

HYDROGEN SULFIDE IN VRLA CELLS

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Abstract

This investigation of hydrogen sulfide (H₂S) in VRLA cells produced three major results. First, VRLA cells produce significant amounts of H₂S even at normal float voltages. Second, the lead dioxide in the positive plates absorbs much of this H₂S. Third, this "H₂S cycle" in VRLA cells results in an equilibrium concentration level of no more than 1 ppm of H₂S in the gas space of a typical cell. The data further suggests that even this low amount may decline over time.

1. Introduction

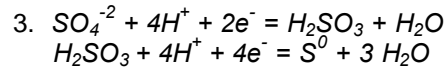
What causes the rotten egg smell that is sometimes associated with batteries? The answer is hydrogen sulfide (H₂S). This smell is common around flooded lead acid batteries, but rarely noted around VRLA batteries under normal operating conditions. H₂S is also produced naturally in the intestines of humans and animals. While there is much known on the formation process of H₂S in living beings, there is relatively little known about the formation of this gas in batteries. Common opinion states that it is not readily formed in VRLA cells except under extreme conditions such as thermal runaway. However, we have produced H₂S in lab experiments where we have allowed charged negative active material to undergo chemical self-discharge in pure sulfuric acid. The fact that we could so easily produce this poisonous gas piqued our curiosity and has led to this paper.

2. Background

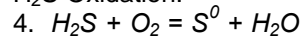
At the start of the investigation, a literature review was conducted that provided some background chemical and electrochemical reactions involving sulfur^{1,2,3}. This literature search included the reactions related to the liberation of H₂S and revealed the following chemistries for sulfur:

H₂S Evolution:

- $MeS + 2H^+ = H_2S + Me^+$
 $Me = Na^0, Fe^0, Ag^0 \text{ Sulfides, etc.}$
- $S^0 + Pb^0 + 4H^+ = H_2S + H_2 + Pb^{++}$

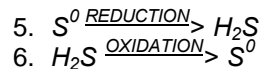


H₂S Oxidation:



From the above it is seen that metal sulfides placed in dilute sulfuric acid will liberate H₂S. The literature further relates that the sulfide reaction rate decreases from the sodium to silver cation. In all cases the metal sulfide reaction rate is such that evolution of H₂S is immediate upon the metal sulfide contacting the electrolyte. These sulfides are likely spent in cell formation unless they are not exposed to the acid at that time.

The activation energy of Reaction No.3 may preclude its taking place at other than high temperatures and voltages as reported in a VRLA battery thermal runaway study.⁴ In our work the reaction rate of the reduction of the sulfate ion to H₂S is studied in some detail. Most importantly, from above the following oxidation-reduction cycle is seen to exist,



It is possible that sulfur from the oxidation of H₂S is deposited on the negative plate surfaces as well as suspended in the electrolyte. This sulfur is then reduced back to H₂S. It is the formation and destruction of H₂S we define as the H₂S oxidation-reduction cycle.

This paper will present our efforts to understand and experimentally evaluate the cycle as described theoretically above. We will discuss H₂S formation, H₂S oxidation and absorption, and the resulting equilibrium concentration developed.

3. Hydrogen Sulfide can be produced under everyday conditions.

One goal of our work was to prove, despite common opinion, that hydrogen sulfide (H₂S) could be produced at normal float voltages and operating temperatures. Another goal was to identify the major source, or sources, for hydrogen sulfide production so that we might minimize or eliminate its production. A series of experiments quickly eliminated many candidates, such as expander, for example, and allowed us to focus on a reaction between pure lead and sulfuric acid as the primary mechanism for production of the poisonous gas.

We designed and constructed a testing rig to electrolyze sulfuric acid and to specifically capture the gas that evolved from a negative electrode. From our literature search and earlier work, we were aware that H₂S was not being produced on the positive electrode. The largely hydrogen gas evolved was analyzed using a gas chromatograph (GC). The test was run at a variety of voltages to determine if there was a change in concentration of the H₂S produced. Figure 1 shows a schematic of our test setup.

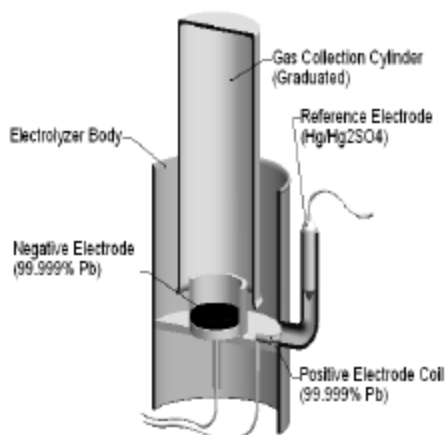


Figure 1: The testing rig developed to electrolyze sulfuric acid and capture the hydrogen evolved from the negative electrode.

The negative electrode is a disk of ultra pure lead (99.999% Pb) that sits directly under a graduated cylinder. The gas evolved from the lead disk is captured for later analysis. The positive electrode (also 99.999% pure Pb) is located outside the cylinder; oxygen produced during the test is not captured. The two electrodes are submerged in an electrolyte of Trace Metal Grade sulfuric acid (H₂SO₄) that is diluted to 1.300 specific gravity using distilled water. All materials were analyzed to guarantee that there were no contaminating sources of outside sulfur present. Current was recorded and a reference electrode (Hg/Hg₂SO₄) was employed to measure the polarization voltage of the negative electrode. Three such test setups were built and placed in an oven at 40°C with each test cell connected to its own power supply. Tests were conducted at voltages of 2.65, 2.50, 2.40, 2.30, and 2.25 volts. The tests were allowed to run until we had collected sufficient gas to allow a GC analysis -- somewhere on the order of 50 ml. The first round of testing produced very consistent concentrations of H₂S at all test voltages; 300 to

600 ppm as measured by our GC. Figure 2 displays the results of this testing.

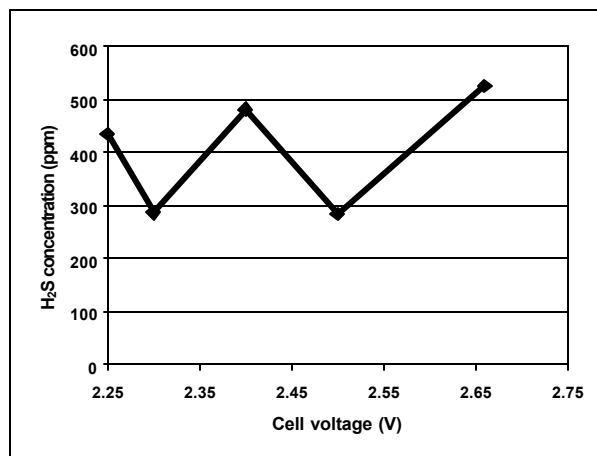


Figure 2: H₂S in ppm vs. the cell voltage

These extremely high concentrations of H₂S were surprising. Even more so was the fact that we could consistently produce these amounts over such a wide range of voltages and, especially, at the low end of the range. The results of this testing led us to hypothesize that H₂S was produced at a consistent rate *regardless of the negative polarization* and that it could be produced very readily. Of more concern, we were now also convinced that H₂S could be produced at normally prescribed float voltages.

The finding of such high concentrations of H₂S in the first round of testing begged to be confirmed by repeated testing. As our testing continued for four rounds, we noted the gradual decline in H₂S concentrations in our test cells from our high of 600 ppm to a low of zero ppm. This was dramatically less than our original 600 ppm and definitely contrary to our original hypothesis. Figure 3 is a graph of declining H₂S concentration measured in one of the three test cells, held at 2.40 volts, over four successive rounds of testing.

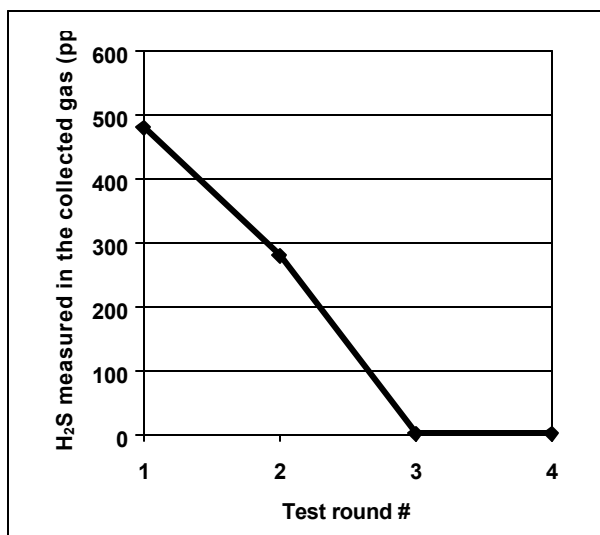


Figure 3: Hydrogen Sulfide concentration in the collected gases measured for four consecutive runs in the cell placed at 2.40 volts.

The next series of tests conducted were designed to quickly determine what was happening. The pure lead disks were individually oxidized and sulfated to see if this had any effect on the H₂S concentration, which it did not. We then changed the acid that was used in the test setup; we had not changed the acid at all in our series of test runs.

Immediately upon the first test run with the fresh acid (made to the same recipe as the original acid) we measured the exact same 600 ppm of H₂S that was first produced. This result was repeated in all three test setups, and the same declining H₂S concentration over successive runs was reproduced. This repeatability gave us confidence in the results and led us to a new hypothesis.

We now theorized that either a natural component of the sulfuric acid, such as SO₃, or a contaminant in the acid itself that might have evaded our analysis, was responsible for liberating the H₂S upon electrolysis. We also theorized that this H₂S liberation rate was not a constant but would gradually decrease to zero as the contaminating factors present in the acid were used up. It must be noted that all of our testing was done with pure Trace Metal Grade sulfuric acid and that the use of normal battery acid could produce higher concentrations of H₂S. As of the writing of this paper, we have not discovered the source of the H₂S in the sulfuric acid. This will be left for future research.

In summary, the experimental results indicate that:

- Components of pure sulfuric acid when in contact with a charged negative plate can liberate H₂S.
- Liberation of H₂S from sulfuric acid is not voltage dependent. The indication is the H₂S reaction is diffusion controlled and thus should also occur when the negative plate is on open circuit. (Note: This is confirmed by the Negative Active Material testing already reported upon)⁵.
- H₂S levels will decrease over time as the precursor components are eliminated.

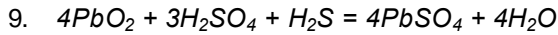
Despite our testing and theories, we were still puzzled by the fact that we do not normally smell H₂S around VRLA cells. Human noses are finely tuned detectors of this noxious gas and can detect it to the parts per billion level. Not only could we not smell it, we were unable to consistently measure it, with a GC, in the gas taken from the VRLA cells on float service in our lab. The question then became: if H₂S is being produced where is it going?

4. Hydrogen sulfide is absorbed by the positive plate.

Based on the test results, one would expect to smell hydrogen sulfide in every battery room in existence, but this is just not the case. In instances of thermal runaway in VRLA cells, there have been documented cases of blackened copper connectors and strong rotten egg smells in battery rooms, both telltale signs of hydrogen sulfide, but these occurrences are the exception and not the norm.⁴ If H₂S is not being emitted outside the cell in large amounts, then it must either be absorbed or oxidized by something inside the cell. Our literature search revealed that H₂S could be readily oxidized to sulfur at the positive plate. This oxidation of H₂S to sulfur can be due to oxygen (see Equation 4 in Background Section 2) or other oxidizing agents. We also suspected that PbO₂ could react to absorb H₂S on its own.

Berndt⁶, in private correspondence, agreed with our reaction mechanisms and proposed lead oxide reactions. Whether H₂S is oxidized to sulfur by oxygen or contact with lead oxides is not known at this time. The equations that include those of lead oxides and H₂S proposed by Berndt are the following:





The above equations do not give an indication of the rate of the reactions. One would expect that the oxidation reaction of H₂S and oxygen would proceed quite rapidly since it is a homogeneous gaseous phase reaction. However, the activation energy of this reaction is quite high indicating that this reaction requires a catalyst (e.g. water, activated carbon or precious metal) to proceed at an appreciable rate in a cell^{1,2}.

On the other hand, the H₂S and lead oxide reactions might be quite slow, especially because these are heterogeneous reactions between solid oxide and gaseous H₂S. The reactions might be slowed down even further by the fact that the PbS and PbSO₄, which are formed as a result, might further block the active oxide surface thus limiting the access of the hydrogen sulfide to the lead oxide.

There are also, most likely, differences in the reaction rates between cells that have different levels of wetness. Positive plates that are wetter (with sulfuric acid) are not able to absorb as much H₂S as dryer plates due to the fact that the acid physically blocks the surface of the PbO₂. In this case, cells that are fully recombinant are able to absorb more H₂S than cells that are new. In either case, we cannot make a definitive statement about which is the dominant mechanism without empirical testing.

Lead dioxide, PbO₂, is the form of oxide that constitutes the positive plate of all lead acid cells, including VRLA cells. Although the oxygen evolution rate is calculable, that of the subsequent oxidation rate of H₂S is not at this time. The fact that Reactions Nos. 7, 8, & 9 are thermodynamically possible indicates that some H₂S will be absorbed on the positive plates of VRLA cells. At this time, we cannot separate the two mechanisms (H₂S oxidation by oxygen or H₂S absorption by lead oxide) to determine which is the dominant. The key question is whether the combined oxidation and absorption rate of H₂S is fast enough to compensate for the H₂S generation that is occurring at the negative plate. To answer this question, two simple experiments were conducted.

4.1. Experiment 1: Absorption of H₂S by PbO₂ through a simple packed filter bed.

Figure 4 shows the packed filter bed built and used in this experiment.



Figure 4: Packed Filter bed reactor used to determine the H₂S absorption capacity/rate of PbO and PbO₂.

The filter bed reactor consisted of the following parts:

- A body composed of polycarbonate pipe (3 inches long X 9/16 inch OD) with gas chromatograph compression fittings at both ends.
- A filter bed of filter material that is confined at both ends by porous Teflon® disks. Polypropylene static mixers were used as compression springs to keep the filter bed packed.
- PFA Gas Chromatograph.

A gas mixture of 108 ppm of H₂S in hydrogen was fed into the bed at a rate of 50 ml per minute. The outlet of the filter bed was connected to the gas chromatograph (GC) to allow direct measurement of the output concentration of the H₂S. The GC automatically measured the H₂S concentration at 15 minute intervals. The test was run (1) empty; (2) with a ½ inch packed bed of PbO; and (3) with a ½ inch packed bed of PbO₂. The time to “breakthrough” was measured in all cases. Breakthrough is defined as the length of time that it takes for the GC to detect H₂S above 1 ppm (the lowest level of detection of our GC). Table 1 presents the results of the experiment:

Test Material	Amount (Grams)	Breakthrough Time (minutes)
Empty	0	0.01
PbO	2.194	120
PbO ₂	1.978	360

TABLE 1: Table of H₂S Breakthrough times for different filter materials tested.

It is evident that both PbO and PbO₂ absorb H₂S fairly well. Even though the breakthrough times for the two oxides are much longer than that of the

empty bed, the theoretical calculations indicate that the capacity of the two oxides is far from exhausted. The given amounts of PbO and PbO₂ should be able to eliminate H₂S for 44,820 minutes and 37,860 minutes respectively, according to the equations presented earlier. We believe that the differences may be due to blockage of the oxide surfaces by the reaction products PbS or PbSO₄.

Now that we had proven that H₂S is indeed absorbed by lead oxide, we wanted to demonstrate that this absorption is possible in a real battery.

4.2. Experiment 2: Absorption of a known concentration of H₂S as it is passed through a VRLA Cell.

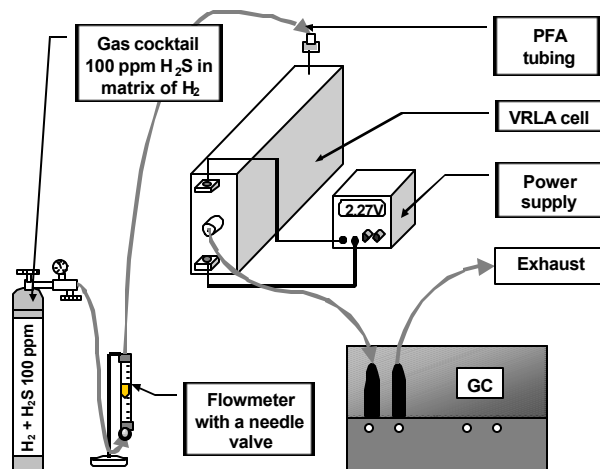


Figure 5: Schematic of the setup for Experiment 2.

In this test, a constant flow of a gas mixture of 100 ppm of H₂S in a hydrogen matrix was introduced into a 200 Ah VRLA cell. The cell was placed on float at a voltage of 2.27 volts. The resultant H₂S concentration was measured in the gas outflow by connecting the cell to the GC as shown in Figure 5. Measurements were taken every 20 minutes. The H₂S/H₂ gas mixture was fed into the bottom of the cell through a syringe needle that was sealed into the cell. The gas outflow was fed into the GC via PFA tubing that was sealed to the top of the cell and connected directly to the GC. A combustible gas detector was used to ensure that there were no leaks in the system.

Figure 6 is a graph of the data collected from the experiment. Time in hours is plotted on the X-axis. H₂S concentration of the outflow gas is plotted on the left Y-axis. The gas inflow rate is plotted on the right Y-axis.

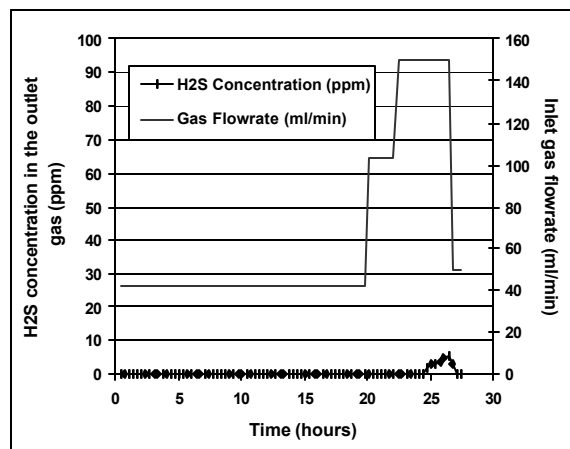


Figure 6: Absorption of H₂S from a gas mixture as it was passed through a VRLA cell at different flowrates.

The experiment was started with a gas inflow rate of 42 ml/minute. From Figure 6 it is evident that for the first 20 hours the GC could detect no H₂S. In order to determine how fast the cell absorbs H₂S, the gas flowrate through the cell was increased to 103 ml/min. From Figure 6 it is again evident that for the 2 hour period that the flowrate was increased no H₂S was detected in the outlet gas. We then imposed an even greater gas flowrate at twenty-two hours from the start of the experiment and increased the gas input flowrate to 150 ml/min. As can be seen, it took 2 additional hours for the GC to detect the presence of H₂S. Even then, the concentration of H₂S remained below 10 ppm, which is well below the inlet H₂S concentration of 100 ppm. At this point in the test, the input flowrate was reduced to what it was initially (50 ml/min) to determine if the battery had undergone irreversible changes as a result of the high H₂S input rate. From Figure 6 it can be seen that after returning the inlet flow to its initial value, the outflow H₂S concentration dropped below the level of detection of the GC in less than 30 minutes.

This experiment clearly indicated that H₂S was being reacted at the positive plates of the battery. This could only be a result of either a direct interaction with oxygen or with the lead oxides. It is also important to note that the full incoming concentration of 100 ppm of H₂S was never reached, which indicated continuing absorption. The results of this experiment were confirmed by subsequent testing.

Based on both experiments, at this point, we still cannot determine which mechanism in the H₂S removal is the dominant one. We can say that in

both experiments the level of H₂S was dramatically decreased and that this removal occurs in VRLA cells on float. We can conclude that this significant fact is very important in our modeling of the cycle of H₂S.

5. Hydrogen Sulfide in VRLA cells exists at an equilibrium state of less than 1 ppm.

We now have independent testing to support the generation and absorption of H₂S in VRLA cells. Our testing indicates that there exists a cycle in VRLA cells whereby H₂S is produced by a reaction at the negative plate between the lead and the hydrogen and sulfur containing compounds. Our testing also indicates that the PbO₂ of the positive plate subsequently absorbs the H₂S. It should be noted that oxidation of H₂S at the positive plate may also be occurring but proof of this will be left for future research. We believe that this cycle of production and absorption occurs on a continuous basis until the amount of H₂S generated gradually diminishes as the required base materials are exhausted through electrolysis. This theory indicates that after a period of time there will be no H₂S produced by the cell, but it also raises the question of is there ever a period in the beginning of this cycle where H₂S can be released by the cell?

To answer this question, GC analysis was carried out on the gas emissions from a variety of VRLA cells produced by a cross section of battery manufacturers. The cells were all housed in our lab and were on float service at 2.27 volts per cell and were at either 25°C or 32°C. The cells all ranged in age between brand new and 6 years old. We had sampled gas on a weekly basis for a period of six months and plan on continuing this analysis for the foreseeable future. The results of our analysis indicated that H₂S was emitted from our test cells in a range from 0 ppm to just under 1 ppm, but never more than 1 ppm. Since we were at the limit of detection of our GC, we sent verification samples of the gasses to an outside lab that had a GC that was capable of measuring H₂S down to the ppb level. The results of the outside lab's testing confirmed our own GC's measurements and gave us confidence to believe our own results. In other words, the results that we had obtained were real.

Since we were sampling gases from a variety of cells, we looked for patterns to explain the variation in concentration of H₂S that we could tie back into our theories. However, we could discern no pattern to the measurements as of the writing of this paper, but the key point is that there was never greater

than 1 ppm detected on any of these cells. The other point of emphasis is that we had successfully measured very low level emissions of H₂S from VRLA cells on float service at 2.27 volts per cell at very normal operating temperatures. Not only did this analysis establish a preliminary maximum equilibrium threshold for our proposed cycle under float conditions, but it also was direct evidence that VRLA cells can and do produce hydrogen sulfide.

A point to remember is that this proposed equilibrium level is for float service only and that at higher voltages, such as those experienced in thermal runaway conditions, the resultant concentrations emitted by a cell could be larger. Even if the resultant concentrations are not much higher than what we have measured, in thermal runaway conditions the current drawn by the battery is much higher than normally experienced. This high current causes the cell to emit larger quantities of gas than on float. So even if the concentration level is as similar to what we have measured on float, at high gas rates the total quantity of H₂S emitted will be large. This accounts for the blackened copper connectors that have been reported when such thermal runaway events have occurred.⁴

There are obviously many more questions raised by this work. One such question is whether the absorption of H₂S and the subsequent equilibrium concentration changes during the discharge or open circuit conditions of a cell? The answer to this question and others will be left to future investigation.

6. Conclusion

What started out as a curiosity about H₂S in VRLA cells led to a complex theory about another series of reactions that take place in an already electrochemically "busy" battery. We have shown that:

- H₂S can be produced by VRLA cells through the reduction of sulfur-containing compounds.
- H₂S can be absorbed within a VRLA cell.
- The equilibrium concentration levels of H₂S in the gas emitted from the VRLA cells in our test did not exceed 1 ppm. It must be noted that these cells were on float and that the concentration levels could be higher in non-float or non-normal conditions.

Even at these low concentrations, H₂S can still cause damage to electronics and to items such as precious metal catalysts. For example, if an

unprotected precious metal catalyst is exposed to H₂S for prolonged periods of time, its life can be shortened as the catalyst is deactivated. Based upon our findings, we have developed an improved catalyst design (patent pending) that employs a filter material specifically chosen for its H₂S absorbing ability. This filter material captures the H₂S before it can reach the catalyst and deactivate it. It is expected that the new filter will substantially increase catalyst life in the presence of H₂S.

Our ultimate goal, however, is more ambitious. If possible we would like to help isolate and eliminate the H₂S precursors or contaminants from VRLA cells during the cell's production and thereby prevent the evolution of H₂S at its source.

7. Acknowledgments

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8. References

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