



# The initial voltage drop in lead–acid cells: the influence of the overvoltage

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## Abstract

The initial voltage drop at the switching on process in lead–acid batteries used as UPS may cause the breakdown of the battery and the failure of the external load when this operates within low fluctuations of the set-up voltage. One of the main components of the initial voltage drop is the overvoltage, whose effects can be considered more important than the ones caused by the electrolyte resistance and other contributions. The use of electrolyte circulation has proved, especially at high rate discharges, to reduce the overvoltage, thus the influence onto the initial voltage drop, and the risk of a sudden breakdown. The voltage drop caused by the overvoltage has been reduced with the use of the electrolyte circulation at high rate discharges, by 57% to 79%, depending on the current rate. Besides, the number of elements required in the battery block to meet the external load demand has been reduced, on average, by 6% to 12% depending on the maximum fluctuation allowed in the external load voltage. The energy required to recirculate the electrolyte, which is taken from the own battery, is overcompensated by the saving of energy because of the reduction of the voltage drop, with an excess of energy of up to 20%, for the heaviest working conditions of the external load. © 1998 Elsevier Science S.A.

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## 1. Introduction

Lead–acid batteries are widely used as uninterruptible power source (UPS) for many applications, such as telephone stations, medical equipments, computers, data acquisition systems, etc. The battery block that supplies current to these systems is usually sized according to the minimum required voltage of the external load and the ohmic voltage drop along the electrical line. Although currently rated at 2 V/e for sizing purposes, lead–acid batteries operate at a starting voltage of 2.1 V/e when fully charged. This voltage drops suddenly when the external load is connected and current is driven out from the battery. The voltage drop at the beginning of the discharge may cause, under circumstances such as heavy work or high rate discharge, the battery to exceed the minimum voltage required by the external load. The main consequence is an early collapse of the supplying power and the

failure of the external load system. This is of especial importance if the extracted current is high as in the case of a sudden failure of the main power. To avoid the problem, it is a current practice to oversize the battery increasing the number of elements of the battery block, where the excess of elements compensate for the voltage drop at the beginning of the discharge. Therefore, if the initial voltage drop is reduced by any means, the number of extra elements as well as the initial investment and maintenance costs will be accordingly reduced.

### 1.1. Theory of the discharge process

The discharge curve of a lead–acid cell is illustrated in Fig. 1. The instantaneous voltage drop, A, after switching on the current is due to the cell internal resistance, electrolyte resistance in the electrolyte-filled pores of the separators, ohmic resistance in the grids, active material resistance, solid–solid and solid–liquid interface, and electrolyte resistivity. The sloping portion, B, arises from double layer capacity discharge, as coupled through the ohmic electrolyte resistance in the pores of the active mass. Supersaturation, nucleation and crystallization phe-

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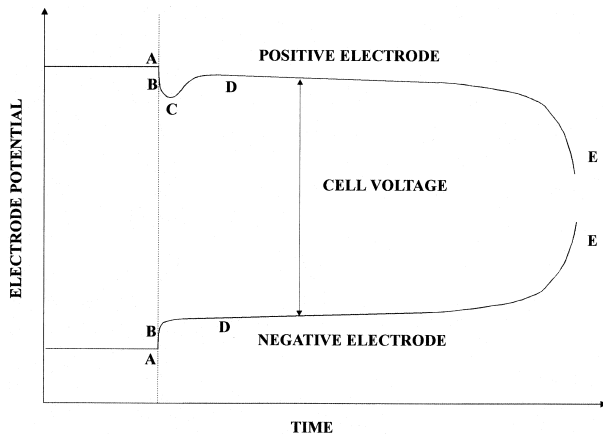


Fig. 1. Schematic discharge curves for positive and negative plates in lead-acid batteries.

nomena lead to the initial voltage dip, C, in the discharge curve of the positive electrode [1].

The different contributions to the voltage drop in the lead-acid cell can be grouped in three main groups: those affecting the electrolyte resistance, those related to the material structure, electrodes and separators, and those involved in the electrochemical reactions at the double layer. The contribution of the material structure to the initial voltage drop can be reduced to a minimum if the material structure is appropriately chosen, using expanders which inhibits the growth of large  $\text{PbSO}_4$  crystals and reduces the crystallization overvoltage [2], and  $\beta\text{-PbO}_2$  as active mass for the positive electrode which minimizes the nucleation overpotential [3–6]. Ohmic resistance in the grids and in the active material can also be minimized using the appropriate elements and developing the forming process in the better possible conditions.

The contribution of the electrolyte resistance is related to the electrolyte concentration and its changes in the electrolyte-filled pores of the separators and in the bulk solution; it will be the focus of a separated study. Therefore, only the terms related to the overpotential have been included in the present analysis.

### 1.2. The overpotential

Experiments carried out in laboratories have shown that the voltage drop at the switching on process in lead-acid cells cannot be justified by the only contribution of the internal resistance of the cell. In fact, the overpotential is, by far, the most important factor in the voltage drop, especially when high rate discharges are demanded.

In the loaded cell neither the vanishing current density at the reversible equilibrium,  $i$ , nor the variation of the voltage from the reversible voltage,  $\Delta E$ , can be neglected. By omitting the effect of the potential drop on the ionic resistance,  $\Delta E$  is composed of the overpotentials (polariza-

tion potentials) of the two electrodes, being positive for the anodic process and negative for the cathodic.

The overpotential or overvoltage depends on the current density, therefore it is greatly influenced by the discharge rate.

The total overvoltage of an electrode is made up additively of all the overvoltage components:

$$\eta = \eta_t + \eta_r + \eta_d + \eta_k + \eta_o \quad (1)$$

being  $\eta_t$ ,  $\eta_r$ ,  $\eta_d$ ,  $\eta_k$ , and  $\eta_o$  the activation, reaction, diffusion, crystallization and polarization overvoltage, respectively, and where the term  $\eta_t + \eta_d$ , accounts for the concentration overpotential.

However, as chemical reactions in lead-acid batteries take part generally only in the dissociation equilibria, they are very fast and usually do not affect the overvoltage; therefore,  $\eta_r$  tends toward zero. Also, the resistance polarization accounts for the ohmic potential drop in the electrolyte and for the resistance in the Nernst diffusion layer as well as in the layers or coatings on the electrode. That portion is usually ascribed to the electrolyte resistance and can be compensated experimentally at least within certain limits. Therefore, as the crystallization overvoltage can also be neglected if compared to the other terms when using the appropriate materials, the overvoltage is mainly formed by the contributions of the activation and concentration components.

### 1.3. The activation overpotential

The activation overpotential, which reflects the change in energy when the charge transfer reaction occurs, is given by the Tafel equation:

$$\eta_t = a - b * \log(i) \quad (2)$$

where,

$$a = - \frac{2.30RT}{\alpha F} \log(i_o); \quad b = - \frac{2.30RT}{\alpha F} \quad (2a)$$

being  $\alpha$  the called ‘transfer coefficient’.

When the overpotential is small, Eq. (2) becomes:

$$\eta_t = i * R_t \quad (3)$$

where  $R_t$  is the activation overpotential resistance, given by:

$$R_t = \frac{RT}{i_o F} \quad (4)$$

The above expression can be extended to 10 mV in lead-acid batteries.

If the exchange current is large, the activation overpotential will be small. On the contrary, if the exchange current is small, the resistance is large. The activation

Table 1

Current rate of the discharge processes in conventional and electrolyte circulation batteries in function of the discharge time and cut-off voltage

Discharge time	Cut-off voltage (element)	Type of battery						
		6 SB 25	6 SB 50	6 SB 72	6 SB 75	6 SB 100	6 SB 125	6 SB 150
		Cell capacity (Ah) [rated at C10]						
		25	50	72	75	100	125	150
		<i>I</i> (max)						
5 min	1.55	51.5	98.0	122.5	126.0	184.0	229.0	275.0
	1.60	47.0	89.0	109.0	115.0	171.0	212.5	255.0
	1.65	44.0	78.5	100.0	106.0	152.0	190.0	228.0
	1.70	39.0	74.5	93.5	98.0	140.0	172.5	207.0
10 min	1.55	42.0	80.0	102.0	106.0	157.0	189.0	226.5
	1.60	39.0	74.0	93.0	98.0	142.0	177.5	213.0
	1.65	37.0	67.0	86.5	91.0	131.0	164.0	196.5
	1.70	33.7	63.0	81.0	85.0	120.0	150.0	180.0
15 min	1.55	35.0	68.0	88.0	90.5	128.0	160.0	192.0
	1.65	32.0	58.0	76.5	80.0	114.0	142.5	171.0
	1.70	29.5	55.0	71.5	75.0	106.0	132.5	159.0
	1.75	26.7	50.0	64.5	68.0	95.0	120.0	144.0
20 min	1.60	30.0	57.5	76.5	80.5	110.5	137.5	165.0
	1.65	27.0	51.0	68.5	72.0	100.5	125.5	150.5
	1.70	25.0	47.0	61.5	64.5	90.5	113.0	135.5
	1.75	23.0	42.5	56.5	58.5	82.5	103.5	124.0
30 min	1.60	23.0	44.0	59.0	62.0	85.0	106.0	127.0
	1.65	22.0	41.5	56.0	59.0	82.0	102.5	123.0
	1.70	21.2	40.0	52.5	55.0	77.0	96.0	115.0
	1.75	20.0	37.0	49.5	51.0	72.0	90.0	108.0

overpotential acts, therefore, opposite to the internal resistance, partially compensating the cell voltage drop as the exchange currents raises or falls. It is difficult to define the limit from which an exchange current can be considered small or large, thus a certain undefinition may affect the analysis of the voltage drop.

#### 1.4. The concentration overpotential

The concentration overpotential accounts for the effect of changes in concentration on the surface of the electrode when the charge transfer occurs. The concentration overpotential can be determined from the Nernst equation:

$$\eta_c = \left( \frac{RT}{zF} \right) \ln \left[ \frac{a(0,t)}{a_o} \right] \quad (5)$$

where the activity  $a_o$  lies in the bulk solution and  $a(0, t)$  occurs at the surface of the electrode ( $x = 0$ ) at time  $t$ .

In the derivation of the transfer processes the assumption is that the activity of the reacting ions in the solution remains constant, therefore the concentration overpotential only depends on the activity at the surface of the electrode.

During the discharge process an equalization of the concentration change can occur by diffusion or migration

as well as by natural or forced convection. If only diffusion is considered, from the Fick's law [7]:

$$J_D = \frac{i}{zF} = -D \left( \frac{\partial a}{\partial x} \right)_{x=0} \approx -D \frac{a_o - a(0,t)}{\delta} \quad (6)$$

$D$  being the diffusion coefficient, and  $\delta$  the thickness of the Nernst diffusion layer. The approximation relates to a simplified assumed linear concentration gradient within the Nernst diffusion layer.

The concentration, say the activity of the species, at the electrode surface changes with time according to the Sand relation [8]:

$$a(0,t) = a_o - \frac{2i}{zF} \left( \frac{t}{\pi D} \right)^{1/2} = a_o - c\sqrt{t} \quad (7)$$

If there is an impoverishment of flow of current at the surface of the electrode, after a certain 'transition time',  $\tau$ , the activity tends toward zero and the potential drops simultaneously; then, the diffusion overvoltage is given by:

$$\eta_d = \frac{RT}{zF} \ln a(0,t) = \frac{RT}{zF} \ln(a_o - c\sqrt{\tau}) \quad (8)$$

or:

$$\eta_d = \frac{RT}{zF} \ln \left( 1 - \frac{i}{i_L} \right) \approx \frac{RT}{zF} \frac{i}{i_L} \quad (9)$$

where  $i$  is the current density at a time  $\tau$ , and  $i_L$  the diffusion limiting current density, given by:

$$i_L = \frac{zFDa_0}{\delta} \quad (10)$$

Mass transport is also affected by all movement of the electrolyte such as forced convection by flow of electrolyte (electrolyte circulation), which makes the thickness of the Nernst diffusion layer to decrease, and the limiting current

to increase. Therefore, the electrolyte circulation reduces the concentration overvoltage and increases the cell output voltage.

### 1.5. The effects of the electrolyte concentration

In high rate discharges the transient time reduces rapidly, and the term  $c\sqrt{\tau}$  in Eq. (8) can be neglected if compared

Table 2

Voltage drop due to concentration overvoltage in conventional and electrolyte circulation lead–acid batteries at various discharge rates (see Table 1)

Discharge time	Cut-off voltage (element)	Type of battery							Voltage drop allowance
		6 SB 25	6 SB 50	6 SB 72	6 SB 75	6 SB 100	6 SB 125	6 SB 150	
<i>Conventional battery</i>									
5 min	1.55	0.333	0.317	0.309	0.307	0.315	0.313	0.311	0.550
	1.60	0.325	0.309	0.299	0.299	0.308	0.307	0.305	0.500
	1.65	0.320	0.298	0.291	0.292	0.298	0.297	0.295	0.450
	1.70	0.309	0.293	0.285	0.285	0.291	0.289	0.287	0.400
10 min	1.55	0.316	0.299	0.293	0.292	0.301	0.296	0.294	0.550
	1.60	0.309	0.293	0.285	0.285	0.292	0.291	0.289	0.500
	1.65	0.305	0.284	0.279	0.278	0.285	0.284	0.282	0.450
	1.70	0.297	0.279	0.273	0.272	0.277	0.276	0.274	0.400
15 min	1.55	0.300	0.285	0.280	0.278	0.283	0.282	0.280	0.550
	1.65	0.292	0.271	0.268	0.267	0.273	0.272	0.270	0.450
	1.70	0.285	0.267	0.262	0.262	0.267	0.266	0.264	0.400
	1.75	0.276	0.259	0.253	0.253	0.257	0.257	0.255	0.350
20 min	1.60	0.286	0.271	0.268	0.268	0.270	0.269	0.267	0.500
	1.65	0.277	0.260	0.258	0.258	0.262	0.261	0.259	0.450
	1.70	0.271	0.253	0.249	0.248	0.253	0.252	0.250	0.400
	1.75	0.263	0.244	0.242	0.240	0.245	0.244	0.242	0.350
30 min	1.60	0.263	0.247	0.245	0.245	0.247	0.246	0.244	0.500
	1.65	0.259	0.242	0.241	0.241	0.244	0.243	0.241	0.450
	1.70	0.256	0.239	0.235	0.235	0.239	0.238	0.236	0.400
	1.75	0.251	0.232	0.230	0.228	0.233	0.232	0.230	0.350
<i>Electrolyte reservoir</i>									
5 min	1.55	0.140	0.133	0.130	0.124	0.127	0.134	0.134	
	1.60	0.116	0.110	0.103	0.103	0.110	0.115	0.115	
	1.65	0.112	0.094	0.097	0.096	0.093	0.099	0.099	
	1.70	0.094	0.096	0.093	0.089	0.089	0.092	0.092	
10 min	1.55	0.114	0.109	0.108	0.104	0.108	0.111	0.110	
	1.60	0.098	0.093	0.090	0.089	0.089	0.097	0.098	
	1.65	0.095	0.082	0.085	0.083	0.083	0.089	0.088	
	1.70	0.083	0.080	0.080	0.078	0.076	0.080	0.080	
15 min	1.55	0.095	0.092	0.093	0.089	0.088	0.094	0.094	
	1.65	0.079	0.067	0.070	0.070	0.070	0.074	0.074	
	1.70	0.074	0.071	0.071	0.069	0.068	0.072	0.072	
	1.75	0.066	0.062	0.062	0.061	0.059	0.064	0.064	
20 min	1.60	0.081	0.078	0.081	0.079	0.076	0.080	0.080	
	1.65	0.066	0.061	0.065	0.063	0.063	0.067	0.067	
	1.70	0.063	0.059	0.058	0.057	0.056	0.060	0.059	
	1.75	0.057	0.052	0.055	0.052	0.052	0.055	0.055	
30 min	1.60	0.062	0.060	0.062	0.061	0.059	0.062	0.062	
	1.65	0.057	0.053	0.056	0.055	0.055	0.058	0.058	
	1.70	0.055	0.052	0.052	0.051	0.050	0.053	0.052	
	1.75	0.051	0.046	0.049	0.047	0.046	0.049	0.049	

Table 3

(a) Minimum number of extra elements required in conventional lead–acid batteries to meet the external load demand operating within low voltage fluctuations (Group I =  $\pm 2.5\%$ ; Group II =  $\pm 5\%$ ); (b) Minimum number of extra elements required in conventional lead–acid batteries to meet the external load demand operating within low voltage fluctuations (Group I =  $\pm 2.5\%$ )

Discharge time	Cut-off voltage (element)	Type of battery						
		6	6	6	6	6	6	6
		SB	SB	SB	SB	SB	SB	SB
		25	50	72	75	100	125	150
Number of elements: 107; required voltage: 220/110 V ( $\pm 2.5\%$ ); minimum voltage: 2.005 V/e; maximum voltage: 2.100 V/e								
<i>Required extra elements in conventional batteries: Group I</i>								
5 min	1.55	15	14	13	13	14	14	13
	1.60	14	13	13	13	13	13	13
	1.65	14	13	12	12	13	12	12
	1.70	13	12	12	12	12	12	12
10 min	1.55	14	13	12	12	13	12	12
	1.60	13	12	12	12	12	12	12
	1.65	13	12	11	11	12	12	11
	1.70	12	11	11	11	11	11	11
15 min	1.55	13	12	11	11	12	11	11
	1.65	12	11	11	11	11	11	11
	1.70	12	11	10	10	10	10	10
	1.75	11	10	10	10	10	10	10
20 min	1.60	12	11	11	11	11	11	11
	1.65	11	10	10	10	10	10	10
	1.70	11	10	9	9	10	10	9
	1.75	10	9	9	9	9	9	9
30 min	1.60	10	9	9	9	9	9	9
	1.65	10	9	9	9	9	9	9
	1.70	10	9	9	8	9	9	9
	1.75	10	8	8	8	8	8	8
Number of elements: 110; required voltage: 220/110 V ( $\pm 5\%$ ); minimum voltage: 1.900 V/e; maximum voltage: 2.100 V/e								
<i>Required extra elements in conventional batteries: Group II</i>								
5 min	1.55	9	8	7	7	8	7	7
	1.60	8	7	7	7	7	7	7
	1.65	8	6	6	6	6	6	6
	1.70	7	6	6	6	6	6	6
10 min	1.55	8	7	6	6	7	6	6
	1.60	7	6	6	6	6	6	6
	1.65	7	6	5	5	6	6	5
	1.70	6	5	5	5	5	5	5
15 min	1.55	7	6	5	5	6	5	5
	1.65	6	5	5	5	5	5	5
	1.70	6	5	4	4	4	4	4
	1.75	5	4	4	4	4	4	4
20 min	1.60	6	5	5	5	5	5	5
	1.65	5	4	4	4	4	4	4
	1.70	5	4	3	3	4	4	3
	1.75	4	3	3	3	3	3	3
30 min	1.60	4	3	3	3	3	3	3
	1.65	4	3	3	3	3	3	3
	1.70	4	3	3	3	3	3	3
	1.75	4	2	2	2	2	2	2
Number of elements: 107; required voltage: 220/110 V ( $\pm 2.5\%$ ); minimum voltage: 2.005 V/e; maximum voltage: 2.100 V/e								
<i>Required extra elements in electrolyte circulation batteries: Group I</i>								
5 min	1.55	3	3	2	2	2	3	3
	1.60	2	1	1	1	1	2	2

Table 3 (continued)

Discharge time	Cut-off voltage (element)	Type of battery							
		6	6	6	6	6	6	6	6
		SB	SB	SB	SB	SB	SB	SB	SB
		25	50	72	75	100	125	150	
	1.65	1	0	1	1	0	1	1	1
	1.70	0	1	0	0	0	0	0	0
10 min	1.55	2	1	1	1	1	1	1	1
	1.60	1	0	0	0	0	1	1	1
	1.65	0	0	0	0	0	0	0	0
	1.70	0	0	0	0	0	0	0	0
15 min	1.55	0	0	0	0	0	0	0	0
	1.65	0	0	0	0	0	0	0	0
	1.70	0	0	0	0	0	0	0	0
	1.75	0	0	0	0	0	0	0	0
20 min	1.60	0	0	0	0	0	0	0	0
	1.65	0	0	0	0	0	0	0	0
	1.70	0	0	0	0	0	0	0	0
	1.75	0	0	0	0	0	0	0	0
30 min	1.60	0	0	0	0	0	0	0	0
	1.65	0	0	0	0	0	0	0	0
	1.70	0	0	0	0	0	0	0	0
	1.75	0	0	0	0	0	0	0	0

to the activity  $a_o$ ; then, the diffusion overvoltage becomes:

$$\eta_d = \frac{RT}{zF} \ln a_o \quad (11a)$$

and replacing the activity in terms of concentration:

$$\eta_d \approx \frac{RT}{zF} \ln(\gamma^\pm c_o^\pm) \approx 2 \frac{RT}{zF} \ln(\gamma^\pm c_o) \quad (11b)$$

where  $\gamma^\pm$  represents the average value of the activity coefficient of the ions, and  $c_o$  the concentration.

If concentration diminishes the activity diminishes too, and because  $a_o$  ranges from 1 to 0, the absolute value of the logarithm, thus the concentration overvoltage, increases with the reduction of concentration. Considering the linear concentration gradient within the Nernst diffusion layer, the concentration can be expressed as:

$$c_o = c^0 - C_1 \delta \frac{t}{\tau} \quad (12)$$

where  $c^0$  is the initial concentration before the discharge starts,  $t$  the elapsed time, and  $C_1$  the slope constant.

In electrolyte circulation batteries, the ratio  $t\sqrt{\tau}$  is lower [9], which added to the fact that the thickness of the diffusion layer is smaller leads the battery with electrolyte circulation to maintain the output voltage of the cell more constant than in conventional batteries during the transient period at the switching on process.

## 2. Experimental

The influence of the concentration overpotential onto the initial voltage drop in lead–acid batteries at the switching on process has been experimentally determined. Since

reaction, crystallization and polarization overpotentials can be neglected or minimized at high rate discharges, where the chemical reactions are fast, only activation and concentration play a relevant role in the initial voltage drop. Moreover, the activation overpotential has little influence compared to the concentration overpotential; therefore, in most of the tested cases it has been discarded, being the contribution of the concentration overpotential the only one accounted.

The experiments have been carried out in seven blocks of lead–acid batteries submitted to different discharge cycles. The limit discharge current rate,  $I_{\max}$ , for every battery, at which the tests have been developed, has been presented in Table 1 in function of the type of discharge (discharge time and cut-off voltage). Half of the battery block elements included an electrolyte circulation system, half were not modified. The electrolyte circulation system consists of a pump that circulates the acid from bottom to top through an outer conduct. The electrolyte circulation flow ranged from 6 l/h to 40 l/h depending on the size of the battery. This corresponds to approximately twice the volume of the electrolyte in the main cell. The batteries were discharged through a DIGATRON unit model 300, which allows discharge rates up to 300 A. The unit is self-controlled and maintains the limit discharge current,  $I_{\max}$ , constant until the battery reaches the set-up cut-off voltage. The cut-off voltage has been fixed as the point at which the discharge slope suddenly drops; their values have been experimentally determined previously to the tests. These values lower as the discharge rate increases because the discharge slope raises with the discharge rate. The battery voltage was controlled by a high precision

voltmeter (6 1/2 digits), and automatically recorded. Tests were developed in both conventional and electrolyte circulation batteries simultaneously.

The voltage drop due to overvoltage has been determined as the difference between the total voltage drop, experimentally measured, and the electrolyte resistance voltage drop [10]. This voltage drop has been obtained

from the value of the discharge current and the electrolyte resistance measured with the aid of an AC bridge.

### 3. Results and discussion

The calculated values have been presented in Table 2. Note that the voltage drop due to overvoltage increases

Table 4

Difference, in terms of percentage, for applications of groups I and II, respectively, between the energy saved by the use of electrolyte circulation in lead–acid cells and the energy used to recirculate the electrolyte

Discharge time	Cut-off voltage (element)	Type of battery						
		6 SB 25	6 SB 50	6 SB 72	6 SB 75	6 SB 100	6 SB 125	6 SB 150
Electrolyte circulation cells								
<i>Excess energy as percentage of energy used: Group I</i>								
5 min	1.55	32	30	23	20	26	24	23
	1.60	29	27	25	20	22	23	23
	1.65	28	26	21	17	21	20	21
	1.70	25	23	20	17	20	19	19
10 min	1.55	26	27	21	17	22	18	19
	1.60	25	23	22	17	20	19	20
	1.65	23	23	18	15	19	19	18
	1.70	21	20	17	14	16	16	17
15 min	1.55	22	21	17	15	18	16	16
	1.65	20	18	16	13	15	16	16
	1.70	19	17	14	11	13	13	14
	1.75	16	14	12	10	11	12	12
20 min	1.60	19	18	16	13	14	15	15
	1.65	16	14	13	11	12	12	13
	1.70	15	13	11	9	11	11	10
	1.75	12	11	10	8	9	9	9
30 min	1.60	12	11	10	8	9	9	10
	1.65	12	11	10	8	9	9	9
	1.70	11	10	9	6	8	9	9
	1.75	11	8	8	6	7	7	7
<i>Excess energy used percentage of energy used: Group II</i>								
5 min	1.55	25	22	19	15	17	18	19
	1.60	22	20	15	12	16	17	15
	1.65	19	16	14	11	13	13	14
	1.70	17	15	11	9	12	10	11
10 min	1.55	18	16	14	11	13	13	13
	1.60	17	15	11	9	12	12	11
	1.65	14	11	10	8	9	10	10
	1.70	13	11	8	6	9	9	9
15 min	1.55	13	12	10	8	9	9	10
	1.65	12	8	7	6	7	7	7
	1.70	9	8	7	5	6	7	7
	1.75	9	7	5	4	4	5	5
20 min	1.60	10	8	7	6	7	7	7
	1.65	9	7	7	5	6	6	6
	1.70	7	5	5	4	4	4	5
	1.75	6	5	3	3	4	4	4
30 min	1.60	6	5	5	4	4	4	4
	1.65	6	5	3	3	4	4	3
	1.70	5	3	3	2	3	3	3
	1.75	4	3	3	2	3	3	3

Table 5

Percentage of the overvoltage reduction by the use of electrolyte circulation in lead–acid cells

Discharge time	Cut-off voltage (element)	Type of battery						
		6 SB 25	6 SB 50	6 SB 72	6 SB 75	6 SB 100	6 SB 125	6 SB 150
Percentage of the overvoltage reduction								
Electrolyte circulation cells								
5 min	1.55	0.58	0.58	0.58	0.60	0.60	0.57	0.57
	1.60	0.64	0.64	0.66	0.65	0.64	0.62	0.62
	1.65	0.65	0.68	0.67	0.67	0.69	0.67	0.66
	1.70	0.70	0.67	0.68	0.69	0.69	0.68	0.68
10 min	1.55	0.64	0.64	0.63	0.64	0.64	0.63	0.63
	1.60	0.68	0.68	0.68	0.69	0.70	0.67	0.66
	1.65	0.69	0.71	0.69	0.70	0.71	0.69	0.69
	1.70	0.72	0.71	0.71	0.71	0.73	0.71	0.71
15 min	1.55	0.68	0.68	0.67	0.68	0.69	0.67	0.67
	1.65	0.73	0.75	0.74	0.74	0.74	0.73	0.73
	1.70	0.74	0.73	0.73	0.74	0.74	0.73	0.73
	1.75	0.76	0.76	0.76	0.76	0.77	0.75	0.75
20 min	1.60	0.72	0.71	0.70	0.70	0.72	0.70	0.70
	1.65	0.76	0.76	0.75	0.75	0.76	0.74	0.74
	1.70	0.77	0.77	0.77	0.77	0.78	0.76	0.76
	1.75	0.78	0.79	0.77	0.78	0.79	0.77	0.77
30 min	1.60	0.76	0.76	0.75	0.75	0.76	0.75	0.75
	1.65	0.78	0.78	0.77	0.77	0.78	0.76	0.76
	1.70	0.78	0.78	0.78	0.78	0.79	0.78	0.78
	1.75	0.80	0.80	0.79	0.80	0.80	0.79	0.79

with current rate. This is in good agreement with the theoretical statement which establishes the overvoltage depends on the concentration gradient.

The experimental results show that voltage drop due to overvoltage never attains the maximum voltage drop allowance;<sup>1</sup> therefore, the battery maintains, even at high rate discharges, the output voltage above the limiting value for current applications such as SLI, traction, automotive, mechanics, and small appliances. Nevertheless, many applications of the lead–acid batteries can only operate if the fluctuation around the set-up voltage is small; this is the case of telephone networks, computers, data acquisition systems, medical care control units, stabilized power sources, very precise power units, etc., systems that can not operate at voltages as low as the cut-off voltage indicated in Table 1. We, therefore, have divided these external load applications into three main groups according to the maximum fluctuation of the required voltage, say 2.5%, 5% and 10%. These voltage fluctuations correspond to stabilized power sources and very precise power units (group I), computers, data acquisition systems, and medical care control units (group II), and telephone networks (group III), respectively between the before mentioned applications. According to these fluctuations, the maxi-

imum voltage drop allowed in the cell is 0.095 V, 0.200 V, and 0.378 V/e, respectively.

The results of Table 2 show that conventional batteries fulfil the minimum voltage requirement for the applications of group III, but not for those of groups I and II. In electrolyte circulation batteries, however, the fulfilment is extended to groups II and III, and to discharges longer than 10 min for group I; this indicates the advantages of the use of the electrolyte circulation. A comparative study shows that the minimum number of elements in the battery block necessary to meet the external load voltage requirement can be reduced if the electrolyte circulation is used in lead–acid batteries. Data shown in Table 3 indicate the minimum number of extra elements required to meet the external load demand; we can appreciate that conventional batteries need a minimum number of 12 and 6 elements, on average, for applications of groups I and II, respectively, while electrolyte circulation batteries barely require 1 or 2 only for the highest rate discharge in case of group I. The experimental results of Table 2 indicate there is no need of extra elements in the battery block for applications of group III with conventional batteries, and for applications of groups II and III with electrolyte circulation batteries.

The difference between data from Table 3a and b gives the absolute reduction in the number of elements of the battery block required to meet the external load demand. This reduction not only compensates for the initial investment, cost maintenance of the device, and energy used by

<sup>1</sup> The voltage drop allowance is the difference between the initial output voltage of the cell and the cut-off voltage at which the battery collapses.



the electrolyte circulation device, 5 W/e for the biggest battery (6SB150), and only 0.8 W/e for the smallest (6SB25), but also saves energy and money respect to the conventional system because of the higher output voltage and the lower number of elements in the battery block. The excess of energy, energy saved minus energy used by the circulation device, in terms of percentage, is presented in Table 4. Note that the difference increases as the battery size decreases for constant discharge current, and as the current rate decreases for the same type of discharge (same cut-off voltage). The difference is also higher for the external load group which operates within the lowest voltage fluctuation. This result is in good agreement with the fact that the systems operating within low voltage fluctuation are more sensitive than any other to sudden changes in the output cell voltage, as it happens at the switching on process; therefore, they require more additional elements to compensate for these changes. The electrolyte circulation cushions the sudden drop in the output voltage; the cushioning effect increases with the difference between the voltage drop and the voltage fluctuation allowed by the external load. As the systems operating within low voltage fluctuation have the largest difference, they get the best results, say the biggest excess of energy. This makes these systems to be the best candidates for the application of the electrolyte circulation to lead–acid cells in order to save money and energy.

It can also be noticed that the percentage values are always positive, which indicates the electrolyte circulation system saves more energy than it uses to recirculate the electrolyte.

Table 5 shows the percentage of the overvoltage drop reduction in electrolyte circulation cells. The reduction of the initial voltage drop because of this effect can be evaluated in 68%, on average, a significant improvement in the battery performance which encourages the use of the circulation system. It can be noticed that the percentage reduction of the overvoltage, say initial voltage drop, due to electrolyte circulation is more effective at low rate discharges, reducing its influence as the current rate increases. This is a consequence of the mass transport to the interface that improves the performance of the cell.

#### 4. Conclusions

The overvoltage causes an initial voltage drop in lead–acid batteries at the switching on process that may cause the breakdown of the battery when they are used to supply current to external load which operates within low fluctuation of the set-up voltage. The problem affects to data

acquisition systems, computers, very precise power units, etc., systems that do not accept voltage fluctuations higher than 5%. The use of electrolyte circulation inside the lead–acid cell improves the behavior of the cell at the switching on process, reducing the initial voltage drop to values under the limit. The main consequence of the reduction of the initial voltage drop is the no need of extra elements to compensate for the voltage drop; only in few cases, at very high rate discharges, for external load applications within very low voltage fluctuation ( $\pm 2.5\%$ ), the use of extra elements, only 2%, has been necessary. The influence of the electrolyte circulation on the performance of the cell increases as the current rate decreases, reaching a maximum reduction of the initial voltage drop due to overvoltage of 79% at the lowest rate discharge (30 min). Besides, the energy saved by the use of the electrolyte circulation compensates for the energy that must be used to recirculate the electrolyte; only at low rate discharges in external load applications within voltage fluctuations of 5%, the small difference between the energy saved and the energy used may do to doubt the user of the possible benefits of the electrolyte circulation.

The cost of a commercial electrolyte circulation system must be also taken into consideration. The additional elements required to configure the proposed system are all commercially available, and they only require minor changes to be adapted to this especial purpose. It is clear that the cost of the prototype used for the tests cannot be considered as a reference, so a commercial set would cost much less. However, the first calculations indicate that a commercial electrolyte circulation system would cost only a 5% more than the conventional set.

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