Journal of Power Sources 187 (2009) 599–604

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Lead-acid batteries for micro- and mild-hybrid applications[☆]

J. Valenciano*, M. Fernández, F. Trinidad, L. Sanz

Exide Technologies, R&D Centre, E-19200 Azuqueca de Henares, Spain

ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 11 November 2008
Accepted 12 November 2008
Available online 28 November 2008

Keywords:
Valve-regulated lead-acid batteries
Improved flooded batteries
Spiral wound
Stop–start
Microhybrid
Mild-hybrid vehicles

ABSTRACT

Car manufactures have announced the launch in coming months of vehicles with reduced emissions due to the introduction of new functions like stop–start and regenerative braking. Initial performance request of automotive lead-acid batteries are becoming more and more demanding and, in addition to this, cycle life with new accelerated ageing profiles are being proposed in order to determine the influence of the new functions on the expected battery life. This paper will show how different lead-acid battery technologies comply with these new demands, from an improved version of the conventional flooded SLI battery to the high performance of spiral wound valve-regulated lead-acid (VRLA) battery. Different approaches have been studied for improving conventional flooded batteries, i.e., either by the addition of new additives for reducing electrolyte stratification or by optimisation of the battery design to extend cycling life in partial state of charge conditions. With respect to VRLA technology, two different battery designs have been compared. Spiral wound design combines excellent power capability and cycle life under different depth of discharge (DoD) cycling conditions, but flat plate design outperform the latter in energy density due to better utilization of the space available in a prismatic enclosure. This latter design is more adequate for high end class vehicles with high electrical energy demand, whereas spiral wound is better suited for high power/long life demand of commercial vehicle. High temperature behaviour (75 °C) is rather poor for both designs due to water loss, and then VRLA batteries should preferably be located out of the engine compartment.

1. Introduction

New requirements for automotive batteries have been increasing significantly for a number of years, particularly due to the integration of more and larger loads into vehicle electrical systems. In addition, fuel saving measures are being considered that actively utilise the battery. Such measures involve different levels of powertrain hybridisation, ranging from micro to full hybrid applications [1]. Depending on the power requirements and location of the battery (in the engine compartment or the trunk) different battery designs could be proposed. No battery design alone represents up to date a solution, in terms of energy/power performance, life and cost goals, industrial development and recycling facilities, to cope with the stringent performance and cost demands of car manufacturers [2]. However, new vehicle functions demand battery working regimes mainly under partial-state-of-charge (PSoC) conditions that, in conventional flooded batteries, lead to premature capacity loss provoked by electrolyte stratification [3] and active material irreversible sulphation [4]. Changes in the demands on automotive batteries [5] are caused by increasing on-board power requirements, due to the introduction of new features in the vehicles, such as the replacement of mechanical by electrical functions (steer- and brake-by-wire, air conditioning, etc.) to provide enhanced safety and comfort, as well as of novel functions (stop–start, regenerative braking, etc.), aimed at achieving significant fuel consumption and emission savings.

Taking into account the above, two ways have been explored in order to meet these growing electrical demands. First, efforts have been made to increase the initial performance and partial-state-of-charge cycle life in "conventional" flooded batteries. Because AGM technology has a limited applicability in terms of heat sensitivity, improved 12 V systems could be an alternative to VRLA batteries in micro-hybrid applications (stop–start system that do not include regenerative braking capability) with the battery located in the engine compartment where high temperatures can be reached. However, AGM VRLA batteries are today the most effective solution for micro- and mild-hybrid applications due to their increased high rate perfomance (HRPSoC operation), extended cycle life, and reliability, although at the expense of a higher cost than the flooded ones. Two VRLA designs have been compared, a spiral wound design

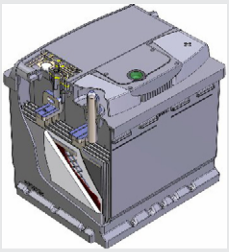
---

[☆] Presented at the 11th European Lead Battery Conference, Warsaw, Poland, 23–26 September 2008.

* Corresponding author. Tel.: +34 949 263 316; fax: +34 949 262 560.
E-mail addresses: jesus.valenciano@eu.exide.com (J. Valenciano), melchor.fernandez@eu.exide.com (M. Fernández), francisco.trinidad@eu.exide.com (F. Trinidad), leticia.sanz@eu.exide.com (L. Sanz).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.11.089

Table 1
Characteristics of improved flooded batteries for micro-hybrid applications.

Dimensions/$L \times W \times H$ (mm)	278 × 175 × 190	
Weight (kg)	20.1	
Nominal voltage (V)	12	
Nominal capacity, C_{20} (Ah)	72	
Reserve capacity (min)	120	
Cold cranking (A) (−18 °C, EN 50342)	640	

that provides an outstanding power capability and life under different cycling conditions [6–8], and a flat Plate design that has found to give a better capacity per volume and weight inside prismatic enclosures.

2. Design characteristics

2.1. Improved flooded batteries

Improved flooded 12 V batteries have been redesigned starting from current production batteries, by introducing a combination of a corrosion resistance alloy to withstand high operation temperatures and an optimised active material formulation to extend cycle life in moderate PSoC cycling. In a further development, batteries having a novel electrolyte recipe and a two-layer separator have been also built. The dimensions and electrical characteristics of improved flooded batteries are indicated in Table 1.

2.2. AGM VRLA batteries

Spiral wound VRLA batteries use lead–tin corrosion resistant grid alloys, thin plate highly compressed cell designs that allow for an efficient battery thermal management by means of air draught cooling systems, thus increasing operating life in warm environments. On the other hand, flat plate VRLA battery designs as presently used for automotive applications are optimised in terms of utilization of the available space for improving energy density and cycle life at low temperature. Comparative tests have been made on two different battery designs, shown in Fig. 1: spiral wound VRLA 12 V/50 Ah battery specifically developed for micro-hybrid vehicles with stop–start and regenerative braking functions, and a 12 V/70 Ah prismatic flat plate design currently used for high end class vehicles, mainly with high energy demand. Although sizes are not exactly the same due to cell configurations, the importance of cold cranking performance has been considered as the main criterium for battery selection (around 800 A is the typical demand for a medium size engine).

For both types cell design and active material formulations were optimised for increased charge acceptance and life under partial state of charge conditions. The dimensions and electrical characteristics of both battery types are indicated in Table 2.

3. Experimental

3.1. Electrical testing

Electrical testing of the batteries was carried out with computer controlled cycling equipment Bitrode LCN and Digatron BTS 500 for initial characterisation and cycle life tests of the batteries. Digatron UBT BTS-500 mod. HEW 2000-6BTS was used for high-rate discharges.

Preliminary characterisation of the batteries to determine specific energy and power capability of every system included capacity at 20 h rate and 5 h rate and reserve capacity (according to EN 50342 and car manufacturers standards), cold cranking at −18 °C (EN 50342 and SAE standards) and cold cranking simulation (CCS) at −25 °C (car manufacturer standard).

3.1.1. Stop–start profile

This test was carried out at 60 °C in a water bath. The cycling profile includes first a discharge period at a moderate current that

Table 2
Characteristics of VRLA batteries for mild-hybrid applications.

	Spiral wound design	Flat plate design
Dimensions/$L \times W \times H$ (mm)	260 × 173 × 206	278 × 175 × 190
Weight (kg)	18.0	20.6
Nominal voltage (V)	12	12
Nominal capacity, C_{20} (Ah)	50	70
Reserve capacity (min)	100	120
Cold cranking (A) (−18 °C, EN 50342)	800	760

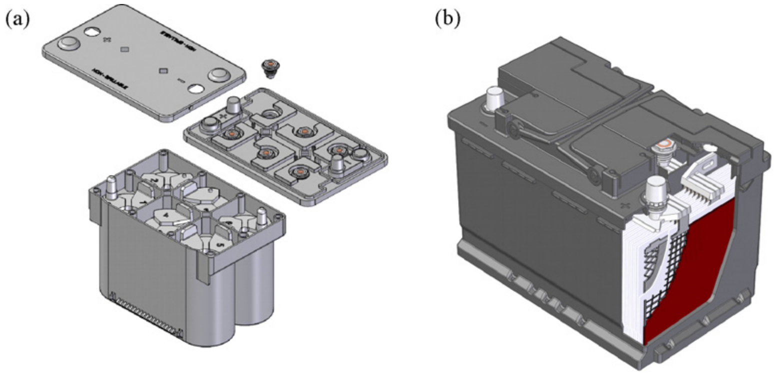


Fig. 1. Design of (a) 12 V/50 Ah spiral wound and (b) 12 V/70 Ah flat plate.

takes into account the standard consumptions of the vehicle. These consumptions are simulated by a discharge at about 1C rate. After that, a simulation of vehicle starting by means of a short duration (<1 s) high current discharge (300 s) is carried out, followed by a charge (at 14 V, limited to 80 A) to recover 90% of the previous discharged Ah. Every 50 cycles a boosting recharge is performed for 30 min at 14.5 V (limited to 80 A) and thus maintained SoC level along the cycling test.

3.1.2. Life test at 75 °C

The following test simulates automotive service when the battery operates at high temperature. The battery is tested in a water bath maintained at 75 °C, with series of 428 cycles that comprise 4 min discharges at 25 A and 10 min charges at 14.8 V (current limited to 25 A). After a stand time on open circuit in the 75 °C water bath to complete a week of testing, the battery is submitted to a cold cranking test (cut off voltage of 7.2 V or 30 s).

3.1.3. Shallow PSoC cycling at 17.5% DoD

Performance of the batteries according to moderate rate PSoC cycling conditions has been also checked at 50% SoC, with C/3 rate charges and discharges a 17.5% DoD. Every 85 cycles the batteries are fully recharged to check available capacity, weight and AC internal resistance.

3.1.4. Cycling at 50% DoD

This test is carried out in a water bath at a temperature of 40 °C after a deep discharge test, that consist of a C20 h capacity followed by a further discharge with a 10 W bulb. Depending of battery technology, batteries must fulfill at least 120 cycles for flooded design and 360 cycles for VRLA design, as follows: 2 h discharge at C/4 rate and 5 h charge at C/4 rate (14.4 V for VRLA and 16 V for flooded batteries).

4. Results and discussion

4.1. Specific energy

The sequence of initial capacity tests has been defined taking into account the requirements of car manufacturers for mild-hybrid vehicles with stop–start and/or regenerative braking functions. Basically consist in several capacity tests at different rates (20 h, 5 h and reserve capacity) followed by full recharge (24 h) at constant voltage (14.8 V for VRLA and 16 V for flooded version). As the technologies (flooded or VRLA), sizes and nominal values are not the same, for comparison purposes, the specific energy (in Wh kg^{-1}) has been calculated and shown in Fig. 2. The clear advantage of prismatic design (well above 40 Wh kg^{-1} in capacity at 20 h rate) is a consequence of better space utilization, whereas spiral wound design has lower specific energy due to heavy straps connection and acid limitation inside the cell. Under the particular requirement for high energy content (high end class vehicles), flat plate is a better choice than spiral wound design.

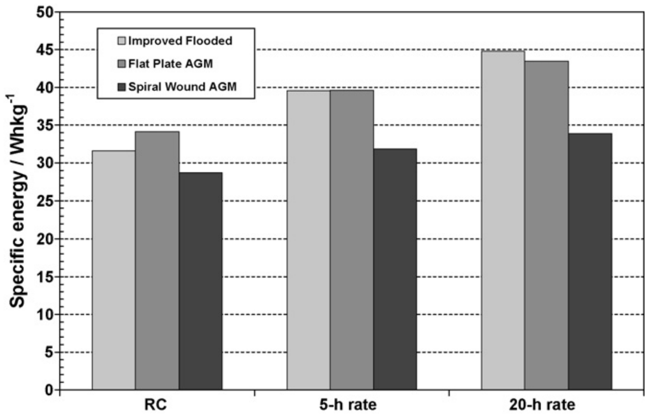


Fig. 2. Specific energy of improved flooded and VRLA batteries.

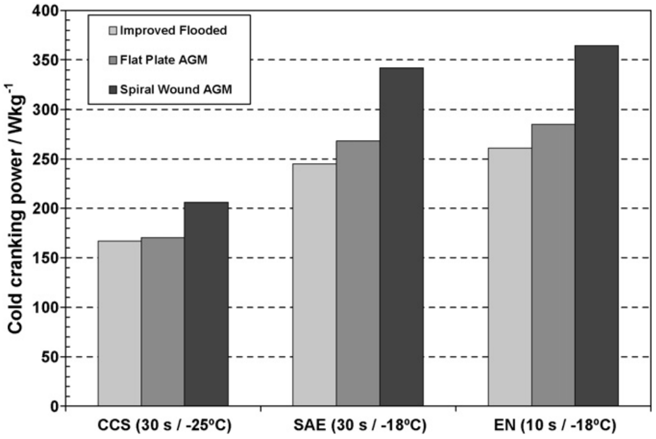


Fig. 3. Cold cranking power of improved flooded and VRLA batteries at different temperatures.

4.2. Cranking power

There are several cold cranking tests typically demanded by different car manufacturers depending on regional requirements (EN or SAE) and temperatures (−18 °C or −25 °C). In order to compare the results of the three types of batteries tested, a similar approach to the previous tests have been considered, that is calculating the specific power (in W kg^{-1}) at the time requested (10 or 30 s) and temperature. Cold cranking at −25 °C has been carried out at 410 A for 30 s independently of the design. Fig. 3 shows that spiral wound design is much better suited for high cold cranking demands (around 350 W kg^{-1} according to EN and SAE standards), i.e. for diesel engines and commercial vehicles, than prismatic design due to the possibility to use very thin plates with highly corrosion resistant alloys (soft lead–tin). Another reason for such high cold cranking power is the small distance between plates due to high compression applied to the wound cells. As a consequence, spiral wound design requires the use of heavy straps (for current conduction) that limits the energy density as previously mentioned. As expected, improved flooded batteries generally show the poorer cold cranking capability, although they present an enhanced performance at −25 °C when compared to their VRLA prismatic counterparts, probably due to a higher electrolyte availability at such temperature.

4.3. Cycle life tests

The batteries have been tested according to five different cycle life profiles and temperatures, simulating the most typical working conditions in mild-hybrid applications.

4.3.1. Stop–start profile

The battery working conditions in stop–start operation as described above represent around 1% depth of discharge (DoD) for prismatic designs but 1.4% DoD for spiral wound design due to the different rated capacity. Trying to simulate the most demanding ambient conditions in the engine compartment, temperature was controlled at 60 °C.

Fig. 4 shows the voltage evolution during the high rate discharge period along the stop–start profile test. As regards VRLA batteries,

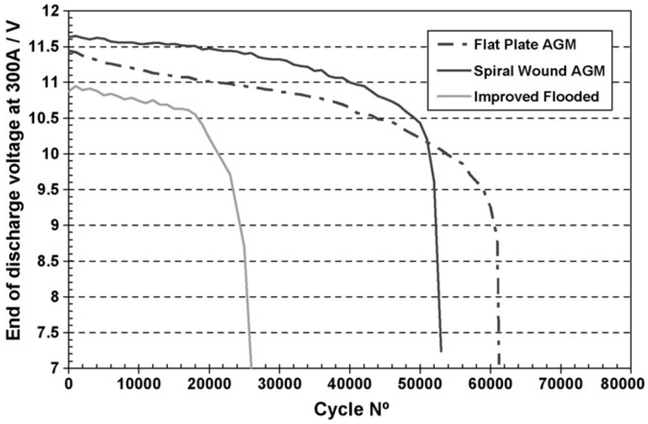


Fig. 4. Voltage evolution of improved flooded and VRLA batteries along stop–start cycle life test.

spiral wound samples completed 52,000 cycles before failure due to positive grid corrosion, whereas flat plate batteries fulfilled 61,000 cycles. Teardown analysis of prismatic samples confirmed also that the end of life of the batteries could be mainly due to positive grid corrosion in such a high temperature test. In spite of a shorter life when compared to flat plate AGM batteries, cranking performance along cycling for the spiral wound design is slightly higher due to the high plate surface and thinner space between the plates, which allows sustaining better the power demanded during the cranking period.

On the other hand, improved flooded batteries fulfilled only 25,000 cycles, being in this case the softening of positive active material the failure mode of this battery design. The advantages of a well-compressed cell configuration are demonstrated in this particular cycling profile.

4.3.2. *High temperature shallow cycling (SAE J240 at 75 °C)*

In order to evaluate possible differences at high temperature environments, like those achieved in hot regions with the battery in the engine compartment, the three battery designs were subjected to the well known SAE J240 cycling test at 75 °C. Fig. 5 shows the specific power evolution after every cycling unit. Both VRLA designs completed 6 units of 428 cycles, which is below the current car manufacture requirements for equivalent flooded battery types (7–10 units). Failure mode was found to be grid corrosion for spiral wound battery and negative active mass shrinkage for flat plate battery, although a significant water loss and grid corrosion were measured in both AGM types. With respect to flooded design, a conventional battery was tested in this case as control group. As can be seen in Fig. 5, this battery fulfilled 7 units, although with lower specific power values. This is a demonstration that, at the moment, VRLA batteries are not the best option for high temperature environments.

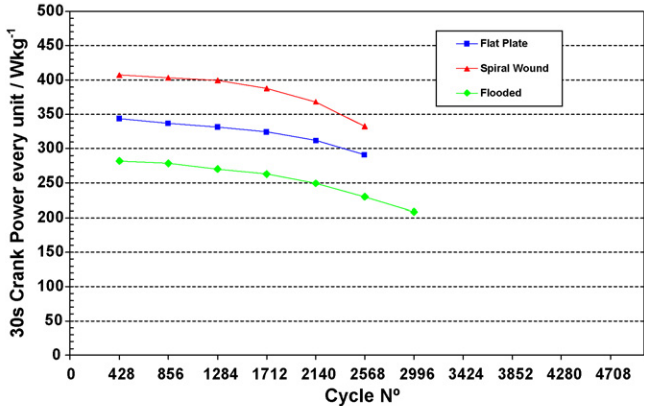


Fig. 5. Specific power evolution of flooded and VRLA batteries at 75 °C (SAE J240 cycling profile).

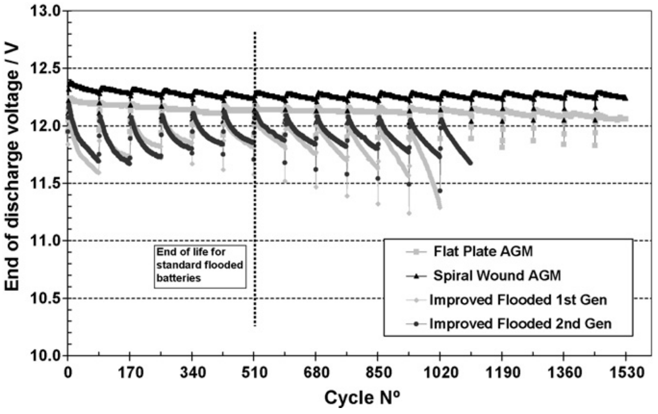


Fig. 6. End of discharge voltage evolution of improved flooded and VRLA batteries along 17.5% DoD PSoC cycling.

4.3.3. *Partial-state-of-charge cycling at 17.5% DoD*

The three different 12 V systems object of this study were tested under a moderate PSoC cycle life test, according to the profile that has been described above. Fig. 6 shows the end of discharge evolution during the shallow cycling at 50–67.5% SoC. Both the spiral wound and flat plate AGM designs completed the 18 life units requested by the car manufacturers for VRLA batteries, with higher end of discharge values measured in spiral configuration. Records of voltage evolution along every cycling unit show very small changes between the initial cycles and the end of cycling (due to the absence of stratification in properly designed VRLA batteries). The application of this type of batteries located out of the engine compartment is clearly most favoured than using standard flooded batteries.

However, some car manufacturers are trying to introduce improved flooded batteries for micro-hybrid applications that are capable at least to double the actual performance (6 units) of conventional batteries under this particular testing procedure. For that, an initial approach has been to modify the active mass (positive and/or negative) in order to cope with this new demand. Surprisingly, a first attempt just modifying the composition of the positive active mass in a standard flooded battery has been successful as the prototype with the new recipe has completed 12 units at 17.5% DoD (Fig. 6). In view of this encouraging result, a second generation of improved flooded batteries has been designed and built, further enhancing the positive mass formulation of the first prototypes. As can be seen in Fig. 6, higher values of end of discharge voltage have been measured when compared to 1st generation prototypes, and as consequence the cycle life has been extended by 1 unit (85 cycles).

Although a significant extension of required PSoC cycling life has been achieved just modifying the active mass recipe, the end of life of both “prototype generations” has been attributed to electrolyte stratification, which is the standard failure mode for current flooded batteries subjected to this particular cycling test. This “unavoidable” design defect that bring a calcium battery with it can be easily seen in Fig. 6: whereas AGM batteries maintain a quite stable end of discharge voltage through the cycling operation, flooded designs show a remarkable voltage decay that is only partially recovered after a fully recharge at the end of every unit.

For that, additional efforts have been directed in stabilise the voltage decline under PSoC conditions, trying to comply with the

Table 3
Initial electrical test results of 12 V/61 Ah batteries with novel electrolyte and/or non-woven separator.

Battery characteristics	C_{20} capacity (Ah)	Cold cranking EN 50342	
		$V_{10\,s}$ (V)	Duration to 6 V (s)
Standard	65.3	8.44	131
Novel electrolyte	56.4	8.10	122
Non-woven separator	61.7	7.90	108
Novel electrolyte + non-woven separator	51.7	7.57	109

current demands for micro-hybrid vehicles. The starting point has been the use of current flooded batteries, in which the novel modifications would be more easily followed. Two approaches have been considered, that are the use of a sulphuric acid electrolyte containing a special silica additive and/or a new separator including non-woven material.

A previous work showed that batteries containing low amounts of silica had higher and more stable end of discharge voltage along life [9]. Also, preliminary tests with non-woven polymeric materials combined with a standard polyethylene separator have shown an improved life by means of delaying positive active material softening and stratification.

Taking into account the above, new tests were planned trying to combine the effects of both silica-containing electrolyte and non-woven separator materials. These developments were introduced on a standard flooded battery size, that is, a 61 Ah/540 A rated battery. Initial electrical characterisation included capacity and cold cranking performance, as shown in Table 3. A control battery was also tested with standard electrolyte and current polyethylene separator.

Electrical results from Table 3 show a loss of electrical performance, both in capacity and cold cranking capability, for the batteries in which the new materials have been introduced. This negative impact is more acute for batteries containing the novel electrolyte, as capacity values of 56.4 and 51.7 Ah have been measured. However, the batteries with the non-woven separator, although with capacity and cold cranking values lower than those of the control sample, have shown to comply with the specification requirements.

However, more encouraging results have been found when the batteries were subjected to the PSoC life test at 17.5% DoD. Fig. 7 shows the end of discharge evolution through the cycling operation. The main effect of the new electrolyte composition was to significantly reduce the EDV drop when compared either to standard or non-woven mat-containing batteries. Additionally, the use of silica electrolyte allowed extending cycle life by two units. The use of non-woven separator had also a positive contribution as the batteries with this material endured 1 unit more than those with the standard polyethylene separator.

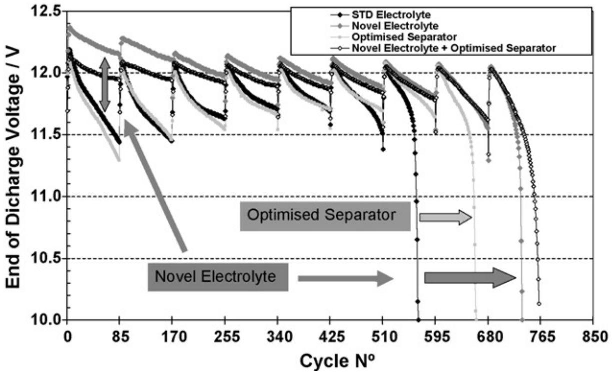


Fig. 7. End of discharge voltage evolution of flooded batteries with novel electrolyte and/or non-woven separator along 17.5% DoD PSoC cycling.

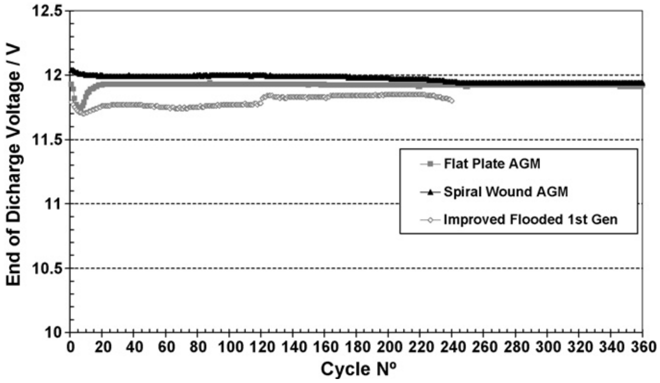


Fig. 8. Voltage evolution of improved flooded and VRLA batteries at 50% DOD cycling.

Taking into account these results together with the life improvements described above in batteries with optimised active mass formulation, a further work is directed in to combine properly all these findings. However, some drawbacks have to be overcome, as i.e. the loss of initial performance mainly in batteries with the silica electrolyte.

4.3.4. 50% DoD cycling tests after overdischarge

In order to determine the influence of the battery technology and cell design, a very demanding test has been performed consisting in an initial deep discharge of the batteries, followed by a cycling test at 50% DoD as described above.

Fig. 8 shows end of discharge voltage through the cycling operation. It can be observed a small initial decay (maybe due to some lead sulphate layers at the grid/active material interphase that disappear later during cycling) for batteries with flat plate design, although voltage is more quickly recovered for AGM technology. On the other hand, voltage for spiral batteries remains stable from the beginning not showing any signal of premature capacity loss (probably thanks to the high compression applied to the spiral wound cells). Anyway, the two VRLA systems have amply completed the 360 cycles requested by car manufacturers.

With respect to improved flooded 12 V system, a remarkable extension of cycle life at 50% DoD has been achieved for 1st generation prototypes, i.e., the ones with a modification in positive active material formulation when compared to standard flooded batteries. The improved prototypes have fulfilled at least 240 cycles, whereas the standard duration for current flooded batteries is around 120 cycles.

5. Conclusions

Depending of the final battery application, i.e., in micro- and/or mild-hybrid systems, different choices arise for a car manufacturer. Spiral wound VRLA batteries can provide above 350 W kg^{-1} as 10 s average cold cranking power at −18 °C, whereas flat plate battery can hardly deliver 300 W kg^{-1} in the same conditions. However, specific energy density is much higher for flat plate (40 Wh kg^{-1}) than spiral wound designs (30 Wh kg^{-1}). Applications of these two designs are strongly driven by power and energy requirements being more adequate the prismatic design for high end class with high energy demand, whereas commercial vehicle with diesel engines may better fit with spiral wound design due to the longer cycling achieved under deep cycling conditions [10]. Life tests under different partial state of charge conditions, simulating different hybrid vehicle operation conditions showed that both VRLA battery designs can provide a cost effective solution for energy storage systems in mild-hybrid applications, provided that the battery temperature do not exceed 60 °C. Because of the higher battery temperature in the engine compartment (up to 75 °C), spiral wound VRLA design is probably a better choice due to the possibility to reduce internal cell temperature by air cooling. Finally, deep discharge behaviour (>50% DoD) could be a very important requirement for mild-hybrid applications due to the fact that under heavy traffic conditions the average state of charge could be very low. Both VRLA battery design exceed the cycling performance of flooded batteries, although spiral design have longer cycle life due to the higher compression applied to the wound cells.

However, for high temperatures in the engine compartment (up to 75 °C) and/or a desired lower cost, an improved flooded battery is probably the best choice for micro-hybrid applications, since new developments in active material formulation, electrolyte composition and the use of two-layer separator materials, have permitted to increase significantly cycle life of standard flooded batteries, both in moderate PSoC and 50% DoD cycling operation.

References

[1] E. Karden, S. Ploumen, B. Fricke, T. Miller, K. Snyder, Journal of Power Sources 168 (2007) 2–11.
[2] E. Karden, P. Shinn, P. Bostock, J. Cunningham, E. Schoultz, D. Kok, Journal of Power Sources 144 (2005) 505–512.
[3] D. Berndt, Journal of Power Sources 100 (2001) 29–46.
[4] P. Ruetschi, Journal of Power Sources 127 (2004) 33–44.
[5] P.T. Moseley, D.A.J. Rand, Journal of Power Sources 133 (2004) 104.
[6] F. Trinidad, F. Sáez, J. Valenciano, Journal of Power Sources 95 (2001) 24–37.
[7] J. Valenciano, A. Sánchez, F. Trinidad, A.F. Hollenkamp, Journal of Power Sources 158 (2006) 851–863.
[8] M.L. Soria, F. Trinidad, J.M. Lacadena, A. Sánchez, J. Valenciano, 168 (2007) 12–21.
[9] J.C. Hernández, M.L. Soria, J.C. Hernández, M. González, E. García-Quismondo, A. Muñoz, F. Trinidad, Journal of Power Sources 162 (2006) 851–863.
[10] F. Trinidad, J. Valenciano, Proceedings of the Eighth International AABC Conference, Tampa, USA, May, 2008.