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Carbon reactions and effects on valve-regulated lead-acid (VRLA) battery cycle life in high-rate, partial state-of-charge cycling

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ABSTRACT

VRLA batteries in hybrid electric vehicles are operated at a partial state of charge with high current draws for acceleration and regenerative braking. Adding larger amounts of carbon particles to the negative plate material extends battery life. Water loss and increasing internal resistance are a cause of a subsequent failure mode that is related to the carbon and other organic additives in the negative plate. Previous studies of the composition and volume of gases vented from valve-regulated lead-acid (VRLA) batteries and acid-limited batteries at various temperatures and current levels are reviewed and used to develop an understanding of carbon reactions and their effects on battery state of health.

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1. Introduction

In HEV applications, batteries are charged at high rates by regenerative braking and discharged at high rates when the vehicle accelerates. Because the batteries are charged only while the vehicle is operating, they generally operate at an intermediate state of charge, often around 50–53% [1]. In acid-limited VRLA batteries, this typically corresponds to a range of about 27–29% acid at room temperature. This type of application is termed high-rate, partial state-of-charge (HRPSoC) cycling.

VRLA batteries in HRPSoC cycling typically fail because of heavy sulfation of the negative electrode, accompanied by higher internal resistance and cell dry out. Increasing the weight% and surface area of carbon in the negative plate expander extends the cycle life of valve-regulated lead-acid (VRLA) batteries in hybrid electric vehicles (HEVs) [1,2]. Mixtures of barium sulfate, carbon black and "organic expanders" made from wood products, such as ligno-sulfonates, are added to negative plates in both VRLA and flooded batteries.

2. Negative plate additive composition and effects

The main documented benefit of organic expanders such as Vanisperse A is maintaining an open crystal structure in the negative plate during cycling [3]. Organic expanders are at least partially soluble in battery electrolyte and can adsorb on the negative plate. They increase the polarization of the positive plate to a value that allows the negative plate to become less polarized [4]. This may contribute to negative plate sulfation. Peters [5] reported some recent concern that in VRLA batteries, "the strong oxidizing atmosphere and higher temperature of the surface of the negative plate under the internal oxygen cycle will degrade the organic component and thus cause premature battery failure. While there is little quantitative evidence of such degradation, some manufacturers increase the amount of barium sulfate. . . to maintain a small crystal size for the discharge product in the event of loss of effectiveness of the organic component." About 2 wt.% barium sulfate is sometimes added to the negative active material instead of expander organics to avoid voltage change on charge.

Barium sulfate is an insulator with a solubility in sulfuric acid that is even lower than that of lead sulfate. Unlike carbon and ligno-sulfonates, it does not change the over-potential of the negative plate. Myrvold [6] concluded that barium sulfate and lead sulfate interactions with ligno-sulfonates are very similar.

Because barium sulfate is iso-morphous with lead sulfate, it is added to the negative plate to nucleate lead sulfate crystals and thereby reduce crystal size. The optimum amount of barium sulfate in a negative plate with other additives is typically 0.3–0.5 wt.% when used in either flooded or VRLA batteries. Concerns about the stability of organic additives and their effect on the half-cell potentials in lead-acid batteries have led to using higher levels of barium sulfate to replace some of the organic additives in VRLA batteries [2]. The purpose is to make the negative plate easier to recharge by maintaining plate conductivity. Recent studies show that 1% $BaSO_4$ yields better cycle life on ECE 15L cycling than 0.5% [5].

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For VRLA batteries in HEV applications, the amount of high-surface-area carbons has been increased from 0.28 to 2.8% relative to the % lead oxide in the negative paste mix [1,2,5]. This approach reduces negative plate sulfation and hydrogen evolution. Carbon decreases negative sulfation as its particle diameter decreases from about 50 to 30 μm.

When cycled on the EUCAR ECE 15L test regime, the capacity decline per cycle of acid-limited VRLA cells proceeds at a reduced but linear rate. Progressive weight loss and increasing internal resistance accompany this capacity decline. These observations suggest that carbon additions shift the failure mode of VRLA cells in HEVs from negative plate sulfation to progressive water loss.

Evaluating the impact of carbon over a range of temperatures and understanding the sources of water loss are critical to good battery life in HRPSoC applications, especially in hot environments. High-surface-area carbons in the negative plate limit its sulfation and preserve its capacity, but the reaction mechanism is not fully understood. This paper reviews thermodynamic and experimental data on carbon reactions with oxygen and considers a new mechanism for water loss.

3. Chemical self-discharge reactions in VRLA batteries

In 1958, Ruetschi and Angstadt [7] studied the kinetics of self-discharge reactions at 35 °C in single positive or negative plates and in flooded lead-acid cells with two positive and one negative plate. Table 1 shows reactions that they found. The rates of these reactions were determined under various conditions by measuring the concentrations of lead sulfate formed on the positive and negative electrodes.

Soluble antimony compounds form during when antimonial lead grids corrode. These compounds greatly accelerate hydrogen evolution (reaction (4)) at the negative plate. In typical antimony-free alloys used in VRLA batteries, grid corrosion products (reaction (1)) are localized at the interface between the positive active material (PAM) and lead grid. Since their only effect on carbon reactions is dilution of the sulfuric acid electrolyte, this reaction will not be considered further here.

Reaction (2) discharges the positive plate and forms oxygen gas. Reaction (4) discharges the negative plate and forms hydrogen gas.

Ruetschi et al. identified reaction (3) at the positive plate by the change in the self-discharge rate of a single positive plate in sulfuric acid in contact with a hard rubber separator. They concluded that the oxidation of organic material from separators in sulfuric acid to lead sulfate "is responsible for a slight amount of positive self-discharge. The reaction can be minimized by reducing the contact of the separator with the positive plate" or "by using separators most resistant to oxidation". They did not specifically consider possible effects of carbon and ligno-sulfonates in the expander on negative plate self-discharge in this study [7], although carbon may have been added to the hard rubber separator. Carbon dioxide solvates in water to form carbonic acid, which is the most stable form of carbon in acidic aqueous solutions [8]. CO and CO_2 are only slightly soluble in sulfuric acid [8].

Information on carbon thermodynamics is available for carbon dioxide that shows lead carbonate is not stable in a highly acid solution. It is vented rapidly when acid is added to a dry-charged battery that has lead carbonate on the plate surfaces. It has unit activity at about 2.5 pH in water saturated with CO_2 at 1 atm. Carbonic acid, H_2CO_3, is the most stable form of carbon in strong aqueous acids in equilibrium with H_2O and CO_2 at 1 atm and 25 °C [8]. Aqueous $HCOOH \Leftrightarrow CO + H_2O$ is another equilibrium that occurs when water is saturated with carbon monoxide [9].

IUPAC [9] lists the free energy of formation in KJ/mol for $PbSO_4$ as −813.83, compared to −356.0 for aqueous HCOOH, −137.268 for CO (g), −623.42 for aqueous H_2CO_3, −394.383 for CO_2 (g), and −386.2 for CO_2 (aq).

The entropy [9] of these species in $J(mol^{-1}\,K^{-1})$ is 140.2 for $PbSO_4$ compared to 163.6 for aqueous HCOOH, 197.91 for CO (g), 191 for aqueous H_2CO_3, 213.64 for CO_2 (g), and 121 for CO_2 (aq). All of these formation reactions are therefore exothermic and will increase the internal temperature of the battery. But some of this heat will be released if gases are vented from the battery.

In water, the solvated phase of CO is formic acid. If this equilibrium occurs in sulfuric acid, carbon could be transported to the positive plate, in either solvated or gaseous form, where it could react according to reaction (3) to form CO_2 in equilibrium with carbonic acid. Measurements described below on the gas compositions of acid-starved and VRLA batteries show a significant percentage of CO_2. Hydrogen produced at the negative plate by reaction (4) does not directly participate in the carbon reaction. But it may change the vapor pressure of CO and CO_2, the internal cell pressure, and the vent opening frequency.

Table 1
Self-discharge reactions in lead-acid batteries [7,12].

At the positive plate	
Gridcorrosion : $PbO_2 + Pb(grid) + 2H_2SO_4 \Leftrightarrow 2PbSO_4 + 2H_2O$	(1)
Oxygenevolution : $PbO_2 + H_2SO_4 \Leftrightarrow PbSO_4 + H_2O + 1/2O_2$	(2)
Organicoxidation : $PbO_2 + \text{organics} * + H_2SO_4 \Leftrightarrow PbSO_4 + H_2O + CO_2$	(3)
At the negative plate	
Hydrogenevolution : $Pb + H_2SO_4 \Rightarrow PbSO_4 + H_2$	(4)
Oxygenrecombination : $Pb + 1/2O_2 + H_2SO_4 \Rightarrow PbSO_4 + H_2O$	(5)

4. Voltage and gassing measurements of VRLA and acid-starved lead-acid cells on open circuit

The self-discharge reactions in Table 1 reduce the sulfuric acid concentration and acid activity in VRLA AGM cells at a faster rate than in flooded lead-acid cells. Increasing the acid concentration and reducing the acid volume limit the amount of water in the cell. The lower electrolyte volume causes self-discharge to reduce the acid concentration faster than in a flooded battery. Therefore the self-discharge reaction rate can be determined by measuring the open circuit voltage and calculating the ln acid activity. Fig. 1 shows the relationship between the ln of the acid activity and the open circuit voltage of an acid-starved VRLA cell at room temperature [11]. The formula shown was determined by fitting the data from a 12 V VRLA telecom battery.

First order rate equations can be written as a function of the acid concentration in these VRLA AGM cells as follows [12]:

$$\ln a_a - (\ln a_o)_o = -kt$$

where the rate constant at a given temperature is t, the acid activity at time $t = a_a$ and the acid activity at time $t_o = (a_o)_o$.

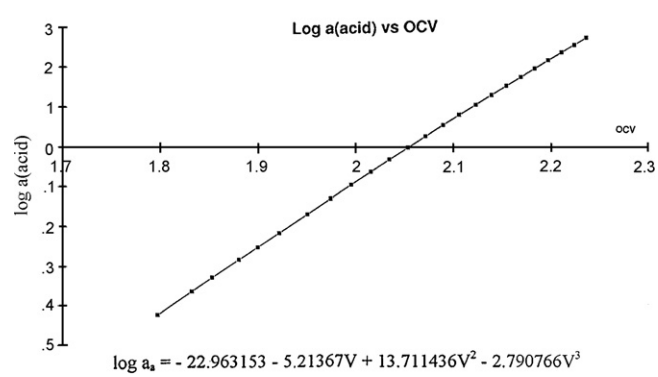

Fig. 1. Relationship between open circuit voltage (OCV) and the acid activity in acid-starved lead-acid batteries [11].

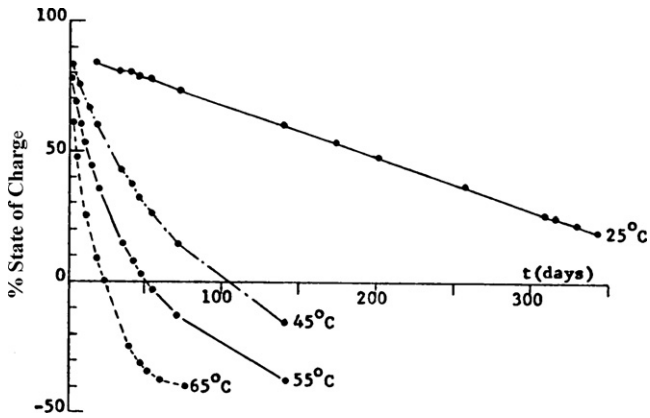

Fig. 2. Relationship between open circuit voltage (OCV) and the acid activity in acid-starved lead-acid batteries [12].

Fig. 2 [12] shows self-discharge curves for the earliest commercial VRLA AGM cells developed by Gates Rubber Co. They have a cylindrical cell design similar to cells that have recently been tested in HEV cycle life studies [1,2]. The linear plot at 25 °C indicates that the rate of self-discharge is a function of the rate of decay of the acid concentration.

The curves in Fig. 2 have a higher initial slope that increases with the storage temperature. The higher the temperature, the faster the self-discharge and the larger the voltage drop before the slope becomes linear. The self-discharge rate constant is determined as a function of T from the limiting slope of a plot of V_{OC} versus time. Self-discharge rates at all temperatures were determined from the limiting slope of the ln activity–storage time curves. At room temperature and above, the limiting slope is easy to determine, but at higher temperatures it becomes difficult to determine this condition. The cause(s) of the initial rapid drop in the cell voltage at high storage temperatures has not previously been explained.

After for the self-discharge rate reaches the limiting slope shown in Fig. 2, gas evolution decreases to a very low level but the acid concentration continues to decrease. Two different reactions could explain the limiting slope where the self-discharge process produces little or no gas. One is the chemical "Oxygen Cycle". Oxygen evolution at the positive plate (reaction (1)) initiates this mechanism. Then at the negative plate, O_2 from the positive plate oxidizes Pb and suppresses H_2 by oxygen recombination (reaction (5)).

$$Pb + 1/2O_2 + H_2SO_4 \Rightarrow PbSO_4 + H_2O$$

In the absence of other reactions, oxygen chemically couples these two reactions to produce an open circuit version of the double sulfate reaction:

$$PbO_2 + Pb + 2H_2SO_4 \Rightarrow 2PbSO_4 + 2H_2O$$

These curves were measured at 55 °C for cells with varying expander compositions. The self-discharge curve did not change when the lignin in the negative plate changed from 0.4 to 0.8%. Likewise, varying the carbon from 0 to 0.2% in the negative plates did not affect the limiting self-discharge rate [12]. However, measurement of the cell voltage or acid concentration alone would not detect either lignin or carbon reactions unless they participate in reactions that dilute the acid concentration.

One way to determine the effects of carbon materials is to measure the composition of gases that evolve from a battery on open circuit. Bullock and Laird [13] measured fairly high levels of carbon dioxide in vent gas from lead-acid batteries formed in acid and then stored on open circuit in a semi-wet condition at temperatures from 25 to 55 °C. Flooded batteries were made and formed as typical automotive designs. Most of the acid was then removed by dumping and centrifuging. Gases were collected through latex tubing using a syringe to sample gases. The gases were then analyzed using a dual column gas chromatograph for CO_2, N_2, H_2, and O_2. The total volume of gas was also recorded. Open circuit voltage readings of the batteries at open circuit were used to monitor the sulfuric acid concentration as a function of storage time. Fig. 3 shows the concentrations of hydrogen, carbon dioxide and sulfuric acid as a function of storage time at 45 °C.

Throughout the test at 45 °C, oxygen was less than 1% of the total gas. The amount of CO_2 detected in the gas space during storage was nearly constant and was independent of the declining acid concentration over the first part of the shelf life. After 45 days, the uncertainty in the volume measurement grew too large to allow measurement of the gas volume. Up to that point, however, the percentage of CO_2 in the total gas collected was 10–20% at 45 °C. Initially the H_2:CO_2 ratio decreases because the rate of CO_2 evolution is independent of acid concentration and fairly constant. But then both the H_2 and CO_2 drop off quickly.

Nelson and McClelland [14] described the composition of vented gases from Gates cells by gas chromatography over an initial 60-day period on open circuit. They concluded that "the composition of the released gases is primarily H_2 and CO_2, along with what appears to be small amounts of CO... initially there is a large excess of H_2 relative to CO_2, probably due to the formation process at the end of which the cells are in overcharge and large quantities of H_2 are generated. As the cells then undergo self-discharge, the relative amount of CO_2 increases slowly and uniformly until at the end of the 60-day test period the molar ratio of H_2:CO_2 is about 7:1, a roughly 10-fold decrease from the initial ratio... Oxygen due to the self-discharge reaction was not detected at any time..." They also speculated that the small amount of CO is derived from the organics present in the cell, possibly as a precursor to CO_2 or by a parallel low-potential pathway, since its presence is noticeably lower under high-level charge conditions.

In the acid-starved SLI battery with antimonial positive grid and low internal pressure, H_2 evolution should be higher. But the self-discharge curves are similar to the Gates VRLA cell with pure lead grids and a 50 psi vent. Possible self-discharge reactions other than the oxygen cycle that could explain carbon dioxide and hydrogen evolution are considered below.

If the reactions in Table 1 are the only self-discharge reactions, CO_2 must be formed by reaction (3) from oxygen that is generated at the positive plate by reaction (2). Elemental carbon particles are usually considered to be stable at the negative plate. So organic expanders that adsorb on the lead dioxide must react to form CO_2

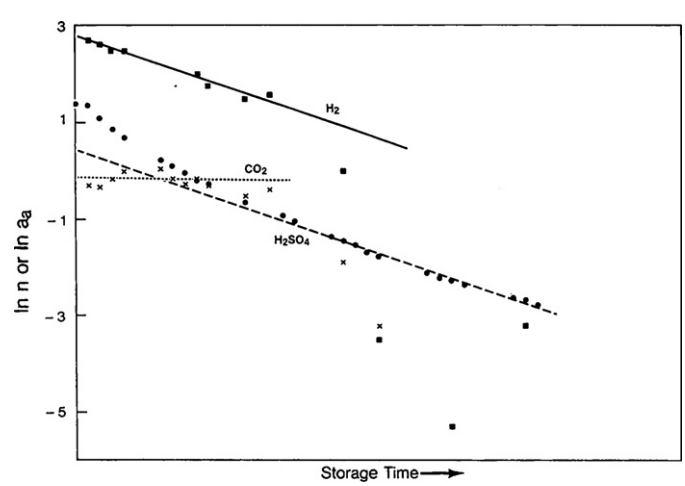

Fig. 3. Composition of vent gas in acid-starved lead-acid battery on open circuit: solid square is H_2, X is CO_2 and solid circle is H_2SO_4.

at the positive plate. If the oxygen is used up before it can diffuse to the negative plate, reaction (5) is suppressed. The dominant self-discharge process at the negative plate is reaction (4), which discharges the sulfates in the lead electrode and forms hydrogen gas.

Dietz et al. [15] studied the resistance of carbon black to oxidation at the lead dioxide positive plate on open circuit. They found that after 56 days of storage in a wet condition, tablets of lead dioxide powder with 2% carbon black contained only 1.4% carbon. They concluded "the oxidation of carbon black already occurs under open circuit conditions of the $PbO_2/PbSO_4$ electrode, i.e. by electrochemical oxidation with PbO_2." Their study confirms that carbon black can be the organic material in reaction (3).

But the carbon black and ligno-sulfonates are not added to the positive plate and have been considered stable in the negative plate. So the question remains, how does carbon black move from the negative plate to the positive plate in a VRLA battery? Still unknown is whether or not oxygen can oxidize organic materials at the negative plate at 45 °C. This reaction would also suppress hydrogen evolution and negative plate sulfation by the following "oxygen/carbon" cycle.

Hypothetical reactions in this scenario are italicized. If O_2 from reaction (2) in Table 1 oxidizes C instead of Pb at the negative electrode: $PbO_2 + H_2SO_4 \Leftrightarrow PbSO_4 + H_2O + 1/2\ O_2$ at the positive plate and $1/2\ O_2 + C \Rightarrow CO$ at the negative plate yield the net reaction: $PbO_2 + H_2SO_4 + C \Rightarrow PbSO_4 + H_2O + CO$. CO is soluble in electrolyte: $H_2O + CO \Leftrightarrow HCOOH$ (aqueous).

So HCOOH (aqueous) can move to the positive plate and oxidize at its surface:

$$PbO_2 + CO + H_2SO_4 \Rightarrow PbSO_4 + H_2O + CO_2$$

The net overall reaction would be :

$$2PbO_2 + 2H_2SO_4 + C \Rightarrow 2PbSO_4$$
$$+ 2H_2O + CO_2 \text{ (equilibrium is } 2H_2O + CO_2 \Leftrightarrow H_2CO_3\text{)}$$

Combining measurements of gas evolution volumes and compositions with measurements of the retention of organic materials in negative plates is needed to determine whether this hypothetical reaction is possible.

5. Carbon reactions during charge and overcharge

When VRLA batteries are on float charge, the oxygen cycle begins with the oxygen formation from water instead of lead dioxide at the positive plate:

$$H_2O \Rightarrow 2H^+ + 1/2O_2 + 2e^- \quad (6)$$

$$Pb + 1/2O_2 + H_2SO_4 \Rightarrow PbSO_4 + H_2O$$

If the oxygen reacts chemically at the negative plate by reaction (5), it produces lead sulfate and water. The lead sulfate can then react with the hydrogen ions and electrons from reaction (6) to recharge the negative electrode.

$$PbSO_4 + 2H^+ + 2e^- \Leftrightarrow Pb + H_2SO_4 \quad (7)$$

No net reaction occurs in a perfect oxygen cycle (reactions (6), (5) and (7)). Because the cell is sealed and acid-limited, oxygen generated at the positive plate can diffuse to the negative plate and chemically discharge it. In an HEV, the high charge currents from regenerative braking and Joule heating from high acceleration currents will cause oxygen evolution at moderate states of charge.

The oxygen is transported to the negative plate as shown in chemical reaction (5) in Table 1. This chemical reaction generates additional heat in a VRLA cell. It will occur even when a disconnected but active negative plate, wet with acid, is lifted from a lead-acid cell and exposed to the oxygen in the air. A charged plate will become almost too hot to touch and produce steam within about 20 min.

Bose and Hampson have studied the reduction of oxygen on lead in sulfuric acid using a rotating disc electrode. Using a mercury/mercurous sulfate reference electrode, they found that the process of oxygen reduction on lead is independent of voltage up to 1.3 V in sulfuric acid at concentrations up to 6 M. The rate of oxygen reduction on lead is faster at lower acid concentrations because the diffusion coefficients of oxygen in sulfuric acid solutions increase with decreasing acid concentrations [17].

The chemical recombination of oxygen at the negative plate will occur at a moderate state of charge because of the high internal temperatures and low acid concentrations associated with VRLA batteries in HRPSoC cycling in HEVs. The effect of the oxygen recombination reaction is to discharge the negative plate chemically at the same time that it is being charged electrochemically. The water and oxygen cancel in Eqs. (6) and (2), so the net effect is the reverse of reaction (7):

$$Pb + H_2SO_4 \Leftrightarrow PbSO_4 + 2H^+ + 2e(\text{areversiblereaction}) \quad (8)$$

When the oxygen cycle is working well, the lead sulfate will recharge quickly. Overall, the water that was decomposed by reaction (6) at the positive plate has been chemically reformed at the negative plate. So there is no net chemical change in the cell.

If reaction (8) is not efficient because of high currents and cell temperatures, some of the hydrogen ions and electrons may be used for hydrogen evolution at the negative plate [6,7].

$$2H^+ + 2e^- \Rightarrow H_2 \quad (9)$$

Reaction (9) maintains the required electro-neutrality of the cell but leaves a sulfated negative plate and hydrogen gas. When hydrogen forms, the effect is permanent sulfation of the negative plate and increased venting of hydrogen. Although the negative plate still contains active lead, the cell capacity is reduced by the loss of H_2SO_4 [5] in the electrolyte.

The reverse of reaction (8) is the only known mechanism for recharging the negative plate. The lack of another known mechanism leaves a gap in our understanding of how the lead sulfate formed by chemical reaction (2) can be recharged when reaction (9) occurs, causing hydrogen loss from the cell.

Gas evolution has been monitored in rectangular, multi-cell VRLA batteries during a float charge at 2.27 V and 46 °C [16]. The measurements show that CO_2 forms at a rate that increases significantly with temperature but decreases after an initial, temperature-dependent time.

Charge reactions have also been monitored at room T in Gates VRLA cells. Total gas volumes over 2 months were 367 ml for D cells and 1688 ml for X cells. Gas compositions were H_2 and CO_2 and about 0.1% CO, with no measurable O_2, and the amount of CO_2 was fairly constant.

In a 72-h charging test with a 1 amp limit, Nelson and McClelland [14] reported that "as the charge V increases to 2.50 V and above, the CO_2 level decreases (as does the CO peak) and O_2 appears. . . .it appears that O_2 recombination is effective in this range and so O_2 levels are moderate."

Gas composition versus charge rate at 120% charge input [14] is shown in Table 2 for a Gates D cell. At 120% state of charge, the current increases from the C/100 to the C rate on the first charge. As the rate increases, the % O_2 increases, and the % of CO_2 and % H_2 decrease. O_2 recombination efficiencies at 120% SOC and STP decrease from 100% at C/100 to 97.7% at C/20, then to 86.6% at C/2 and 13.2% at C/1. The gas volume at 200% SOC at the C/10 rate decreases from the 1st to the 3rd cycle.

Table 2
Composition versus charge rate in Gates D cells 9 [14].

Charge rate	Cycle number	Gas volume, cm^3 at 200% SOC	Gas Composition at 120% SOC		
			$\%H_2$	$\%CO^2$	$\%O_2$
C/100	1	160.4	92.9	5.11	
C/60	1	354.5	94.4	2.78	1.85
C/50	1	432.2	95.4	1.69	1.97
C/40	1	158.9	92.3	4.51	2.22
C/30	1	242.9	90.2	3.98	4.87
C/20	1	349	90.6	2.87	5.54
C/10	1	740	87.8	1.46	9.77
C/2	1	452	84.3	0.42	15.2
C	1	1485	65.7	0.52	33.8
C/50	2	113.1	91.6	2.84	4.56
C/40	2	113.7	94.2	2.95	1.87
C/30	2	114.1	88.1	3.4	7.52
C/10	2	248	74.1	0.79	24.1
C/10	3	129.9	83.4	0.99	14.53

Increases in cell resistance and weight loss with cycling suggest that dry out from water loss is a likely failure mode in batteries with high-carbon levels. But water is not lost in either the oxygen cycle (reactions (6), (5) and (7)) or when an incomplete oxygen cycle causes negative plate sulfation and hydrogen evolution (reactions (6) and (9)):

$$H_2O \Rightarrow 2H^+ + 1/2O_2 + 2e^-$$

and

$$2H^+ + 2e^- \Rightarrow H_2$$

These reactions do not have to be coupled, but if they are, no net reaction occurs.

Weight loss cannot be explained by loss of H_2SO_4 in the latter mechanism. Sulfate ions are retained in the cell, even though they are lost from the acid by reactions with the positive and negative plates. Hydrogen evolution alone does not account for all the observed weight loss in the battery because it weighs so little. The cell weight loss is more than the total weight of available hydrogen in the sulfuric acid contained in the battery.

But if the hydrogen ions and electrons that come from oxygen evolution at the positive are used to form hydrogen gas, how can a sulfated electrode be recharged and electro-neutrality be maintained in a VRLA cell?

Positive grid corrosion (A) and positive plate sulfation (B) are common failure modes that will discharge the plate in normal cycling or standby applications. However, they are not a typical failure mode in HRSoC cycling. A more likely possibility is that hydrogen ions and electrons and carbon oxides can be formed from organic materials.

Batteries in HEVs fail mainly by sulfation of the negative plate. Adding larger amounts of carbon to the negative plate maintains the half-cell potential below the hydrogen evolution potential and reduces negative plate sulfation [1]. The sulfuric acid concentration is thereby maintained and capacity retention improves because capacity is a function of the acid concentration [11,12].

This effect has been demonstrated in recent tests [2], but how carbon maintains the half-cell potential below the hydrogen evolution potential has not been fully explained. It has been reported that the conductivity of a discharged negative plate favors lead sulfate recharge rather than hydrogen evolution [1,19]. Also, carbon black has little effect on plate over-potentials. But high amounts of carbon can delay the potential change to hydrogen evolution during charging [2,5] by improving lead sulfate reactivity. Other chemical and electrochemical effects of high-carbon VRLA batteries have not yet been fully explored. Two other beneficial effects of carbon are evaluated below:

(1) Competition of carbon with lead for oxygen from formation of formic acid (HCOOH), which reduces the amount of lead sulfate formed by an incomplete oxygen cycle. The data in Figs. 4 and 5 on carbon dioxide and oxygen measurements show an apparent competition between oxygen and carbon dioxide formation in a VRLA battery on float at 46 °C.

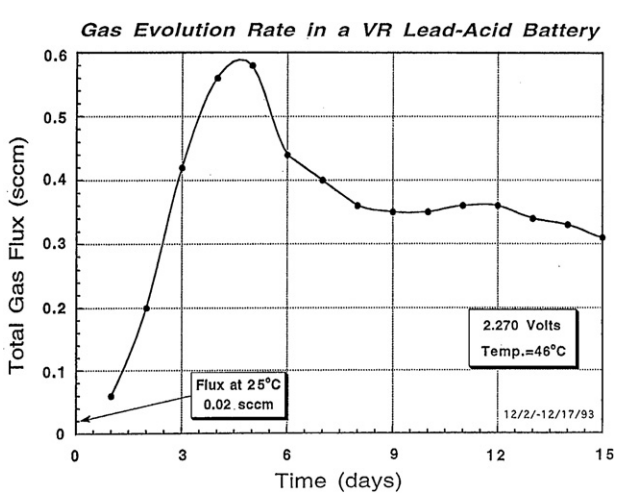

Fig. 4. Gas evolved from a rectangular VRLA battery at 46 °C.

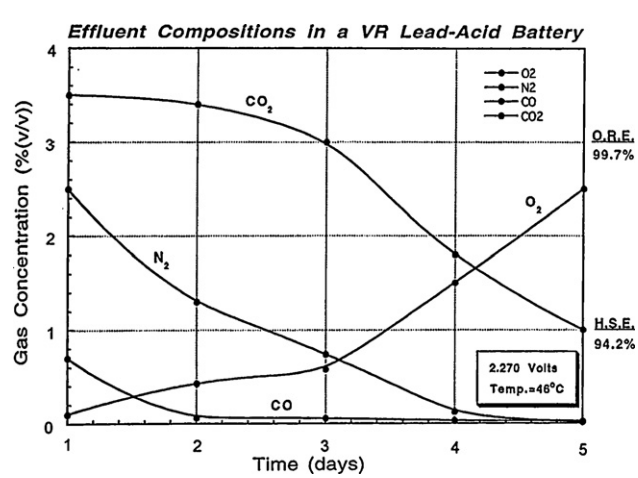

Fig. 5. Composition of gas evolved from VRLA battery at 46 °C.

(2) Providing additional hydrogen ions and electrons for the recharge of lead sulfate by the oxidation of formic acid to carbon dioxide or carbonic acid during charging.

Formic acid (HCOOH) or CO in equilibrium with formic acid can be further oxidized to form carbonic acid, H_2CO_3 (aqueous) $\Leftrightarrow H_2O + CO_2$ at the positive electrode on open circuit or charge. This reaction will accelerate separator dry out by the loss of 2 moles of water for every mole of carbon dioxide that is vented. Water vapor may also be carried out of the cell with the carbon dioxide. This is consistent with the observed failure modes of weight loss and increased resistance in the HEV cycling.

6. Carbon reactions on charge and their effects on cell failure modes in HRPSoC applications

Shiomi et al. [18] showed that large quantities of high-surface-area carbons in the negative plate expander form a conductive network within the lead sulfate matrix of a discharged negative electrode. This conductive matrix facilitates high rate recharge by providing a conductive path for the electrochemical conversion of lead sulfate back to lead. The effect is greater with the addition of larger amounts of carbon and also increases as the surface area of the carbon increases.

However, even with the addition of carbon to the negative plate, the resistance of VRLA batteries increases during EUCAR ECE 15L cycling.

In recent EUCAR tests of VRLA batteries with high-carbon negative plates, the capacity at the 5-h rate is over 80% of rating at the end of the test. But even though negative plate sulfation has decreased [1,2], the power requirements cannot be met. Higher cell resistance is consistent with the reduced power that has been observed.

Gas composition studies described above show that oxygen reacts with carbon in a lead-acid cell to form CO_2 and possibly CO. High-surface-area carbon apparently competes with lead to react with oxygen instead of sulfating the negative plate (reaction (8)). The addition of high-surface-area carbons will also accelerate the formation of carbon dioxide at the positive plate (reaction (3)) if the carbon material can diffuse to the positive plate in the liquid or gas phase or as a gas such as CO. A VRLA battery AGM separator could facilitate the diffusion of oxidized carbons to the positive electrodes if they are either a gas or are solvated.

In HEV applications, the carbon in the negative plate increases the HRPSoc cycle life as the amount of C in the negative plate increases and C diameter decreases from about 50 to 30 μm.

Formation of CO_2 increases the internal cell pressure and causes the cell to vent gas and water vapor.

Carbon reduces negative plate sulfation and capacity loss by competing with lead to react with O_2 during charge. Carbon also increases the conductivity of the negative plate and may add capacitance, and it reduces cell heating on overcharge. These effects all contribute to increased cycle life for VRLA batteries in high-rate, partial state-of-charge cycling applications, such as hybrid electric vehicles.

Gas composition measurements on open circuit and during charge show that hydrogen vents when C oxidizes instead of Pb. Water is lost when small amounts of CO_2 form. The positive plate also discharges when CO or CO_2 form. So although C oxidation protects the negative plate from premature capacity loss, it also promotes positive plate discharge at open circuit and dry out on charge. High temperatures greatly accelerate these processes.

Dietz et al. [15] suspended carbon black in acid and partially oxidized it in 1.05 g cm^{-3} sulfuric acid on a gold electrode at about 300 mV versus a mercury/mercurous sulfate electrode in a potentiodynamic sweep. Small, pasted positive electrodes were prepared with 0.2% or 10% carbon black. They were cured, formed and cycled using a 10-h rate discharge for 1 h with a 5-h charge. Analyses showed that 40% of the carbon was left in the electrodes after formation and only 0.05% after cycling.

Kimura et al. [19] wrote that carbon is intrinsically hydrophobic, but becomes dispersible as a result of electrochemical oxidation. They made a solution of 0.018 wt.% carbon colloid by electrochemical oxidation of a graphite anode in water. Then they added the colloidal solution to dilute battery electrolyte to produce a solution containing 0.018% carbon. A 6 V lead-acid battery containing this solution was discharged down to 4.8 V. The colloidal carbon enhanced its charge–discharge capacity and extended life compared to the same battery design without the additive. ESCA studies showed that in dilute sulfuric acid in a lead-acid battery, both the lead and lead dioxide electrodes are electrochemically doped with oxidized carbon particles, including carbon particles with carboxyl group (HCOO−) on their surfaces. Lead dioxide and lead electrodes could be doped in the potential range from −0.8 to 1.2 V versus a gold electrode. Kimura's electrochemical doping reaction may be a first step in a mechanism for the formation of carbon monoxide and formic acid at the negative plate from the very fine carbon particles added to the paste.

The standard reduction potential for $CO_2 + 2H^+ + 2e^- \Rightarrow HCOOH$ (aqueous) is −0.16 V. It becomes more positive as the pH decreases but also depends on the activity of HCOOH and the partial pressure of CO_2. This will depend on kinetic effects during the acceleration phase of an ECE 15L cycle.

This potential is between the standard reduction potentials for $PbSO_4 + 2e^- \Rightarrow Pb + SO_4^=$ at −0.3505 V and $Pb^{2+} + 2e^- \Rightarrow Pb$ at −0.1251 V [10]. In dilute aqueous electrolyte, carbon particles with carboxyl group or formic acid in equilibrium with CO may be produced when the negative plate discharges at high currents. Alternatively, gas evolution at the negative electrode may break off oxidized carbon particles during a high rate charge, and the particles could then be oxidized at the positive plate.

The crystallization processes of lead oxide and lead sulfate that form at the negative plate during discharge are kinetically hindered. The voltage dip (coup de fouet) that occurs when a fully charged battery is discharged at high rates is evidence for this kinetic hindrance. So it is conceivable that in a dynamic HRPSoC cycle, a very high-surface-area carbon can compete with lead to react with oxygen and water, forming a product that is either in a solution or gas phase.

When C forms HCOOH, two hydrogen ions are released, and these can react to form either hydrogen gas or lead sulfate.

$$C + 2H_2O \Rightarrow HCOOH(\text{aqueous}) + 2H^+ + 2e^- \quad (10)$$

The hydrogen ions and electrons can be used to either recharge lead sulfate at the negative plate or form hydrogen gas.

The overall effect of adding excess high-surface-area carbon to the negative plate is that sulfuric acid is preserved in the cell and capacity can thus be recovered that would otherwise be lost by one or more of these mechanisms. This is a better outcome because the negative plate is less sulfated and HCOOH formation conserves some water in the cell. But when CO is oxidized to form CO_2 2 moles of water are lost.

Further work to understand the kinetics of carbon reactions in VRLA batteries during ECE 15L cycling is needed to optimize battery life, particularly in hot climates.

7. Summary and conclusions

Water loss mechanisms in VRLA batteries are as follows:

- Carbon oxides form by oxidizing carbon or soluble lignin derivatives and then vent from the VRLA cell.
- For every mole of CO vented, 1 mole of water is lost.
- 2 moles of water are consumed in the formation of 1 mole of CO_2.
- For every mole of O_2 or CO_2 vented, 2 moles of water are lost.
- Formation of CO or CO_2 increases vapor pressure and water vapor loss from the cell.

Dry out increases with increasing temperature and charge and discharge currents. Efforts to further extend life, especially for hot climates, should focus more on the high current and high temperature effects. Measurements of gas compositions vented from the cell and battery weight loss are non-destructive methods of following carbon reactions during cycling. Determining carbon concentrations in the negative and positive plates and electrolyte before and after formation and cycling will increase our understanding of the reaction mechanisms. More studies are required at high ambient temperatures to understand potential failure modes of VRLA batteries containing carbon in hot climates.

The new "UltraBattery" design, a capacitor/battery hybrid in a single cell [20] should be effective in reducing high currents and temperatures at the negative plate. The results described above are probably a major reason for the improved cycle life of the UltraBattery in HEV tests. Similar studies of side reactions at the carbon capacitor in parallel with the lead negative plate should be pursued to evaluate its benefits and to determine its stability at high ambient temperatures.

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