

Hydrogen sulfide and sulfur dioxide evolution from a valve-regulated lead/acid battery

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Abstract

Two incidents concerning the contamination of copper-conductor surfaces associated with uninterruptible power systems (UPS) were recently observed. Valve-regulated lead/acid (VRLA) batteries used in the UPSs for backup powering were diagnosed as a possible source of the contamination. One of the VRLA batteries from the UPS unit was subjected to overcharge in the laboratory, to simulate the incident. Overcharge currents greater than 10 A, coupled with battery temperatures over 60 °C, can cause a VRLA battery to release significant amounts of hydrogen sulfide and sulfur dioxide. Under extreme conditions, hazardous levels of hydrogen sulfide could be generated. We conclude that the contamination was due to copper sulfide, Cu_2S , and copper oxide, Cu_2O , formed on copper surfaces as a consequence of hydrogen sulfide evolution and the high humidity inside the UPS enclosure resulting from battery venting.

Introduction

Recently, we learned of a problem related to the contamination of copper surfaces near an uninterruptible power supply (UPS), which used valve-regulated lead/acid (VRLA) batteries for power buffering. Corroded Cu samples from the UPS were covered by a greyish film. Simple chemical tests and X-ray powder diffraction (XRD) showed that the corroded material is mainly a mixture of Cu_2O and Cu_2S , implying the presence of sulfide within the UPS enclosure. It was essential to determine the origin of the corrosion in order to prevent the problem from recurring.

The electrochemical reduction of sulfate to sulfide in aqueous sulfuric acid electrolyte is unexpected under the electrochemical conditions and the temperatures normally encountered in lead/acid batteries, because sulfate ion is generally considered to be highly resistant to chemical reduction. However, we have created conditions in the laboratory where sulfide can be generated, at high current density and in strong sulfuric acid. Such conditions are possible under abnormal, thermal runaway battery conditions. The high temperature can cause battery venting, loss of water, and hence enhancement of the electrolyte concentration. This causes the battery internal resistance to increase, from electrolyte loss. If this battery is required to deliver power, a large voltage can appear across such a cell, producing high current densities. These observations were transferred to a laboratory experiment using an intact VRLA battery from the contaminated UPS, showing that H_2S can be generated from a VRLA battery under the abnormal operating conditions encountered during battery thermal runaway.

Experimental

Generation of H₂S in a laboratory electrochemical cell

An electrochemical cell was fitted with Pb (10 cm²) or Pt (1 cm²) electrodes. Because concentrated H₂SO₄ is a relatively poor conductor, it was diluted 3:1 (v./v) with water. At 20 V, the current through the cell was ~0.6 A (Pb) or 1.7 A (Pt). The electrochemical cell was covered to minimize the escape of evolved gases, and Cu coupons were placed inside the cover, exposed to the evolved gas. The coupons became blackened within several hours, and the black film on the coupons was analyzed.

Test for evolution of H₂S from a VRLA battery

The test battery was a three-cell valve-regulated monoblock lead/acid battery, capacity 160 Ah, taken from the contaminated UPS. The battery had been in service less than 4 months. The battery case was intact, with no signs of physical damage. The battery was placed inside a bell jar, which was inclined to allow a 1 cm opening at the bottom for gas sampling and instrumentation cables. A thermocouple was attached to the end of the battery, about half way down from the top of an end cell, which was used for the test. The battery was wrapped in a fiberglass insulating blanket to simulate the thermal retention in the middle of a closely-packed, multibattery string (Fig. 1). The insulation doubled the temperature rise of the battery for the same overcharge current (when tested at 10 A). Cleaned Cu coupons were hung inside the bell jar, away from surfaces where water condensation could occur. After the overcharge runs, the coupons were analyzed for corrosion products. The battery was subjected to two overcharge runs. The first run was made without gas analysis instrumentation, to verify (with Cu coupons) that corrosive gases were evolved during prolonged battery overcharge at excessive current, and to find the best overcharge parameters for cell failure. The battery was allowed to cool to ~43 °C after the first run, and another cell of the battery was used for the second experiment, with gas monitoring. The inlet port of the gas analyzer was placed 4 cm from the bottom of the bell jar, near the side of the jar.

Test for chemical sources of copper corrosion

To determine the chemical source of the Cu corrosion, Cu coupons were exposed to dry or humid H₂S or SO₂ for 48 h, and analyzed with XRD.

Results and discussion

Analysis of corrosion film for sulfide

Wet-chemical analysis of insoluble sulfides involves treating the sample with strong acid, liberating H₂S. For Cu₂S, Zn is used to reduce the Cu²⁺ produced from disproportionation of Cu⁺, to help drive the reaction [1]:



With the bus bar sample or our intentionally contaminated (from electrolysis of H₂SO₄) Cu coupons, a strong odor of H₂S was detected. A common chemical test for H₂S is the formation of PbS from a soluble lead compound, and the evolved gas also darkened a piece of filter paper moistened with lead acetate solution.

The deposited film at the surface of the sample was identified with XRD (Cu Kα₁). Two areas of the sample were examined with identical results. Besides the strong



Fig. 1. Photograph of valve-regulated lead/acid battery, with thermal insulation, inside bell jar.

peaks from Cu metal, weaker peaks can be unambiguously identified as Cu_2S and Cu_2O .

H_2S evolution from a VRLA battery

Corroded, blackened Cu coupons from the first battery overcharge run were analyzed. The black film was composed of Cu_2S and Cu_2O . A second run was started with continuous gas analysis to determine the overcharge conditions which cause evolution of H_2S .

A recording of battery voltage and temperature, and H_2S and SO_2 concentration inside the bell jar as a function of time and applied current are shown in Fig. 2. The cell temperature trace begins at $\sim 43^\circ\text{C}$ because of heating from the first overcharge run. $[\text{H}_2\text{S}]$ monitoring was started at ~ 6 h into the run, after disconnecting the battery for 2 h to establish a baseline concentration. The H_2S evolution depended on both

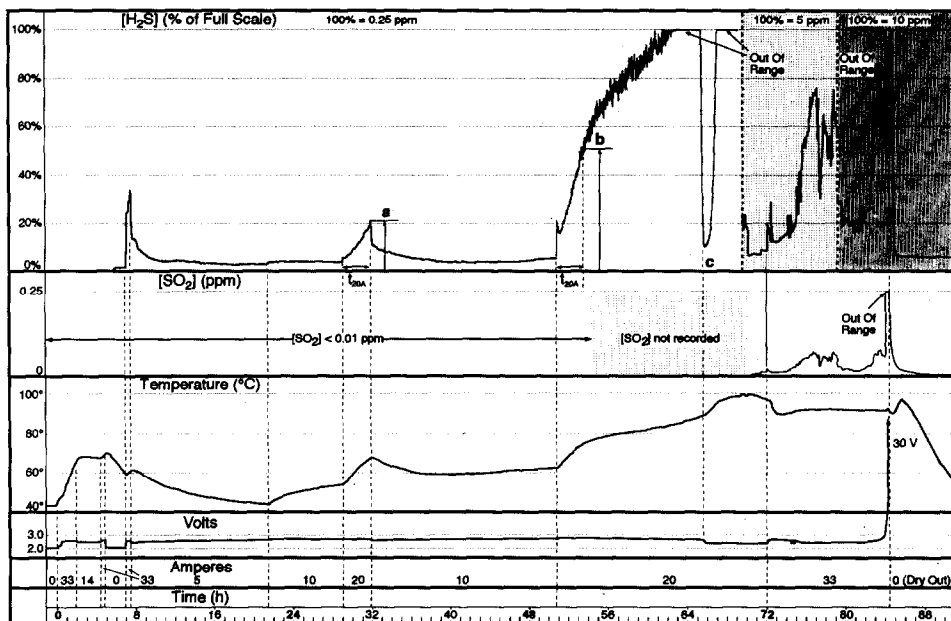


Fig. 2. Recording of H_2S and SO_2 concentration in bell jar, cell temperature, and cell voltage as a function of time and applied current. The dashed lines extending to the time axis indicate when the cell current was changed.

the applied current and temperature. Above 60°C , higher currents produced corresponding increases in H_2S evolution, shown by the 33 A current step at 7 h and the 20 A step at 51 h. Likewise, reducing the current (at ~ 7.5 h and 32 h) caused an immediate decrease in H_2S evolution. Lower evolution rates were observed at battery temperatures below 60°C and currents of 10 A and below. The temperature dependence is shown best by the 20 A current pulses at 29 h and 51 h. Both the instantaneous increase in $[\text{H}_2\text{S}]$ and the maximum $[\text{H}_2\text{S}]$ after an elapsed time of $t_{20\text{A}}$ (a and b in Fig. 2) were greater at the higher temperature, and the shape of the $[\text{H}_2\text{S}]$ curve following the first pulse, when applying 10 A, also qualitatively tracked the temperature curve.

The cell was then subjected to prolonged, extreme overcharge to determine maximum gas-evolution rates. $[\text{H}_2\text{S}]$ increased with increasing battery temperature. At the point marked c in Fig. 2 ($t=65.5$ h) the battery sealing valve failed, as indicated by the decrease in battery voltage. The drop in $[\text{H}_2\text{S}]$ may reflect the interference of water vapor, evolved after the valve failure, with the gas analysis equipment. The current was then increased to 33 A and $[\text{H}_2\text{S}]$ increased to ~ 2 ppm inside the bell jar, compared with ~ 0.25 ppm at lower temperatures. This is well above the olfactory threshold of 0.13 ppm [2]. Here, SO_2 also was detected, and the recording of its concentration was started. At this time, 80% of the interior surface of the bell jar was heavily coated by condensed water vapor.

Finally, as electrolyte was depleted, reflected by the increase in cell voltage at ~ 84 h, $[\text{H}_2\text{S}]$ and $[\text{SO}_2]$ both increased dramatically. At what appeared to be cell dry out, the cell voltage exceeded 30 V, followed by the cell becoming an open circuit, and current dropping to zero. During this time, $[\text{H}_2\text{S}]$ increased to over 10 ppm, which

was the limit of the analyzer. From the shape of the peak, its concentration was probably between 30 and 50 ppm. For $[\text{SO}_2]$, the analyzer was operating at its most sensitive setting, 0.25 ppm full scale, and saturated; but $[\text{SO}_2]$ probably remained below several ppm. Nearly all of the condensed water inside the bell jar had evaporated. After the test the battery was inspected. The case was distorted, but intact, except for the damaged valves.

Chemical source of copper corrosion

A summary of the XRD results are given in Table 1. XRD showed only Cu_2S in the samples treated in H_2S^* . Samples exposed to humid SO_2 produced a mixture of Cu_2O and Cu_2S , consistent with previous studies [3–5]. The corrosion rate was much faster with H_2S present. The formation of Cu_2S from Cu and H_2S is a simple reduction reaction, but the mechanism of reduction of SO_2 on Cu is unknown [3–5]. The Cu surface was not affected by dry SO_2 .

Copper samples from the UPS enclosure and from our VRLA test were covered with Cu_2O and Cu_2S , as indicated by XRD (Fig. 3). This implies the formation of H_2S and SO_2 gases during the battery failure, as was experimentally verified. However, it is important to recognize that Cu can be corroded by moist SO_2 alone. Thus, the humidity as well as the SO_2 content inside a UPS enclosure should be closely monitored and minimized, to prevent Cu contact problems.

Our results show that appreciable H_2S evolution occurs from a VRLA battery when its temperature exceeds 60 °C. However, it is important to note that VRLA batteries are not intended for operation under the severe conditions used in our tests, and should not evolve corrosive gases during normal operation. However, abnormal conditions could be induced in a healthy battery by charging with float currents exceeding several amperes for a long time, promoting thermal runaway if the temperature was allowed to increase. In a UPS installation, this also may occur with a deficient cell in a battery string, e.g., a cell with a damaged case, causing evaporation or loss of electrolyte, drawing large currents from charging rectifiers that were not current limited.

Prolonged overcharging that leads to valve failure and cell dry-out could cause the accumulation of hazardous $[\text{H}_2\text{S}]$ in an enclosed, unventilated space. Olfactory fatigue (loss of ability to detect the 'rotten egg' odor) occurs at 100 ppm. Potentially lethal concentrations lie above ~250 ppm; a single inhalation at concentrations above 1000 ppm may cause convulsions, coma, and death [2]. The ultimate $[\text{H}_2\text{S}]$ depends on the efficiency of electrochemical reduction of sulfate, which is unknown. This is likely a function of temperature, electrolyte concentration, and current density. However, in lieu of further study, we note in the interest of safety that complete conversion of sulfate in the electrolyte of a single cell to H_2S , under the conditions above, would give $[\text{H}_2\text{S}] > 10\,000$ ppm.

Since H_2S evolution depends upon the cell temperature and the amount of charging current, it would be wise to either monitor continuously the temperature of each cell or control the amount of current supplied by the charging rectifier. Limiting the current of the rectifier could be a solution, but large currents should be available following a power outage, to recharge the cells. This would have to be accounted for in the

*There are two forms of Cu_2S , one denoted $\beta\text{-Cu}_2\text{S}$, and the other called chalcocite. The ratio of these two forms within the corrosion film depends on the corrosion conditions. For instance, $\beta\text{-Cu}_2\text{S}$ is predominant within the field samples.

TABLE 1

Summary of X-ray analysis results for Cu samples from the UPS enclosure and the laboratory test

Test condition	H ₂ SO ₄ electrolysis	Dry H ₂ S	Humid H ₂ S	Dry SO ₂	Humid SO ₂	Humid H ₂ S+SO ₂	Field sample	VRLA test
Appearance	grey-black film	metallic grey film	matte grey film		grey-black film	grey-black film	grey-black film	grey-black film
Analysis								
Cu ₂ S	+	+	+		+	+	+	+
Cu ₂ O	+				+	+	+	+

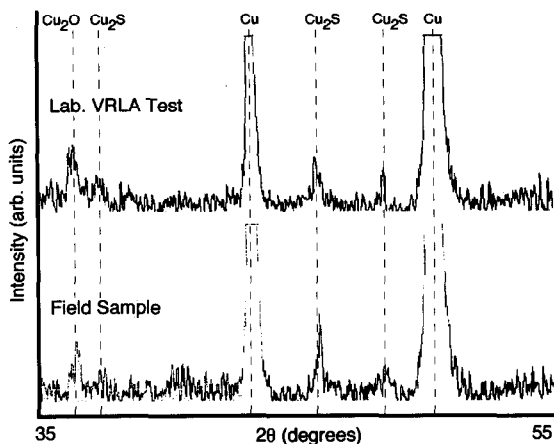


Fig. 3. X-ray diffraction curves of Cu samples from the UPS enclosure and the laboratory valve-regulated lead/acid battery test.

rectifier design, and would increase the complexity and cost of the rectifier. A better solution would involve monitoring the temperature of each cell with a feedback loop going to the rectifier. If the temperature of a cell were above 50 °C the rectifier could automatically decrease the current, preventing a thermal runaway condition and allowing enough time for service (e.g., Sparton Technology, Model 5353 battery monitoring system). We also are working on a monitoring system that will allow temperature monitoring, as well as measuring the energy reserve capacity of each cell, so that failures such as these could be detected or even anticipated.

Conclusions

H₂S and SO₂ were evolved in significant amounts from a valve-regulated lead/acid battery under abnormal operating conditions, with a cell temperature above 60 °C and overcharge current above 10 A. These gases can cause contamination and corrosion of Cu contacts in electronic equipment. Furthermore, prolonged overcharging that leads to valve failure and battery dry-out could cause the accumulation of potentially hazardous levels of H₂S in an enclosed, unventilated space. The problem may be prevented through battery temperature monitoring and the control of battery current.

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