Development of high power VRLA batteries using novel materials and processes

M.L. Soria[a,*], J. Valenciano[a], A. Ojeda[a], G. Raybaut[b], K. Ihmels[c],
J. Deiters[c], N. Clement[d], J. Morales[e], L. Sánchez[e]

[a]*Global R&D Centre, Tudor (Exide Technologies), Carretera N-II, km 42, E-19200 Azuqueca de Henares, Spain*
[b]*R&D Department, MGE UPS Systems, 140 Av. Jean Kuntzmann, ZIRST Montbonnot Saint Martin, F-38334 Saint Ismier, France*
[c]*Technology Centre, Daramic, Erlengang 31, D-22844 Norderstedt, Germany*
[d]*Bernard Dumas, B.P. 3, Rue de la Papeterie, F-24100 Creysse, France*
[e]*Departamento de Química Inorgánica, Universidad de Córdoba, Campus Rabanales, Edificio C3, 1° Planta, E-14071 Córdoba, Spain*

Abstract

Nowadays UPS manufacturers demand batteries with very high specific power and relatively low specific energy, because most mains failures can be defined as ''microfailures'', usually of the order of seconds. Due to this fact, it is not necessary to provide energy but power. Within a 3-year EU funded project, a new AGM valve-regulated lead–acid battery with weight and volume substantially reduced, as well as a substantial improvement in its reliability, is under development. These aspects can provide the achievement of a more efficient, safe and economic energy supply.

Battery specific power is practically related to electrode area, so that its increase, and therefore an electrode thickness reduction, appear essential to achieve the project objectives. Furthermore, it is necessary to achieve a similar reduction in the conventional glass microfibre separator. But such thin material should have improved mechanical properties and can make the battery more prone to develop short circuits across the separator. In order to avoid this problem, a new microporous polyethylene membrane has been developed and tested, with excellent mechanical properties, high porosity and low pore size. For these reasons, the final separator configuration includes a combination of both materials, improved non-woven glass microfibre and the polyethylene membrane.

Batteries are designed and assembled by Tudor (Exide Technologies) as battery manufacturer and will be tested in real conditions by MGE UPS Systems as end user. Daramic for the membrane and Bernard Dumas for the glass microfibre mat, have developed and supplied the separators, while the Inorganic Chemistry Department of Córdoba University carries out fundamental research studies on very thin electrodes.
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1. Introduction

High power lead–acid batteries have traditionally been linked to automotive applications, mainly for vehicle starting, even at low temperatures. However, novel industrial and automotive applications, such as 42 V and hybrid vehicles, demand an improved battery performance in terms of ultra high power capability and cyclability. The use of advanced battery technologies, such as nickel–metal hydride or lithium-ion batteries, can provide such a performance, but cost is a quite restrictive factor for most of the industrial and automotive applications. This fact has led to the definition in past years of new research projects aimed at the development of advanced lead–acid batteries, with increased power capability, life and reliability, provided through the use of novel materials currently under development [1–4].

One of these running projects is focused on the development of ultra high power valve-regulated lead–acid (VRLA) batteries for uninterruptible power supply (UPS) applications [5]. Nowadays UPS manufacturers demand batteries with very high specific power and relatively low specific energy, because most mains failures can be defined as ''microfailures'', usually of the order of seconds. Due to this fact, it is not necessary to provide energy but power.

UPS systems have achieved a widespread use in a lot of electronic equipment, especially for consumer, office and telecommunication applications. For consumer and office applications the most important use is for computers to protect information. In telecommunications, they must support the commutation systems in case of mains failure. Today, from smaller to bigger installations, VRLA batteries

* Corresponding author. Tel.: +34-949-263-316; fax: +34-949-262-560.
E-mail address: soriaml@tudor.es (M.L. Soria).

are the preferred choice, due to their intrinsic characteristics of lack of maintenance, ease of installation, even in the rack of the commuting equipment, no gas release, clean product, and cost [6].

Although some applications require a long autonomy, in most of cases the general trend is to a reduction of the autonomy. The main reasons are:

- Due to the type of mains failure normally occurring, electrical failures are generally of short duration, in the range of seconds or minutes, most of them being included in what can be termed as "microfailures".
- Besides, some customers have a motor generator, and the battery is used only during the motor starting (15–30 s).

For small power UPSs, with conventional AGM lead batteries currently used, the minimum back-up time is around 3 min. The discharge rate is up to $8C_{10}$. At this rate, only 33% of the battery capacity can be used and therefore the limit of conventional VRLA technology is reached. The increasing demand for short autonomies is today satisfied by alternative and more expensive technologies such as flywheels and supercapacitors.

The trends for future needs in the UPS market are:

- *Footprint reduction*: In a computer room, footprint is expensive.
- *Size reduction*: As an example, for a rack version, not to exceed 44.45 mm.
- *Back-up time reduction*: Today, most power failures are short. In case of a customer equipped with a motor generator, the battery power is needed only during the starting period (15 s to 1 min).
- *Cost reduction*: A battery optimisation should induce a cost reduction.

The aim of this project is therefore to develop a new battery with weight and volume significantly reduced, as well as a substantial improvement in its reliability. These aspects can provide the achievement of a more efficient, safe and economic energy and power supply. Table 1 summarises the performance targets.

The battery under development is mainly focused on the UPS market, in order to be able to use such equipment in portable applications as well as in telecommunication cabinets. The improved performance of this new battery could also have application in 42 V automotive systems [7].

Battery specific power is practically related to electrode area, and its increase appears essential to achieve the project objectives. Within this project, the use of novel grid materials and grid manufacturing techniques that would allow an electrode thickness reduction, are studied. Therefore, the use of alloys with improved corrosion resistance is required [8]. Furthermore, it is necessary to achieve a similar size reduction in the conventional glass microfibre separator. But such thin material should have improved mechanical properties, for an adequate handling during the battery manufacturing processes, and can make the battery more prone to develop short circuits across the separator during the filling and formation (hydration shorts) or during battery life. In order to avoid this problem, a new microporous polyethylene membrane has been developed and tested, with excellent mechanical properties, high porosity and low pore size. For these reasons, the final separator configuration includes a combination of two materials: improved non-woven glass microfibre and the polyethylene membrane.

Moreover, the microporous membrane can provide an adequate barrier to oxygen generated during charge: as the saturation level in the separator decreases, the oxygen cycle draws an increasing amount of charging current, thus causing the negative plate depolarisation observed as the failure mode in VRLA batteries during stand-by and cyclic use [9]. The membrane should slow down the transfer of oxygen to the negative plate, allowing a more complete recharge of the plate before oxygen recombination takes place.

Therefore, several separator manufacturers are developing novel separator materials, as key components to improve the AGM battery life, such as multilayered AGM materials and hybrid separators. Multilayered materials [10] are composed of two layers of materials with finer fibres close to the positive plates to provide suitable electrolyte delivery during battery cycling and to avoid acid stratification and coarser fibres close to the negative plates to allow for free electrolyte access and increased gas diffusion. It has also been reported to include a membrane between the two AGM layers (80% porosity and 3–5 μm average pore diameter). Hybrid separators [11] include synthetic fibres that provide not only improved mechanical properties, but hydrophobic sites to

Table 1
Project performance targets

Characteristics	At start	Mid-term performance	At the end of the project
Weight (kg)	16	6	6
Volume (dm³)	5.5	2	2
Specific power[a] (W/kg)	80–100	>400	>600
Power density[a] (W/dm³)	230–290	>1000	>1500
Specific energy (Wh/kg)	30	30	30
Cycle life (IEC 896-2)	>300	400	>600
Calendar life (floating, in years)	3	>3	3–5
Cost (€/kWh)	<100	<100	<100

[a] Specific power measured in a 30 s discharge at $20C$ A, 70% SOC and room temperature.

offer controlled wetting properties and modification of the recombination process as well.

2. Experimental

The parallel development of the different battery components has been performed by the specific project partners.

Daramic has prepared and characterised polyethylene membrane samples in three consecutive steps. The material characteristics were redefined in each step according to the physical and electrical properties of the samples and to the results obtained in the electrical testing of cells and batteries prepared with the membranes in comparison to batteries with a standard AGM separator. Membrane samples were prepared as sheets in the laboratory and finally as rolls of optimised material prepared in pilot installation. The physical, mechanical and electrical characterisation of the samples was performed using internal procedures. Volume porosity was calculated from water-filled separator buoyancy and water-filled pore volume as measured by dry weight and wet weight in air and water. Average pore size was determined with a mercury intrusion porosimeter Porotec model 2000, the electrical resistance was measured in a cell with constant dc current in sulphuric acid, density $1.28 \, g/cm^3$, at $27 \, ^\circ C$ and the puncture strength with a motorised Chatillon TCM-201-M test stand.

Bernard Dumas has prepared and tested AGM materials as laboratory handsheets, in comparison to standard composition samples. They have also prepared samples of AGM materials with different thicknesses, to be used in the different groups of prototypes, according to the acid reservoir needs. Characterisation included both physical parameters as well as mechanical properties. Tensile strength and elongation were measured with a MTS DY20B according to BCI IIX34-1 specification, the specific surface with a BET nitrogen micromeritics analyser, according to BCI VI34-1, the capillarity rise with an internal procedure in sulphuric acid $1.26 \, g/cm^3$, the porosity was calculated from the basis weight measurement (g/m^2) according to BCI III34-1 and the thickness was measured under 10 kPa according to BCI II34-1 using an Adamel Lhomargy model MI-21 micrometer.

For the investigation of thin layer electrodes at the University of Córdoba, the positive plates were prepared by mixing lead oxide with water and sulphuric acid and using lead–tin–low calcium grids of dimensions $40 \, mm \times 75 \, mm \times 0.35 \, mm$ as substrate. The plates were obtained by applying manually the paste on both sides and by controlling the plate thickness with a roller, consisting of two metallic cylinders, whose separation can be varied according to the electrode thickness required. Curing was done at $55 \, ^\circ C$ at a relative humidity about 98% for 2–12 days. Then, the plates were dried at $55 \, ^\circ C$ for 1 day. Negative plates and AGM separators were conventional ones used in standard batteries. The electrolyte used in all measurements was a sulphuric

acid solution of specific gravity $1.28 \, g/cm^3$. The electrochemical formation of the positive active material (PAM) was accomplished by charging the cell 600% over the nominal capacity as calculated from the amount of deposited material and a typical benchmark of 8.5 Ah/g. The process was carried out in two steps: 8 h to reach 60% of the total capacity and 12 h for the remaining 40%. After formation, cells were subjected to cycling tests under different discharge regimes. All discharge measurements were performed up to a depth-of-discharge (DOD) of 60%. The cells were recharged 110% of the previous discharge capacity. Phases were identified, and their composition and morphology determined by combining X-ray powder diffraction (XRD), chemical analysis and scanning electron microscopy (SEM). Formation and cycling tests were carried out using a Solartron battery testing 1740 A model.

Finally, Tudor (Exide Technologies) has prepared 2 V cells and 12 V batteries with commercial ABS containers sized $180 \, mm \times 75 \, mm \times 150 \, mm$, which are commonly used in the manufacturing of 15 Ah gel VRLA batteries for stand-by applications. Positive and negative plates were prepared in a standard continuous manufacturing line, cured under standard conditions and then they were cut to size and stacked manually. A manual cast-on-strap (COS) tooling was used to weld the plate lugs and finally the ABS case and cover, and the valves were welded with a laboratory ultrasound device. The nominal capacity of the cells and batteries was defined as 18 Ah at the C_8 rate and 15 Ah at the C_1 rate. Electrical testing was carried out with computer controlled cycling equipment: Bitrode LCN-3-100-12 with modules CSM-6-100-12 for the 2 V cells and Bitrode LCN-7-100-12 and Digatron UBT BTS-550 ZLEG 300/150 for the 12 V batteries. High rate discharges of cells and batteries were performed with a computer controlled Digatron UBT BTS-500 model HEW 2000-6BTS. Electrical testing included initial capacity check at different rates, power capability under constant power discharges, at rates ranging from 500 to 3000 W down to 9 V, and life under floating and deep cycle conditions. The floating test at 2.27 V per cell was accelerated at $55 \, ^\circ C$. Capacity evolution at the C_8 and C_1 rates was checked every 42 days. According to the Arrhenius law, each 42-day unit at $55 \, ^\circ C$ corresponds to 1.3 years of floating life at room temperature $(20 \, ^\circ C)$. Cycle life was carried out according to IEC 896-2 specification, with 60% DOD discharges. Capacity evolution at the C_{10} rate was checked every 50 cycles. A tear-down analysis of the batteries was performed to establish the failure mode.

3. Results and discussion

3.1. Development of membrane separator

The development of thin membranes for AGM batteries with thin plate designs has been based on previous experience of Daramic in microporous polyethylene materials for

Table 2
Properties of membrane separators

	Preliminary samples (02.01)		Alternative separator (optimised version)	
	Alternative separator (first version)	AJS	Sheets (09.01)	Rolls (05.02)
Thickness (mm)	0.36	0.36	0.15	0.14
Electrical resistance (mΩ cm^2)	44	25	20	20
Porosity (%)	71.5	80.7	75.2	75.1
Average pore size (μm)	0.14	0.22	0.13	0.16
Drying shrinkage (%)	−4.2	−15.1	−4.1	−3.3
Puncture strength (N)	6.3	4.0	6.8	4.8

SLI conventional batteries [12] and for VRLA batteries for deep cycling applications [13,14]. Besides microporosity for the prevention of short circuits, high porosity and low electrical resistance, as well as good mechanical properties at lowest possible thickness, are the desired features for this separator.

At the project start, preliminary samples of two separator versions with a backweb thickness of 0.36 mm were produced and characterised. The first version was the Daramic development product Acid Jellying Separator (AJS) as described in the US Patent 6,124,059. The second version was an alternative separator with a lower porosity and higher electrical resistance, but advantages for the drying shrink and some mechanical properties. The physico-chemical properties of both separators are compiled in Table 2.

These preliminary membrane samples were tested in valve-regulated 2 V cells and compared to standard AGM materials.

To assure the acid content and a high stack compression degree, two layers of AGM material were used in combination with the membranes. The discharge capability of the cells at different discharge rates is shown in Fig. 1. Results show that the capacity and power capability of the three groups of cells with different separator combinations are quite similar, even though the electrical resistance of the membranes is higher than that of the AGM standard separator, due to the lower membrane porosity. Moreover, Fig. 2 shows that the specific power in a 10 s discharge and the internal resistance of the three types of cells at different states of charge is quite similar whichever separator combination is used. This behaviour indicates that any interlayer contact resistance between the different separators materials can be neglected, due to the high stack compression.

Due to the equivalent cell test results obtained with both membrane types, it was decided to proceed with the
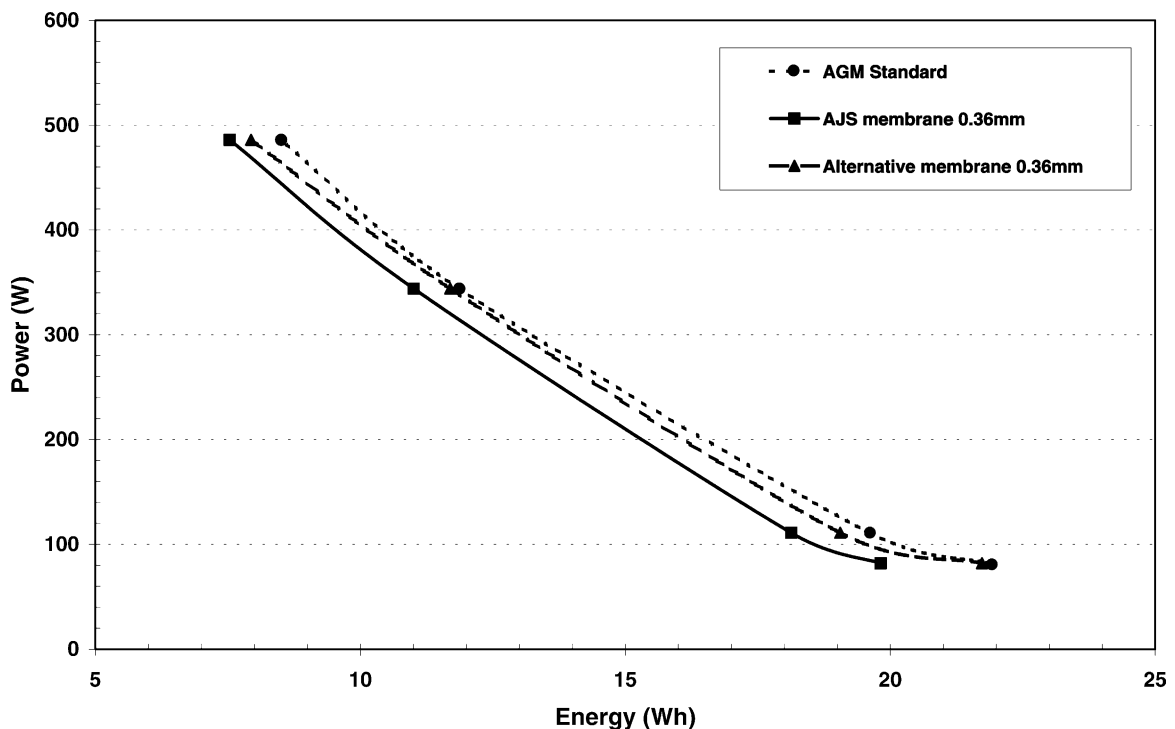

Fig. 1. Plot of battery power vs. energy of 2 V cells with preliminary membranes and AGM separator.
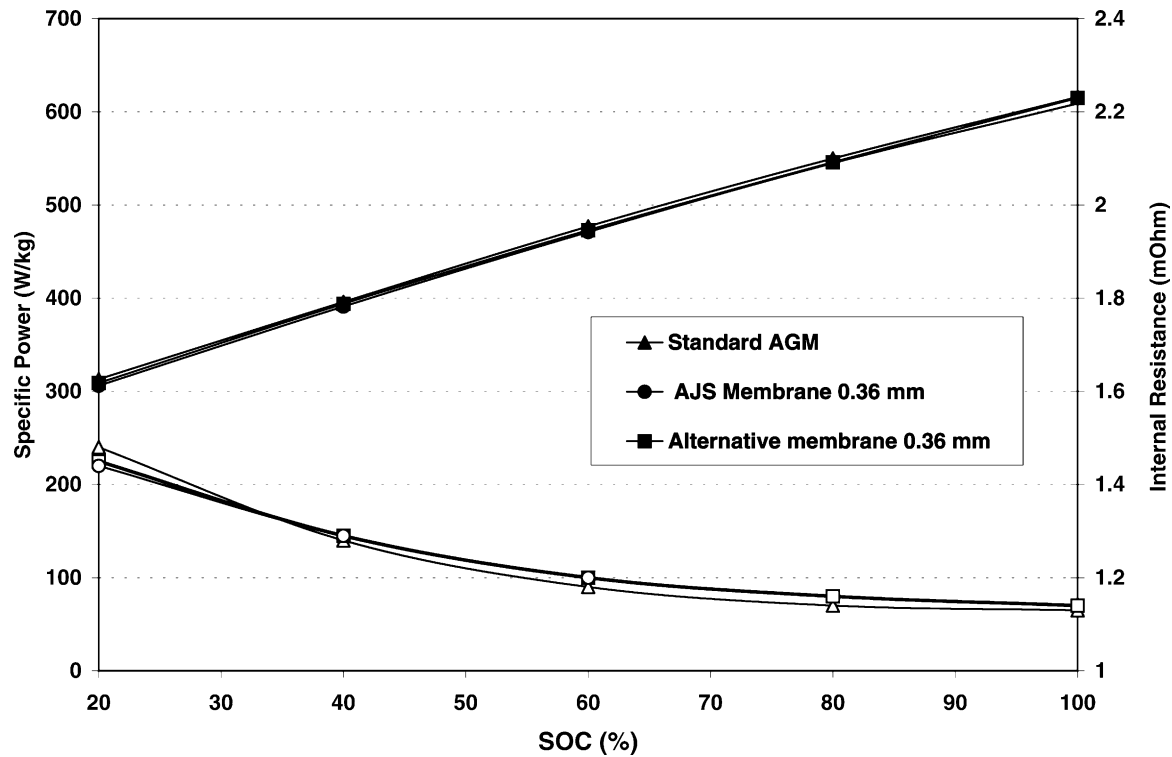
Fig. 2. The 10 s power capability (■) and internal resistance (□) at different SOC of 2 V cells with preliminary membranes and AGM separator.

alternative separator due to its favourable drying shrink and cost, as well as its potential for further thickness and electrical resistance reduction. Pilot trials for the optimisation of thickness, electrical resistance and porosity were performed, which resulted in separator properties as compiled also in Table 2. As shown, a strong reduction in the material electrical resistance (from 44 to 20 $m\Omega\ cm^2$) was achieved by means of the thickness reduction and the porosity increase up to 75%. The average pore diameter was 0.13 μm. Sheet samples of the optimised alternative membrane with a thickness of 0.15 mm were provided for extended testing in 12 V batteries, in comparison to standard AGM separator. Two different thickness of AGM materials

were used in the batteries with the optimised alternative membrane, leading to two different compression degrees of 20 and 28%, whereas the compression degree in the standard AGM batteries was 25%.

The electrical testing conditions and results are shown in Table 3. Although the three groups of batteries show similar initial internal resistance values, the constant power discharge durations are shorter in the batteries with the membrane and the thinner AGM material. The higher compression degree in prototypes with the membrane and thicker AGM material seems to prevent any contact resistance between the different separator layers. This effect is also shown in the electrical resistance values, which are

Table 3
Electrical testing of batteries with AGM separator and optimised alternative membrane (09.01)

|	Testing conditions	Standard AGM	Optimised membrane, low compression	Optimised membrane, high compression
Capacity (Ah)	C_{20} (0.9 A)	17.2	17.6	18.0
	C_8 (2.25 A)	17.0	17.1	17.6
	C_1 (15 A)	14.0	14.2	13.9
Constant power discharges ($V_{min} > 9.0$ V)	500 W	14.7 min	14.3 min	14.9 min
	650 W	10.6 min	10.4 min	10.45 min
	1100 W	5.1 min	5.15 min	5.2 min
	1500 W	3.15 min	3.10 min	3.15 min
	2500 W	1.35 min	1.15 min	1.30 min
	3000 W	50 s	43 s	48 s
Internal resistance (mΩ)		5.8	5.9	5.8
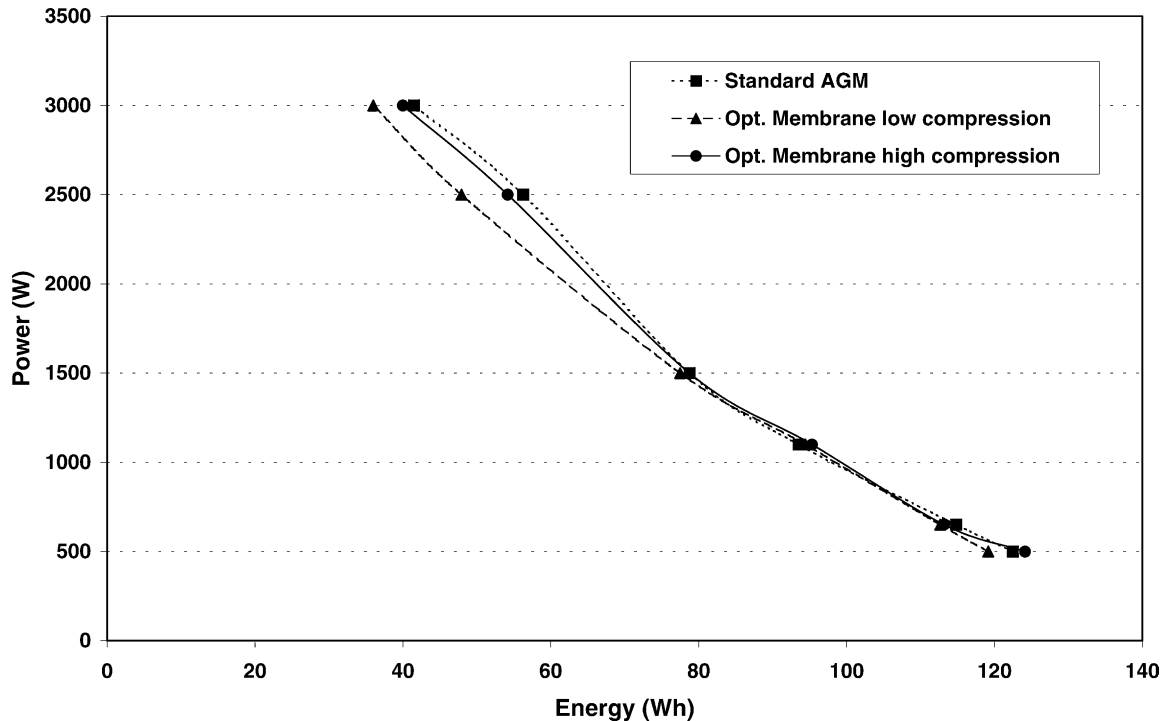
Fig. 3. Plot of battery power vs. energy of 12 V prototypes with optimised membrane and standard AGM separator.

quite similar for the batteries with standard AGM and with optimised membrane and high compression.

The power capability of the three prototype groups is shown in Fig. 3, where it is clearly shown that the rate capability of the three groups, with standard AGM separator and optimised membrane, is similar up to the 1500 W discharge. Over that value, the prototypes with optimised membrane and a high compression degree show a behaviour similar to prototypes with standard AGM separator, whereas the batteries with optimised membrane and lower compression degree show poorer constant power discharge durations. Therefore, the compression degree is critical for the power capability when membranes are used: the inter-phase resistance between the different separator layers becomes significant when the stack compression decreases.

In the accelerated floating test at 55 °C, the prototypes showed significant capacity decay after the third testing unit, which is equivalent to around 3 years of floating service at 20 °C.

The capacity evolution of the three types of batteries in the cycle life test according to IEC 896-2 specification (60% DOD) is represented in Fig. 4, and is quite similar: batteries fulfil over 300–350 cycles and tear-down analysis showed softening of the positive active material. This result can be considered quite satisfactory taking into account the low thickness value of the electrodes used to prepare the batteries.

Furthermore, in order to check the recombination efficiency of the batteries with membrane separator, 12 V batteries with optimised alternative membrane and standard AGM separator have been continuously overcharged at the

C_{50} rate (0.36 A) during 530 h. The weight loss was used to calculate the minimum recombination efficiency figures shown in Fig. 5. After initial poor recombination values (50–60%) ascribed to a too high separator saturation degree (slight electrolyte excess), both types of batteries reached high recombination efficiency values, around 96–98%, which are considered quite satisfactory for the application as the charging rate used in this test was much higher than the real rate on floating conditions.

Finally and due to the satisfactory testing results obtained, roll form samples of alternative optimised membrane have been extruded, extracted and evaluated. The main material characteristics are also included in Table 2. This material will be used to prepare the batteries to be tested in benches and in real UPS working conditions.

3.2. Development of non-woven AGM material

The thin microglass paper developed by Bernard Dumas had to combine mechanical strength, to be able to be used in the battery manufacturing process, and good acid absorption. Work has focused on the investigation of different compositions to find out what could be the best compromise of strength and good AGM behaviour (through specific surface area and capillarity rise). Fields of investigation explored and results obtained are detailed in Table 4 and can be summarised as follows:

- *Microfibre glass mixture*: Using experimental design, the best ratio of fine, coarse and chopped strand has been explored. At this step the conclusion was that the best
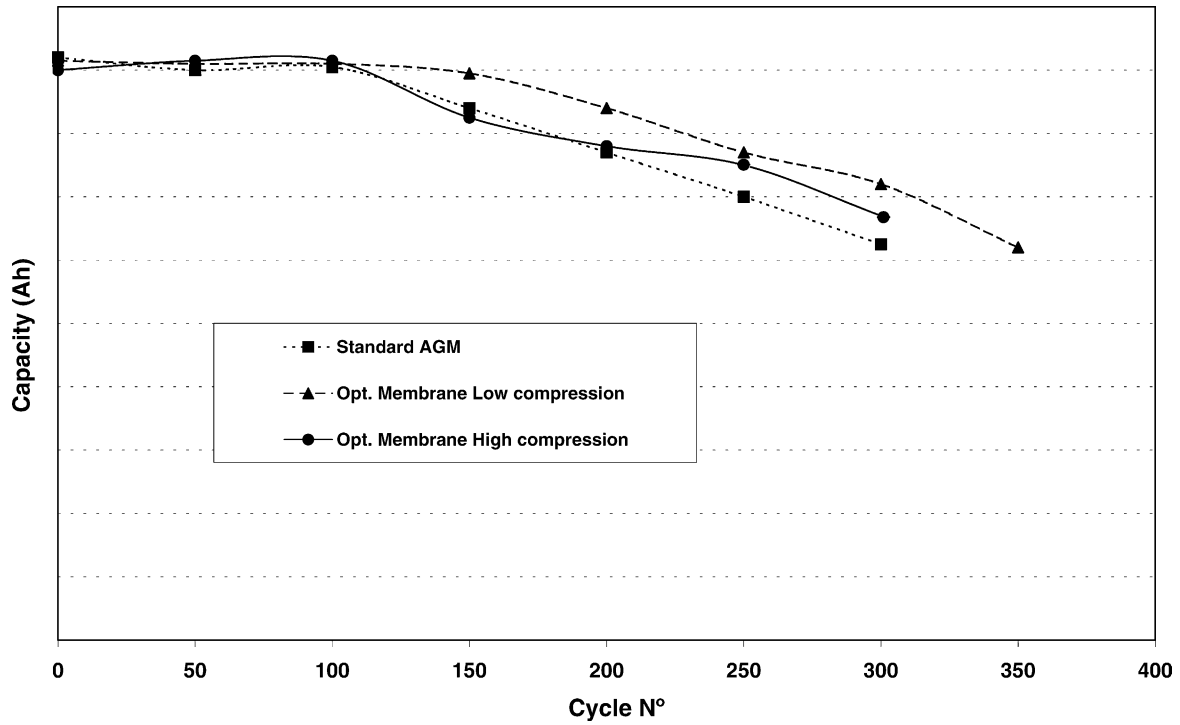
Fig. 4. Cycle life of 12 V prototypes with optimised membrane and standard AGM separators (IEC 896-2, 60% DOD).
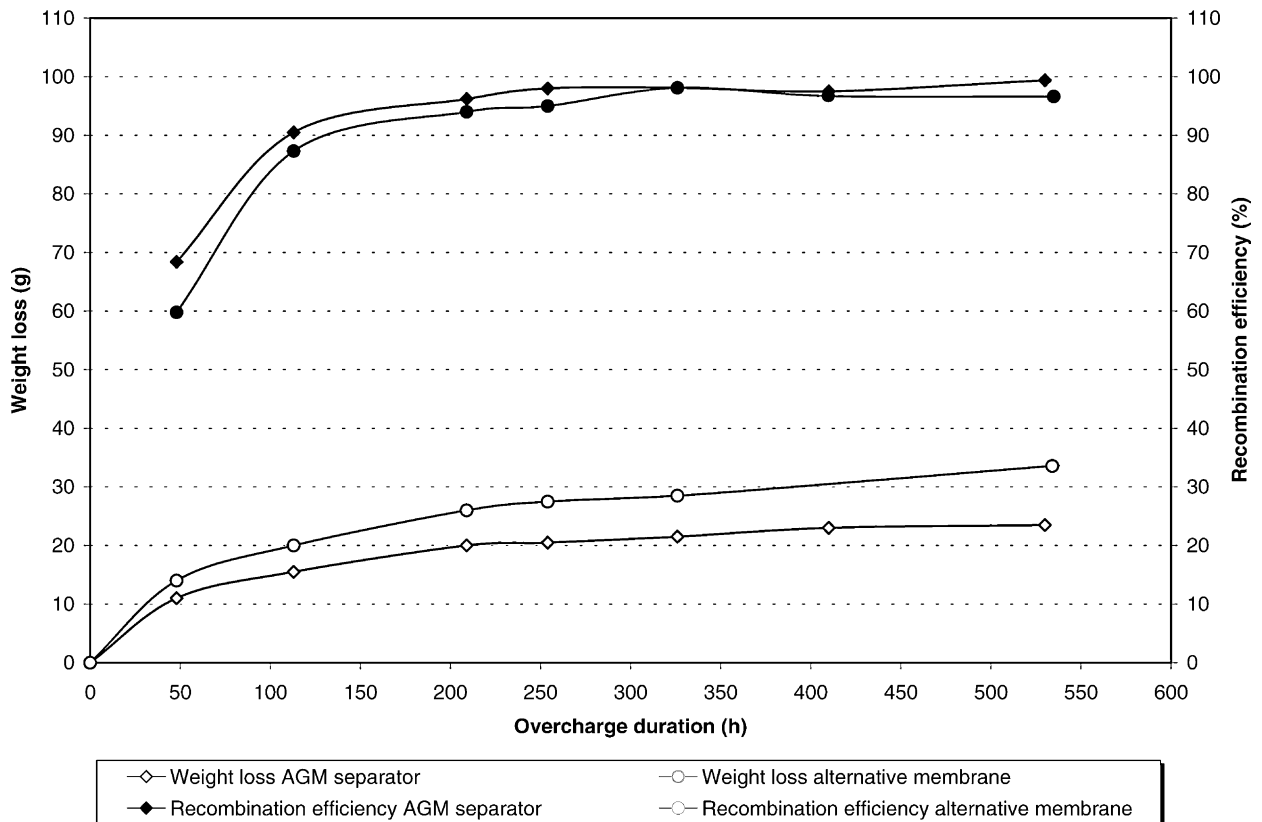

Fig. 5. Recombination efficiency and water loss of 12 V batteries with optimised membrane and AGM separators.

Table 4
Optimisation steps and characteristics of AGM materials

	Standard pasting paper	Experimental design, glass composition	Synthetic fibre content	Synthetic fibre length	Synthetic fibre diameter	Latex binder addition	Hydrophilic soluble binder addition (1%)
Glass composition	12% Chopped strand + 88% fine fibre	30% Chopped strand + 70% fine fibre	30% Chopped strand + 70% fine fibre	12% Chopped strand + 88% fine fibre	30% Chopped strand + 70% fine fibre	12% Chopped strand + 88% fine fibre	30% Chopped strand + 70% fine fibre
Synthetic fibre							
Percentage	14	14	30	14	30	14	30
Length (mm)	5	5	5	10	5	5	10
Diameter (dtex)	2.2	2.2	2.2	2.2	1.7	2.2	2.2
Tensile strength (daN/in., 100 g/m²)	1.8	2.38	3.74	2.01	3.56	2.7	4.55
Percentage improvement vs. standard	–	37	110	12	98	50	150
Elongation (%)	3.29	2.23	3.53	6.02	6.02	1.4	5.05
SSA (m²/g)	1.6	1.32	1.09	1.49	1.09	1.47	0.91
Capillary rise (mm, 2 min H₂SO₄)	43	42	42.3	43.5	43	37	43
Porosity (%)	92.7	92	92	92.8	92.6	92.4	92.2

results concerning glass ratio were obtained at 30% chopped strand and 70% glass.

- *Synthetic fibres type*, *amount*, *diameter and length*: This large study has shown that the best results were obtained with 10 mm, 2.2 dtex bicomponent fibres.
- *Binder addition*: Results concerning this point have shown a very high improvement in mechanical characteristics but with a high decrease in acid absorption. Latex solutions were sprayed on the humid handsheets and some hydrophilic binders have been added to the mixture.

Results obtained show that the final best compromise (fifth column in Table 4, under synthetic fibre length) was a mixture of:

- fine microglass fibre for acid absorption properties (77% glass, $\varnothing < 1\,\mu m$);
- chopped strand, for stiffness at low price (9%, 6 mm length, $\varnothing = 11\,\mu m$);
- long and big diameter bicomponent synthetic fibre (14%, 10 mm length).

3.3. Development of thin electrodes

One of the main drawbacks of conventional lead–acid batteries is the low energy density due to the excessive weight of the active and non-active components. Substantial weight reductions can be achieved in two complementary ways, viz.: (i) by using very thin lead-based alloy substrates (e.g. in the form of foil) [15]; or (ii) by reducing the layer thickness of the active paste applied to the lead substrate, thus increasing the active material efficiency.

The University of Córdoba has recently demonstrated the usefulness of a spray method for preparing lead oxide thin films and their potential as positive active mass for lead−acid batteries [16]. Furthermore, they have also explored a controlled pasting method using a special roller to obtain thin electrodes with improved adhesion of the active material to the grid, in order to avoid a premature electrode capacity decay. The coatings thus obtained have been characterised in textural and structural terms, and the electrochemical properties of the resulting cells have been determined. The positive electrodes prepared had a final thickness of 0.55 mm, a value notably lower than those commonly reported [17].

Fig. 6a and b show the X-ray diffraction patterns for the lead oxide before soaking and after curing at 55 °C for 6 days. These processes promote formation of new phases, 3BS (14%) and 1BS (7%), with the subsequent reduction in the content of the starting phases, Pb (14%) and PbO (65%). Table 5 shows the phase composition of PAM after formation obtained by combining X-ray diffraction and chemical analysis. A significant amount of PbO (about 30%) was observed at the formation step, the origin of which could be associated with conductivity problems that make difficult the proton and electron transfer between particles. However, the presence of $PbSO_4$, observed in pastes of different
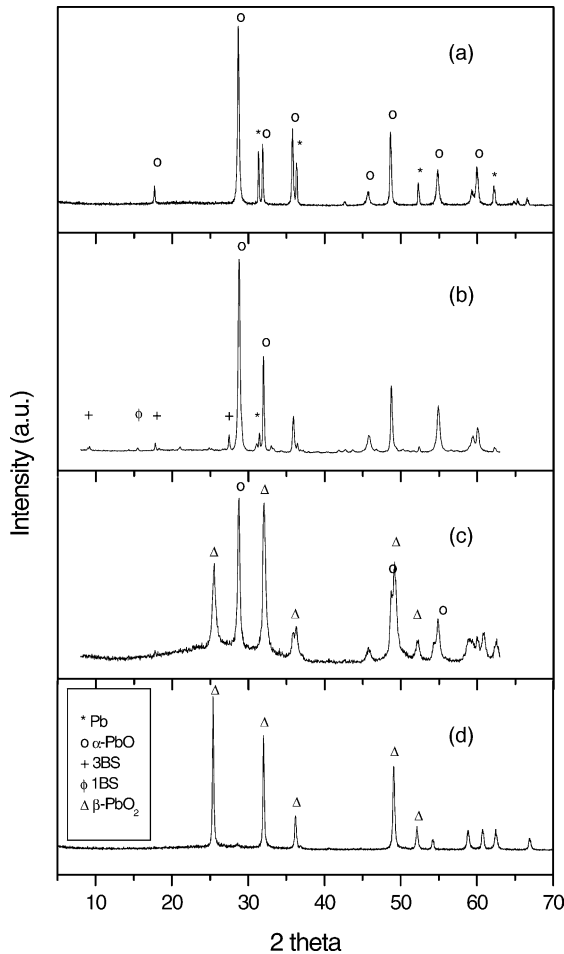
Fig. 6. XRD pattern of thin layer positive electrode: (a) lead oxide; (b) after soaking and curing for 6 days; (c) after electrochemical formation; (d) after the 110th cycle.

Table 6
Initial capacity and cycle life of electrodes prepared with different curing and formation conditions

	Curing period (days)			
	2	6		12
Formation (% overcharge)	600	400	600	600
First capacity control C_{10} (Ah)	0.76	0.95	0.97	0.75
Second capacity control C_{10} (Ah)	0.77	1.03	1.03	0.81
Cycle life (60% DOD, in cycles)	45	35	120	>90

initial capacity and cycling tests are shown in Table 6. If the electrochemical formation process is 400% the calculated theoretical value, the cell capacity fades after the first thirty cycles. If the overcharge reaches 600%, the cell capacity is maintained for more than 100 cycles. In this case, the curing time plays a major role. A reduced curing period of 2 days is insufficient to obtain a thin electrode with a good electrochemical performance. This can be achieved by prolonging the curing conditions. Thus, the gradual increase in the cell life must reflect improved adherence of the particles to the substrate. It seems plausible that on increasing the curing time, the corrosion layer formed between the active material and the grid develops further, thus favouring the charge transfer at the active particle–substrate interface. In fact, the conversion degree at the formation step is also improved, as shown in the capacity control values of Table 6.

3.4. Battery development

Tudor (Exide Technologies) has performed several studies in order to optimise the design and the manufacturing procedures of 12 V prototype batteries to achieve the project objectives. Several parameters have been studied to improve the battery performance in terms of power capability, life and reliability. They deal mainly with the density of positive active material, the active material ratios (plate weight and stack configuration) and acid density. On the other hand, according to the early failure modes detected in the preliminary batches, several toolings and assembly processes have been optimised to assure a reliable assembly of batteries and to avoid premature battery failure due to assembly faults.

Table 7 summarises the characteristics and electrical performance of three groups of ultra high power (UHP) prototypes as well as the conventional AGM batteries of the same size for stand-by applications. It is important to point out the great difference in the number of plates used in the standard AGM battery (three 3.5 mm positives and four 1.9 mm negatives) and in the UHP prototypes (eight 1.1 mm positives and seven 1 mm negatives).

The power capability of the batteries is shown in Fig. 7. There is a huge difference between the standard AGM batteries and the UHP prototypes due to the thinner electrodes. However, the three groups of UHP prototypes show

particle size [18] was undetected. On the other hand, the curing time slightly increased the conversion degree, especially if the curing was performed for more than 2 days. However, particle morphology scarcely changes with the curing time. The α-PbO content decreases on cycling and at the 10th cycle, β-PbO$_2$ was the unique phase detected. This was also the common behaviour of all cells tested at the end of life, a monophasic system formed by β-PbO$_2$ of improved crystallinity (see Fig. 6c and d).

In addition to the curing time, the influence of the formation conditions has been studied. Preliminary results of

Table 5
Phase composition of PAM after formation (wt.%)

Curing period (days)	β-PbO$_2$	PbO
2	66	34
6[a]	71	29
12	69	31

[a] After the 10th cycle: 98% of β-PbO$_2$.

Table 7
Electrical testing of 12 V ultra high power (UHP) VRLA prototypes

	Testing conditions	Standard AGM (12 V, 15 Ah)	UHP prototype		
			AGM + 4.0 g/cm^3	AGM + 4.3 g/cm^3	Optimised membrane + 4.3 g/cm^3
Battery weight (kg)		6.5	6.1	6.4	6.4
Internal resistance (mΩ)		8.4	6.2	6.3	6.4
Capacity (Ah)	C_{20} (0.9 A)	16.1	18.5	19.0	18.8
	C_8 (2.25 A)	15.5	18.2	18.3	18.4
	C_1 (15 A)	15.0	15.7	15.3	15.6
Constant power discharges ($V_{min} > 9.0$ V)	500 W	10.4 min	17.4 min	17.0 min	17.0 min
	650 W	6.9 min	11.9 min	12.3 min	12.4 min
	1100 W	2.7 min	5.8 min	6.3 min	6.0 min
	1500 W	1.1 min	3.45 min	3.8 min	3.4 min
	2500 W	15 s	1.39 min	1.55 min	1.4 min
	3000 W	–	55 s	56 s	50 s
Floating life at 20 °C	13.6 V, 55 °C	>8 years[a]	>4–5 years[a]	–[a]	–[a]
Cycle life (IEC 896-2)	60% DOD		350–400	>250[a]	>350[a]

[a] Under testing.

similar high rate capability performance with small differences between the AGM and the membrane groups.

The results obtained in the accelerated floating test at 55 °C show that, to date, UHP prototypes have fulfilled at least four units, equivalent to over 4–5 years floating life at room temperature. On the other hand, standard AGM batteries have already fulfilled six units at 55 °C, equivalent to nearly 8 years floating life at 20 °C, due to the thicker plate design: positive grids are three times thicker in standard AGM batteries than in UHP prototypes.

Cycle life at 60% DOD is being tested according to IEC 896-2. The capacity evolution every 50 cycles of the three types of UHP prototypes is represented in Fig. 8. As shown, up to date 400 cycles have been completed with the prototypes prepared with AGM separator and lower positive paste density (4.0 g/cm^3), whereas the batteries with higher
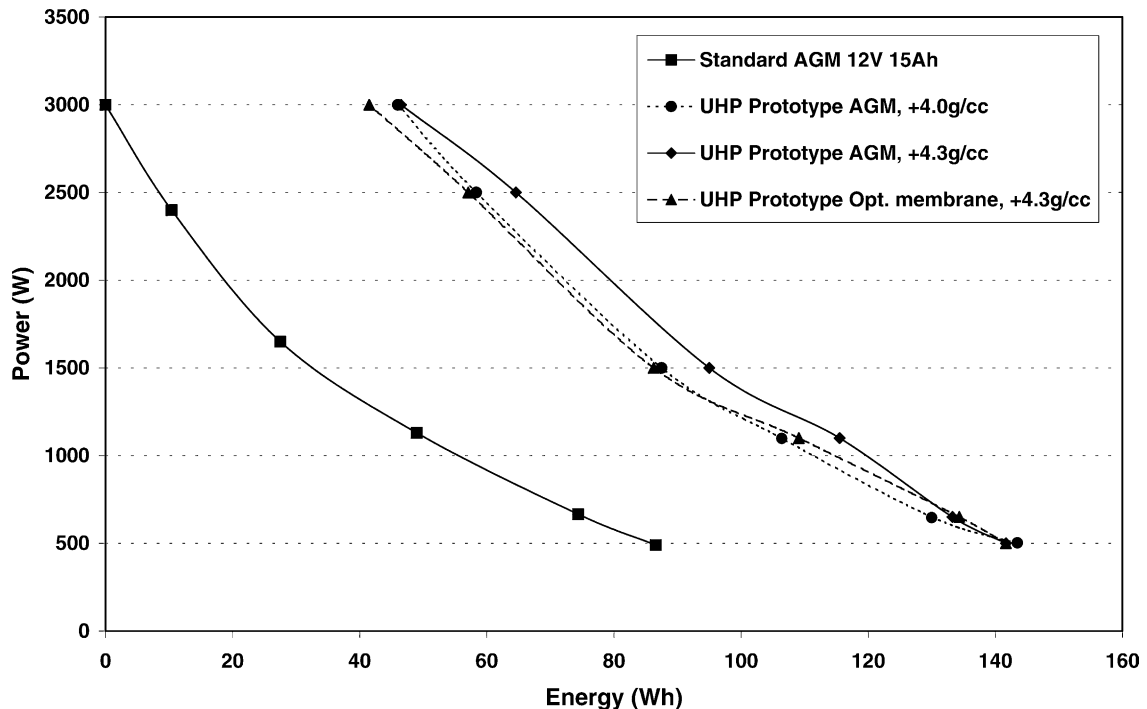

Fig. 7. Plot of battery power vs. energy of standard AGM batteries and UHP prototypes with different separators.
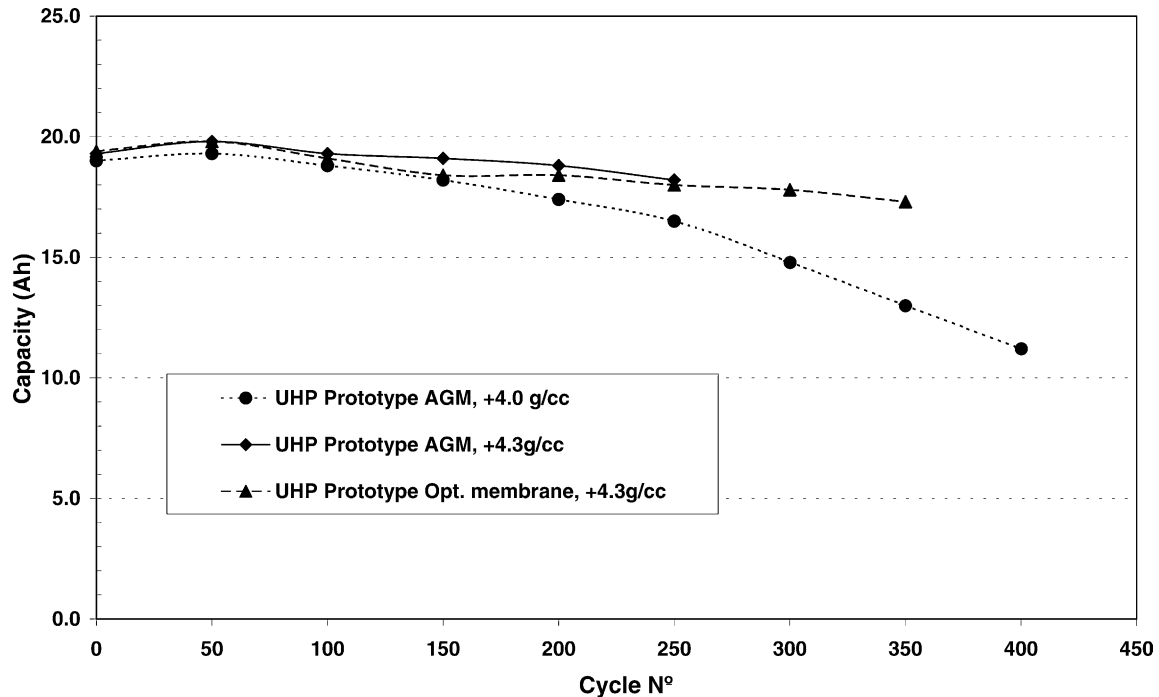
Fig. 8. Cycle life of UHP prototypes with AGM and alternative optimised membrane separators (IEC 896-2, 60% DOD).

positive paste density (4.3 g/cm^3) have fulfilled 250 and 350 cycles, for the AGM and optimised membrane version, respectively. Although the initial performance of the three types of UHP prototypes is similar, after 150 cycles the capacity decay slope is stronger in the prototypes with lower positive paste density. The behaviour of the two other groups to date indicates that around 450–500 cycles could be fulfilled.

4. Conclusions

Several European companies and one university are working together in the development of ultra high power valve-regulated lead–acid batteries for UPS applications. During the first half of the project novel materials and battery components have been developed and optimised and the final battery design and manufacturing procedures have been established.

Daramic has developed a 0.15 mm polyethylene membrane with characteristics adequate for high power batteries: low thickness and high porosity to provide low electrical resistance, adequate drying shrink behaviour and good mechanical properties to avoid problems during the manufacturing processes. The product is based on the technology currently used to manufacture separators for flooded SLI batteries, which is beneficial for cost and industrialisation. The membrane has been tested in batteries leading to satisfactory results concerning power capability and recombination efficiency, provided an adequate stack compression degree is achieved.

Bernard Dumas has studied thoroughly the factors that affect the mechanical properties of the thin AGM materials,

and defined the optimised composition to obtain the best performance compromise between physical, electrical and mechanical characteristics for the ultra high power batteries. The final thickness of the AGM material has to be adjusted in each case according to the electrode and membrane thickness, to provide adequate acid reservoir and compression degree within the plate stacks.

Córdoba University has studied two methods to prepare thin layer lead electrodes: spray pyrolysis (mainly focused to lead oxide precursors) and pasting with a roller. The objective is to create a conductive inter-phase between the smooth grid surface and the active material in order to avoid the problems encountered of capacity fading due to loss of contact between the grid and the active material. Results obtained to date show that a prolonged curing process improves the cycling life due to an enhanced adherence of particles to the substrate and thus the charge transfer at the PAM–grid interface is favoured.

Tudor (Exide Technologies) has studied several design parameters to optimise the battery performance and find the best compromise between the power capability and life endurance: electrode configuration, acid density, PAM density, electrode thickness, etc. To date, 472 W/kg and 1440 W/dm^3 in a 30 s discharge at 70% SOC have been obtained and, according to the results of running tests, over 5 years floating life and around 500 cycles at 60% DOD can be expected. The design characteristics of the batteries, to be tested by MGE UPS Systems in the coming months, have therefore been defined and prototype manufacturing has already started.

The development of high power lead–acid batteries with improved life and reliability can provide a cost-effective

solution for high power cyclic applications in which other battery types are used today (Ni–Cd, Ni–MH, etc.). In all these applications UHP VRLA batteries can be considered a short term option, because the manufacturing and recycling installations are already available.

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