Oscillations of electrode potentials in sealed lead/acid cells

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Abstract

Oscillations (fluctuations) of both positive and negative electrode potentials of a laboratory sealed lead/acid cell were observed during galvanostatic overcharging, accompanied with a gradual pressure increase. The frequency of the oscillations and the highest potential of the negative electrodes increased with the applied current. The oscillations are discussed in terms of nonuniform penetration of oxygen through the separator. Oxygen accumulates at the positive electrode and, after reaching a critical local pressure, it penetrates into the negative electrodes causing their depolarization. As long as the oxygen is reduced, the cell pressure remains steady. During accumulation of oxygen at the positive electrode, the potential of the negative electrode increases to negative values causing evolution of hydrogen and, thus, an increase of the cell pressure. This interpretation is supported by the results obtained during overcharging at limited voltage.

Introduction

Accumulators with aqueous electrolytes suffer from an undesirable phenomenon, termed gassing: besides the desired, current-generating reactions, also parasitic reactions, namely decomposition of water proceeds at the electrodes, the decomposition voltage (1.23 V) being lower than the open-circuit voltage of the accumulator. Accordingly, during overcharging, oxygen is evolved at the positive and hydrogen at the negative electrode. The water thus lost must be replenished, when necessary.

During galvanostatic charging, continuous changes of the electrode potentials take place, as illustrated in Fig. 1. It can be seen that the potentials change only little during charging, but more profoundly at the end of charge. The cell voltage of a vented accumulator changes proportionally until it reaches 2.6 V.

The course of the electrode potentials may be different with a sealed cell. If an efficient oxygen cycle is realized (the oxygen formed at the positive electrode is reduced at the negative electrode according to the equation $O_2 + 4H^+ + 4e^- = 2H_2O$), then the negative electrode is depolarized by oxygen resulting in a suppression of the hydrogen evolution towards the end of charging and, especially, during overcharging. So the negative electrode potential (Fig. 1, dashed curve) does not reach the region of hydrogen evolution.

During our studies of the oxygen cycle in sealed lead/acid cells [1, 2], we observed a transient increase of the negative electrode potential towards the end of charging. This increase was dependent on the charging current, and after the start of the oxygen

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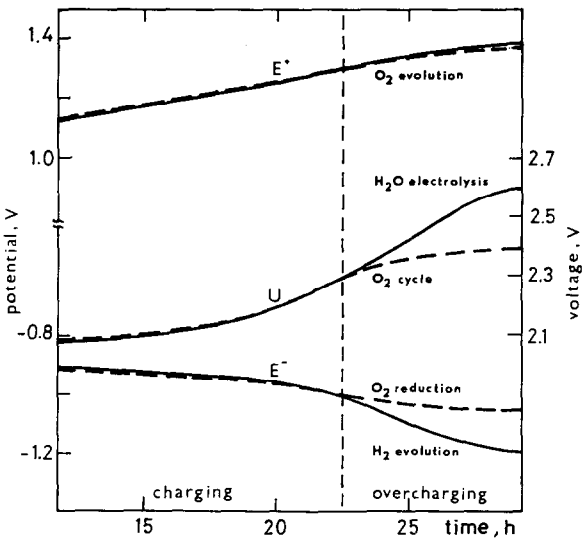

Fig. 1. Electrode potentials (vs. Hg/Hg_2SO_4) and terminal voltage of lead/acid accumulator during galvanostatic charging and overcharging: (——) vented accumulator, and (– – –) sealed accumulator operating on oxygen cycle.

cycle, gradually disappeared as a result of the depolarization of the negative electrode by oxygen.

If the oxygen cycle has a low efficiency, i.e., if the current due to reduction of oxygen is much smaller than that due to evolution of oxygen (which is equal to the charging current during overcharge), then the depolarization of the negative electrode by oxygen is prevented, its potential increase becomes steady, and the evolution of hydrogen is made possible [3]. As a result, the internal cell pressure increases.

Our further studies of sealed laboratory cells revealed an anomalous phenomenon during galvanostatic overcharging, namely some cells showed oscillations (fluctuations) of both electrode potentials. These are dealt with in the present work.

Experimental

Dry-charged electrodes, prepared by pasting pure-lead grids under laboratory conditions, were placed in laboratory cylindrical cells [2]. The electrode dimensions were 80 mm×50 mm×2 mm. A 1.4 mm thick glass fiber web of 95% porosity served as a separator, which covered entirely the surface of the working electrodes. Two separator layers were placed between the central, positive electrode and the adjacent negative electrodes, while the outer faces of the negative electrodes were covered with one layer only. One of these outer separator layers was in contact with an additional charged positive electrode which served as a reference, and, which communicated with the working electrodes through the separator, soaked with the electrolyte.

The cell was assembled in the dry state. The electrode pack was pressed and fixed at 65 kPa outside the cell vessel and then it was put into the cell vessel. After evacuation, the cell was filled with 23 ml of 5 M H_2SO_4, whereby the electrodes and the separator layers were wetted to about 75%. The cell pressure was measured with an electronic manometer with an accuracy to 0.1 kPa.

Results and discussion

During charging at various rates, it was found that the oxygen cycle in the cell functions well: a dynamic equilibrium was established between the formation and consumption of oxygen, characterized by a moderate overpressure (up to 100 kPa). At the same time, fluctuations of potentials of both electrodes were observed.

Galvanostatic overcharging

The potential fluctuations of electrodes of both polarities were recorded during overcharging, the current being gradually increased in 100 mA steps, up to 800 mA and then decreased to 100 mA. At each selected value, the current was maintained constant for 10-min intervals, or a constant charge of 100 to 150 mAh was maintained at each level. The overpressure increase was also recorded. It reached a maximum value of 52 kPa. A record of the potential fluctuations and gas overpressure is shown in Fig. 2. It can be seen that the potential of the positive electrode increases with the current (from 100 to 300 mA) and at the same time oscillates. The negative electrode potential oscillates between a minimum value, which is nearly independent of the current, and a maximum value, which increases with the current (Table 1).

The average number of the potential oscillations of the negative electrodes increases with rising current: per 10-min interval this number was 5, 8, and 15 at $I = 100$, 300, and 800 mA, respectively. The changes of the charging current result in pressure changes, which are stepwise and related with the fluctuations of the negative electrode potential: the pressure increases during the periods when E^- is at its maximum value, and remains steady during periods when E^- is at its minimum value. This is well observable, e.g., at $I = 200$ mA. The minimum potential of the negative electrode, E^-_{min}, corresponds to oxygen reduction on lead, and the maximum potential, E^-_{max}, to hydrogen evolution at the particular current.

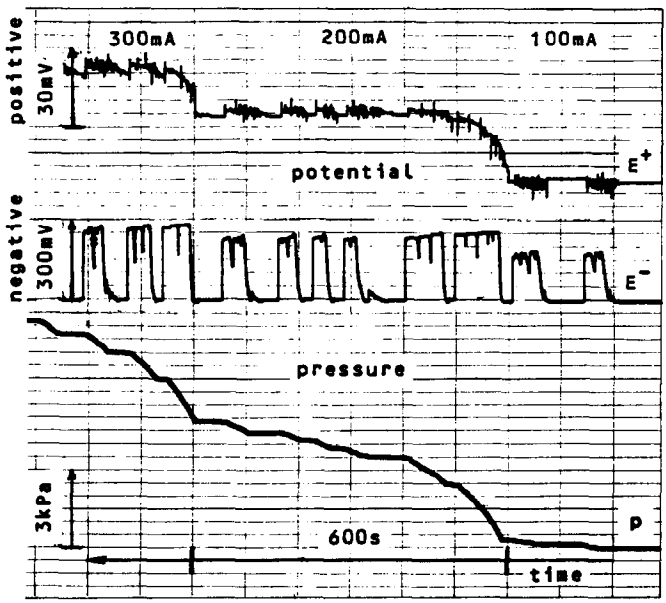

Fig. 2. Electrode potentials and pressure during overcharging of a sealed lead/acid accumulator at stepwise-increasing currents.

TABLE 1

Dependence of negative electrode potentials, E^-_{max}, on the overcharging current, I

	I (mA)							
	100	200	300	400	500	600	700	800
E^-_{max} (mV)	−2185	−2245	−2275	−2300	−2315	−2330	−2340	−2350

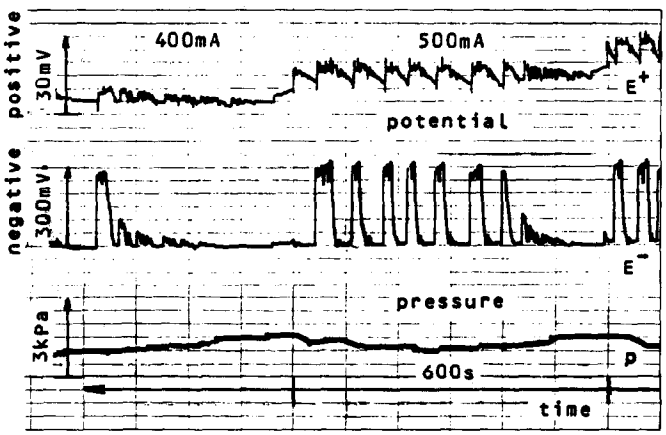

Fig. 3. Electrode potentials and pressure during overcharging of a sealed lead/acid accumulator at stepwise-decreasing currents.

The pressure changes and the related potential fluctuations of the negative electrodes proceed analogously at higher currents. The pressure increase between subsequent current changes ranged from 4.5 to 6.8 kPa during 10 min.

In parallel to the potential fluctuations of the negative electrodes, small positive electrode potential excursions were observed, amounting up to 20 mV for the highest overcharging current of 800 mA.

When the charging (overcharging) current is gradually lowered (see Fig. 3), the course of both electrode potentials is different from that observed when the current is gradually increased. As soon as the current is lowered, the potential fluctuations of the positive and negative electrodes disappear; they reappear after some time, namely the later the lower is the current. If the current is in the range of 300 to 100 mA, no fluctuations appear in the course of 10 min.

As an example, the potential courses at currents of 500 and 400 mA are shown in Fig. 3 together with the corresponding pressure. The pressure changes at decreasing overcharging current are quite different from those at increasing overcharging current: as long as no fluctuations appear, the pressure decreases; during potential fluctuations the pressure increases moderately at E^-_{max} and remains constant at E^-_{min}.

We propose the following elucidation of the observed phenomena. During overcharging, the cell having a strongly compressed electrode stack, oxygen is accumulated at the positive electrode, where the local pressure increases up to a critical value at which the gas penetrates through the separator towards the negative electrode. Here

the oxygen is reduced (ionized). The accumulation and penetration of oxygen proceed periodically, bringing about potential changes of both the positive and negative electrodes. As soon as the oxygen reaches the negative electrodes, they are depolarized (their potential decreases in absolute value), the current efficiency of oxygen reduction at the lead electrodes being high (98–99%). The positive electrode potential oscillations might be related to variations of the local oxygen pressure.

Since the cell electrodes were not ideally plane-shaped, the compression of the separator was not uniform and it is probable that the transport of oxygen was undisturbed at some points, while it was hindered at others.

In our previous paper [4], devoted to the impedance characteristic of sealed lead/acid cells during galvanostatic charge, we observed at the end of charging a sharp increase of the impedance and potential (up to hydrogen evolution) of negative electrodes. This is probably caused by blocking of electrode pores with hydrogen. During overcharging, the cell overpressure rises due to the oxygen evolution and the impedance falls and stabilizes. In this situation, the ionization of oxygen at the negative electrodes becomes important and is apparently responsible for the observed decrease of the impedance and the potential (up to oxygen reduction) of negative electrodes.

In the same study of the cell showing the fluctuations of both electrode potentials [5] fluctuations of impedance were observed during cell overcharging. These fluctuations reached values similar to the above mentioned maximum and stabilized impedance. If the transport of oxygen to the negative electrode is continuous and its electroreduction is sufficiently fast then the impedance of negative electrodes is stabilized. Hence the fluctuations of impedance may be explained by the nonuniform transport of oxygen.

Overcharging at limiting cell voltage

An anomalous behaviour of the cell under study was observed even during overcharging at limiting cell voltage. The cell was overcharged at a maximum current of 200 mA and, at the same time, the limiting cell voltage was changed in 30-min intervals from 2.42 to 2.27 V in steps of 30 mV each.

In normal cells the potentials of both electrodes are constant and the current decreases when the limiting cell voltage is reached. In our case, the fluctuations of the voltage, electrode potentials, and also the current were observed whereas the cell overpressure was nearly constant (9 kPa) during the whole measurements (see Fig. 4).

Figure 4 shows the variations of the current and of the electrode potentials. It can be seen that the limiting cell voltage influences mainly E^-_{max} values. On the contrary, if the potential of the negative electrode reaches the E^-_{min} value the cell voltage decreases under the adjusted limiting cell voltage, hence the cell voltage fluctuates also. The character of fluctuations of the current and of the electrode potentials changes when the limiting voltage passes from 2.33 to 2.30 V. When the limiting voltage decreases from 2.42 to 2.33 V, the character of the fluctuations does not change, only the amplitude of the current fluctuations increases: at a limiting voltage of 2.42 V (region A) the current varied between 200 and 130 mA, whereas at 2.33 V (region B) it varied between 200 and 80 mA. The maximum current of 200 mA occurs less frequently when the limiting voltage is lower; at 2.30 V (region C) and less, the lower current values prevail and the limit of 200 mA is attained only at certain intervals which increase with the duration of overcharging.

The oscillating current attains its maximum value of 200 mA at the potential E^-_{min}, which is best apparent at the limiting voltage of 2.3 V.

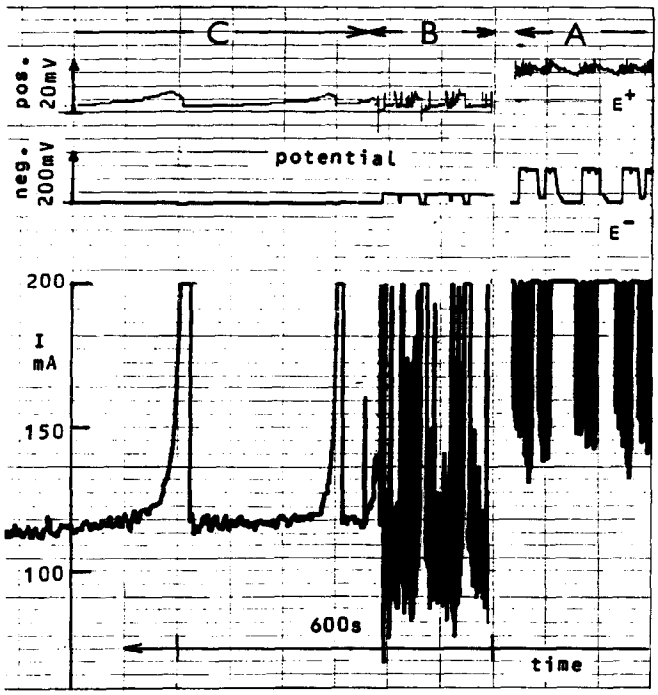

Fig. 4. Influence of voltage limitation on the time courses of electrode potentials and current during overcharging a sealed lead/acid accumulator at limited voltage. The illustration for different limiting voltages: 2.42 V in region A, 2.33 V in region B, and 2.30 V in region C.

The observed phenomena can, in our opinion, be discussed in terms of our concept about accumulation of oxygen at the positive electrode and its subsequent penetration through the separator to the negative electrode, where it is reduced. During reduction, the current immediately reaches its maximum value on which level it persist as long as there is a sufficient quantity of oxygen at the negative electrodes. A conjugated process is the evolution of oxygen at the positive electrode, where it is accumulated. Accordingly, oxygen is exhausted at the negative electrodes, whereby the current drops to a value corresponding to the limited transport of oxygen. The whole process is periodically repeated.

Conclusions

Potential oscillations of positive and negative electrodes of sealed lead/acid cell during overcharging are caused by accumulation of oxygen at the positive electrode and its subsequent penetration through the separator to the negative electrodes, i.e., by nonuniform transport of oxygen. During accumulation of oxygen, the potential of the negative electrodes increases up to hydrogen evolution, accompanied by an increase of overpressure. The oxygen that penetrated through the separator is reduced at the negative electrodes, which are thus depolarized, while the cell pressure remains constant.

Acknowledgements

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