

# Water Loss Predictive Tests in Flooded Lead-Acid Batteries

Mattia Parnigotto,<sup>[a]</sup> Marco Mazzucato,<sup>[a]</sup> Daniele Fabris,<sup>[b]</sup> Lorenzo Dainese,<sup>[a]</sup> Silvia Cazzanti,<sup>[b]</sup> Nicola Bortolamei,<sup>[b]</sup> and Christian Durante<sup>\*[a]</sup>

Different aging processes rates of flooded lead-acid batteries (FLAB) depend strongly on the operational condition, yet the difficult to predict presence of certain additives or contaminants could prompt or anticipate the aging. Linear sweep current (LSC) and gas test (GT) characterizations were reported here to fasten the water consumption evaluation. The two methods were proposed to evaluate the water consumption effect at 60 °C, on a custom cell with a (1 + 2-) plate configuration. The predictive ability of the proposed tests was verified on

## Introduction

Despite major technological developments in storage devices, lead-acid technology represents a large share of the battery market, with moderate constant growth forecasted in the next decades both for the Automotive and Reserve Power markets. The association of European Automotive and Industrial Battery Manufacturers (EUROBAT) declares that "The EU lead-based battery industry will maintain a strong position and will be able to meet projected growth, but ongoing investments in R&D and production enhancement are required".<sup>[1]</sup> Such considerations have brought industry and university research facilities to study extensively one of the main aging problems for the simplest and most competitive lead-acid technology: the water consumption (loss) effect on the flooded lead-acid batteries (FLAB).

Water loss and corrosion of the positive plate grid represent two of the main aging processes in FLAB and are closely interdependent.<sup>[2,3]</sup> To date, the most widely used industrial method to determine the water consumption in generic LAB is the weight loss test. However, this method doesn't allow to understand the different origins of water loss (for example, hydrogen, oxygen evolution and water vapor itself<sup>[4]</sup>).

The water consumption characterizations of the LAB reported in literature use either full size cells, where a series of

[a]	Dr. M. Parnigotto, Dr. M. Mazzucato, L. Dainese, Prof. C. Durante
	University of Dadeya
	Via Marrada, 1. 25121 Dadava Italia
	VIA MATZOIO, 1, 35131 PAAOVA, Italy
	E-mail: christian.aurante@unipa.it
[b]	Dr. D. Fabris, Dr. S. Cazzanti, Dr. N. Bortolamei
	FIAMM Energy Technology S.P.A.
	Viale Europa 75, 36075, Montecchio Maggiore (VI), Italy

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© 2022 The Authors. ChemElectroChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. 9 batches of plates for FLAB preliminary tested with the European standard CEI EN 50342-1:2019-11 method. LSC and GT tests showed the capability to identify plate batches with anomalous behaviour for the water consumption and good agreement with the European standard CEI EN 50342-1:2019-11 method. Furthermore, it was found that Tafel parameters determined from LSC and GT tests correlated well with the concentration of Te.

batteries group of circa 2 V are collected in series assembling, or alternately a reduced cell comprising different combinations of positive and negative plates (e.g., 1 + and 2 -, 1 - and 2 +, etc.) in an appropriate customized cage. The determination of water consumption in full size configuration is mainly detected by the weight loss and gas analysis tests.<sup>[3,5–9]</sup> In the latter case, the tests on the outing gas, obtained during the working condition, are carried out exploiting the variation in pressure<sup>[10,11]</sup> or evaluating the composition and volume of the vented gas with a gas chromatograph.<sup>[7,8,12-15]</sup> Such tests, carried out on full size cell, are developed in constant current or constant voltage mode for at least one day or more (weeks/ months), and in most cases the applied or collected potential is limited to the cell potential without discriminate the positive potential from the negative potential in the overcharging period. On the other hand, the water consumption effect in reduced size configuration is mainly detected through Cyclic Voltammetry (CV) or Linear Sweep Voltammetry (LSV) using a third electrode (reference), in order to investigate the reactions governing the water consumption of the single plate (either negative or positive) or to determine the inhibition and the retarding behaviour toward the H<sub>2</sub>/O<sub>2</sub> evolution caused by additives/contaminants in electrolyte and plate compositions.<sup>[16-21]</sup> Non-conventional designs, namely reduced size cell, are used also for the gas guantification during floating water consumption tests, where the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER) are detected by the volume variation and the monitoring of vented gas rate.<sup>[19,22-29]</sup> Unfortunately, LSV, CV and GT characterization are often limited to electrode with small surface, far even from the dimension of a single plate of a lead acid battery. Moreover, when massive plate are used in reduced cell, the time required for the gas developed quantification is very long, that means that it takes at least 10 hours.<sup>[24]</sup> To the best of our knowledge, no work in the literature has yet combined the information deducible from voltametric techniques, with the determination of gassing rates in floating overcharging tests. Furthermore, effective, and fast methods to predict the water consumption behaviour have not yet been proposed. Thus, this work provides to join the observation of a linear sweep with the information collected during fast gas tests at different applied current steps in a thermostatic bath at 60 °C, limiting the evaluation test to a single day for sample.

## **Experimental Section**

#### Chemicals, materials and cell design

All the electrochemical experiments were carried out 5 M sulfuric acid provided from FIAMM Energy Technology (FET), all the 9 batches of plate were as well provided by FET. A reduced cell configuration (with a limited number of positive and negative plates) was preferred over a full-size cell because of a greater flexibility in terms of space or employable components and versatility for the insertion of a reference electrode, a temperature probe and an inlet/outlet gas line for the gas sampling. Moreover, working with a low number of plates allows to analyse a consistent but overall limited surface area and therefore, from an electrochemical point of view, to collect more accurate, reliable, and reproducible information. An adaptable design becomes fundamental to take advantage of different water loss evaluation techniques, namely, to compare electrochemical information with respect to the volume of gas evolved in order to find a guick diagnostic method to distinguish excessive water consumption behaviour. Being aware of this, it was decided to use a reduced electrochemical cell, able to host from 2 (configuration 1 + and 1 -) to 12 plates configuration 6+ and 6-) alternately arranged and containing three plates 12.2 cm height and 14.3 cm width (showed in Figure 1), in a (1 + 2) configuration. The choice for cell cage material fell on polyvinyl chloride (PVC) and specifically a cell with 1.5 cm thick walls was made. As suggested by Berndt et al.[28] hydrogen loss, due to the high permeation through polymer can be the biggest source of systematic errors, which is why great attention has been given to welds and cell sealing. The choice of PVC was therefore strengthened considering that the diffusion of oxygen and hydrogen through the PVC is lower than materials such as polymethyl methacrylate, (PMMA), polypropylene (PP) and polyethylene (PE),<sup>[30,31]</sup> along being sufficiently chemically inert in

presence of sulphuric acid. The cell also has two quartz windows which allow the inside inspection of the cell in operative conditions.

The pictures of the homemade FLAB cell are shown in Figure 1. The cell (Figure 1b and c) allows to host from 3 (set-up 1+2-) to 12 plates to (set-up 6+6-) considering also that every positive plate is covered by a PE bag to avoid short-circuit during the test (namely to prevent contact between positive and negative plates). The top of the cell (Figure 1d) is equipped with: 2 gas valves, which allow the inlet and outlet of the gas carrier (N2), a glass Luggin capillary to limit the distance between the reference electrode and the plates (limiting the ohmic drop), and a small tube close at one end to lodge the thermocouple for temperature monitoring. All the elements are sealed on the cover to avoid leak of gas during the analysis. As internal connections two long screws (Figure 1b) made from lead linchpin are inserted through two drilled holes in one of the front faces of the cell, each plate is fixed by two lead bolts made from the same linchpin alloy. Such design allows to study the entire system using only material not susceptible to corrosion in strong acidic condition (like steel or copper that could also contaminate the electrolyte and the plate if corroded), in an experimental set-up that simulates as closely as possible the conditions of a real FLAB.

The cell is gas-proof and the tightness near the screw insertion is guaranteed by two O-rings for each screw. The outside of the lead screw is drilled to allow the insertion of a common pin for connecting the potentiostat cables. This cell layout allows an electrochemical monitoring of the system in a three-electrode configuration with a Working Electrode (WE), a Counter Electrode (CE), and a Reference Electrode (RE). The use of a RE  $(Hg/Hg_2SO_4/$ SO4 MSE SCHOTT® Instruments) allows to impose the potential of the plate of interest and, by changing the external cabling, it is possible to reverse the polarity of the cell moving the WE from the positive plate to the negative plate while using always the same RE. The insertion of a reference electrode allows to split the negative and the positive overvoltage contributes when the cell is in overcharging phase. Such condition permits to understand if the higher water consumption is due to the positive or the negative plate or both.



Figure 1. Cell design: front and lateral view (a, b), front view and view from above on the cell inside (c, d), screws and bolts obtained from lead rod (e), plate and PE bag (f).

## Plate formation

The plates are preliminary formed by a specific galvanostatic formation process: 8 steps of charge in galvanostatic mode; one step of small discharge; a phase where the acid of formation is substituted with a new fresh acid; a bubbling step to mixing the new acid with the acid remained into the pore of the plate and finally a rest phase of 2 days. Water consumption tests are carried out two days after the formation allowing the cell potential to equilibrate. The electrolyte is an aqueous solution of sulphuric acid, 1.290 g mL<sup>-1</sup> (checked by a densimeter, Anton Paar; DMA35) as specific gravity.

### Water consumption test

For the standard water consumption test proposed by the EN 50342-1:2019-11, each sample is assembled to constitute a 12 V FLAB. After being charged, the battery shall be cleaned, dried, and weighed ( $W_i$ ), in grams. Successively the battery is placed in water bath and maintained at a temperature of 60 °C and charged at 14.40 V without adding water for 21 days. Immediately after this overcharge period, the battery is cleaned, dried and weight under the same conditions as initial ( $W_e$ ). The final WL is calculated as (g/ Ah) [Eq. (1)]. Where  $C_e^{max}$  is the maximum effective capacity.

$$WL = \frac{W_i - W_e}{C_e^{max}} \tag{1}$$

#### **Electrochemical test**

Once the cell is formed, two types of electrochemical tests were carried out at 25 and 60 °C in a thermostat bath (Julabo mod. Corio CD): LSC were carried out with a potentiostat/galvanostat (Amel 7060) from 0 to 600 mA with a scan rate of 3 mA s<sup>-1</sup> to verify the potential response when the WE is the positive plate or, from 0 to -600 mA with the same scan rate to verify the potential response, when the WE is the negative plate. Every scan was collected at both 25 and 60 °C to evaluate the effect of temperature on the predictive fast test for the water consumption characterization.

From such type of test is possible to extrapolate a set of parameters useful for the predictive evaluation of the water consumption behaviour. Indeed, one way to relate the applied current to the collected voltage is plotting the voltage as function of the logarithm of the applied current. This correlation is the well-known Tafel plot and could be expressed with the homonymous Equation (2), (which finds its theoretical basis in the Butler-Volmer equation<sup>(32)</sup>).

$$\eta = a + b \ln |i| \tag{2}$$

It correlates the logarithm of the current with the overvoltage ( $\eta$ ) in a linear dependence [Eq. (3)], where:

$$b = \frac{\mathsf{R}T}{\alpha n\mathsf{F}} \tag{3}$$

is the slope of the linear Tafel region, which describes the mechanism of the reaction in relation to the electron transfer coefficient  $\alpha$ , R is the gas constant, T is the temperature, n is the number of exchanged electrons and F is the Faraday constant. The intercept a is described by:

$$a = \left(\frac{\mathsf{R}T}{\alpha n\mathsf{F}}\right) ln |i_0| \tag{4}$$

which, in addition to the parameters described above [Eq. (4)], also contains the exchange current  $i_0$ , which is defined as:

$$i_0 = nFAC_0^* k^0 e^{-\frac{anFAE}{RT}}$$
(5)

Where A is the electrode area and  $k^0$  is the standard rate constant, all the other terms assuming the common meaning [Eq. (5)]. The linear Tafel region falls at overpotential far from the open circuit potential and only if the electron transfer is sufficiently slower than the mass transfer.

Electrolysis test from 0 to 600 mA with steps of 100 mA were also carried out. The first step of 100 mA is applied for 50 minutes (time required to achieve potential stabilization), the following steps (from 200 to 600 mA) are applied only for 30 minutes because the potential stabilization is easier to obtain. During the application of the current a controlled flow of  $N_2$  of 80 mL min<sup>-1</sup> enters the cell to allow the collection of 10 mL of gas sample from the outlet gas valve with the aid of a sampling system (a copper tube, connected to the outlet valve, equipped with a T-adapter with a rubber septum at one end from which the gas is retrieved) and a syringe. For every step a sample of gas is collected concurrently with the potential stabilization and then injected into the loop of a GCsystem (Agilent 7820, TCD detector, Ar as carrier gas) equipped with a first column HP-PlotQ, that allows the separation of CO<sub>2</sub> and water from the other gases, and a secondary molecular sieve column (Molesieve 5 A), used for the separation of O<sub>2</sub>, H<sub>2</sub>, CO and N<sub>2</sub>. The electrode potential of the positive plate is measured versus the MSE RE and at the same time the cell potential in monitored by using an auxiliary multimeter (Keithley 197A) connected between the two poles. Therefore, the potential of the negative plate can be determined being the difference between the positive pole potential and the cell potential. With the employed set-up, the potentials of the two pole and of the full cell are recorded as a function of the applied current. Likewise to the LSC test, also the gas tests are carried out at 25 and 60°C in order to verify the effect of temperature.

The moles of  $H_2$  and  $O_2$  gases obtained from the GAS-TCD analysis are associated to the current for the HER and OER processes as function of the overvoltage. Equations (6) and (7) which link the evolved gases to the theorical faradaic currents flowing in the negative and positive plates are:

$$i_{H_2} = 2F\hat{n}_{H_2}$$
 (6)

$$i_{O_2} = 4F\hat{n}_{O_2}$$
 (7)

Where 2 and 4 are the electrons exchanged at the negative and positive plate, respectively, and  $\hat{n}_{H_2}$  and  $\hat{n}_{O_2}$  are the moles production rates (mol s<sup>-1</sup>) for the negative and positive plate, respectively. The permeation of hydrogen gas through container walls and sealings was evaluated by calibrating the hydrogen loss. The oxygen recombination current and the corrosion current were then corrected by considering the effect of H<sub>2</sub> loss (see S1 and S2 for more details). In both the tests, the potential is compensated considering the resistance values obtained by impedance tests performed on both the negative and positive plates with a potentiostat (Ametek PARSTAT 3000 A-DX). Impedance tests are executed from 0.1 Hz to 10 MHz at the Open Circuit Potential (OCP) with 5 mV (RMS) of amplitude, 10 points per decade. In all the tests,

the cell resistance did not exceed 60 m $\Omega,$  all the results are showed in Table S1.

#### ICP – MS

Metal contaminations into the negative and positive active mass are relieved through ICP – MS characterization. Te concentration is measured in all the considered batches, removing the active mass from the centre of the plate to the angle, in diagonal direction. approximately 0.2 mg of material is accurately weighed and solubilized in 5 ml of HNO<sub>3</sub>, 20 ml of distilled water and 30  $\mu$ l of H<sub>2</sub>O<sub>2</sub>. The suspension is successively heated at 100° C up to the complete solubilization of the lead active mass. The prepared samples are analysed through as AGILENT ICP-OES 5800, with the torch in axial mode. The measurement conditions provide for a read time of 5 s, a power amplification of 1.20 kW and a stabilization time of 15 s, 0.7 l/min as nebulizer flow, 12 l/min as plasma flow and 1 l/min as aux flow.

## **Results and Discussion**

#### Weight loss result

The values obtained by the weight loss tests according to the CEI EN 50342-1:2019-11 are showed in Table 1, where the weight loss of every sample is compared with the contamination of Te found in the positive and negative plate before the immersion in the acid formation cell (both the weight loss and the contamination are normalized to the lowest value found in the nine studied samples). The plates showing the higher water consumption are 3, 4 and 9, followed by 5, while all the others maintain a water loss behaviour within the normal range. The contaminant element most affecting the WL appears to be Te. In fact, water consumption was observed to increase along with the increasing of Te content in the positive or negative active mass.<sup>[33]</sup> Such type of test, as mentioned before, does not allow to discriminate whether the major roles for water consumption comes from the negative or the positive plate, or both and how the contaminants influence such phenomena.

**Table 1.** Water consumption test (CEI EN 50342-1:2019-11) results for all the investigated plates. Tellerium contents are determined by ICP-MS for both positive and negative plates before the formation process. For trade secret protection reasons, all the values are not reported in absolute value but are normalised to the lowest value found among the nine batches. The reported values are necessarily to be considered adimensional.

Batch	WL	Te <sub>pos</sub>	Te <sub>neg</sub>
1	1.08±0.1	2.60	2.08
2	$1.60 \pm 0.4$	1.11	1.00
3	$3.85\pm0.4$	6.42	6.28
4	$3.55\pm0.4$	3.75	5.72
5	$1.73\pm0.1$	1.53	3.08
6	$1.00 \pm 0.02$	1.05	1.58
7	$1.08 \pm 0.04$	1.00	1.89
8	$1.13 \pm 0.03$	1.81	2.53
9	$2.08 \pm 0.1$	2.44	4.39

#### Linear sweep current results

LSC results brings additional detailed information. Comparing the LSC collected at 25°C and at 60°C of the sample 1 (Figure 2), it is possible to notice that all the overcharging reactions occur at a lower overvoltage when the temperature increases to 60 °C, according to an Arrhenius behaviour already verified by Laman et al.<sup>[12]</sup> The LSC at the negative plate (Figure 2a) identifies two distinct regions: a first one (from 0 to -300 mV) which is assigned to the reduction of lead sulphate to lead (charging reaction). The second region (from -300 mV) is inherent to the hydrogen evolution. On the other hand, the positive plate (Figure 2b) shows a substantial monotonic increase without evident changes in slope of the current, which corresponds to the sum of different mechanisms, i.e. the oxidation of PbSO<sub>4</sub> to PbO<sub>2</sub>, the oxygen evolution reaction (OER), and the grid corrosion reaction. The corresponding Tafel plots in Figure 2c and d, show a linear region in the range of -0.5 and -0.22 V and between -0.35 and -0.22 V for the negative and positive plate, respectively. The corresponding current values are approximately between -316 and -600 mA for the negative plate and 450 to 600 mA for the positive one.

The comparison of the LSC for the negative plates of all the 9 samples carried out at 25°C (Figure S3a) is indicative of a slightly higher activity towards the HER of samples 3 and 4, while sample 9 (take as an example of medium water consumption) falls among the other less catalytic samples. Conversely on the positive plate at 25 °C (Figure S3b), sample 3 and 4 clearly stands out while sample 9 stands among the samples with low water consumption. When the temperature is set to 60°C, the aging effect increases, and the water consumption behaviour becomes more noticeable. Figure 3 reports the LSC and the relative Tafel plots at 60°C for the positive and negative plate of batch 3 and 4 (high WL), 8 (low WL) and 9 (medium WL). In the Tafel plot recorded at 60 °C for the negative plate the higher kinetic for the HER for the sample 3, 4 and 9 results accentuated (Figure S3c). A similar effect is found on positive plates 3 and 4 at 60 °C (Figure S3d), whereas sample 9 remains in the average of the low WL plates. Such discrepancy suggests that the higher water loss observed on the samples 3 and 4, which have a WL almost four times higher than the lowest value found, is an additive effect of both the negative and the positive plate. Instead, the intermediate water consumption of sample 9 (two times than the lowest value found) is mainly due to the negative plate. Looking now at Figure 3e some more quantitative evaluation can be made, i.e. a confidence range of values may be given within which tests from LSC are indicative of unacceptable or acceptable WL. In particular, among the different parameters obtainable from the Tafel plot, the current exchange determined from LSC recorded at 60°C appears to be a good indicator matching the results obtained from the water loss analysis determined according to the CEI EN 50342-1:2019-11 test (Table 2). In particular I<sub>0</sub> below 4 mA ( $j_0 \approx 11.5 \mu$ A/cm<sup>2</sup>, considering that for negative plates only the surfaces facing the positive plate are active) are indicative of acceptable water loss, whereas above this value the batches are to be considered out of the acceptable range Figure 3e.



Figure 2. LSC curve for the plates of batch 1 negative (a) and positive (b) plates at 25 °C (black line) and 60 °C (red line). Corresponding Tafel plot for negative (c) and positive (d) plates.

Table 2. Tafel parameter from LSC test (left) and from gas test (right) collected at 60 °C for all the analyzed samples.												
Sample	Linear Sweep Negative plate <i>a</i> [mV]	Current parame e b [MV]	eters <i>I<sub>o</sub></i> [mV]	Positive plat <i>a</i> [mV]	te b [mV]	<i>l₀</i> [mV]	Gas test par Negative pl a [mV]	rameters ate <i>b</i> [mV]	<i>l<sub>o</sub></i> [mV]	Positive p <i>a</i> [mV]	late b [mV]	<i>l₀</i> [mV]
1 2 3 4 5 6 7 8 9	$\begin{array}{c} -410.5\pm0.1\\ -415.8\pm0.2\\ -388.3\pm0.2\\ -388.1\pm0.2\\ -409.1\pm0.2\\ -407.0\pm0.2\\ -414.2\pm0.2\\ -421.6\pm0.2\\ -404.4\pm0.2\end{array}$	$\begin{array}{c} -169.4\pm0.4\\ -171.0\pm0.4\\ -172.7\pm0.5\\ -163.6\pm0.5\\ -164.6\pm0.5\\ -165.2\pm0.4\\ -161.4\pm0.5\\ -181.3\pm0.5\\ -155.9\pm0.5\end{array}$	$\begin{array}{c} 3.77 \pm 0.6 \\ 2.15 \pm 0.5 \\ 5.36 \pm 0.8 \\ 5.66 \pm 0.1 \\ 3.15 \pm 0.07 \\ 3.36 \pm 0.06 \\ 3.11 \pm 0.06 \\ 2.44 \pm 0.06 \\ 5.88 \pm 0.1 \end{array}$	$\begin{array}{c} 65.4 \pm 0.9 \\ 95.8 \pm 0.4 \\ 267.1 \pm 0.4 \\ 163.5 \pm 0.5 \\ 91.4 \pm 0.4 \\ 91.8 \pm 0.6 \\ 101.4 \pm 0.4 \\ 86.2 \pm 0.4 \\ 92.6 \pm 0.4 \end{array}$	$\begin{array}{c} 121\pm 3\\ 183\pm 1\\ 375\pm 1\\ 285\pm 2\\ 180\pm 1\\ 179\pm 2\\ 197\pm 2\\ 172\pm 2\\ 172\pm 2\\ 178\pm 1\end{array}$	$\begin{array}{c} 288 \pm 4 \\ 299 \pm 1 \\ 194 \pm 1 \\ 267 \pm 1 \\ 311 \pm 1 \\ 307 \pm 2 \\ 306 \pm 1 \\ 315 \pm 1 \\ 302 \pm 1 \end{array}$	$\begin{array}{c} -460\pm1\\ -453\pm2\\ -470\pm8\\ -443\pm10\\ -451\pm2\\ -443\pm1\\ -448\pm2\\ -449\pm1\\ -455\pm2 \end{array}$	$\begin{array}{c} -178\pm 2 \\ -145\pm 3 \\ -259\pm 20 \\ -211\pm 24 \\ -201\pm 4 \\ -157\pm 2 \\ -148\pm 3 \\ -174\pm 1 \\ -200\pm 6 \end{array}$	$\begin{array}{c} 2.55 \pm 0.2 \\ 0.74 \pm 0.1 \\ 15.3 \pm 6.1 \\ 8 \pm 5 \\ 5.8 \pm 0.8 \\ 1.5 \pm 0.1 \\ 0.9 \pm 0.1 \\ 2.7 \pm 0.1 \\ 5.3 \pm 1 \end{array}$	$\begin{array}{c} 151\pm 4\\ 153\pm 2\\ 424\pm 20\\ 204\pm 3\\ 161\pm 3\\ 158\pm 2\\ 162\pm 3\\ 158\pm 8\\ 155\pm 2\\ \end{array}$	$97 \pm 4$ $96 \pm 2$ $239 \pm 20$ $116 \pm 4$ $100 \pm 3$ $92 \pm 3$ $97 \pm 3$ $99 \pm 9$ $99 \pm 3$	$\begin{array}{c} 28 \pm 1 \\ 26 \pm 1 \\ 17 \pm 3 \\ 17 \pm 1 \\ 25 \pm 1 \\ 19 \pm 1 \\ 21 \pm 1 \\ 26 \pm 4 \\ 27 \pm 1 \end{array}$

Given that the tests carried out at 60 °C allow to accentuate the phenomenon of water consumption and appears to be the most indicative for determining parameters suitable for a fast water consumption evaluation, it was decided to restrict the data analysis of the gas tests only at this temperature.

## Electrolysis tests

The gas tests allow to build current-potential plot as the one shown in Figure 4a, where the applied current is reported with

respect to the resulting overvoltage (the cell potential is specified in the middle of the 2 profile). Each points in Figure 4a corresponds to a volume of gas sampled from the battery at a precise applied current and then injected into the GC-system (calibration curve for  $H_2$ ,  $O_2$  and  $N_2$  are showed in Figure S5), where hydrogen and oxygen produced from the electrolyte water electrolysis are separated in column and quantified by a TCD detector. An example of chromatogram is reported in Figure S4. An example of  $H_2$  and  $O_2$  evolution rate (batch 1) is displayed in Figure 4b, where the hydrogen and the oxygen evolution rates are reported as function of the negative and

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Figure 3. LSC and relative Tafel plot at 60 °C for the representative batches with high (3 and 4), medium (9), and lower (8) water consumption. a, c) negative and positive (b, d) plate. Inserts in figure (a) and report the entire curve profile (c). e) current exchange determined by LSC analysis on negative plate versus water loss as determined by weight loss tests. f) Overpotential determined by gas tests versus normalized water loss (where all the WL values are normalized to the WL of batch 6 which presents the lowest WL result) as determined by weight loss tests.

positive plate overvoltage, respectively. It is obvious how the content of the two gases and, as a consequence of the water consumption, increases at the increase on the overvoltage. As reported later, these set of data along with the LSC will allow to discriminate the plate behaving according to CEI EN 50342-1:2019-11 method with respect to those out of the bunch. The gas analysis data on water consumption tests allow also to discriminate the contribution of the different electrode processes such as the lead grid corrosion (on the positive plate) or the oxygen recombination reaction (on the negative plate) to

the total flowing current.<sup>[28,34]</sup> Such model assumes that in the overcharging phase, the charge contribution to the total applied current ( $I_{cha}^-$  and  $I_{cha}^+$ ) can be neglected for both positive and negative plates. The net current at the negative plate is composed of three contributions

$$I_{tot}^{-} = I_{cha}^{-} + I_{H_2}^{-} + I_{rec}^{-}$$
(8)

Where, besides  $(I_{cha}^{-})$ , the other two contributions  $I_{H_2}^{-}$  and  $I_{rec}^{-}$ , are the hydrogen evolution current and the recombination



**Figure 4.** a) Applied current as function of the overvoltage collected in gas test at 60 °C for sample 1. b)  $H_2$  and  $O_2$  evolution rate for respectively the negative (light blue) and the positive (red) as function of the overvoltage collected for sample 1 at 60 °C, the error associated to each point is determined from the error propagation. c) Current rationalization on the negative plate and on the positive plate for the sample 1 at 60 °C (d).

current, respectively [Eq. (8)]. Symmetrically, at the positive plate

$$I_{tot}^{+} = I_{cha}^{+} + I_{O_{2tot}}^{+} + I_{cor}^{+}$$
(9)

the  $I_{cor}^+$  is the current contribution due to the corrosion of the lead grid, while  $I_{O_{2tot}}^+$  is a comprehensive value for the oxygen evolution current [Eq. (9)], which is in turn composed of two terms due to the O<sub>2</sub> leaving the cell ( $I_{O_{2out}}^+$ ) and the one that recombine on the negative plate [Eq. (10)]:

$$I_{O_{2tot}}^{+} = I_{O_{2out}}^{+} + I_{rec}^{-}.$$
 (10)

By considering negligible the  $I_{cha}^{-}$  contribution in Equation (9) it is possible to explicit the oxygen recombination current contribution on the negative plate as:

$$I_{rec}^{-} = -I_{H_2}^{-}$$
(11)

Then, the combination of Eq. (10) and (11) affords the corrosion current on the positive plate

$$I_{cor}^{+} = I_{tot}^{+} - I_{O_{2tot}}^{+} = I_{tot}^{+} - \left(I_{O_{2out}}^{+} + I_{rec}^{-}\right)$$
(12)

The current contributions at the negative plate are showed in Figure 4c, where the applied current, the HER current and the recombination current, are compared as function of the negative overvoltage. It is worth to mention that the recombination current contribution for all samples is on the average 12% to the total current. A small recombination contribution in FLAB batteries is indeed expected, in fact in this type of technology the oxygen diffusion in solution is slow and limited by the absence of electrolyte-free channels as is the case of AGM technology. On the positive plate, the contribution of oxygen recombination to the negative plate can be added to the OER current detected through the gas chromatograph, determining the total OER current (Figure 4d). The remaining positive current is associated at the corrosion current, which at 60 °C has a bell-shaped pattern. Such trend differs from the one measured at 25 °C (Figure S8b and d), where the corrosion currents maintain an almost linear trend as the applied current and thus the positive overvoltage increases. This behaviour is not influenced by a different recombination current at the negative plate, which remains similar despite the different temperature (Figure S8a and c). For positive plates with higher water consumption, the gas tests suggest that at 60°C there is a greater tendency to evolve oxygen than to corrode the internal grid, and therefore a higher overcharging potential is required to distribute the same overcharging current. This observation allows to anticipate that metal contaminants have a great influence on water consumptions effect: samples **3** and **4** have been shown to have a higher concentration of Te in the positive plate before formation, and Guo et al.<sup>[33]</sup> demonstrate that Te can suppress the growth of PbO<sub>2</sub> on the lead grid and accelerates the oxygen evolution reaction, in line with the assumption of gas rationalization results.

It is interesting to observe that the results from the gas tests match those of the LSC determined in the same condition. In fact, according to both the LSC and the gas tests the samples 3, 4, 9 are those showing higher water consumption. Looking at the negative plate response for the gas test at 60°C it is possible to identify the samples with higher water consumption (grey circled points in Figure 5). The samples 3, 4, 9 have a lower overvoltage to supply the required current of 200 mA and are those with the higher water consumption. The water consumption and overpotential for HER in 3, 4, 9 matches well also with the water consumption measured in tests carried out using the CEI EN 50342-1:2019-11 method (Figure 3f). Indeed, overpotentials more negative than 250-300 mV vs. RHE are indicative of lots with lower water losses, whereas more positive values than this are correlated to the sample with higher water losses (Figure 3f). On the other hand, at the positive plate, only samples 3 and 4 need more voltage to guarantee the applied current, in line with the LSC made on the positive plate. For sake of comparison the results from gas analysis at 60 °C for all the nine samples are resumed in Figure S6 (Figure S7 at 25  $^{\circ}\text{C}$ ).

Tafel parameters for HER and OER were extrapolated from reconstructed  $\eta$  vs.  $\log |i|$  positive and negative branch resulting from the gas test profiles (Table 2). Unfortunately, the low number of points detected does not guarantee optimal statistics and the exchange current values obtained are indicative but not effective in identifying a diagnostic parameter. However, these tests remain qualitatively useful as a comparison with the parameters obtained from LSC. It is therefore appropriate to emphasize that the LSC and GT tests give results that qualitatively coincide with the results of the CEI EN 50342-1:2019-11 method and therefore make it possible to identify batches with the highest water consumption. The



**Figure 5.** Gas test outputs for batch 4 taken as representative one and comparison of positive and negative plate at 60°, HER currents when 200 mA are applied are cycled in a grey dashed line oval.

kinetic parameters that can be obtained from the Tafel plots are only indicative in a qualitative sense, while in order to have a greater quantitative solidity, it would be necessary to collect a greater number of data, which would however increase the time for the evaluation of the materials in the face of a need for a quick screening for the identification of suspect lots on which to carry out more in-depth investigations.

#### Correlation with Te contaminant

The next step was to verify whether there was any correlation between the Tafel parameters (intercept, slope, and the exchange current) determined from the LSC and GT at 60 °C for the water consumption and the metal concentrations of other element than Pb present even in ppm in the positive and negative active masses. Among other metal contaminants, Te, proves to be the element that most strongly influence the kinetics of water consumption. Figure 6 reports the correlations between the intercept, the slope, and the exchange current obtained from the LSC on both negative and positive plate recorded at 60 °C versus the concentration of Te. It is interesting to observe how all the correlation are indicative of a strong influence of Te on the water consumption kinetics. Looking at the negative plate (Figure 6a-c), while the Tafel slope does not change and remains around 170 mV/dec (Figure 6b), the absolute value of intercept decreases and consequently the exchange current increases as the tellurium concentration increases (Figure 6a and c). These results are indicative of a boosted HER catalytic activity in active masses containing increasing amount of Te, while remaining unchanged the HER mechanism. Similarly, the overpotentials collected on the negative plate in the gas tests at 60 °C when applying a current of 200 mA well correlate with the Te concentration (Figure 7a and c). On the other hand, in the positive plate (Figure 6d-e), both the intercept and the slope growth as the concentration of Te increases, and the final effect leads to a decrement in the exchange current.

These results clearly stem the validity of both LSC and gas tests methods or the combination of the two in foreseen the water consumption behaviour of negative and positive plates as a function of the metal content impurities. In fact, it clearly identifies the effect of contaminants in both the negative and positive plates, making it possible to understand whether excessive water consumption is due to contamination of the sole negative or positive plate only, avoiding the time consuming CEI EN 50342-1:2019-11 method.

## Conclusions

In this paper, 9 different batches of both positive and negative plates coming from flooded lead-acid batteries (FLAB) production line were tested for verifying whether linear sweep potentiometry and gas analysis of H<sub>2</sub> and O<sub>2</sub> evolved during the overcharge of a reduce (1 + , 2 -) flooded lead acid battery could be used as indicative and fast screening test for the evaluation



Figure 6. Correlations between normalized Te content (Te concentration is related to the lowest value found among the 9 batches) and intercept (a, d), slope (b, e), and exchange current (c, f) obtained from the LSC on the negative (a–c) and positive (d–f) plate at  $60^{\circ}$ C.



Figure 7. Normalized [Te] (Te concentration is normalized to the lowest value found among the 9 batches) correlations with respect to the overpotentials recorded when 200 mA are applied on the negative plate, in the gas test at  $60\,^{\circ}$ C.

of water consumption in place or for supporting the recommended CEI EN 50342-1:2019-11 method. The results of the alternative proposed method were compared to those obtained from the CEI EN 50342-1:2019-11 method leading to the following considerations. It was possible to electrochemically characterise the overcharge behaviour of a lead-acid battery with flooded technology using a reduced cell suitably modified to accommodate the plates produced by LAB manufacturers. The test proposed developed over three days versus the 21 days of the CEI EN 50342-1:2019-11 method, where only the results obtained at 60°C proved to be truly relevant. The effect of contaminants like Te on water consumption could be verified for both positive and negative plates. The current exchange and overpotential of LSC and gas tests, respectively determined at 60°C were fully consistent with the CEI EN 50342-1:2019-11 method to identify the plate with the highest water loss. Current exchange above 4 mA and overpotential more positive than 250–300 mV vs RHE could identify lots of plate with higher water consumption. The Tafel parameters of both LSC and gas tests determined at 60°C correlated well with the concentration of Te contaminant, that was considered responsible for the increased water consumption in the active masses.

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# **Conflict of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.



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