

# New developments in separators for valve-regulated lead–acid batteries

W. Böhnstedt

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

## Abstract

In valve-regulated lead–acid (VRLA) batteries the electrolyte solution has to be immobilized to ensure tiny channels left open for the transfer of oxygen from the positive to the negative electrode. So far microfibre glassmats have predominantly been used, which based on their high porosity and good wettability of the glass fibres are able to retain durably large electrolyte volumes. The tensile strength of such microfibre glassmats remains unsatisfactory. Developments to produce absorbing mats from organic fibres have recently succeeded due to advanced developments in polymers and in fibre production processes as well as in achieving permanent hydrophilisation. Such polypropylene-microfibre mats have excellent tensile and puncture strength and—as pockets—can be well integrated into highly automated assembly processes. Test data for polypropylene-microfibre mats are presented and compared to microfibre glassmats. Another approach to hamper the electrolyte in its free mobility is to gel it: batteries with gelled electrolyte have been shown to require conventional microporous separators—both for secure fixing of plate spacing as well as for preventing electronic shorts. Despite their complex filling process gel batteries are well accepted for cycling applications, when simultaneously freedom from maintenance is required. Due to the high power requirements for EV batteries there is a trend towards thinner plates and thinner separation; also substantial pressure on the positive electrode and thus also on the separator is desirable to improve the cycling life decisively. A new separator development is presented, which in spite of high porosity (> 80%), suffers only little deformation even under very high pressure. It effectively prevents acid stratification, forms no filling profile and permits oxygen transfer. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Valve-regulated lead–acid batteries; Separators; Microfibre mats; Gel electrolyte; Acid jelling separator; Compression

## 1. Introduction

The basic principle of valve regulated lead–acid batteries is founded on the oxygen formed during charging at the positive electrode being internally transported to the negative electrode and being reduced there. The negative electrode thus becomes partially discharged and does not reach the overcharging phase and simultaneous hydrogen evolution. Therefore, no water consumption occurs; the total charging current—viewed externally—is converted into heat [1].

In order to keep tiny channels from the positive to the negative electrode open for this oxygen transfer the electrolyte has to be immobilized, i.e., hindered in its free mobility. For this purpose, two rather different approaches have turned out: in one the electrolyte filling the space between the electrodes can be absorbed by a highly porous structure, e.g., a microfibre mat [2]; in the other, the electrolyte by addition of gel formers, such as, e.g., pyrogenic silica, can be incorporated into a three-dimensional lattice.

## 2. Valve-regulated lead–acid batteries with liquid electrolyte

### 2.1. Microfibre-glassmats

Today for electrolyte immobilization in valve regulated lead–acid batteries predominantly microfibre glassmats are in use, which at the same time assume the function of the separator, i.e., a distance fixation of the electrodes being permeable for ionic current flow. Extremely high porosity (> 90%), large internal surface area ( $\geq 1 \text{ m}^2/\text{g}$ ), and a good wettability are the prime characteristics to absorb a maximum quantity of electrolyte. Large internal surface area is achieved by finest fibre diameter, e.g., glass fibres of  $10 \text{ }\mu\text{m}$  diameter reach  $\sim 0.15 \text{ m}^2/\text{g}$ , whereas  $0.5 \text{ }\mu\text{m}$  fibres result  $\sim 3 \text{ m}^2/\text{g}$ .

The pore distribution of fibre mats is anisotropic, which is desirable: whereas within the plane between the electrodes due to the fibre diameter very fine pores ( $\sim 1 \text{ }\mu\text{m}$ ) are formed, effecting high capillary forces, in the direction perpendicular to this plane, pores of  $\sim 10\text{--}20 \text{ }\mu\text{m}$  diame-

ter can be found, which are required to assure the oxygen transfer [3].

The separator has to have long-term stability against the various chemical and electrochemical attacks inside a lead–acid battery and, of course, its susceptibility increases with the internal surface area. It also must not give off any substances increasing gassing rate, corrosion or self-discharge. Finally, it should be robust enough that it can be handled in the production process of the battery, i.e., it should not be punctured by sharp edges or small particles. This last requirement might suggest the use of binders which, however, detrimentally affect the wettability and thus may not be used.

Microfibre glassmats meet these generally formulated requirements quite comprehensively [4–11]. Blends of glass fibres of various diameter are processed on paper machines into voluminous mats while the blending ratio gains particular emphasis for balancing technical properties against economical considerations. Expensive microfibrils below 1  $\mu\text{m}$  diameter effect a large internal surface area and the desired pore size distribution, but due to their shortness they contribute only little to tensile strength. Fibres of larger diameter improve the handling, but increase the tendency to break on compression of the glass mat. A microfibre content of some 20–30% has shown to be quite sufficient for optimizing the desired properties [12].

Microfibre glassmat can be procured from a variety of suppliers; Table 1 shows typical data.

The extreme porosity of microfibre glassmats—despite some 10 vol.% free channels for oxygen transfer—assures the acid displacement and also the electrical resistance to be very low, although considerably higher than results of fully soaked samples would indicate [3]. The actual electrical resistance ‘experienced’ by the battery is within the order of magnitude of other modern separation systems ( $\sim 50\text{--}70 \text{ m}\Omega \text{ cm}^2/\text{mm}$  of thickness).

The low pore size of microfibre glassmats in the plane between the electrodes effects capillary forces, which should allow cell heights of some 30 cm. However, the electrolyte adopts a filling profile: due to gravity, the voids required for oxygen transfer will accumulate in the upper part of the electrolyte.

A further limitation for the battery height is caused by acid stratification. Finally, the electrolyte is still just liquid

and acid of higher density, which, e.g., is formed during the charging step, will—even with some delay—diffuse downward, which is detrimental, especially for deep-cycling applications. In contrast to batteries with fully liquid electrolyte, there is the lack of acid agitation by bubble formation at the end of charging.

All of this has led to microfibre glassmats prevailing up to now only in smaller-sized—not particularly long-lived—stationary or consumer batteries. In severe cyclic service applications or for larger battery heights, valve-regulated batteries with gelled electrolyte—mainly due to their lower acid stratification—have significant advantages (cf. Section 3.1).

Despite all the efforts for many years to introduce the valve-regulated construction with microfibre glassmats in starter batteries, until now only few results have been published: the cold crank performance is excellent, the cycling life, despite the required lead–calcium alloys, was found to be very good [13], probably due to the support of the positive active material. In spite of these advantages—in addition to the freedom from maintenance—valve-regulated starter batteries have yet failed to succeed, mainly due to their cost structure. Stable containers and precise electrode geometry, voluminous separators and reliable valves, lower productivity and costly filling process are difficult to justify in times of cost cutting in the automotive industry.

One interesting new development, the addition of a few percent of organic fibres to microfibre glass fleeces [14] is claimed to essentially simplify the acid filling of cells: surplus acid can be poured out simply by overturning the batteries. The organic fibres for their hydrophobicity will facilitate the oxygen transfer and are sufficient to allow welding these mats into pockets. Experience from the field practice has not yet been published.

## 2.2. Polymeric microfibre mats

One significant step ahead attempts to produce such absorbing mats totally from organic fibres. Only recently, further developments in polymers as well as refinements in the fibre production processes have resulted in successfully manufacturing mats with a high percentage of fine fibre diameter below 1  $\mu\text{m}$ , and—in parallel—achieving a lasting hydrophilisation [15].

In the production of these polypropylene microfibre mats in a melt-blown process, an optimum between fine fibres share and productivity is to be achieved. Depending on the intended application, the fine fibres portion can be adjusted within certain limits. For hydrophilisation there is a choice of several processes: grafting of hydrophilic macro-molecules can be justified costwise only for special applications. Coextrusion of polypropylene and hydrophilic polymers is considerably more cost efficient; such microfibre mats currently undergo battery testing.

Table 1

Typical properties of microfibre glassmat separators<sup>a</sup> for VRLA batteries with liquid electrolyte

Basis weight [ $\text{g}/\text{m}^2$ ]	200
Porosity [%]	93–95
Pore size (mean) [ $\mu\text{m}$ ]	5–10
Thickness (acid filled)	
at 10 kPa [mm]	1.3
at 35 kPa [mm]	1.0
Puncture strength [N]	7.5

<sup>a</sup>100% Glass fibres.

Table 2  
Comparison microfibre-glassmat vs. PP-microfibre-mat

	Microfibre-glassmat	Polypropylene-microfibre-mat
Basis weight [g/m <sup>2</sup> ]	240	185
Porosity [%]	93–95	90–92
Pore size (mean) [μm]	5–10	5–15
Fibre diameter [μm]	0.5–5	0.5–30
Thickness (acid filled) at 10 kPa [mm]	1.7	1.8
at ~ 35 kPa [mm]	1.3	1.3
Puncture strength [N]	7.5	15
Tensile strength		
MD [kN/m]	0.32	0.75
CMD [kN/m]	0.25	0.92
Seal strength [kN/m]	n.a.	0.7

Generally, polypropylene microfibre-mats distinguish themselves by excellent tensile and puncture strength; they can be welded ultrasonically, thermally or mechanically into pockets and can thus be integrated into highly automated assembly processes.

Table 2 shows a comparison between typical data of a microfibre glassmat and of a polypropylene microfibre-mat. Glassmats attain a slightly higher porosity, probably based on higher stiffness of the individual fibres, beyond this the portion of microfibres is also higher in glass mats.

Because of the different densities of the materials used and because of the differing porosities, any conclusive comparison of mechanical properties should be based on equal final mat thickness inside the battery, i.e., the thickness under a pressure of some 35 kPa corresponding to a 25% compression of the microfibre glassmat. Despite a significantly lower area weight of the polymeric microfibre-mat, this results typically in twice the puncture strength as well as in at least twice the tensile strength. In addition, tear resistant pockets can be welded, which facilitates automated handling of pocketed plates, e.g., for batteries which are produced in large quantities, like SLI batteries for cars or motor cycles.

### 3. Valve-regulated lead–acid batteries with gelled electrolyte

#### 3.1. Conventional separation

As already pointed out, VRLA batteries with liquid electrolyte have not yet prevailed for severe cycling service; the main reasons for this may be found in acid stratification and susceptibility to lead microshorts. A remedy can be achieved by VRLA batteries with an electrolyte which is hindered in its free mobility by gelling. The addition of some 5–8 wt.% pyrogenic silica to the electrolyte develops a gel structure due to its immense internal surface area (200–300 m<sup>2</sup>/g), fixing the molecules of the dilute sulfuric acid within a lattice by Van-der-Waals

forces. These gels have thixotropic properties, i.e., by mechanical stirring they can be liquefied for filling the batteries, where they again gel within a few minutes. Initially, these batteries experience some water-loss during overcharging; the gel thus dries partially and forms cracks, enabling the oxygen to reach the negative electrode, where the internal oxygen consumption occurs, which prevents additional water loss and drying out [16,17].

Batteries with gelled electrolyte have been shown to require a separator in the conventional sense—both for secure fixing of the distance between the electrodes as well as to prevent electronic shorts; the latter is achieved by microporous separators. A further important criterion is minimal acid displacement, because these batteries compared to batteries with liquid electrolyte lack the electrolyte volume share, which is taken up by gel and crack formation. Typical data for such a microporous separator predominantly used in VRLA batteries with gelled electrolyte can be found in Table 3.

#### 3.2. Acid jelling separators

For severe cyclic loads, as they occur, e.g., in electrotraction applications, the use of lead–calcium alloys, required for freedom from maintenance, shows premature capacity loss [18]. This effect has been shown to occur delayed or even not at all, if a continuous pressure on the electrodes is exerted [19–23], like that effect which is known to extend the service life for lead–antimony alloys [24–27]. The capacity loss over the cycle life is accompa-

Table 3  
Typical properties of microporous separators<sup>a</sup> for valve-regulated lead–acid batteries with gelled electrolyte

Backweb thickness [mm]	0.3
Porosity [%]	70
Pore size (mean) [μm]	0.5
Acid displacement [ml/m <sup>2</sup> ]	145
Electrical resistance [mΩ cm <sup>2</sup> ]	120

<sup>a</sup>With 0.3 mm glassmat on the positive side.

Table 4

Typical properties of acid jellifying separators for valve-regulated lead–acid batteries in cycling applications

Basis weight [g/m <sup>2</sup> ]	320
Porosity [%]	81
Pore size (mean) [μm]	0.2
Acid shrinkage [%]	+1
Thickness (acid filled)	
at 10 kPa [mm]	1.0
at 35 kPa [mm]	0.995
at 100 kPa [mm]	0.99
Electrical resistance [mΩ cm <sup>2</sup> ]	90

nied by an expansion of the battery cells; this again is caused by a partially irreversible expansion of the positive electrode during each individual cycle [28]. While using conventional microfibre glassmat separators attempts at exerting considerable pressure on the electrodes—and thus vice-versa also on the separators—suffer from these separators experiencing fibre fracture at high compression and thus irreversible loss in thickness, which again decreases the pressure on the electrodes [22,29].

Instead of designing the separator to follow the expansion and contraction of the electrodes during each individual cycle, the conception of the ‘acid jellifying separator’ is based largely on preventing this expansion: for this, gelled electrolyte is tied into a stable, microporous separator structure, which occupies the whole void volume between the electrodes. Ideally, the strived for separator is therefore ‘stiff as a board’ to resist any expansion of the positive active material beyond the geometric electrode dimensions, and also not to invade the electrode (between the grid bars) at high external pressure and thus decreasing the electrode porosity. Thus, an effective limitation of the originally existing electrode space is strived for by suppressing any expansion of positive active material also during the cycle

life and hereby maintaining the internal contact sites in their initial state. An adaptation and optimization of the porosity of the positive active material is expected to essentially contribute to an extension of cycle life.

To prevent a loss of positive active material by shedding or crystal growth, the separator has to be microporous on its surface, and inside its pores, to fix the electrolyte as a gel which also counteracts the acid stratification.

What pressure should such a separator be able to withstand? From the literature, one may assume for lead–antimony batteries a pressure of at least 40 kPa [24], but at best some 100 kPa [25]; for lead–calcium alloys at least 40 kPa or more are considered necessary. On the other hand, for weight reasons of the total battery—still presuming a prismatic construction—mechanical pressure in excess of 200–300 kPa is difficult to imagine. The pressure within an electrode/separator stack varies widely (up to 20%) from the nominal pressure during each individual cycle in a complex manner, which has been reported on in the literature with contradictory results and theories [24,26]. Based on the above, a separator design for very high cycle life should stand a pressure range of 50–150 kPa.

Recently, microporous acid jellifying separators have been introduced [30], which in spite of surprisingly high porosity of more than 80%, show excellent mechanical properties. In Table 4, the most important properties for 1 mm thick separators are compiled as an example; the material can also be produced as thin as some 0.1 mm.

Remarkable is the fact that this acid jellifying separator is slightly growing, when filled with acid, opposite to the troublesome shrink behaviour of microfibre glassmats.

Of excellence is the very low dependency of the thickness on the mechanical pressure, which becomes even more obvious in comparison to microfibre glassmats, as shown in Fig. 1. For a design pressure of 100 kPa, its

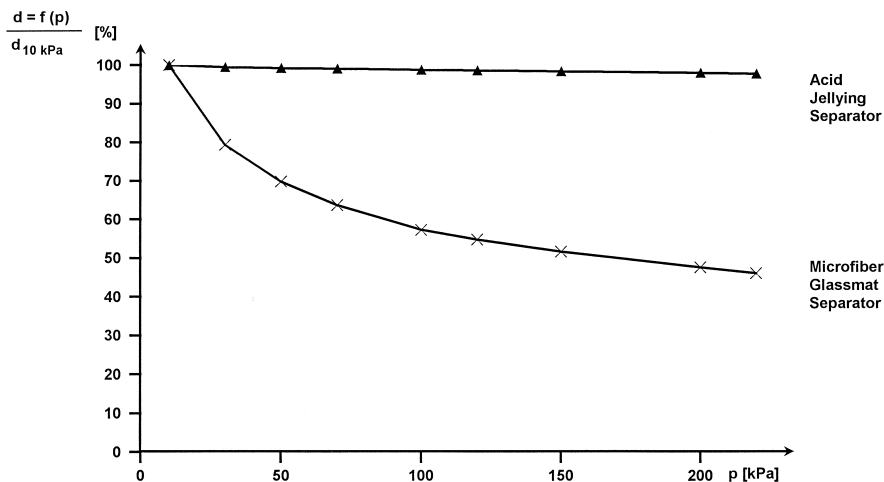


Fig. 1. Compressibility of VRLA battery separators (acid filled).

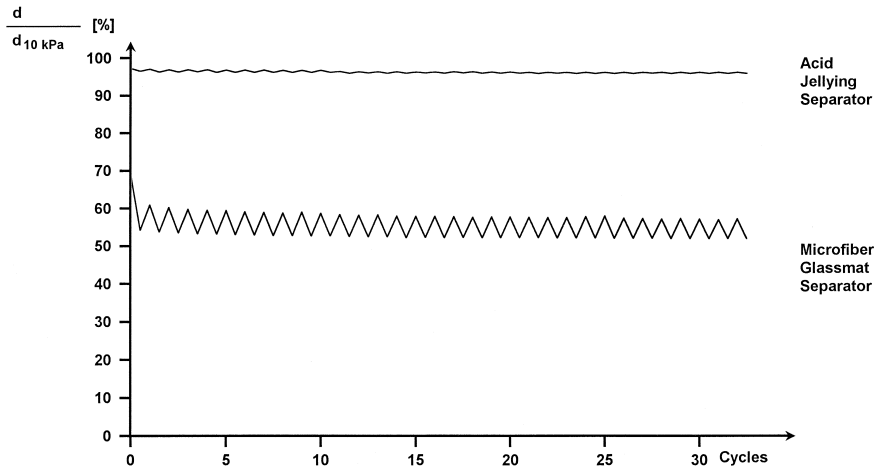


Fig. 2. Compressibility of VRLA battery separators (pressure cycles: 50 kPa/150 kPa; acid filled).

thickness decreases by only some 1% in contrast to more than 40% for microfibre glassmats.

Also, the sensitivity against pressure changes is minimal, as can be seen in Fig. 2, again in comparison to microfibre glassmat separators. For this test, acid filled separators have been subjected for 15 min each alternately to either 50 kPa or 150 kPa, respectively. This low pressure sensitivity of acid jellying separators should suffice to confine—a defined, limited space for the positive active mass, each between the adjacent ribs of the cast grid and the form-stable separator, to suppress any expansion of the positive active mass from the start. The microporosity will largely prevent shedding.

Acid stratification is also not expected to have a significant effect on cycle life, since the electrolyte is fixed like a gel inside these separators, which is due to the extremely large internal surface area of some  $150 \text{ m}^2/\text{g}$ . The following experiment proves this quite impressively: separator strips ( $8 \times 2.5 \text{ cm}$ ) are soaked with sulfuric acid, half of it

with a density of  $1.6 \text{ g/cm}^3$  and half with  $1.2 \text{ g/cm}^3$  and then suspended to have the higher density acid in the top half. Due to gravity effects with time the densities will equalize from top to bottom. Fig. 3 shows the acid densities measured for acid jellying separators in comparison to microfibre glassmat separators. The intersection of the straight lines yields the extrapolated time for acid density equalization within the separator. Due to the substantially larger internal surface for acid absorption and the lower average pore size the acid density change proceeds some six times slower in acid jellying separator than in microfibre glassmats. This should effectively delay acid stratification in cycling service or even completely eliminate it, because the time for forming denser acid within the few hours of one charge–discharge cycle is short in comparison to the time of acid diffusion exchange inside the separator over some 50 h.

Acid jellying separators are currently being tested and optimized for electric vehicle batteries within the ALABC program [31], especially with respect to its oxygen trans-

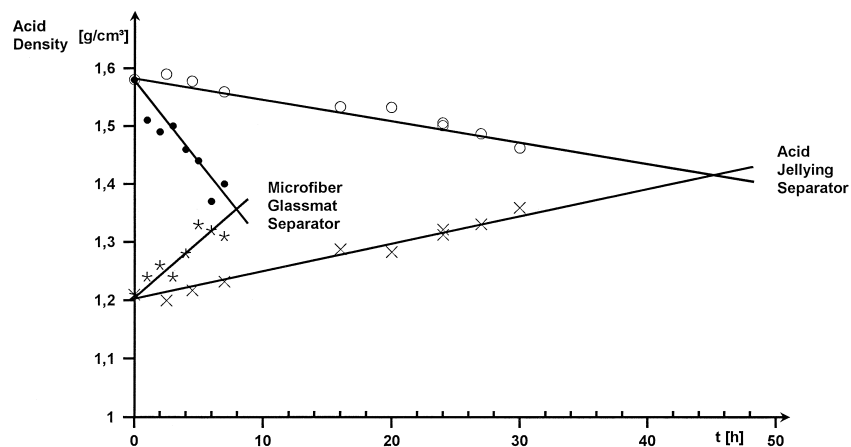


Fig. 3. Acid equalization under gravity.

fer. The share of larger pores permitting gas transfer can be varied within a certain range. Here, an optimum between sufficient oxygen transfer and least penetration susceptibility is to be achieved, which strongly depends on separator thickness and thus on battery design. For electric vehicle applications with their high power requirements, a clear trend toward thin electrodes and thus also toward thin separators can be observed. This should not present any limitation to acid jellying separators, because—as already pointed out—they can be produced in very low gauges tear-resistant down to some 0.1 mm to enable problem-free automatic processing, even for other applications, such as, e.g., spirally wound cells or super-capacitors.

#### 4. Outlook

Just as already for conventional lead–acid batteries with liquid electrolyte, where optimum battery designs for the various applications have evolved with optimized separators, so also for VRLA batteries different requirement profiles demand special separator characteristics. The recent developments have shown strengths, but also weaknesses for the existing separation systems and thus have given impetus to intensive further development. Probably none of the alternatives presented here will displace any other completely; on the contrary, they will be forced to compete in ever optimized versions for the various applications. It certainly will remain interesting!

#### References

- [1] D. Berndt, *Maintenance-Free Batteries*, 2nd edn., Research Studies Press, Taunton, Somerset, England, 1997.
- [2] D.H. McClelland, J.L. Devitt, US Patent 3,862,861 (1972).
- [3] B. Culpin, J.A. Hayman, in: L.J. Pearce (Ed.), *Power Sources* 11, International Power Sources Symposium Committee, Leatherhead, UK, 1986, p. 45.
- [4] K. Peters, *J. Power Sources* 42 (1993) 155.
- [5] G.C. Zguris, D.W. Klauber, N.L. Lifshutz, in: T. Keily, B.W. Baxter (Eds.), *Power Sources* 13, International Power Sources Symposium Committee, Leatherhead, UK, 1991, p. 45.
- [6] R.F. Nelson, in: T. Keily, B.W. Baxter (Eds.), *Power Sources* 13, International Power Sources Symposium Committee, Leatherhead, UK, 1991, p. 13.
- [7] R.F. Nelson, *J. Power Sources* 46 (1993) 159.
- [8] D.A. Crouch Jr., J.W. Reitz, *J. Power Sources* 31 (1990) 125.
- [9] B. Culpin, *J. Power Sources* 53 (1995) 127.
- [10] H. Miura, H. Hosono, *J. Power Sources* 48 (1994) 233.
- [11] W. Böhnstedt, Separators, in: J.O. Besenhard (Ed.), *Handbook of Battery Materials*, Wiley-VCH Verlag GmbH, 1999, p. 245.
- [12] F.J.T. Harris, US Patent 4,465,748 (1982).
- [13] E. Nann, *J. Power Sources* 33 (1991) 93.
- [14] J.P. Badger, US Patent 4,908,282 (1987).
- [15] J. Zucker, International Patent Application (PCT) WO 98/31060 (1997).
- [16] O. Jache, German Patent 1,671,693 (1967).
- [17] H. Tuphorn, *J. Power Sources* 46 (1993) 361.
- [18] A.F. Hollenkamp, *J. Power Sources* 59 (1996) 87.
- [19] K.K. Constanti, A.F. Hollenkamp, M.J. Koop, K. McGregor, *J. Power Sources* 55 (1995) 269.
- [20] K. Peters, *J. Power Sources* 59 (1996) 9.
- [21] A.F. Hollenkamp, R.H. Newnham, *J. Power Sources* 67 (1997) 27.
- [22] K. McGregor, A.F. Hollenkamp, M. Barber, T.D. Huynh, H. Ozgun, C.G. Phyland, A.J. Urban, D.G. Vella, L.H. Vu, *J. Power Sources* 73 (1998) 65.
- [23] G.C. Zguris, *J. Power Sources* 67 (1997) 307.
- [24] K. Takahashi, M. Tsubota, K. Yonezu, K. Ando, *J. Electrochem. Soc.* 130 (1983) 2144.
- [25] Z. Alzieu, J. Robert, *J. Power Sources* 13 (1984) 93.
- [26] J. Alzieu, N. Koechlin, J. Robert, *J. Electrochem. Soc.* 134 (1987) 1881.
- [27] J. Landfors, *J. Power Sources* 52 (1994) 99.
- [28] D. Pavlov, E. Bashtavelova, *J. Electrochem. Soc.* 133 (1986) 241.
- [29] G.C. Zguris, *J. Power Sources* 59 (1996) 131.
- [30] W. Böhnstedt, J. Deiters, K. Ihmels, J. Ruhoff, German Patent Application 19702757 (1997).
- [31] EALABC Project No. -BE 1 (b) Brite-Euram Project IMPLAB BRPR-CT97-0602 Task 1 b.