Composite grids are a new kind of battery grids with significantly improved properties. Hans Warlimont, Matthias Seidel and Thomas Hofmann describe this novel grid material, the novel galvanic production technology, and the results of comparative battery tests performed by major battery producers.

Novel composite grid technology to improve the performance of lead acid batteries

Composite grids are a new kind of battery grid with superior properties and potentially lower costs of production. Their unique feature is a multilayer composite structure which achieves significantly improved grid and battery properties.

The layer structure is illustrated in figure 1 which shows the cross section of a composite grid wire.

Each layer contributes a particular property such as strength, electrical conductivity or corrosion resistance, or to obtain the total cross section required. .

The basic advantage of using composite grids for batteries is to overcome the disadvantages of present alloy grids. Their alloying elements impart conflicting effects: calcium or antimony are used as a hardening element, but both reduce the corrosion resistance; tin is added to increase the corrosion resistance, but while tin is required near the surface only, this expensive element is contained in the entire volume.

These inherent technical and economic disadvantages of alloy grids can be overcome by using composite grids which offer additional advantages because the layer structure permits one to optimize each property separately and to incorporate additional layers such as a copper one to increase the conductivity.

Process and equipment

In composite grid technology the grid pattern and its composite layer structure are produced by an economical, continuous galvanic process without any emission of CO_2 because no pyrometallurgical processing is required.

Figure 2 shows the layout of the equipment for the two-stage electrochemical deposition process which is based on well established galvanic technology.

It comprises a small unit for forming a thin grid strip by continuous galvanoforming first and a galvanic coating line to deposit the various layers which constitute the composite structure of the final grid.

The photograph on the lower right shows the finished grid strip as it leaves the last module of the coating line.

Product and properties

The product is a grid strip which is one or two grids wide and which may be produced with any predetermined grid pattern and thickness. Figure 3 (on following page) shows examples of composite grids and of a composite foil produced.

It should be noted that a grid strip

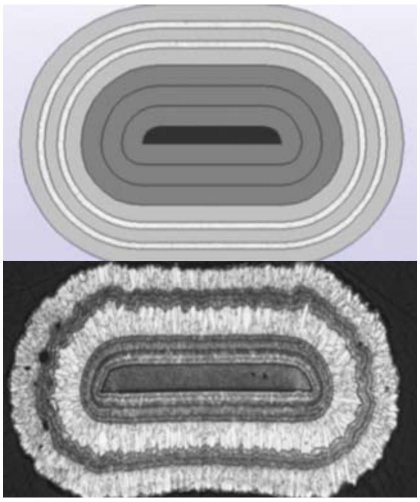


Figure 1: Cross section of a composite grid wire. The drawing on top indicates schematically that each layer of the composite grid may consist of a different metal or alloy. The micrograph below shows the microstructure of a real grid wire.

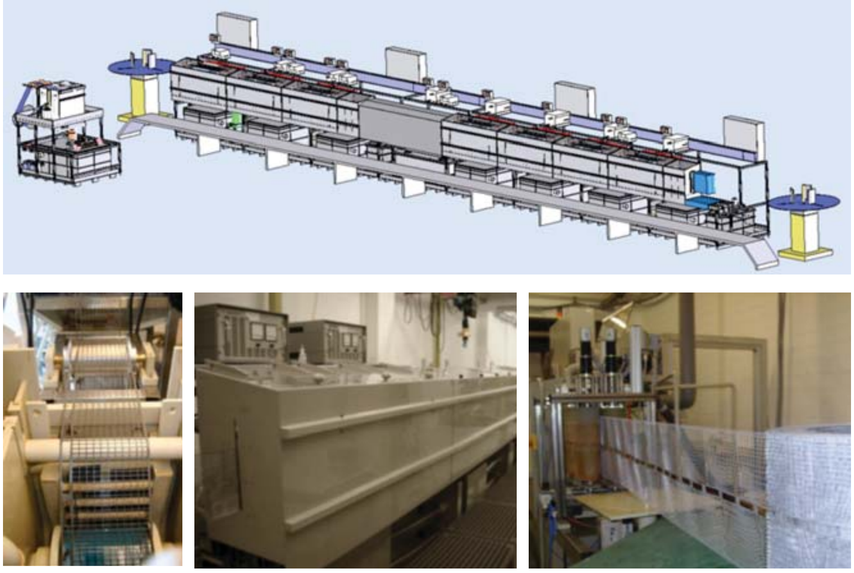


Figure 2: Production equipment for composite grids. Left: strip galvanoforming unit (open, without electrolyte); centre and right: multi-layer strip forming line consisting of a number of independent galvanic strip coating modules

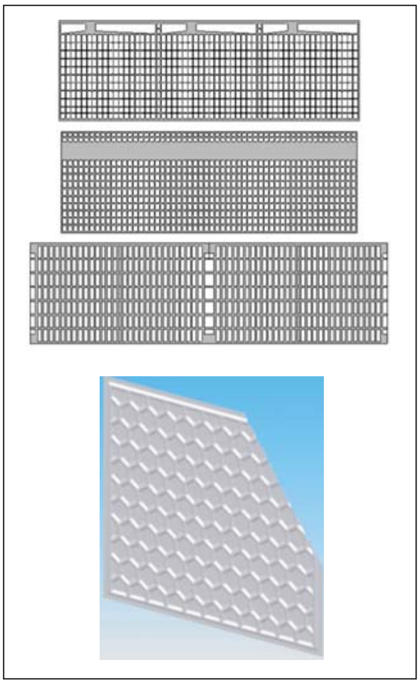


Figure 3: Examples of grids for lead acid batteries in strip form and a foil for spirally wound batteries produced by the composite grid technology

OVERVIEW

The composite battery grids and the galvanic process for their production have been developed to the state of a mature technology. The multilayer composite imparts superior grid properties compared to present grids. In particular, the use of a copper layer to decrease the resistivity improves the electrical properties and the performance parameters significantly.
The table summarizes the improvements demonstrated by battery tests.

Battery improvements by composite grids vs. gravity cast grids

Improved battery property	Improvement	
	Amount	%
Decrease of internal resistance	- 0.5 mΩ	20
Decrease of voltage drop after cranking	- 250 mV	2.5
increase in test cycle life	+ 400 cycles	50
Decrease in degree of sulfation	3 vs. 12 units by weight of PbSO4	75

The new technology combines making improved battery grids with the recycling of battery scrap and, thus, lower cost compared to present grid production. Therefore it is expected to find its place in the battery industry despite its innovative technical approach.

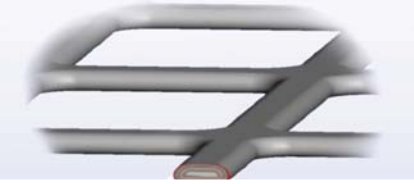


Figure 4: Grid contour

produced by conventional processes such as continuous casting, punching or expanding of prefabricated strip can be coated in the same strip coating line to add the superior properties of a multilayer composite structure.

As shown schematically in figure 4 the grid wires produced galvanically have rounded edges which contribute to increasing the adherence of the active material around their contour.

The characteristic internal layer structure of a composite grid is shown in figure 5. The drawing on the top gives an example of a typical design of a layer sequence while the microstructure below shows the real layer structure in the cross section of a grid wire.

It should be noted that a pure copper layer will always be located far enough below the free surface such that it is not exposed to the electrolyte during the life time of the battery. A final rough surface coating may be deposited by a suitable setting of the deposition conditions to increase the adherence of the active material.

Grid properties

The layer structure imparts a combination of grid properties by design such as reduced electrical resistivity, increased corrosion resistance or simply an adjustment of cross-sectional volume.

The reduction of electrical resistivity can be achieved by incorporating a copper layer as shown in figure 5 above. The quantitative dependence of the effective resistivity of a typical composite grid wire with a copper layer on the thickness of this layer has been calculated, the result is presented in figure 6. It shows that a layer thickness of 0.05 mm is sufficient to reduce the resistivity by 50%.

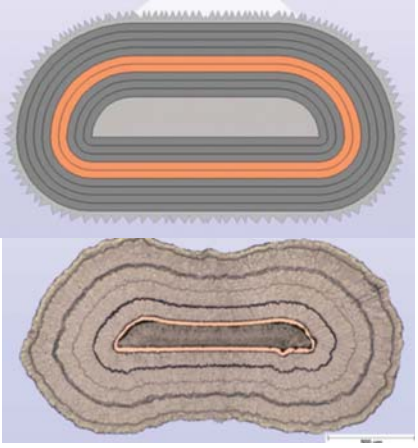


Figure 5: Typical layer structures of a composite grid with an internal copper layer to reduce the resistivity

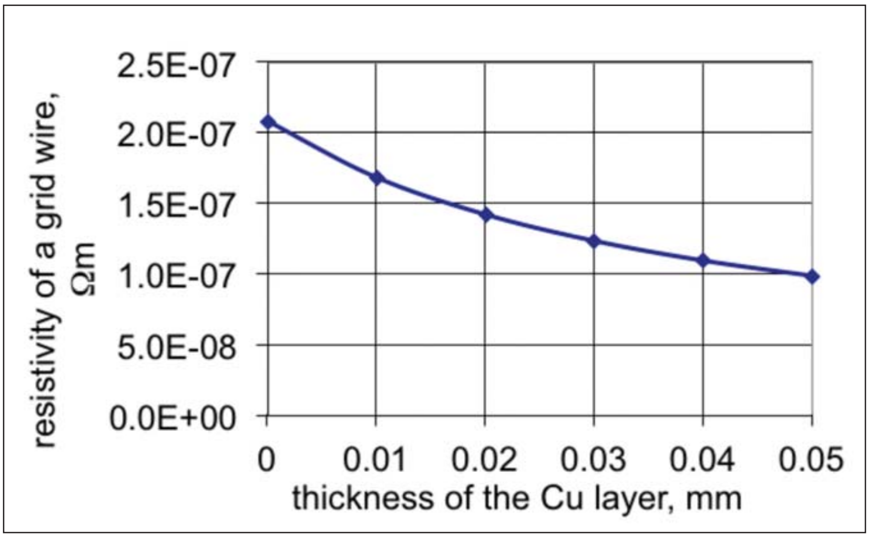


Figure 6: Resistivity of a composite grid wire as a function of the thickness of an internal copper layer

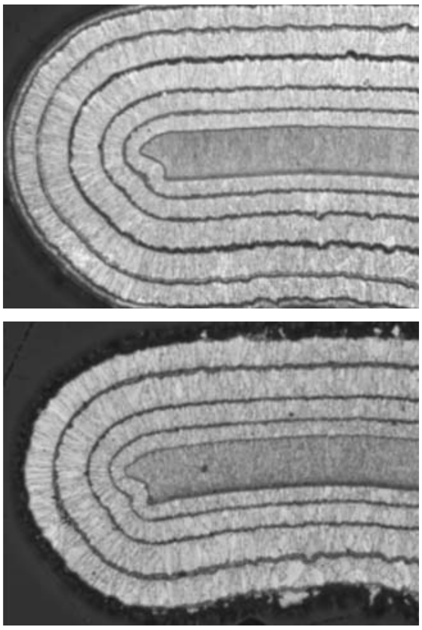
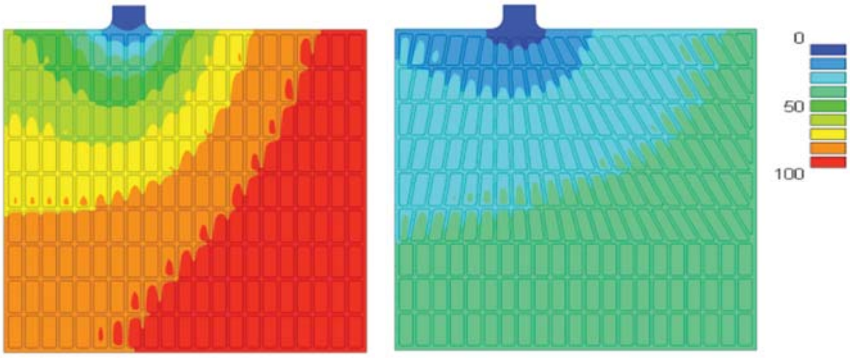


Figure 7: Cross section of a grid wire before and after a corrosion test. Just one layer has been dissolved. Test conditions: 10 days, 75°C, 6 mA/cm^2, H_2SO_4



Pure Pb grid

Composite grid with a copper layer

Figure 8: Comparison of the potential variation across positive plates with different grids. Simulation calculations

The increase in corrosion resistance is based on alternating layers of pure lead and lead-tin with a tin content, of 1.0%-1.4%, near the surface, and on the layer structure of the grids as such.

The effect of the layer structure is illustrated in figure 7. It shows that the corrosion attack proceeds layer-wise. Thus, the grid stays intact even after considerable weight loss. The composite structure prevents the formation of deep crevices and cracks. Therefore, the effective corrosion life is increased considerably.

Plate properties

The reduction in electrical resistivity of the composite grids by an internal copper layer affects the plate properties significantly. This can best be shown by the comparison of plate properties as assessed by simulation calculations. Typical results are illustrated in figure 8.

The steep potential gradient of the plate with the pure lead grid will result in a reduced utilization of the active material with increasing distance from the lug. However, the plate based on the composite grid with a copper layer has a much lower potential gradient which leads to a significantly more uniform and, thus, higher degree of utilization of the active material across the entire plate, resulting in a higher effective charge capacity.

Battery properties

Two battery companies — Moll Batteries in Germany and Shandong Sacred Sun Power Sources in China — have carried out extensive comparative battery tests by using conventional and composite grids in different combinations for the positive and negative battery plates. Standard test procedures were applied.

The subsequent figures show some of their results. The obvious basic effect of composite grids with a copper layer is to decrease the internal resistance of the batteries which is shown quantitatively in figure 9.

An immediate effect of the composite grids with a copper layer on battery performance is observed in the cranking test. Figure 10 illustrates that the voltage after 10 seconds of cranking remains higher by more than 250mV compared to batteries with gravity cast grids.

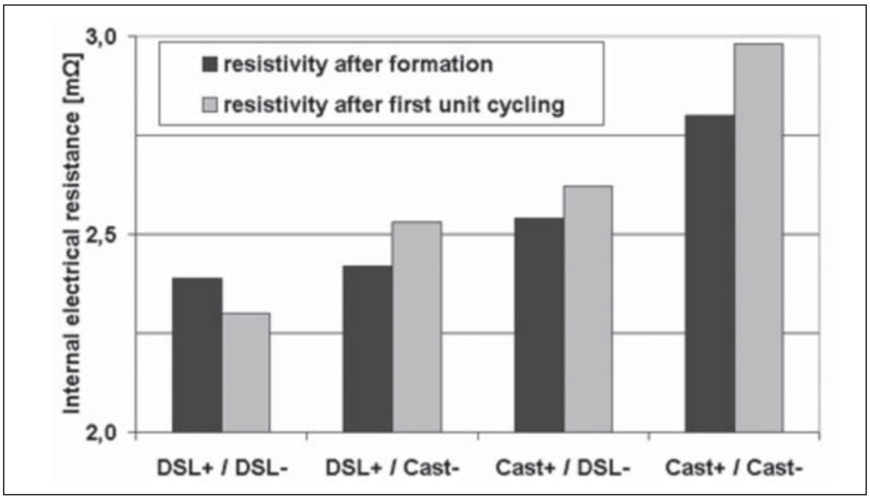


Figure 9: Lowering the internal resistance of the battery by using composite grids with a copper layer (Moll). DSL = plates containing composite grids with a copper layer, Cast = plates containing gravity cast grids

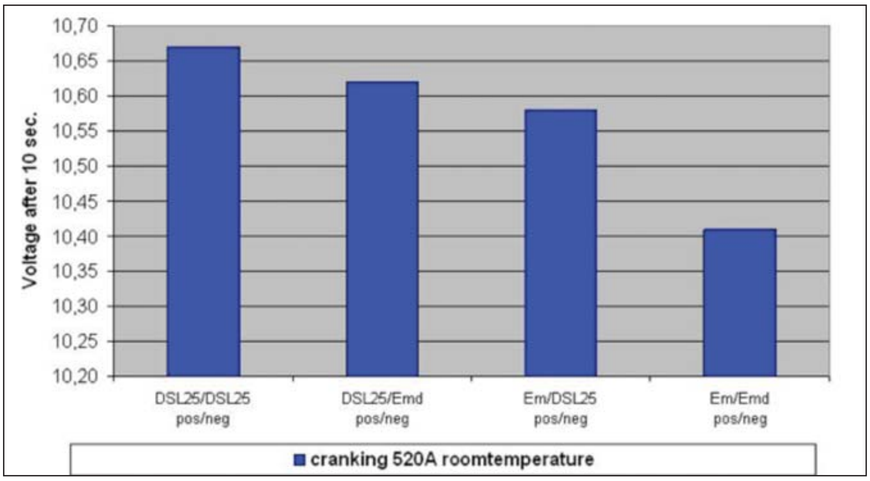


Figure 10: Comparative cranking test results show the lowered voltage drop associated with the use of composite grids (Moll). DSL25 = plates with composite grids with a copper layer, Emd = plates with gravity cast grids

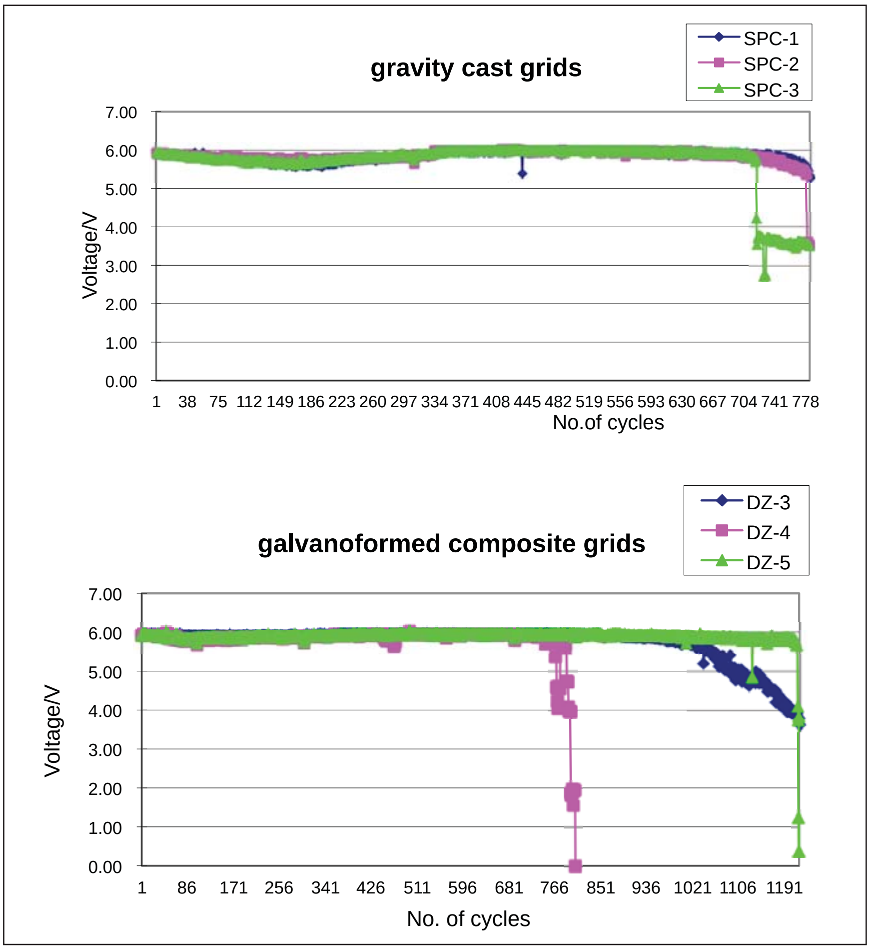


Figure 11: Cycling behaviour (Sacred Sun). Cycle: discharge at 14A (0.5C2) for 1.40h to 70% of nominal capacity, charge at 4.2 A (0.15C2) followed by 8.0 V to a total of 5.6h.

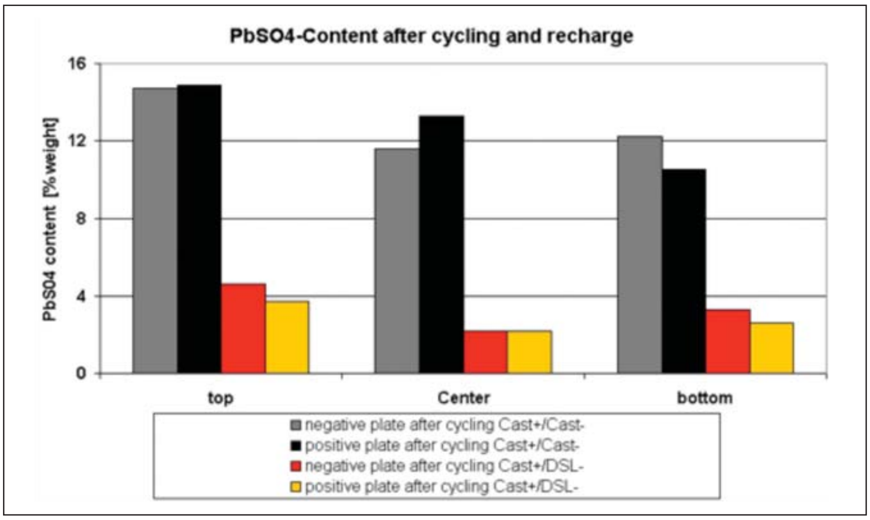


Figure 12: Comparison of sulfate content after cycling (Moll)

THE AUTHORS

Professor emeritus Dr **Hans Warlimont** has held several positions in fundamental research and industrial development in physical metallurgy. He has published over 200 original papers, several reviews and books in the field of materials science. He initiated the development of composite battery grids.

Dr **Thomas Hofmann** has used his electrochemical background to develop the novel product and process technology for composite grids by extensive research first and by industrial development subsequently.

Dipl Ing **Matthias Seidel** is senior manager of OTA Surface Technology and Plant Manufacturing in Berlin, where the experimental equipment and the industrial production plant for composite grids were designed and built.

Figure 11 shows the test data obtained for the cycle life which is the most relevant battery property from a cost point of view.

Despite some early failures due to unavoidable defects owing to the experimental production conditions, there is a clear difference in maximum cycle life which is increased significantly from about 780 cycles for the cast grids to about 1190 cycles for the composite grids made from lead alloys, ie by about 50%.

Another favorable consequence of using composite grids with a copper layer is a drastic reduction of sulfation during cycling as shown in figure 12. It indicates that the amount of sulfation of both the positive and the negative plate is lowered by 75% if composite grids with a copper layer are used.

Direct use of scrap as raw material

A unique economic advantage of grid production by galvanic deposition arises from the fact that electrolytic dissolution and re-deposition of a metal has a refining effect simultaneously. Therefore, the scrap and even the active material of spent batteries can be used as raw material for the galvanic production of composite battery grids.

Various kinds of scrap and active material have been studied as raw material systematically by deposition experiments and subsequent analyses to prove that the deposits satisfy the impurity limits of battery grade material.

Figure 13 is a schematic flow diagram of the processing options resulting from the possible use of scrap and of the active material of used batteries as direct feed in the process.

The economic gain by the use of scrap is obvious because scrap cost is typically about 30% lower than the cost of pure lead. The gain is even higher if the cost of grid alloys is compared.

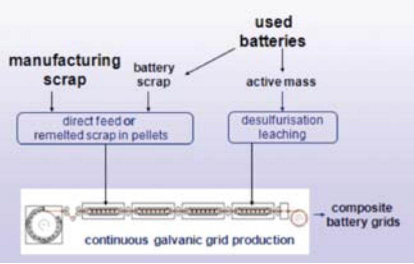


Figure 13: Flow diagram indicating the options to couple the galvanic production of composite battery grids with the electrolytic recycling of scrap