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Aspects of optimizing polyethylene separators

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Abstract

Battery separators are characterized largely by their material and by their shape. In this paper options to achieve optimization of polyethylene separator properties are discussed, based on reasonable variations in material and shape, in particular with respect to electrical resistance and chemical stability.

The raw materials of polyethylene separators, i.e. silica, ultrahigh-molecular weight polyethylene, mineral oil and some additives are presented, their relative amounts are varied, and the resulting properties are evaluated with regard to oxidation stability, deposits generated, puncture strength, and electrical resistance.

Distinct consideration must be given to the dimensional parameters of both the separator sheet and the distance-setting ribs. Various proposals, in particular for the latter, are referred to in the literature without critical evaluation of their effect on battery performance. Some considerations for optimized profile design and initial battery results are reported.

Keywords: Automotive batteries; Polyethylene separators; Materials and composition; Profiles

1. Introduction

Battery separators are largely characterized by their material and by their shape [1], other properties rank secondary. This paper discusses aspects of optimizing polyethylene separator properties, based on reasonable variations in material composition and shape. The essential separator properties, which are to be considered primarily, will be electrical resistance and chemical stability. If these are optimized, the separator should satisfactorily meet both of its main functions, i.e. on the one hand to keep the positive and negative electrodes physically apart for preventing flow of any electronic current directly between them, and on the other hand to allow the optimum flow of ionic current. These two opposite requirements are met by a compromise: a porous non-conductor.

The requirement of electronic insulation — the origin of the term separator — has to be met durably, i.e. often over many years within a wide range of temperatures and in a highly aggressive medium. The unhindered ionic charge transfer requires many open pores and these to be of the smallest possible diameter in order to prevent electronic bridging by deposition of metallic particles. The large number of microscopic pores form immense internal surfaces, which inevitably are subject to increased chemical attack. Not only the electrolyte, but also the electrodes, directly or indirectly, exert a chemical attack, either by a high oxidation potential of the electrode materials themselves, or by generating soluble aggressive substances.

The above requirements can appropriately be translated into measurable data by established test methods for separator electrical resistance and oxidative stability (PEROX 80).[1,2]

2. Materials and composition

The term "polyethylene separator" is somewhat misleading, since such a separator consists mainly of agglomerates of precipitated silica, being held within a network of extremely long-chain ultrahigh-molecular weight polyethylene. A typical polyethylene separator formulation comprises precipitated silica (SiO_2 about 60%wt., based on the final product), ultrahigh-molecular weight polyethylene (UHMW PE about 20%wt.), mineral process oil (about 15%wt.), as well as some processing aids, like antioxidants and/or proprietary surface tension or other modifiers [2].

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[1] Battery separators test methods: electrical resistance; BCI–TM 3.218 (1997), cf. DARAMIC BS–TE, 2000–2002 (1995).

[2] Degradation testing (sulfuric acid/hydrogen peroxide oxidation): BCI–TM 3.219 (1997), cf. DARAMIC BS–TE, 2100 (1995).

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2.1. Silica-polyethylene ratio

It is obvious that for obtaining high porosities, and thus, finally low electrical resistances, maximizing the content of highly porous precipitated silica, is essential. This again can only be achieved by reducing the relative share of the polyethylene content, assuming a constant amount of residual oil and additives.

For reasons of chemical stability polyethylene of the highest processable molecular weight is used. Currently polyethylene grades are used with a molecular weight of about 5–9 mio AMU. Higher molecular weights cannot be processed with the existing technology without partial fracture of the molecular chains. The UHMW polyethylene macromolecules form connecting strings between the silica particles. It is evident that a higher content of such connecting chain molecules improves the mechanical performance, which may, for example, be measured in terms of puncture strength, as well as the chemical stability. For the latter, the decrease in elongation of a separator sample after a defined chemical attack (such as PEROX 80) is a reliable test. Based on a total separator content of polyethylene plus silica of about 80%wt. the correlations as shown in Figs. 1–3 result.

An optimum compromise between electrical resistance, chemical stability and mechanical performance has to be found. Experience has shown that for a backweb thickness of about 200 μm and a backweb oil content of about 10–12%, even under extreme climatic conditions, 20 wt.%, but preferably 22 wt.% of polyethylene guaranteed sufficient chemical, as well as mechanical, stability, especially with the use of appropriate wetting agents. This does not cause a significant increase in electrical resistance, and thus, results in excellent cold-crank performance.

2.2. Oil type

After this first optimization step with respect to the ratio of silica to polyethylene content, a suitable oil type must be selected and the proportion of this oil in the separator must be decided. The oil, of course, has to meet certain prerequisites of thermochemical stability. It must exhibit limited flammability, if it is to be used at all in the extrusion process with UHMW polyethylene. The selection of the specific oils also affects all of the performance properties.

Mineral oils consist of a multitude of chemical compounds, largely very similar to each other. Thus, mineral oils are generally classified simply as paraffinic, naphthenic or aromatic, according to the ratio present of these components. Oils with a high aromatic content have long been known to contribute considerably to the oxidative stability of separators [3]. Pure paraffinic oils, such as e.g. medicinal white-oil, do not show any effect of this kind. The protective mechanism relies on the oxidizing substances, which derive from the positive electrode, attacking the relatively easily oxidizable aromatic components and becoming themselves reduced and thus, innocuous. While aromatic compounds sacrifice themselves, paraffins evidently are sufficiently stable to resist this oxidative attack [4].

Oils with polar components, among them the aromatic ones, are known to be partly soluble in battery electrolyte. Since, they are lighter than sulfuric acid, they accumulate at the electrolyte surface and form a film, to which floating lead particles can adhere and give rise to an unsightly smudge around the top of translucent battery containers. An optimum between the least tendency for such contamination and sufficient oxidation protection has to be found. It may be remarked that measuring the extent of such contamination is subject to personal bias in evaluation. Independent views by

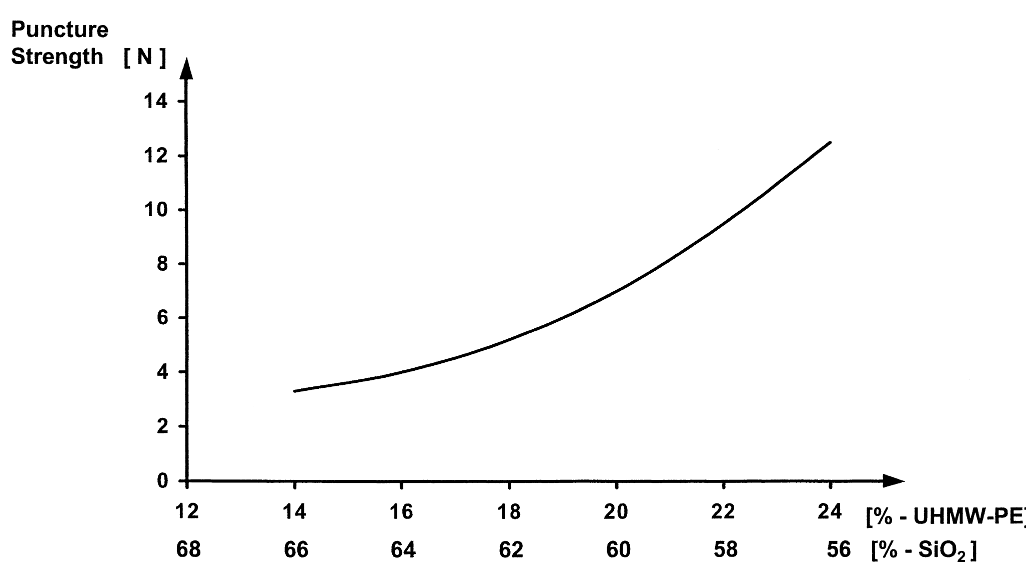

Fig. 1. Puncture strength as a function of SiO_2/PE ratio (backweb thickness 0.2 mm).

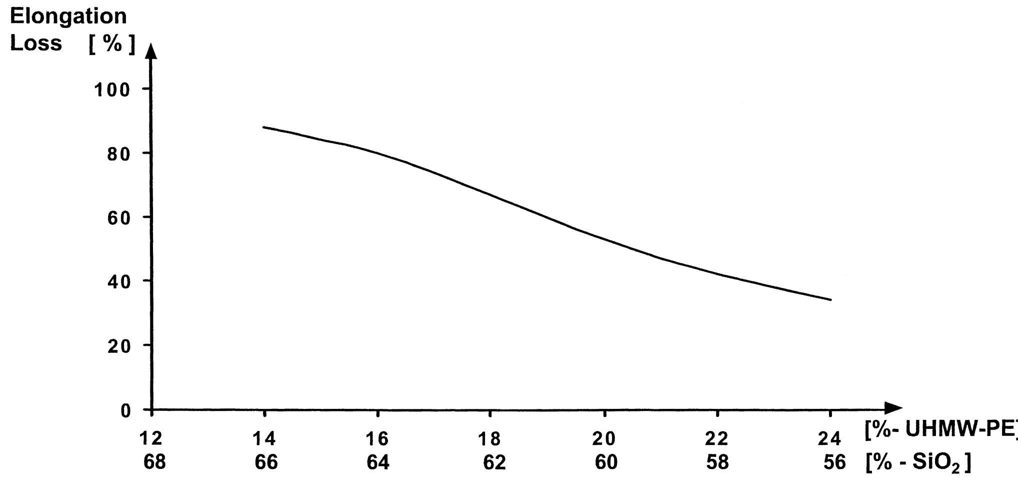

Fig. 2. Oxidation test elongation loss as a function of SiO_2/PE ratio (PEROX 80–20 h; backweb oil content 12%).

a panel of several observers, however, yield sufficiently reproducible results.

Extended test series have been able to identify oil types offering an optimum between low extent of contamination and high oxidation protection [5] (Fig. 4). Separators with such oils have proven in practice to provide an excellent oxidation stability.

2.3. Oil content

With the composition of the oil decided, it remains for the oil content of the separator to be fixed. As shown elsewhere in the literature in detail [4] the separator oil content, and in particular the backweb oil content, must be high enough to provide adequate oxidation stability. On the other hand with increasing oil amount the tendency towards deposit contamination is raised. Experience with hundreds of millions of starter batteries has convincingly demonstrated, that with 10–12% oil content in the separator backweb — of course of a reasonable thickness — excellent oxidation protection is provided, even under extreme climatic conditions.

Silica, UHMW polyethylene, and oil are the primary ingredients of each polyethylene separator. As mentioned above, wetting agents or other surface tension modifiers can also be included. If any additives are used, for example, to enhance processability, then the effect of any residues on potentially adverse electrochemical reactions must be considered.

2.4. "High performance" process

Antioxidants may help to protect the long-chain molecules during extrusion. Despite many attempts, they failed to impart the separator with an improved oxidation stability

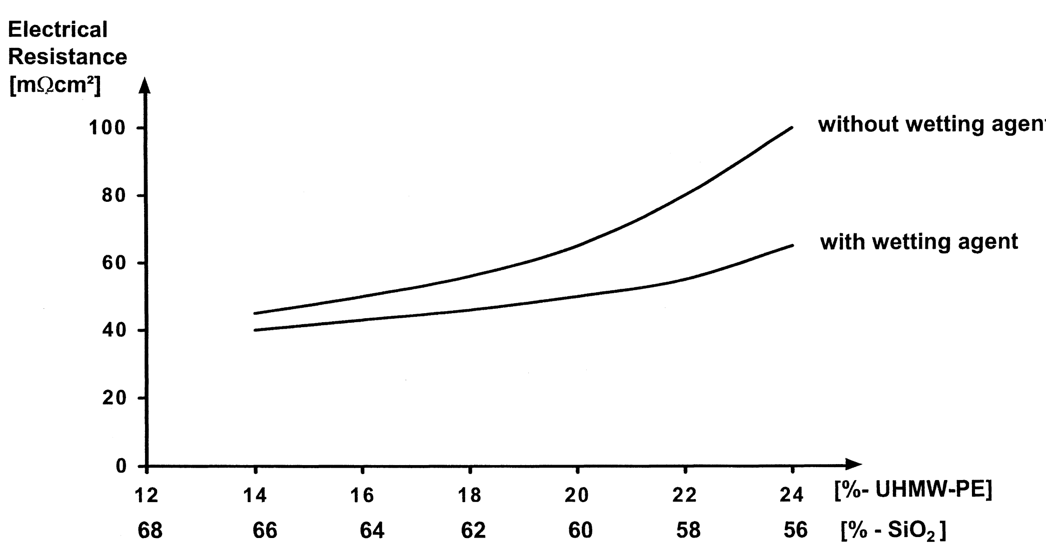

Fig. 3. Electrical resistance as a function of SiO_2/PE ratio (backweb thickness 0.2 mm).

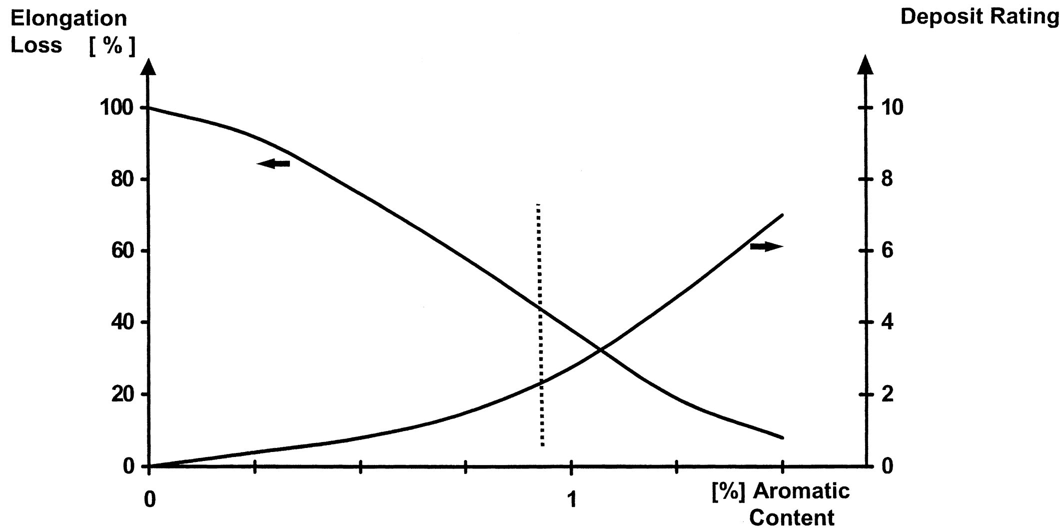

Fig. 4. Oxidation test elongation loss, and deposit rating as a function of oil aromatic content.

in battery service. In order to prevent any premature chain deterioration of the polyethylene macromolecules, a modified separator production process has been found to be a significant advantage [4]. A decisive improvement in puncture strength can be achieved, which allows safe handling with expanded metal electrodes. The impressive increase in oxidative stability provided by this "high performance" process assures safe processing and use of these separators under most severe service conditions even at low backweb thicknesses without any noticeable increase in electrical resistance.

In conclusion, an optimized formula for polyethylene separators may be summarized as follows: at about 58%wt. silica, around 22% UHMW polyethylene and approximately 16% of a suitable "clean" formulated oil, with typically about 10–12% in the separator backweb, as well as some additives, produced in the "high performance" process, results in an optimum polyethylene separator.

3. Separator shape

What effect on battery properties does the shape of a separator have?

Basically a lead-acid battery separator consists of the backweb as the separating element and ribs, or something similar, keeping it at a distance from the positive electrode. In modern starter batteries the separator backweb is microporous and the pores preferentially do not provide a straight path through the sheet in order to give optimum protection against penetration by lead particles. However, micropores involve large internal surfaces and increased susceptibility to chemical attack. The material properties necessary to withstand this attack have already been dealt with in detail above. Ribs both prevent a direct contact of the thin backweb with the positive electrode and also maintain a maximum distance to the origin of all aggressive oxidative substances.

3.1. Separator backweb

The microstructure of a separator has an essential influence on its electrical resistance. For homogeneous separators the electrical resistance is generally known to be a function of the square of the tortuosity factor T and to depend inversely on the porosity P [1]. These parameters are largely defined for polyethylene separators by the chosen chemical composition. The electrical resistance of a separator is further known to increase, as a first approximation, in proportion to the backweb thickness. This would let the thinnest backweb appear to be most desirable. However, processing difficulties, and problems of oxidation stability at elevated temperatures, also have to be considered, thus, for modern starter batteries, a backweb thickness of about 0.2 mm has proven to be optimum.

3.2. Profiles

Once the optimum backweb thickness is established, only the distance-setting ribs remain to be optimized. Their function is to maintain, reliably and durably, the distance to the positive electrode in order to protect the microporous separator backweb and also to achieve the desired acid assignment to both electrodes. This would call for as many closely spaced distance-keeping elements as possible without unduly increasing electrical resistance and acid displacement. For starter batteries, generally a microporous polyethylene separator with a backweb thickness of about 0.2 mm and some 10–20 vertical ribs has become standard. The number of ribs depends primarily on the electrode spacing but of course also on the targeted reliability.

Several proposals for alternative rib geometries have been published in the literature, and these are generally supposed to improve the processability of the separator. In this way additional vertical ribs have been proposed in order to increase the stiffness in the machine direction and flat ribs transverse to the main rib direction have been proposed to improve the cross-stiffness, which is particularly low for very thin backwebs [6]. So-called "compressible rib" arrangements [7], allow a certain compression of the electrodes/separators stack in order to compensate one-sided deviations from the design thickness for electrodes or separators. This could both simplify insertion into the container and assure a properly tight fit there. Other proposed rib geometries aim at reducing puncture risk at the sensitive separator edge zone by pointed wires from expanded metal grids. For this purpose, the separator areas forming the pocket seals are either designed thicker or even covered with a protective film [8]. They can also be designed with many, very closely parallel, vertical ribs [9] or, alternatively, with cross-ribs in the area of the plate edge [10–12].

3.3. Electrical resistance

All these rib geometry proposals serve to ameliorate weaknesses in conventional construction in terms of processability or reliability, they do not refer to their effect on battery performance data.

Separator rib elements exercise a direct influence on electrical resistance as a result of the volume of acid that they displace.

The rib elements are therefore, required to occupy a minimum volume in order to prevent the already acid-limited design of starter batteries becoming even more susceptible to deep discharge. Proposals to form the distancing elements by embossing the backweb [13] were unsuccessful, since, they did not offer enough rigidity inside the battery to withstand vibration, and direct contact of the backweb with the positive electrode led to premature damage. Therefore, rib elements should be solid.

Rib element design also affects cold-crank performance.

Assuming a given backweb and a given distance of the electrodes it is clear that the space elements contribute an additional electrical resistance proportional to their base area (Fig. 5). According to Kirchhoff's laws, this resistance is to be connected in parallel with the resistance of the surrounding electrolyte and in series with the resistance of the backweb (Fig. 6).

This rigorous formula can be simplified by assuming that the electrical resistance for the current flow through the spacer element itself is very large compared with the electrolyte resistance (Fig. 7). This effect of the spacer elements on the electrical resistance suggests that their base area should be as small as possible. Again an optimum has to be found, this time between minimum distances between the supporting rib locations on the one hand, and their total volume and total base area on the other. In this connection, continuous ribs appear not to be the optimum, and "dot-like" spacers would be preferred. However, such profiles have the disadvantage of not positioning the electrode precisely in relation to the separator backweb, and to the bottom of the battery container. This can lead to processing problems or even premature battery failure by direct oxidative attack on the separator backweb. These considerations have been taken into account in the profile proposal of Fig. 8 [14]; in addition, this design offers the least electrical resistance and the optimum proximity of supporting points.

3.4. Cold-crank performance

Cold-crank tests of this profile compared to a separator of equal overall and backweb thickness, but with continuous vertical ribs have shown an increase in cold-crank performance beyond the effect of the electrical resistance of the separator alone. This is due to the fact, that the separator

Generally is $R = \frac{1}{\sigma}\frac{l}{A}$ with l = length of ionic path and A = area

and R (Separator) = R (Separator + Electrolyte) - R (Electrolyte)

$$R\,(\text{Sep. Sheet + Electrolyte}) = \frac{1}{\sigma}\frac{d}{q}\frac{T^2}{P}$$

$$R\,(\text{Spacer + Electrolyte}) = \frac{1}{\sigma}\frac{(D-d)}{q_S}\frac{T^2}{P}$$

$$R\,(\text{Electrolyte; free}) = \frac{1}{\sigma}\frac{D-d}{q-q_S}$$

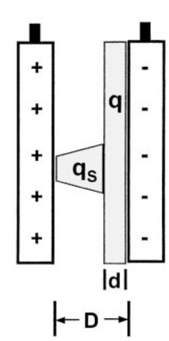

Fig. 5. Electrical resistance of a separator (theoretical considerations).

(I) Resistances "in parallel" : $$\frac{1}{R_{Total}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \ldots$$

(II) Resistances "in series" : $$R_{Total} = R_1 + R_2 + R_3 + \ldots$$

result in :

$$\frac{1}{R_{(Spacer + Electrolyte;\ free)}} = \frac{1}{R_{(Spacer)}} + \frac{1}{R_{(Electrolyte;\ free)}}$$

As $R_{(Spacer)} >> R_{(Electrolyte;\ free)} \Rightarrow R_{(Spacer + Electrolyte;\ free)} \sim R_{(Electrolyte;\ free)}$

follows :

$$R_{(Separator)} = R_{(Sep.\ Sheet + Electrolyte)} + R_{(Electrolyte;\ free)} - R_{(Electrolyte)}$$

Fig. 6. Kirchhoff's laws.

$$R_{(Separator)} = R_{(Sep.\ Sheet + Electrolyte)} + R_{(Electrolyte/\ free)} - R_{(Electrolyte)}$$

$$R_{(Separator)} = \frac{1}{\sigma}\,\frac{d}{q}\,\frac{T^2}{P} + \frac{1}{\sigma}\,\frac{D-d}{q-q_S} - \frac{1}{\sigma}\,\frac{D}{q}$$

With $\frac{D}{q} = \frac{D-d}{q} + \frac{d}{q}$ follows

$$R_{(Sep)} = \frac{1}{\sigma}\,\frac{d}{q}\left(\frac{T^2}{P} - 1\right) + \frac{1}{\sigma}\left(\frac{(D-d)}{q-q_S} - \frac{(D-d)}{q}\right)$$

$$R_{Separator} = R_{Sep.\ Sheet} + R_{Electrolyte\ (D-d)} \cdot \frac{q_S}{q-q_S}$$

Fig. 7. Electrical resistance of a separator consisting of a backweb and spacer elements.

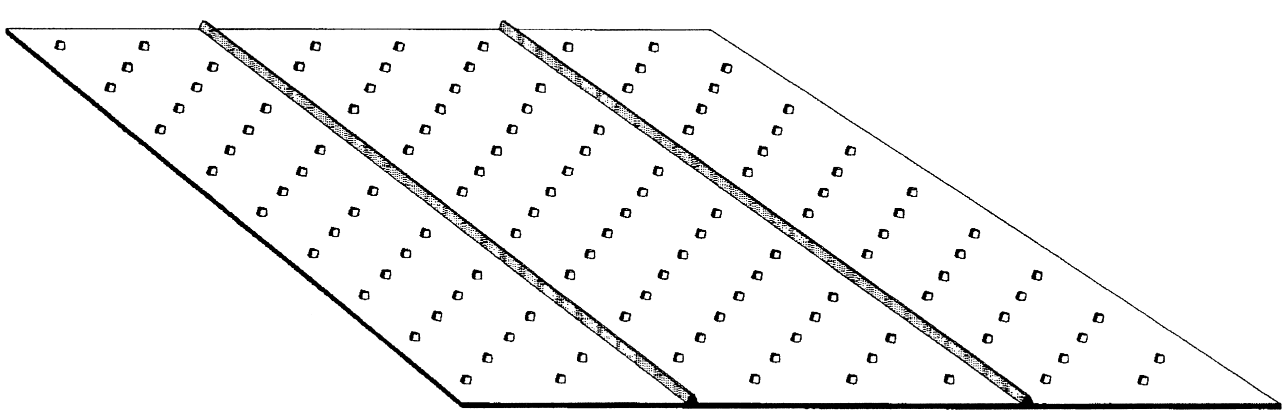

Fig. 8. "Studs–ribs–combi" profile.

electrical resistance is only defined macroscopically and does not take account of microscopical inhomogeneities. Inside the electrodes under the rib area of the separators the ion passage is considerably impeded, increasing the overvoltage and thus, decreasing the cold-crank performance. A comparison of the two designs shows an advantage of about 6% in terms of cold-crank current for this optimized version versus the standard design with a multitude of vertical ribs, whereas the difference in electrical resistance alone would only anticipate 3% improvement.

4. Concluding remark

Material's properties and geometric design characterize a separator. Aspects of the optimization of both factors have been presented here. Designs which are apparently optimized today may have to be further modified in order to meet the challenges of new applications in the future.

References

[1] W. Böhnstedt, Separators, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Wiley, Weinheim, Germany, 1999.
[2] D.W. Larsen, C.L. Kehr, US Patent 3,351,495 (1966).
[3] N. Sugarman, Brit. Patent 2,044,516 (1979).
[4] W. Böhnstedt, J. Power Sources 67 (1997) 299–305.
[5] H. Bünsch, K.H. Ihmels, F.O. Theubert, Eur. Patent EP 0,425,784 (1989).
[6] W. Böhnstedt, US Patent 5,776,630 (1994).
[7] W. Böhnstedt, W. Lindenstruth, US Patent 4,927,722 (1988).
[8] L. Lemorini, G. Fossati, Eur. Patent EP 0,484,295 (1991).
[9] D.W. Hercamp, T.E. Key, Eur. Patent Application EP 0,899,801 (1997).
[10] K. Nakano, US Patent 5,716,734 (1991).
[11] D.J. Knauer, US Patent 5,558,952 (1995).
[12] H. Okamoto, K. Yonezu, S. Murochi, Eur. Patent Application EP 0,994,518 (1998).
[13] D.D. O'Rell, N.J. Lin, G. Gordon, J.H. Gillespie, UK Patent GB 2,097,174 (1981).
[14] W. Böhnstedt, J.K. Whear, US Patent Application 09/372,531 (1999).