

A SYSTEM EVALUATION OF LEAD-ACID BATTERY CHARGERS: PART II. CELLS WITH CAST LEAD-CALCIUM GRIDS

E. G. SIWEK

*General Electric Company, Corporate Research and Development, P.O. Box 8,
Schenectady, N.Y. 12301 (U.S.A.)*

(Received July 27, 1977)

Summary

Lead-calcium grid batteries were life tested by modified constant potential, gas flow, and gas pressure controlled charging methods.

The longest lived lead-calcium grid battery was life tested by the gas pressure charge controlled method followed by the mass flow controlled method and the modified constant potential method at 185, 130, and 110 cycles respectively.

The results of this program indicate that lead-calcium grid batteries can be charged by gas flow controlled charging methods and deep discharged for cycle lives comparable with lead-antimony grid batteries cycled by the same methods.

Results also indicate high ampere-hour efficiencies during the entire cycle lives of lead-calcium grid batteries with small electrolyte loss due to gassing.

Cycle lives of lead-calcium grid batteries can be extended by deliberate slight undercharging during normal cycling with gas flow controlled charging coupled with periodic overcharging at low rate constant current.

Gas flow controlled charging of lead-calcium grid batteries results in a 15 to 40% improvement in cycle life over the modified constant potential method.

Battery failure results from the loss of adhesion of the positive active material to the grids.

Introduction

The work described in this report covers three charging systems for lead-acid batteries: modified constant potential (MCP), charging current controlled by the rate of gas flow from the battery during charging (FM), and charging current controlled by the gas pressure developed within the battery during charging (GP). The three charging systems were selected as a

result of a screening of the following charging methods [1]: constant current, *modified constant potential*, *first order mass flow control*, second order mass flow control, first order gas pressure control, *second order gas pressure control*, impedance control, pulse.

The measurement techniques developed during the screening program were refined and applied to the current program and expanded to include life testing under the three most promising charging methods.

Work described in Part I covered cells with antimonial positive grids. This work covers cells with cast lead-calcium grids.

Current profile selection

The shape of the charging current profile, current *versus* time, for a gas flow or gas pressure controlled charge is determined by the initial charging current, I_0 , and the rate of gas evolution from the battery electrodes. Since the charging efficiency and battery cycle life are heavily dependent on the charging current profile, the optimum charging profile must be selected for each battery type. Inasmuch as the 2 C rate was used for the initial charging current for the lead-antimony grid batteries covered in Part I, an attempt was made to charge the lead-calcium grid battery at its 2 C rate, 16 A at 2.67 V/cell. This resulted in an initial spike followed by a current profile similar to that shown in Fig. 2 of Part I. The current spike was thought to be due to the small amount of free electrolyte and/or the relatively small electrode surface area. A subsequent investigation established that the electrolyte level could be made equivalent to the lead-antimony grid battery by the addition of electrolyte and the initial charging current could be adjusted downwards in direct ratio to the electrode surface areas of the two battery types. As verified experimentally these adjustments resulted in a smooth charging current profile for the modified constant potential charge at 2.67 V/cell, which is the recommended charging potential for lead-calcium grid batteries. End of charge potentials, electrode areas, electrolyte volumes, and other battery parameters used in adjusting the initial charging current are discussed in detail later.

The end of charge current for the series of charging characterizations and life tests covered in this program should have been set at C/50, (0.16 A) or less. This would have resulted in complete charging and minimal loss of electrolyte even on prolonged overcharge. However, this very low end of charge current would have resulted in unduly long charging times. Secondly, the operational amplifier controls used in regulating the output of the power supplies for the gas controlled charging circuits could not discriminate current values as low as 0.16 A. The same type of problem was encountered with the power supply set in the constant voltage mode for the modified constant potential charge. With the end of charge potential set at 2.67 V, the end of charge current varied from cycle to cycle. For this reason commercial modified potential chargers often switch to a low rate constant current at the end of the voltage controlled part of the charge.

End of charge currents used for this program were as follows: modified constant potential charge, 0.24 - 0.74 A; mass flow controlled charge, 0.6 A; gas pressure controlled charge, 0.7 - 0.9 A.

Description of the charging modes

The three charging modes; modified constant potential (MCP), mass flow (MF), and gas pressure (GP), are described in Part I.

The use of lead-calcium grid rather than lead-antimony grid batteries necessitated several changes in the charging constants used for life testing and characterization. For example, the lead-calcium grid battery operates at a higher end of charge voltage than the lead-antimony grid battery, 2.67 and 2.50 V respectively when charged by the MCP method. Ideally, all three charging modes should have had end of charge voltages of 2.67 V/cell. This was not the case since the MF and GP controlled charging methods are not end of charge voltage controlled and have end of charge voltages less than 2.67 V/cell.

Preliminary work with gas pressure controlled charging of lead-calcium grid batteries showed that a 0.2 lb/in² (gauge) differential pressure controlled charge, rather than 0.5 lb/in² (gauge) as used in Part I, was necessary in order to result in an acceptable end of charge voltage 2.64 V and temperature 36 °C, as compared with 2.83 V and 48 °C at 0.5 lb/in² (gauge). This adjustment is necessary since the lead-calcium grid batteries evolve less gas at a given charge level than lead-antimony grid batteries.

The mass flow controlled charge circuit was adjusted for a gas flow of 3.5 cm³/min at the end of charge. This represents the electrolysis of water at 0.32 A (C/25). The charging current tapers during charging at a rate dependent on the gas flow from an individual cell until the gas flow reaches 3.5 cm³/min. At this time the charging current is at its preselected cut-off value of 0.32 A and all of the charging current results in the electrolysis of water. In practice the characterization and life testing by mass flow (MF) resulted in charge cut-off at approximately the predetermined gas flow but at end of charge currents almost twice as high as anticipated, 0.58 A rather than 0.32 A. Part of the variation is due to the sensitivity of the end of charge controller. Other possible reasons for this anomaly are covered in the discussion.

Description of batteries

A search was made of lead-acid batteries to locate a lead-calcium grid battery equivalent to either battery reported on in Part I. An 8 Ah lead-calcium grid battery was found and adapted as equivalent to battery A of Part I. Table 1 shows the dimensions of battery C, lead-calcium grid, and battery A, lead-antimony grid, and Table 2 the normalized plate volumes,

TABLE 1

Battery dimensions, 12 ampere hour lead-antimony grid (A) vs. 8 ampere hour lead-calcium grid C

	12 Ah battery A	8 Ah battery C
Weight/cell (g)	570	568
Volume/cell (cm ³)	326	246
Discharge rate for nominal capacity (h)	10	20
Number of positive plates/cell	8	5
Number of negative plates/cell	9	4
Positive plate thickness (cm)	0.165	0.267
Negative plate thickness (cm)	0.140	0.299
Positive plate area		
two sides, total/cell (cm ²)	463	213
Negative plate area		
two sides, total/cell (cm ²)	521	170
Positive plate volume/cell (cm ³)	38	28
Negative plate volume/cell (cm ³)	36	25
Separator area, two sides		
total/cell (cm ²)		
microporous rubber	1401	492
glass mat	1121	1170
Separator volume/cell (cm ³)		
microporous rubber	48	9.3
glass mat	37	38
Electrolyte volume/cell (cm ³)		
below plates	10	0
separator and electrodes	101	[95]
between plates	22	
above plates	20	0
total elect. vol./cell (cm ³)	153	95

TABLE 2

Normalized battery parameters

	12 Ah battery A	Battery A normalized to 8 Ah	Battery normalized C
Positive plate volume (cm ³)	38	25.3	28
Negative plate volume (cm ³)	36	24	25
Electrolyte volume (cm ³)	153	102	95
Positive plate area (cm ²)	463	309	213
Negative plate area (cm ²)	521	347	170

plate areas, and electrolyte volumes of both batteries. Plate area, plate volume, electrolyte volume, and nominal capacity are the critical parameters. The addition of 7 cm³ of electrolyte to battery C results in electrolyte equivalence to battery A.

The smaller plate area of the lead-calcium grid battery C, necessitates the adjustment of its initial charging current, I_0 , so that it is equivalent to the lead-antimony grid battery A:

$$24 \text{ A} \times \frac{213 \text{ cm}^2}{463 \text{ cm}^2} = 11.0 \text{ A}$$

The above calculation assumes that true plate areas are directly proportional to apparent plate areas.

These two adjustments, electrolyte volume and initial charging current, result in battery C, lead-calcium grid, being equivalent to battery A, lead-antimony grid, for characterization and life testing.

The results of X-ray analyses of grid specimens cut from batteries A and C were as follows:

Battery type	Grid type	% Antimony	% Tin	% Calcium
A	Lead-antimony	3.95	0.08	–
C	Lead-calcium	0	0.01	~ 0.20

Characterization and life test data

Each of the three batteries was characterized three times; immediately after conditioning, after 30% degradation in discharge capacity, and after 50% degradation in discharge capacity. Battery conditioning is described in the Experimental section.

Each characterization consisted of two parts. The first part was a 12 hour charge at a constant current of 0.80 A, (C/10), followed by a 0.80 A constant current discharge to 1.75 V/cell. The second was a charge at one of the three charging modes followed by a constant current discharge to 1.75 V/cell. The charging modes were: MCP, charge to 2.67 V/cell at $I_0 = 11 \text{ A}$; MF, charge at $I_0 = 11 \text{ A}$ to a gas flow of 2.35 cm³/cell to a finishing current of 0.6 A; GP, charge at $I_0 = 11 \text{ A}$ at 0.2 lb/in² (gauge) gas pressure to a finishing current of 0.7 A.

Characterization data were collected with a Fluke 2200A Data Logger and included the following:

Time	Hr
Cell voltage	V_c
Positive electrode to Hg/HgSO ₄ ref.	V_+
Negative electrode to Hg/HgSO ₄ ref.	V_-
Charging current	I_t
Gas flow (%)	F_t
% Oxygen in gas flow (%)	O_2
Temperature (°C)	T

From the directly measured data, the following were calculated:

Oxygen flow (cm ³ /min)	F_o
Hydrogen flow (cm ³ /min)	F_h
Charging current, positive electrode (A)	I_+
Charging current, negative electrode (A)	I_-
Total ampere hour charge (Ah)	Aht
Ampere hour charge, positive electrode	Ah ⁺
Ampere hour charge, negative electrode	Ah ⁻
Total watt hour charge (Wh)	Wht
Watt hour charge positive electrode	Wh ⁺
Watt hour charge, negative electrode	Wh ⁻
Total ampere hour efficiency (%Ah)	(Ahd _{is} /Aht)
Ampere hour efficiency, positive electrode (%Ah ⁺)	(Ah ⁺ /Aht)
Ampere hour efficiency, negative electrode (%Ah ⁻)	(Ah ⁻ /Aht)
Total watt hour efficiency (%Wh)*	(Wh _{dis} /Wht)
Watt hour efficiency, positive electrode (Wh ⁺)	(Wh ⁺ /Wht)
Watt hour efficiency, negative electrode (Wh ⁻)	(Wh ⁻ /Wht)
Charge retention, positive electrode (%CR ⁺)	(Ahd _{is} /Ah ⁺)
Charge retention, negative electrode (%CR ⁻)	(Ahd _{is} /Ah ⁻)

* Assuming an average discharge voltage of 1.95 V/cell.

Life testing

Life test data were gathered from Rustrak recorders during charging at one of the three charging modes, MCP, MF, and GP, followed by constant current discharging at 0.80 A to 1.75 V/cell. Life test data logging included time on charge and discharge, (Hr), calculation of discharge capacity, (Hr × I_t), and the calculation of percentage of initial discharge capacity, (Ahd_{is}/Ahd_{is}, init).

Experimental

Battery identification

A coding system was used in identifying each of the three batteries used for this program. For example, MCP-Ca-CC-1 identifies the battery as life tested by the modified constant potential method; having lead-calcium grids, charged by constant current (in this instance), characterization number 1. Conversely, MCP-Ca-MCP-1 identifies the same battery charged by a modified constant potential charge, characterization number 1.

Battery pretest conditioning

This consisted of three cycles of constant current charge at 0.8 A for 12 h followed by constant current discharge at 0.8 A to 1.75 V/cell. Since this discharge rate, C/10 exceeded the manufacturer's rating at C/20, discharge capacities of less than 8 Ah were observed: battery MCP-Ca, 7.52 Ah; battery GP-Ca, 7.32 Ah; battery MF-Ca, 7.98 Ah. These discharge capacities were used in determining 30% and 50% degradation in discharge capacities for characterizations 2 and 3.

Battery pretest conditioning also included the addition of 7 cm³ of 1.26 s.g. H₂SO₄ to each cell. This acid addition resulted in equivalent acid volume per ampere hour of nominal capacity between the 8 Ah lead-calcium grid battery C and the 12 Ah lead-antimony grid battery A used in Part I.

Characterization data

These include measured and calculated data:

Measured

Hr (hours) preset on Fluke No. 2200 A Data Logger

V_c (cell volts)

V^+ (positive to ref. volts)

V^- (negative to ref. volts)

I_t (charge current) mV drop across precision 1 mohm resistor

F_t (gas mass flow) mV output of Hastings Mass Flowmeter, calibration constant 2.57 cm³/min/mV

O₂ (% oxygen) mV output of Beckman Oxygen Analyzer, calibration constant 0.5 mV/1% oxygen

T (temperature) mV iron-constantan thermocouple, 0 C reference, 19.3798 C/mV

Calculated

F_o (oxygen flow, cm³/min) $F_t \times \% O_2 / 100$

F_h (hydrogen flow, cm³/min) $F_t - F_o$

I_+ (charge current, positive electrode) $I_t - F_o / 3.7355$

I_- (charge current, negative electrode) $I_t - F_h / 7.4834$

Aht (total ampere hour charge) $\Delta Hr \times \Delta I_t$

Ah⁺ (Ah charge, positive electrode) $\Delta Hr \times \Delta I_+$

Ah⁻ (Ah charge, negative electrode) $\Delta Hr \times \Delta I_-$

Wht (total watt hour charge) Aht $\times V_c$

Wh⁺ (watt hour charge, positive electrode) (Ah⁺) $\times V_c$

Wh⁻ (watt hour charge, negative electrode) (Ah⁻) $\times V_c$

Discharge after charge (discharge time $\times 0.8$ A)

Ampere hour efficiency (Ah discharge/Aht)

Watt hour efficiency (Ah discharge $\times 1.95$)/Wht

Results

Table 3 represents measured and calculated quantities at the end of charge.

TABLE 3
End of charge characterization data

Cell	Char. no.	Mode	Time (h)	Volts		Current (A)	Gas flow (cm ² /min)	O ₂ (%)	Gas flow (cm ³ /min)		Current (A)		Ampere hours		Watt hours		Ah discharge			
				V _c	V ₋				F _t	F _o	F _h	I _t	I ₊	I ₋	Aht	Ah ⁺		Ah ⁻	Wh ⁺	Wh ⁻
MCP-Ca	1	CC	12.5	2.79	1.33	1.46	0.83	7.16	45	3.21	3.95	0.50	0.30	10.67	8.00	8.29	29.76	22.32	23.12	7.46
	2	CC	12	2.80	1.40	1.40	0.78	1.82	33	0.60	1.21	0.62	0.62	9.63	8.42	9.04	26.97	23.57	26.31	5.58
	3	CC	12.4	2.82	1.39	1.43	0.81	4.28	30	1.28	3.00	0.40	0.41	10.07	6.68	6.55	28.38	18.83	18.46	3.56
MF-Ca	1	CC	11.7	2.77	1.35	1.42	0.82	6.84	33	2.25	4.58	0.22	0.21	9.73	8.50	8.73	26.95	23.53	24.18	8.38
	2	CC	11.8	2.81	1.34	1.46	0.81	7.78	39	3.04	4.74	0.00	0.18	9.69	5.23	6.90	27.24	14.70	19.38	7.16
	3	CC	12	2.82	1.34	1.48	0.82	3.70	33	1.22	2.48	0.50	0.49	9.70	8.24	7.32	27.35	23.24	20.64	6.32
GP-Ca	1	CC	12.3	2.78	1.37	1.40	0.79	1.37	21	0.29	1.08	0.72	0.65	9.93	9.64	9.58	27.61	26.81	26.64	7.54
	2	CC	12.5	2.80	1.36	1.44	0.78	8.02	32	2.67	5.45	0.10	0.06	9.94	7.71	7.56	27.83	21.59	21.17	5.72
	3	CC	11	2.81	1.34	1.48	0.80	8.33	33	2.75	5.58	0.07	0.06	8.83	6.70	5.78	24.81	18.83	16.24	5.73
MCP-Ca	1	MCP	3	2.71	1.31	1.40	0.74	3.06	31	0.96	2.10	0.48	0.46	8.48	8.03	8.40	22.98	21.76	22.76	7.26
	2	MCP	1.8	2.66	1.35	1.31	0.82	1.22	20	0.24	0.98	0.26	0.19	5.57	5.34	5.46	14.81	14.19	14.53	5.25
	3	MCP	1.6	2.68	1.34	1.34	0.84	1.56	21	0.33	1.23	0.15	0.07	3.73	3.45	3.60	9.53	8.83	9.19	3.60
MF-Ca	1	MF	2.1	2.69	1.31	1.38	0.61	3.26	24	0.78	2.48	0.40	0.28	8.24	7.40	8.02	22.17	19.91	21.58	8.19
	2	MF	1.62	2.70	1.30	1.40	0.57	1.15	19	0.22	0.93	0.51	0.45	6.92	6.06	6.36	18.67	16.32	17.18	6.77
	3	MF	1.60	2.70	1.27	1.43	0.57	3.60	14	0.50	3.10	0.44	0.16	5.97	5.37	5.72	16.12	14.50	15.44	6.08
GP-Ca	1	GP	1	2.64	1.29	1.35	0.87	2.25	82	1.85	0.41	0.47	0.92	7.08	6.58	7.03	18.69	17.37	18.56	7.00
	2	GP	1.2	2.64	1.31	1.33	0.88	1.80	100	1.80	0.00	0.20	0.68	7.00	6.54	6.99	18.45	17.23	18.42	6.04
	3	GP	1.8	2.50	1.23	1.26	0.93	1.86	99	1.84	0.02	0.44	0.93	6.66	5.87	6.66	17.02	15.00	17.02	4.89

TABLE 4
Summary data of characterizations

Battery no.	Char. no.	Charge mode	No. of cycles	Ampere hour		Watt hour		% Charge acceptance**		% Charge retention***		% Nom	
				Charge	Dis. Eff.	Charge	Dis.*	Pos	Neg	Pos	Neg		
MCP-Ca	1	CC	4	10.67	7.46	29.76	14.55	49	75	78	93	90	99
	2	CC	65	9.63	5.58	26.97	10.88	40	87	94	66	62	74
	3	CC	117	10.07	3.56	28.38	6.94	24	66	65	53	54	47
MF-Ca	1	CC	4	9.73	8.38	26.95	16.34	61	87	90	99	96	105
	2	CC	46	9.69	7.16	27.24	13.96	51	54	71	137	104	90
	3	CC	98	9.70	6.32	27.35	12.32	45	85	75	77	86	79
GP-Ca	1	CC	6	9.93	7.54	27.61	14.70	53	97	96	78	79	103
	2	CC	59	9.94	5.72	27.83	11.15	40	78	76	74	76	78
	3	CC	126	8.83	5.73	24.81	11.17	45	76	65	86	99	78
MCP-Ca	1	MCP	5	8.48	7.26	22.98	14.16	62	95	99	90	86	97
	2	MCP	66	5.57	5.25	14.81	10.23	69	96	98	98	96	70
	3	MCP	116	3.73	3.60	9.53	7.02	74	93	96	104	100	47
MF-Ca	1	MF	5	8.24	8.19	22.17	15.97	72	90	97	111	102	103
	2	MF	47	6.92	6.77	18.67	13.20	71	88	92	112	106	85
	3	MF	99	5.97	6.08	16.12	11.85	74	90	96	113	106	77
GP-Ca	1	GP	7	7.08	7	18.69	13.65	73	93	99	106	100	96
	2	GP	60	7.00	6.04	18.45	11.78	64	93	100	92	86	82
	3	GP	127	6.66	4.69	17.02	9.14	54	88	100	80	70	64

* Average voltage during discharge = 1.95 V.

** Ah⁺/Aht.

*** Ahdis./Ah⁺.

Table 4 contains calculated quantities used in determining changes in battery performance with age.

Table 5 is used in evaluating electrolyte utilization as related to cell degradation with life. This possibility is considered below.

Table 6 indicates decay in discharge capacities with life.

Tables 7, 8, and 9 summarize comparison data between lead-antimony and lead-calcium grid batteries.

TABLE 5

Electrolyte specific gravity and water makeup

Battery number	Character number	Cell 1			Cell 2			Cell 3		
		Volts	Sp. Gr.	cm ³ Makeup	Volts	Sp. Gr.	cm ³ Makeup	Volts	Sp. Gr.	cm ³ Makeup
MCP-Ca	1	-	*1.26	**7	-	*1.26	**7	-	*1.26	**7
	2	2.17	1.22	21	2.17	1.25	21	2.17	1.17	21
	3	2.14	1.24	14.4	2.14	1.24	14.2	2.14	1.23	14.2
GP-Ca	1	-	1.26	7	-	1.26	7	-	1.26	7
	2	2.03	1.13	3	2.01	1.12	3	2.02	1.17	3
	3	2.05	1.15	30	2.05	1.15	30	2.05	1.17	30
MF-Ca	1	-	1.26	7	-	1.26	7	-	1.26	7
	2	-	1.15	19.2	-	1.15	19.2	-	1.16	19.2
	3	2.02	1.14	25	2.02	1.15	24	2.02	1.14	25

*Specific gravity of electrolyte in charged state prior to Char. 1. All other electrolyte sp. gr. in discharged state prior to indicated water makeup and characterization.

**7 cm³ 1.26 H₂SO₄ added to each cell to make electrolyte volume/Ah equivalent to 12 Ah cell used in Part I.

TABLE 6

Life tests

Cycle No.	Nominal capacity, Ah								
	(7.52) MCP-Ca			(7.92) MF-Ca			(7.32) GP-Ca		
	Charge time (h)	Dis. Ah	% Nom.	Charge time (h)	Dis. Ah	% Nom.	Charge time (h)	Dis. Ah	% Nom.
5	(1) 3.0	7.26	97	(1) 2.10	8.19	103			
6	2.9	6.45	86	1.80	7.86	99			
7	2.05	6.56	87	1.80	7.60	96	(1) 2.64	7.00	96
8	2.15	6.35	84	1.52	7.14	90			
9	2.10	5.84	78	1.50	6.77	85			
10	2.02	5.62	75	1.52	6.53	82	1.36	7.04	96
15	2.10	5.81	77	1.22	6.16	78	1.16	6.34	87
20	2.10	5.94	80	1.22	5.94	75	1.35	5.86	81
25	1.90	5.70	76	1.15	5.76	73	1.22	5.49	75
30	1.96	5.84	78	1.10	5.49	69	1.00	5.44	74

(continued on facing page)

TABLE 6 (continued)

Cycle No.	Nominal capacity, Ah								
	(7.52) MCP-Ca			(7.92) MF-Ca			(7.32) GP-Ca		
	Charge time (h)	Dis. Ah	% Nom.	Charge time (h)	Dis. Ah	% Nom.	Charge time (h)	Dis. Ah	% Nom.
35	1.86	5.33	71	1.02	5.25	66	0.76	5.14	70
40	2.52	5.38	72	0.98	5.00	63	0.80	4.82	66
45	2.16	5.22	69	0.86	4.72	60	0.80	4.62	63
47	2.22	5.18	69	(2) 1.62	6.77	85	0.78	4.68	64
50	2.42	5.13	68	1.15	5.64	71	0.80	4.60	63
55	2.28	5.04	67	1.02	5.01	63	0.72	4.28	58
60	2.04	3.52	47	0.96	4.72	60	(2) 1.15	6.00	82
65	-	-	-	0.86	4.42	56	0.72	4.30	59
66	(2) 1.80	5.25	70	0.96	4.50	57	0.70	4.13	56
70	2.70	5.06	67	0.82	4.30	54	0.84	3.68	50
75	2.56	4.74	63	0.96	4.29	54	0.80	4.44	61
80	2.50	4.82	64	0.95	4.22	53	1.15	4.50	61
85	2.30	4.46	59	0.86	4.13	52	1.16	4.43	61
90	2.25	4.27	57	0.88	4.02	51	0.78	4.06	55
95	2.02	4.10	55	0.82	3.94	50	1.20	4.29	59
99	1.90	4.06	54	(3) 1.60	6.08	77	1.16	4.18	57
100	2.00	4.05	54	1.20	5.62	71	0.72	3.90	53
105	1.80	3.84	51	0.98	4.92	62	1.86	4.40	60
110	1.76	3.72	49	0.90	4.54	57	0.86	4.20	57
115	1.56	3.17	42	0.90	4.28	54	0.85	3.97	54
116	(3) 1.60	3.56	47	0.82	4.27	54	1.20	4.24	58
120	1.36	3.52	47	0.82	4.18	53	1.15	4.05	55
125	1.30	3.26	43	0.80	4.10	52	0.70	3.68	50
127	1.26	3.17	42	0.76	4.02	51	(3) 1.80	4.69	64
130	1.22	3.15	42	0.78	3.98	50	1.75	5.86	80
135				0.80	3.98	50	1.64	5.20	71
140	1.12	2.88	38	0.75	3.94	50	1.44	5.07	69
145				0.76	3.84	48	1.30	4.83	66
150	1.02	2.62	35	0.75	3.82	48	1.30	4.58	63
155				0.75	3.74	47	1.20	4.29	59
160	0.98	2.32	31	0.70	3.68	46	0.70	3.84	53
165				0.70	3.70	47	0.76	3.89	53
170	1.02	1.97	26	0.70	3.60	45	0.78	3.95	54
175				0.82	3.70	47	1.10	4.00	55
180	0.86	1.94	26	0.70	3.64	46	1.10	3.96	54
185				0.80	4.08	52	0.66	3.60	49
190	0.80	1.78	24	0.80	4.24	53	0.65	3.34	46
220							0.62	2.96	40

() Characterization number.

TABLE 7

Comparison summary of life test data, lead-antimony *vs.* lead-calcium grid type batteries

Battery type	Grid type	Total cycles to failure		
		MCP	MF	GP
A	Pb/Sb	129	*111	175
B	Pb/Sb	325	188	172
C	Pb/Ca	110	130	185

*Sudden failure.

Discussion

Discussion of the experimental results covers two broad areas: (1) the performance of the lead-calcium grid batteries cycled by three charging methods selected for this program; and (2) the comparison of the lead-calcium grid batteries evaluated for this part of the program with the lead-antimony grid batteries covered in Part I.

Life tests

For this program, batteries reached the end of useful lives when discharge capacities degraded to 50% of initial discharge capacity. Discharge capacity was measured in ampere hours required for battery voltage to drop to 1.75 V/cell when discharged at 0.80 A. From Table 6, battery cycle lives were: gas pressure controlled charge, 127 cycles; modified constant potential charge, 110 cycles; mass flow charge, 99 cycles.

There are several possible reasons for the gradual lessening in discharge capacity of batteries cycled for this program. Among these is water loss through gassing during charging. For this program, electrolyte volumes and specific gravities were measured for fresh batteries and immediately prior to each characterization (Table 5).

Since the 102 cm³ of 1.26 s.g. acid represents approximately twice the amount of acid necessary for an 8 Ah discharge, of the lead-calcium battery, and since water loss was small for the charging methods used for this program, electrolyte limitation was not considered likely for the anticipated cycle life of these batteries. The end of discharge electrolyte specific gravity measurements, as shown in Table 5, indicate that electrolyte specific gravities were such that acid limitation was not the chief contributor to discharge capacity degradation.

Another possibility for the gradual lessening in discharge capacity of batteries cycled for this program could result from repeated undercharging. Since the gas flow and gas pressure controlled charging methods selected for this program and applied to life testing did not allow for deliberate overcharging, as in the case for most commercial chargers, repeated undercharging

TABLE 8

End of charge characterization data lead-antimony vs. lead-calcium grids

Battery type	Char. No.	Time (h)	Volts		Current (A)	Gas flow (cm ³ /min) F_t	O ₂ (%)	Gas flow (cm ³ /min)		Current (A)	
			V_c	V_+				V_-	F_o	F_h	I_t^+
MCP-A-MCP 1		4	2.58	1.28	1.30	4.87	—	—	—	—	—
MCP-A-MCP 2		3.5	2.48	1.27	1.21	8.16	30	2.48	5.68	0.33	0.23
MCP-A-MCP 3		6.2	2.34	1.31	1.02	7.79	32	1.48	3.13	0.63	0.61
MCP-Ca-MCP 1		3	2.71	1.31	1.40	3.06	31	0.96	2.1	0.48	0.46
MCP-Ca-MCP 2		1.8	2.66	1.35	1.31	1.22	20	0.24	0.98	0.26	0.19
MCP-Ca-MCP 3		1.6	2.68	1.34	1.34	1.56	21	0.33	1.23	0.15	0.07
GP-A-GP 1		4.0	2.42	1.25	1.18	3.88	17.7	0.69	3.19	0.26	0.01
GP-A-GP 2		3.33	2.38	1.26	1.12	3.37	26.1	0.89	2.48	0.52	0.43
GP-A-GP 3		5.83	2.37	1.25	1.12	2.75	27.4	0.75	2.00	0.29	0.32
GP-Ca-GP 1		1	2.64	1.29	1.35	2.25	82	1.85	0.41	0.47	0.92
GP-Ca-GP 2		1.2	2.64	1.31	1.33	1.80	100	1.80	0	0.20	0.68
GP-Ca-GP 3		1.8	2.50	1.23	1.26	1.86	99	1.84	0.02	0.44	0.93
MF-Ca-MF 1		2.05	2.69	1.31	1.38	3.26	24	0.78	2.48	0.40	0.28
MF-Ca-MF 2		1.62	2.70	1.30	1.40	1.15	19	0.22	0.93	0.51	0.45
MF-Ca-MF 3		1.60	2.70	1.27	1.43	3.60	14	0.50	3.10	0.44	0.16

A Lead-antimony grid (Part I).

Ca Lead-calcium grid.

Battery type MF-A-MF failed prematurely and no data are available.

TABLE 9
 Characterization at MCP, MF, and GP charges lead-antimony vs. lead-calcium grid

Characterization number	1						2						3							
	Efficiency		Charge accept.		Ah Recovery		Efficiency		Charge accept.		Ah Recovery		Efficiency		Charge accept.		Ah Recovery			
	Ah	Wh	Pos.	Neg.	Pos.	Neg.	Ah	Wh	Pos.	Neg.	Pos.	Neg.	Ah	Wh	Pos.	Neg.	Ah	Wh	Pos.	Neg.
MCP-A	83	66	-	-	-	-	74	61	73	75	102	100	67	57	58	91	115	74		
MCP-Ca	86	62	95	99	90	86	94	69	96	98	98	96	97	74	93	96	104	100		
GP-A	92	75	81	81	113	113	89	77	84	87	105	102	91	76	88	89	103	101		
GP-Ca	99	73	93	99	106	100	86	64	93	100	92	86	70	54	88	100	80	70		
MF-A	88	72	97	91	88	93	-	-	-	-	-	-	-	-	-	-	-	-		
MF-Ca	99	72	90	97	111	102	98	71	88	92	112	106	102	74	90	96	113	106		

Watt hour efficiency, assume 1.95 av. V during discharge.

Percent charge acceptance, Ah[±]/Aht.

Ampere hour recovery, Ahdis./Ah[±].

A = Lead-antimony (Part I).

Ca = Lead-calcium.

is a possible reason for the gradual degradation in discharge capacity. The life test data in Table 6 suggest this possibility particularly near the end of battery life of the gas flow controlled charges. As stated in the experimental section, each characterization included a C/10 constant current charge for 12 h. This type of charge allows for a 20% overcharge. As the batteries age their discharge capacities decrease, thus the C/10 charge for 12 h for an aging battery represents proportionately more overcharge than for a new battery.

The first part of each characterization, a constant current charge and discharge, as indicated above preceded the life test cycles indicated as (1), (2), and (3) in Table 6. Increases in discharge capacities for the mass flow and gas pressure controlled charges are noted at characterizations (2) and (3). The effect is more temporary after characterization (2) than after characterization (3) but shows that discharge capacity restoration can be achieved by overcharging at constant current.

The battery charged by modified constant potential did not increase in discharge capacity after constant current charges (2) or (3). This results from battery MCP being charged to a higher potential during life testing than either battery MF or battery GP, therefore it received some overcharge during life testing.

By including the perturbation in the life test resulting from the overcharge occurring during constant current characterization charges, the useful lives of the batteries can be revised as follows: GP, from 127 cycles to 185 cycles; MF, from 99 cycles to 130 cycles; MCP, 110 cycles (no increase).

Table 6 shows that the lead-calcium grid battery, which was life tested by the GP method, retained 40% of its initial discharge capacity after 220 cycles, with a similar retention of capacity for the battery charged by the MF method.

Comparison of life test data obtained on the lead-calcium grid batteries with the lead-antimony grid batteries covered in Part I is shown in Table 7. The lead-calcium grid battery C has a shorter life than the lead-antimony grid batteries A and B when cycled by the MCP and MF methods, but a longer life when cycled by the GP method. The reasons for the longer life of the lead-calcium grid battery C, when cycled by the gas pressure method, are related to its lower voltage, lower gas flow, and higher current at the end of charge.

Table 6 shows that charging time decreases with battery age. The exception to this is immediately after a constant current charge. Lessening in charging time results from gradual reduction in battery charge acceptance with battery aging. It requires progressively less time to arrive at the end of charge current, a controlling gas pressure, a controlling gas flow, or a controlling voltage for the GP, MF, and MCP charge methods respectively.

End of charge voltages V_c , V_+ , and V_- (Table 3)

The average end of charge voltages, V_c for the constant current characterization charges show that the end of charge voltages increase slightly during cycle life; 2.78 V for characterization number (1), to 2.82 V for

characterization number (3). Individual electrode voltages V_+ and V_- vary slightly with age but suggest an increase in V_- and a decrease in V_+ . The increased end of charge voltages reflect less charging efficiency for constant current charging of aging batteries.

Battery MCP, life tested by the MCP method, was charged to a preset voltage of 2.67 V/cell; however, its end of charge voltage during characterization varied from 2.71 to 2.66 V, 2%. The individual electrode end of charge voltages for the MCP characterizations varied slightly during battery life; the positive electrode voltage V_+ (+ 3%) and the negative electrode V_- (− 6%), without a pattern relatable to life.

The end of charge voltages for the batteries characterized by the MF and the GP methods did not vary with age. The exception to this was characterization number (3) for battery GP, which had an end of charge voltage of 2.50 V. Battery GP operated at a lower end of charge voltage than either battery MF or battery MCP. The end of charge voltages are relatable to the battery cycle life; the lower the end of charge voltage, the longer the cycle life. This observation plus recovery of capacity resulting from constant current overcharging suggests that for maximum life, lead–calcium grid batteries should be deliberately undercharged by limiting the end of charge voltage, and periodically overcharged to recover capacity lost by repeated undercharging.

The lead–antimony grid batteries, unlike the lead–calcium grid batteries when charged at constant current, exhibited decreased end of charge voltages with age. This drop in battery voltage is due to a decrease of 17% in the end of charge voltage of the negative electrode between characterization number (1) and characterization number (3). This negative electrode voltage difference between the lead–calcium grid and the lead–antimony grid batteries is attributable to the composition of the grids. A similar decrease in the end of charge negative electrode potential is observed when the lead–antimony type batteries are charged by the MCP, MF, and GP methods. However, it is less noticeable for the gas controlled charges. Regardless of the grid composition, the gas controlled charges are current regulated by the sum of the gasses evolved from both electrodes. For example, if the negative electrode of the lead–antimony grid battery becomes poisoned by the migration of antimony to it during successive cycling, its hydrogen gassing potential is reduced and it gasses hydrogen earlier in the charge. The gassing of hydrogen results in a reduction in the charging current when the charge is controlled by gas flow or differential gas pressure. The reduction in the charging current results in a lowering of the potential of both cell electrodes. Since the negative electrode normally begins gassing at a higher potential than the positive electrode, the reduction in the cell potential with aging is more pronounced for the negative electrode.

End of charge currents I_+ , I_- , and I_c (Table 3)

The end of charge current, I_c , for the constant current charges was fixed at 0.80 A. I_+ and I_- were variable end of charge currents for this charging

method. The end of charge currents, I_t , for the MF-Ca and the GP-Ca charging methods were also fixed at 0.60 and 0.80 A respectively, with I_+ and I_- being variable. The end of charge current, I_t , for the MCP charging method is directly related to the end of charge voltage, V_c . This is consistent for MCP-Ca characterizations (2) and (3). The relatively high end of charge current for MCP-Ca characterization number (1) plus the relatively high end of charge gassing rate is probably attributable to an upward drift in the power supply voltage during characterization. This type of anomalous charging behavior is a defect inherent in the MCP charging method. The limiting or "bus" voltage must be extremely stable since small variations in the limiting voltage result in large variations in charging current.

The actual charging currents are represented by I_+ and I_- . At the end of a complete charge I_+ and I_- should be zero, with all of the charging current, I_t , resulting in gassing; the amount of gassing being minimal but just sufficient to maintain the battery in the charged state. This does not apply to the constant current charging method where substantial overcharge is applied. For constant current characterization the end of charge current, I_t , should be 0.80 A. I_+ and I_- should be zero; all of the charging current, I_t , resulting in gassing. These conditions were met for some of the constant current characterizations: MF-Ca-CC-2, GP-Ca-CC-2, and GP-Ca-CC-3; but not for the remaining characterizations and, because of the complex nature of the charging process, the reasons for this are not readily explainable. The end of charge current, I_t , may include current part of which results in gasses which are recombined, oxidized or reduced, within the cell and do not appear as gas flow, F_t , external to the battery. Total gas flow, F_t , is then smaller than is the case where no recombination occurs and I_+ and I_- appear to be larger. Since gas recombination is not directly proportional to the applied charging current, but to the diffusion rates of oxygen and hydrogen, the gas recombination effect on total gas flow, F_t , is more evident for smaller end of charge currents. Since oxygen is more readily recombined than hydrogen, the division of the gas flow between oxygen flow, F_o , and the hydrogen flow, F_h , results in less oxygen measured external to the cell and a larger I_+ than calculated.

Another contribution to the charging current not readily measurable is that part of the charging current which results in grid corrosion. Overcharging causes oxidation of the positive grid which results in the charging current for the positive electrode, I_+ , being less than would be the case where less or no grid corrosion occurs.

Comparison of the end of charge currents of the lead-calcium grid batteries with the end of charge currents for the lead-antimony grid batteries is difficult since different end of charge voltages were used for the GP charges, and different end of charge flow rates were used for the MF charges.

Gas flow F_t , % O_2 , F_o , and F_h

The charging current applied to a fully charged battery results in the electrolysis of water, 33% oxygen and 67% hydrogen. Accordingly, the lead-

calcium grid batteries, charged at 0.80 A constant current, should have an end of charge gas flow, F_t , of 8.98 cm³/min; 33% oxygen and 67% hydrogen. As shown in Table 3, the percentage of hydrogen and oxygen are as expected but the flow rates tend to be less than 8.98 cm³/min, probably due to charging of residual active material previously uncharged during life testing.

The end of charge oxygen flow for the lead-calcium grid batteries charged by the MCP, MF, and GP methods suggests that the GP mode results in undercharging, while the MF mode and characterizations (2) and (3) of the MCP mode reflect overcharging. These observations also apply to life test data summarized in Table 6.

As shown in Table 8, the lead-antimony grid batteries exhibit end of charge oxygen flows of approximately 33% which indicate full charge. Accordingly, life test data in Part I do not show recuperation of discharge capacity for lead-antimony grid batteries as evidenced by the lead-calcium grid batteries.

Ampere hour efficiency and watt hour efficiency

Shown in Tables 4 and 9 are efficiency, charge acceptance, and charge retention summaries for the lead-antimony and lead-calcium grid batteries. The average ampere hour efficiencies for three characterizations of each battery type are:

Charge mode	Ampere hour efficiency (%)	
	Pb/Sb	Pb/Ca
CC	66	65
MCP	75	92
GP	91	85
MF	84	100

Table 4 shows that the lead-calcium batteries, when characterized by the MCP, MF, and GP methods, exhibit higher and virtually constant ampere hour efficiencies as compared with the lead-antimony grid batteries.

The stability of the lead-calcium grid battery in terms of gassing potential results in a higher average ampere hour efficiency for the MCP mode where the battery is always charged to the same limiting potential. This also applies to the MF charging mode. The gassing potential of the negative electrode remains constant during battery life of the lead-calcium grid battery which results in a more consistent controlling gas flow rate during battery life. The low average ampere hour efficiency for the GP-Ca battery results from the very low ampere hour efficiency measured during characterization (3), 70%. The average of characterizations (1) and (2) for this battery is 93% which is comparable to the lead-antimony battery charged by the same method.

The end of charge voltages (Table 8) are higher for the lead-calcium batteries than the lead-antimony batteries. This suggests lower watt-hour

efficiencies. However, the improved ampere hour efficiencies of the lead-calcium batteries for the MCP, MF, and GP characterizations compensate for the higher end of charge voltages. The result is that the watt-hour efficiencies of both grid type batteries are approximately equal for the MCP, MF and GP characterizations.

Charge acceptance and charge recovery

Summaries of charge acceptance and charge recovery data are given in Tables 4 and 9 for the two types of battery. These quantities are approximately the same for the lead-calcium and the lead-antimony grid batteries when characterized by the constant current method. Similar data for the two battery types obtained for the MCP, MF, and GP charging modes show that the lead-calcium grid batteries have better charge acceptances, (Ah^+/Aht) and (Ah^-/Aht) than the lead-antimony grid batteries over the entire life of the batteries. Differences between the two battery types in terms of charge retention, $(Ah\ dis./Ah^+)$ and $(Ah\ dis./Ah^-)$ are not as obvious.

Failure analysis

The three batteries, MCP-Ca, MF-Ca, and GP-Ca, were disassembled in the charged state after the third characterization. The negative electrodes were in excellent condition, having metallic luster and good "smear" properties. Adhesion of the negative active material to the negative grids was excellent. The negative active material was removed from one negative electrode of each of the three batteries. The negative grids were intact and showed no signs of corrosion or buckling.

The appearance of the positive electrodes was good; a uniform black color. However, the fine, black, sandy material was easily removed from the grids indicative of poor cohesion of the positive active material and poor adhesion of the positive active material to the grids. One positive electrode grid from each of the three batteries was stripped using a mannitol solution. The grids, while slightly roughened in texture, were not corroded or buckled.

Failure of the batteries appears to be due to the loss of adhesion of the positive active material to the positive grids. Because of the tight cell construction with thick absorbent separators and "bagged" positive electrodes, the loosened material was retained adjacent to the electrodes. No cell shorting occurred.

Conclusions

(1) Lead-calcium grid batteries can be charged rapidly by gas controlled charging and deep discharged for more than 150 cycles before the discharge capacity degrades to less than 50% of its initial value.

(2) The cycle life of lead-calcium grid batteries can be improved by slightly undercharging during cycling by a gas controlled method coupled with periodic overcharges at constant current.

(3) The cycle lives of lead-calcium grid batteries evaluated by the charging methods covered in this report are inversely proportional to the end of charge voltages.

(4) The ampere hour and watt hour efficiencies of lead-calcium grid batteries charged by gas controlled charging methods are independent of battery age.

(5) The charge acceptance (Ah^{\pm}/Aht) and charge retention ($Ah_{dis.}/Ah^{\pm}$) of lead-calcium grid batteries, when charged by the MCP, MF, and GP methods, are independent of battery age.

(6) The ampere hour efficiencies of lead-calcium grid batteries, when charged by the MCP, MF, and GP methods, are higher than the ampere hour efficiencies of the lead-antimony grid batteries during the entire lives of the batteries.

(7) The watt hour efficiencies of lead-calcium grid batteries, when charged by the MCP, MF, and GP methods, tend to be lower than the watt hour efficiencies of the lead-antimony grid type batteries because of higher charging voltages.

(8) The charge acceptance (Ah^{\pm}/Aht) of the positive and negative electrodes of lead-calcium grid batteries, when charged by the MCP, MF, and GP methods, are higher than the charge acceptance of the lead-antimony grid batteries.

(9) The ampere hour recovery ($Ah_{dis.}/Ah^{\pm}$) of lead-antimony grid batteries is higher than the ampere hour recovery of lead-calcium grid batteries.

(10) Battery failure for lead-calcium batteries charged by the MCP, MF, and GP methods is due to the loss of adhesion of the positive electrode active materials to the positive electrode grids.

Acknowledgement

This work was sponsored and partly financially supported by the International Lead Zinc Research Organization.

Reference

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