ELSEVIER

Journal of Power Sources 85 (2000) 157–163

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

# Grid technology and silver additive influence on VRLA-AGM batteries performances for electric vehicle application

L. Torcheux *, A. Villaron, M. Bellmunt, P. Lailler

*CEAC — Exide Europe Holding, 5 à 7 allée des Pierres Mayette, F-92636 Gennevilliers Cedex, France*

Accepted 22 September 1999

**Abstract**

With the purpose to develop improved positive grids for electric vehicles (EVs), tests on valve-regulated lead acid (VRLA)-AGM prototype batteries have been carried out. Batteries were made using positive grids from gravity cast technology or rolled expanded technology, with and without silver additive at 0.025% and 0.05%. Batteries were submitted to self-discharge tests, deep discharge tests and TC69 cycling. The effect of silver after the self-discharge test of batteries is not significant, or very small, for both technologies; the differences observed between grid technologies are small, but give a better behaviour of batteries using rolled expanded grids, taking into account the lower weight of such grids for the EV application. The effect of silver in deep discharge test of batteries is only significant for gravity cast technology, but even then is limited. No effect of silver is observed for the rolled technology. The differences observed between grid technologies show a better electrical behaviour of batteries using gravity cast grids. However, the voltage limitation should be adjusted to higher values for better rechargeability of the rolled expanded technology according to EV application. The evolution of specific energy of batteries with TC69 cycling shows an important difference between the specific energy of the two battery technologies without over significant effect of silver. The batteries using rolled expanded technology give better results in specific energy and better stability during the TC69 test. However, due to the softening failure mode, it is very difficult to relate directly the role of grid alloy composition and grid technology to the behaviour of batteries in the cycling test. Other parameters like positive active mass elaboration and battery design play a major role in such test. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Gravity cast; Rolled expanded; Lead calcium tin silver alloys; Self discharge; Deep discharge; Cycling

## 1. Introduction

For electric vehicle (EV) application, valve-regulated lead acid batteries (VRLA) require a substantial increase of specific energy. A solution in order to reduce the quantity of lead in the battery and subsequently to improve specific energy could be to use thinner grid collectors for positive plates. Therefore, the role of alloy and grid manufacturing process becomes a major point for the corrosion behaviour of such grid for the EV application.

The influence of calcium, tin and silver content in these alloys has already been widely studied. Some studies reported the effectiveness of tin to prevent the development of a high impedance passivation layer at the grid/active material interface [1–3]. Other studies showed that microstructure and mechanical properties depend on the weight ratio of tin/calcium [4] and on the grid manufacturing process [5–7]; all these parameters having a significant influence on the corrosion of such grids [8,9]. Silver addition has been found to improve the corrosion behaviour of lead calcium tin alloys [10].

This paper reports the performances of VRLA-AGM batteries with different positive grids manufacturing technologies and alloys which were submitted to self-discharge test, deep discharge test and cycling TC69 test. Batteries using rolled expanded grid technology instead of gravity cast technology allow an important reduction of battery weight; this should lead to a major improvement of specific energy for the battery in EV application.

## 2. Experimental

Battery prototypes were specially designed for the purpose of this study. The aim was to compare different grid alloys from different grid technologies with maximum agreement on the battery conception. Table 1 reports the

* Corresponding author. Tel.: +33-1-41-21-24-63; fax: +33-1-41-21-27-09; e-mail: torcheuxl@exide.fr

0378-7753/00/$ - see front matter 
PII: S0378-7753(99)00395-X

Table 1
VRLA-AGM batteries tested with different positive grids technology and alloys

| Battery type | Positive grid technology | Positive alloy composition |
|---|---|---|
| A-65 Ah AGM VRLA | Gravity cast (GC) | $Pb-Ca_{0.08\%}-Sn_{1.2\%}$ (REF) |
| B-65 Ah AGM VRLA | Gravity cast (GC) | $Pb-Ca_{0.08\%}-Sn_{1.2\%}-Ag_{0.025\%}$ |
| C-65 Ah AGM VRLA | Gravity cast (GC) | $Pb-Ca_{0.08\%}-Sn_{1.2\%}-Ag_{0.05\%}$ |
| D-40 Ah AGM VRLA | Rolled expanded (RE) | $Pb-Ca_{0.08\%}-Sn_{1.2\%}$ (REF) |
| E-40 Ah AGM VRLA | Rolled expanded (RE) | $Pb-Ca_{0.08\%}-Sn_{1.2\%}-Ag_{0.025\%}$ |

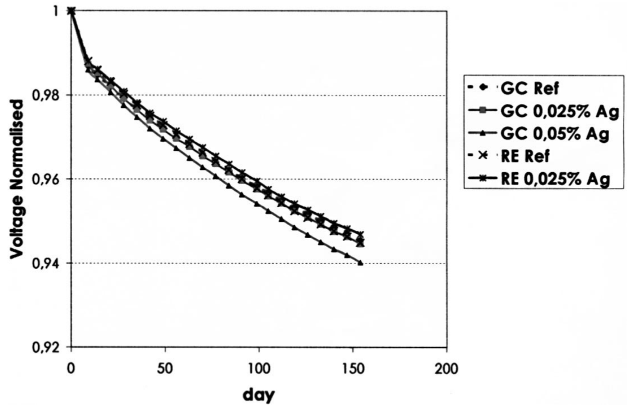


Fig. 1. Batteries voltage evolution in self-discharge.

battery types manufactured and the positive grid alloy and technology used. The batteries with gravity cast grids were made with grids thickness 1.75 mm giving 75 g per grid, whereas batteries with rolled expanded grids were made with the same positive grid conformation thickness, but with thinner bare grids giving 45 g in weight for the complete grid.

However, due to manufacturing reasons, it was difficult to obtain exactly the same design for both battery technologies and some differences were necessarily implemented in the conception of each battery type concerning plate thickness, compression of separator, ratio PAM/NAM, ratio electrolyte/AM). Therefore, exact comparison in the battery behaviour is sometimes difficult to make without taking into account these differences in the battery prototypes conception from different grid technologies.

Battery prototypes were submitted to self-discharge test, deep discharge test and cycling TC69 test.

For self-discharge test, three batteries per case (five cases: GC Ref, GC 0.025% Ag, GC 0.05% Ag, RE Ref, RE 0.025% Ag) were placed in a water bath at 50°C after 6 h charge. For each battery, the voltage, internal resistance and weight loss were monitored during 150 days. Sample batteries from each case were dismantled after 8, 16 and 22 weeks.

For the deep discharge test, two batteries per case (five cases: GC Ref, GC 0.025% Ag, GC 0.05% Ag, RE Ref, RE 0.025% Ag) were discharged at C/5 rate at 25°C after 6 h charge. The cutoff voltage was 10 V. Afterwards, batteries were placed on resistance 10 Ω at 25°C during 2 weeks and disconnected and placed in open circuit at 50°C during 4 weeks. At 25°C, batteries were recharged with limited voltage 14.4 V during 48 h. After a rest period, batteries were discharged at C/5 as previously, recharged and dismantled.

For TC69 cycling test, two batteries per case (four cases: GC Ref, GC 0.05% Ag, RE Ref, RE 0.025% Ag) were cycled at 25°C following the TC69 cycling test: (1) charge complement, (2) discharge $I = 8/5_{C/5}$ during 10 s until 9 V, (3) discharge $I = 2/5_{C/5}$ during 20 s until 9 V, (4) rest 30 s, (5) charge 14.4 V maxi limited to 105% of discharged Ah, (6) rest 3 h.

## 3. Results and discussion

### *3.1. Self-discharge test*

Fig. 1 presents the voltage evolution of batteries during the self-discharge test. The voltages have been normalised at the origin in order to better compare the evolution. Note that the initial voltages for all batteries were closely grouped between 12.85 and 13.05 V (12.96 V with $\sigma = 0.05$ V).

Fig. 1 shows that the voltage evolution is not significantly affected by the presence of silver for gravity cast technology and also for rolled expanded technology until 150 days (22 weeks). In the same way, there was no significant difference between both technologies. Small differences observed are within confidence limits, especially for the gravity cast alloy with 0.05% silver giving a more pronounced voltage decrease in comparison with other cases.

Fig. 2 presents the normalised internal resistance evolution in milliohms during the self-discharge test. For batter-

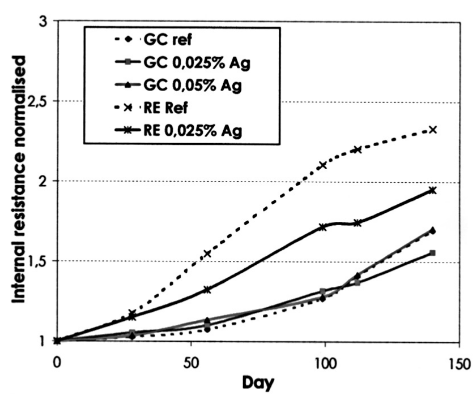


Fig. 2. Internal resistance evolution in self-discharge.

ies using gravity cast grids, the internal resistance is lower than batteries using rolled expanded grids, during 150 days without any effect of silver. For rolled expanded technology, the silver at 0.025% seems to give a lower internal resistance.

Fig. 3 presents the weight loss of batteries during the self-discharge test in grams per kilogram of initial electrolyte. For gravity cast technology, the weight loss reaches about 27 g/kg after 150 days of self-discharge; no difference with the silver presence or content is observed in comparison with reference. For rolled expanded technology, the weight loss is smaller than gravity cast technology giving 13 g/kg. The rolled expanded grids with 0.025% silver give 10 g/kg after 150 days of self-discharge at 50°C.

Fig. 4 presents grid weight loss during self-discharge test in grams per grid. It is observed for gravity cast grids that the effect of silver is not significant, the total weight loss for gravity grids reaches about 14 g after the test, corresponding to 18% of the grid mass (without tab). For rolled expanded grids, the effect of silver is also not significant, the total weight loss for expanded grids is lower than that for gravity cast grids, about 12 g after the test corresponding to 26% of the grid.

Fig. 5 presents photographs of grid sections after the self-discharge test (22 weeks) for all cases. It is observed that gravity cast grids present nonregular surfaces with some small penetrations especially for the reference without silver. The rolled expanded grids present also irregular surface, but no penetrating corrosion is observed.

Grid deformation after 22 weeks self-discharge test is reported in Fig. 6 in several directions. It shows that the percentage of deformation is independent of silver for both technologies, but the rolled expanded grids suffer from more deformation than the gravity grids, corresponding to about 2 mm in height and 3 mm in width, whereas grid deformation is lower than 1 mm for gravity cast grids.

After self-discharge test, chemical analysis of the positive and negative active mass was carried out. No differences were observed for the gravity cast alloys, the lead sulphate is about 20–25% in the positive and in the negative without effect of silver. For rolled expanded alloys, results are similar.

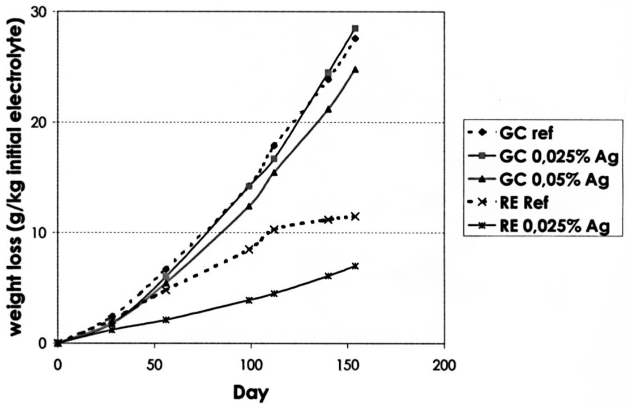


Fig. 3. Weight loss evolution in self-discharge.

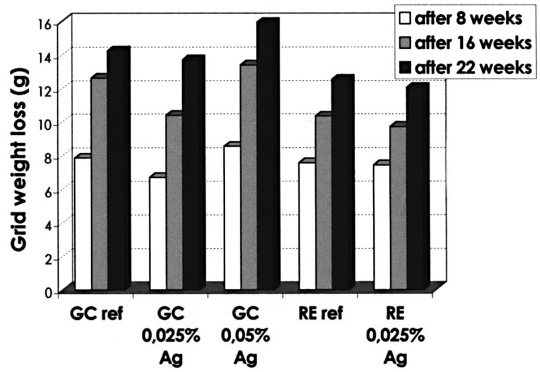


Fig. 4. Grid weight loss evolution in self-discharge.

After self-discharge test of the batteries with different alloy composition and technologies, it can be pointed out that no very significant effect of silver for gravity cast technology is observable, except the corrosion layer which seems more homogeneous in the presence of silver. A slight positive effect of 0.025% silver after the self-discharge test for rolled expanded technology is observed concerning internal resistance and also for water loss during the test. For comparison between the technologies, it can be observed that a higher internal resistance of such batteries is obtained, but also better behaviour of rolled expanded technology, in terms of water loss compared to gravity cast technology. This behaviour could also be partially explained from the difference in battery design conception although grid technology can play also a significant role.

From the point of view of corrosion, a better behaviour of rolled expanded grids in terms of corrosion is obtained, although the corrosion layers seem more developed after the test, the corrosion proceeds more homogeneously (Fig. 5) and the weight loss of such grids is smaller than that of gravity cast grids, but with more deformation. The effect of silver is not significant.

In conclusion, the effect of silver after self-discharge tests of batteries is not significant or very slight for both technologies tested. The differences observed between grid technologies are weak, but lead to a good behaviour of batteries using rolled expanded grids taking into account the weight of such grids (45 g of positive grids instead of 75 g).

### 3.2. Deep discharge test

Fig. 7 presents the time needed to reach $I_{max}$ during the recharge after a deep discharge test. It is observed that the time to reach $I_{max}$ is slightly influenced by the silver content for gravity cast grids. The higher is the silver

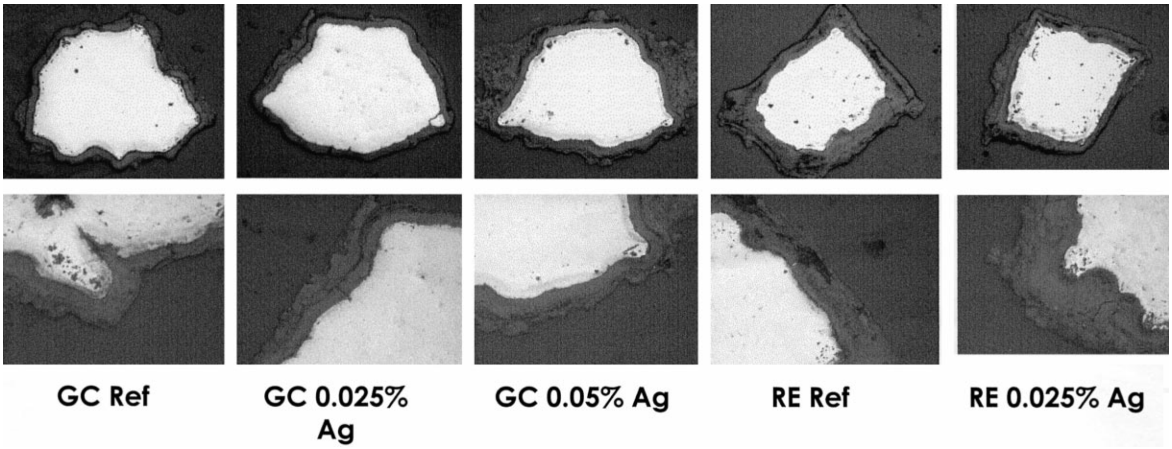


Fig. 5. Photographs of grid sections after self-discharge test 22 weeks.

content, the lower is the time to reach the maximum intensity at the recharge step.

For rolled expanded grids, the time to reach $I_{max}$ is 10-fold more important in comparison with that for gravity technology; this result shows that recharge at 14.4 V after deep discharge for rolled technology is more difficult than for gravity cast technology. No beneficial effect of silver is observed for this technology.

Fig. 8 presents grid weight loss after a deep discharge test in grams per grid. It is observed for gravity cast grids that the effect of silver is weak, the total weight loss for gravity grids reaches about 6 g after the test corresponding to about 7% of the grid. For rolled expanded grids, the effect of silver is not significant, the total weight loss for expanded grids is higher than for gravity cast grids, about 9.5 g after the test corresponding to 21% of the grid.

Fig. 9 presents the photographs of grid sections after the deep discharge test for all cases. It is observed that gravity cast grids present nonregular surfaces with some small penetrations more pronounced for the reference without silver. The rolled expanded grids present a very regular surface without sign of penetrating corrosion. The corrosion depth has been measured for gravity cast grids and it shows that the corrosion layer thickness evolution after deep discharge test is slightly affected by silver for gravity cast technology. Higher silver content leads to smaller corrosion layers. The corrosion layer thickness for rolled expanded technology is not affected by silver.

The composition of the positive active mass and the lead sulphate content in the negative mass have been investigated using wet chemical analysis. Analysis was performed at the top and at the bottom of plates. Concerning the positive active material, no difference was observed for all the cases. The lead dioxide and sulphate contents are similar for all the batteries, a similar acid stratification is also observed giving about 15–20% difference in composition between the top and the bottom. No significant difference between $PbO_2$ and $PbSO_4$ levels can be observed between the two technologies and the effect of silver is not detectable. For the negative active material, the lead sulphate content is between 1% and 6% for the top of plates and between 4% and 12% for the bottom. The references without silver seem to present larger sulphating than batteries having silver, but it is difficult to draw firm conclusions due to the slight difference between the analysis.

After deep discharge test of the batteries with different alloys composition and technologies, a slight effect of silver in deep discharge test for gravity cast technology

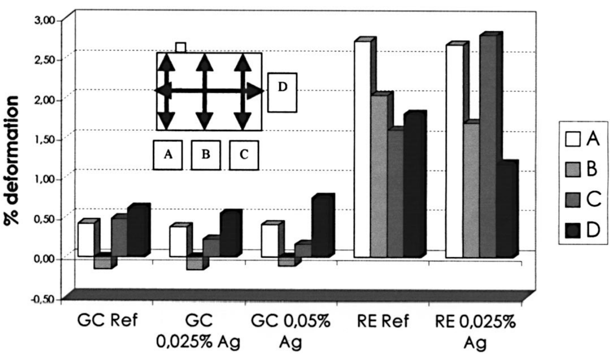


Fig. 6. Grid deformation after self-discharge test 22 weeks.

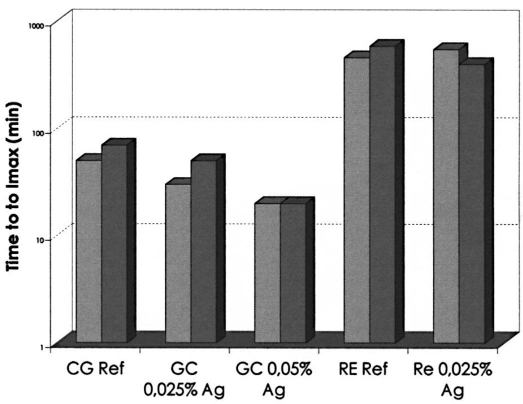


Fig. 7. Time needed to go to $I_{max}$ after deep discharge test.

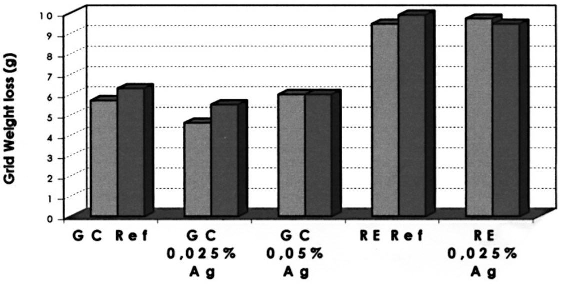


Fig. 8. Grid weight loss in grams after deep discharge test.

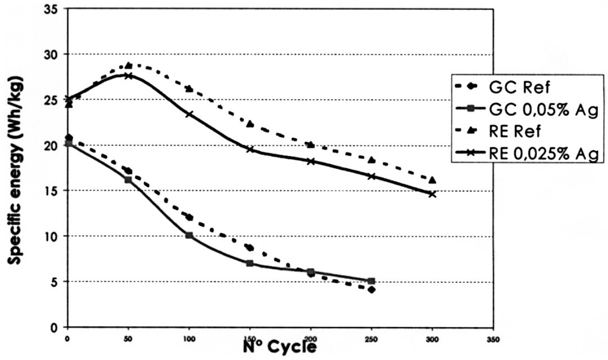


Fig. 10. Specific energy of batteries with TC69 cycling test.

can be pointed out. The higher is the silver content, the lower is the time to reach the maximum intensity at the recharge step after deep discharge. The corrosion layer thickness is also weakly decreased by silver. No effect of silver with deep discharge test for rolled expanded technology has been observed.

The comparison between the technologies shows that a better behaviour for gravity cast technology in terms of rechargeability after deep discharge test is obtained. However, it is well known that recharge at 14.4 V is not so efficient for rolled technology. A better rechargeability is usually obtained with 14.8 V.

From the point of view of corrosion behaviour, the corrosion layer is again observed to be more homogeneous for rolled expanded technology, although the rate of grid corrosion is higher for this technology compared to gravity cast technology. There is no difference between all the batteries in terms of chemical composition of active material nor of acid stratification.

In conclusion, the effect of silver with deep discharge test of batteries is significant only for gravity cast technology, but even then is limited. No effect of silver for rolled technology is observed. The differences observed between grid technologies show a better electrical behaviour of batteries using gravity cast grids; however, the test of rechargeability should be revised for the rolled expanded technology.

### 3.3. TC69 cycling test

Fig. 10 presents the evolution of specific energy in watt hour per kilogram during the TC69 test; dotted lines are references and the full lines are batteries with silver alloys.

It is observed that batteries with gravity cast technology give poor results during the TC69 cycling test. The specific energy decay is continuous until cycle 250. The effect of silver is not detectable. For batteries with rolled expanded grid technology, the results are better, the specific energy delivered is more stable until 250 cycles. An important difference is found between the specific energy of the two battery technologies. The smaller batteries using rolled expanded technology give a better result in specific energy and better stability during the TC69 test.

Fig. 11 presents photographs of grid sections after the TC69 cycling test. It is observed that gravity cast grids

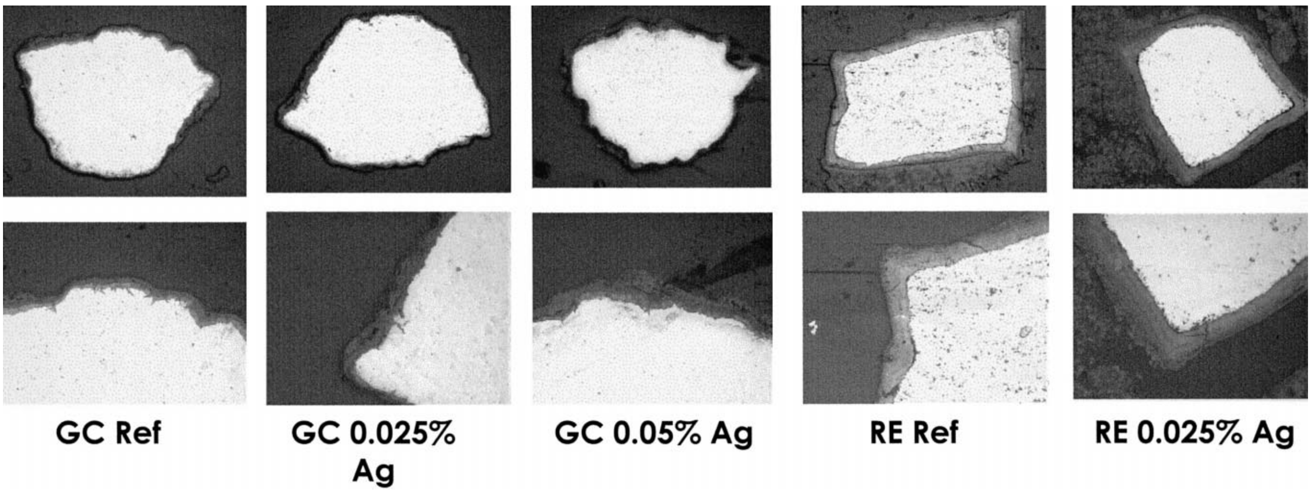


Fig. 9. Photographs of grid sections after deep discharge test.

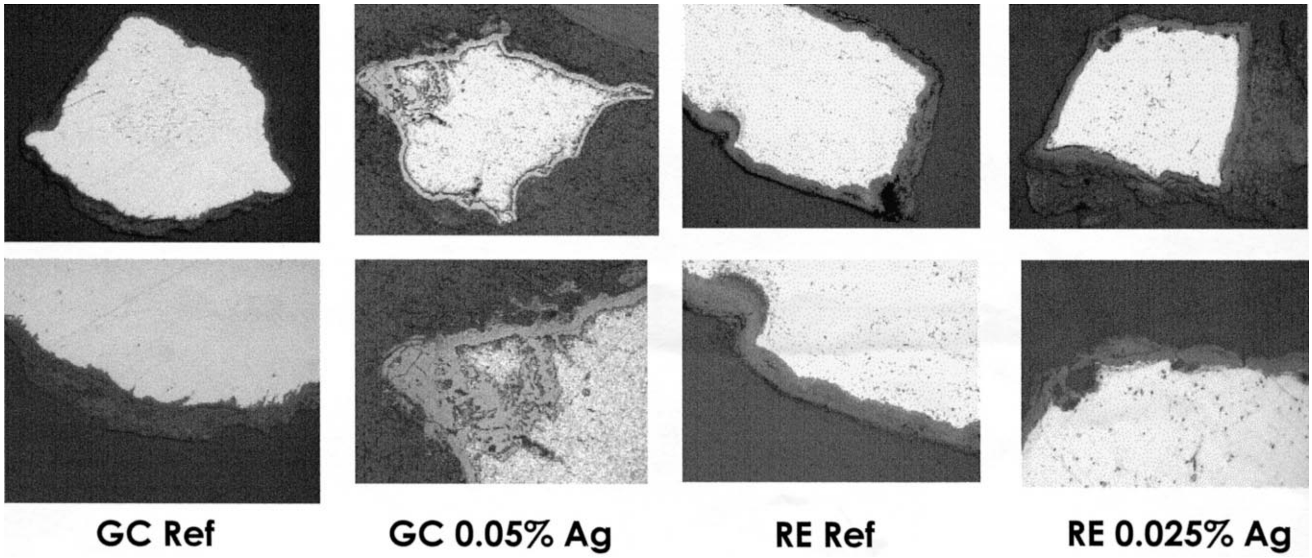


Fig. 11. Photographs of grid sections after cycling test TC69.

present nonregular surfaces with some penetration. The rolled expanded grids present more regular section without sign of penetrating corrosion. The corrosion depth has been measured; it shows that the corrosion layer thickness evolution after cycling test is not, or very weakly, affected by silver for gravity cast technology and for rolled expanded technology.

The grid weight loss after cycling test has been measured and it is observed that for gravity cast grids, the effect of silver is not detectable, the total weight loss for gravity grids reaches about 9 g after the cycling test corresponding to about 10% of the grid. For rolled expanded grids, the effect of silver is also not significant, the total weight loss for expanded grids is lower than for gravity cast grids, about 7 g after the test, corresponding to 16% of the grid.

The chemical analysis of the positive active mass and of the negative mass were performed using wet chemical analysis and X-ray diffraction. Concerning the positive active material, no differences were observed for all the cases. The lead dioxide contents were near 100% for all the batteries. X-ray diffraction showed differences between the ratio $\beta/\alpha$ $PbO_2$, the positive grids from gravity cast technology showing a lower ratio. The measurement of $PbO_2$ crystallite size and the visual inspection of positive plates after cycling showed unambiguously that the failure mode for all batteries was softening of positive material. The analysis of the negative AM did not show any difference for all the cases.

After the TC69 cycling test of the batteries with different alloy composition and technologies, it can be pointed out that no effect of silver in the TC69 cycling test for both technologies was obtained.

Batteries with gravity cast technology gave poor results during the TC69 cycling test, whereas the batteries with rolled expanded grid technology gave better results, the capacity delivered was more or less stable until 250 cycles. A better behaviour of rolled expanded grids in terms of corrosion was observed, the corrosion proceeded more homogeneously and the weight loss of such grids was smaller than for gravity cast grids.

Analysis with X-ray diffraction showed unambiguously that the failure mode for all batteries was due to a softening of positive material.

In conclusion, the smaller batteries using rolled expanded technology gave better results in specific energy and better stability during the TC69 test. However, due to the softening failure mode, it is very difficult to relate directly the role of grid composition and grid technology to the behaviour of batteries in a cycling test.

## 4. Conclusion

The study of the influence of positive grid technology (gravity cast or rolled expanded) and the effect of silver additive has been carried out using battery prototypes tested in self-discharge, deep discharge and TC69 cycling with the view of electric vehicle application.

The effect of silver after self-discharge test of batteries is not significant or very low for both technologies. The differences observed between grid technologies are weak, but show a good behaviour of batteries using rolled expanded grids taking into account the weight of such grids for EV application.

The effect of silver with deep discharge test of batteries is significant only for gravity cast technology, but is limited. No effect of silver for rolled technology is observed. The differences observed between grid technologies show a better electrical behaviour of batteries using gravity cast grids after this test. However, the rechargeability test should be revised for the rolled expanded technology because recharge at 14.4 V is not the most efficient for rolled technology. The reason for this behaviour is probably the very fine and homogeneous metallographic structure for rolled expanded grids which, after deep discharge, can give more dense sulphate layers at the grid/active material interface. This phenomenon results in more difficult exchange with active material at the beginning of recharge after deep discharge. However, this good structural homogeneity will clearly prevent the risk of penetrating corrosion.

The evolution of the specific energy of batteries with TC69 cycling shows an important difference between the battery technologies, without any significant effect of silver. The batteries using rolled expanded technology give better results in specific energy and better stability during the TC69 test. An explanation of this behaviour could be again a more homogeneous grid/active mass interface giving a more homogeneous use of positive active mass. However, due to the softening failure mode, it is very difficult to relate directly the role of grid composition and technology to the behaviour of batteries in the cycling test; other parameters like positive active mass elaboration and battery design play a major role in such test.

## Acknowledgements

Authors would like to express their thanks to ILZRO — ALABC for financial support (AMC011 contract) and to Metaleurop and University of Nancy for collaboration. Special thanks are due to G. Mologni from CGA/Sinac for battery prototypes manufacturing.

## References

[1] P. Simon, N. Bui, F. Dubosi, J. Power Sources 50 (1994) 141–152.
[2] H.K. Geiss, in: K.R. Bullock, D. Pavlov (Eds.), Proc. Symp. Advances in Lead Acid Batteries, Proc. Vol. 84-14, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 241–251.
[3] R. Miraglio, L. Albert, A. El Gacham, J. Steinmetz, J.P. Hilger, J. Power Sources 53 (1995) 53–61.
[4] L. Bouirden, J.P. Hilger, J. Hertz, J. Power Sources 33 (1991) 27–50.
[5] D. Prengaman, J. Power Sources 67 (1997) 267.
[6] G. Clerici, J. Power Sources 33 (1991) 67–75.
[7] G. Fossati, R.C. Reuters, Batteries International 29 (1996) 40–46.
[8] D. Kelly, P. Niessen, E.M. Valeriotte, J. Electrochem. Soc. 132 (1985) 2533–2538.
[9] H. Geiss, J. Power Sources 53 (1995) 31–43.
[10] P. Rao, European Patent, No. 0 506 323 A1, 1992.