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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

CONTENTS

Abstract  
Number

Page

ACCELERATED TESTING OF BATTERIES

1	Accelerated Deep Cycling Test for Lead-Acid Load-Leveling Cells A. M. Chreitzberg, T. M. Noveske, and W. P. Sholette.....	11
2	Continuous Overcharge Accelerated Positive Grid Corrosion Test on Lead Antimony Pasted Flat Plate Cells T. M. Noveske and A. M. Chreitzberg.....	13
3	Accelerated Positive Material Shedding Test for Pasted Flat Plate Lead-Acid Cells J. C. Sklarchuk and A. M. Chreitzberg.....	16
4	Correlation of Accelerated Test Results to In-Service Cycle Life E. A. Wagner and W. P. Sholette.....	18
5	Electrode Impedance and State-of-Charge of Tubular-Type Lead-Batteries C. Gabrielli, M. Keddah, H. Takenouti, and N. Yahchouchi.....	20
6	Battery Capacity Measuring Device for Electric Vehicles V. R. Simas and W. F. Hammersley.....	23
7	Testing of Batteries for Solar Applications D. M. Bush, A. E. Verardo, P. C. Butler, and D. W. Miller.....	25
8	Accelerated Cycling Tests for Redox Electrodes R. F. Gahn and L. H. Thaller.....	28
9	Synthetic Battery Cycling as an Aid in Battery Development H. F. Leibecki and L. H. Thaller.....	31
10	Accelerated Discharge Testing of Lithium-Iodine Pacemaker Batteries and Longevity Projections W. D. Helgeson.....	34
11	Accelerated Testing of Lithium/Bromine Chloride in Thionyl Chloride Low Rate Cells R. L. McLean, W. R. Brown, and M. J. Brookman.....	37

12	Predictive Testing for Fuel Cells D. N. Patel, H. C. Maru, M. Farooque, and C. H. Ware.....	39
<u>ENVIRONMENTAL SAFETY AND RECYCLING OF BATTERIES</u>		
13	Treatment and Disposal of High Energy Density Lithium Cells W. V. Zajac, Jr.....	42
14	Shock Sensitivity of Discharge Lithium-Sulfur Dioxide Cells S. C. Levy and C. C. Crafts.....	44
15	Disposal of Large Li/SOCl <sub>2</sub> Batteries N. Marincic, R. C. McDonald, and J. S. Shambaugh....	46
16	Deactivation and Disposal of Large 10,000 Ah Li/SOCl <sub>2</sub> Batteries R. C. McDonald, F. Goebel, J. S. Shambaugh, and M. A. Slavin.....	48
17	Recycle of Battery Components J. P. Pensler and R. A. Spitz.....	50
18	Recovering Nickel from Zinc/Nickel Oxide Batteries B. L. Tiwari and D. D. Snyder.....	53
19	Application of a High Surface Area Electrochemical Reactor System to the Pollution Control and Recovery of Metals from Process Effluent Streams in the Battery Manufacturing Industry R. K. Kalia, B. Fleet, S. Mohanta, and R. Valencia.....	56
<u>THE NICKEL ELECTRODE</u>		
20	The Alkaline Nickel Electrode - Introduction to the Symposium J. L. Weininger.....	60
21	Recent Contributions to the Kinetics and Mechanism of the Nickel Hydroxide Electrode J. R. Vilche and A. J. Arvia.....	61
22	Nickel Oxide Electrode Model M. Sinha and D. N. Bennion.....	64

23	Structural Studies of Alkaline Nickel Electrode Powders J. F. Jackovitz and J. Seidel.....	66
24	Difficulties in Using Voltammetric Peak Potentials for the Identification of Nickel Hydroxide Type R. Barnard, C. F. Randell, and F. L. Tye.....	68
25	Reactivity of Hydrous Oxide Films Grown on Nickel under Potential Cycling Conditions L. D. Burke and T. A. M. Twomey.....	71
26	Properties of Chemically Derivatized Nickel Electrodes A. B. Bocarsly, S. A. Galvin, and S. Sinha.....	73
27	An Electrochemically Impregnated Ni(OH) <sub>2</sub> Electrode and Its O <sub>2</sub> Evolution Behavior T. Shirogami, K. Murata, and M. Ueno.....	76
28	Oxygen Generation and Recombination in Nickel-Hydrogen Cells R. L. Kerr.....	78
29	Chargeability of Ni Electrodes Studied by Optical Microscopy C. K. Dyer.....	80
30	Acceptance of Charge in Analog Nickel Electrodes R. F. Sma, L. R. Lemmer, and T. Katan.....	81
31	Application of Cobalt in Sintered Type Sealed Nickel-Cadmium Batteries X-f. Wang, Z-k. Zhang, and J-b. Tao.....	83
32	Zinc Hydroxide as a Substitute for Cobalt Hydroxide in Nickel Electrodes D. H. Fritts.....	86
33	Selenium-Modified Nickel Electrodes for Alkaline Batteries D. Cipris.....	89
34	Alkaline Nickel Electrode Voltage vs. Current Performance N. J. Maskalick.....	90



Abstract  
Number

Page

35	Electrochemical Studies of the Nickel Electrode in the Nickel-Cadmium Cell A. H. Zimmerman and M. C. Jannecki.....	92
36	Studies of the Effect of Aging on the Components of Sealed Nickel Cadmium Cells S. DiStefano, R. M. Williams, R. Fedors, I. Schulman, D. Tench, C. Ogden, and R. Haack.....	95
37	Analysis of Nickel Electrode Behavior in an Accelerated Test P. P. McDermott.....	98
38	Nickel Powders into Sintered Structures for the Alkaline Battery V. A. Tracey.....	101
39	Performance of Nickel Cathodes as "Free Standing" Electrodes in the Ni-Zn VIBROCEL <sup>TM</sup> S. Thornell and E. Pearlman.....	103
40	Surface Studies of Composite Nickel-Graphite Battery Electrodes W. W. Lee, C. R. Anderson, W. A. Ferrando, R. A. Sutula, and R. N. Lee.....	106
41	The Electrochemical Behavior of Thin Nickel Hydroxide Electrode with Composite Substrate W. W. Lee, R. A. Sutula, C. R. Crowe, and W. A. Ferrando.....	109
42	Cycle Life Characteristics of Composite Nickel Electrodes W. A. Ferrando and R. A. Sutula.....	111
<u>THERMAL ANALYSIS IN BATTERY DESIGN</u>		
43	Thermal Analysis of a Thin Cell, High Rate Li/SOCl <sub>2</sub> Battery L. Parnell and S. Szpak.....	113
44	Calorimetric Study of Li/SOCl <sub>2</sub> Cell Discharge K.-Y. Kim.....	115
45	Calorimetric Studies of Li/SOCl <sub>2</sub> Cell Reversal J. C. Hall and L. W. Wiechmann.....	117



Abstract  
Number

Page

46	Thermal Characterization of Ultra-High-Rate Li/SOCl <sub>2</sub> Batteries J. C. Hall, C. C. Chen, and H. F. Gibbard.....	120
47	Thermal Behavior of Various Cell Components in Li/SO <sub>2</sub> Systems N. Doddapaneni, D. L. Chua, and R. F. Bis.....	123
48	Thermal Behavior of an Experimental 2.5-kWh Lithium/ Iron Sulfide Battery C. C. Chen, T. W. Olszanski, and H. F. Gibbard.....	126
49	Generation of Thermal Energy in High-Temperature Lithium/Iron Sulfide Cells H. F. Gibbard and D. M. Chen.....	129

GENERAL SESSION

50	The Buckling of Lead-Acid Battery Positives during the Formation Process H. K. Giess.....	132
51	Defect Structure of Lead Dioxide P. T. Moseley and J. L. Hutchison.....	133
52	Analysis of Tellurium in Lead and Lead Oxide by Differential Pulse Polarography D. F. Wilkinson, K. R. Bullock, and C. L. Wang.....	135
53	Linear Potential Sweep of Lead-Acid Battery Electrodes Containing Trace Te, Sb, As, Co and Ni B. K. Mahato and W. H. Tiedemann.....	138
54	Development of a Sealed, Starved Electrolyte Lead-Acid Battery for Photovoltaic Applications J. Szyborski and M. L. Eggers.....	140
55	Charging Characteristics of a Sealed, Starved Electrolyte Lead-Acid Cell Designed for Photovoltaic Applications S. S. Misra and K. K. Ogata.....	142
56	Self-Discharge in Acid-Starved Lead-Acid Batteries K. R. Bullock and E. C. Laird.....	144
57	Alumina "Fiber FP" Reinforced Pure Lead Composites for Battery Electrodes H. S. Hartmann and R. A. Sutula.....	147

**Abstract  
Number**

**Page**

58	Assessing the Corrosion Behavior of Lead Metal Matrix Materials Using Potentiodynamic Polarization Measurements C. M. Dacres, S. M. Reamer, and R. A. Sutula.....	149
59	The Evaluation and Design of Battery Grids by Potential Distribution Y. L. Chen.....	150
60	Recent Advances in Nickel-Zinc Cell Technology A. Himy and O. C. Wagner.....	153
61	Conditions in Electroforming Zinc Electrodes H. F. Bauman and T. Katan.....	155
62	Charging Studies on Maintenance-Free Nickel-Zinc Cells O. C. Wagner, A. Almerini, and R. Smith.....	157
63	Effect of Inorganic Additives on Zinc Electrodes in Alkaline Batteries J. McBreen and E. Gannon.....	160
64	Mossy Zinc Growth Induced by Zincate Ion Gradients T. Katan and P. J. Carlen.....	162
65	Parametric Behavior of the Circulating Zinc-Bromine Battery E. Kantner, R. J. Bellows, H. Einstein, P. Grimes, P. Malachuk, and K. Newby.....	164
66	Development of Zinc Bromine Batteries for Stationary Energy Storage R. A. Putt.....	165
67	Foreign Gas Removal from a Zinc-Chloride Battery M. J. Hammond.....	167
68	Coulombic Efficiency of Zinc-Chloride Battery: The Isolated Contribution of Bubble-Induced Convection A. Shah, S. Argade, and J. Jorne.....	170
69	Reverse Disproportionation of AgO T. Katan and P. J. Carlen.....	173
70	Common Pressure Vessel Ni/H <sub>2</sub> Battery G. L. Holleck, V. Feiman, and D. H. Longendorfer....	175

- 71 An Elastomeric Binder for  $\text{TiS}_2$  Cathodes in Secondary Lithium Cells  
S. P. S. Yen, D. Shen, and R. B. Somoano..... 177
- 72 Electrochemical Domain of the Components of Ambient Temperature Secondary Lithium Batteries  
B. J. Carter, S. P. S. Yen, D. Shen, R. M. Williams, and R. B. Somoano..... 179
- 73 Development of High-Rate Lithium/Sulfuryl Chloride Cells  
D. J. Salmon and J. C. Hall..... 181
- 74  $\text{Li}/\text{SO}_3$  Soluble Cathode Cells: The 4.5 Volt Lithium Battery  
R. Gary, C. R. Schlaikjer, and R. J. Staniewicz..... 184
- 75 Transport Properties and Structure of Aluminum Chloride Thionyl Chloride Based Electrolytes for  $\text{Li}/\text{SOCl}_2$  Battery  
H. V. Venkatesetty and S. Szpak..... 188
- 76 Lithium/Sulfuryl Chloride Electrochemical Cells  
K. A. Klinedinst..... 190
- 77 Surface Analysis of Lithium/Gas Reactions  
P. A. Lindfors and K. M. Black..... 193
- 78 Complex Impedance of  $\text{Ca}/\text{CaCrO}_4$  Thermal Batteries  
R. A. Guidotti and F. M. Delnick..... 194
- 79 Thermodynamic Properties and Concentration Fluctuations in Galvanic Cells of Molten Na-Se and Na-Pb  
G. F. Fishler, L. Viswanathan, and A. V. Virkar..... 198
- 80 Effect of  $\beta$ "Alumina-Sodium Interface Due to Additives in Liquid Sodium  
L. Viswanathan, G. F. Fishler, and A. V. Virkar..... 199

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  $70 \pm 3^\circ\text{C}$ . 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:

<u>Test</u>	<u>Current</u> A	<u>Time</u> h	<u>Capacity</u> 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  $70 \pm 3^\circ\text{C}$  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  $25-35^\circ\text{C}$ . The observed capacity, average voltage and energy output is plotted against the number of cycles completed at  $70^\circ\text{C}$ , and against the  $25^\circ\text{C}$  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  $70^\circ\text{C}$  is equivalent to 6 cycles at  $25^\circ\text{C}$  and two cycles per day at  $70^\circ\text{C}$  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  $70^\circ\text{C}$ . 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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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 4% 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<sup>2</sup> 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 tests 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 subjected 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<sub>oc</sub>/cm<sup>2</sup> grid surface at 70±3°C. The equivalent corrosion rate at 50-55°C is estimated to be 0.015 mg/Ah<sub>oc</sub>/cm<sup>2</sup>. The overcharge corrosion rate at 50-55°C was 0.011 mg/Ah<sub>oc</sub>/cm<sup>2</sup>. 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<sub>2</sub> 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 additive. Since  $\beta$ -PbO<sub>2</sub> is the high capacity form (discharges at higher potentials than  $\alpha$ -PbO<sub>2</sub>) (5), the higher  $\alpha$ -PbO<sub>2</sub> 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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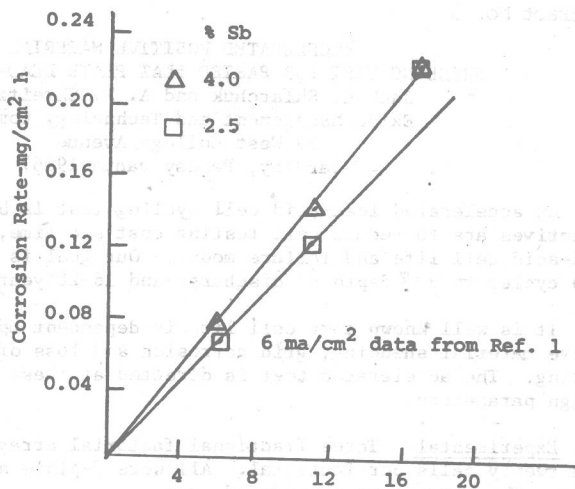


FIGURE 1  
Overcharge Current Density-ma/cm<sup>2</sup>  
Effect of Overcharge Current Density  
on Corrosion Rate at 50-55°C

TABLE 1

Accumulated Overcharge Ah	Alloy Composition		Rate of Gas Evolution mg/Ah (OC)/1000 Ah 5-h Rated Capacity	
	Sb	As	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  $\alpha/\beta$  PbO<sub>2</sub> 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

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.