Short communication

Analysis of gassing processes in a VRLA/spiral wound battery

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Abstract

An experimental analysis of the gassing processes has been conducted on a modified commercial spiral wound AGM battery. Single electrode potential, cell and battery voltage and internal gas pressure have been monitored on a modified battery at different current rates in the steady-state regime. At low polarization, the oxygen recombination cycle proceeds properly. At large polarization of the negative electrode, careful examination of the evolution both of the electrode potential and the inner gas pressure indicates that, instead of the expected adverse evolution of hydrogen gas, oxygen continued to be reduced.
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1. Introduction

In conventional flooded lead-acid batteries, completion of charge is followed by heavy "gassing", i.e., oxygen evolution at the positive plate and that of hydrogen at the negative one. This operation results mainly in a substantial water loss, tendency to leak electrolyte and positive grid corrosion at high electrode potentials. The valve-regulated design of lead-acid batteries (VRLA) offers solutions to such drawbacks by simply reducing, at the negative plate, oxygen evolved at the positive one, thereby regenerating water at the negative electrode. This process keeps the overpotential of the negative electrode low since the kinetics of the oxygen reduction is fast. However, when the negative electrode is highly polarized, the reaction may switch from oxygen reduction to hydrogen evolution, just like what occurs in flooded-type cells. These processes have been widely investigated experimentally as well as by mathematical modeling to identify the kinetically determining parameters [1–6]. It has been particularly shown that oxygen gas transport from the positive to negative electrode is promoted by a level of electrolyte saturation in the porous separator lower than 90% [7]. Besides, an extremely slow hydrogen evolution rate can be achieved by the use of highly purified lead [3].

The purpose of this study is to analyze the gassing processes occurring in a VRLA battery when in overcharge conditions.

To get a better understanding of the overcharge behavior, we used a setup in which the following parameters were monitored continuously: battery voltage, individual cell voltage, separate potentials of the positive and negative plates using a suitable mercury/mercurous sulfate reference electrode (Ref) in one cell and internal gas pressure.

2. Experimental

All experiments were conducted on a 12 V Optima AGM–VRLA battery, manufactured by Johnson Controls, with a nominal capacity of 44 Ah at room temperature. The electrolyte has a concentration of $1.33 \, \text{kg} \, \text{l}^{-1}$. The battery has been equipped with a differential gas pressure sensor and a reference electrode through holes created at the top part of the battery (Fig. 1). It is necessary to mention that the battery has a common gas space for all cells. Therefore, the measured pressure cannot be attributed directly to the cell where electrode potentials have been measured. Multiple electrical contacts to the individual plates have been achieved by means of screws to record individual cell voltages. Epoxy seals were used to make modifications tight. The pressure relief valves were deliberately obstructed to make gas accumulate inside the battery. Finally, the whole battery was submerged into an oil-bath to control permanently possible gas leakage.

A mercury/mercurous sulfate reference electrode, of standard design, in the same sulfuric acid concentration as the cell electrolyte in fully charged conditions, was used to measure the
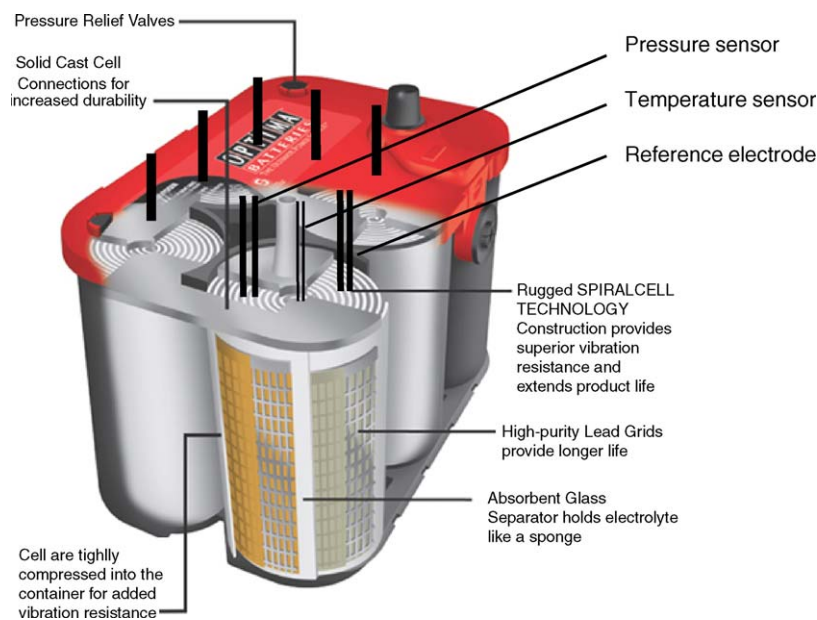
Fig. 1. Optima AGM–VRLA battery equipped with a pressure sensor, a reference electrode and multiple electrical contacts for individual cell voltage measurements. The battery, with all its accessories, is submerged in an oil-bath for gas leakage control (by courtesy of Johnson Controls).

electrode potentials separately without liquid junction potential error during overcharge measurements. Its thermodynamic potential, in the $1.33\,kg\,l^{-1}$ H_2SO_4 solution at $23\,°C$, is estimated to be $554.4\,mV$ versus SHE [8]. The use of Ref with a conventional Luggin capillary for long-term experiments may be problematic since electrolyte may be drawn from the capillary into the separator. In order to avoid such an electrolyte flow, Ref was prolonged with a thin extension glass tube, at the end of which was fixed a small porous Vycor glass. It is through this tip that solution contact is maintained between the reference electrode and the cell separator.

The cycling and polarization tests have been conducted with the ISEA-*EIS*meter, which is a multi-channel instrument, suitable for precise measurements on industrial batteries including impedance measurements. Overcharge polarization for the investigation of the gassing processes has been performed galvanostatically in steady-state conditions for current rates ranging from 0 to $500\,mA$. All experiments were carried out at a room temperature of $23\,°C$.

3. Results and discussion

The voltage of a typical cell and the positive and negative half-cell potentials recorded during a discharge–charge cycle of the complete battery are shown in Fig. 2. The discharge was made at a $C/5$ rate, while the charge consisted in a $C/5$ constant current rate up to $14.7\,V$ ($2.45\,V\,cell^{-1}$), followed by a constant voltage at $14.7\,V$ till the current drops below $C/50$. Finally, an overcharge current of $C/50$ was held for $2\,h$. The cell voltage at any time matches exactly the difference between the two half-cell potentials. However, it is noteworthy that the electrode potentials recorded during discharge and charge require correction for the junction potential, since during discharge, the concentration of the cell electrolyte drops

significantly from its initial value, creating a junction potential between the cell electrolyte and Ref which amounts to few tens of millivolts. The actual potential curves actually lie at somewhat lower values, stressing the limiting character of the positive electrode kinetics over the whole discharge–charge cycle. During measurements on gassing reactions, however, the liquid junction potential can be neglected since the average acid concentration in the cell is the same as that in the reference electrode.

During the overcharge step, oxygen is evolved at the positive electrode. The potential of the negative electrode increases first moderately in the domain labeled I, corresponding to normal recombination process, i.e., oxygen produced at the positive is reduced at the negative. No gas accumulation normally occurs in this case. Next, the potential of the negative plate increases much more in domain II to reach a value of $-1.35\,V$ versus Ref. This jump has been usually related with the switch from oxy-
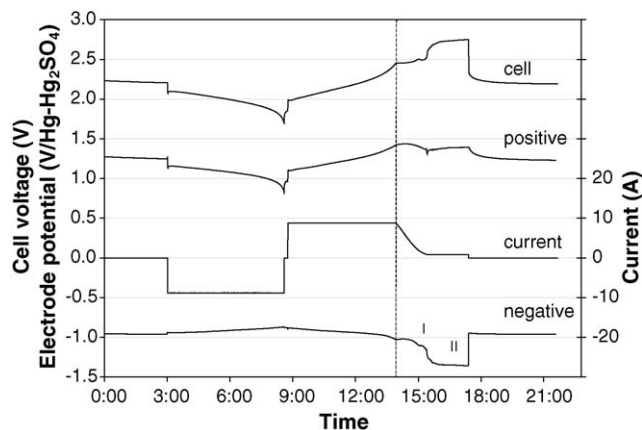

Fig. 2. Current, cell voltage and half-cell potentials during a discharge–charge cycle of a 44 Ah Optima AGM–VRLA battery at $23\,°C$.
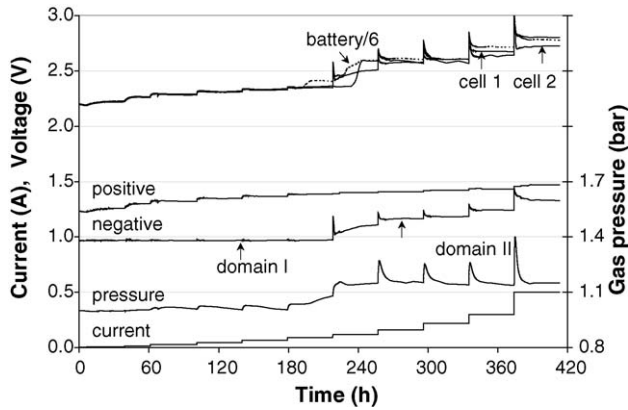
Fig. 3. Current, battery and cell voltages, half-cell potentials and internal gas pressure at various overcharge current rates of a 44 Ah Optima AGM–VRLA battery at 23 °C.

Fig. 4. Overcharge Tafel plots for battery, cell and half-cells of a 44 Ah Optima AGM–VRLA battery at 23 °C.

gen reduction at the negative plate to the evolution of hydrogen. When this happens, oxygen and hydrogen gas mixture accumulates leading to a continuous build-up of the internal pressure, unless the outlet valves open for gas escape.

Fig. 3 shows the evolution of battery and cell voltages, the potential of the positive and negative electrodes and gas pressure for different currents. For each current intensity, the test lasted 40 h allowing for a perfect stabilization of the electrode potential.

The potential of the positive electrode increases monotonously with the current. For the negative electrode, the two domains, I and II, can again be distinguished: for low currents, as expected, the overpotential of the negative amounts to few mV, whereas at high currents, it increases considerably. Strikingly, the gas pressure increases only slightly, i.e., from 1 to 1.2 bar after 17 days testing under load. The volume of oxygen and hydrogen gas mixture which would have evolved (if no O_2 recombination occurred) is estimated to 38 l per cell (i.e., 228 l for the whole battery). This corresponds to an increase in the internal gas pressure of 60 bar. Stabilization of the pressure at a low value indicates particularly that no gas accumulation took place. The only plausible explanation, if re-oxidization of hydrogen at the positive plate as well as the unlikely gas escape are discarded, is that hydrogen gas was not formed at all in these conditions; only oxygen recombination cycle was involved.

Besides, at the end of this long-lasting test, which was additionally prolonged by further 8 days at 500 mA load, the valves were allowed to vent. Unlike the huge quantity expected to escape in case hydrogen was formed, only a limited quantity of gas has been noticed. This confirms once more the proper occurrence of the oxygen recombination process during the whole overcharge period, whatever the potential of the negative electrode was.

Immediately after incrementing the current, the pressure increases and then stabilizes at a lower value (Fig. 3). This may be interpreted by a momentary increase in the content of oxygen gas in the free volume at the top part of the battery before it diffuses inside the separator. Meanwhile, for balancing the reaction at the negative electrode, the required quantity of oxygen is
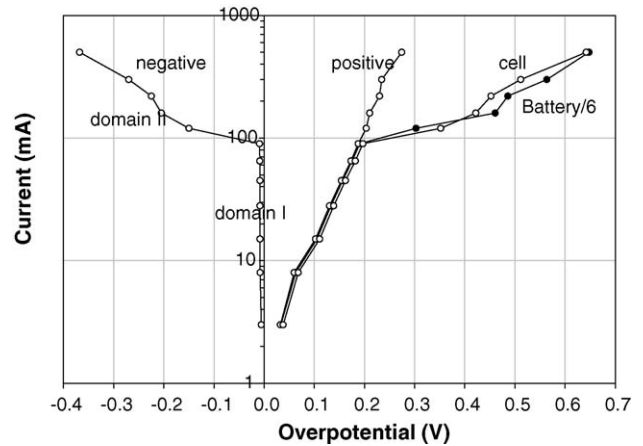
withdrawn from the gas available inside the separator channels near to the negative electrode.

The current–overpotential plots are presented in a semi-logarithmic scale in Fig. 4. For the oxygen evolution on the positive electrode, a constant Tafel slope of 110 mV dec^{-1} is determined. For the negative plate, the two polarization domains are indicated: at low currents (domain I), a very low polarization is measured. For large currents (domain II), the polarization increases almost linearly as a function of current, with an average slope of 600 mΩ. These data do not correspond to hydrogen evolution which is expected to produce a linear semi-logarithmic relationship with a typical slope of 120 mV dec^{-1} in this region [9]. Hence, this statement diminishes the likelihood of hydrogen evolution; the reduction of oxygen continued further on the negative electrode even at such large overpotentials.

The increase in the negative electrode polarization seems to be mainly related with an additional hindrance caused by water formation at this electrode, produced by the oxygen reduction. Indeed, growth of the thin liquid film through which oxygen must diffuse to reach the surface of the electrode makes oxygen diffusion slower, which entails increased polarization (domain II; in Figs. 2–4). Besides, together with proton consumption in this recombination process, water formation results in a dilution, with respect to the protons concentration, near to the active zone inside the pores of the negative electrode. If a significant decrease in the protons concentration occurs, hydrogen evolution will kinetically slow further down and call for a large cathodic polarization. Add to this the high purity of lead anode in the Optima battery which makes the hydrogen evolution extremely hindered. Consequently, although slower than in domain I, the reduction of oxygen would continue to occur preferentially to the protons reduction equally in domain II.

4. Conclusions

The experiments presented in this work describe a successful implementation of various sensors in a VRLA battery that allows for monitoring individual cell voltages, half-cell potentials and

gas pressure. Knowledge of these parameters is of great importance for reliable characterization of the internal processes. Investigation of the gassing reactions in the overcharge conditions indicated particularly that oxygen recombination cycle occurs over a range of negative electrode polarization wider than what is typically established. It is believed that this behavior results basically from accumulation of water, at quite large current rates (domain II), at the inner surface of the negative electrode pores, although slowing down the oxygen reduction reaction but still favoring it to the evolution of hydrogen. This statement deserves further confirmation by other techniques, such as impedance measurements, since it broadens the performances of VRLA batteries.

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