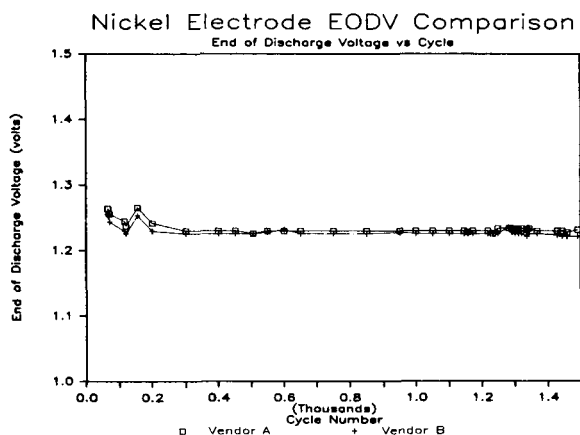
Nickel Electrode EODV Comparison

FIGURE 3

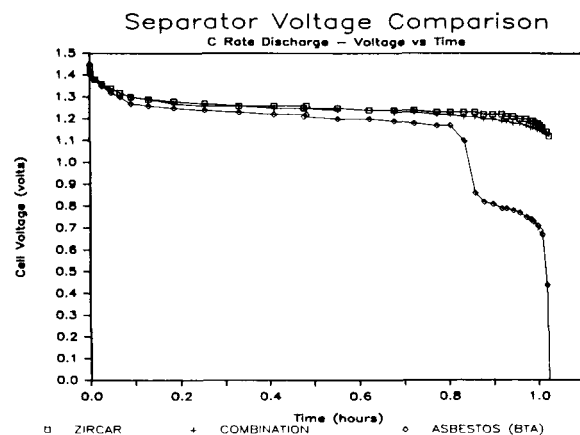Separator Voltage Comparison

FIGURE 4

Figure 4 shows a C rate discharge curve for a representative cell with each of the types of separator. The cells with zircar and the combination separator demonstrated comparable performance. The cell with asbestos operated at a lower voltage throughout the discharge. There was a 50 millivolt difference in voltages between asbestos and the other separator types. In addition, the cell with asbestos had a lower capacity above 1 volt and exhibited a second plateau.
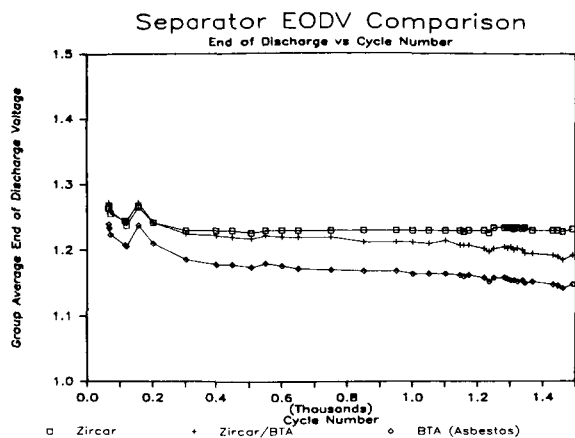
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Separator EODV Comparison
End of Discharge vs Cycle Number

FIGURE 5

Group 10 — EODV vs Cycles
LEO Cycle Regime — 40% DOD

FIGURE 7

Group 5 — EODV vs Cycles
LEO Cycles — 40% DOD

FIGURE 6

Group 10 — Voltage Comparison
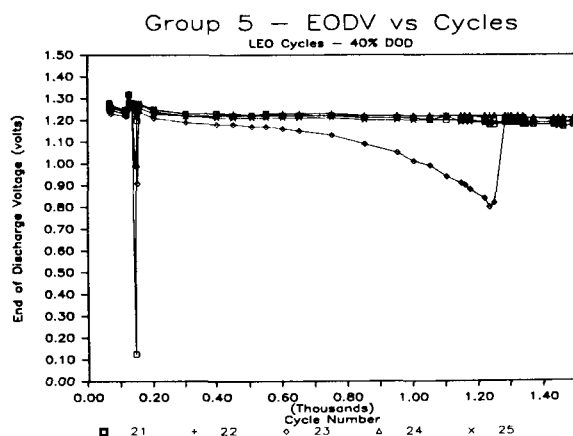### C Rate Discharge — Voltage vs Time

FIGURE 8

Similar trends can be observed in figure 5, which compares group average end of discharge voltages vs cycle numbers for the three types of separators.

During the course of LEO cycling the voltage and capacity performance of several cells degraded significantly. Figure 6 and 7 show the end of discharge voltages vs cycles for the cells in groups 5 and 10. From cycle 150 on, performance began to decline for cells 23 and 46-50, and kept getting worse. The component configuration for the cells in group 10 is basically representative of the 'standard' bipolar configuration that has been used in the majority of the stacks built and tested at the Lewis Research Center. The 'standard' configuration has demonstrated much better performance in all previous tests[1,2,6]. The cells appeared to have a resistance problem. For this group of cells the capacity appears to be available; however, much of it is obtained below 1.0 volt.

One cell, number 23, from group 5 (with the zircar/BTA separator) exhibited a similar, but much more uniform, degradation. In this cell there was very little capacity obtained between 1.0 volts and 0 volts on the full discharges, indicating that all of the capacity had been removed by the time the voltage fell off, suggesting a shorting mechanism of some sort or a charge acceptance problem. At cycle 1280 the vessel was opened and electrolyte was added to cells 23 (group 5), 46, 48 and 50 (group 10). With the addition of elec-
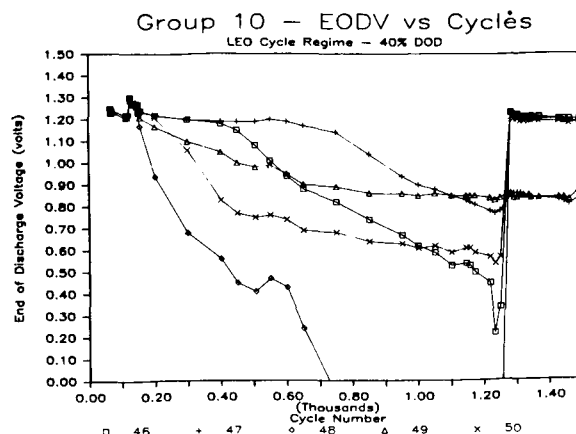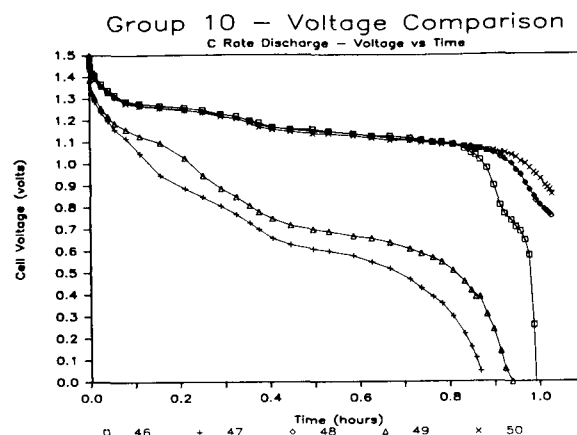
trolyte, all of these cells improved to the level of the rest of the stack. The battery was run for 200 cycles following the electrolyte addition and the cells maintained their improved performance levels. Since the cells did improve and the capacity was recovered with the addition of electrolyte, we can conclude that the poor performance was the result of high resistance associated with electrolyte loss. There was no apparent nickel electrode capacity loss or degradation.

The data from the open circuit stands substantiate the above conclusions concerning a shorting mechanism in cell 23 and high resistance in cells 46-50. Since the open circuit stand time varied from 65 to 72 hours, and the capacity measurements following the open circuit stands were made at various discharge rates, the capacity to 1.0 volt was compared for all cells as a percentage of the total capacity obtained to a battery voltage of 40 volts. In some cases one or two cells from a group exhibited consistently lower capacities to 1.0 volt than the rest of the group. As above, these variations appear to be the result of true available capacity variations as in these cases there was typically very little capacity obtained below 1.0 volt. Flooded capacity tests will be run to determine if these variations rest with the electrodes themselves or developed as a result of conditions within the cell. The cells in group 10 generally had poor capacity to 1.0 volt but the capacity was available at a lower voltage indicating a low rate of self discharge. Figure 8 shows C rate discharge curves from group 10 fol-

lowing the addition of electrolyte to cells 46, 48, and 50. The cells with the added electrolyte show vastly improved voltage performance.

Battery Teardown - Preliminary Analysis - All components were visually inspected upon removal from the stack. In general there was no obvious, extensive damage to any hydrogen electrodes even though in the cells with zircar oxygen could freely cross the separator and recombine on the hydrogen electrode surface. However, slight pinholes may have gone unnoticed because all of the negatives had been used previously. Some of the nickel electrodes in cells with asbestos separators exhibited growth primarily in the areas that did not correspond to recombination strip locations. This was not observed in cells with zircar separators. The cells with asbestos appeared to be much drier than those with zircar. Evaluation of electrolyte content (by weight) in the cells shows that in general the cells with asbestos or combination separators had the least amount of electrolyte after cycling, even though this was not generally the case after the original fill. The change in electrolyte fill for the total cell ranged from +15% to -53% of the initial fill. The average change was a loss of 20%. The battery was suspended horizontally in the vessel with gas access ports from the hydrogen or ERP areas open to the bottom of the vessel. In the bottom of the vessel, there was a puddle of electrolyte that leaked from the cells; however, the amount found was not enough to account for the total electrolyte lost from the stack. A shunt current mechanism can be used to explain the transfer of electrolyte from one cell to another resulting in a net increase in the electrolyte content in the cells at the negative end of the loop.

Table II summarizes the electrolyte distribution changes that occurred with cycling. In general the nickel electrodes gained electrolyte during the cycle period while all other components lost it. In a few individual cases, separators and

COMPONENT	% CHANGE IN ELECTROLYE FILL LEVEL			
	OVERALL	SEPARATOR TYPE		
		ZIRCAR	ZIRCAR/BTA	BTA
NICKEL ELECTRODE	+ 42	+ 47	+ 53	+ 20
HYDROGEN ELECTRODE	- 50			
SEPARATOR	- 22	- 15	- 28	- 40
ERP	- 54	- 43	- 68	- 80

TABLE II
ELECTROLYTE FILL VARIATIONS AFTER CYCLE TESTS

ERP's gained electrolyte. While initial separator/rings fill levels were comparable for asbestos and zircar separators, the asbestos separators lost more KOH than their zircar or combination counterparts. A similar trend was observed when comparing ERP fill levels in cells with asbestos or zircar separators. There is a better correlation of electrolyte fill levels with separator types than with any of the other variables tested.

Component thicknesses were measured before and after cycling. The nickel electrodes expanded from 1 to 13 mils over the 1500 cycles. There is no apparent correlation of nickel electrode electrolyte weight gain and the amount of nickel electrode expansion. Pore size distribution analyses are planned to further evaluate the final

nickel electrode electrolyte fill vs total pore volume. As found with earlier stacks[7] the ERP compressed to accommodate nickel electrode expansion. The nickel electrodes expanded an average of 6.25 mils and the ERP's compressed by an average of 4.6 mils.

Further testing is planned to help identify the causes for the electrolyte loss from cells with asbestos separators. Electrolyte is being extracted from the separators and rings of selected cells for analysis of KOH and carbonate concentrations. Flooded capacity tests are planned to evaluate if capacity variations can be attributed to nickel electrode differences as opposed to specific cell cycling conditions, such as electrolyte content and distribution.

Concluding Remarks

We were able to demonstrate successful operation of a 50 cell, high voltage bipolar nickel-hydrogen battery. Although shunt currents may have been operating within the stack they were not severe enough to prevent the stack from operating. This evaluation of component variations has led to the conclusion that in this specific test, only separator variations had any significant effect on cell performance. Further studies are planned to try to separate the effects of relative cell position in the stack from the specific separator and/or nickel electrode characteristics.

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15. Supplementary Notes

16. Abstract

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