Irreversible sulphation in photovoltaic batteries

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Abstract

In order for the number of individual photovoltaic installations, to increase rapidly, it is necessary for such systems to be reliable and cheaper. The analysis of these systems when running shows indeed that the weakest element is the battery, and extremely variable lengths of service life can be observed. It is, therefore, increasingly important to optimise this component and its management mode.

In this study, post mortem analyses have been performed on batteries, which have been operating in PV installations. Irreversible sulphation has been identified as a major ageing effect in many investigations. Moreover, the positive electrodes were particularly affected by this degradation.

The objective of this present work is the experimental observation of the evolution of the lead sulphate during deep and prolonged discharge of the positive electrodes. An experimental set-up was built to identify the influence of parameters (electrolyte specific gravity, temperature) on the lead sulphate distribution and ''rechargeability''. These experiments have shown that there is a recrystallisation mechanism during prolonged discharge periods leading to low poor rechargeability.
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1. Introduction

The lead–acid battery is the most commonly used technology for photovoltaic energy storage due to its low cost and its great availability. However, in the light of experience gained to date, we must recognise that the battery is the component which most strongly influences the photovoltaic system cost and reliability [1–3]. There are three possible reasons which could explain this situation:

1. Photovoltaic systems impose specific and penalising operating conditions.
2. The battery characteristics (lifetime, efficiency) are very different from one model to another, even within one type of battery.
3. The battery management is often not appropriate to the battery technology and does not take into account the intermittent PV recharge.

At present time, the potentialities for improvement are the choice of the best-suited battery for the specific application and the optimisation of its management. In order to reach these objectives, our first approach is the identification of the degradation modes by characterising batteries from the field,

followed by laboratory study of their mechanisms. Better understanding of the different degradation modes will allow us to

- identify them as quickly as possible in order to aid battery selection;
- optimise the battery management to limit or rehabilitate the degradation.

2. Experimental

2.1. Battery capacity measurement

When a battery arrives at our laboratory for expert study, the first step of the analysis consists of capacity measurements, which are performed on a test bench. The test benches are composed of a power supply for charging the battery, an electronic load for discharging it with controlled current, and an acquisition system from HP (Agilent). Each test bench is computer-controlled, and the battery voltage and current are monitored. The batteries are placed in a temperature-controlled water bath. The capacity measurements are performed after the full recharge of the battery: the battery is recharged with a constant current (I_{10}) until its voltage reaches a constant value. In order to perform the capacity measurements, the batteries are discharged at

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different constant current rates (I_{10} and I_{100}), and the discharge capacities are compared with the nominal values. Finally, the batteries are recharged again to perform the physico-chemical analyses of the electrodes.

2.2. Physico-chemical analysis of electrodes

After opening the battery tank, a first analysis allows identifying qualitatively some of the degradation modes: brittle grids (indicating corrosion), white marks (indicating hard sulphation), active mass softening and shedding. The electrodes are then rinsed and dried, under neutral atmosphere for the negative plates to avoid oxidation of the active mass. Samples are taken from the top, middle and bottom of each electrode, in order to assess the potential electrolyte stratification and its consequences.

The chemical titration of the active mass components indicates the Pb, PbO, and $PbSO_4$ content for the negative electrodes, and PbO_2, PbO, and $PbSO_4$ for the positive electrodes. As, before tear-down analysis, the batteries are always fully charged, the $PbSO_4$ content gives the hard or "irreversible" sulphation of the battery plates.

SEM analysis allows location of the lead sulphate crystals, while chemical titration only gives the overall $PbSO_4$ content. If these crystals are located close to the grid, the conductivity will be decreased.

Cross-sections of the positive grid are observed after encapsulating samples in transparent epoxy resin and polishing using a PRESI Mecapol P220U automatic polishing machine, on abrasive paper, then on cloth with diamond suspension. Samples are examined using an Olympus BX51M optical microscope, under polarised light in order to emphasise the different zones of the sample (grid, corrosion layer, active mass). This observation gives information about the corrosion layer width and morphology [4].

3. Results and discussion

3.1. Characterisation of the lead–acid batteries used in PV systems

Various analyses have been conducted on batteries which have been operating in photovoltaic installations. Within these analyses, different types of system have been studied.
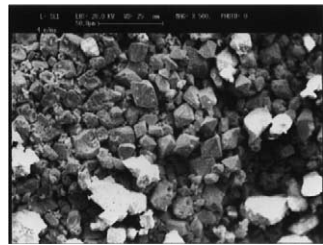
3.1.1. Professional systems

The characterisation results are summarised in Table 1.

The two batteries characterised were installed in lighthouses for 6 (battery 1) and 8 (battery 2) years. These batteries were 2 V cells of flooded type, with tubular positive plates and lead–antimony grid alloys.

Some cells of battery 1 show a polarity inversion, which induces a high capacity loss to the whole battery: 89% at C_{10}. The second battery (battery 2) presents high capacity value: only 12% capacity loss at C_{10}.

Table 1
Characteristics of the autopsied batteries from professional systems

Battery characteristics	Management/operating constraints	Positive electrodes degradation
Battery 1		
Lifetime : 6-year-old; nominal capacity (C_{10}): 575 Ah; capacity loss (%C_{10}): −89%	Conventional BMS; low maintenance	Positive electrode sulphation at the bottom of the electrodes X500
Battery 2		
Lifetime: 8-year-old; nominal capacity (C_{10}): 1400 Ah; capacity loss (%C_{10}): −12%	Conventional BMS; low maintenance	Positive electrode sulphation specifically at the interface electrolyte-active mass X100

Several degradation mechanisms have been observed in this kind of system:

- *Irreversible sulphation of positive and negative active mass*: High levels of lead sulphate in charged positive and negative active mass indicate the presence of irreversible sulphation. Different locations of the irreversible lead sulphate crystals have been identified: a homogeneous sulphation is observed in the negative active mass. In the positive plate, the electrolyte—active mass interface is particularly affected by irreversible sulphation leading to a limitation of diffusion (Table 1, battery 2). In other parts of the positive active mass (namely active mass cross section) large lead sulphate crystals (>20 μm) are formed in the macropores (Table 1, battery 1).
- *Electrolyte stratification*: Electrolyte stratification is observed on the positive plates: lead sulphate crystal content is higher in the lower part of the electrodes than in the upper part (Table 1). The phenomenon is less visible on the negative plates.
- *Formation of a corrosion layer at the positive grid–active mass interface*: The PbO content of 6% in the upper part of some cells indicates the presence of a corrosion layer. This result is confirmed by SEM observation of the grid–active mass interface.
- *Shedding of the active mass*: Negative active mass is found at the bottom of the container, indicating a loss of grid–active mass connection (the positive active mass is kept in place by a gauntlet).

3.1.2. Stand-alone domestic installation

The batteries characterised were of flooded stationary type with tubular positive plates and lead antimony grid alloys. The characterisation results are shown in Table 2.

Battery 3 belonged to a photovoltaic system representing a typical domestic stand alone installation operating in a farm and has been replaced after 11 years of service. Two other batteries (batteries 4 and 5) have been characterised after premature failures (after 3 and 5 years of service, respectively). Battery 6 was installed in an advanced PV system with optimised management and has been running for 14 years.

Different degradation mechanisms have been observed by characterising the electrodes of the stand-alone domestic installations.

- *Irreversible sulphation*: A high lead sulphate presence in the charged positive and negative plates is indicative of irreversible sulphation.
- *Electrolyte stratification*: The lead sulphate gradient between the top and the bottom of the positive plate and negative plate indicates the presence of electrolyte stratification in both plates. However, electrolyte stratification was particularly prominent in the positive active mass. As in the case of the batteries studied above, a lead sulphate layer is observed at the electrolyte–positive active material interface, especially in the lower part of

the plates (Table 2, battery 3). The crystal formation may be linked to the high local electrolyte density values in this part of the plate.
- *Formation of a corrosion layer at the positive grid–active mass interface*: Some positive plates show up to 5% PbO concentration in the top part and the corrosion layers observed approach 500 μm (Table 2, battery 5).
- *Textural change of the active mass*: For battery 6, the main ageing phenomenon observed is a decrease in the porosity of the positive active mass (Table 2, battery 6).

3.1.3. Lighting kits

Different types of lighting kit systems have been studied in our laboratory: rural community systems used to supply electricity to a whole village, and individual solar kits. All the batteries in these installations were of flat plate construction with positive grids made of antimony alloy (batteries 7–11, local SLI batteries) or calcium–tin alloy (battery 12, solar battery).

These batteries were being replaced because of very high capacity losses (Table 3).

- *Irreversible sulphation*: High lead sulphate levels in the charged positive and negative active masses indicate the presence of irreversible sulphation, and this is more pronounced for the positive plate.

  In the case of individual systems, large crystals located in the macropores have been observed using SEM. The batteries were often in overcharge and thus, the gassing has enlarged active mass pores.
- *Absence of electrolyte stratification in individual kits*: In the case of the rural community equipment, electrolyte stratification was observed in the positive and negative plates of the batteries. Moreover, the SEM observation shows that the large irreversible lead sulphate crystals (20–30 μm) are mostly located at the electrolyte–active mass interface, in the lower part of the plate.
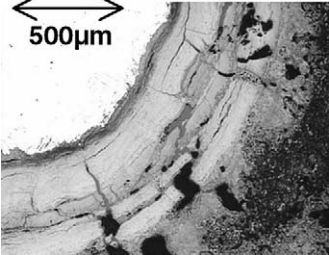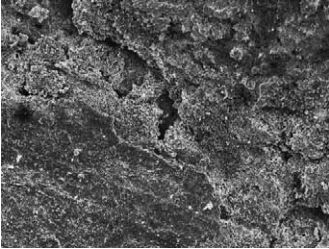
  In the case of some individual kits (Table 3, batteries 7–9), the lead sulphate gradient is inverted for both positive and negative plates. This phenomenon is a reflection of the use of this battery: the gassing induced by the "quasi-floating" condition has inhibited the stratification usually seen in PV applications.
- *Formation of a corrosion layer at the positive grid–active mass interface*: In some cases, the corrosion layer reaches up to 400 μm and was favoured by the battery use at high SOC (Table 3, batteries 7–9).

A summary of the types of damage observed in flooded batteries from several types of PV system, as a function of the operating constraints, is presented in Table 4.
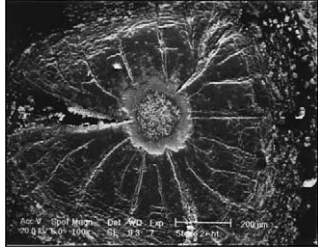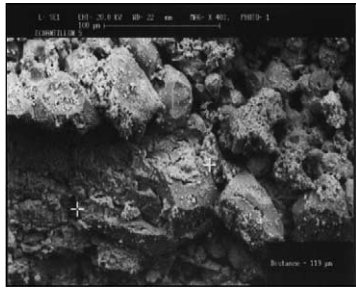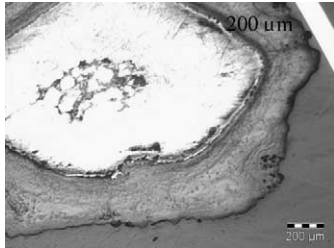
1. The main degradation observed in batteries used in professional systems and stand-alone domestic systems (stationary type, tubular positive plates) is the sulphation of the positive and negative electrodes, with higher lead sulphate contents in the positive plates. The formation of

Table 2
Characteristics of the autopsied batteries from stand-alone domestic systems

Battery characteristics	Management/operating constraints	Positive electrodes degradation X500
Battery 3		
Lifetime: 11-year-old; nominal capacity (C_{10}): 500 Ah; capacity loss (%C_{10}): −53%	Conventional BMS; good maintenance	Positive electrode sulphation at the bottom of the electrodes X500
Battery 4		
Lifetime: 3-year-old; nominal capacity (C_{10}): 375 Ah; capacity loss (%C_{10}): −30%	Bad system sizing; low maintenance	Positive electrode sulphation specifically at the interface grid–active mass X500
Battery 5		
Lifetime: 5-year-old; nominal capacity (C_{10}): 600 Ah; capacity loss (%C_{10}): −57%	Conventional BMS; extremely low maintenance	Corrosion of the positive grid + sulphation
Battery 6		
Lifetime: 14-year-old; nominal capacity (C_{10}): 350 Ah; capacity loss (%C_{10}): −27%	High performance BMS; good maintenance	Textural change of the active mass X200

the irreversible lead sulphate gradient, its higher percentage located in the lower part of the plates, is due to electrolyte stratification developed in the absence of prolonged gassing.

2. The batteries used in the lighting kits (SLI type, flat plates) are subjected to irreversible sulphation but are mostly susceptible to positive grid corrosion.

3. The premature failures which have been observed in several batteries (batteries 4 and 5) leading to battery replacement are due to bad systems characteristics:
   ○ *Maintenance*: Poor maintenance appears to strongly decrease the battery lifetime (down to 3 years for stationary type instead of 10 years expected). The batteries with very low electrolyte level present severe corrosion.

Table 3
Characteristics of the autopsied batteries from lighting kits

Battery characteristics	Management/operating constraints	Positive electrodes degradation
Batteries 7–9 (200 μm)		
Lifetime: 6 months to 2 years; nominal capacity (C_{10}): 50 Ah; capacity loss (%C_{10}): −100%	Individual solar kits; conventional BMS; low maintenance	Positive electrode corrosion
Batteries 10–11		
Lifetime: 6 months to 1 year; nominal capacity (C_{10}): 75 Ah capacity loss (%C_{10}): −100%	Rural community systems; Conventional BMS; low maintenance	Positive electrode sulphation X500
Battery 12		
Lifetime: unknown; nominal capacity (C_{10}): 80 Ah; capacity loss (%C_{10}): −80%	Individual solar kits; BMS and maintenance unknown	Positive electrode corrosion

○ *Initial sizing*: In the case of battery under sizing, very short lifetime has been observed (6 months) corresponding to the high sulphation of the electrodes.

In order to learn more about the irreversible sulphation of the positive active mass, which is the most important degradation mechanism found in the field applications, our approach is the simulation of this phenomenon in the

Table 4
Summary of damages observed on ex service batteries

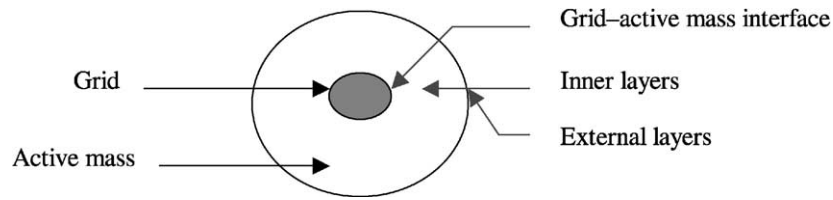| Damage	Main causes	Examples of PV systems
Irreversible sulphation	Sustained deep discharge Acid stratification	Stand-alone domestic systems Navigation systems Lighting kits
Active mass shedding	Cycling Overcharge	Navigation systems Lighting kits (rural community equipment)
Corrosion of positive grid	Overcharge	Lighting kits in rural community equipment (intergranular) Lighting kits in individual applications (uniform)

Fig. 1. Tubular electrode cross-section—the different active mass zones characterised.

laboratory and the detection of parameters which can cause or accelerate the damage.

3.2. The sulphation mechanism

This study consists of the characterisation of the positive active mass after storage in very low SOC conditions and with various parameters (electrolyte specific gravity, temperature). The same testing and characterising facilities as previously have been used.
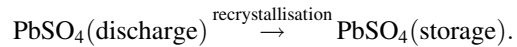
3.2.1. Lead sulphate distribution during deep and prolonged discharge

The study has allowed us to see the evolution of the active mass during deep and prolonged discharge. Characterisations have been performed both immediately after the discharge, and 1 month after the discharge. Different active mass zones have been observed by the SEM: the inner layers, the external layers and the grid–active mass interface (Fig. 1).

The results are presented in Tables 5 and 6.

The characterisations show an evolution of the positive active mass during the storage of the discharged cells. An ionic exchange between the $PbSO_4$ crystals and the electrolyte has been observed. This is the recrystallisation mechanism [5–7]:

$$PbSO_4(discharge) \xrightarrow{recrystallisation} PbSO_4(storage).$$

It appears that the experimental cell storage in discharged conditions has homogenised the lead sulphate distribution in

Table 5
SEM micrographies of different zones of the active mass of charged positive plates (X500)

External layers	Inner layers	Grid–active mass interface
Immediately after the discharge: 1.75 V, 25 °C, 1.238 g cm^{-3}, I_{10}		
One month after the discharge, storage at 25 °C: 1.75 V, 1.238 g cm^{-3}, I_{10}		
One month after the discharge, storage at 50 °C: 1.75 V, 1.238 g cm^{-3}, I_{10}		

Table 6
SEM micrographies of different zones of the active mass of charged positive plates (X500)

External layers	Inner layers	Grid–active mass interface

Immediately after the discharge: 1.75 V, 25 °C, 1.200 g cm^{-3}, I_{10}

One month after the discharge, storage at 25 °C: 1.75 V, 1.200 g cm^{-3}, I_{10}

Immediately after the discharge: 1.75 V, 25 °C, 1.300 g cm^{-3}, I_{10}

One month after the discharge, storage at 25 °C: 1.75 V, 1.300 g cm^{-3}, I_{10}

the horizontal cross-section. Moreover, both a high temperature (50 °C) and a low specific gravity (1.2) applied during the cell storage favour the decrease of the amount of lead sulphate aggregates.

3.2.2. Evolution of the lead sulphate content during the storage

The previous observations are confirmed by the PbSO$_4$ content measured by chemical titration. As shown in Table 7, the lead sulphate content changes during the storage period with some parameters: the lead sulphate content increases with high electrolyte specific gravity and decreases with

high temperatures. The storage conditions (temperature, and electrolyte density) seem to influence the "recrystallisation" mechanism towards the dissolution or the formation of lead sulphate crystals aggregates.

3.2.3. Electrochemical properties of the lead sulphate

The electrochemical properties of the lead sulphate formed during the storage period have been characterised. In order to evaluate the "rechargeability" of the experimental cells after the deep and sustainable discharge, they have first been recharged (I_{10} with a recharge coefficient of 1.2). Then, capacity measurements (C_{10}) have been

Table 7
Comparison of the compositions of discharged positive active mass: after the discharge, after 1 month of deep discharge

Test condition	PbSO$_4$ content (%)	
	Immediately after the discharge	One month after the discharge
Storage at 25 °C, 1.238 g cm^{-3}	22	34
Storage at 50 °C, 1.238 g cm^{-3}	22	15
Storage at 25 °C, 1.200 g cm^{-3}	18	18
Storage at 25 °C, 1.300 g cm^{-3}	24	42

performed for the capacity loss evaluation. Then, after final recharge, other chemical titration has allowed to measure the irreversible lead sulphate content and to determine the influence of the storage parameters on the lead sulphate "rechargeability" (Table 8).

3.2.3.1. Influence of the electrolyte specific gravity.

- In the case of a specific gravity of 1.2, the capacity loss measured after 1 month of deep discharge is very low: 5% of the initial capacity. The irreversible lead sulphate content of the discharged positive active mass is stable during the cell storage (around 11%).
- In the case of high specific gravity, the analyses show higher capacity losses (48%) due to an increase of the lead sulphate content (25%). Moreover, the analyses of the discharged positive active mass just after the discharge and at the end of the storage period show the formation of more lead sulphate (respectively, 24 and 42%).

Thus, two different hypotheses can be given for the influence of specific gravity:

- The specific gravity influences the recrystallisation process, a high value involving the formation of numerous aggregates.
- The specific gravity influences lead sulphate dissolution during the recharge leading to easy recharge of the lower acid specific gravity cells.

3.2.3.2. The influence of temperature.
The irreversible lead sulphate content are higher at 25 °C (21%) than at 50 °C

Table 8
Composition of recharged positive active mass and capacity measurements after 1 month of deep discharge

Test condition	Irreversible PbSO$_4$ content (%)	Capacity losses (% of initial capacity)
Storage at 25 °C, 1.238 g cm^{-3}	21	43
Storage at 50 °C, 1.238 g cm^{-3}	12	14
Storage at 25 °C, 1.200 g cm^{-3}	11	5
Storage at 25 °C, 1.300 g cm^{-3}	25	48

(12%), and low capacity losses have been measured at 50 °C (14% of the initial capacity). In short, a high temperature seems to decrease the recrystallisation process. The irreversible lead sulphate formation corresponds to a thermodynamic equilibrium between the lead sulphate crystals and the electrolyte. A high temperature increases the crystal's solubility.

In conclusion, we have shown the existence of an ionic exchange between the lead sulphate formed during the discharge and the electrolyte, when the battery remains at a low state of charge. This chemical process has been initially observed by SEM: after storage of the experimental, the lead sulphate distribution has been homogenised. This process has been identified in the literature as a recrystallisation phenomenon [5–7].

This recrystallisation phenomenon consists of a thermodynamic equilibrium:

- A high temperature leads to a decrease in the number of aggregates.
- A high electrolyte density involves the opposite.

These parameters have an influence on the equilibrium between lead sulphate crystals and electrolyte.

In a second part of this work, the electrochemical properties of the lead sulphate crystals have been studied after the recharge of the experimental cells by measuring the irreversible lead sulphate content and the capacity losses. For all the experimental cells, the low SOC storage has favoured the formation of poorly rechargeable lead sulphate.

A first hypothesis can be given: as lead sulphate is redistributed during the prolonged discharge, it forms electronic contacts with the positive active mass leading to poor rechargeability.

The irreversible sulphate formation during deep and prolonged discharge can be related to the formation of new aggregates as a result of the crystal—electrolyte equilibrium with poor positive active mass contact.

4. Conclusion

Lead–acid battery types are numerous and photovoltaic applications (therefore the charge and discharge profiles of the batteries) are varied. Within this context, two questions have to be solved: how to adequately select in a reasonable time period the battery best suited to a specific application? Then, how to improve the management in order to decrease or to rehabilitate degradation of the electrodes?

The general approach we have selected is to understand first the degradation mechanisms linked to this application. Most degradation results in capacity loss. But a capacity loss does not indicate the real cause of degradation. In this regard, the extensive characterisations made on field-operated batteries were rich in information, with one main result: the irreversible sulphation of the positive active mass was observed frequently. Then the strategy to optimise

the battery was to get a better understanding of this degradation.

This mechanism has been studied in prolonged periods at low SOC. The influence of parameters (temperature, electrolyte specific gravity) has been observed during the storage period showing that there is a recrystallisation process corresponding to a thermodynamic equilibrium between the crystals and the sulphate ions in the electrolyte. Poor ''rechargeability'' can be related to the distribution of new crystals leading to poor electronic contact.

Acknowledgements

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