# EXTENDED ABSTRACTS

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Corrosion
Dielectrics and Insulation
Electrodeposition
Electronics
Electrothermics and Metallurgy
Industrial Electrolytic
Physical Electrochemistry
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Extended Abstracts
of
BATTERY DIVISION

Subjects:
Accelerated Testing of Batteries
Environmental Safety and Recycling of Batteries
The Nickel Electrode
Thermal Analysis in Battery Design
General Session

The Electrochemical Society, Inc., 10 South Main St., Pennington, NJ 08534

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Abstract No. 1

# ACCELERATED DEEP CYCLING TEST FOR LEAD-ACID LOAD-LEVELING CELLS

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Electric utility requirements for load-leveling batteries with very long cycle life has stimulated renewed interest in accelerated testing of advanced lead acid batteries. Cell design objectives are 4000 deep cycles in a 16-20 year life span and a cycle regime including a 5-h discharge and a 10-h recharge, one cycle a day, 200 to 250 cycles a year. Our goal for the accelerated test is a demonstration of the equivalent of 4000 cycles in a one year test time.

Accelerated Test Design. The proposed test requires 2 deep cycles per day (to 80% of 5-h rated capacity), each having controlled overcharge, and performed at a cell temperature of 70 ± 3°C. Experimental cells are slightly less than half the capacity of the ultimate prototype cell but have full size plates, and a rated capacity of 1785 Ah. The test regime is as follows:

| Test | Current A | Time h | Capacity Ah |
|---|---|---|---|
| • Discharge | 324 | 4.4 | 1426 |
| • Charge | | | |
| Step 1 | 324 | 4.3 | 1393 |
| Step 2 | 115 | 3.3 | 380 |
| TOTAL: | | 7.6 | 1773 |
| | Overcharge: | % | 24 |

Cell temperature of 70 ± 3°C is maintained by a combination of each cell's internal heat during cycling and a 100 W heater-insulation blanket-thermostat on each cell.

Capacity measuring catch-out cycles are performed on the test cells at 5-6 week intervals at 25-35°C. The observed capacity, average voltage and energy output is plotted against the number of cycles completed at 70°C, and against the 25°C equivalent cycles, to relate the effect of cell design variables on cycle life and relative performance. Based on temperature compensating factors proposed by Maskalick and by E. A. Wagner one cycle at 70°C is equivalent to 6 cycles at 25°C and two cycles per day at 70°C thus gives an acceleration factor of 12:1. (1)(2)

Experimental Results. At this time 52 of 60 each 17-plate 1785 Ah cells have completed 450 plus 80% depth cycles at 70°C. The eight failing cells reached the 80% rated capacity test end point prematurely. All had lower negative active material densities and lower negative to positive active material ratios. This method for cost reduction, the reduction of negative active material reserves, has given short life and is not a viable alternative.

Energy output versus cycle life to 2500 equivalent 25°C cycles will be shown for the more successful cell designs in the three factorial experiments in progress.

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Abstract No. 2

## CONTINUOUS OVERCHARGE ACCELERATED POSITIVE GRID CORROSION TEST ON LEAD ANTIMONY PASTED FLAT PLATE CELLS

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A continuous overcharge test is one of three tests now in progress to provide cell design information for a 4000 deep cycle load-leveling battery. Five-plate 400 Ah cells, differing only in alloy composition of the positive grid, were continuously anodically polarized at 4½ and 3 times the normal finishing rate, and at a test temperature of 50-55°C. Periodically 5-hour-rate catch-out cycles were run to measure residual capacity. After each discharge test selected cells were dissected and positive grid corrosion measured by grid weight loss.

Four different alloys with two levels of antimony (4 and 2.5) and arsenic (0.3 and 0.05) were tested.

Figure 1 illustrates the linear effect of the overcharge current density on corrosion rate for the 4 and 2.5% antimony alloy with 0.3% As. The referenced data at 6 ma/cm$^2$ was extrapolated from the recent paper by Papazov et al. (1) An approximately linear relationship is observed between corrosion rate and overcharge rate in the range tested. Papazov utilized spines from a tubular positive plate. We tested flat plates but the area used for both overcharge and corrosion rates is that of the spine or cast grid in the pasted flat plate. Both tests indicate little difference in the corrosion rate of alloys with varying antimony at the same overcharge rate. The effect of arsenic concentration on corrosion rate is not clear to date and is an objective for future work.

A comparison was made between the corrosion rate of grids subjected to continuous overcharge at 50-55°C and the same grids subject to a deep cycle test at 70±3°C. The deep cycle cell was a 17-plate design rated at 1800 Ah at the 5-hour rate to 1.60 vpc. These cells were cycled twice a day on a regime consisting of a 4-hour discharge to 80% of 5-hour rated capacity, 8-hour recharge with 24% overcharge each cycle. The measured corrosion rate on the deep cycle grid was 0.031 mg/Ah$_{oc.}$/cm$^2$ grid surface at 70±3°C. The equivalent corrosion rate at 50-55°C is estimated to be 0.015 mg/Ah$_{oc.}$/cm$^2$. The overcharge corrosion rate at 50-55°C was 0.011 mg/Ah$_{oc.}$/cm$^2$. The corrosion on the cycled cells was 1.4 times more than for the same alloy under continuous overcharge, using ampere-hours overcharge per unit positive grid surface area as the baseline for comparison. This confirms the conclusions of others. (2)

Results to date suggest that at least one of the test alloys will be suitably corrosion resistant for a 4000 deep cycle life battery. Since a continuous anodic polarization produces lower positive grid corrosion than on cycled plates, continuous polarization corrosion must be correlated with the corrosion observed on a specific duty cycle if meaningful cycle life data is to be estimated.

While these cells were on continuous overcharge at 50-55°C, arsine/stibine generation was monitored by the method of Varma and Yao. (3) The results are shown in Table 1. The general trend indicates an increase in both arsine and stibine with accumulated overcharge. This type of behavior would be expected as long as the corrosion process exposes fresh grid surface area having new antimony and arsenic rich areas. The results suggest that the presence of arsenic decreases the rate of stibine evolution at 50-55°C. Holland (4) found that stibine generation increases with increasing temperature. It is likely that the results in Table 1 measured at 55-55°C are higher than would be observed in a battery operating at a cell temperature up to 40°C.

X-ray diffraction measurements made on the positive active material showed a trend to higher levels of $\alpha$-$PbO_2$ with increasing accumulative overcharge capacity (Table 2). The effect appears to be more dominant in active material with no additive than for active material with addative. Since $\beta$-$PbO_2$ is the high capacity form (discharges at higher potentials than $\alpha$-$PbO_2$) (5), the higher $\alpha$-$PbO_2$ content in the non-additive paste predicts a more rapid loss in cell capacity in cells of this type. This loss in capacity was verified by catch-out cycle data on the accelerated deep cycle test.

Other data as well as photographs of grid corrosion will be presented.

Acknowledgement: This work was performed under Argonne National Laboratory Contract 31-109-38-4951. Special thanks go to Exide Management and Technology Company for the opportunity to present this data and to INCO Research and Development Center, Sterling Forest, N.Y. for the arsine analysis.

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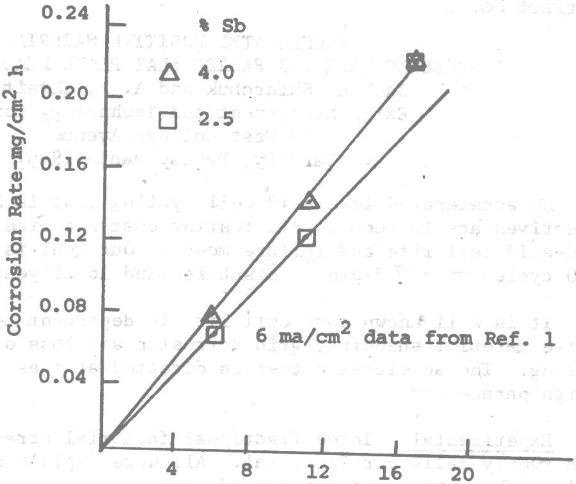


FIGURE 1
Overcharge Current Density-ma/cm$^2$
Effect of Overcharge Current Density on Corrosion Rate at 50-55°C

TABLE 1
Stibine/Arsine Evolution from 400 Ah Cells Overcharging at 50-55°C

| Accumulated Overcharge Ah | Alloy Composition Sb | As | Rate of Gas Evolution mg/Ah (OC)/1000 Ah 5-h Rated Capacity Stibine | Arsine |
|---|---|---|---|---|
| ~10,000 | 4 | 0.30 | 0.06 | 0.05 |
| ~20,000 | 4 | 0.30 | 0.07 | 0.04 |
| | 4 | 0.05 | 0.14 | 0.005 |
| | 2.5 | 0.30 | 0.07 | 0.03 |
| | 2.5 | 0.05 | 0.03 | 0.002 |
| ~40,000 | 4 | 0.30 | 0.18 | 0.08 |
| | 4 | 0.05 | 0.25 | 0.01 |
| | 2.5 | 0.30 | 0.13 | 0.04 |
| | 2.5 | 0.05 | 0.10 | 0.006 |
| | 4* | 0.05 | 0.13 | 0.006 |

*Additive in positive active material

TABLE 2
Ratio α/β $PbO_2$ in Positive Active Material

| Positive Mix Composition | Accumulative Overcharge - Ah 88,000 | 127,000 | 166,000 |
|---|---|---|---|
| No additive | 0.2:1.0 | 1.2:1.0 | 1.0:1.0 |
| Additive | 0.2:1.0 | 0.4:1.0 | 0.6:1.0 |

Abstract No. 3

# ACCELERATED POSITIVE MATERIAL SHEDDING TEST FOR PASTED FLAT PLATE LEAD-ACID CELLS

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An accelerated lead-acid cell cycling test is being studied. The objectives are to reduce cell testing cost and time, and to predict lead-acid cell life and failure modes. Our goal is a cell capable of 4000 cycles to 80% depth of discharge and 16-20 years of life.

It is well known that cell life is dependent upon reduction of active material shedding, grid corrosion and loss of capacity with cycling. The accelerated test is directed at these important cell design parameters.

Experimental. Three fractional factorial arrays were designed with twenty cells per factorial. All were 3-plate nominal 200 Ah cells. The parameters considered are:

- Positive and negative plate active material past density
- Anti-shedding additives to positive and negative plate active material
- Electrolyte specific gravity
- Positive plate wrap and retaining system
- Spacing between plates

In addition, twelve other 3-plate cells, designed from data obtained from the 60 original factorial test cells, were assembled and tested.

Cycling Regime. The cells were subjected to the following treatment:

- Formation (180 Ah/lb wet paste weight)
- Capacity building cycles (5-12 at 5 h discharge rate, 13-15 h charge rate)
- Characterization cycles (4 discharge rates at 13 h charge rate, 3 charge rates at 5 h discharge rate)
- Catch-out cycles discharge @ 35 A to 1.6 V, charge step 1. 27.5 A to 2.45 V, charge step 2. 20% overcharge at 10 A.
- Accelerated cycle regime

Catch-out Cycles. Cell capacity maintenance during the accelerated test was monitored by means of the catch-out cycles. Two catch-out cycles were obtained after the characterization tests and just before initiation of accelerated testing. The cell capacities obtained were recorded as the base-line capacities. Future catch-out capacities were compared to the base-line values.