Received by OSTI

AUG 0 3 1989

ZINC/BROMINE BATTERY EVALUATION AT SNL

SAND--89-1852C

DE89 015847

S. L. Lott, P. C. Butler, J. M. Freese
Sandia National Laboratories

Three prototype zinc/bromine batteries were evaluated at Sandia during the last year. The objectives of these tests were to determine performance, cycle life, durability of the auxiliary components, and failure mechanisms. All three were deliverables from a Sandia development contract with Energy Research Corporation (ERC). The test results were communicated to ERC along with suggestions for improving battery design and reliability.

Each battery system consisted of a cell stack, two electrolyte pumps, in-line electrolyte filters and other plumbing, reservoirs, bromine mixing baffles in the catholyte reservoir, and an electrolyte level sensor in the zinc electrolyte reservoir. Two of the cell stacks utilized 872 cm^2 electrodes, and one had the newer 1500 cm^2 electrodes. Electrolyte was supplied by ERC and contained approximately 2 molar zinc chloride. The batteries are identified in Table 1.

A typical test cycle consisted of a timed, constant current charge followed by a 5-minute open circuit wait. This was followed by a constant current discharge until the battery voltage dropped below a predetermined cutoff level of 1.2 volts per cell. To insure a uniform zinc deposit, the battery was periodically completely discharged to remove all residual zinc. A failure criteria of less than 40% energy efficiency for five consecutive cycles was imposed. A summary of the performance data is included in Table 2.

One 5-cell battery, number 456, completed 100 cycles at Sandia. Efficiency data are shown in Figure 1. Charge and discharge rates were varied from 34 to 43 mA/cm^2 and zinc loading on charge ranged from 137-170 mAh/cm^2 The slight drop in voltaic efficiency after Cycle 9 was due to an increase in the charge and discharge rates. The fluctuation in coulombic efficiency from Cycles 47 to 53 was due to self-discharge testing described below. Performance was inconsistent on subsequent cycles but stabilized at reduced efficiency levels after Cycle 70. One cell was identified as limiting battery capacity and voltage performance at this point. Performance then dropped substantially at Cycle 98 to below the failure criteria.

The self-discharge rate of the battery with the electrolyte pumps running was measured between Cycles 31 and 43. The maximum open-circuit stand time was one hour, and self-discharge was not significant (less than 2% of the discharge capacity). Between Cycles 47 and 53, self-discharge tests were run with the pumps off for periods of 24 and 48 hours. The effect on capacity was significant with losses of 12 and 16%, respectively.

The battery was disassembled and the cause of failure determined. A gasket used to seal the end electrode to the end block had enlarged during exposure to bromine. By enlarging, it partially blocked the flow of electrolyte to the end cell, thus limiting its capacity. ERC had also observed this degradation mechanism. Subsequently, ERC redesigned the battery end blocks to eliminate the gasket completely.

The 30-cell battery, Number 459, had completed 84 cycles by the end of July 1989. Charge and discharge currents and zinc loadings were similar to those described above for Battery 456. Battery performance is shown in Figure 2. Initially, battery performance was comparable with the 5-cell battery. However, after about 20

cycles, the coulombic efficiency began to vary significantly. After 52 cycles, coulombic efficiency decreased sharply, and battery performance dropped below the failure level. Electrolyte analysis indicated that the battery was not deficient in zinc or bromine. However, rapid and uncontrollable increases in electrolyte pH required frequent additions of hydrobromic acid. Over 270 milliliters of acid was added per cycle between Cycles 60 and 66.

The battery was disassembled after 73 cycles to determine the cause of the observed performance. The loss in performance was due to a swollen gasket which blocked electrolyte flow as described above for Battery 456. The end blocks were replaced by parts built with the new design which eliminated the gasket. Several electrodes and separators were also replaced, and the battery was reassembled and placed back on test. Performance improved substantially at first, and then dropped off again. This performance decline will be investigated during the next few months.

Finally, another 5-cell battery, Number 481, was placed on test in late May 1989. This unit contained larger electrodes, flow frames with improved electrolyte distribution features, and improved bromine mixing in the catholyte reservoir. This battery had completed 29 cycles by the end of July 1989. Its performance is illustrated in Figure 3. While initial efficiency values were close to the expected levels, voltaic performance dropped approximately 10% during the testing. Coulombic efficiency also decreased significantly during this period. Adjustments were made to the electrolyte flow rates in an attempt to reverse this behavior. Further testing will be conducted to fully characterize this new design.

These tests have demonstrated that maximum energy efficiencies of about 65% are possible on the most recent ERC designs. Cycle lives of approximately 100 cycles were achieved. One key design change was made due to degradation of a gasket. This change should result in increased cycle life and improved overall performance. Testing will continue in the next several months on these units as well as on new batteries scheduled to be delivered in the near future.

This work is supported by DOE Contract #DE-AC04-76-DP00789.

TABLE 1
ERC ZINC/BROMINE BATTERIES TESTED AT SNL

SNL ID NO.	ERC ID NO.	START/END TEST DATE	NO. OF CELLS	RATED CAP. (Ah) @ C/4
456	SNL-5-5D	2-88/12-88	5	125
459	SNL-30-1D	2-88/ -	30	125
481	1500-5-1D	5-89/ -	5	200

TABLE 2
ERC ZINC/BROMINE BATTERIES DATA SUMMARY, JULY 1989

SNL ID NO.	MEAN COULOMBIC EFF. %	MEAN VOLTAIC EFF. %	MEAN ENERGY EFF. %	TOTAL NO. OF CYCLES	STATUS
456	86±2	70±1	61±2	100	FAILED
459	69±3	70±1	49±3	84	ON TEST
481	81±2	66±1	53±2	29	ON TEST

NOTE:
Uncertainties are expressed as 95% confidence limits.

Figure 1

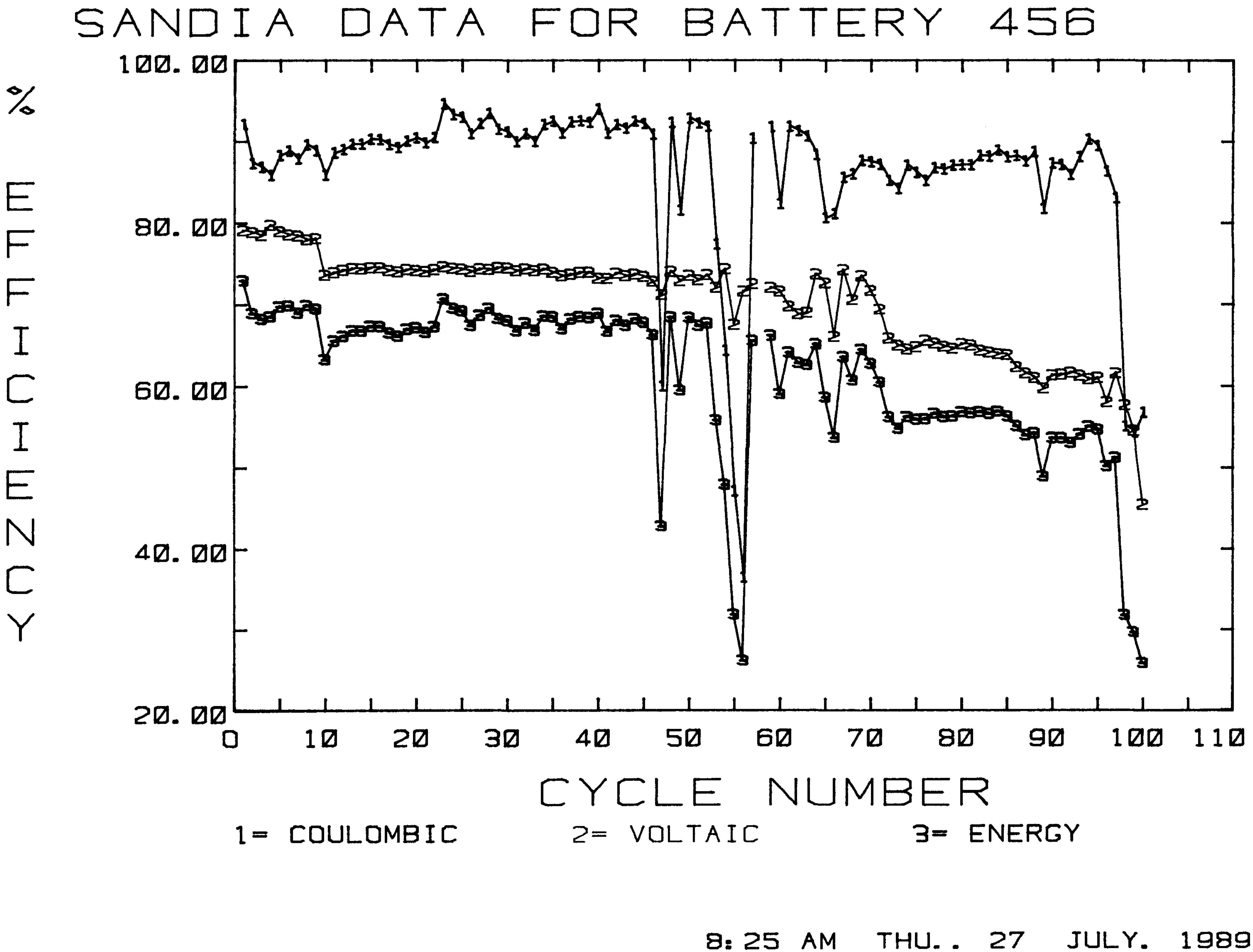

SANDIA DATA FOR BATTERY 456
% EFFICIENCY
100.00
80.00
60.00
40.00
20.00
0
10
20
30
40
50
60
70
80
90
100
110
CYCLE NUMBER
1= COULOMBIC
2= VOLTAIC
3= ENERGY
8:25 AM THU.. 27 JULY. 1989

Figure 2

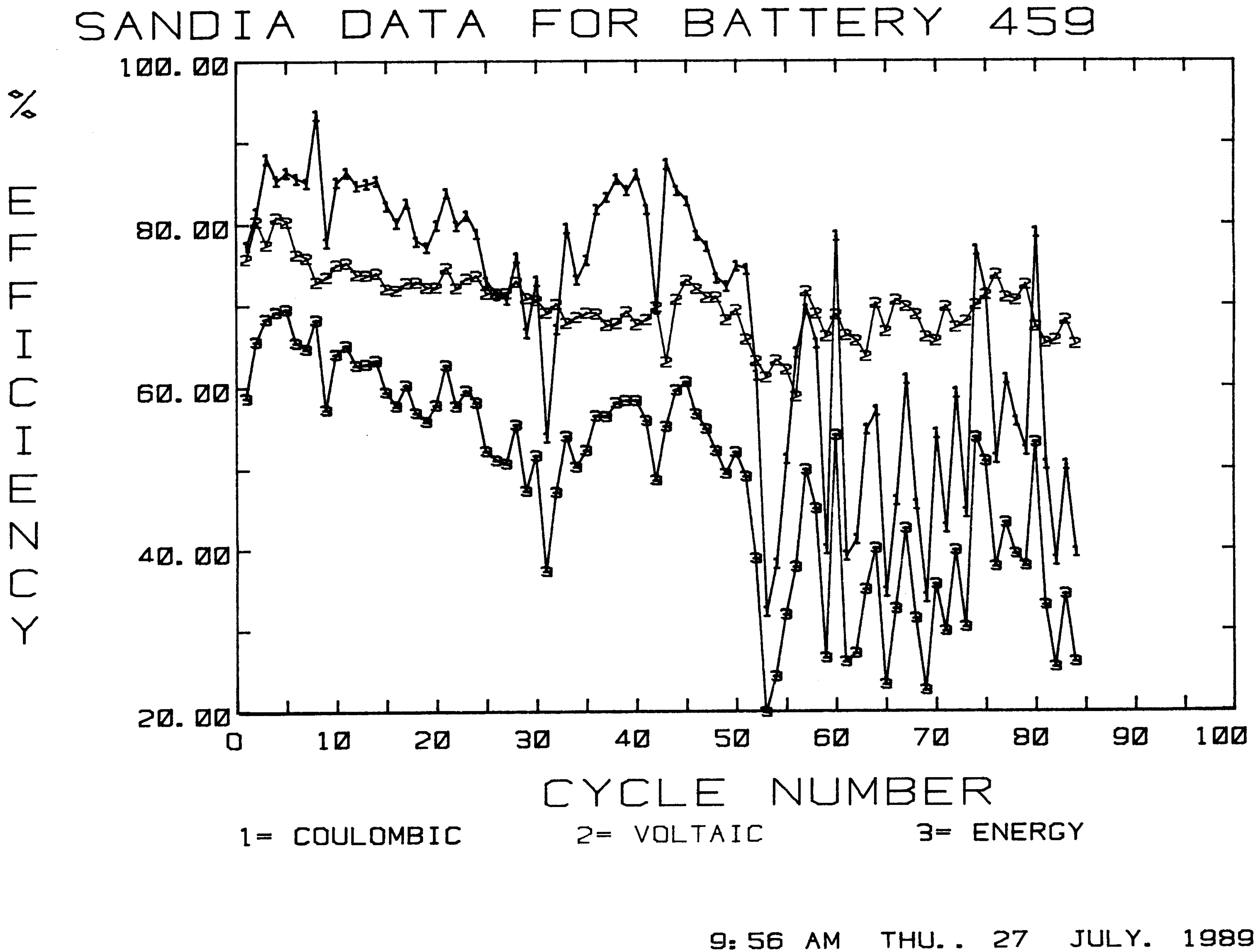
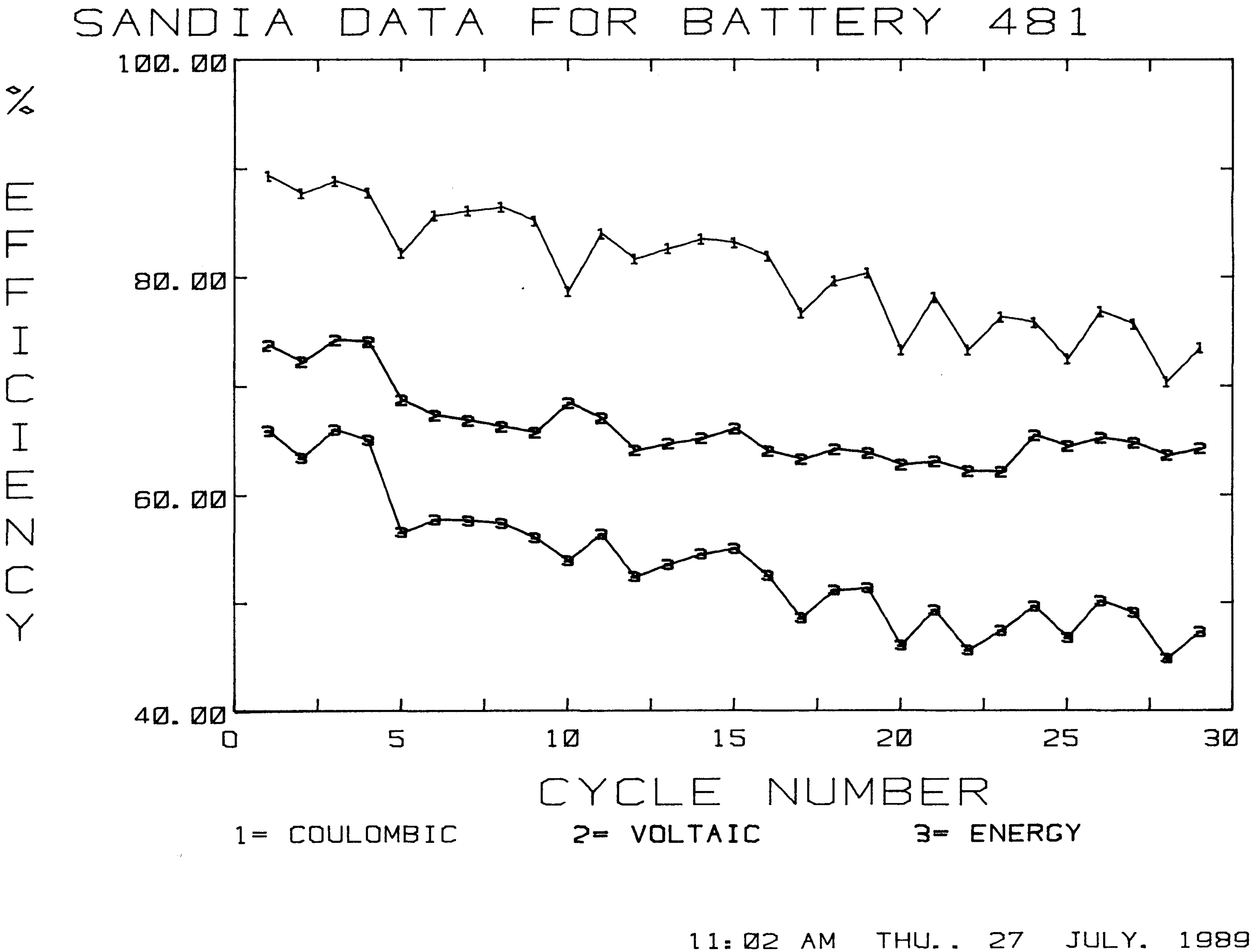

SANDIA DATA FOR BATTERY 459
% EFFICIENCY
100.00
80.00
60.00
40.00
20.00
0
10
20
30
40
50
60
70
80
90
100
CYCLE NUMBER
1= COULOMBIC
2= VOLTAIC
3= ENERGY
9:56 AM THU.. 27 JULY. 1989

Figure 3


SANDIA DATA FOR BATTERY 481
100.00
80.00
60.00
40.00
% EFFICIENCY
0
5
10
15
20
25
30
CYCLE NUMBER
1= COULOMBIC
2= VOLTAIC
3= ENERGY
11:02 AM THU.. 27 JULY. 1989