

# A review of future directions in automotive battery separators

W. Böhnstedt\*

*Daramic Inc., Erlengang 31, D-22844 Norderstedt, Germany*

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## Abstract

During recent decades the design of modern automotive batteries has undergone a fundamental change from leaf-type separators to microporous polyethylene envelope separation. The increased energy content and higher cold-crank performance of automotive batteries, especially in combination with application at elevated temperatures, has significantly increased the demand on separators with regard to puncture strength and oxidative stability. This paper describes recent achievements, together with typical battery test results, and gives an outlook on probable automotive battery developments from the separator manufacturer's point of view.

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Automotive batteries are by far the largest individual commercial segment of all battery types; they account by value for approximately 30% of all batteries of all chemistries, and for more than 70% of all lead-acid batteries [1]. In 1970, about 100 million automotive batteries were produced worldwide; all of them used leaf-type separators, predominantly PVC and cellulosic types. Since then, the production of automotive batteries has grown to around 300 million, of which nowadays almost 90% are built with microporous pocket separation (Fig. 1). The balance are still leaf-type separators, like sintered PVC, synthetic pulp with stiff glass-mat, and some cellulosic types. Absorptive glass-mat separation is used only in special cases—in total, in less than 1% of all automotive batteries—and this is mainly for cost reasons.

The transition to microporous polyethylene envelope separators started in the USA in the 1970s, followed by Europe in the 1980s, and is essentially completed now in these two regions. In Asia-Pacific, for several reasons, this conversion started a few years later, and a similar development to that in the Western Hemisphere is to be expected (Fig. 2), primarily for technical reasons. The polyethylene pocket separation is in almost all aspects significantly superior to leaf separation.

Table 1 shows a summary of some typical parameter values for the different separator types. Leaf separators—as stackable separators—according to the stiffness of the ma-

terial do require a certain minimum thickness for handling. This, of course together with their porosity, expresses itself in higher acid displacements and especially in higher electrical resistances. While sintered or fibrous separators, because of the diameter of their components, necessarily have pore sizes of 15–25  $\mu\text{m}$ , polyethylene pocket separators are microporous, i.e., their pores are significantly smaller than 1  $\mu\text{m}$ .

How do these differences reflect themselves in the performance of automotive batteries? Such a comparison is slightly impeded by the different battery construction principles for leaf versus pocket separation in general. Conventional construction uses stiff leaf separators, inserted between two electrodes of opposite polarity—frequently still with a grid antimony content of 1.6–2.5 wt.%. The aligned sets are placed into the cells of the battery boxes and stand there on bottom spacers in order to reserve room for lead particles, which precipitate during battery service, to accumulate without causing premature bottom shorts. On the other hand, the use of microporous pocket separators has enabled a type of battery construction without a ‘mudroom’, which allows a more complete use of the space available. About 8% higher capacity and cold-crank performance can be achieved with identical box dimensions.

Lead–calcium alloys—known for their tendency towards increased shedding—require the use of a microporous pocket. The micropores of a polyethylene separator have, on average, a diameter of 0.1  $\mu\text{m}$  or less, while the lead dioxide and lead sulfate particles precipitating from the

\* Tel.: +49-40-535960.

E-mail address: [wbohnstedt@daramic.com](mailto:wbohnstedt@daramic.com) (W. Böhnstedt).

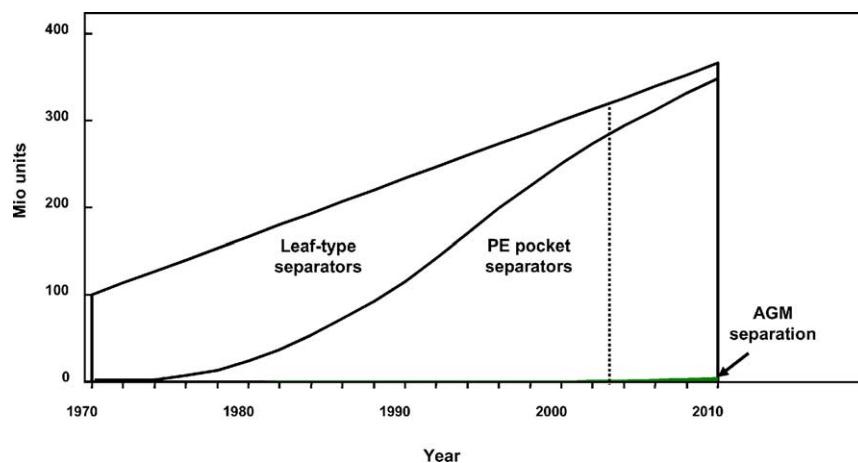


Fig. 1. World automotive battery production by separator type.

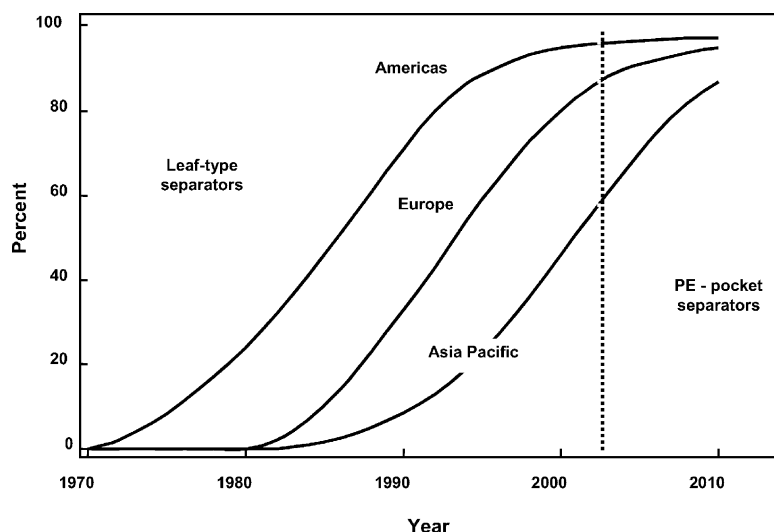


Fig. 2. Conversion rate to polyethylene pockets.

electrodes—especially in cycling service—have a diameter typically 10-fold larger and are retained by a kind of sieve or filter effect. The pocket not only protects against shorts on both vertical edges as well as on the bottom edge, but, because of its pore size, also prevents direct penetration by lead particles. Thus, the automotive battery with microporous pocket separation allows all conceivable alloy combinations: lead–antimony for both electrodes, hybrid, i.e., positive electrode in lead–antimony and negative electrode

in lead–calcium, and finally lead–calcium for both electrodes. The use of expanded metal grids for lead–calcium electrodes is especially cost-effective, since they require less weight of inert lead.

A comparison of the influence of leaf versus pocket separation on automotive battery properties is given in Table 2. In the  $-18^{\circ}\text{C}$  cold-crank test, the differences in separator resistance are of course reflected in the 30 s voltage. Although the battery in pocket construction gains by its larger

Table 1  
Comparison of automotive battery separators

	Backweb thickness (mm)	Pore size (average) ( $\mu\text{m}$ )	Acid displacement ( $\text{ml m}^{-2}$ )	Electrical resistance ( $\text{m}\Omega \text{cm}^2$ )
Sinter PVC separators	0.30	15	200	150
Cellulosic separators	0.50	22	140	100
Polyethylene pocket separators	0.20	0.1	110	55

Table 2  
Comparison of automotive batteries

Battery type	Cold-crank voltage (V)	Water loss (g Ah <sup>-1</sup> )	Cycle-life (cycles)
Pb–Sb 1.6/Pb–Sb 1.6			
Sinter PVC separators	9.20	4	120
Cellulosic separators	9.30	2	145
Pb–Ca/Pb–Ca			
Polyethylene pocket separators	9.45	0.5	300

electrode surface, to which an increase of some 50 mV over the best leaf separators is traceable, about 100 mV is due to the lower electrical resistance of the polyethylene separator.

The standardized water consumption during 21 days at 14.4 V and 40 °C amounts, for PVC separation, to about 4 g per nominal 'Ah', and is known to be positively affected by cellulosic separators, which reduce the water loss to about 2 g Ah<sup>-1</sup>. The freedom from maintenance, achievable by lead–calcium alloys, is clearly shown by the significant lowering of water consumption to only around 0.5 g Ah<sup>-1</sup> in the same test. The water consumption increases at elevated temperature, about linearly with lead–calcium and noticeably more than that with lead–antimony alloys.

The decisive advantage of the pocket construction type however is in cycle-life, which can be demonstrated especially in cycle-life tests conducted at elevated temperature (Fig. 3). While batteries with leaf separators fail relatively early, and this is due to bottom shorts, the capacity of polyethylene pocket-separated batteries begins to decrease only later—and then only slowly. This is not caused by shorts around or through the separator, but by a slow capacity decrease of the active material by loss of internal electrical contact, grid corrosion or material shedding, or even a combination of these three factors. The pocket separator remains undamaged and is not the life-limiting component.

This result is in agreement with the experience gained from investigations on failed batteries. In moderate climates—as a rule—the separator is not life-limiting for

automotive batteries. At elevated temperature, however, and especially with significant cycling service, the picture changes. Batteries with leaf separation often fail prematurely due to bottom shorts, whereas batteries with pocket separation experience their life limit due to capacity loss of the positive electrode—but considerably later.

During recent years, some trends in the use of automotive batteries have become apparent. These are increasing the demands on the chemical stability of separators even further. Elevated battery temperatures by flat, aerodynamically styled engine hoods and, statistically, a growing share of vehicles operated in warmer climates are both leading to a considerably aggravated oxidative attack on the separator. These effects certainly do not concern the majority of automotive batteries being operated predominantly in moderate climates, but a still small, though steadily growing share in warmer climates. As mentioned before, the higher operating temperatures increase also the water loss, and thus the use of lead–calcium alloys as an antidote is gaining acceptance and this—for cost reasons—preferentially in the form of expanded metal grids, at least for the negative electrodes. As these are known to present a danger to the separator backweb through their sharp edges and protruding wires, an increased puncture resistance is also required.

In order to meet these requirements, separator manufacturers have developed and presented premium qualities, such as the DARAMIC 'High Performance' (Table 3). It distinguishes itself from standard polyethylene pocket material, above all, by an increased puncture resistance, as well as a by far improved oxidative stability and this without raising the very low electrical resistance.

During separator production an especially protective manufacturing process avoids damaging the polyethylene macromolecules with an average molecular weight of about 8 million atomic weight units. These macromolecules constitute the polymeric network, which invests to the polyethylene separators with their excellent mechanical properties. With an identical chemical composition, but only by the more gentle treatment, the DARAMIC 'High Performance'

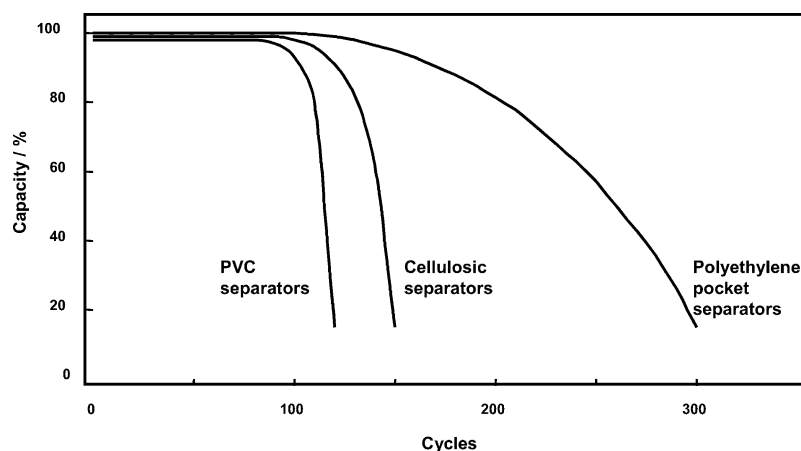


Fig. 3. Cycle-life test of automotive batteries.

Table 3  
Polyethylene separators for automotive batteries

Product	Backweb thickness (mm)	Electrical resistance ( $\text{m}\Omega \text{ cm}^2$ )	Puncture resistance (N)	Oxidation stability <sup>a</sup> (h)
Polyethylene pocket separator	0.20	55	7.5	20
DARAMIC® 'High Performance'	0.20	55	13	48
DARAMIC® 'DuraLife'	0.20	65	18.5	72

<sup>a</sup> PEROX 80 duration (h) to 100% residual CMD elongation.

process increases the puncture resistance from typically 7 to 8 N for standard separators to about 13 N. Even more than a doubling has been achieved in oxidative stability, sensibly measured by the PEROX method [2], which in all experience best reflects the requirements placed on the separator in actual battery service. The improvement of both these properties, while maintaining the well-balanced profile of all other properties, confers on this generation of polyethylene separators with an excellent stability even under aggravated conditions of use.

Relentless intensive cost pressure on the automotive battery industry, and thus also on separator manufacturers, has led to the offer and use of ever thinner separator backweb thicknesses. This should not happen without giving it a second thought! Especially in combination with the trends towards ever higher battery temperatures, the limits of demands on the separator can be well reached—thus resulting in calls for a further increase in mechanical and chemical stability.

'DuraLife' is a new product generation in which, with the inclusion of all product and process-related experiences, the properties puncture resistance and oxidation stability can be improved further [3] (Table 3). This recent achievement can be seen clearly from a graph of puncture strength versus separator backweb thickness (Fig. 4). Starting from standard polyethylene separators, as offered by several manufacturers, an initial major step was reached with DARAMIC 'High Performance', which now is still surpassed by far by 'DuraLife'. This puncture resistance should be more than meet all the mechanical demands normally arising. In parallel to this—and even more impressive—is the improvement

achieved in oxidative stability (Fig. 5). Again starting with the standard polyethylene separator, 'High Performance' results in doubling the PEROX stability, and 'DuraLife' even in quadrupling the values of standard qualities.

Will these differences ever show up in battery tests? The cold-crank capacity is shown in Fig. 6 as a function of cycle number for batteries with a standard polyethylene separator, for DARAMIC 'High Performance', as well as for 'DuraLife'. It should be mentioned that a hybrid construction has been chosen with positive electrodes made from lead–antimony alloy with 1.6 wt.% Sb and negative electrodes from lead–calcium expanded metal. This hybrid construction, based on experience, promises to give the best cycle-life under aggravated conditions. Up to the end of this battery test, after some 400 cycles, only a minor difference in electrical performance could be recorded.

On the other hand, the residual elasticity of the separators after the battery test in comparison to the initial values shows quite significant differences (Fig. 7). Whereas 'DuraLife' loses only about 3% of its elasticity by oxidative attack during the cycling test, for 'High Performance' it is about 22%, and for standard polyethylene separators even 73%. This is a significant proof of the enhanced oxidation stability, possibly of decisive importance under critical conditions of use! Decreased elasticity reflects a degradation of the polyethylene macromolecules, which finally could lead to embrittlement and thus tears within the separator backweb.

The advances in polyethylene separator development are summarized in Fig. 8 with puncture strength and oxidation stability as y- and x-axes, respectively. 'High Performance' offered the first significant step towards higher puncture

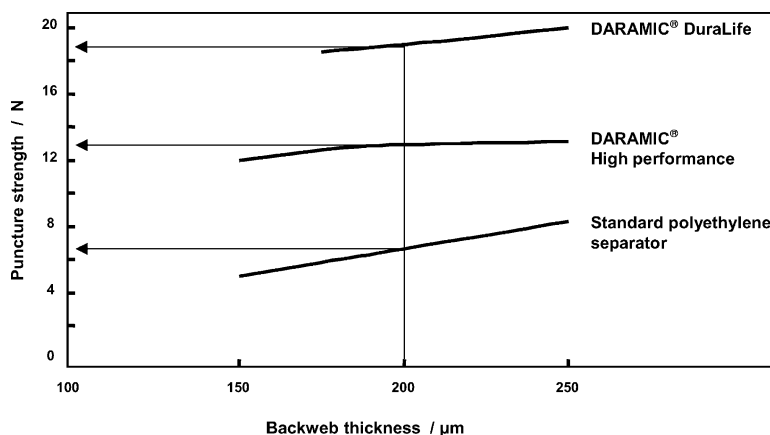


Fig. 4. Puncture strength =  $f$  (backweb thickness).

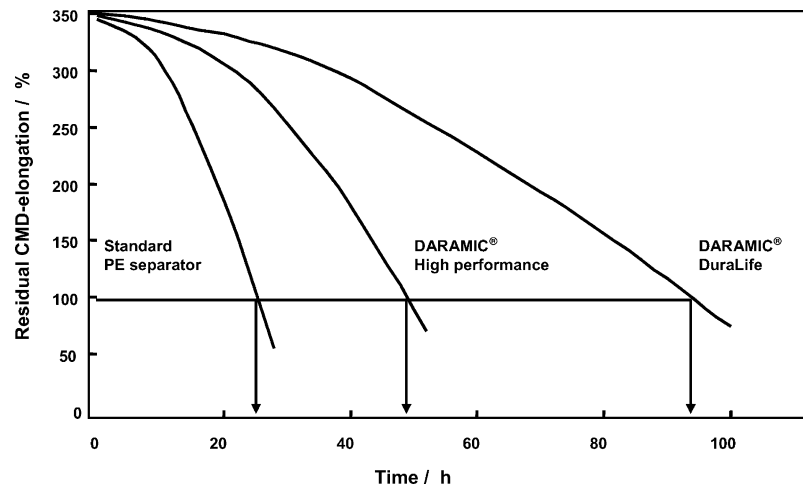


Fig. 5. Oxidation resistance =  $f$  (PEROX 80 duration to 100% residual elongation).

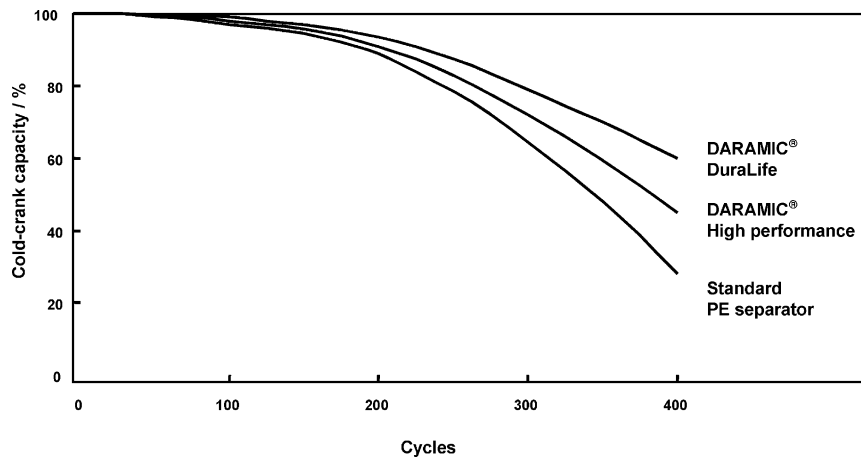


Fig. 6. Cycle-life test.

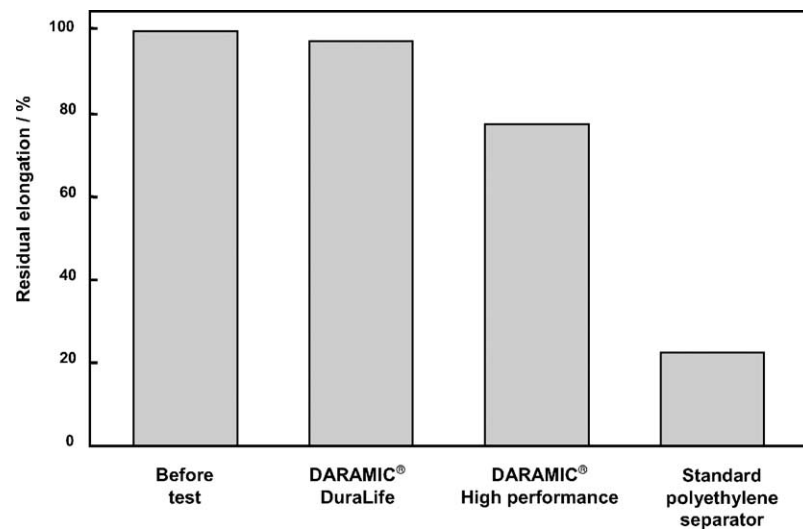


Fig. 7. Residual elongation after battery test.

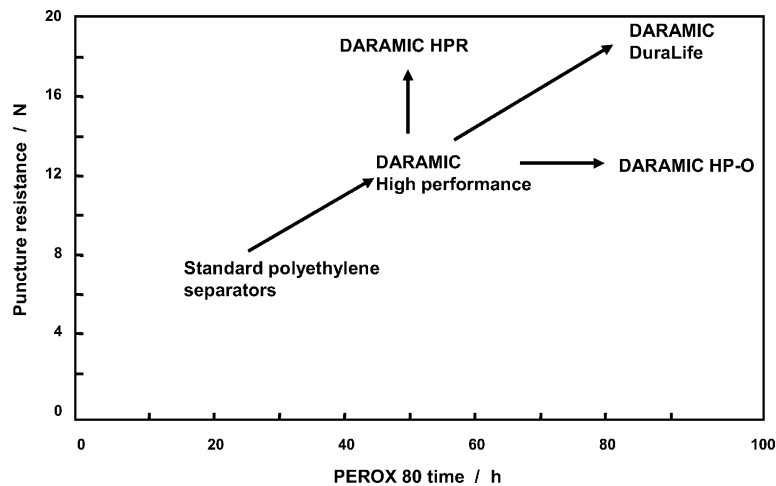


Fig. 8. Product family 'DuraLife'.

strength and increased oxidation stability, and 'DuraLife' shows a further large improvement.

But why 'DuraLife family'? It is possible by suitable process conduction and separator formulation to optimize in this case both parameters separately. Under the name 'HPR' a material can be offered with a puncture strength far improved beyond the 'High Performance' product, and 'HP-O' is a separator with an oxidative stability far beyond 'High Performance'. Thus, according to the expected conditions of use it is now possible to provide an exactly adapted separator quality at the best cost.

The future of the automotive battery separator is, of course, most closely linked with the further development of the automotive battery itself. The trends presented so far assume that the automotive battery will continue to be in a prismatic 12 V construction. Will the 36 V battery come and when will it come? This appears to be a moving target—always 5 years away! In a foreseeable prediction

period of about 5–10 years, it will most likely not be introduced to a large extent! Cost/benefit considerations are essentially responsible for this; in most cases, the intended purpose can be achieved at lower cost by other means!

Therefore, what will be the near future for the automotive battery? It is most likely that, for the next few years, the prismatic 12 V battery in lead–calcium or hybrid construction with a microporous polyethylene pocket separation will prevail. Within the prediction period, the VRLA battery with glass-microfiber separation—mainly for cost reasons—will be justified only in special cases.

The cold-crank power of present automotive batteries in relation to their energy content is presented in Fig. 9. This may serve to understand another direction of development, which appears to be promising. In those cases where the power supply of a vehicle is assessed to be critical, two batteries may be considered, most likely both in a 12 V construction. This has major advantages. By this division, the

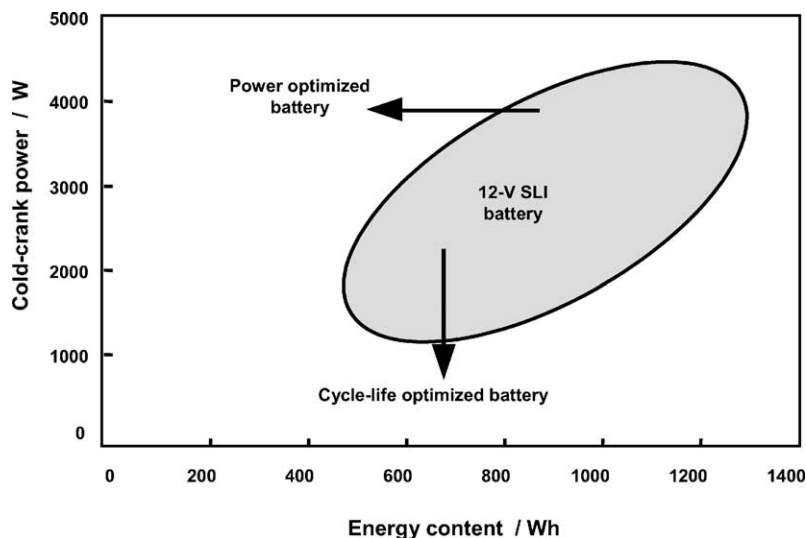


Fig. 9. Power vs. energy diagram for automotive batteries.

two contradictory demands on automotive batteries can be separated, because present batteries present a compromise. On the one hand, they have to provide a very high cold-crank current for a very short time, and on the other hand for longer periods, when the engine is not running, they have to provide some energy for electronic equipment, warning lights, etc. To a certain degree, present high-power batteries are over-dimensioned with respect to capacity. These contradictory demands ideally would require different types of construction, i.e., thin electrodes and narrow spacing in order to minimize the internal resistance for the cold-crank function, and thick electrodes with sufficient acid between them for the supply battery. One quite essential positive factor in favor of a two-battery system is the increased reliability due to the redundancy, especially when safety-relevant components, such as electric brake assistance, etc., are to be operated.

By the way, in a two-battery concept even a decrease in total weight can be achieved—despite the fact of having two batteries—by optimizing the designs for each purpose. Further advantages can be achieved by their separate placement. Short, and thus not too heavy, cable connections can be used between the high-power battery and the automotive motor, whereas the supply battery, due to the low current demands and thus low gauge cables, could be located anywhere, such as in the boot, where low ambient temperature will extend battery life.

What is to be expected for these premium vehicles with regard to their two-battery design? First, there will be a 12 V high-power battery with about 3–4 kW cold-crank power mainly for starting purposes at a relatively low capacity, such as 20–30 Ah, using very thin electrodes of around 0.5–0.6 mm spacing. This battery initially will be designed in conventional prismatic construction, while spirally wound designs are under development at various battery manufacturers. Due to the narrow spacings of high-power batteries, microporosity of the separators appears to be indispensable,

since otherwise penetration shorts are almost unavoidable. The narrow electrode spacings place special demands on the oxidation stability, since necessarily the distance from the positive electrode, the source of all aggressive, oxidative substances, to the endangered separator backweb also decreases. The developments toward highest oxidative stability, such as HP-O or DuraLife, should ideally fit into this requirement profile. In a two-battery concept it is therefore considered very likely that the high-performance battery will have microporous polyethylene separation.

Second, a 12 V service battery will be required for low currents, i.e., less than 1 kW, at discharge periods of typically hours with a capacity of about 40–60 Ah and good cycling stability. Prismatic construction with relatively thick electrode plates and sufficient distance for their adequate acid supply characterize this construction. With regard to separation, the desire for cycling stability is especially important besides the ever-present cost considerations. Cycling stability requires support of the positive active material against premature shedding, e.g., with a glass- or an organic-fiber mat placed directly against the positive electrode. This could be achieved either by completely filling the space between the electrodes with a microfiber glass-fleece (AGM), as in the VRLA battery construction, or conventionally by attaching a fiber mat on the ribs of a microporous separator pocket. The latter construction certainly is more cost-effective, since many of the cost-increasing components of VRLA batteries, such as valves, voluminous microfiber glass-mats, or the tedious formation processes, are avoided.

The performance of two batteries with low-antimony alloy electrodes, one with a polyethylene pocket separation and one with an additional polyester-fleece towards the positive electrode, is given in Fig. 10. Because of the intended service profile, a depth-of-discharge of 50% has been selected, i.e., significantly more demanding than the former battery tests. As mentioned earlier, the capacity loss in such tests is mostly due to shedding of the positive mass, which—as can

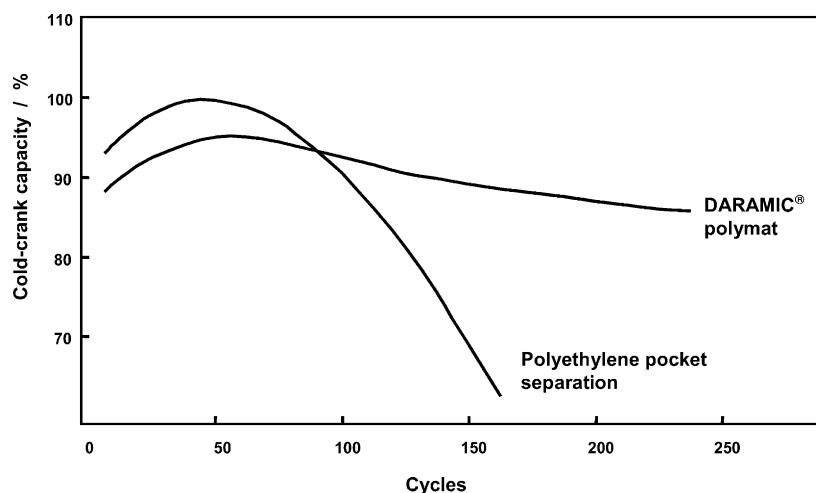


Fig. 10. Impact of surface mat on cycle-life.

be seen—is effectively delayed. Certainly a cost-efficient solution for improving the cycling stability of the service battery! The future will have to show which construction for the supply battery will prevail, whether it be a VRLA battery with microfiber glass-mat separation or a more conventional construction with microporous polyethylene pocket with a surface mat addition in order to support the positive active material.

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