

Lead/acid cell capacity improvement: the use of additional electrolyte volume

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Abstract

The performance of lead/acid batteries can be improved considerably by modifying the design according to certain criteria. One of the problems that have been detected is the low ratio of the volume of electrolyte to the amount of active matter content in the plates; with this goal, the influence that a greater quantity of electrolyte, in relationship to the active matter to be used, could have on the behavior of the battery, and especially on its capacity, has been studied. The tests carried out in this sense proved that the increase of the quantity of available electrolyte improves the behavior of the battery by increasing the discharge capacity between 5% and 20% depending on the discharge current. This increase in capacity is directly related to the increase in volume of the electrolyte. The addition of extra electrolyte from an external tank with electrolyte recirculation presents considerable advantages over the extra electrolyte addition into the battery casing. © 1998 Elsevier Science S.A.

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1. Introduction

Lead/acid batteries play a major role in the storage of electric energy in many applications. The basic design of a typical stationary battery, used in photovoltaic (PV) systems, reminds of the design of SLI batteries, large number of plates in a reduced space and low amount of electrolyte. This strategy is useful when dealing with cars, trucks, elevating wheelbarrows, etc., as they require high current densities for a short time. However, the use of the same design in batteries for PV system leads to a decrease in energy delivered when the battery operates at low currents for a long time.

The main requirement of a lead/acid battery used in PV utilities is current supply during a long period of time, especially in cloudy days. It is well known that the capacity of a lead/acid battery increases as the discharge current is reduced according to the Peukert equation. In lead/acid cells the shortage of electrolyte quantity inside the cell accelerates the acid depletion at the electrode surface when the system operates at low rate discharges, making the battery to collapse earlier. The problem can be

solved by the addition of electrolyte to the cell. Following this principle, the British Petroleum company has developed a modified cell with an electrolyte reservoir at the top of the cell [1]. The new design allows the more concentrated electrolyte from the reservoir to fall down by gravity and mix with the depleted electrolyte in the cell as discharge is proceeding, thus maintaining the electrolyte concentration. The system works properly during discharge, but needs an extra overcharging process to homogenize the electrolyte reservoir. This reduces the cycle efficiency and accelerates the electrode corrosion and plate ageing. The author proposes to supply the extra electrolyte from an external reservoir (Fig. 1). This method not only maintains the electrolyte concentration in the cell, but benefits from the electrolyte circulation [2], and avoids excessive overcharging.

2. The electrolyte concentration and the diffusion process

It has been proved by a number of investigators [3–5] that voltage decay and battery breakdown may be caused by electrolyte depletion, especially during low rate discharges, while the capacity limitation is due to the blocking of the electrode pores by PbSO_4 .

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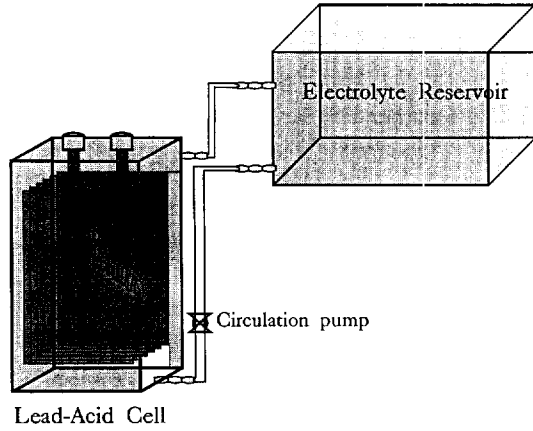


Fig. 1. Scheme of the experimental device.

In lead/acid batteries, the cell performance has noticeably been improved with the use of a circulation system that homogenizes the electrolyte concentration, achieves longer discharge time, and increases the output voltage [6]. Further improvements have been obtained when the battery has been attached to an electrolyte reservoir supplying sulfuric acid to the main cell. In this case, the acid depletion at the electrode interface is compensated by the forced flow created by the electrolyte circulation [7], and hence the higher concentration gradient between the bulk solution and the interface. The result is the enhancement of the discharge process.

During the discharge process the reactions at the electrode surface cause the electrolyte concentration to drop; then, the diffusion process starts and generates a concentration gradient across the Nernst diffusion layer, whose thickness tends to grow with the square root of the time if the diffusion process is not perturbed by natural or forced convection. Thus, the electrolyte concentration at the electrode surface drops [8].

Once the steady state is reached, because of the action of the natural or forced convection, and the concentration profile is established, the concentration gradient persists if the discharge current is kept constant. The process continues until the diffusion flux cannot compensate for the acid depletion at the electrode surface; thus, the battery breaks down.

It is generally assumed that diffusion controls the electrochemical process during the cell discharge. Therefore, the basic transport equation for the ion motion [9] can be replaced by Fick's law for the diffusion process

$$J_i = -D \frac{dc_i}{dx} \quad (1)$$

where D is the diffusion coefficient, c the electrolyte concentration, and x the distance from the electrode surface.

According to the Nernst diffusion layer theory, we can linearize the concentration gradient when forced convection takes place as is the case in electrolyte circulation. Therefore, Eq. (1) can be transformed into

$$J_i = -D \frac{c_o^* - c_s^*}{\delta^*} \quad (2)$$

where c_o^* represents the concentration in the electrolyte reservoir, c_s^* the concentration at the electrode surface for the modified lead/acid cell, and δ^* the diffusion layer thickness when the forced flow appears.

If there is no electrolyte reservoir, the concentration in the bulk solution decreases with discharge time, and the diffusion flow may be expressed from the linearized Fick law as

$$J_i = -D \frac{c_o - c_s}{\delta} \quad (3)$$

where c_o is the concentration of the bulk solution, c_s the concentration at the electrode surface in the non-modified lead/acid cell, and δ the diffusion layer thickness when the diffusion flux is the only ion-transport mechanism.

In the steady state, the rate of every step involved in the overall electrochemical reaction is the same; therefore, the current density of the charge transfer is equal to the current density due to the ion transport, the electrolyte flow is constant, and

$$\frac{c_o^* - c_s^*}{\delta^*} = \frac{c_o - c_s}{\delta} \quad (4)$$

On setting $c_o^* = c_o + \Delta c$ and $\delta^* = \delta - \Delta \delta$, we obtain

$$c_s^* - c_s = \Delta c + \frac{\Delta \delta}{\delta} (c_o - c_s) \quad (5)$$

where Δc accounts for the decrease of the bulk electrolyte concentration in the conventional cell, and $\Delta \delta$ is the reduction of the diffusion layer thickness because of the electrolyte circulation.

From the definition of Δc and $\Delta \delta$, these terms are positive, and because the concentration in the diffusion layer is always lower than in the bulk solution, the term $c_o - c_s$ is also positive, therefore, $c_s^* > c_s$.

The last term on the right hand side of Eq. (5) remains constant once the steady state is established and the discharge conditions do not change. Nevertheless, while the battery is discharged the bulk electrolyte concentration is reduced gradually, and c_o decreases accordingly; on the contrary, if we maintain the concentration of the bulk solution by supplying electrolyte from an internal or external reservoir, c_o would be maintained practically constant during the discharge or would vary only slightly. In this case, $c_s^* - c_s$ increases, leading to a greater electrolyte concentration at the surface of the electrode of the modi-

fied cell, which increases the discharge time and improves the cell behavior.

Eq. (5) relates the changes in electrolyte concentration at the electrode surface for the modified and non-modified cells. As the cell capacity depends on the concentration at the electrode surface, the improvement in cell capacity will be related to the difference $c_s^* - c_o$. On the other hand, the concentrations c_s^* and c_o depend on the concentration gradient across the boundary zone; therefore, the capacity improvement factor should be related to the ratio of the concentration gradients rather than to the concentration difference itself. Mathematically

$$f = 1 - \frac{c_s^* - c_o^*}{c_s - c_o} = \frac{\Delta \delta}{\delta} \quad (6)$$

with $0 < f < 1$.

The factor f increases with decreasing diffusion layer thickness, according to the expected behavior of the lead/acid cell.

Since the thickness of the boundary zone depends on the discharge current, the factor f must be expressed, in general as $f = f(I_D, c_o^*)$.

3. Experimental

The tests have been carried out in two blocks of lead/acid batteries with capacities of 425 and 240 Ah, respectively. In each block a fraction of the batteries has stayed without changes while the other has been connected to an electrolyte reservoir. Two types of test have been carried out, one with a reservoir volume equal to twice the volume of electrolyte contained in the main cell ($r = 2$), and the other with a reservoir volume equal to the volume of electrolyte contained in the main cell ($r = 1$). The

electrolyte reservoir has been connected to the cell by using a peristaltic pump whose flow rate could be regulated between 0.5 and 4 l/h. Most of the tests have been carried out at a flow rate of 3 l/h. The experimental device is given in Fig. 1.

The batteries have been submitted to continuous charge/discharge cycling from very low current ($C/70$) to accelerated discharges ($C/5$). The bulk electrolyte density has been continuously monitored during the process by a digital electronic specific gravity meter.

The capacity of the cell was obtained by the Ah-accounting method [10] while the efficiency was computed as the ratio of the delivered Ah during discharge to the supplied Ah during charge [11].

The discharge process ends at a sudden drop of the potential. With the purpose of establishing the influence of the electrolyte contribution from the external reservoir, the discharge curves of two identical batteries, one without external electrolyte supply and the other with said supply have been represented in the Fig. 2. We can observe the increase in discharge time before the collapse of the battery for the system with external electrolyte supply.

3.1. Capacity improvement

The experimental capacity improvement has been computed as the ratio of the capacity of the modified to the non-modified cell. The improvement capacity factor has been defined as the exceeding fraction of the non-modified cell capacity, according to

$$f_{cf} = \frac{C_{mc}}{C_{cc}} - 1 \quad (7)$$

where C_{mc} and C_{cc} are the capacities of the modified and non-modified cell, respectively, rated at the same dis-

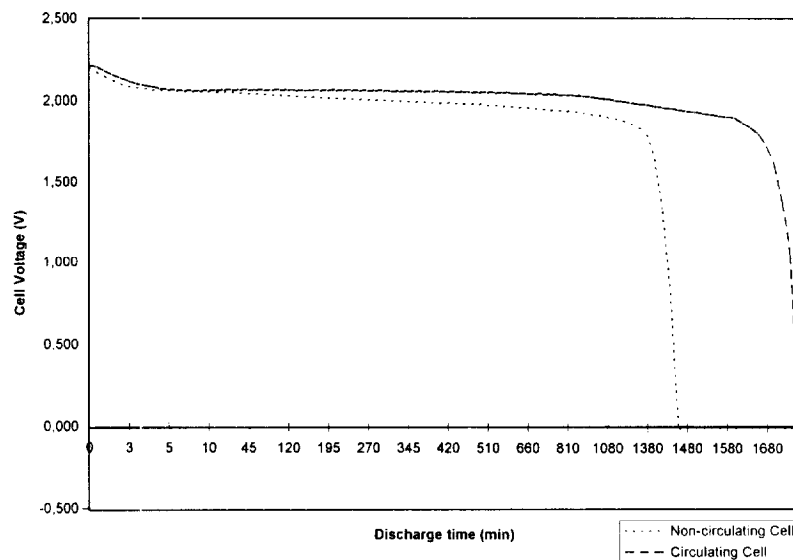


Fig. 2. Cell voltage for a lead/acid battery with electrolyte circulation from a reservoir and for a conventional battery.

Table 1
Experimental capacities of the lead/acid batteries with (C_{mc}) and without (C_{cc}) external electrolyte supply

I_D (A)	425 Ah				240 Ah			
	$r = 2$		$r = 1$		$r = 2$		$r = 1$	
	C_{mc}	C_{cc}	C_{mc}	C_{cc}	C_{mc}	C_{cc}	C_{mc}	C_{cc}
12.5	728	607	668	607	411	342	377	342
15.0	697	590	632	590	394	333	357	333
17.5	666	571	605	571	375	322	342	322
20.0	636	549	580	549	360	310	328	310
22.5	604	525	553	525	340	296	312	296
25.0	569	500	525	500	322	282	296	282
3.0	765	638	703	638	431	360	397	360
6.0	715	606	697	606	405	342	365	342
9.0	630	541	666	541	357	306	324	306
12.0	585	504	636	504	331	285	301	285
15.0	515	448	604	448	290	253	266	253
18.0	472	414	569	414	267	234	245	234

charge rate. Table 1 shows the experimental data for the two types of batteries tested.

To summarize the dependence of f_{cf} on the discharge current, we correlated the experimental values with the factor r , by the equation

$$f_{cf} = 0.0182 r \left(\frac{C_{10}}{I_D} \right)^{0.428} \quad (8)$$

where C_{10} is given in Ah and I_D in A.

Table 2 shows the improvement factor, both experimental and calculated. It is interesting that the factor f_{cf} decreases with the increase in discharge current. The discharge time for the batteries with electrolyte reservoir, i.e. delivered capacity, has been increased by 5 to 20%, de-

Table 2
Comparison of predicted values (f_{cal}) and experimental results (f_{exp}) of the improved available capacity of circulating lead/acid batteries with electrolyte reservoir

I_D (A)	425 Ah				240 Ah			
	$r = 2$		$r = 1$		$r = 2$		$r = 1$	
	exp	cal	exp	cal	exp	cal	exp	cal
12.5	0.199	0.193	0.100	0.098	0.201	0.196	0.102	0.099
15.0	0.181	0.182	0.071	0.073	0.184	0.185	0.071	0.072
17.5	0.166	0.165	0.060	0.061	0.166	0.166	0.061	0.062
20.0	0.158	0.158	0.057	0.058	0.162	0.161	0.058	0.059
22.5	0.151	0.150	0.053	0.050	0.149	0.150	0.053	0.051
25.0	0.137	0.135	0.050	0.048	0.143	0.139	0.051	0.048
3.0	0.200	0.195	0.102	0.099	0.197	0.194	0.103	0.099
6.0	0.180	0.182	0.070	0.071	0.182	0.184	0.068	0.069
9.0	0.165	0.166	0.058	0.060	0.167	0.166	0.059	0.060
12.0	0.160	0.160	0.056	0.057	0.161	0.162	0.056	0.057
15.0	0.150	0.150	0.051	0.050	0.148	0.149	0.052	0.051
18.0	0.140	0.138	0.048	0.046	0.141	0.139	0.049	0.047

pending on the discharge rate. The correlation factor was determined as 0.992, which encourages us to extend the method to other batteries.

3.2. Effects of the electrolyte addition

The main function of the external electrolyte reservoir is to maintain the concentration of the electrolyte in the bulk solution of the battery as uniform as possible. The time during which this process is maintained depends on the quantity of the electrolyte in the external reservoir; the greater is the external reservoir, the longer is the time that elapses before the depletion of the electrolyte and the collapse of the battery.

The extra electrolyte can be placed inside the battery casing or in an external tank. Both methods fulfil the same function, but the electrolyte addition from an external tank promotes the electrolyte circulation which increases the capacity of the battery [7]. Furthermore, the forced flow created by the electrolyte circulation is more efficient than the laminar flow due to the electrolyte addition from the upper part of the recipient. Thus, the combined effect of the electrolyte circulation and the greater concentration in the bulk solution increase considerably the capacity of the battery.

4. List of symbols

- c_o, c_o^* concentration of the electrolyte in the bulk solution for the conventional and the modified cell, respectively
- c_s, c_s^* concentration of the electrolyte at the electrode surface for the conventional and the modified cell, respectively
- c_i concentration of species i
- C_{10} cell capacity at 10 h discharge time
- C_{mc} capacity of the modified battery
- C_{cc} capacity of the non-modified battery
- D diffusion coefficient
- f theoretical capacity improvement factor
- f_{cf} experimental capacity improvement factor
- I_D discharge current
- J_i overall ion flux for the species i
- r ratio of volume of the electrolyte reservoir to the main cell
- t_d discharge time for the non modified cell
- x distance from the electrode surface

Greek symbols

- δ, δ^* boundary layer thickness for the conventional and the modified cell, respectively

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