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Gelled-electrolyte batteries for electric vehicles

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Abstract

Increasing problems of air pollution have pushed activities of electric vehicle projects world-wide and in spite of projects for developing new battery systems for high energy densities, today lead/acid batteries are almost the single system, ready for technical usage in this application. Valve-regulated lead/acid batteries with gelled electrolyte have the advantage that no maintenance is required and because the gel system does not cause problems with electrolyte stratification, no additional appliances for central filling or acid addition are required, which makes the system simple. Those batteries with high density active masses indicate high endurance results and field tests with 40 VW-CityStromers, equipped with 96 V/160 A h gel batteries with thermal management show good results during four years. In addition, gelled lead/acid batteries possess superior high rate performance compared with conventional lead/acid batteries, which guarantees good acceleration results of the car and which makes the system recommendable for application in electric vehicles.

During the last years many serious activities in the development of electric vehicles have been done world–wide with a different goal than the first projects, which started in the 1970s. The goal of the projects for electric vehicles 20 years ago was a replacement of conventional vehicles, because of the world-wide anxiety about the resources of oil and natural gas. For such a goal the range of the car, due to the energy storage capability of the battery and the possibility for fast charging in order to compete with gasoline cars, has been of very high priority. Considering that the batteries in the electric VW-Golf, the CityStromer, have a weight of approximately 500 kg and an energy capacity of 15 kW h, which is less than the energy equivalent of 2 litres of gasoline, the problem for those projects becomes obvious. To develop batteries with energy contents in the range of a gasoline tank, that will be impossible for ever. But in the last years world–wide problems of air pollution, especially as a consequence of the increasing individual traffic, became more and more critical, so that world–wide some capital areas are planning to close their centres for the individual traffic with the exception for cars with very low or no emissions. And this is the goal for all the electric vehicle projects today.

Comparing the hydrocarbon emissions of cars with different energy sources (Fig. 1) the best solution to the pollution problem is the electric vehicle.

For introducing electric vehicles instead of conventional cars for inner-city traffic, the range of the vehicle has less priority, considering that in most cases those cars do not need ranges more than 50 km a day and than there is time enough to recharge the battery overnight. For those applications the life of the battery has at least the

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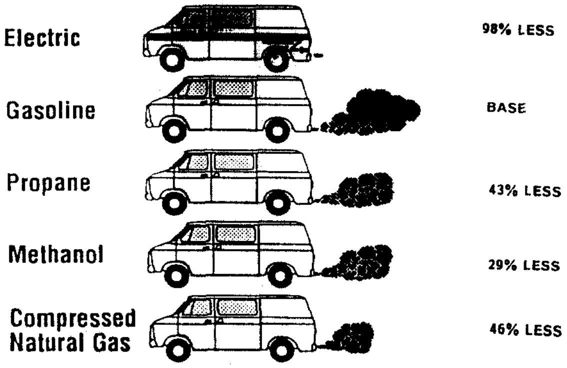

Fig. 1. Comparison of hydrocarbon emissions. Source: California Air Resources Board, Mobile Sources Division, *Definition of a Low-Emission Motor Vehicles in Compliance with the Mandates of Health and Safety Code Section* 39 037.05, *May* 1989.

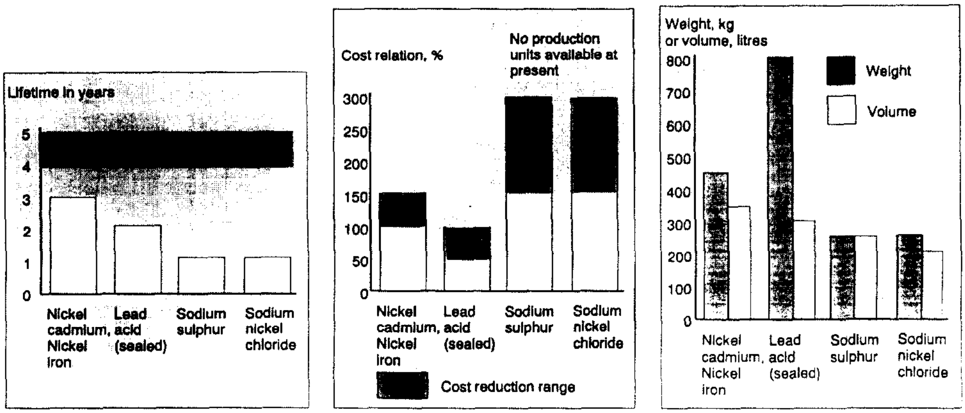

Fig. 2. Comparison data of electric vehicle batteries. Source: *Batteries International* issue 7, April 1991.

same priority as the energy density, because it determines the current costs of the vehicle.

When we compare the different battery systems competing for vehicle propulsion, the lead/acid battery is the cheapest system, and is also easy to recycle (Fig. 2).

The life of the lead/acid battery in the present technical state is superior to those of the high-temperature systems with high energy density by weight. What I will point out is that our system achieves a 4-years life in the field under rigorous technical conditions. Also, the specific energy of our valve-regulated gel battery is better than published last year in the *Batteries International.*

In comparison with Ni–Cd batteries, the sealed lead/acid system (SLA) has the advantage that because of the voltage characteristic, the state-of-charge controls the charging current, while the Ni–Cd system needs a special indicator system to switch off the charge when charging is finished (Fig. 3).

In DIN 43 549 traction block batteries for light applications are specified between 45 and 160 A h in 6 V and 12 V units.

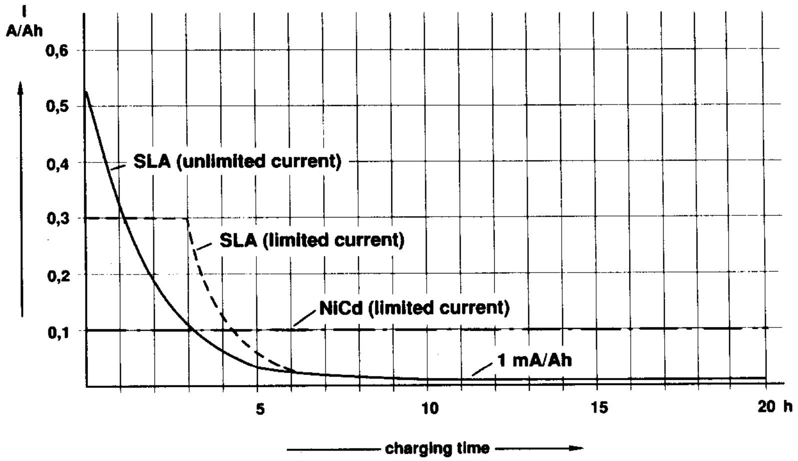

Fig. 3. Current characteristic during charging of batteries: lead/acid (SLA) and Ni–Cd systems.

						
	12V-50	12V-70	12V-90	12V-110	6V-160	12V-160
Ref. No.	02 1920 5000	02 1920 7500	02 1920 9000	02 1921 1500	02 1921 6000	02 1921 8500
Voltage (V)	12	12	12	12	6	12
Capacity C_5 in Ah	50	70	90	110	160	160
Power-to-weight ratio Wh/kg	30	28	28	28	31	30
Power-to-weight volume Wh/kg	76	70	66	68	77	71
Dimensions length width height	 306 175 190	 330 171 235.5	 513 189 223	 513 223 223	 244 190 275	 518 291 242
Weight (kg)	20	30	39	48	31	64

Fig. 4. Traction monoblock batteries – System Dryfit (Sonnenschein).

Because we had the capability for maintenance-free lead/acid batteries in gel technology, Sonnenschein (Büdingen, Germany) developed a line of valve-regulated traction monoblock batteries, according to the dimensions in this draft, which is still valid for these batteries (Fig. 4). In these batteries the electrolyte is gelled and each cell is sealed with a valve. As it will be pointed out later, the 6 V/160 A h unit is used today for many applications in electric vehicles.

While flooded batteries for traction applications contain relatively high antimony amounts in the grid alloys in order to achieve good cycle life, Dryfit batteries with gelled electrolyte have antimony-free grids. The electrolyte contains phosphoric acid, which increases the cycle life and it is solidified as a gel by highly-dispersed SiO_2.

The antimony-free grid alloy imparts a high hydrogen overvoltage, so that during the main charge operation water decomposition is negligible. By ageing the gelled electrolyte, many capillary cracks are formed, which allow the anodically-developed oxygen to penetrate to the surface of the negative electrode, where it recombines with protons to form water, as is illustrated in Fig. 5.

Due to the antimony-free alloy and the oxygen recombination, these batteries do not require maintenance. Figure 6 shows over a long overcharging time, that the gas extrication of the Dryfit batteries is negligible compared with flooded batteries, and after ageing the loss of water and the gas extrication of gel batteries is minimal, so that the loss of water never limits the life of those batteries. That means that for these batteries no complicated system for central water topping up is required; such a system would require additional space beside the battery. Another property of gel batteries is important for these applications. For flooded lead/acid batteries, which can be charged without gassing — which is general requirement for maintenance-free batteries — the problem of acid stratification is well known. This problem becomes more serious with increasing height of the battery and Fig. 7 shows that even after ten cycles acid stratification can change the nominal acid gravity of 1.23 to 1.29 at the bottom and 1.17 at the top of the cell, yielding to a difference of concentrations of almost 1:2.

This stratification causes a capacity decrease because of electrolyte limitation and an early desintegration of the lower parts of the plates by corrosion and sulfation. While this stratification can be eliminated by complicated so-called 'Mono Pump-Systems', which require capillaries in each cell for agitating the electrolyte by air-bubbles, gel batteries do not have problems with acid stratification and do not require those appliances. Therefore, the installation of gel batteries is very simple, it requires less space and that is one of the reasons for introducing this system in electric vehicle applications.

The first positive reaction for our gel batteries in electric vehicle applications we heard already in 1986 from a small US company, Soleq Corporation, Chicago, IL.

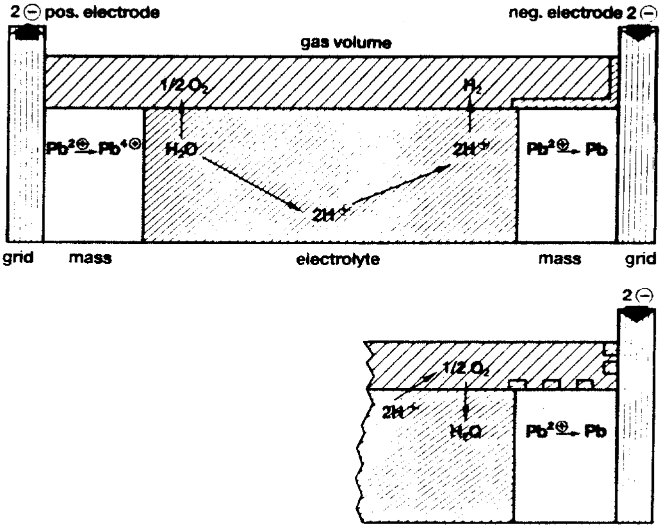

Fig. 5. Oxygen recombination: electrode reactions of valve-regulated lead/acid cells during charging.

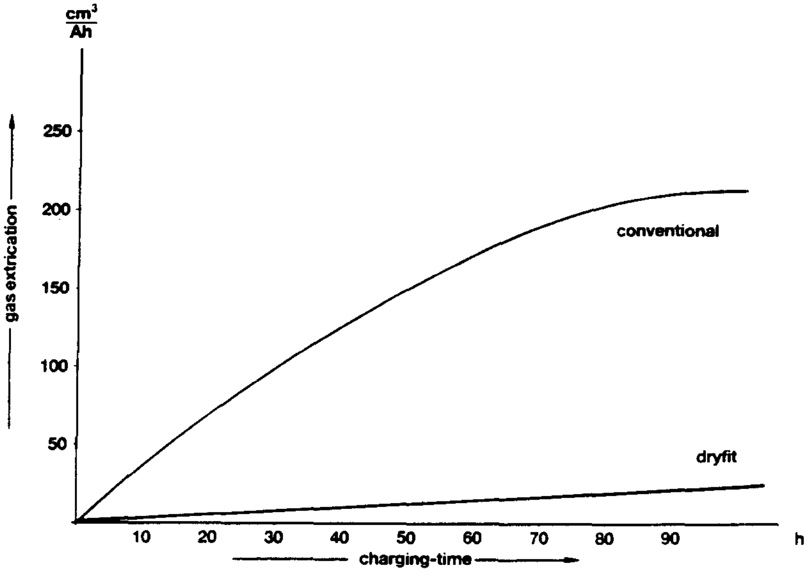

Fig. 6. Comparison of gas development of conventional and valve-regulated lead/acid batteries during charging with $U = 2.3$ V/cell at 20 °C.

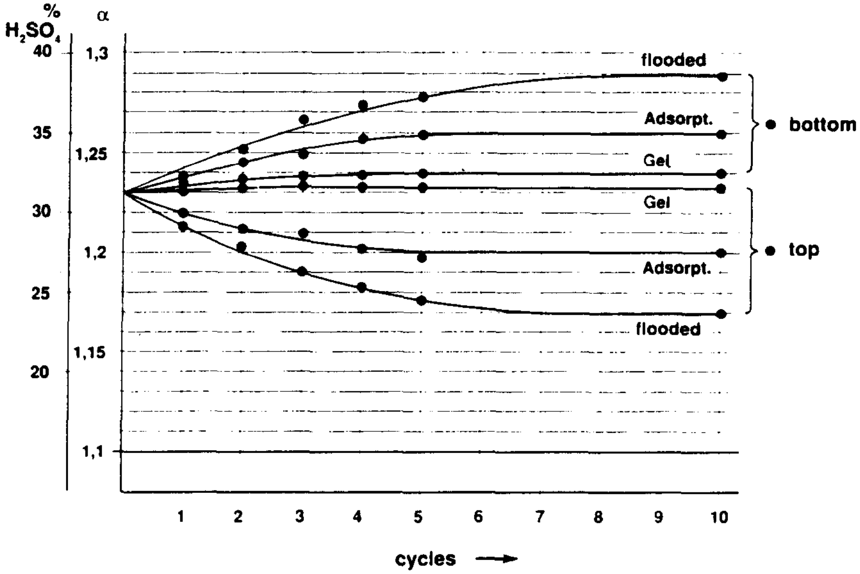

Fig. 7. Electrolyte stratification of 350 A h PzS cells of different systems.

They tested our valve-regulated Golf-car-battery type GC2 in comparison with some competitor products and were pleased with our gel battery, especially because of the life.

Figure 8 shows the battery installation in the trunk of the CityStromer provided by Volkswagen — RWE (Rhein. Westf. Elektrizitätswerke, Essen). The car uses 16

Fig. 8. Dryfit-battery installation in the trunk of the CityStromer by Volkswagen – Rhein. Westf. Elektrizitätswerke, Essen.

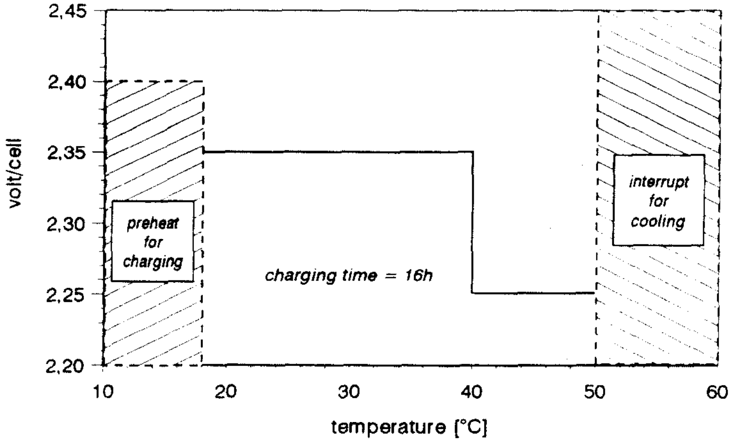

Fig. 9. Recommended charge voltage for *IU*-charging ($I_{max} = I_5$) of Dryfit batteries according to the temperature.

modules with a 6 V/160 A h configuration and its range is approximately 70 km at 50 km/h. The maximum speed is 120 km/h.

All maintenance-free lead/acid batteries are to be charged with controlled voltage, which is below the water-decomposition voltage and which has to be adapted to the temperature. We recommend to charge the battery with an *IU*-characteristic with $I = I_5$ ($C/5$ rate). While theoretically the temperature influence on the charging voltage of our batteries requires a ΔU of -5 mV/K, for the application in the CityStromer it was sufficient to regulate the voltage according to Fig. 9.

That means, between 18 and 39 °C, we recommend a voltage of 2.35 V/cell, which has to be decreased to 2.25 V/cell between 40 and 50 °C. Above 50 °C charging shall be stopped until the battery is cooled, in order to prevent thermal runaway, and below 18 °C voltage should be increased to 2.4 V/cell or if possible the battery should be preheated to 18 °C.

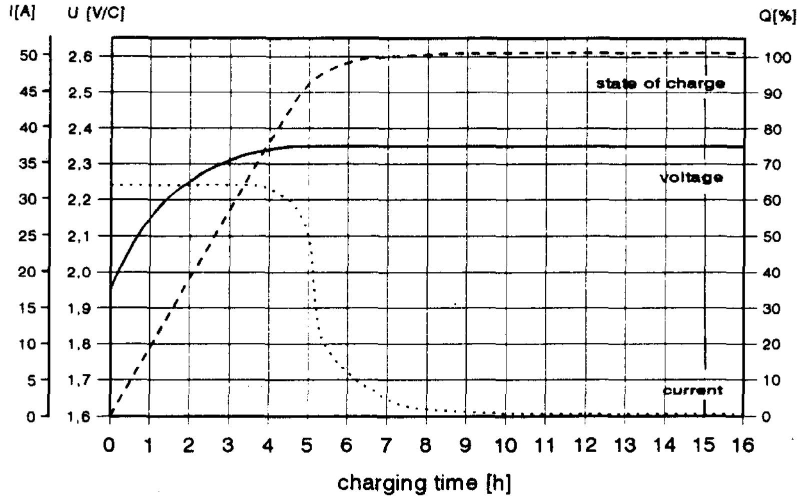

Fig. 10. Charging characteristic of a 6 V/160 A h electric vehicle module at 20 °C with *IU*-characteristic, $I=I_5$, $U=2.35$ V/cell, charge coefficient = 1.05.

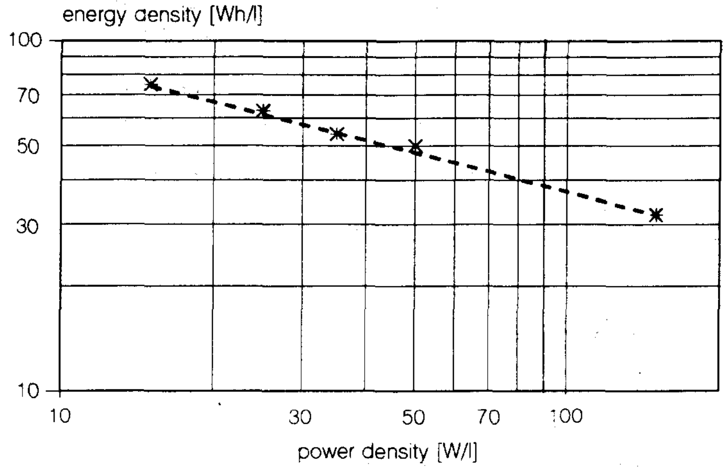

Fig. 11. Volumetric performance of traction monoblock 6 V/160 A h batteries.

Figure 10 indicates the charge characteristic of this method for a fully-discharged battery. While valve-regulated lead/acid batteries are not suitable for fast charging, Fig. 10 shows that the described method, to recharge 90% of the total capacity only requires 5 h charging time, while the last 10% require at least an additional 10 h.

While conventional lead/acid batteries always require full charge operation, Dryfit batteries with gelled electrolyte have consistent performance if they are only partly charged as long as the full recharge is done once a week. We have cycled batteries — which we use for solar-applications — between 30 and 60% state-of-charge over two years, with only one full charging every week, without any capacity decrease. That means that for electric vehicles short-time opportunity charging is useful, in order to extend the range of the car between charge operations.

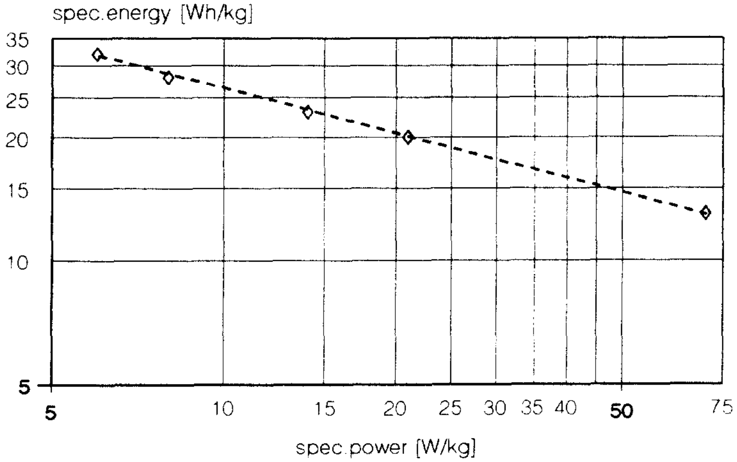

Fig. 12. Gravimetric performance of traction monoblock 6 V/160 A h batteries.

Figures 11 and 12 indicate the specific volumetric and gravimetric performance of our traction block batteries according to the discharge rate. The values were obtained on the 6 V/160 A h battery, and to get this performance, the batteries have to be precycled approximately ten times.

This precycling today is still necessary, because in order to obtain an extended cycle life we use thick plates with a high density of the positive mass of nearly 4.5 g/cm^3.

For developing the full capacity, this treatment with full discharging has to be done before installing the battery in the car.

For precycling the ready-connected modules are cycled with the following parameters:

charge: $I = I_5$ with $U = 2.35$ V/cell
$U = 2.35$ V/cell to $I = 0.08 \times I_5$
$I = 0.08 \times I_5$ for $t = 4$ h

discharge: $I = 71.5$ A/160 A h$\triangleq 2.2 \times I_5$ to $U = 1.7$ V/cell

This treatment is finished as soon as a capacity is achieved of 100 min$\triangleq$120 A h$\triangleq$75% of $C/5$.

These are the requirements set up by Volkswagen — RWE for all EV-applications and to achieve this capacity, 5 to 10 cycles are required, as can be seen in Fig. 13.

Figure 14 indicates the cycle life of traction block batteries with $C/5$ cycles, which is achieved after the described precycling operation. The high endurance of 800 cycles can only be achieved with the high density mass, which on the other side requires the mentioned precycling operation.

Test samples of 160 A h batteries with a slightly lower mass density achieved the full required capacity without precycling and for reduction of the production cost here we see a good possibility (Fig. 15).

It will be checked now in a field-simulating endurance test, if the slightly lower capacities of the lower density mass after 650 cycles will have a significant influence on the long-term performance of the batteries in practice.

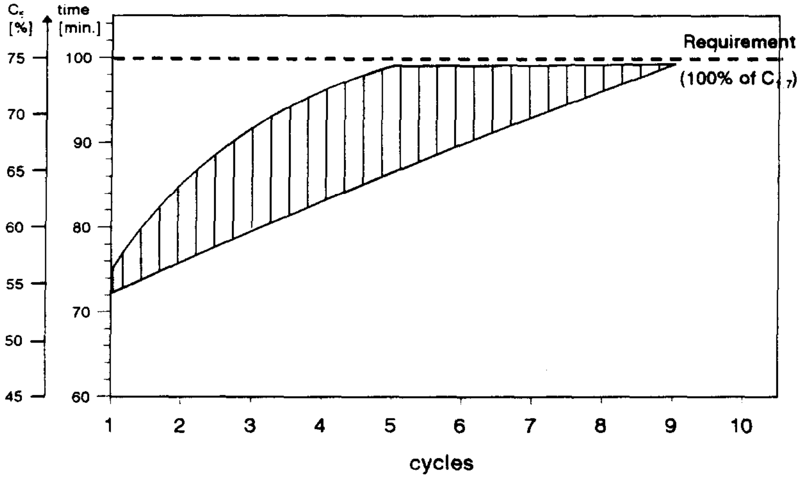

Fig. 13. Influence of precycling of traction block batteries for electric vehicle application on performance; charge *IUI* (see above), discharge $I=2.23\times I_5$.

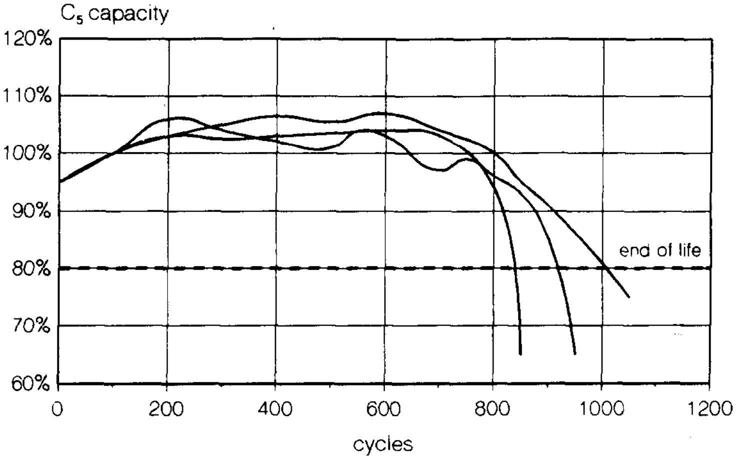

Fig. 14. *C*/5 cycle test of a Dryfit traction block 12 V/160 A h battery.

RWE, which has the longest practice in Germany in the field of electric vehicles, has set up an endurance test for field simulation and Fig. 16 indicates a life of a total energy supply of almost 1800 times the battery capacity for our gel battery.

Hereby the batteries are discharged every day with 100 pulses as shown in Fig. 17, simulating acceleration, constant drive and utility braking.

Every day three times 34 of those pulses with a daily opportunity charging of 60% and 17 h charging are applied to the battery, so that every day 120% energy return of the discharge capacity is achieved (Fig. 18).

These good laboratory test results have been confirmed in the field. By RWE, a fleet of 40 CityStromers is equipped with Dryfit 6 V/160 A h gel batteries and the oldest are now four years old. Figure 19 shows the performance of the first battery

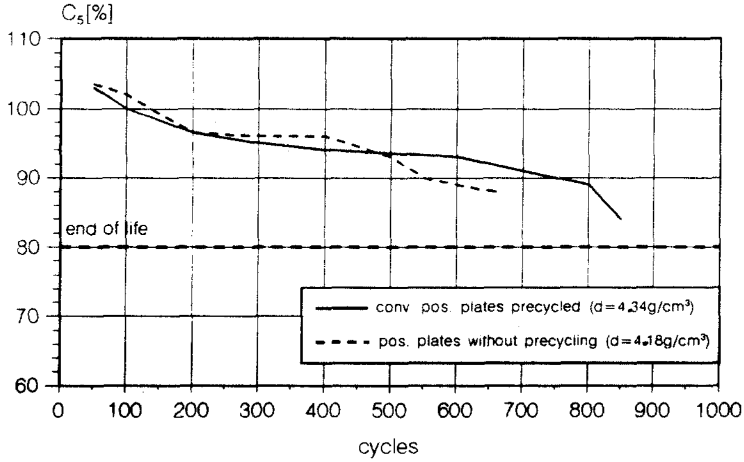

Fig. 15. Cycle life according to DIN 43 539 P3, for 6 V/160 A h traction block modules.

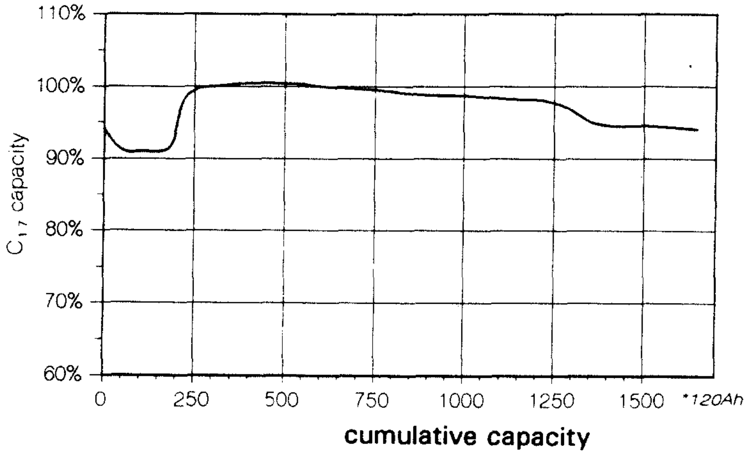

Fig. 16. Field-simulated endurance test with a 6 V/160 A h electric vehicle module system Dryfit.

in the field for the first three years; after this time the residual capacity of the battery was still above 90% of the rated capacity at the 71.5 A discharge rate.

To achieve these life results, thermal management for the battery is necessary, which guarantees a temperature range between the single modules of the battery not exceeding 5 K.

In the new design of the CityStromer 16 single 6 V-modules are switched together in a twin tray, which becomes installed in the trunk of the car. Water flown through rubber pillows are placed between the single modules, connected with plastic hoses and water is pumped by an 11 W pump with an output of 95 l/h, powered by the battery itself.

Because the charge efficiency of lead/acid batteries depends on the rate of the water-decomposition reaction, which is influenced by the temperature, the thermal

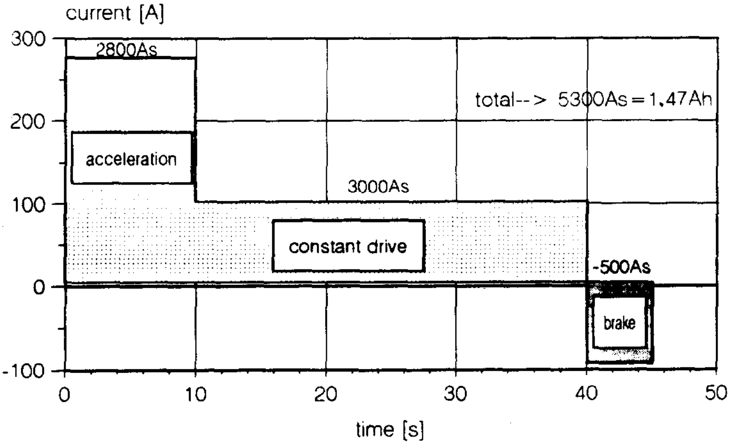

Fig. 17. Field-simulated endurance test: pulse characteristic.

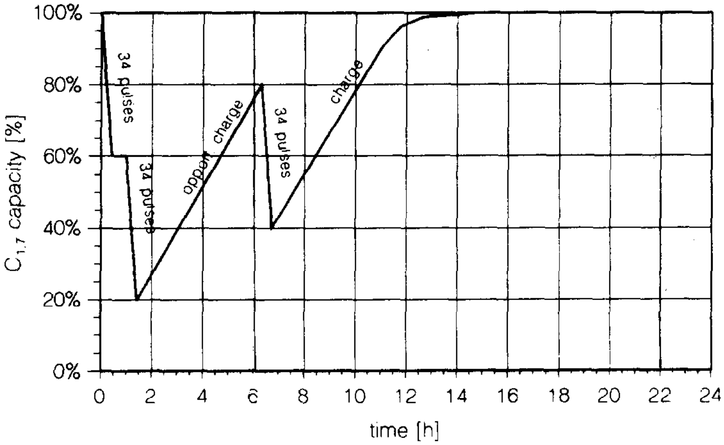

Fig. 18. Field-simulated endurance test: daily profile.

management system provides a uniform state-of-charge during charging, to prevent deep discharging of single modules, which causes early end-of-life of those units.

In addition, the thermal management system together with a small electric heat exchanger can be used for preheating the battery at low temperatures. However, its main importance is to equalize the module temperatures during charging.

In spite of the solidified electrolyte, Fig. 20 indicates a superior performance of gel batteries compared with flooded ones with increasing discharge rate.

A similar superiority of gel batteries is indicated in Fig. 21. This graph compares the high-rate performance of gel batteries and conventional batteries during pulse discharging with an average discharge rate of 70 A with discharge peaks between 70 and 280 A. It is obvious, that this behaviour promises good acceleration properties for the gel batteries. The high performance can be explained with a higher state-of-charge of the positive plate and as a consequence of O_2 recombination, which depolarizes the negative electrode.

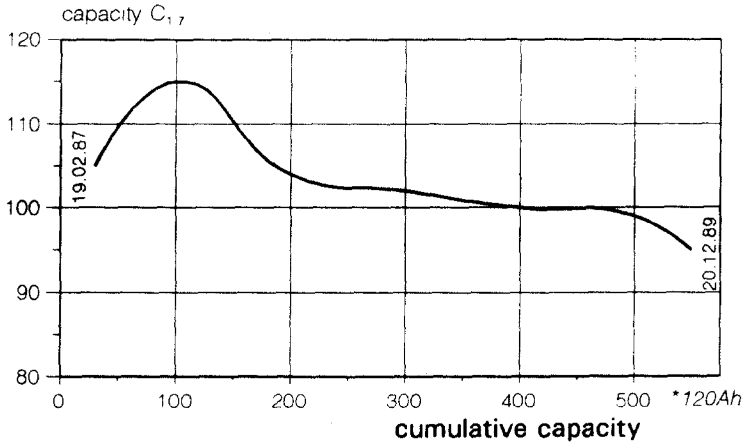

Fig. 19. Life of 96 V/160 A h dryfit battery with thermal management in a VW-CityStromer during three years.

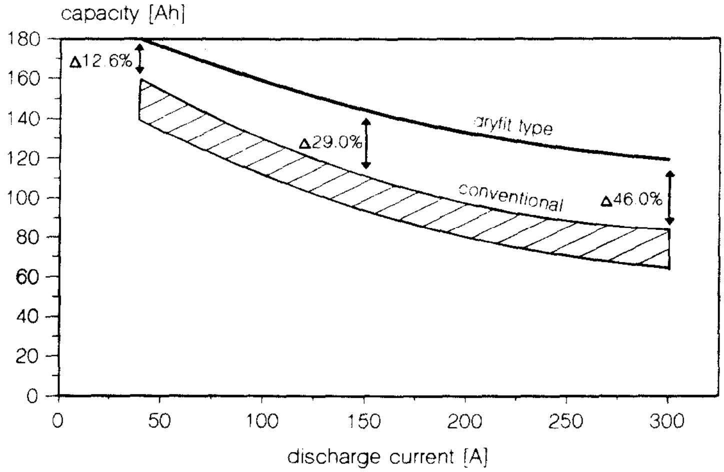

Fig. 20. Influence of discharge rate on performance of 6 V/160 A h electric vehicle modules.

Oxygen recombination influences the voltage distribution of the single cells during the end-of-charge. As pointed out in Fig. 22, the voltage range of gel cells is ±30 mV, roughly twice as much as for conventional batteries. It is important to know that this anomaly does not indicate battery failures. It is influenced by two different possible reactions at the negative electrodes, which are in competition – the hydrogen formation by proton reduction and the oxygen reduction to water – so that such a voltage range anomaly is noticed for all valve-regulated lead/acid systems. That means that with increasing oxygen penetration to the negative plate, the voltage decreases and in consequence, the voltage of cells with lower oxygen-decomposition must increase. This has no influence on the performance of the battery and must not become mixed up with problems of wide voltage ranges of conventional batteries, often caused by antimony poisoning or failures in single cells.

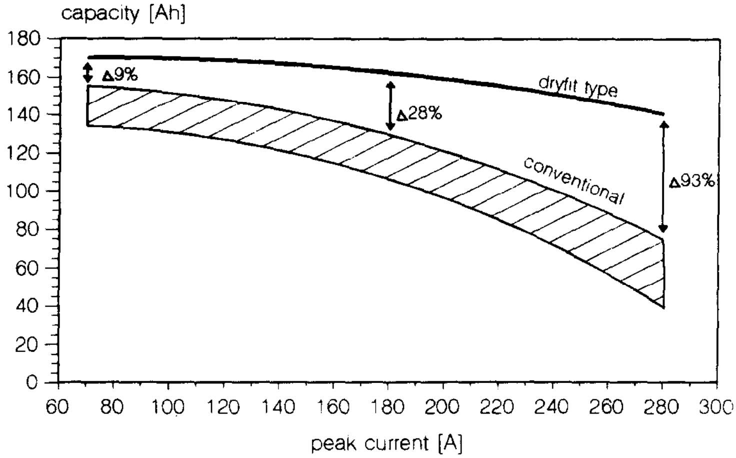

Fig. 21. Influence of peak-current during pulse discharging of 6 V/160 A h electric vehicle modules; average discharge rate $i = 70$ A.

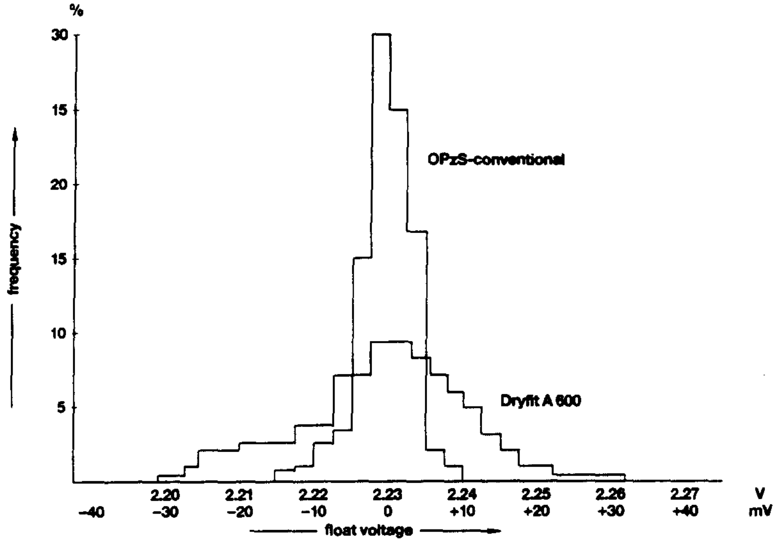

Fig. 22. Distribution of cell voltages of new 370 V uninterruptable power supplies (UPS) batteries during float charging with $U = 2.23$ V/cell.

One other property of lead/acid batteries with gelled electrolyte has to be mentioned, namely the resistance for failure in deep discharging. We are testing the deep-discharge resistancy of our batteries by connecting the terminals with the resistor calculated for an initial discharge rate of I_5 for one week. After this treatment and recharging with $U = 2.35$ V/cell for 48 h, a capacity of the battery of at least 90% is obtained.

Beside of the CityStromer, a small Japanese transport vehicle 'Colenta' is equipped with a 90 V/160 A h battery.

For Electrotek in Chattanooga, TN, USA, we provided a 216 V/160 A h battery, for a Chrysler TEVan-car (Fig. 23), which is in a test programme for an electric vehicle study in Los Angeles, CA, USA, sponsored by EPRI in California.

The modules are installed in a tray, which becomes mounted underneath the car. The total battery consists on 36 Drifit 6 V/160 A h modules and includes a water pillow thermal management system which guarantees a temperature range in the single cells below 5 K. In the tray there is also a fuse, the water pump for three parallel strings, each for twelve modules, combined with a heat exchanger and a temperature control device. The total water system is usually connected with the radiator of the car as a water reservoir. While the pump is powered by the battery itself and pumps during charge and drive, the electric heat exchanger is powered by the electric plug and heats only during charging, if the temperature is below 18 °C.

The range of the TEVan with a speed of 35 miles/h is 73 miles. Since June 1991, the status of the field test is 4900 miles corresponding to 141 cycles. The capacity at 75 A discharge rate started with 114 A h with a present state of 131.5 A h.

Most of the electric vehicles are equipped with a battery monitoring system, which collects information about the

- charge condition of the battery
- voltage comparison in different branches of the battery
- temperature of the modules
- charge and discharge current and voltage

It also prevents deep discharging of single modules.

Our main objectives for the future, considering increasing demand for electric vehicle batteries, are:

- replacing the precycle operations by optimization of active masses and final development operation
- weight reduction by optimization of grid designs

This has to be done without influence on battery life, which was the key point for the decisions of many companies of the automotive industry to introduce this system in this application.

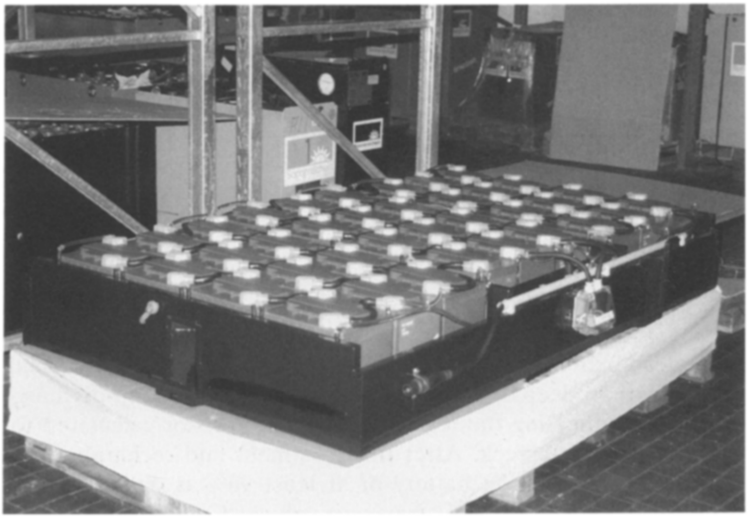

Fig. 23. 216 V/160 A h battery for Electrotek.

We know, that there are other battery systems under development, especially for electric vehicles, which are superior in energy density and which can become recharged faster than valve-regulated lead/acid batteries, so that they many have some advantages in range and speed compared with lead/acid batteries. However, the present system:

- is today available
- is cheap compared with all other systems
- has a long life
- has a capacity to fulfill the demand of 80% of the inner-city traffic
- is easy to recycle

So, even if other high-energy battery systems are developed, we are sure that the valve-regulated lead/acid battery will participate in the applications for electric vehicles for special applications in the inner-city traffic.

References

1 H. Tuphorn and E. Zander, *Proc. Int. Conf. Electric Vehicles for Europe, Stoke on Trent, UK, 1991.*
2 E. Zander and Kalker, RWE, personal communication.
3 J. H. Barnett, Electrotek Concepts Inc., personal communication.
4 *Batteries Int.*, Issue 7, April (1991).