

The influence of different operating conditions, especially over-discharge, on the lifetime and performance of lead/acid batteries for photovoltaic systems

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Abstract

A study is made of the influence of different operating conditions (i.e., cycling, self-discharge, floating) on the lifetime of different types of lead/acid battery (vented: flat plate, tubular; valve-regulated: gel, AGM) recommended by manufacturers for solar applications. A bench test has been conducted for more than six years and is based on practical photovoltaic operating conditions. The best performance is exhibited by gel batteries and by vented, pasted-plate batteries with electrolyte agitation. The over-discharge of series-connected cells in large solar battery packs influences the lifetime. Results are given for the discharge and over-discharge characteristics of lead/acid batteries, i.e., battery voltage, cell voltage, positive and negative electrode potentials, gassing rate, oxygen evolution, and sulfuric acid density. The same characteristics are also examined for the recharge of over-discharged batteries. In the over-discharge period, inactive PbO_2 and Pb are activated and can react in a further electrochemical discharge or/and in a chemical disproportionation reaction. © 1997 Elsevier Science S.A.

Keywords: Gel lead/acid batteries; Valve-regulated lead/acid batteries; Oxygen evolution; Electrolyte agitation; Photovoltaic cells; Lead/acid batteries

1. Introduction

In order to obtain a continuous supply of energy from photovoltaic (PV) systems, an energy-storage buffer is required. Rechargeable batteries are typically used for this purpose. The behaviour of batteries in such photovoltaic applications is different from that in more traditional duties and can result in reduced lifetime of the batteries.

The study reported here presents the results of a battery test with different types of lead/acid battery technology. The test is based on simulations of solar insolation and typical loads and has now been in operation for more than six years. Three typical working conditions are considered in the test, namely: cycling, self-discharge and floating.

Because the charging of solar batteries is stochastic, the state-of-charge (SOC) of the battery is equally stochastic. Therefore, deep-discharge can take place. If the cells in a series-connected battery have different capacities (the nominal voltage of PV systems can be between 12 and 400

V), then over-discharge of individual cells can occur. It is well known that such differences in capacity can be caused by variances in cell manufacturing, different degrees of ageing, and deviations in temperature. For example, it has been found [1] that a temperature deviation of only 2 °C leads to the development of differing capacities. Because over-discharge (cell reversal) can be a serious problem with solar batteries, this phenomenon is investigated in detail in the work presented here.

2. PV battery test

2.1. Test batteries

Vented, and valve-regulated (gel type and adsorbed) lead/acid cells, either with pasted or tubular plates, were investigated. All the batteries were recommended by their manufacturers for solar applications. The technical data of the batteries given by the respective manufacturers are summarized in Table 1. The LAB-PP design has an air-forced, electrolyte agitation system.

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Table 1
Technical data of test batteries. All data are for monoblocs

Parameter	Vented		Valve-regulated	
	LAB-PP	LAB-PP	VRLA-gel	VRLA-AGM
Positive plate	pasted	tubular	tubular	pasted
Negative plate	pasted	pasted	pasted	pasted
Electrolyte	flooded	flooded	gelled + H ₃ PO ₄	adsorbed
Rated C ₁₀ /10 capacity (Ah)	125	150	180	168
Rated voltage (V)	6	6	2	12
Dimensions (l × w × h)	283 × 229 × 300	226 × 221 × 405	208 × 109 × 360	340 × 170 × 527
Total weight (kg)	39.7	38	19.5	123
Electrolyte weight (kg)	10.43	11.2		
Rated electrolytespecific density	1.24	1.24		
Specific energy (Wh kg ⁻¹)	18.89	23.7	18.46	16.39
Charge voltage (V/cell)	2.35	2.35	2.33	2.27
Charged charge voltage (V/cell)				2.33

2.2. Test methods

The batteries were tested in a water bath held at 25 °C. Three test procedures were conducted, namely: cycling, self-discharge, and floating. All the batteries were subjected to capacity tests at three-monthly intervals.

2.2.1. Cycling batteries

Cycling batteries were operated according to typical solar conditions. Solar data, repeated weekly, and a load profile, repeated daily, were superimposed (for further details see Ref. [2]). The batteries were stressed by a shallow daily cycle and by a deeper weekly cycle.

2.2.2. Self-discharge batteries

Self-discharge batteries were held at open-circuit at 33% of the rated capacity at the beginning of the tests.

This represents typical operation during periods of bad weather. The low SOC causes increased corrosion and sulfation.

2.2.3. Floating batteries

Floating batteries were charged continuously at 2.25 V/cell.

2.3. Results

The discharge capacity is a key descriptor of the state-of-health of a battery. The change in capacity versus operating time for the three types of test battery are shown in Figs. 1–3. The batteries exhibit different behaviour. With the exception of the VRLA-AGM type, all batteries deliver an initial capacity that is more than 120% of the rated value. The highest initial capacity is obtained for the pasted-plate battery.

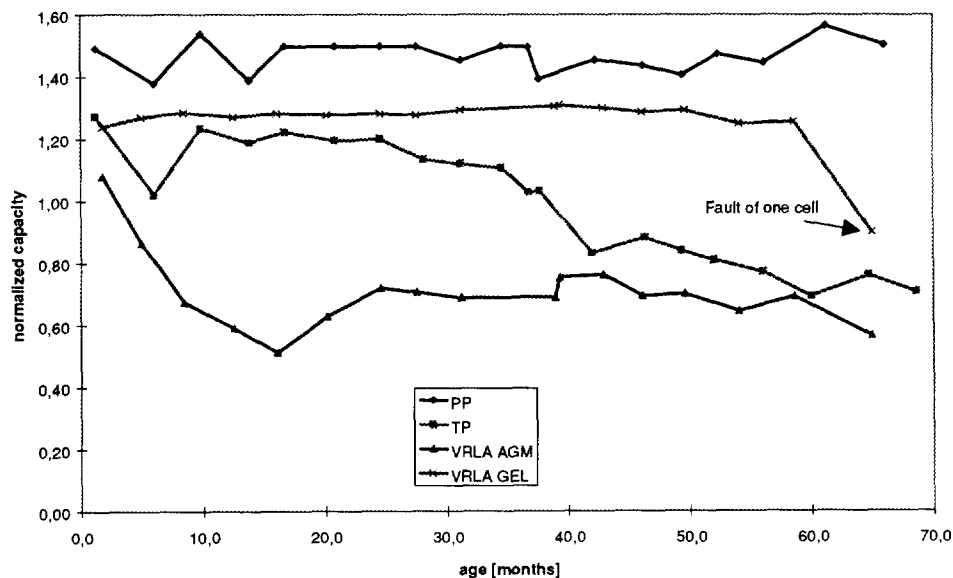


Fig. 1. Capacity vs. time for cycling batteries.

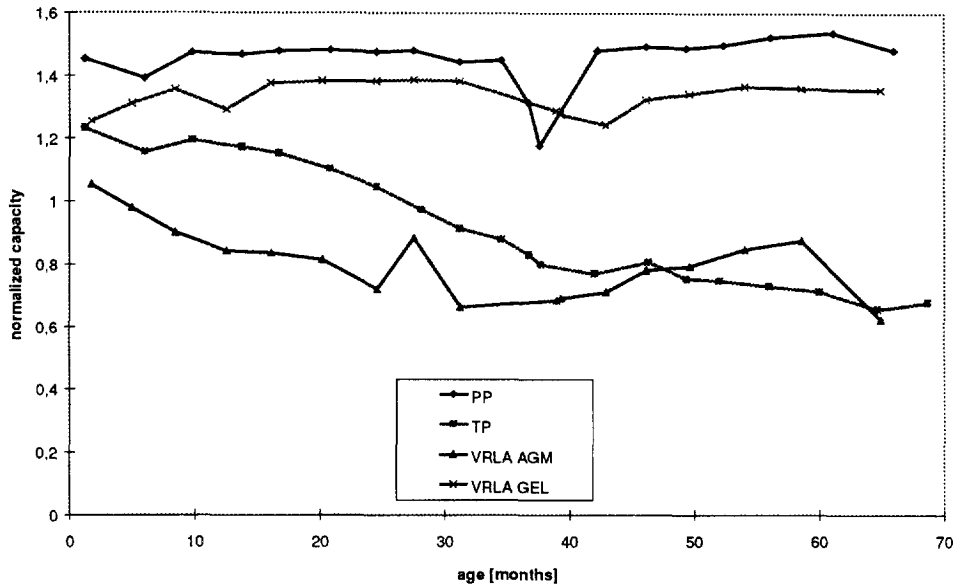


Fig. 2. Capacity vs. time for self-discharge batteries.

2.3.1. Cycling batteries

The capacity versus time relation for cycling batteries is shown in Fig. 1. The vented pasted-plate battery and the valve-regulated gel battery have displayed no significant changes in capacity during five years of cycling. The valve-regulated gel battery then suffered a rapid loss in capacity. This was due to a connection failure in one of the cells.

The AGM battery showed a very fast capacity degradation within the first year of cycling. An equalization charge was carried out and the charge voltage was increased (see Table 1) from 2.27 V (manufacturer’s specification) to 2.33 V. By this method, it was possible to recondition the

battery and the capacity increased during the second year of operation. Significant acid stratification was found in the glass mat. This stratification gave rise to very high contents of lead sulfate in the lower parts of the negative plates.

The tubular-plate battery exhibited a linear decrease in capacity while cycling. The 80% limit was reached after four years of operation. The capacity loss was caused primarily by penetration corrosion of the positive grids.

2.3.2. Self-discharge batteries

The capacity versus time relation for self-discharge batteries is presented in Fig. 2. The ageing of the self-dis-

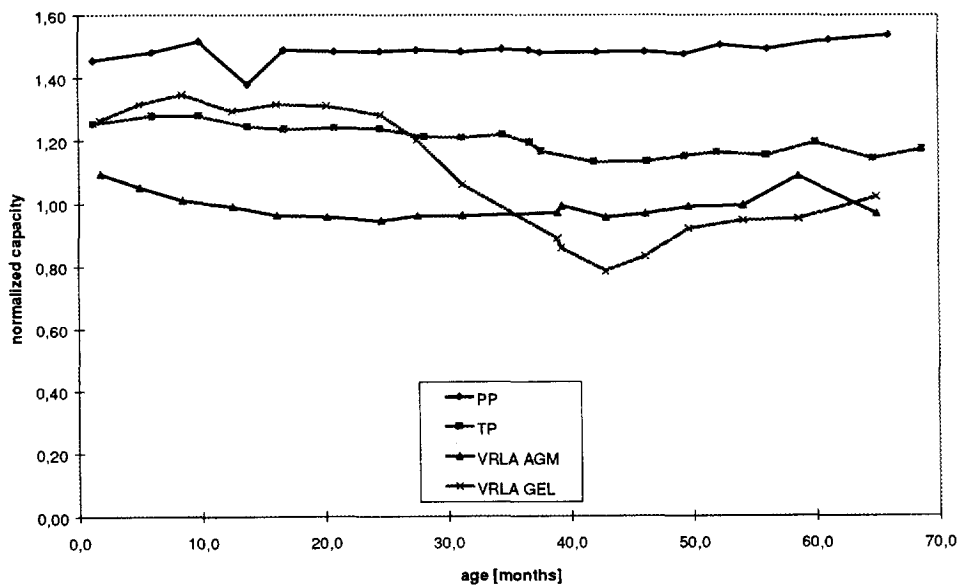


Fig. 3. Capacity vs. time for floating batteries.

charge batteries is very similar to that of the cycling batteries. The vented pasted-plate and the gel batteries did not experience any significant capacity losses during more than five years of operation. The tubular-plate battery reached the 80% capacity limit after three years, and the AGM battery failed after 20 months. The causes of capacity loss were the same as those observed the cycling batteries.

2.3.3. Floating batteries

The capacity versus time relation for floating batteries is given in Fig. 3. The vented-battery types showed no marked degradation in capacity: the AGM battery experienced a small decrease in capacity during the first 12 months, whereas the gel battery suffered a rapid loss in capacity after two years of operation. The latter was due to failure of a single cell. Analysis of this cell revealed that the capacity loss was caused by the development of a crack (due to corrosion) in the top lead-bar junction.

3. Over-discharge tests

3.1. Experimental

To investigate the overcharge characteristics, the experimental set up shown in Fig. 4 was implemented. A Hg/Hg₂SO₄ (5 M H₂SO₄) reference electrode was used to measure the half-cell potentials.

The gas flow and the oxygen content were measured with the following sensors:

1. gas flow: Tylan FM 360-KZ, range 0–10 sccm, accuracy: ± 0.1 sccm; an overload of up to 120% is possible (sccm = standard cubic centimetre per minute)
2. oxygen content: KE 25, Japan Storage Battery, range 0–100%.

The sulfuric acid concentration was measured by conductometry with a WTW LF 537 conductivity meter.

The battery was connected to a computer-controlled test system. To charge the battery with a negative voltage, a potential shift was necessary. Therefore, a parallel circuit of an electronic load and a power supply were connected in series with the battery (not shown in Fig. 4).

From Faraday's laws, it can be calculated that a current flow of 1 A produces 7.48 cm³/min of hydrogen and 3.74 cm³/min of oxygen under normal conditions. For both gases, a flow of 1 cm³/min (atmospheric pressure, 25 °C) is equal to 1 sccm.

The following two types of batteries were used for over-discharge investigations.

(i) For potential and gas measurements: 'battery a': VARTA, Vb 614, 6 V/50 Ah (C₁₀/10), vented type, with pasted plates, Pb–1.6wt.%Sb grids, 2.5 years operation under PV conditions

active mass	PbO ₂	760 g (4 plates) per cell, Faraday equivalent = 170 Ah
	Pb	650 g (5 plates) per cell, Faraday equivalent = 168 Ah
	H ₂ SO ₄	1.108 l ($d = 1.24 \text{ g cm}^{-3}$) per cell, Faraday equivalent = 122 Ah

(ii) For sulfuric acid concentration measurement: 'battery b': Moll, 12 V 36 Ah (C₂₀), vented type with pasted plates, Pb–1.8wt.%Sb grids, new battery

active mass	PbO ₂	282 g per cell, Faraday equivalent = 63 Ah
	Pb	349 g per cell, Faraday equivalent = 90 Ah
	H ₂ SO ₄	0.467 l ($d = 1.285 \text{ g cm}^{-3}$) per cell, Faraday equivalent = 62.6 Ah

To determine the over-discharge characteristic, the test procedure outlined in Table 2 was performed.

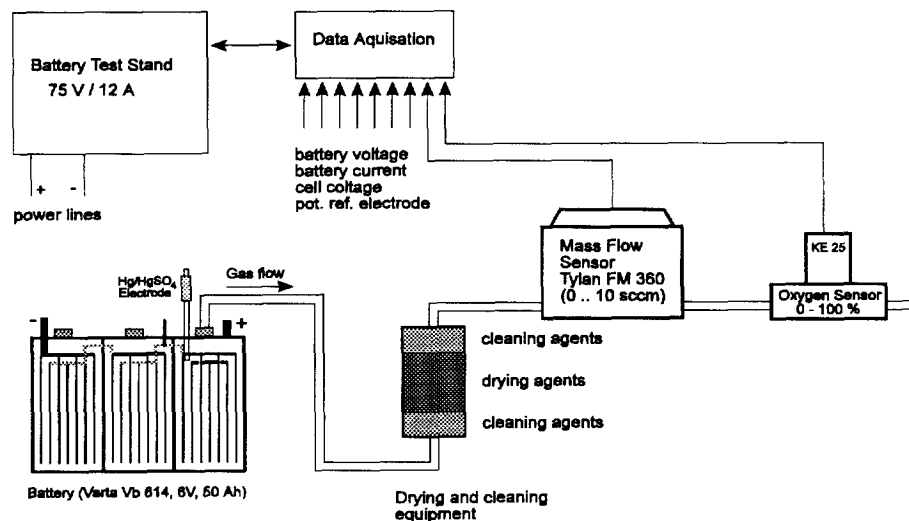


Fig. 4. Experimental setup for overcharge experiments.

Table 2
Procedures for over-discharge tests

	Battery 'a'	Battery 'b'
Step 1	Equalization charge; a SOC of 100% will be reached	
Step 2	Discharge with I_{10} (5 A) until a cut-off voltage of 5.4 V (1.8 V/cell) is reached; the DOD will then be 100%	Discharge and over-discharge with I_{20} (1.8 A) until the total amount of electricity is 108 Ah
Step 3	Over-discharge (reverse charge) with a current of $0.5I_{10}$ (= 2.5 A) until the total amount of electricity will be 180 Ah (= Faraday equivalent of the electrodes)	Open-circuit for 1 h
Step 4	Open circuit for 24 h	Recharge with a constant current of I_{20} (= 1.8 A) until the full SOC is reached
Step 5	Recharge with a constant current of $0.5I_{10}$ (= 2.5 A) until the full SOC is reached	

3.2. Results

3.2.1. Measurement of voltage, electrode potential and gas evolution (battery a)

3.2.1.1. Discharge / over-discharge (steps 2, Table 2). Fig. 5 presents the voltages of the battery (3 cells) and one, arbitrarily selected, cell of this battery. The battery voltage shows a potential step with a large slope (> 400 mV/min, after about 4 h) and a step with a smaller slope (< 5 mV/min, after about 10 h). The voltage of the battery is the sum of the three cell voltages. Given the variations in cell characteristics, the battery voltage should display three potential steps with large slopes and three with small slopes. By contrast, the data show only two potential steps with large slopes, and one with a small slope. The large step with high slope is caused by two cells that exhibit a large slope at the same time. The step with the small slope is caused by the merging of the small slopes of the three cells.

Fig. 6 shows the potential of the positive and the negative electrodes, together with the voltage of the single cell shown in Fig. 5. It is found that the potential step with the steep slope (after about 4 h) is caused by the negative

electrode, while the potential step with the smaller slope (after about 10 h) is caused by the positive electrode. The potentials of both electrodes exhibit an overshoot at the first moment of reverse charging. These overshoots are due to the high resistance of the lead sulfate and the onset of cracking of the sulfate layer.

The total gas flow together with the oxygen content of the gas atmosphere in a single cell (see Fig. 5) are given in Fig. 7. The gas evolution during the reverse charge test is very small (a total cell gas flow of 0.1 sccm is equal to a gassing current of 9 mA at both electrodes). The gas evolution is increased, however, in the first moments of the change in polarity of the electrode.

Measurement of the oxygen content is problematical because of the large gas volume of the battery cell (~ 100 cm³), the low evolution of oxygen, and the temporary reverse gas flow.

3.2.1.2. Recharge after over-discharge (step 5, Table 2). Recharging of the over-discharged battery or cell was achieved with the same constant current as the discharge current, namely, $0.5I_{10}$ (2.5 A). The voltages of the battery and a single cell (from Fig. 5) during recharging of an over-discharged battery are given in Fig. 8. A few minutes

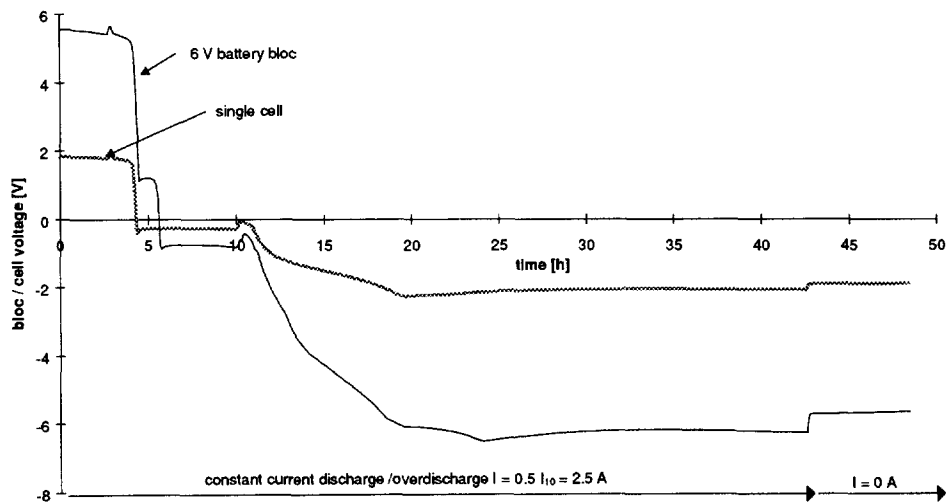


Fig. 5. Battery voltage and cell voltage during over-discharge experiment.

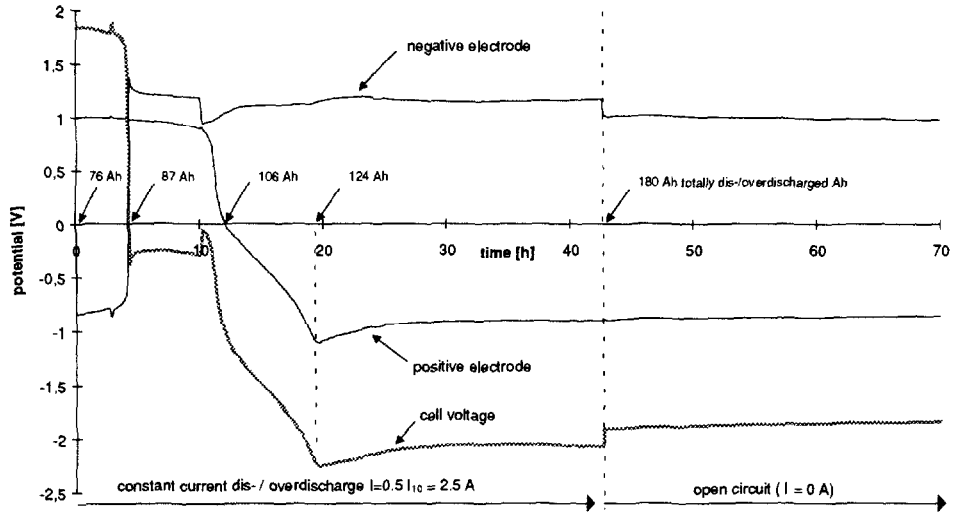


Fig. 6. Electrode potentials vs. Hg/Hg₂SO₄ and voltage of a single cell during over-discharge experiment.

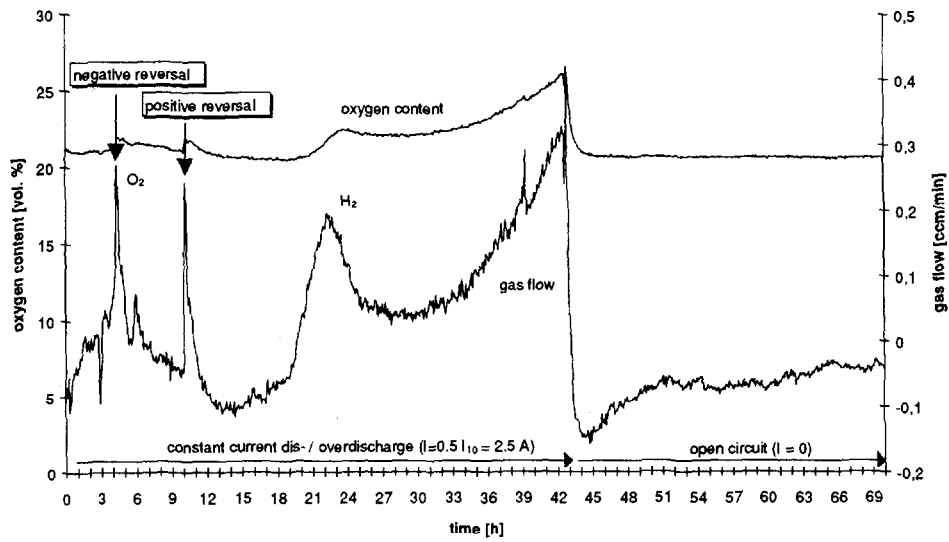


Fig. 7. Gas flow and oxygen content of a single cell during over-discharge experiment.

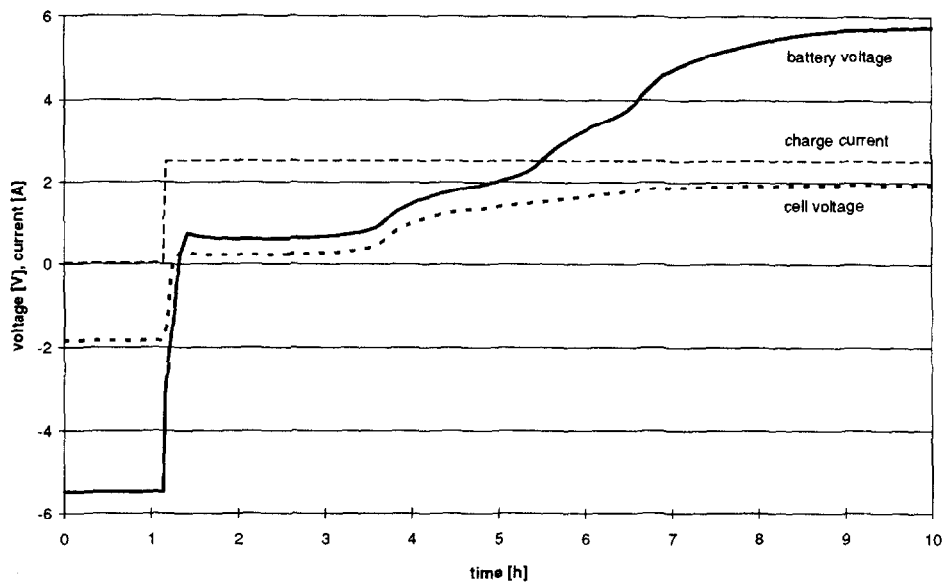


Fig. 8. Battery voltage and cell voltage during recharging (first ten hours) of a over-discharged battery.

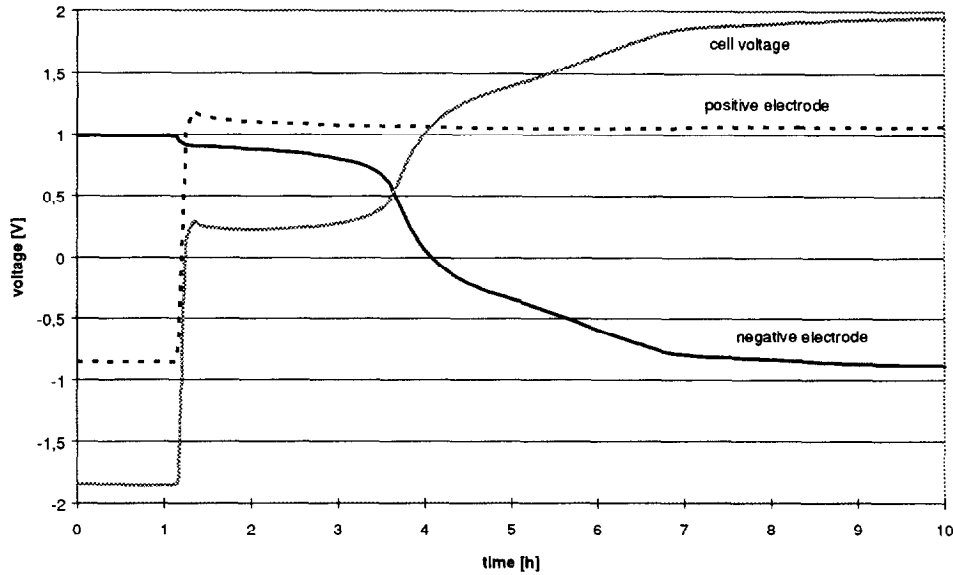


Fig. 9. Cell voltage and electrode potentials during recharging (first ten hours) of a over-discharged cell.

after the recharging was started, the cell and battery voltages increased within 5 min to values of about 230 mV/cell and 630 mV/battery. Further recharge (2.5 h) resulted in a very slow increase in cell voltage; the normal level (about 2 V) was reached within 3 h. By contrast, the battery voltage exhibited a stepwise rise to the normal value (about 6 V) during the first nine hours of charge. This was caused by the different behaviour of the three component cells.

The electrode potentials and the voltage of a single cell (from Fig. 5) are presented in Fig. 9. The first potential increase (rapid, after about 5 min of charge) is caused by

the positive electrode, and the second, slow, potential increase (after about 2.5 h charge) is caused by the negative electrode. It is interesting that, in both cases (over-discharge and recharge), the rapid potential change is caused by a change of only one electrode potential from a negative to a positive value. The slower potential change is caused by the other electrode that changes the potential from a positive to a negative value.

The gassing characteristics of a single cell (from Fig. 5) during the whole recharge procedure is presented in Fig. 10. Significant gassing starts only after 50 h ($Q_C = 125$ Ah) and increases linearly with time. At a cell voltage of

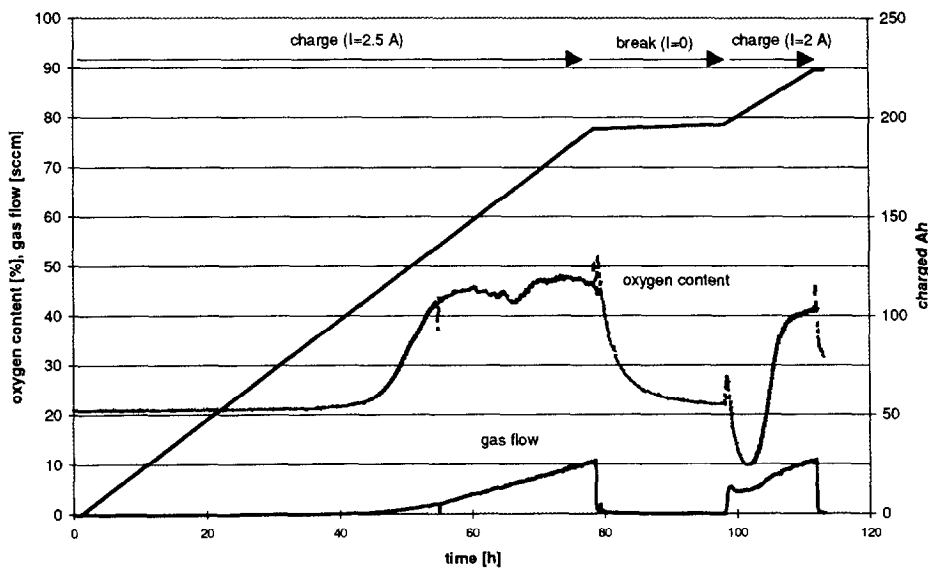


Fig. 10. Gas flow and oxygen content during recharging of a over-discharged cell.

2.35 V, the gassing increases to values up to 10 sccm (900 mA). This is rather a high value for a 50 Ah lead/acid battery at 20 °C. Nevertheless, it should be recognized that the battery had been cycled for 2.5 years. According to the oxygen content, the high gas flow is caused by both electrodes. The positive electrode generates more than the expected stoichiometric value of 33%.

3.2.2. Measurement of sulfuric acid concentration (battery b)

The changes in sulfuric acid concentration, voltage and electrode potentials during discharge, over-discharge, and recharge after over-discharge are shown in Fig. 11. The positive electrode of the new battery (battery b) is limiting the battery capacity. As with battery a, there is a difference in the slope between both electrodes at the transition from discharge to over-discharge, and over-discharge to charge. In contrast to battery a, however, the potential gradient is stronger.

The experiment can be divided into various phases by the difference in the electrode potentials:

1. Phase I: both electrodes are operated under normal discharge conditions; energy is flowing out of the battery.
2. Phase II: the negative electrode is discharged under normal operation conditions and the positive electrode is operated in a reverse polarity mode.
3. Phase III: both electrodes are operated in a reverse polarity mode; energy is flowing into the battery.
4. Phase IV: both electrodes are operated in a reverse mode; energy is flowing out of the battery.
5. Phase V: the negative electrode is charged under normal operation conditions and the positive electrode is operated in a reverse polarity mode. This phase can be

divided into two regions: (i) first five hours of phase V: high slope of the sulfuric acid concentration; (ii) second five hours of phase V: low slope of the sulfuric acid concentration.

6. Phase VI: both electrodes are operated under normal charge conditions; energy is flowing into the battery.

The experiment can be divided also into different phases in terms of the different sulfuric acid concentrations:

1. $t_0 \rightarrow t_1$: decreasing sulfuric acid concentration;
2. $t_1 \rightarrow t_2$: increasing sulfuric acid concentration;
3. $t_2 \rightarrow t_3$: decreasing sulfuric acid concentration, and
4. $t_3 \rightarrow t_4$: increasing sulfuric acid concentration.

The turning points are related to:

1. t_1 : increase in potential of the negative electrode to the $\text{PbO}_2/\text{PbSO}_4$ potential region during discharge/over-discharge;
2. t_2 : start of the charge of the over-discharged cell, and
3. t_3 : increase in potential of the 'positive' electrode to the $\text{PbO}_2/\text{PbSO}_4$ potential region during charge.

In this experiment (battery b) the total amount of discharged electricity was 108 Ah. Because the total theoretical capacity of the electrodes was 63 Ah for the positive electrode and 90 Ah for the negative electrode, 45 Ah should be reduced to Pb at the 'positive' electrode and 18 Ah should be oxidized to PbO_2 at the 'negative' electrode. These Ah amounts must go into the reverse electrodes before the normal potentials of the electrodes are reached. The following values were found before the potential change:

1. 'positive' electrode: 31 Ah reduced to Pb.
2. 'negative electrode: 13 Ah oxidized to PbO_2 .

The differences can be explained by gas evolution and also by the oxidation of blocked Pb in phase VI, or reduction of blocked PbO_2 in the phase V.

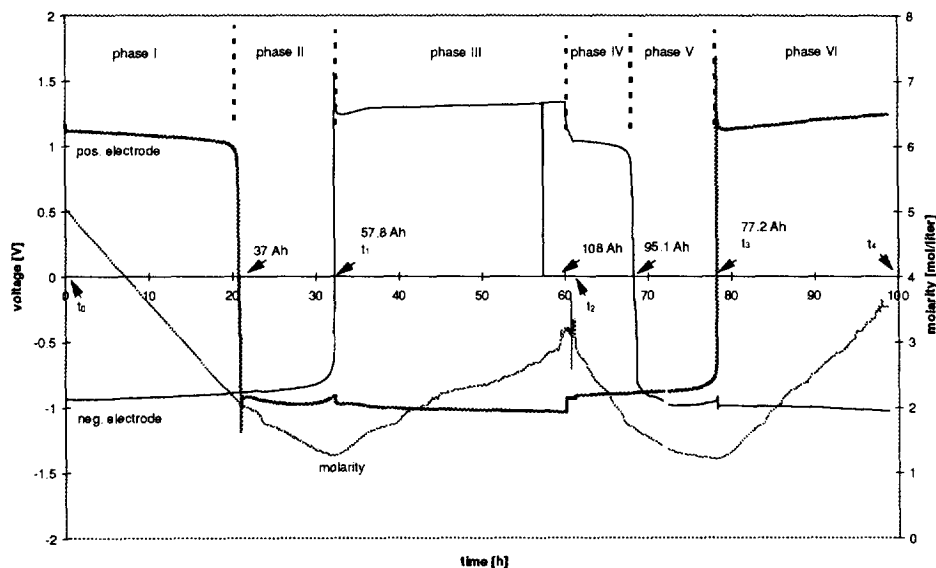
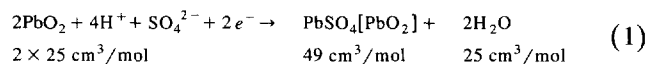


Fig. 11. Sulfuric acid concentration and electrode potentials during the overcharge experiment.

3.3. Discussion

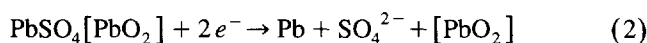
3.3.1. Positive electrode

3.3.1.1. *During discharge.* During discharge, the main reaction (MR) (up to 10 h in Fig. 6) is as follows



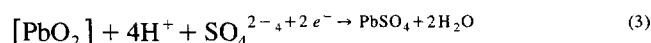
At the end of discharge, PbSO_4 will block the further discharge of PbO_2 , and the remaining PbO_2 ($[\text{PbO}_2]$) will be electrochemically inactive, i.e., $\text{PbSO}_4[\text{PbO}_2]$ is formed. The potential will fall.

3.3.1.2. *Polarity of the positive half-cell.* The polarity of the positive half-cell changes to the Pb/PbSO_4 potential when the lead sulfate is converted to lead in the reverse reaction (RR) (at ~ 10 – 20 h in Fig. 6)

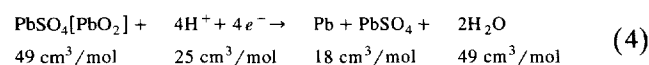


3.3.1.3. *Dense passivating layer of lead sulfate.* The dense passivating layer of lead sulfate will be made porous by the formation of lead because the molar volume relation of the compounds is $V_{\text{PbSO}_4}:V_{\text{Pb}} = 2.64:1$. Therefore, inactive lead dioxide ($[\text{PbO}_2]$) comes into contact with the electrolyte and can be reduced to lead sulfate.

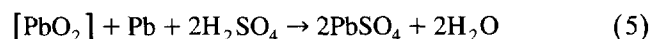
One possibility is a *direct electrochemical reaction*



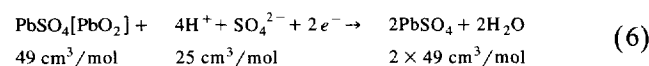
Reactions (2) and (3) yield



The other possibility is a *chemical comproportionation reaction*



Reactions (2) and (5) give



It is difficult to determine whether the electrochemical (Eq. (4)) or the chemical (Eq. (6)) reaction is preferred. The reactions exert different influences on both the porosity and the pH.

The *direct electrochemical reaction* shows a volume decrease of about 2.5% per Faraday. The *chemical comproportionation reaction* leads to a volume increase of about 16% per Faraday (see Table 3). Measurement of the structural parameter as a 'labyrinth' factor (quotient of tortuosity and porosity) and its dependence on the discharge and over-discharge time [3] indicates a preference for the chemical reaction. This is supported by the lead sulfate content [3]. The *direct electrochemical reaction* involves a proton consumption of one mole of protons per

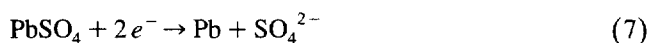
Table 3

Volume change ($\Delta V = V_{\text{end}} - V_{\text{start}}$, $\% = \Delta V / V_{\text{start}}$) and change of proton concentration ($\Delta c_{\text{H}^+} = c_{\text{H}^+, \text{end}} - c_{\text{H}^+, \text{start}}$) for electrochemical (4) and chemical (6) over-discharge reactions at the 'positive' electrode

	ΔV		Δc_{H^+}
	($\text{cm}^3/\text{mol F}$)	(%/F)	(mol/F)
Electrochemical reaction	-1.75	-2.5	-1
Chemical reaction	+12	+16	-2

Faraday. The *chemical comproportionation reaction* leads to a proton consumption of two moles per Faraday (see Table 4).

3.3.1.4. *Remaining PbSO_4 .* The remaining PbSO_4 will be reduced to Pb



This reaction should take place only if the electrode is discharged to 100% of the theoretical (thermodynamic) value. Kinetically, in a positive electrode, Pb, PbSO_4 , and PbO_2 can be in co-existence, e.g., in poorly cured positive electrodes after formation. Therefore, reaction (7) can occur in parallel with reactions (4) and (6).

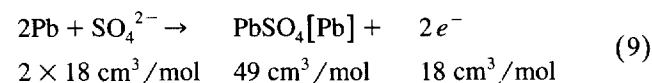
3.3.1.5. *Hydrogen evolution.* Hydrogen evolution can be observed if all the active material is reduced to lead (at about 24 h in Fig. 7)



As dictated by the electrode potential, hydrogen can also be formed at the beginning of over-discharge. High negative potentials (about -2000 mV versus Hg/HgSO_4) will be observed if the positive electrode is passivated [4].

3.3.2. Negative electrode

3.3.2.1. *Discharge.* During discharge, the main reaction (MR) (up to 4.5 h in Fig. 6) is



At the end of discharge, the lead sulfate will block further discharge of Pb and any remaining lead ($[\text{Pb}]$) will be electrochemically inactive, i.e., $\text{PbSO}_4[\text{Pb}]$ is formed. The potential will increase.

3.3.2.2. *Polarity of the negative electrode.* The polarity of the negative electrode will change and the lead sulfate will be oxidized to lead dioxide in the reverse reaction (RR) (at about 4.5 h in Fig. 6)

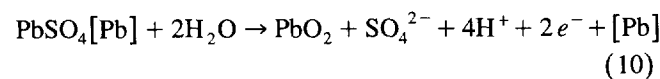


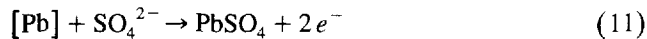
Table 4

Volume change ($\Delta V = V_{\text{end}} - V_{\text{start}}$, % = $\Delta V/V_{\text{start}}$) and change of proton concentration ($\Delta c_{\text{H}^+} = c_{\text{H}^+, \text{end}} - c_{\text{H}^+, \text{start}}$) for electrochemical (12) and chemical (14) over-discharge reactions of the 'negative' electrode

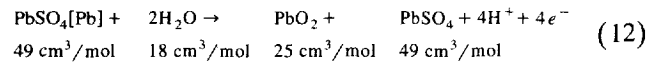
	ΔV		Δc_{H^+} (mol/F)	$\Delta c_{\text{SO}_4^{2-}}$ (mol/F)
	(cm ³ /mol F)	(%/F)		
Electrochemical reaction	+1.75	+2.7	+1	
Chemical reaction	+16	+24		-0.5

3.3.2.3. Lead sulfate layer. The lead sulfate layer will crack due to the formation of lead dioxide. The dense and passivating lead sulfate layer will be made porous by the formation of lead dioxide because the molar volume relation of both compounds is $V_{\text{PbSO}_4}:V_{\text{PbO}_2} = 1.91:1$. Therefore, inactive lead (PbSO₄ [Pb]) comes into contact with the electrolyte and can be oxidized to lead sulfate.

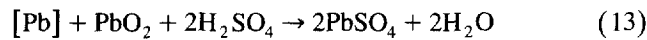
One possibility is a *direct electrochemical reaction*



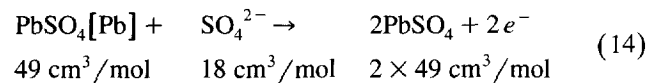
Combined, reactions (10) and (11) yield



The other possibility is a *chemical comproportionation reaction*



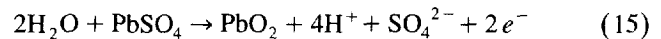
Reactions (10) and (13) yield



The direct electrochemical reaction shows a volume

increase of about 2.7% per Faraday and a proton concentration increase of 1 mol/F. The chemical comproportionation reaction leads to a volume increase of about 24% per Faraday and a sulfate concentration decrease of 0.5 mol/F (Table 4).

3.3.2.4. Remaining PbSO₄. The remaining PbSO₄ will be oxidized to PbO₂ if the electrode is over-discharged



This reaction should take place only if the electrode is discharged to 100% of the theoretical (thermodynamic) value. Kinetically, in a negative electrode, Pb, PbSO₄, and PbO₂ can be in co-existence, e.g., in poorly cured electrodes after formation. Therefore, reaction (15) can occur in parallel with reactions (12) and (14).

3.3.2.5. Oxygen evolution. Oxygen evolution can also take place. Depending on the potential, oxygen can be formed at the beginning of over-discharge (at about 4.5 h Fig. 7) or if all the active material is oxidized to lead dioxide



Table 5

Possible reactions and SO₄²⁻ concentration slope for different phases; calculated by conductivity measurement

Phase	Positive electrode		Negative electrode		Cell		Cell $\Delta c(\text{SO}_4^{2-})$ (mol/1Ah) measured
	possible reaction	$\Delta c(\text{SO}_4^{2-})$ (mol/1Ah) calculated	possible reaction	$\Delta c(\text{SO}_4^{2-})$ (mol/1Ah) calculated	min $\Delta c(\text{SO}_4^{2-})$ (mol/1Ah) calculated	max $\Delta c(\text{SO}_4^{2-})$ (mol/1Ah) calculated	
I ^a	(1)	-0.04	(9)	-0.04	-0.08	-0.08	-0.08
II ^a	(4)	0.0	(9)	-0.04	-0.08		
	(6)	-0.04				0.0	-0.047
	(7)	+0.04					
III ^a	(4)	0.0	(12)	0.0			
	(6)	-0.04	(14)	-0.04	-0.08	+0.08	0.033
	(7)	+0.04	(15)	+0.04			
IV ^a	(4)	0.0	(12)	0.0			
	(6)	+0.04	(14)	+0.04	-0.08	+0.08	-0.1
	(7)	-0.04	(15)	-0.04			
V ^a	(4)	0.0	(9)	+0.04			
	(6)	+0.04			-0.08	0.0	-0.041 ^b
	(7)	-0.04					-0.016 ^b
VI ^a	(1)	0.04	(9)	+0.04	0.08	0.08	0.067

^a Phase I → III are for over-discharge. Phases IV → VI are for charge.

^b Different slopes in phase V.

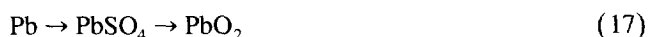
3.3.3. Sulfuric acid concentration

The sulfuric acid concentration provides some additional information about the relationship between the possible reactions during over-discharge. Since the acid concentration is influenced by both electrodes, it is difficult to separate the behaviour at the electrodes. Table 5 provides an overview of the possible reactions and the calculated acid concentration slopes for the different phases in relation to the measured slopes. The minimum and maximum values give the respective minimum and the maximum concentration change in the cell, as calculated from the possible electrode reactions. Depending on the reactions, the slope of the acid concentration can vary over a wide range. In phase I (normal discharge of both electrodes), the slope was -0.08 mol/1Ah. In phase II (over-discharge only of the positive electrode), the measured slope of -0.047 mol/1Ah is mainly caused by the normal discharge of the negative electrode (slope -0.04 mol/1Ah). The positive electrode causes a slope of -0.007 mol/1Ah. This value can be explained by the electrochemical reaction (4) (0 mol/1Ah) superimposed with the chemical reaction (6) (-0.04 mol/1Ah). In phase III (over-discharge of both electrodes), the slope changes from -0.047 mol/1Ah (phase II) to $+0.033$ mol/1Ah (phase III). This shows that, during reverse charging, reactions (15) and (12) should be dominant at the negative electrode, and reactions (7) and (4) at the positive electrode.

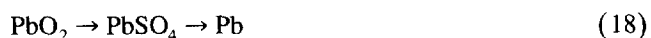
During the recharge of the over-discharged cell, (phase IV–VI), the change in the sulfuric acid concentration should follow the reverse course. Such behaviour can be observed approximately for phases I and IV, and for phases II and V, but not for phases III and IV. This is because of the kinetic hindrance of the thermodynamically possible reaction.

3.3.4. Potential slope

The experimental results with the 2.5-year old battery (battery a) show (see Table 6) that the potential change at the end of the discharge of the negative electrode and at the beginning of the recharge of an overcharged 'positive' electrode



has a much higher potential slope (about two decades) than the potential change at the end of the discharge of the positive electrode and at the beginning of the recharge of an overcharged 'negative' electrode



A different mechanism, which may be associated with a different structural change of the active mass, could be the reason for this behaviour.

For the new battery (battery b), the slope of the change in potential has the same tendency as that for the old battery (battery a), but the differences in the slopes are smaller (Table 6).

Thus, it appears be possible to determine the perfor-

Table 6

Slope of potential change of both electrodes for over-discharge and recharge

Electrode		Slope (V/min)	
		Battery 'a'	Battery 'b'
Positive	$+$ \rightarrow $-$	0.005	0.086
Negative	$-$ \rightarrow $+$	0.15	0.308
'Negative'	$+$ \rightarrow $-$	0.008	0.03
'Positive'	$-$ \rightarrow $+$	0.25	1.4

mance-limiting electrode of a cell by investigation of the cell-voltage slope at the end of discharge. A rapid voltage decrease indicates limitation by the negative plate and a slow voltage decrease indicates limitation by the positive plate. Such a method could be a simple way to obtain more information about battery ageing without the use of complex measuring equipment.

3.3.5. Influence of over-discharge on battery behaviour

Over-discharge of the positive electrode results in the following irreversible changes

- loss of capacity because of morphological changes of the positive active material; these are caused by the mechanical stress ($V_{\text{PbO}_2}:V_{\text{PbSO}_4}:V_{\text{Pb}} = 1.4:2.7:1$) in the active material
- sulfuric acid concentration during the over-discharge period should be (small over-discharge) relatively low, therefore, sulfation can occur
- antimony will be dissolved from the positive grid and enter the electrolyte

Over-discharge of the negative electrode results in the following irreversible changes

- oxidation of the expanders of the negative active-material; this results in a reduced surface area (loss of capacity)
- a loss of capacity because of morphological changes of the negative active-material; this is caused by the mechanical stress in the active material
- open-circuit periods will cause sulfation

With reverse charging, it is expected that the negative electrodes will exhibit a greater degradation in capacity than the positive electrodes. The major reason for this assumption is the fact that the expanders and other additives of the negative plate will be oxidized on reverse charging.

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