

Short communication

# Simultaneous optimisation of the properties of engineered composite grids for lead-acid batteries

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## Abstract

We have developed innovative multilayer composite grids as engineered materials, which are produced in the form of grid strip in a single, highly efficient, multistage electrodeposition process. In the present paper, we are reporting, how the individual requirements for grid properties can be satisfied and optimised individually and then combined simultaneously to an overall optimum in this new family of composite grid materials. The multilayer composite materials are composed of different layers of different structures and properties, which can provide a combination of different functional properties to satisfy a more demanding total specification of mechanical behaviour, electrical performance, corrosion resistance and cycling behaviour.

The paper deals with the improvement of these properties in detail and with the overall simultaneous engineering of the grid material.  
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## 1. Introduction

Present battery grids are made of single-alloy materials that provide sub-optimal combinations of mechanical, electrical, corrosion and cycling properties compared to ideal requirements for optimal battery performance. Current grid materials based on Pb–Sb or Pb–Ca–Sn base alloys are actually incomplete technical compromises not only because of their sub-optimal compositions but also because of their particular microstructures, which result from the conventional manufacturing processes, i.e. casting, rolling, expanding or punching.

Recent more stringent demands such as increased battery-operating temperatures, higher power and energy densities, extended cycle life requirements and others call for improved grid materials. They must be engineered to satisfy the conflicting property demands simultaneously to a maximum, which cannot be attained with single-alloy materials and by present manufacturing processes.

As a response to these new challenges DSL Dresden has developed innovative multilayer composite grids as engineered materials, which are produced in the form of grid strip in a single, highly efficient, multistage electrodeposition process [1–3]. In

the present paper, we are reporting on the particular aspect, how the individual requirements for grid properties can be satisfied and optimised individually and then combined simultaneously to an overall optimum in this new family of composite grid materials.

Since the electroforming process developed by DSL Dresden results in multilayer composite materials this means that combining different layers of different structures and properties can provide a combination of different functional properties to satisfy a more demanding total specification of

- mechanical behaviour;
- electrical performance;
- corrosion resistance;
- cycling stability.

In addition, this unique combination of an innovative material synthesis and manufacturing process is, also, very cost effective and competitive with all present processes used to manufacture grids for batteries.

## 2. Mechanical behaviour

Optimisation of the mechanical behaviour of composite grids means to satisfy several different requirements:

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- hardening of at least part of the cross-sectional area of the grid to provide a sufficiently high basic yield strength;
- composing layers of different yield strength to obtain a sufficient overall yield strength to withstand (i) the tensile stresses arising during pasting and (ii) the tensile stresses causing grid growth;
- controlling the elastic material stiffness, the elastic shape stiffness and the yield strength in such a way as to provide an effective bending stiffness which is sufficient for handling during all stages of the battery production process.

### 2.1. Yield strength

The basic idea of attaining sufficient effective yield strength of the composite grid is to provide one or several internal grid layers of high yield strength. Electrodepositing a Pb–Cu alloy which is dispersion hardened by 0.2–0.6 wt% Cu can provide such a layer of high yield strength. It has been known at least since 1972 that the strength of electrodeposited Pb–Cu layers increases steeply with increasing Cu content [4] whereas conventionally processed chemical lead containing 0.05–0.5 wt% Cu shows a very slight increase with Cu content only [5]. Upon electrodeposition of the dilute Pb–Cu alloy, Pb forms the matrix layer in which Cu is embedded in particle form in the nm size range (5–50 nm). The particles are distributed at random and give rise to dispersion hardening. An example of the concentration dependence of the 0.2% proof stress of dilute electrodeposited Pb–Cu–Sn alloys is shown in Fig. 1. Quantitative microstructural analysis based on TEM micrographs permits to analyse the particle density and relate it to the observed yield stress through the Orowan relation for particle hardening.

Since the Cu rich particles are extremely small in size, isolated and very dilute, they have no deleterious chemical effect on the battery performance because there is no significant amount of Cu dissolution and deposition on the negative plate.

Simple additive material law can be applied in a first approximation to determine the overall tensile properties of

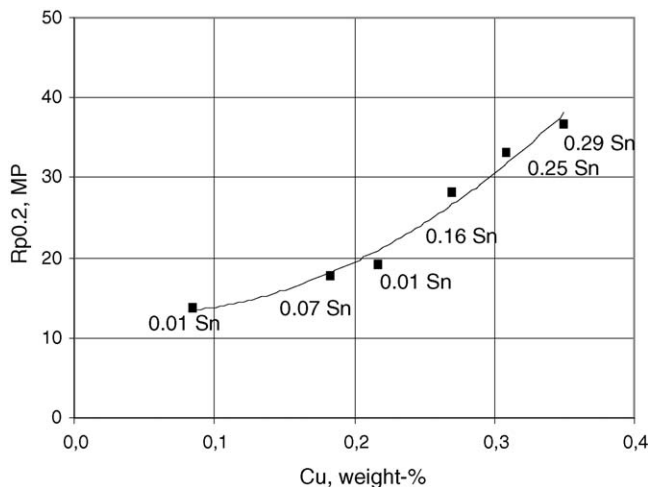


Fig. 1. Concentration dependence of the 0.2% proof stress of dilute, electrodeposited Pb–Cu–Sn alloys.

the composite from those of the core and outer layers [2]. But numeric, FEM-based modelling and simulation can provide more definitive property results and functional relationships for grid design in particular for deformation in bending.

### 2.2. Effective bending stiffness

The deformation behaviour of the composite grids in bending cannot be predicted by simple algebraic relations from the basic mechanical properties of the individual layers. But it is possible to model and simulate the effective bending stiffness, which comprises elastic deformation and plastic yielding. We have studied a number of different variants by numerical FEM computations. One basic variant was to use a dispersion hardened Pb(Cu) core material. On the other hand, it was obvious that the major outer layer of Pb–Sn is soft both elastically, since its Young's modulus is essentially that of pure Pb, and plastically, because its yield strength is almost as low as that of pure Pb. Therefore, we have considered a number of variants which contain an intermediate layer of Cu. This is related to the use of Cu to increase the effective conductivity as discussed in the subsequent section. Young's modulus of Cu (128 GPa) is eight times higher than that of Pb (15.8 GPa). Accordingly, we devised a series of computations with different composite structures.

We have chosen a model consisting of a single grid wire 5 mm in length, 0.9 mm in thickness and based on a width of 0.6 mm in the initial deposition structure. The composites consisted of layers of different thickness and mechanical properties. The wire is fixed at one end and force  $F$  applied to the other end was 0.5 and 0.7 N, respectively. Such a model is a good approximation of an entire grid and of a deflection under its own weight. Since this model disregards the somewhat larger cross sections of the grid frame the computed bending displacements tend to be rather an overestimate of the real displacements occurring for a true grid structure. Qualitatively the cross-sectional variants on which the computations were based, resembled the wire cross sections shown in Fig. 3a and b below, respectively.

Fig. 2a shows a pictorial representation of a typical computational result: the grid wire is bent under the load applied. The maximum displacement  $d$  as a function of composite structure and load is the most decisive indicator of the effective bending behaviour of the composite. It was assessed as a function of different composite variants as shown in Fig. 2b. It should be noted that we have assumed a minimum thickness of 200  $\mu\text{m}$  of the outer Pb–Sn layer in order to ensure that ordinary rates of corrosion would not dissolve this amount of material before the end of life of the battery.

The striking result of these experimental computations is that the overriding parameters of the effective displacement  $d$  by bending are: (i) the shift of the hardened Pb(Cu) and/or the pure Cu layer towards the free surface and (ii) the thickness of those layers. All composite variants can be realised by the DSL deposition process in one single production run.

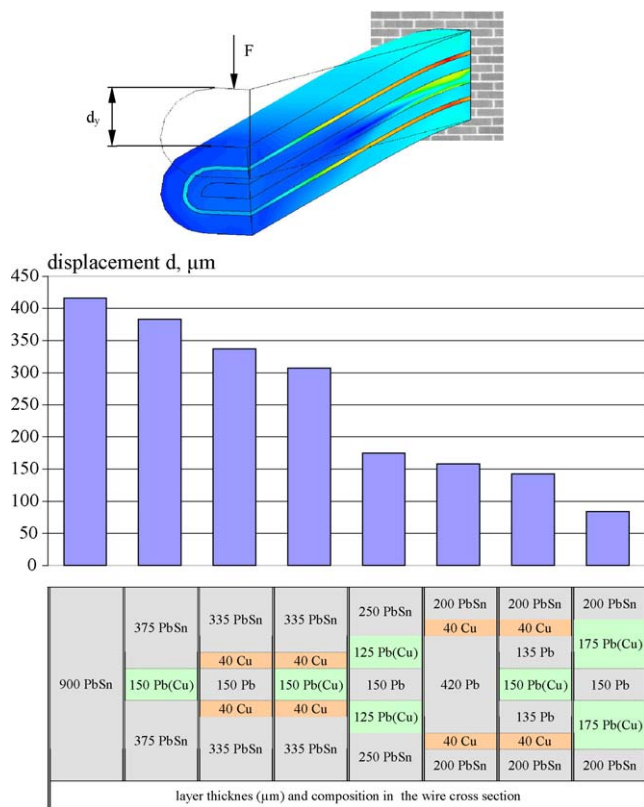


Fig. 2. (a) Typical output graph of the simulation of half a grid wire containing an intermediate Cu layer. (b) Results of the simulation of effective bending displacements under 0.7 N load of full grid wires for different composite structures.

### 3. Electrical performance

The electrical performance of a battery grid can be optimised under two major aspects:

- effective resistivity of the grid material;
- effective resistance resulting from the grid design.

#### 3.1. Effective material resistivity

The resistivity of pure Pb and of a number of characteristic present grid alloys is listed for reference in Table 1. In the commercial grid alloys which are essentially dilute solid solutions of Pb the impurities and the alloying elements contribute to the resistivity by their different specific effects on the residual resistivity. Obviously, this effect is smaller for Sn than for Ca.

Table 1  
Electrical resistivity  $\rho$  of Pb and Pb alloys [5,7]<sup>a</sup>

	$\rho$ (nΩ m)
Pb	192
Pb99.94	206
Pb–5Sn	208
Pb–0.07Ca	218
Pb–0.1Ca–0.5Sn	219
Pb–4Sb	223
Pb–6Sb	253

<sup>a</sup> Concentration in wt%.

Since the DSL grids contain no Ca and the major part of their cross section consists of pure binary Pb–Sn they have a lower effective resistivity than present common Pb–Ca–Sn grids by about 5%. We have shown that the resistivity can be lowered still more drastically by introducing pure Cu layers into the composite structure as shown in two variants in Fig. 3. This unique feature can be realised solely by the DSL manufacturing process [6]. It requires simply adding a Cu deposition bath into the strip galvanising line.

Since the electrical resistivity of pure Cu is 16.8 nΩ m, a wire cross section with a Cu layer of only 3% in fractional area, as realised approximately in Fig. 3b, reduces the effective resistivity from 208 to 155 nΩ m, i.e. by about 25%. Fig. 4 illustrates the changes in effective resistance of grid wires as a function

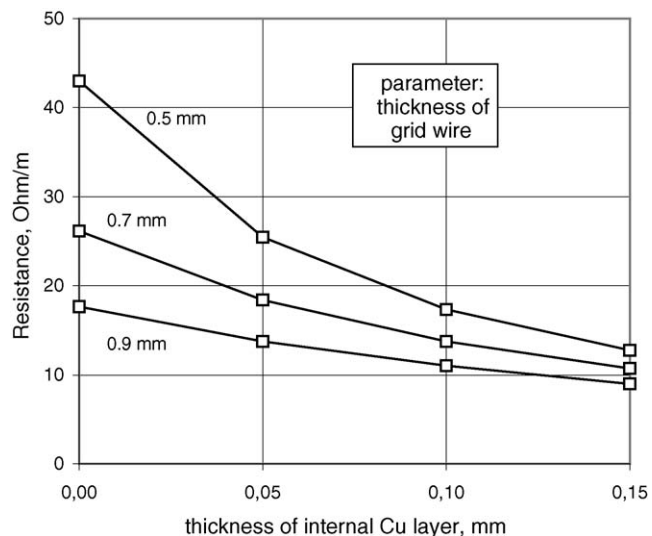


Fig. 4. Effective resistance per unit length of grid wires as a function of thickness of an internal Cu layer.

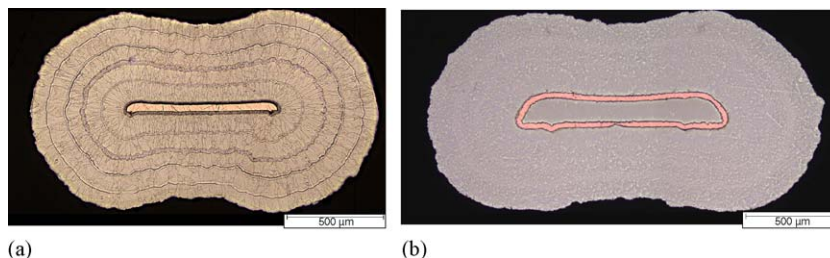


Fig. 3. Micrographs showing the cross sections of grid wires with layers of pure Cu: (a) Cu as a core layer (etched) and (b) Cu as an intermediate layer (as polished).

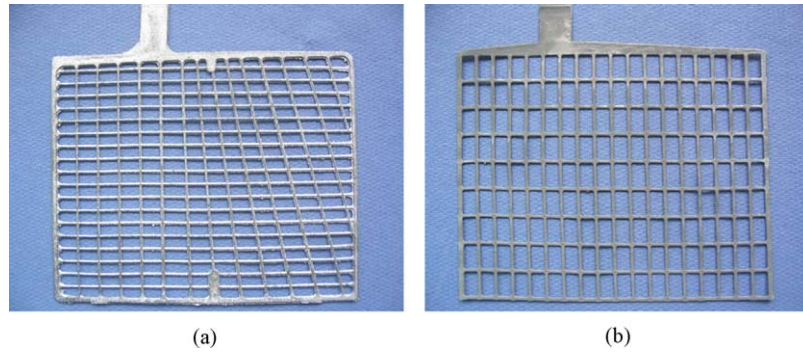


Fig. 5. Grid types compared by electrical measurements and by modelling and simulation: (a) book mould cast grid type Zm and (b) electroformed DSL grid.

of the thickness of the internal Cu layer and the total thickness of the grid wire for a wire cross section of the type shown in Fig. 3a.

It should be noted that this type of low-resistivity variant of a composite grid could be utilised for positive plates without any limitation because the Cu layer is fully encapsulated by a corrosion resistant pure Pb–Sn outer layer, which prevents the Cu from being dissolved in the battery electrolyte throughout the battery life.

Obviously, Pb/Cu composite grids manufactured economically by multistage electroforming provide an unprecedented possibility of improving the current distribution within the grids and of designing lead-acid batteries with an exceptionally high power rating.

### 3.2. Effective grid resistance

The overall resistance of a grid determines the power performance of the battery and depends on the electrical resistivity of the grid material as well as on the grid design. Tiedemann et al. [8] were among the earliest to assess the potential distribution in battery grid both by modelling and by experiment. Different computation methods have been developed since to design grid structures taking the overall resistance into account. But most of the present manufacturing processes do not permit to optimise the grid design completely because the manufacturing process itself is limiting the freedom of design or even determining the grid structure. Thus, for gravity cast grids the requirements of the casting process have to be taken into account. In the expanded grid manufacturing process non-ideal, lozenge shaped grid structures only can be produced.

By contrast, the DSL electroforming process provides essentially full freedom of grid design and optimisation. We have

reported earlier [2] that improvements by as much as 22% of effective resistance over that of a seemingly optimised cast grid could be attained by suitable systematic computations and optimisations based on modelling and simulation of the grid design. Computer aided optimisation of grid design is a current topic [10].

In the meantime, we have developed refined tools of modelling by applying the finite element method (FEM) to simulate electrical grid properties as determined by practical laboratory measurements such as the effective resistance  $R_{\text{eff}}$ , and the weighted conductance (Gittergüte)  $C_w$ . Fig. 5 and Table 2 indicate results of practical measurements by which a conventional cast grid, a regular DSL grid and a DSL grid with a Cu core were compared.

These observations by measurement and by simulation have clearly shown three results: (i) the composite material has a superior conductivity even on the basis of using a pure Pb–Sn outer layer; (ii) the conductivity is increased still more significantly if a pure Cu intermediate layer is incorporated; (iii) modelling and simulation using FEM are ideally suited to predict the electrical grid properties from the geometric and material design parameters such that this numeric method can be used as a design tool.

An additional possibility to optimise the current distribution in the grid is the use of tapered grid wires. Even though this is not a novel idea as such its realisation is limited to a larger or lesser degree by the kind of manufacturing process. The electroforming process, however, offers even two modes of tapering: the entire grid may be tapered from top to bottom in thickness, and the individual grid wires may be tapered in width.

Another aspect requiring the freedom of design may be the future use of dual tab designs [9]. This design feature can be provided by simply designing the tool accordingly when using the electroforming process.

Table 2  
Experimental<sup>a</sup> and simulated results obtained for the effective resistance  $R_{\text{eff}}$  and the weighted conductance  $C_w$  of a book mould cast grid, a regular electroformed grid and an experimental high power electroformed grid with a copper layer of the type shown in Fig. 2b

	Cast, Pb–0.06Ca–Sn–Ag (65 g)		Electroformed, Pb–Sn (67 g)		Electroformed Pb–Sn/Cu (67 g)	
	Measured	Simulated	Measured	Simulated	Measured	Simulated
$R_{\text{eff}}$ (mΩ)	0.69 ± 0.09	0.69	0.43	0.53	0.38	0.39
$C_w$ (S g <sup>-1</sup> )	24 ± 3	24	32	31	40	42

<sup>a</sup> The experimental results were kindly supplied by Akkumulatorenfabrik Moll, Bad Staffelstein, Germany.



#### 4. Corrosion resistance

The basic strategy to obtain the superior corrosion resistance of battery grids is to provide

- an inherently corrosion resistant composition, at least in a major outer layer;
- a microstructure which leads to a uniform and general, rather than a catastrophic and localised, corrosion attack.

We have shown [3] that these two conditions can be fulfilled to an optimum by DSL composite grids. Corrosion resistant layers can be deposited as the major outer layers of the composite grids such as the multilayered outer layer in Fig. 2. It remains functional throughout the life of the battery. In keeping with the two major demands stated above, the corrosion resistance is effectively due to two effects [3]:

- the use of highly corrosion resistant binary Pb–Sn;
- the control of the microstructure in such a way that it consists of crystallites in columnar, fine-grained array and that it exposes a multisublayer structure of slightly varying Sn-content, which corrodes in a layer-like manner without forming deep crevices.

Such a combination of favourable chemical composition and microstructure can only be provided under the particular conditions of electrodeposition. The superior corrosion behaviour of DSL composite grids has been proved in numerous corrosion tests by battery manufacturers in the meantime. Examples are shown in Table 3.

The effective reduction in rate of chemical corrosion of DSL grids permits to produce grids 20–30% thinner than with Ca alloyed grid materials while reaching the same battery life [3].

#### 5. Cycling stability

Present grid manufacturing processes, in particular when based on strip materials with rolled surfaces, tend to yield insufficient interfacial contact between grid alloy and active material. In some cases even “exfoliation”, i.e. delamination of the flat-rolled surface crystallites, may occur during corrosion. This leads to loosening of the contact with the active material. The flexibility of the electroforming process of DSL grids permits to

coat the grid surface with layers of a pre-selected

- specified composition;
- textured microstructure;
- surface roughness.

to increase the adherence of the active material and influence the composition of the oxide formed significantly. If the grids are formed by electrodeposition, a final coating with controlled properties can be applied at essentially no extra cost because it is deposited as part of the continuous grid manufacturing process. Moreover, the improvement can even be applied to grids formed by other processes (such as casting, expanding and punching) in passing them through an electrodeposition line for a coating treatment.

##### 5.1. Specified composition

For optimising surface composition by electrodeposition, different variants can be realised in-line in the DSL process. The optimum surface composition may be chosen according to the type of battery and typical load cycles in service.

If the cycling occurs in a partial state of charge (PSoC) the formation of an oxide is preferable which provides strong bonding between grid and active material and a persistent electrical contact. Using the DSL electrodeposition process Pb–1–2 wt%Sb is one of the alloy variants that may be deposited as a final coating in this case; it promotes the initial corrosion process during plate formation and gives rise to a highly adhesive oxide layer. The thickness of the coating layer may be chosen typically in the range of 5–50  $\mu\text{m}$ .

If improved deep discharge behaviour and charge-acceptance upon re-charging is required, the formation of the highly conducting  $\text{SnO}_2$  phase at the interface between grid and active material has been found to offset the passivating effect of the  $\alpha$ -PbO formed in the increasingly alkaline electrolyte upon deep discharging. A surface layer containing Pb–1–1.5 wt%Sn promotes the formation of  $\text{SnO}_2$  and increases the conductivity of the oxide layer formed upon deep discharge according to the literature [3]. Using the DSL electrodeposition process, a final coating of this alloy composition would be deposited to achieve optimum deep discharge behaviour.

##### 5.2. Increased interfacial area

The electrodeposition process to produce battery grids offers two unique possibilities to increase the contact area between the grid and the active material. On the one hand, the fine-grained columnar microstructure is oxidised in such a way that it forms a serrated surface as shown in Fig. 6a. Moreover, controlling the current density applied for deposition in the final stage of the grid formation by electrodeposition permits to control the surface roughness to a predetermined amount, e.g. in terms of the roughness parameter  $R_a$ , as shown in Fig. 6b. Since a controlled surface roughness is not available with any of the present grid making processes there are no quantitative data of the effects available for comparison to date.

Table 3

Results obtained by battery manufacturers on corrosion behaviour of DSL grids tested according to different industrial standards for automotive applications

Test standard	Conditions	Result
VW 750 73	Corrosion at 60 °C under varying specified loading conditions for a total of 8 weeks	DSL grids fully flexible at end of test
ASI J-240	Cycling at 75 °C, 1500 cycles	DSL grids fully intact at end of test

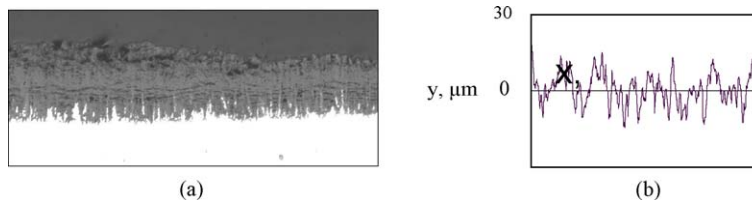


Fig. 6. Two measures to increase the effective surface area of an electroformed grid: by intensive intergrowth of oxide and grid during the formation treatment and by deliberate, controlled surface roughening during grid production. (a) Rough surface contour caused by corrosion of grid wire, (b) deliberate roughening, roughness trace corresponding to  $R_a = 13 \mu\text{m}$ .

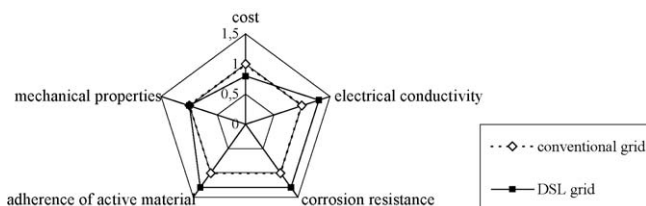


Fig. 7. Semi-quantitative comparison between conventional grids (reference) and DSL grids regarding their major properties and cost.

## 6. Total grid optimisation

Obviously, the layer structure of composite grids provides a variable material system to optimise the desired grid properties deliberately and by design in combining the different layers according to their

- intrinsic properties;
- thickness or volume fraction;
- position or sequence in the composite.

A comparative assessment of the technical and economic efficiency of conventional and DSL grids is derived as shown schematically in Fig. 7.

## 7. Conclusions

The composite structure of electroformed grids permits optimising their properties independently and in combination. As a result, optimised property combinations may be attained, which cannot be provided by present single-alloy grids.

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## References

- [1] PCT patent application WO 02/057515 A2.
- [2] H. Warlimont, T. Hofmann, Technical economic advantages of making lead-acid battery grids by continuous electroforming, *J. Power Sources* 133 (2004) 14–24.
- [3] H. Warlimont, T. Hofmann, Superior corrosion properties and reduced battery cost using electroformed grids, *J. Power Sources* 144 (2005) 486–493.
- [4] Japanese Patent J 48080437 A.
- [5] W. Martienssen, H. Warlimont (Eds.), Springer, Handbook of Condensed Matter and Materials Data, Springer, Heidelberg, New York, 2005.
- [6] Patent pending.
- [7] Properties of Lead and Lead Alloys, Booklet No. 5M, Lead Industries Association, New York, pp. 12–83.
- [8] W. Tiedemann, J. Newman, F. DeSua, Potential Distribution in the Lead-Acid Battery Grid, *Power Sources, Research and Development in Non-Mechanical Electric Power Sources*, vol. 6, Brighton 1976, Academic Press, 1977, pp. 15–23.
- [9] M.J. Kellaway, P. Jennings, D. Stone, E. Crowe, A. Cooper, Early results from a systems approach to improving the performance and lifetime of lead acid batteries, *J. Power Sources* 116 (2003) 110–117.
- [10] K. Yamada, K. Maeda, K. Sasaki, T. Hirasawa, Computer aided optimization of grid design for high power lead-acid batteries presentation at 9th ELBC, Berlin, 2004.