Bipolar lead–acid battery for hybrid vehicles

M. Saakes *, R. Woortmeijer, D. Schmal

TNO-Energy, Environment and Process Innovation, Electric Storage Systems, Laan van Westenenk 501, 7300AH Apeldoorn, The Netherlands

Abstract

Within the framework of the European project bipolar lead–acid power source (BILAPS), a new production route is being developed for the bipolar lead–acid battery. The performance targets are $500\,\mathrm{W\,kg^{-1}}$, $30\,\mathrm{Wh\,kg^{-1}}$ and 100 000 power-assist life cycles (PALCs). The operation voltage of the battery can be, according to the requirements, 12, 36 V or any other voltage. Tests with recently developed 4 and 12 V prototypes, each of 30 Ah capacity have demonstrated that the PALC can be operated using 10 C discharge and 9 C charge peaks. The tests show no overvoltage or undervoltage problems during three successive test periods of 16 h with 8 h rest in between. The temperature stabilizes during these tests at 40–45 °C using a thermal-management system. The bipolar lead acid battery is operated at an initial 50% state-of-charge. During the tests, the individual cell voltages display only very small differences. Tests are now in progress to improve further the battery-management system, which has been developed at the cell level, during the period no PALCs are run in order to improve the hybrid behaviour of the battery. The successful tests show the feasibility of operating the bipolar lead–acid battery in a hybrid mode. The costs of the system are estimated to be much lower than those for nickel–metal-hydride or Li-ion based high-power systems. An additional advantage of the lead–acid system is that recycling of lead–acid batteries is well established.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Bipolar; Lead–acid battery; Power assist life-cycle; Hybrid electric vehicle; Absorptive glass mat; Internal resistance

1. Introduction

For hybrid electric vehicles and 42 V automotive the batteries are required to have systems, much higher specific power ($\mathrm{W\,kg^{-1}}$) than present commercial automotive types. With the latter batteries, the specific power during starting (typically 300 A discharge) is too low for the new hybrid vehicle systems (e.g., $200\,\mathrm{W\,kg^{-1}}$ for starting versus $>500\,\mathrm{W\,kg^{-1}}$ for hybrid vehicles). For high-power applications, various battery types (and for certain applications, supercapacitors) already fulfil the new requirements, e.g., the prismatic nickel–metal-hydride battery in the Toyota Prius. Nevertheless, large-scale application of batteries in hybrid vehicles will only be possible if very stringent cost targets are met (20 € per kW is required). It is expected that only lead–acid battery technology will be able to meet these cost targets (of the order of 200€ per kWh, or even less in mass production) because the price of nickel and cobalt is too high. The price of nickel has doubled during the past 2 years.

Since the power–time profile (discharge and charge behaviour) of the battery in a hybrid vehicle is completely different from that in conventional applications of batteries (including automotive), it is necessary to develop a complete new design of battery, e.g., batteries with prismatic configurations and an increased number of tabs, thin metal-film batteries, bipolar batteries, quasi-bipolar batteries. Only then will it be possible to obtain high specific power, not only during discharge but also during charge (fast charging during regenerative braking). Accordingly, many battery companies are working on hybrid vehicle battery design and development. Most effort is being concentrated on lead–acid, nickel–metal-hydride, lithium-ion, and sodium–nickel-chloride. Good overviews of these newer designs can be found in [1,2]; preliminary results of bipolar battery development are included in [2].

* Corresponding author. Tel.: +31 55 549 3839; fax: +31 55 549 3410.
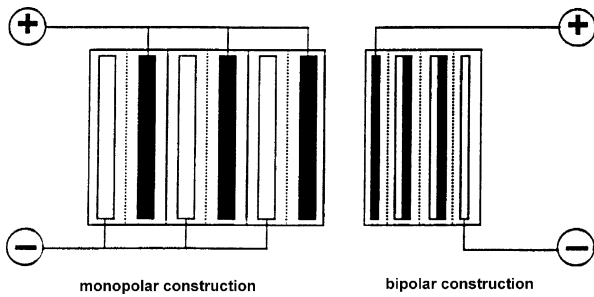 *E-mail address:* m.saakes@mep.tno.nl (M. Saakes).

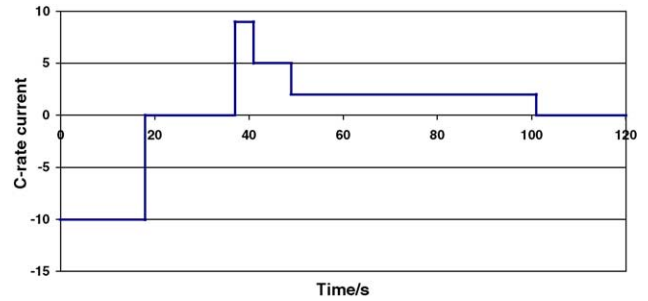Fig. 1. Bipolar and conventional mono polar battery concepts.

Fig. 2. Power-assist life cycle profile. Positive current = charge of battery (regenerative braking); negative current = discharge of battery (acceleration).

2. Bipolar lead–acid battery concept

The specific power (W kg^{-1}) of a battery is not restricted by thermodynamics (like the specific energy, Wh kg^{-1}), but mainly by the structure and the internal resistance of the component materials and the cell construction. Thus, for the lead–acid battery, and indeed for any other battery chemistry, there are no principal restrictions to high-power applications. Of course, the requirement is that under partial state-of-charge (PSoC) operation there exists an electronic pathway for conduction. This requires a special paste formulation. Another requirement is that the materials can sustain long periods under PSoC duty without changes in their properties.

Since lead–acid batteries are produced on a very large scale and lead is a cheap material, the units can be correspondingly inexpensive. Furthermore, there exists an infrastructure for recycling with very high materials reclamation percentages (>98%).

In a previous development of a lead–acid battery for military pulse–power applications (very high power during milliseconds) TNO has chosen the bipolar concept (see Fig. 1). This concept is also applicable to hybrid vehicles for the following reasons.

- In principle, no metallic grids are necessary since the current is moving perpendicular to the surface from one side of the bipolar plate to the other.
- A homogeneous current density is present. By contrast, mono-polar configurations have limited cycle-life (less than 50 000 cycles) at very high charge and discharge rates due to sulfation of the lower parts of the pasted plate.
- Production techniques for lead–acid batteries are well developed and inexpensive, despite the potentially harmful health properties of lead.
- The internal resistance is much lower than that of monopolar designs.
- Lead is a very cheap material. Many other types of batteries use materials that are less abundant (e.g., Ni, Co) and more costly (or will be when the batteries reach the mass-production stage).
- There is the possibility of a much higher stack pressure than in a monopolar design. Of course, this requires the

use of absorptive glass mat separators that can resist the high pressure.
- Within a single module, or a restricted number of modules in series, the required voltage can be reached without external cable connections, etc.
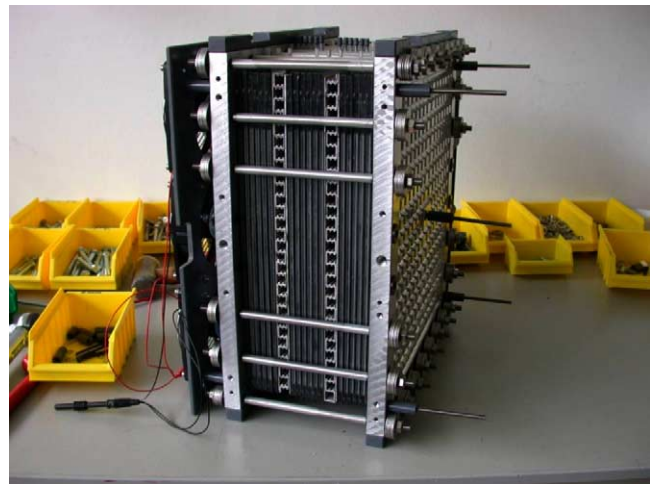

Fig. 3. Photograph of the bipolar lead–acid battery after assembly.

Fig. 4. Photograph of bipolar lead–acid battery under PALC testing.
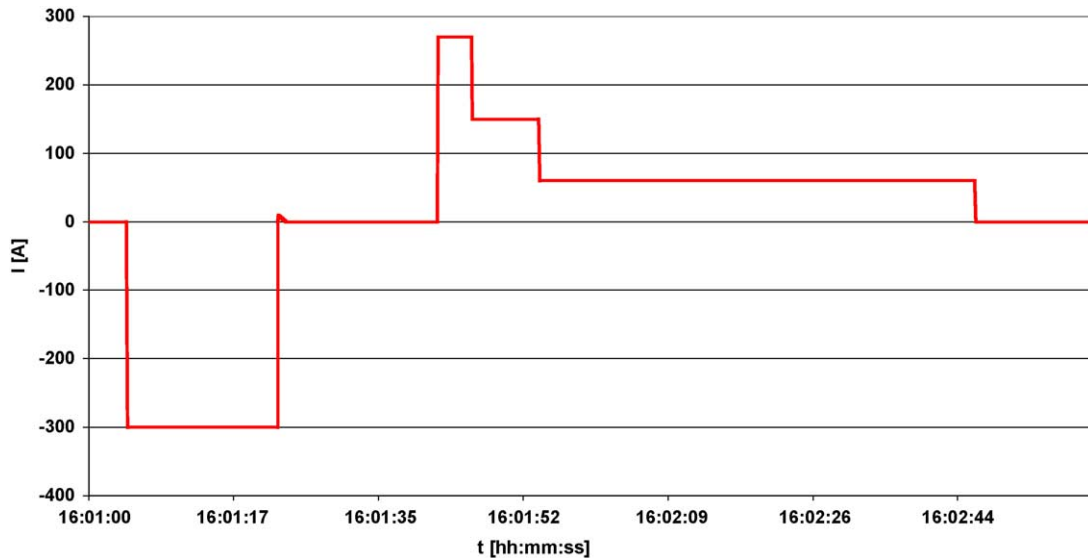
Fig. 5. EUCAR power-assist life cycle for 12 V, 30 Ah bipolar lead–acid battery.

There are, however, some technical obstacles to overcome with respect to the bipolar lead–acid battery before successful commercialization is possible, as follows.

- A corrosion-resistant, lightweight and cheap bipolar plate material is required. Much work has been under taken to find a material that meets all these requirements. Up to now, this has not resulted in a commercial bipolar lead–acid battery system reaching the market; several materials and other problems have still to be solved. Although the bipolar concept is used, in virtually all types of fuel cell, the materials are generally not applicable in a lead–acid battery. This is mainly because of the relatively heavy requirement for good corrosion resistance in lead–acid batteries (i.e.,

at up to 2.5 V per cell in a lead–acid battery as opposed to less than 1 V per cell in a fuel cell). Thus, European project BILAPS (Bipolar Lead–Acid Power Source, has been initiated to develop a new mass-production route for a corrosion–resistant, highly conductive, bipolar plate.
- The application in hybrid vehicles requires > 100 000 shallow charge–discharge cycles to obtain sufficient battery lifetime and acceptable cost (of course these criteria also apply to conventional batteries). Testing is performed using the power-assist life cycle (PALC).
- The state-of-charge (SoC) during cycling is often held somewhere in the range of 40–60% and this introduces the extra risk of recrystallization of lead sulfate during periods of rest and thereby, to a lowering of the capacity and
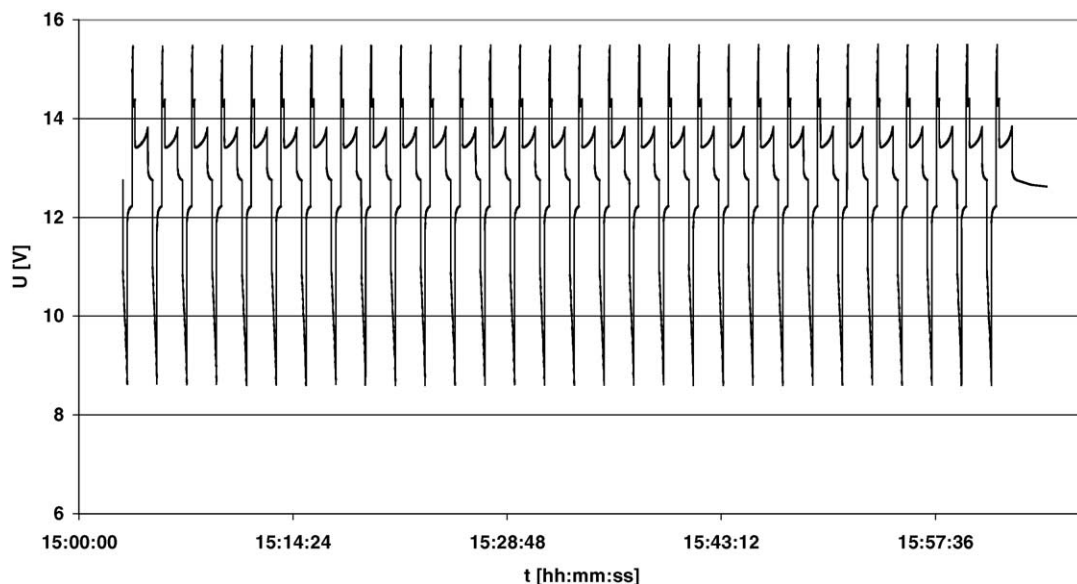

Fig. 6. Voltage of 12 V, 30 Ah bipolar lead–acid battery, sixteenth hour of test during PALC (see Fig. 4).
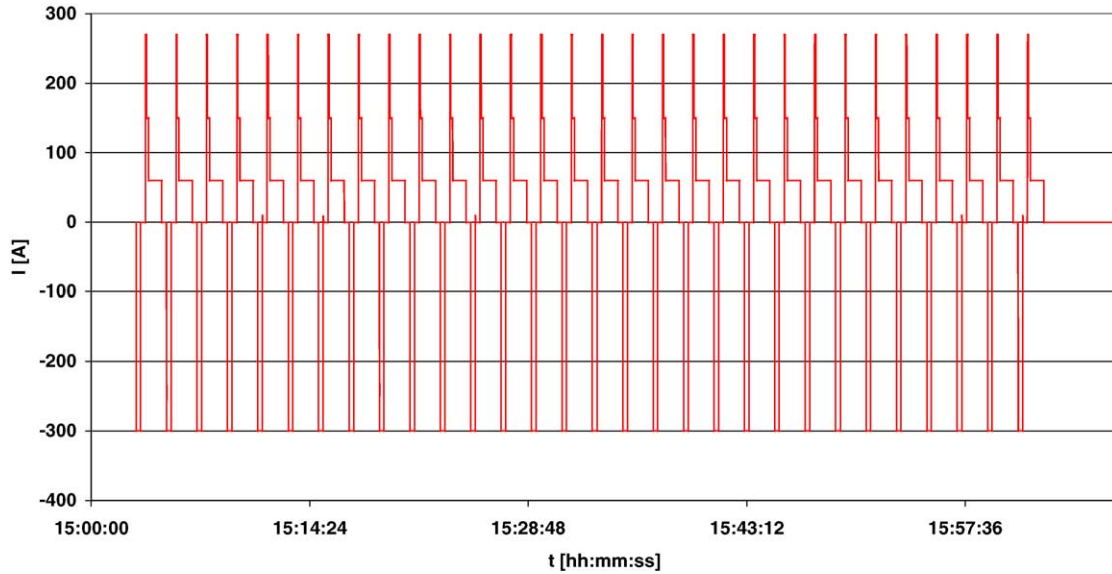
Fig. 7. Current profile of 12 V, 30 Ah bipolar lead–acid battery, sixteenth hour of test during PALC.

an increase in the internal resistance. For more background information on the bipolar battery, the reader in referred to [3–14].

3. Test procedure

The bipolar lead–acid battery was tested using the PALC schedule illustrated in Fig. 2. This drive cycle is comprised of the following stages: 10 C discharge for 18 s; pause for 19 s; charging at 9 C for 4 s; charging at 5 C for 8 s; charging at 2 C for 52 s; pause for 19 s.

4. Stack construction

The construction of the bipolar lead–acid battery was similar to that of fuel cell stacks, i.e., a modular design (see Figs. 3 and 4). The stack pressure was at a higher level than in monopolar designs and was achieved by the use of a special absorptive glass mat (AGM) separator. The bipolar plate was developed using a new process that offers the possibility of high flexibility in the dimensions of the bipolar plate. The bipolar plate is stable against corrosion and does not form lead sulfate. The cell is comprised of a bipolar plate, spacer, the positive active-mass, the
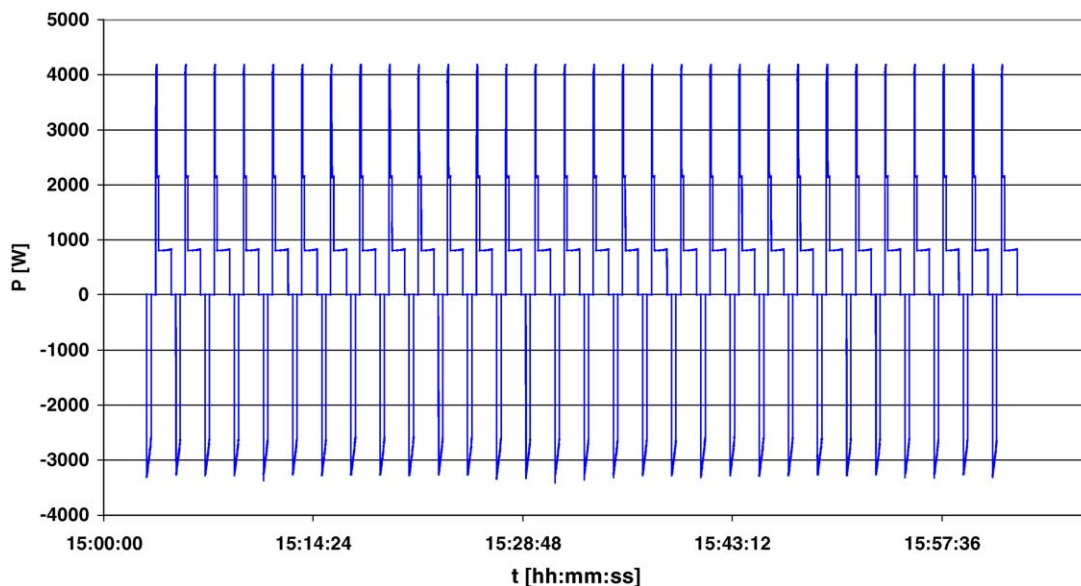

Fig. 8. Power (negative = discharge of battery, i.e., acceleration; positive = charge of battery, i.e., regenerative breaking) of 12 V, 30 Ah bipolar lead–acid battery, sixteenth hour of test during PALC.
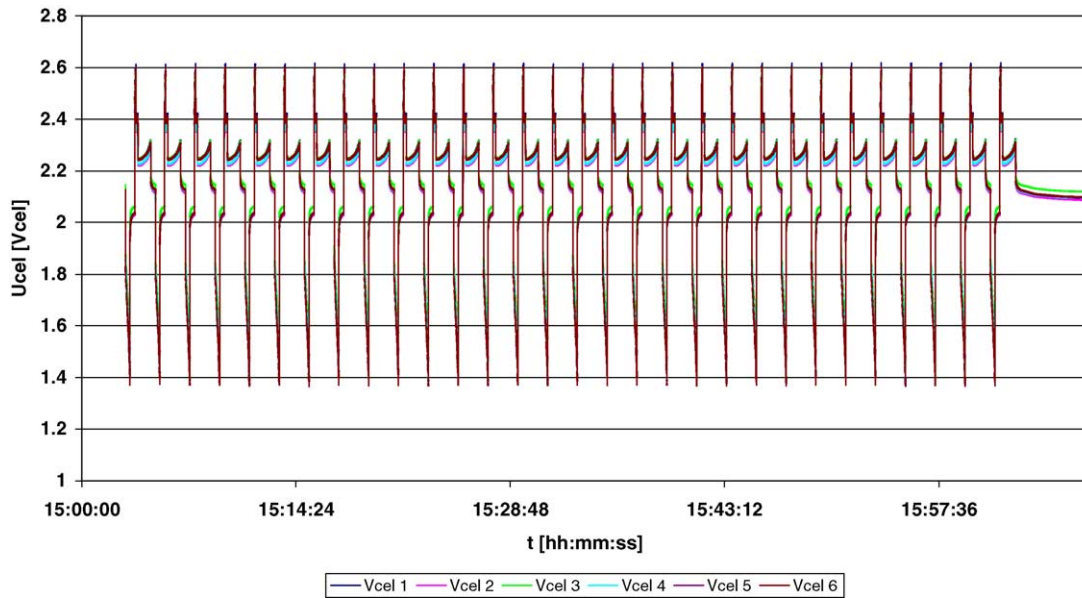
Fig. 9. Distribution of cell voltages during testing of 12 V, 30 Ah bipolar lead–acid battery during PALC tests at 50% SoC.

negative active-mass, and the AGM separator. Sealing was achieved with VITON O-rings in order to facilitate easy autopsy of the battery; in production, another sealing method would be used. The end-plates were provided with connectors for high current (300 A), voltage measurement and facilities for cooling by air. The bipolar plates were made with tabs in order to measure the individual cell voltages during operation.

Manual stack construction of a 36 V battery took 30 min for a trained person. In production, the stacking is only a fraction of this time. The stack was placed under pressure by means of bolts. In order to measure the internal temperature (inside the stack), a special Pt-100 sensor was developed, as well as a dedicated connector to the spacer. With such an

arrangement, it was easy to install or change the Pt-100 in case of malfunction. The complete stacked was filled (under vacuum) cell-by-cell after verification of the stack resistance (must be infinite before filling) and placing the cell under pressure (sealing must be good before filling). After filling, the open-circuit voltage (OCV) was measured together with the internal resistance at 1000 Hz (Hewlett-Packard milliohmmeter). After this, the stack was allowed to rest. A refill was performed 2 days later and was followed by constant-current (CC) and constant-voltage (CV) charging. In order to prevent sulfate build up, an electronic device with high frequency pulses was connected to the battery directly after the final filling. The device is commercially available (Power Pulse) [15].
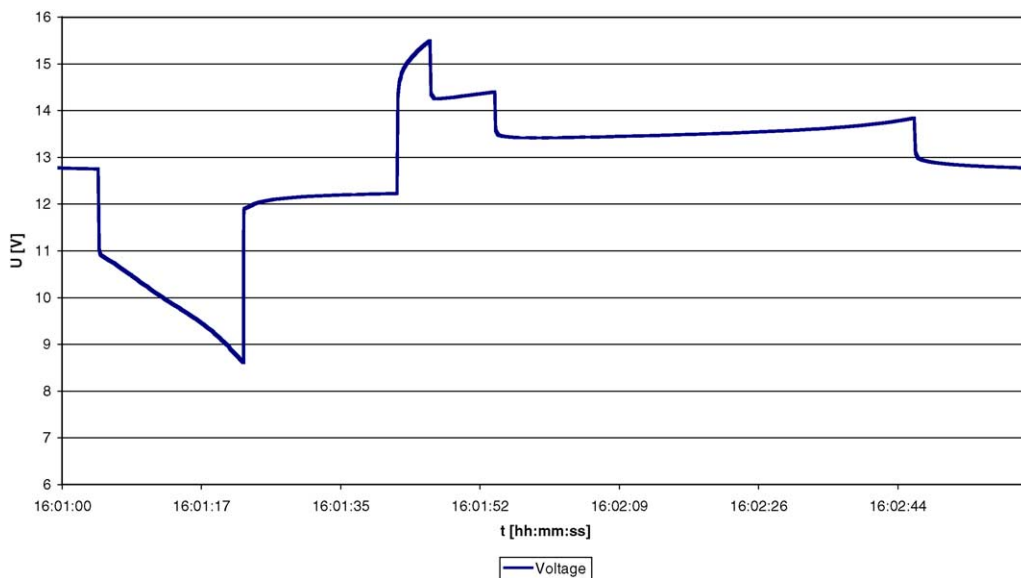

Fig. 10. Voltage of 12 V, 30 Ah bipolar lead–acid battery during PALC tests at 50% SoC for single cycle during the sixteenth hour.
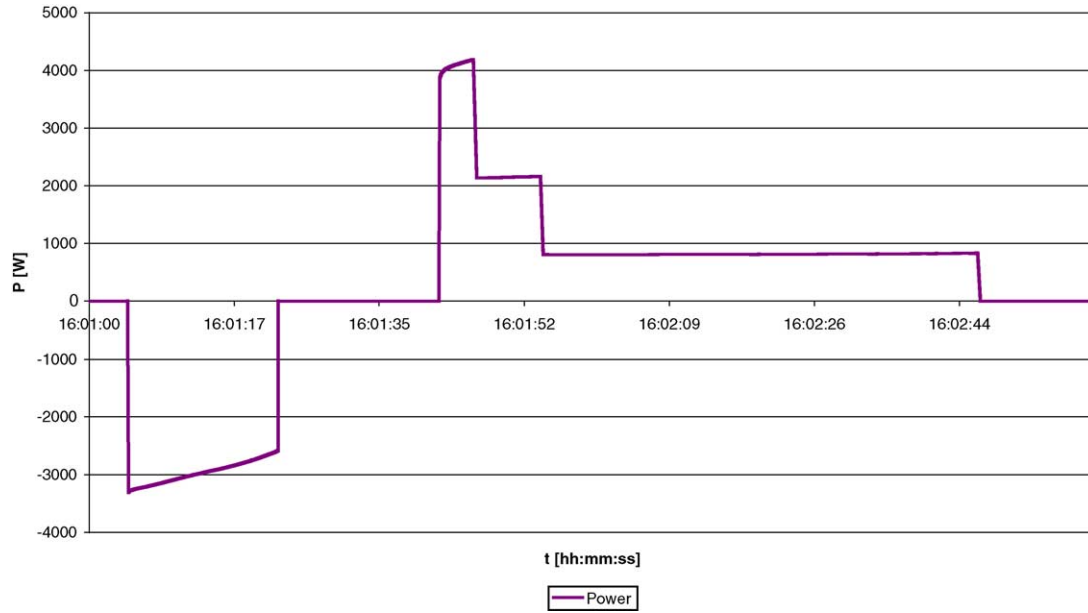
Fig. 11. Power profile during single cycle (positive = charge; negative = discharge) given by 12 V, 30 Ah bipolar lead–acid battery; sixteenth hour of PALC test.

5. Testing of 12 V 30 Ah bipolar lead–acid battery using PALC schedule

The 12 V, 30 Ah bipolar lead–acid battery was discharged at a C/3 rate until 50% SoC was reached. The battery was then tested under the EUCAR profile, as shown in Fig. 5, using 10 C discharge peaks and 9 C charge peaks. The tests were performed for 16 h and were followed by a period of rest for 8 h. The PALC tests were continued and the maximum temperature rise during 16 h of continuous testing was less than 20 °C.

The voltage of the 12 V battery during testing is given in Fig. 6. The minimum voltage is 8.6 V at 300 A discharge during 18 s and a SoC of about 50%. No problems were found with low voltage limits during the tests. The current profile is given in Fig. 7 while the corresponding power profile, as measured, is shown in Fig. 8. The maximum power generated by the 12 V bipolar lead–acid battery is approximately 3.3 kW see Fig. 8. This is equivalent to 10 kW for a 36 V module. For the PALC, 10 kW of power is required. Thus, at 50% SoC, the tested 12 V, 30 Ah bipolar battery fulfills the power requirement. More importantly, charg-
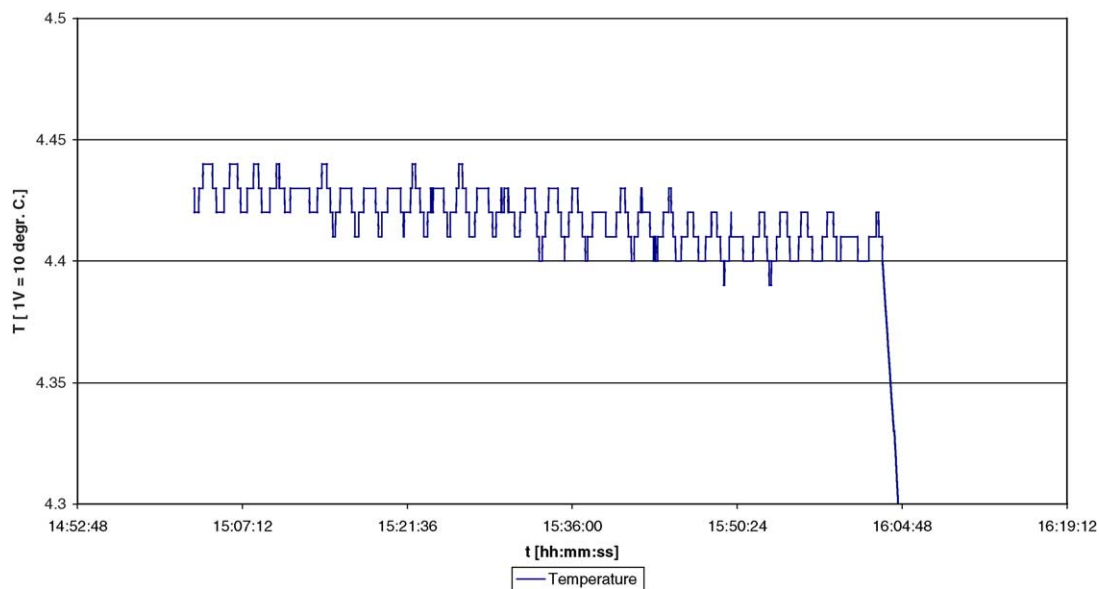

Fig. 12. Internal cell temperature (cell 3) during sixteenth hour of PALC test for 12 V, 30 Ah bipolar lead–acid battery at about 25 °C and with air-cooling on the outside.
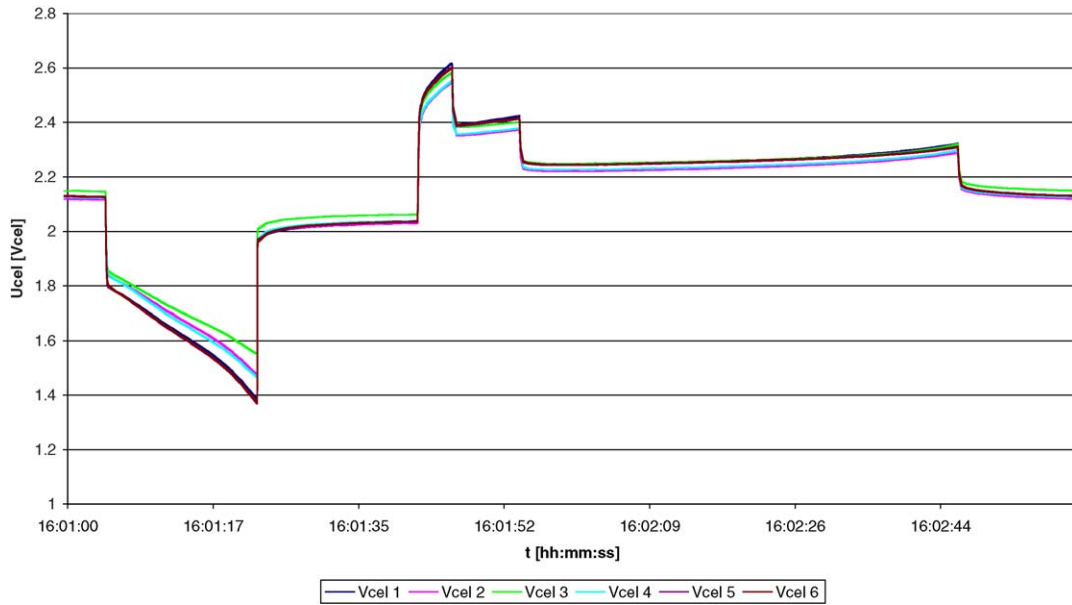
Fig. 13. Cell voltages on single PALC cycle during sixteenth hour of continuous operation for 12 V, 30 Ah bipolar lead–acid battery.

ing with 9 C peaks during 4 s has been demonstrated to be feasible.

The single-cell voltages given in Fig. 9 show only a relatively small variation. Because the battery was hand-made, differences in cell behavior will always exist. The minimum voltage during 18 s of 300 A discharge at a maximum 50% SoC is above 1.35 V per cell. The maximum cell voltage is 2.6 V per cell at 9 C charge during 4 s at 50% SoC. Of course, the cell voltages have to be corrected for the internal resistance per cell to determine the resistance-free charge and discharge voltage. The internal resistance is about 0.94 mΩ per cell at 50% SoC. At 300 A discharge, the ohmic voltage drop is 0.28 V. The cell voltage corrected for the internal

resistance during discharge is then equal to 1.63 V. In case of 300 A discharge, this value is not too low for operation. The charging at 9 C can also be corrected for the ohmic voltage contribution. In this case, the ohmic voltage increase is 0.25 V and therefore the charge voltage at the 9 C rate is 2.35 V per cell. This value is still below the gassing voltage. The voltage profile for one PALC is presented in Fig. 10. The minimum voltage, during discharge at 10 C (300 A), is equal to about 8.7 V. This discharge is under taken while the battery operates at about 50% SoC. The current density is about 0.4 A cm^{-2}.

During PALC tests, started at 50% SoC, the bipolar lead–acid battery shows stable operation without decreases
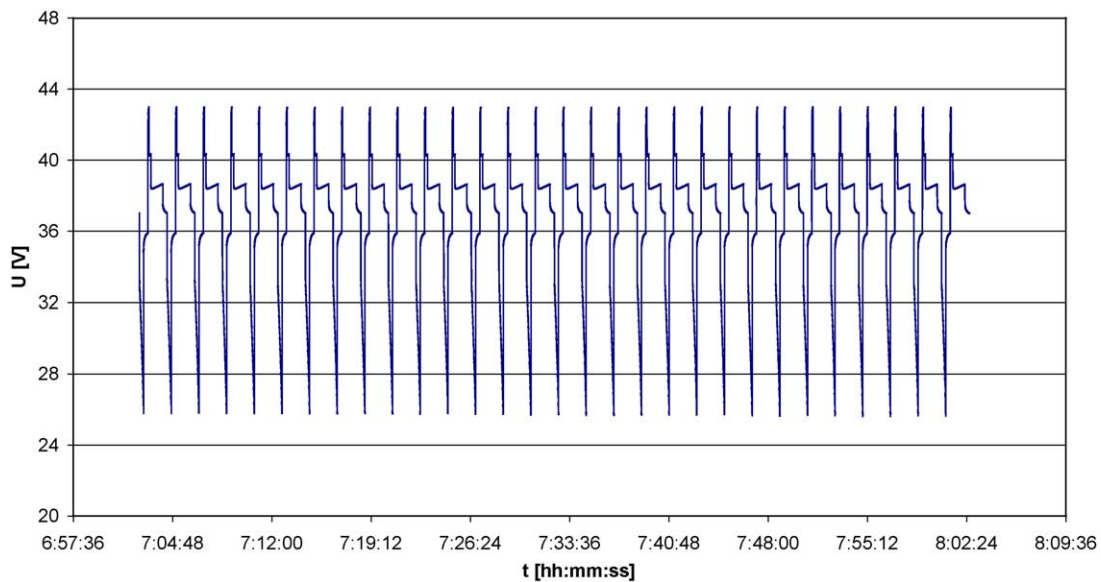

Fig. 14. Voltage vs. time for 36 V, 32 Ah bipolar lead–acid battery during eight hours of PALC test with 7 C discharge and 6.3 C charge peaks.
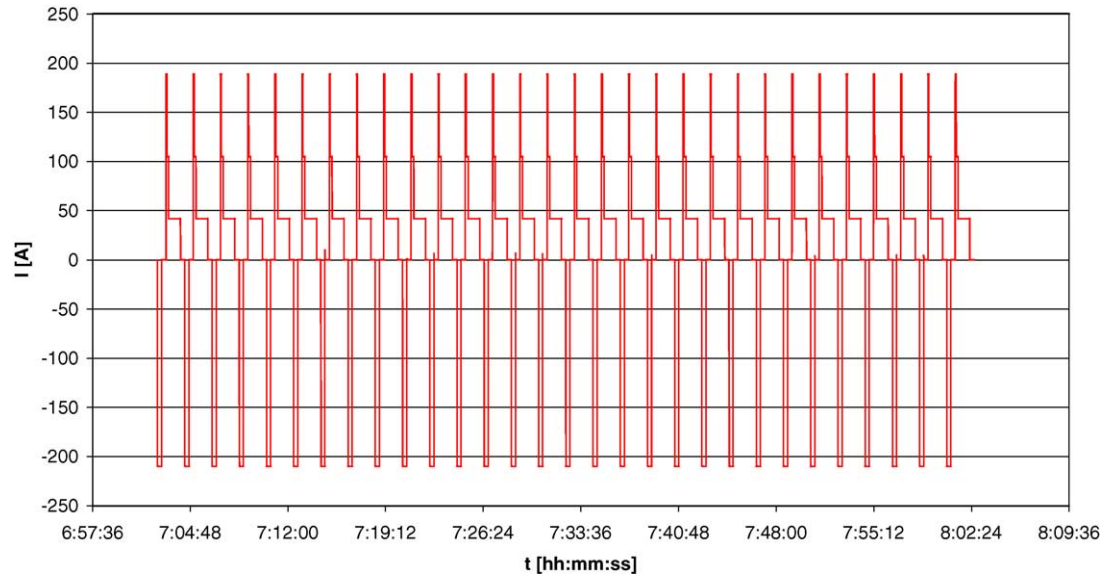
Fig. 15. Current vs. time for 36 V, 32 Ah bipolar lead–acid battery during eight hours of PALC test with 7 C discharge and 6.3 C charge peaks.

in cell voltage. An example of the power profile for the 12 V stack is presented in Fig. 11. It is remarkable that the bipolar lead–acid battery readily accepts very high charging rates (9 C during 4 s) and also delivers 10 C discharge peaks during 18 s while being at only a maximum of 50% SoC. This means that the formation of lead sulfate does not inhibit the passage of high currents. This is due to the fact that conducting pathways are present in the form of a stable conductor added to the paste. Another point is that due to the operation at 50% SoC, corrosion processes are less severe than in operation at almost 100% SoC as is experienced in uninterruptible power supply and automotive applications where the battery is held at (almost) full charge. The relatively high compression of the positive active-material is

another important features has been included in the design of the battery. Differences in acid concentration due to stratification have also been addressed. For this reason, the 12 V, 30 Ah battery (Fig. 2) has been operated horizontally. This orientation also reduces strongly the risk of active-material shedding and the oxygen cycle is improved. Importantly, the bipolar configuration leads to a homogeneous current distribution. The internal heating is also lowered using a bipolar configuration and this decreases the internal resistance, which has been further decreased by adding conductive additives to the paste and by applying a technique to counteract the re-crystallization process. Finally, a battery-management-system at the cell level has been applied to optimize the cell behaviour.
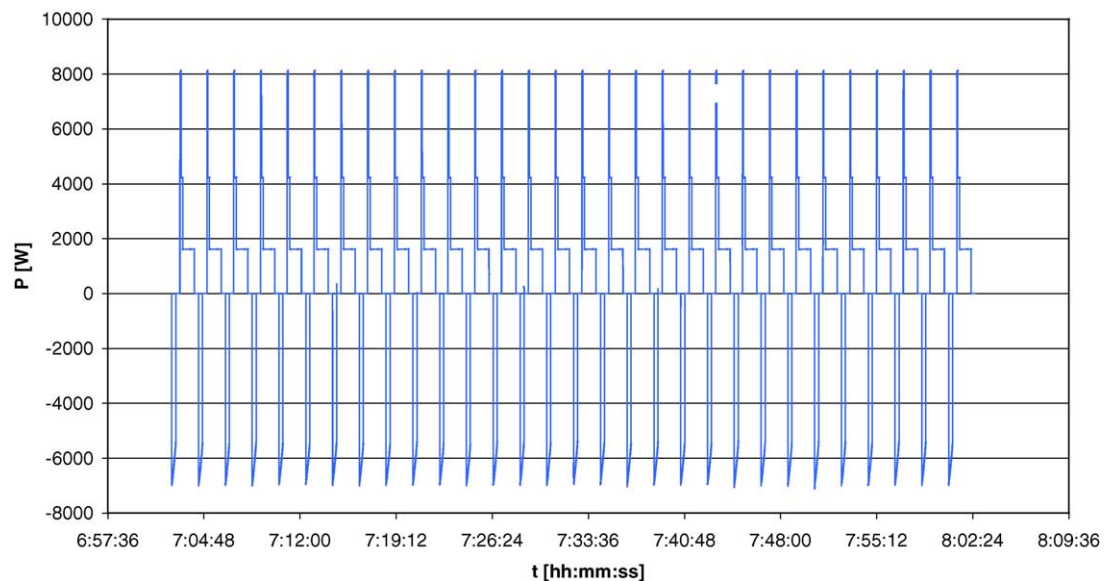

Fig. 16. Power vs. time for 36 V, 32 Ah bipolar lead–acid battery during eight hours of PALC test with 7 C discharge and 6.3 C charge peaks.
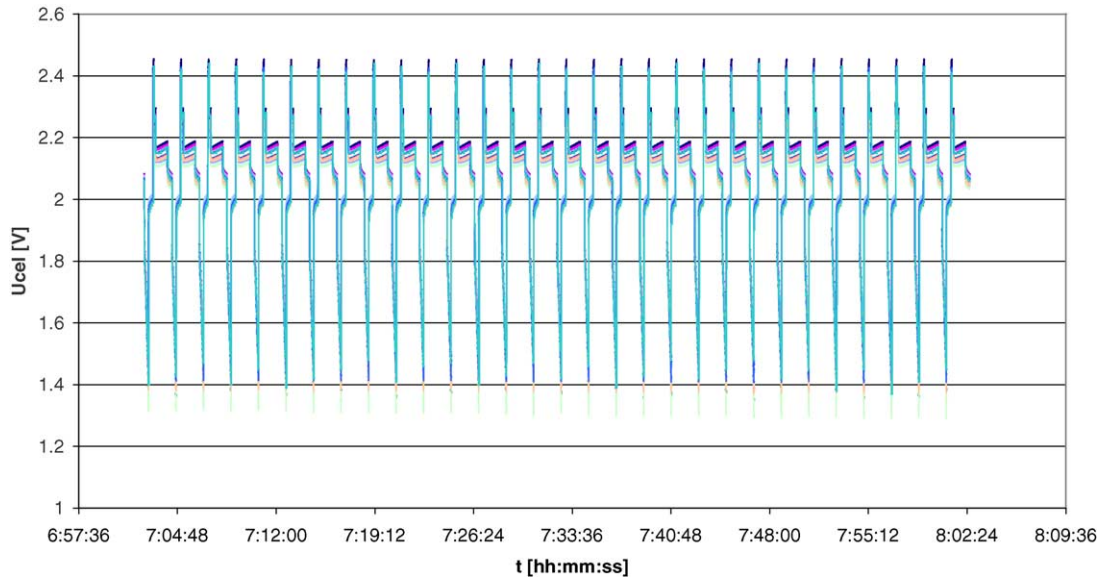
Fig. 17. Cell voltages vs. time for 36 V, 32 Ah bipolar lead–acid battery during eight hours of PALC test with 7 C discharge and 6.3 C charge peaks.

The internal cell temperature during continuous operation on a PALC cycle is shown in Fig. 12. During discharge (18 s at 300 A), the internal temperature decreases as expected. During charge, the internal temperature increases. The temperature during operation stabilizes at about 15 to 18 °C above room temperature. During one run, the ambient was 30 °C and this resulted in a battery temperature of 48 °C. This is well below the temperature of 70 °C when tribasic lead sulfate changes into tetrabasic lead sulfate, i.e., the conversion only takes place at elevated temperatures that normally do not occur during battery operation. The tribasic lead sulfate is present due to the manufacturing method used. Of course, during plate formation, all of the tribasic lead sulfate is converted to active material. During partial state-of-charge duty, tribasic lead sulfate is formed. Further investigations are required to determine the exact composition of the positive and negative plate during hybrid operation. It is postulated that material with a high surface area material is formed as a result of PALC operation with 9 C charge and 10 C discharge. When the temperature becomes too high, the power has to be decreased. The temperature rise can be lowered by other means, e.g., by increasing the conductivity of the bipolar plate. For the 36 V module (see later), the internal resistance was further lowered to 0.5 mΩ per cell, and more such improvements are underway. There is also scope to improve the thermal management system. In this way, the battery can be operated even at outside temperatures that are higher than 30 °C without causing problems with charge acceptance (regenerative breaking) or charge delivery (acceleration). The cell voltages of a 12 V module during one PALC are shown in Fig. 13. The maximum voltage is 2.6 V. The internal resistance of the cell is approximately 0.9 mΩ. The ohmic cell voltage drop or increase is about 0.3 V. This means that the cell voltage corrected for the ohmic voltage contribution is about 2.3 V during charge (9 C charge peak) and 1.7 V during discharge (10 C discharge peak). This voltage window (1.7 to 2.3 V) enables stable operation as is found by the stable continuous operation during 16 h.

6. PALC testing of 36 V, 30 Ah bipolar lead–acid battery

After construction and testing of 4 V and 12 V bipolar batteries (30 Ah), two 36 V versions were assembled from optimized bipolar plates. Testing with 10 C discharge and 9 C charge peaks resulted in heating of the battery due to the fact that the thermal management system required further development. Therefore, it was decided to perform PALC with 7 C discharge peaks and 6.3 C charge peaks. The battery exhibited a stable operational temperature. The voltage, current and power profiles of the 36 V, 32 Ah bipolar battery during 1 h of the PALC test after 7 h of running are presented in Figs. 14–16 respectively. The individual cell voltages are shown in Fig. 17. The data indicate that the bipolar battery experiences a stable operation and gives rise to no problems of overvoltage or undervoltage. Improvements are in progress to decrease further the internal cell resistance and to optimize the installed capacity of the positive active-mass, negative active-mass, and the acid present.

7. Conclusions

From initial tests of a novel bipolar lead–acid technology that uses AGM separator technology, it has been demonstrated that continuous testing for 16 h at 50% SoC with 10 C discharge pulses (18 s) and 9 C charge pulses (4 s) of a 12 V, 30 Ah battery gives stable behaviour, even when the outside temperature is 30 °C. The re-crystallization phenomenon is

actively counteracted by using electric pulses applied to the battery at 50% SoC. PALC to date the 12 V, 30 Ah bipolar battery has operated without any problems and with no decay in capacity after more than 7000 PALCs, each of 2 min duration. The total Ah-throughput is more than 350 times the nominal capacity of 30 Ah. Some differences in cell behavior have been found, but can be attributed to the manual way of assembling. Further tests are being conducted to improve the technology, especially in terms of lowering the internal resistance and reducing the weight of the bipolar cell module.

Acknowledgements

References

[1] Proceedings of AABC-02, 4–7 February 2002, Las Vegas, USA.
[2] Proceedings of AABC-03, June 2003, Nice, France.
[3] http://www.europeanenergyfair.com/download_03/presentation_effpower.pdf.
[4] http://www.sovereign-publications.com/atraverda.htm.
[5] http://www.stormingmedia.us/70/7005/A700543.html.
[6] http://www.trojan-battery.com/welcome.html.
[7] US Patent 6,077,623 Bipolar lead–acid battery plates and method of making same.
[8] A. Cooper, J. Power Sources 133 (2004) 116–125.
[9] V. Toniazzo, U. Lambert, J. Power Sources 133 (2004) 94–103.
[10] D. Pavlov, I. Pashmakova, J. Appl. Electrochem. 17 (1987) 1075–1082.
[11] P.T. Moseley, D.A.J. Rand, J. Power Sources 133 (2004) 104–109.
[12] J.H. Yan, W.S. Li, Q.Y. Zhan, J. Power Sources 133 (2004) 135–140.
[13] L.T. Lam, N.P. Haigh, C.G. Phyland, A.J. Urban, J. Power Sources 133 (2004) 126–134.
[14] D. Edwards, C. Kinney, Final Report (Report Number N01–11), Advanced Lead–Acid Battery Development, NIATI, March 2001.
[15] http://www.pulsetech.net/productinfo/product_sheets/PRS_LIT.pdf.