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ADVANCED TECHNOLOGIES IN ENERGY STORAGE FOR SUBMARINE PROPULSION

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Main subject of the paper is electrochemical energy storage systems in submarines.

In order to give an insight into the requirements to such a storage system, the lead-acid cell, which is state of the art, is described in full detail. This part takes into consideration especially the Copper-Stretch-Metal technology and the usage of other electrode metals within the lead-acid cell.

Non-electrochemical storage systems and a review of the possibilities of different systems including H_2/O_2 fuel-, sodium sulphur- and lithium-cells are subject of the second part.

Finally, results of present developments of a maintenance-free lead-acid submarine cell are presented and discussed under various aspects, e.g. hydrogen evolution, capacity and charging procedures.

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ENERGY STORAGE

There are different kinds of energy and storage possibilities:

- mechanical (pocket-watch, toy cars, hydropower),
- chemical (food, batteries, gasoline, dynamite),
- electrial (electric and magnetic fields),
- nuclear (matter).

The engines of our cars are fed with chemical stored energy, namely gasoline or diesel fuel, and so are the engines of a so-called diesel-electric submarine. At least as long as the boat is not dived. During its operational periods, the submarine is totally dependent on the lead-acid battery installed. A rough calculation on the possibilities to store energy, either as gasoline or as chemical energy in a lead-acid battery, is quite interesting. Image a car with a 30 kW motor running one hour at high speed, thus consuming 10 liters of gasoline. For easy calculation, assume a density of 1 kg/l so that an energy density of 3000 Wh/kg for gasoline results (the true value is even higher). The most sophisticated lead-acid cells come up to values of 60 Wh/kg.

But the only alternative to the lead-acid cell, presently in use, is nuclear power. The underwater endurance of underwater ships is limited by other factors than energy shortage. However, because of the necessary shielding of the hot sections, these ships are big and, therefore, not suitable for use in shallow waters.

To increase the submerged range of a submarine, some options are available. Despite increasing the capacity of the battery, the same could be removed and replaced by another system, or part of the battery is replaced. From the above given estimate, it is plain to see the advantages of fuel storage against batteries. For a submarine, one also has to take the oxygen needed for combustion into the calculations. A car takes more than half of the fuel from the open air, for each kg of fuel burnt, 2 to 3 kg of oxygen are needed! The boat has to carry this oxygen as fuel in one form or another, e.g. as hydrogenperoxide or in elementary form.

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The three approaches for underwater propulsion with combustion engines are the Stirling engine, the Walther turbine and the closed diesel engine. The Walther turbine was developed in Germany during WW II 1), the Stirling engine is presently promoted by a Swedish group and for the closed diesel, recent developments have been reported from Italy 2).

Another alternative to increase the underwater endurance is the use of fuel cells which directly convert chemical energy into electric energy. Therefore, these cells are not Carnot machines and give high degrees of efficiency although working at low temperatures. The fuel cell is described later in more detail 3).

Besides all efforts to use alternatives to the lead-acid cell, this reliable system is and will be the most important storage system for non-nuclear submarines during the next decades. To give the reasons for this opinion, in the following, the state of the art of lead-acid cells and aspects of other electrochemical systems are summarized.

THE LEAD-ACID ACCUMULATOR - STATE OF THE ART

Since 1854, the storage principle	(Sinstedten)
and since 1889, the double-sulphate equation is known and used in storage cells.	(Gladstone and Tribe)
Important steps were the pasting,	(Faure 1881)
the recombination cells, and	(Jache 1958)
copper as material for negative grids.	(Kiessling 1972) 3)

A cell used in submarine batteries, in principle, consists of positive tubular plates and negative flat (pasted) plates. These are immersed in sulphuric acid inside a rubber bag which is surrounded by the rectangular container. There are at least four end terminals, two positive, resp. negative poles. A cooling system inside the cells and an acid circulation system are mandatory for submarine cells, because acid stratification as well as high temperatures decrease lifetime. Some so-called pilot cells are provided with thermocouples to measure temperature.

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Potential of the system:

Theoretically 167 Wh/kg can be stored

Practical values range between 10 and 50 Wh/kg.

Reasons are:

Active mass utilisation only up to 60 %

Passive parts like separator, container, etc.

Water

Inner resistance of cell

All these technically necessary parts increase the weight of the cell without taking part in the reaction and thus reduce specific capacity of the cell. The most sophisticated lead-acid cells, in respect to energy density, are used in submarines. Special mixtures give maximum utilisation in the positive as well as in the negative active mass. Every manufacturer has his own secret procedures for mixing and curing the masses. The passive parts have to be reduced in weight and volume as much as possible. The container for sophisticated cells is made from glass mates glued together with polyester resins. The volume of the acid inside a large cell can be increased by more than two liters if the wall thickness is reduced by one millimeter! But the mechanical stability (shock resistivity) is also very important. Thickness of the container down to four millimeters is state of the art. The separator prevents failure of the cell by preventing shortcutting during lifetime. But the separator also has some resistance for the ions which have to move during charge and discharge. Again a compromise between the two properties has to be made. The water is needed to dilute the acid, again the values are determined by a compromise between lifetime and power of the cell, as in the case of the separators. An acid density of 1.35 g/ml would give an increase in capacity in the range of some percent, but the reduction of lifetime would also be tremendous.

Finally, the inner resistance of the cell. This value is very important for the charging and discharging property of the cell. At first, as in all power optimized circuits, the maximum power can only be obtained if the outer resistance is equal to the inner resistance, thus the designer of a submarine propulsion system has to take note of the inner resistance of the battery.

The lead-acid cell can be looked at as an ohmic resistance. This resistance can be broken down into three main components. There is the resistance of the positive plate, spines out of lead and lead dioxide, the acid resistance, including separator, and the negative grid and active mass, which is lead in a charged state. It is possible to replace the lead grid in the negative plate with copper and thus reduce the total inner resistance of the cell. The reasons to take copper for the negative plate are:

The conductivity is 15 times higher than that of lead. The electrochemical potential of the negative plate is always well below the value necessary to dissolve copper. Copper is a technically available metal.

For the positive, a replacement of the lead has been tried but without success, due to severe corrosion problems. The high potential of the positive plate, in combination with the requirement of high oxygen overvoltage, limits the choice of material very much. Some manufacturers claim to be able to make a titanium grid for the positive, but the benefit has to be examined very carefully. The conductivity of titanium is not better than that of lead. Maybe some advantages in view of the low specific weight of the metal can be reached.

The diagrams 4) show the relative distribution of current in a CSM-grid during discharge. In comparison with a lead grid, the distribution of current is more uniform. In other words, due to the lower voltage drop inside the CSM-plate, the utilization of the active mass, which is directly related to the distribution of current, is better in the lower parts of the plate. Also during charging, the lower parts benefit from the lower inner voltage drop.

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SUMMARY

Power density can be increased by:

a) reduced weight and volume of passive parts

b) better utilization grade of active material

c) lower inner resistance of the cell

ad a) already near the optimum

ad b) subject of research for decades

ad c) use copper as carrier material in the negative plate, copper inserts in the polebridges and terminals, Al-inlay in the positive upper frame

The use of copper as a carrier for the active mass also gives low gassing rates because the negative plate is manufactured antimony free. The well-known effect of "poisoning" the negative electrode, which means lowering the hydrogen overvoltage due to high antimony content, is reduced to the antimony moving from the positive grid alloy to the negative plate. Thus gassing rates increase during lifetime by a factor of three.

FIGURES:

1.0.021	Energy density of lead-acid batteries
1.0.004	Calculation of the resistance of a cell section
1.0.007	Current distribution of a cell section ...

THE MAINTENANCE FREE LEAD-ACID CELL

Why does a lead-acid cell need maintenance? Because the cell is not closed. What does "closed" mean in this context? The cell generates hydrogen and oxygen which have to be released to avoid high overpressure. As hydrogen/air mixtures are dangerous down to an H_2-content of 3 volume percent, it is the task of the submarine designer to remove hydrogen from the battery room and from the boat's atmosphere as a whole. This will need some air compressors, recombinators and monitoring systems. But, of course, the cell also has to get the water back, which was lost during gassing. This topping up has to be done by the crew and is a main point of maintenance.

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The way out of these problems is obvious: Avoid gassing and close the cell.

This does not work with a flooded cell because the gassing charging stage is needed for some reasons, e.g. to avoid acid stratification and to reach full charge. Nevertheless, there are sealed cells available for some thiry years now, not for submarine application, however, the principle of a so-called "recombination cell" is known and used in industrial manufactured batteries.

The term "recombination" refers to the cycle in which oxygen revolves in these cells. The idea is as follows: The ratio of positive to negative mass is such that during charging the positive plate always starts with gassing. The oxygen generated remains inside the container and is recycled to water at the negative plate. As the negative plate contains highly reactive lead, it reacts with oxygen, formally to lead-oxide which is immediately converted to lead-sulphate. The negative plate is discharged through this reaction and thus is never fully charged. Therefore, the generation of hydrogen is reduced to a minimum.

This mechanism does not work inside a flooded cell because the oxygen transport from the positive to the negative plate does not happen inside liquid acid, solubility of oxygen in acid is very low. All the gas is collected above acid level.

If the acid could be porous in some way to provide a direct way to the negative plate, the problem would be solved. In fact one gets something like porosity only in solid bodies, therefore, the acid has to be solidified. This is done by adding definite amounts of silica. During the first cycles, some water is removed, the acid is porous and gas transport takes place.

When the first cells with solid electrolyte were built, the main idea was not recombination but a cell without spilling electrolye if it was turned upside down. The rest was discovered later.

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Nowadays, there also are cells with acid absorbent glassmates between the plates. Also recombination cells, starved electrolyte, which means that there is free space left inside the glassmate to allow oxygen diffusion. For submarine cells, the silica type is prefered because the glassmate type is restricted in cell height due to limited capillar forces within the glassmates.

The first submarine experimental cell contained plates of the normal dimensions for 209-class cells. It is a three plate cell, positive tubular, lead-calcium spines, negative CSM-plates. The comparison of capacity of this cell and a flooded cell has to be done carefully. At first there is silica inside the electrolyte, thus less acid inside the same volume. The second point is the acid level. In a flooded cell above and below the plate set, there is a considerable amount of liquid acid usable for the discharge. This is not possible in a gelled type cell, only the acid in-between the plates is used during cycling. Taking this into consideration, our experimental cell reached between 80 and 90 percent (C_5 and $C_{1.25}$) of the calculated capacity. These values are increased to 100 percent if the discharge takes place immediately after charge. The cell is cycled and reaches 60 cycles more than to date. (80 percent of C_5 discharge in 8 hours, IUI charge, 0.6 I_5 - 2.35 V - 0.6 I_5 until 110 percent of discharged ampere hours are recharged).

Next step is a sealed cell with standard container but with longer plates extending close to the top cover and the bottom of the cell. Both spaces, now necessary for acid and, on bottom, as mud space, can be used for the plates. Further investigations concerning temperature and pressure properties have to be carried out before a final statement, about the possibility to use such a cell inside a submarine, can be given.

LITHIUM CELLS

The high energy content of elementary lithium can be demonstrated easily: The pure metal does not only react vigorously with water and oxygen but also with elementary nitrogen. Some alloys, however, are stable even against water. Lithium is used in nuclear processes as well as for medical purposes. Also lithium is used as electrode material for negative electrodes in primary cells.

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The use of lithium as a negative electrode material has the advantage of high voltage and high energy density. Theoretical values are 3863 Ah/kg, resp. - 3 volt against normal H_2H+. The practical values for lithium thionylcloride cells $Li/SOCl_2$ are in the range of 630 Wh/kg and 1240 Wh/l.

Cell reaction: $4\ Li + 2\ SOCl_2 = S + 4\ LiCl + SO_2$

Cell voltage is 3.67 volts in open loop. Self-discharge is very low. The cells are used in electronic devices, cameras, portable video recorders, etc. Capacities of cells are in the range of .1 to 30 Ah.[5]

However, the cells can not be charged. Therefore, the use of these cells as the main battery in submarines is not possible. If the high potential of the lithium electrode can be utilized in a secondary, rechargeable cell with good cycle-life and shockproofness, this would be superior to the lead-acid cell. Some results of investigations in the field show that the energy density of cells designed for 200 cycles decreases to 125 Ah/kg. This is due to the poor rechargeability of lithium, which leads to an extreme overdimensioning of the negative electrode. Nevertheless, this is much more than the value of a lead-acid cell. The positive electrode is an organic compound, namely polypyrrol; the electrolyte is an organic solvent which contains lithiumperchlorate. Taking into consideration the specific properties of the positive electrode and the electrolyte, the final value for a lithium-polypyrrol cell designed for 200 cycles is 30 Ah/kg. Average discharge voltage is 3 volts, thus the energy density comes up to 90 Wh/kg. Calculated.[6]

Experimental cells reached between 15 and 30 Wh/kg with cells of mignon size.

Summary Lithium Cells:

- lithium electrode gives high voltages
- theoretical high energy density
- small primary cells commercially available

- secondary cell under development
- rechargeability of lithium is poor

HIGH TEMPERATURE SYSTEMS

Besides the lead-acid cell, there is one secondary system which may be suitable for submarine cells. This is the sodium sulphur (Na/S) cell 6) which has been developed for traction application. Prototypes have already been used in electric cars.

The main components of an Na/S cell are the two liquid reactants Sodium and Sulphur. Both are separated by a cylinder made out of alumina, which serves as separator and electrolyte. The surrounding outer metal container is used as a positive pole and it is connected gas-tight to the alumina on the upper edge. Inside the ceramic, there is another metal insert as negative pole. Between the alumina and the outer cylinder, graphite fibres lower the resistance of the liquid sulphur.

The alumina is used as an ionic conductor; here the electrolyte is solid and the reactants are liquid. The cell reaction can be described as:

$$2\ Na + 3\ S = Na_2S_3 \quad \text{at } 350\ c.$$

The open circuit voltage is 2.1 volts. Theoretical energy density is 758 Wh/kg, practical values for batteries of cells are around 85 Wh/kg (for C2).

There are two drawbacks to the system: At first, the high temperature, which always has to be above 300 C. Once the reactants become solid, the user has to heat up the whole system before he can take out energy. The number of these liquid/solid cycles should be very low because they decrease the lifetime of the cells drastically. The heat loss of the battery, which can not be neglected, can be described as "self-discharge". To keep a battery at 300 C, only 10 percent of the stored energy is necessary per day. Thus the battery is discharged after 10 days, unless it is recharged during that period or a separate heating system is installed.

The second problem is the electrolyte. As it is beta-alumina, the mechanical properties are that of industrial ceramic. The number of cycles reached with Na/S batteries is approximately 300.

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At present, there is no sodium sulphur battery commercially avaible, neither for traction application nor for submarine propulsion.

Summary Na/S:

- high temperature 350 C
- liquid sodium and sulphur
- solid ceramic electrolyte

- cell voltage 2.1 V
- practical energy density 85 Wh/kg (C2)
- 300 cycles at most

- self-discharge rate 10 % per day due to heat loss
- shock performance unknown
- not commercially available

THE FUEL CELL

Fuels cells directly convert chemical energy into electric energy. A main difference to the classic electrochemical cell ist the fact that the reactants are constantly fed to the electrodes. The used fuel is also removed, there is no recharge but refueling. Advantages of fuel cells against Carnot cycle machines are: Good degree of transformation, no movable parts and very little noise. 7)

From the various types of fuel cells, the most sophisticated are the H_2/O_2 cells. Very reliable batteries have been built and used, e.g. in spacecrafts. 8) As these cells contain a considerable amount of precious metals, such as platinium, the field of application is somewhat limited by commercial aspects. The development of new electrodes without the use of high priced metals is one condition to be met before the fuel cell can become a more widespread energy storage system.

The principle of a fuel cell is the "cold" reaction between oxygen and hydrogen. Both reactants are fed into highly porous metal electrodes, immersed either in acid or in alkaline aquous media. Product of the reaction is water which has to be removed. New materials developed for the H_2-electrode are nickel and, for the O_2-electrode, a silver based alloy. Pressure of gas approximately 1.5 bar, temperature between 40 and 80 C. The cell voltage is only about one volt in open loop.

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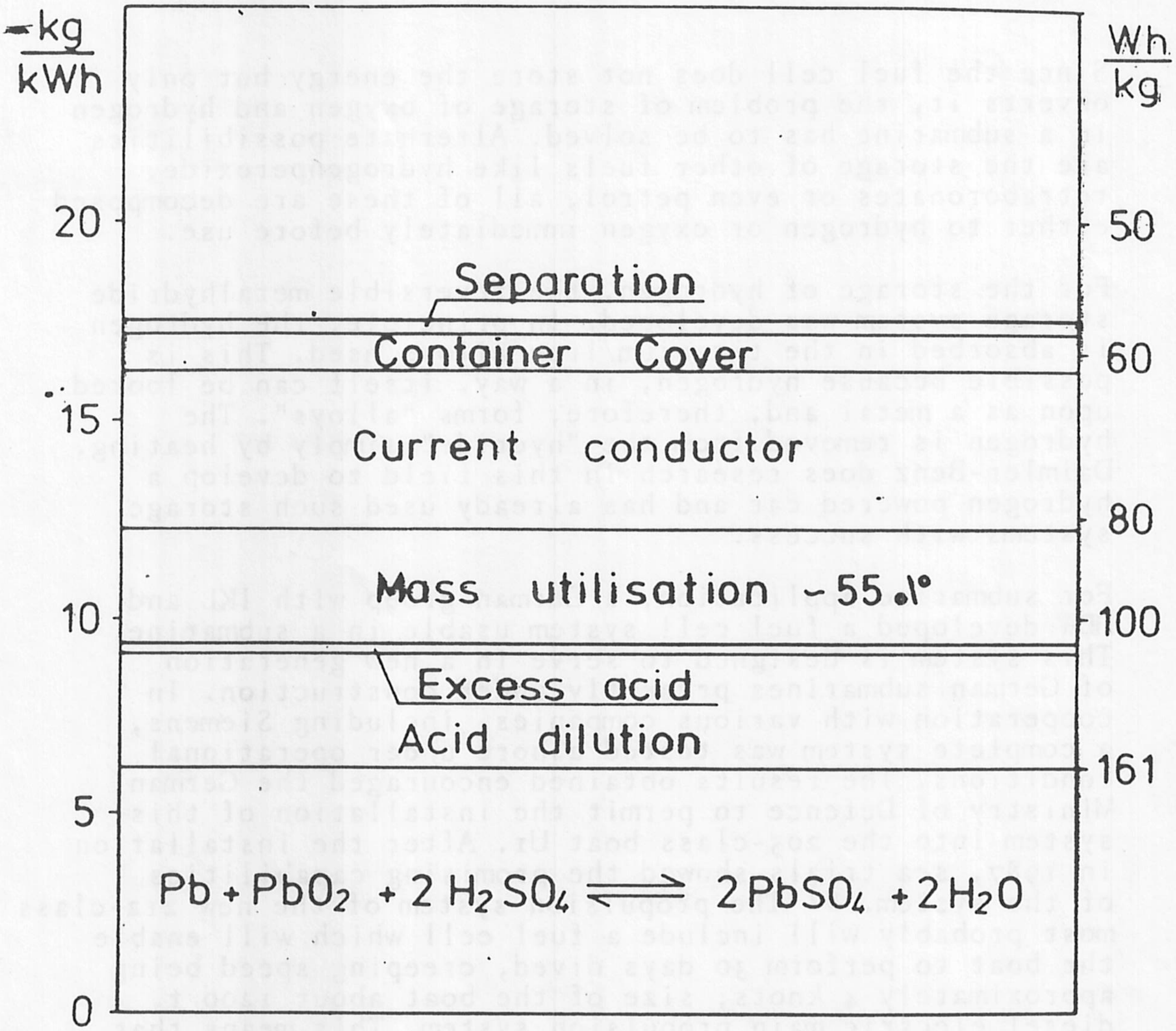
Since the fuel cell does not store the energy but only onverts it, the problem of storage of oxygen and hydrogen in a submarine has to be solved. Alternate possibilities are the storage of other fuels like hydrogenperoxide, tetraboronates or even petrol, all of these are decomposed either to hydrogen or oxygen immediately before use.

For the storage of hydrogen, the reversible metalhydride storage system was developed. In principle, the hydrogen is absorbed in the titanium/iron alloys used. This is possible because hydrogen, in a way, itself can be looked upon as a metal and, therefore, forms "alloys". The hydrogen is removed from the "hydride" simply by heating. Daimler-Benz does research in this field to develop a hydrogen powered car and has already used such storage systems with success.

For submarine application, a German group with IKL and HDW developed a fuel cell system usable in a submarine. This system is designed to serve in a new generation of German submarines presently under construction. In cooperation with various companies, including Siemens, a complete system was tested ashore under operational conditions. The results obtained encouraged the German Ministry of Defence to permit the installation of this system into the 205-class boat U1. After the installation in 1987, sea trials showed the promising capabilities of the system. 9) The propulsion system of the new 212-class most probably will include a fuel cell which will enable the boat to perform 30 days dived, creeping speed being approximately 4 knots; size of the boat about 1200 t, diesel electric main propulsion system. This means that a lead-acid battery is also used for propulsion, especially for high speeds.

12.)



Active mass M $207\,g\ Pb$ $239\,g\ PbO_2$
$196\,g\ H_2SO_4$ $\Sigma\ 642\,g$

Energy E $53{,}6\ Ah \cdot 1{,}93\ V = 103{,}36\ Wh$

Energy density $e = E/M = 161\ Wh/kg$

W. Hagen AG *Soest Kassel Berlin*	**Energy density of lead-acid batteries**	Nr. 1.0.021

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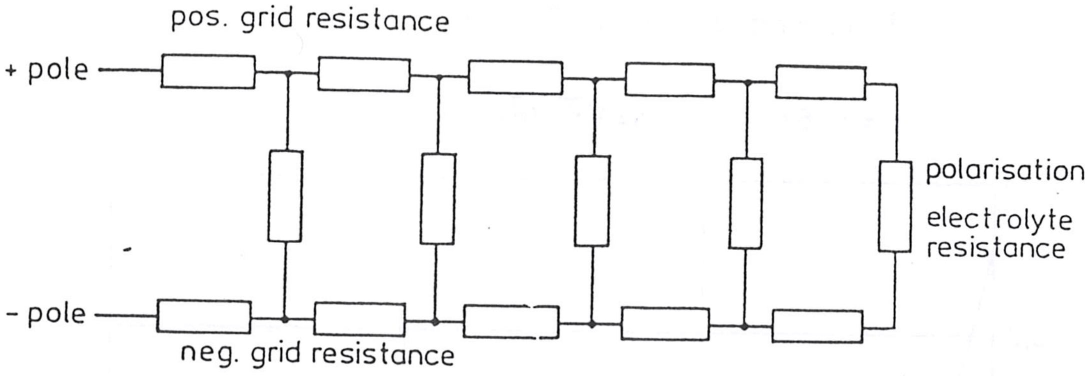
12.5 cm



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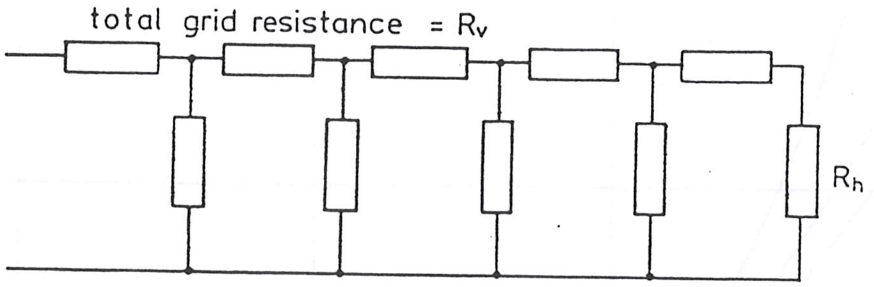


$$R_{tot} = \sqrt{R_v \cdot R_h} \cdot \coth(\sqrt{R_v / R_h} \cdot L)$$

experimental values (strip 9,6 mm wide)

$$\left.\begin{array}{l} \text{pos. grid} : R_p = 7{,}6 \times 10^{-4}\,\Omega\text{cm}^{-1} \\ \text{neg. grid} \quad R_n = 13{,}6 \times 10^{-4}\,\Omega\text{cm}^{-1} \end{array}\right\} R_v = 21{,}2 \times 10^{-4}\,\Omega\text{cm}^{-1}$$

polar. elektr.: $R_h = 1{,}46\,\Omega\,\text{cm}$

Accumulatorenfabriken WILHELM HAGEN AG Soest Kassel Berlin	Fig. 4 Calculation of the Resistance of a Cell Section	Nr. 1.0.004 Soest, 23.08.77

12.5 cm.

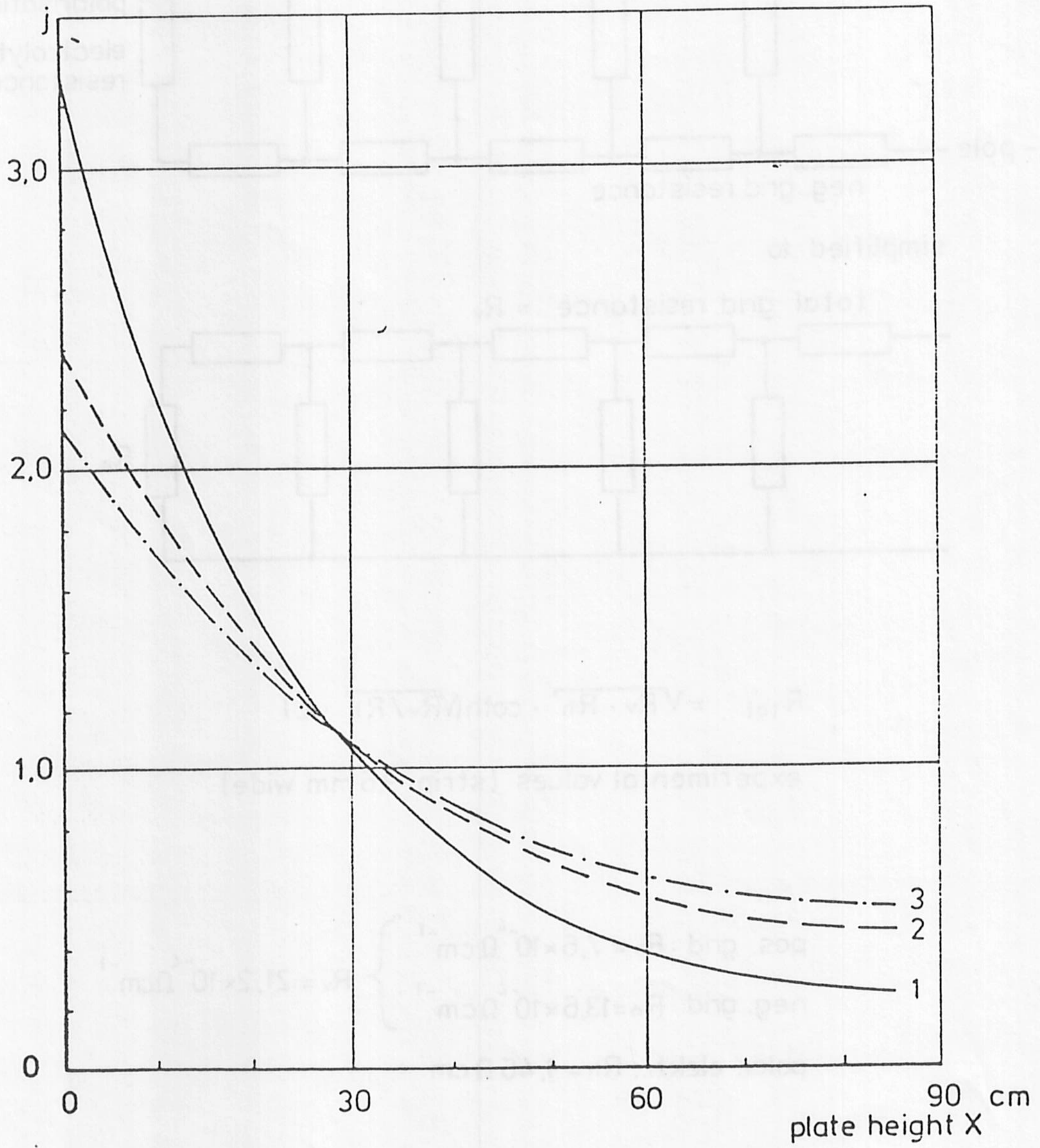
current distribution $j = \frac{\alpha L}{\sinh(\alpha L)} \cosh(\alpha X)$

1: lead grid $\alpha = 0{,}0381\,\text{cm}^{-1}$

2: LCC grid $\alpha = 0{,}0274\,\text{cm}^{-1}$

3: copper grid $\alpha = 0{,}0242\,\text{cm}^{-1}$

$L = 85{,}6\,\text{cm}$ $\alpha = \sqrt{R_v / R_h}$



Accumulatorenfabriken
WILHELM HAGEN AG
Soest Kassel Berlin

Fig. 7
Current Distribution of a Cell Section as a Function of the Plate Height.

Nr 1.0.007
Soest, 29.04.77

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