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A new electrolyte formulation for low cost cycling lead acid batteries

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Abstract

This paper is devoted to the development of a new lead acid battery electrolyte formulation for cycling applications, especially for renewable energy markets in developing countries. These emerging markets, such as solar home systems, require lead acid batteries at very low prices and improved performances compared to automotive batteries produced locally.

The new acid formulation developed is a mixture of sulphuric acid, liquid colloidal silica and other additives including phosphoric acid. The colloidal silica is used at a low concentration in order to decrease the acid stratification process during cycling at high depth of discharge. Phosphoric acid is used for the improvement of the textural evolution of the positive active material during cycling.

After a description of the markets and of the additives used in the new acid formulation, this paper presents the results obtained with normalised photovoltaic cycle testing on low cost automotive batteries modified by the new electrolyte formulation. It is shown that the cycling life of such batteries is much increased in the presence of the new formulation. These results are explained by the improved evolution of positive active mass softening parameters (specific surface and β-PbO_2 crystallite size) and also by a more homogeneous sulphating process on both plates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lead acid batteries; Colloidal silica; Acid stratification; Softening process

1. Introduction

Nearly two-thirds of the world's rural inhabitants have no access to electricity and little hope of connection to national electricity grids. Stand alone renewable energies are the best solution to provide small but vital electricity quantities at low cost from sun, wind, water or biomass for these populations. This emerging market is in rapid growth and is supported by the initiative of world wide organisations and by the mass production of photovoltaic modules.

Lead acid batteries are an essential part of most stand alone renewable systems, particularly solar home systems (SHS). The market for the battery component is presently estimated to be 130 ME/year [1] and for 2010 is expected to reach 820 ME/year. The promise of this emerging market for battery manufacturers can be realised if low cost batteries with convenient performance can be provided and used properly by the end user.

Within SHS, the most important feature of battery operation is cycling [2]. During the daily cycle the battery is charged by day and discharged by the night time load. Superimposed onto the daily cycle is the seasonal cycle which is associated with periods of reduced radiation availability. Moreover, charging conditions are a very important factor and often uncontrollable because of variation in solar irradiation. Batteries generally suffer from acid stratification and deep irreversible sulphating when the battery is insufficiently recharged, and suffer from positive softening when the battery is fully recharged. Furthermore, lack of, or bad, battery maintenance is currently a source of failure. To limit these failure modes different but concomitant options should be examined:

- higher sizing of PV module generator (but this brings extra costs);
- better control of charge/discharge operations, including intelligent regulator control;
- better design of batteries resistant against the failure modes reported.

This paper reports advances made in the European Joule project JOR3-CT98-0203 concerning the improvement of low cost battery design for cycling applications.

The state of the art concerning batteries devoted to stand alone PV systems shows that presently several types of lead acid batteries are used for this application.

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- Flooded tubular technology giving reliability of about 8 years at the rate of 50% depth of discharge (DOD) and cost of about 150 Euro/kWh. This product is the most common in the PV application (rural electrification, domestic applications and large professional systems) but incure significant cost due to maintenance frequency.
- Valve regulated lead acid batteries (VRLA) using tubular gel technology require no maintenance, are as reliable as flooded technology but at a high cost (more than 200 Euro/kWh). This product is generally used for high quality professional systems but is too expensive for widespread use.
- Valve regulated lead acid batteries using flat plates combined with gel or Adsorptive Glass Material (AGM) giving no maintenance but medium reliability (about 5 years at the rate of 50% DOD) and cost about 100 Euro/kWh. This product is often used for small professional PV systems Maritime (Telecom, Maritime).
- Flooded flat plate technology (automotive battery design) giving poor reliability (between 0.5 and 3 years at the rate of 50% DOD) but a low cost of about 50 Euro/kWh resulting from large scale production. Due to this low cost this product is the most commonly used in the PV application in developing countries for SHS but gives high life-time cost due to poor reliability.

The short life-time of this last technology can be compensated by introducing relatively simple modifications to the battery design without changing the fundamental technology. Thus renewable energy batteries have been derived from truck batteries by using thicker electrodes and different separators. This seems to be the best way for improving the service life of batteries for SHS but the extra cost is not always compensated by the performance improvement. The idea developed in this paper is to use a standard automotive battery with thin calcium plates made with a low cost continuous process but to adopt new concepts in order to promote cyclability at the expense of power. The main idea was to substitute the standard electrolyte by a new electrolyte formulation able to provide sufficient improvement in cycling life for renewable energy applications.

2. Experimental

For the development of a new electrolyte formulation different compositions and additives were tested. This work was made at the electrode scale in special cycling cells represented in the Fig. 1.

The procedure used is a very accelerated cycling test at 40°C giving high stratification and high positive active mass softening. The procedure consists of small microcycles at high depth of discharge. Tests have been performed at two overcharge coefficients 103% (stratification test) and 115% (softening test). The cells are based on standard SLI flooded battery technology with excess electrolyte. Several additives in the electrolyte have been tested in this exploratory phase.

1. Colloidal silica at 2, 4 and 6%, this additive aims at reducing the acid stratification processes and promotes good homogeneity of electrochemical reactions.
2. Orthophosphoric acid at 2.2% this additive is well-known to reduce the softening process of the positive plate by decreasing textural evolution of PbO_2 crystals or $PbSO_4$ [3].
3. Perfluoro-alkyl-sulfonic acid at 0.1%, (Forafac 1033D) [4].
4. Polyvinyl pyrrolidone at 0.2% [4].
5. Additive 4 at 1%;
   these additives were also tested to decrease the textural evolution of $PbSO_4$ and to decrease the softening evolution.

Evaluation of the effect of additives was made by monitoring the Ah capacity evolution versus cycle number and from post mortem analysis of the active material using X-ray diffraction with software measuring crystallite size (INEL spectrometer CPS 120) and BET specific surface measurements (Coulter SA 3100).

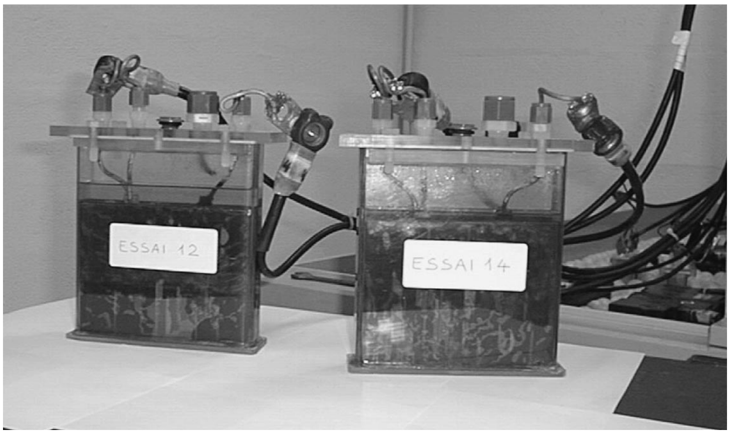


Fig. 1. Cells for tests of additives in real electrode scale.

After determination of the potential of each additive, the best additives were mixed and an electrolyte formulation was determined by taking into account the lead sulphate equilibrium in the acid. This formulation was tested in cells and in different types of standard SLI flooded batteries according to the following matrix including reference batteries (REF) and battery prototypes (BP):

- **REF1** standard SLI, thin plates, laminated expanded all calcium technology Pb–Ca–Sn.
- **REF2** modified SLI, thick plate, gravity cast technology hybrid technology Pb–Sb/Pb–Ca, +new separator.
- **REF3** modified SLI, thin plates, laminated expanded all calcium technology Pb–Ca–Sn, +new separator.
- **BP1** = REF1 + new electrolyte formulation.
- **BP2** = REF2 + new electrolyte formulation.
- **BP3** = REF3 + new electrolyte formulation.

These batteries were tested using a cycling test taking into the account the seasonal variation of state of charge at $T = 40^\circ\mathrm{C}$. This was made with the norm NFC58-510 devoted to secondary batteries for renewable energy applications. This cycle test presents the following characteristics.

Phase A cycling 20% DOD at 0.98 undercharge coefficient until 11.1 V:

- discharge 3 h $0.066.C_{100}$
- charge 4 h $0.0485.C_{100}$

Phase B cycling 20% DOD at 1.10 overcharge coefficient during the number of cycles performed in phase A:

- charge 4 h $0.0545.C_{100}$, voltage limited at 14.1 V
- discharge 3 h $0.066.C_{100}$

Phase A′ cycling 20% DOD at 0.98 undercharge coefficient until 11.1 V:

- discharge 3 h $0.066.C_{100}$
- charge 4 h $0.0485.C_{100}$

After one period ($A + B + A'$), discharge capacities $C/100$ and $C/10$ are made at 25°C, and a new cycling period is carried out at 40°C.

This procedure was originally developed for tubular batteries and one period represents about 1 year of battery service in the field.

Maintenance was not allowed during this test because field experience shows that maintenance operations are often a source of battery failures. The objective with the new electrolyte formulation is a field operation of 5 years without failure using standard low cost batteries (standard low cost batteries give service life between 6 months and 3 years), therefore, in order to assess effect of the new formulation the battery behaviour was judged after four periods of cycle test following three criteria:

- Number of cycles achieved.
- Rate of capacity loss.
- Rate of water loss.

Batteries were dismantled and a complete analysis of plates and active materials was made by XRD, BET and chemical analysis in order to support electrical behaviour observations.

3. Results and discussion

Results of cycling of plates in cells with additives show that it is mainly colloidal silica and phosphoric acid that provide improved results in the accelerating test procedure in cells and give interesting interactions from the point of view of acid stratification and positive active mass softening. Results of the analysis are reported in Table 1.

- Colloidal silica at 2, 4 and 6% plays a beneficial role for capacity evolution (Fig. 2) and acid stratification. The chemical analysis of plates after cycling shows that lead sulphate is present as a trace (about 2%) at the top and at the bottom of the electrodes. The best results on capacity are obtained with 4% silica. However, BET specific surface analysis has revealed abnormal behaviour of the softening parameters (see Table 1); in the presence of silica, the BET surface of the PbO_2 active material is decreased to 1–2 m^2/g (instead of 3–4 m^2/g for the reference). Moreover, some increase in PbO_2 crystallite size has been observed by X-rays. These results point out the possible detrimental effect of the colloidal silica on positive electrode degradation.
- Phosphoric acid at 2.2% does not show improvement of capacity during the electrical tests performed but analysis of the plates after the tests (reported in Table 1) shows

Table 1

Non-cycled PAM	$S_{BET} = 6\ m^2/g$	PbO_2 cryst. = 800 Å
Cycling with 103% overcharge		
Cycled PAM reference	$S_{BET} = 3\ m^2/g$	PbO_2 cryst. = 1400 Å
Cycled PAM reference + H_3PO_4 2.2%	$S_{BET} = 5.2\ m^2/g$	PbO_2 cryst. = 900 Å
Cycled PAM reference + silica 4%	$S_{BET} = 1.5\ m^2/g$	PbO_2 cryst. = 1400 Å
Cycling with 115% overcharge		
Cycled PAM reference	$S_{BET} = 4\ m^2/g$	PbO_2 cryst. = 1147 Å
Cycled PAM reference + H_3PO_4 2.2%	$S_{BET} = 5.8\ m^2/g$	PbO_2 cryst. = 777 Å
Cycled PAM reference + silica 4%	$S_{BET} = 1.85\ m^2/g$	PbO_2 cryst. = 1500 Å

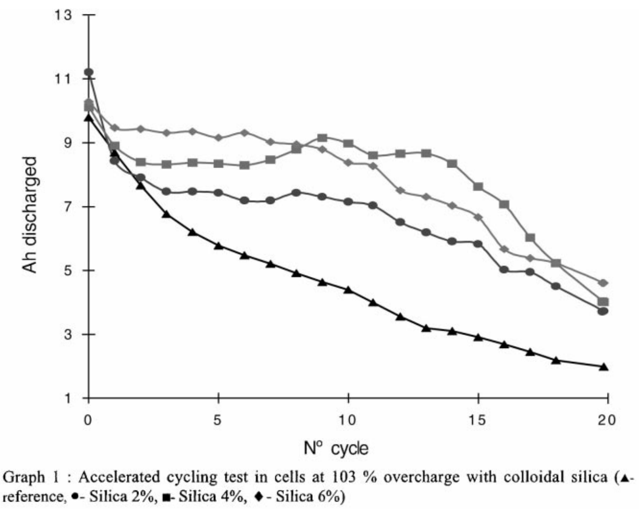


Fig. 2. Accelerated cycling test in cells at 103% overcharge with colloidal silica.

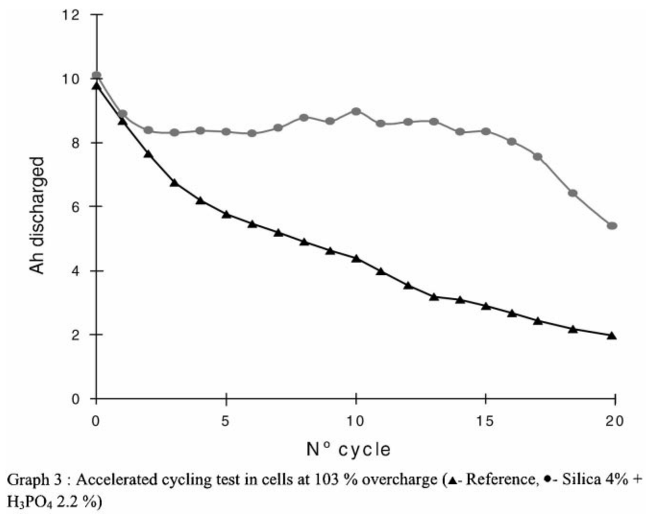


Fig. 4. Accelerated cycling test in cells at 103% overcharge.

unambiguously that the PbO_2 crystallite sizes are decreased in presence of phosphoric acid and that the BET surface is increased. This results is consistent with CSIRO results [5]. This parameter evolution shows clearly that the degradation of the positive active mass is slowed down with phosphoric acid, in fact, values obtained at this stage are typical of non cycled positive active material.

From these results the combined effect of colloidal silica at 2, 4 and 6% in the presence of phosphoric acid 2.2% was tested in cells. It was shown that the best results were also obtained with 4% silica and H_3PO_4 2.2%. This formulation presented very good improvement compared to the reference in terms of capacity evolution (Figs. 3 and 4) and softening parameters. Thus, the analysis results showed that the PAM BET specific surface is increased toward 5 m^2/g and XRD β-PbO_2 crystal size about 985 Å demonstrating that the silica detrimental effect on the softening process is over compensated by the H_3PO_4 positive effect. Note that no negative effect of phosphoric acid was obtained probably due to the use of thin plates and tetrabasic curing, thus the porosity of such an electrode is not influenced by H_3PO_4.

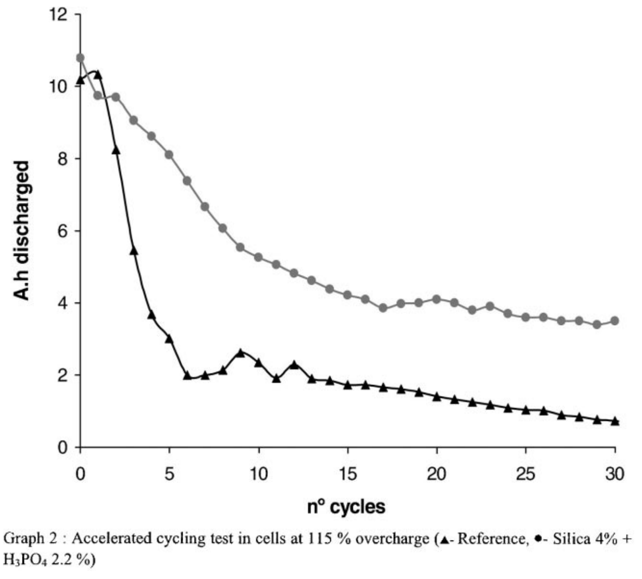


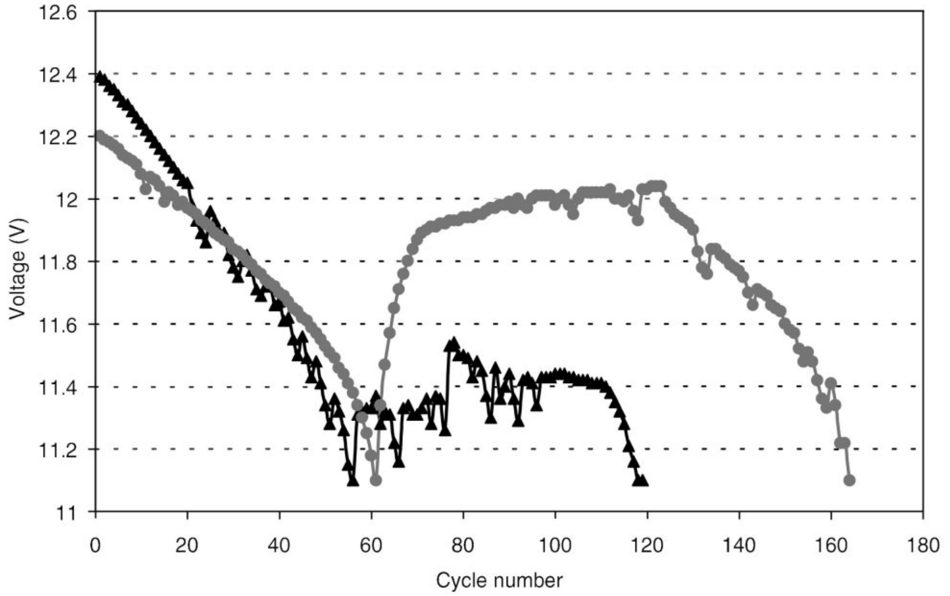
Fig. 3. Accelerated cycling test in cells at 115% overcharge.

Next the novel electrolyte formulation was tested in complete standard batteries. The battery REF1 type was selected because this battery is from low cost advanced automotive technology. One battery was tested with a standard electrolyte $d = 1.28$ and the other battery was filled with new electrolyte at 4% colloidal silica $+2.2\%$ phosphoric acid (BP1). After that, batteries were cycled with NF58-510 procedure.

The results are given in the Fig. 5. It is observed that the BP1 battery using new acid formulation gives very improved results in cycling, especially the slope of voltage loss is decreased during Phase A with small overcharge coefficient, moreover the recharge during Phase B is more efficient with formulation probably due to better homogeneity and less stratification. The number of cycles performed during one period $A + B + A'$ are reported in the Table 2; it can be observed that new formulation exhibits much improved cycle ability in comparison with standard electrolyte. This experiment was reproduced several times giving same result.

Table 2
Number of cycles with and without new electrolyte formulation

	Battery REF1	Battery BP1
Phase A	56	61
Phase A′	8	42
Phase $A + B + A'$	120	164



Graph 4 : First period of Cycling test from NFC58-510 (▲- REF1, ● BP1= REF1 + Silica 4% + H_3PO_4 2.2 %)

Fig. 5. First period of cycling test from NFC58-510.

After preliminary tests concerning new formulation development, four reinforced battery types (see experimental section) were tested by long cycling procedure from NFC58-510 procedure.

The results of cycles performed and capacity loss per cycle after four periods of $A + B + A'$ are reported in Figs. 6 and 7.

Fig. 6 shows clearly that the number of cycles performed by period is significantly increased for BP3 including the new electrolyte formulation. This improvement is by a factor of two by comparison with the references but is not observed for BP2 battery.

Fig. 7 reports the capacity loss per cycle for all batteries. Significant improvement of the capacity decrease during the test is observed for BP2 and BP3.

Fig. 8 reports the water loss per cycle of batteries during the test. It is observed that this water loss is linked to battery technology type and not to electrolyte formulation. Batteries using positive the Pb–Sb alloys in hybrid technology give twice the water consumption of those using calcium

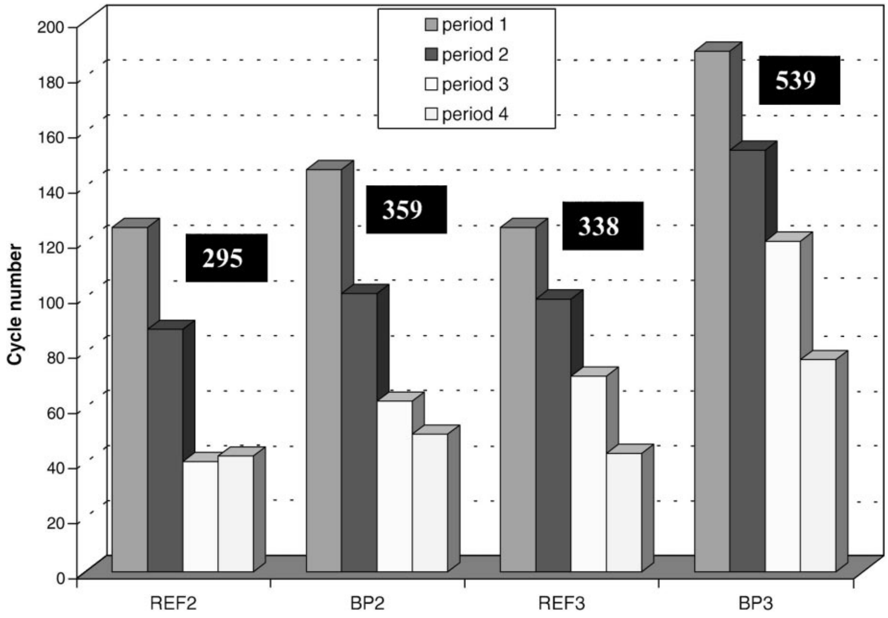


Fig. 6. Cycle number during four periods NFC58-510 cycling test.

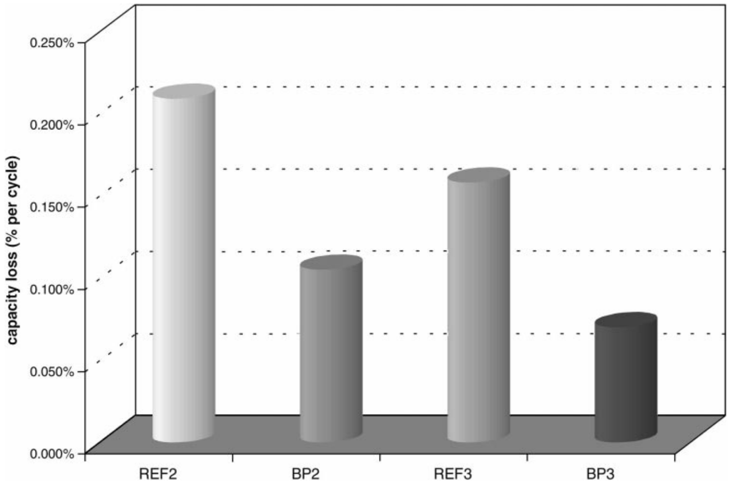


Fig. 7. Capacity loss during NFC58-510 cycling test.

laminated Exmet technology. This observation explains why the improvement of the new formulation is not observed for the BP2 battery. In fact this prototype has failed due to premature dry out. This was confirmed by battery post mortem analysis.

Each battery type was dismantled after the test and analysis carried out. Results are reported in Table 3.

First the analysis was devoted to the control of softening process by XRD analysis. The β-PbO_2 crystal size was measured and a softening index was calculated taking into account the number of cycles achieved and the plate thickness. Note that this calculation gives only the approach of the softening process and should be used carefully. In a general way, the softening failure is observed for crystallite sizes more than 1500 Å but depending on the plate thickness, battery design, compression and electrical application [6]. An estimation of the softening process (Sp) was made in this work using the following formulation:

$$\mathrm{Sp} = \frac{\text{Crystal size}\left(\text{Å}\right)}{\text{Number of cycles} \times \text{Positive plate thickness (mm)}}$$

Results are reported in Table 3 and show that the softening process is well slowed down with the new formulation including 2.2% phosphoric acid.

The specific surface area measurement of the positive active mass is also related to the softening evolution by the relationship between PbO_2 crystal grain growth and the specific surface area decrease. However, this parameter includes the $PbSO_4$ grains component which could be present as irreversible sulphating in the charged state. In fact the BET measurement combines the softening evolution and irreversible sulphating and is also a good parameter for evaluating ageing of PAM. Table 3 reports the BET values

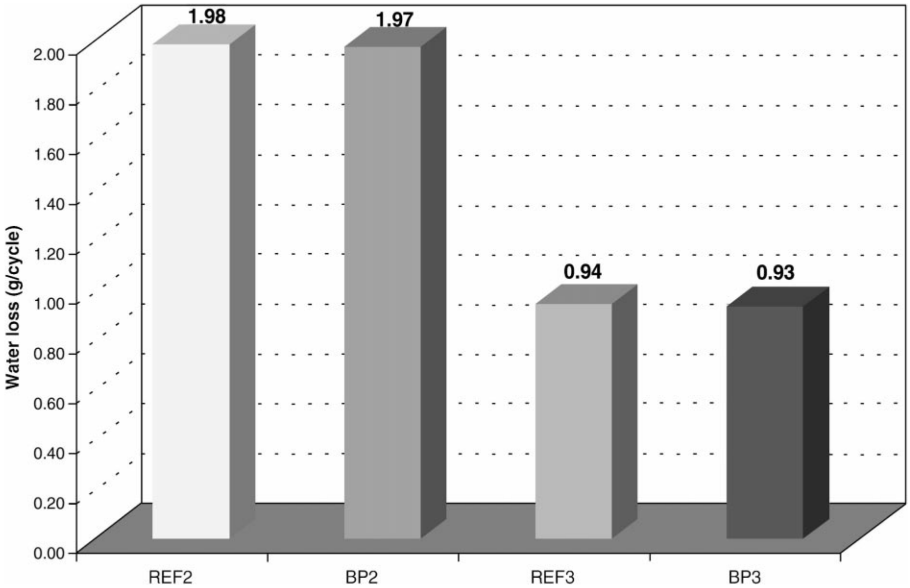


Fig. 8. Water loss per cycle during four periods NFC58-510 cycling test.

Table 3

	REF2	BP2	REF3	BP3
PbO_2 X-ray crystallite size (A)	849	492	581	508
Softening process index	1.15	0.55	0.95	0.52
S_{BET} positive (m^2/g)	1.34	5.41	1.08	4.88
Sulfate positive top %	2.2	2.4	2.1	4.0
Sulfate positive bottom %	24.1	2.6	24.5	4.0
Water loss (g)	583	707	317	501
Water loss (g/cycle)	1.98	1.97	0.94	0.93
Failure mode	Softening + stratification	Dry out	Softening + stratification	No reached

measured for the PAM after the test. A significant improvement of PAM ageing is observed with the new electrolyte formulation, probably due to smaller β-PbO_2 crystals and to the absence of large $PbSO_4$ grains.

The measurement of the $PbSO_4$ content between the top and bottom of the positive electrode is on indication of irreversible sulphating and of stratification. $PbSO_4$ analysis results for the PAM reported in Table 3 show unambiguously that the stratification is prevented with the new electrolyte formulation including 4% colloidal silica.

In conclusion, after four periods of NF58-510 cycling test, ageing of the positive active mass of batteries including the new formulation was significantly delayed by comparison to standard formulation. This is well supported by softening and stratification evolution measurements.

The test was rendered more severe since no maintenance was allowed, in order to prevent the risk of failure in the field. This has shown that the performances of batteries made with hybrid technology and including the new electrolyte was limited by dry out. For the case of batteries made with all calcium laminated Exmet technology, including the new formulation, failure was not reached until four periods of the cycling test. This shows that the electrolyte formulation developed gives major improvement of low cost flooded battery technology for renewable energy cycling applications.

4. Conclusions

This work was devoted to the improvement of low cost batteries for cycling applications in solar home systems which need improved low cost batteries to increase installation reliability and performance.

A new patented acid formulation, using 4% of colloidal silica and 2.2% of phosphoric acid, was developed and tested in standard automotive batteries with seasonal cycling operation. Following, the needs of the application, the results showed that battery life is significantly increased using this formulation and that acid stratification is prevented by colloidal silica and positive active mass softening is delayed by phosphoric acid.

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