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Recent developments on lithium ion batteries at SAFT

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Abstract

Li ion system has been implemented in various cell sizes and technologies, for very different applications. While cobalt oxide is the positive material chosen for voltage compatibility in portable applications, using conventional liquid electrolyte technology or polymer type for thin batteries, nickel-based oxides give excellent performances in the large batteries, designed for electric vehicles or satellites. All these battery designs are described, and some performances presented. These results show that the Li ion concept, widely used presently in small portable batteries, can bring very impressive improvement in power capability as well as long cycle life, besides the well established high energy density. Thanks to basic studies intensively engaged many years ago in its R&D Centres, SAFT is now using the Li Ion electrochemical system in the main development programs for a new generation of power sources. Both fields of expertise of SAFT, small portable and large industrial batteries, are involved in manufacturing or developing these power sources, addressing a very large market from portable phones to EVs. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium ion battery; Cobalt oxide; Nickel-based oxide

1. Portable batteries

Portable Batteries Division of SAFT is now currently producing medium size prismatic cells (MP range), ranging from 2 to 5 Ah. These medium-to-high capacity cells, with high ‘packaging efficiency’ are very well suited for utilisation in portable phones and laptop computers, as well as high capacity/various voltage battery assemblies for specific applications. A new generation of batteries is developed, to satisfy the demand for thin power sources, especially for the portable phones market. This new Li Ion polymer battery type uses a SAFT proprietary technology of microporous gelled polymer electrolyte, which satisfy the key point of industrial process feasibility.

1.1. MP cells

The cell chemistry chosen is based on $LiCoO_2$/graphitized carbons blend, in order to have a fully compatible voltage profile with the existing products on the market. Now classic materials are used for current collector (Cu and Aluminium foil for negative and positive electrode, respectively), and separator PE/PP mixed separator with micropore-closure capability at 125–130°C. Electrolyte is $LiPF_6$ dissolved in a blend of organic carbonates [1].

Cell technology is based on winding electrodes on a flat mandrel, to produce a cell stack with oblong section. The MP cell containers are made of stainless steel, laser-welded, cans and covers. The covers feature the electrolyte fill port (closed with a metal ball after the cell formation), a circuit breaker and a safety vent. The volume left inside the cover can accommodate the electronic protection circuit (Table 1).

They are capable of high drain continuous discharge, up to 2*C* as well as low temperature utilisation, down to −30°C, as described in Fig. 1. The minimum in voltage curve at −30°C is probably due to some limited internal heating due to cell polarisation. Standard temperature range are −30/+60°C in storage, 0/+50°C during charge and −20/+60°C during discharge.

The MP cells can be charged up to 4.1 V at *C*-rate in the usual Li-ion constant current–constant voltage mode. 500 cycles at *C*-rate room *T* and 100% DOD have been demonstrated, this number jumps up to 1000 cycles when the DOD (at *C*-rate) is limited to 80%.

Cycling at 40°C does not noticeably affect the capacity, as shown in Fig. 2.

1.2. Polymer cells

Thanks to years of R&D experience in polymer electrolytes for lithium cells, SAFT took the decision of going

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Table 1
General characteristics of MP cells series

	MP 176065	MP 174865	MP 144350
Size	17.7 × 60.0 × 65.0 mm	17.5 × 48.0 × 65.0 mm	13.9 × 43.0 × 50.0 mm
Cylindrical cell size equivalence	2 side to side D size cells	2.5 side to side 18,650 cells	3 side to side AA cells
Weight (without protection circuit)	150 g	120 g	66 g
Ac impedance (1000 Hz)	50 mΩ	50 mΩ	60 mΩ
Average capacity	4.9 Ah	3.8 Ah	1.9 Ah

4 g and 60 mΩ to be added for the electronic protection circuit (single cell batteries).

into an industrialisation program in mid 1997. A proprietary process has been settled, and first generation products are being tested for qualification. The cell design and performances are presented more in details in an other paper in this volume [2].

The main feature of the technology is the use of the well stabilised electrodes process established for liquid electrolyte Li ion, together with a proprietary process of electrode/polymer laminate manufacturing via a phase inversion process. Cell casing is a now classical 'coffee bag' technology, using aluminium/polymer foils.

The cell chemistry is basically the same as for the MP cells, and 0.65 Ah cells demonstrated the power ability to satisfy the Global System for Mobile communications (GSM) working profile, in the temperature range of −10 to 60°C. Fig. 3 represents continuous discharge voltage profile at different rates.

Manufacturing is scheduled for early 1999, and full industrial mass production for 2000.

2. Industrial batteries

The 'Industrial Batteries' are large batteries used in applications such as stationary or mobile power sources. SAFT is the leader in Ni/Cd batteries used in this field, and has been more recently developing Li Ion batteries for Electric Vehicle (EV), Hybrid Electric Vehicle (HEV), and Space (Low Earth Orbit (LEO) and Geostationary Earth Orbit (GEO) satellites).

2.1. General features

In large batteries, material cost has a major impact on the final system price, and cobalt-based compounds are far too expensive to reach the market price of EV batteries, for example. Manganese-based materials are very attractive, however, the ambient conditions of utilisation can be highly variable, especially towards high temperature, and they suffer from important capacity loss on cycling in these conditions. Nickel-based oxides $LiNi_xM_yO_2$, which should lead to very competitive cost/Wh figures were consequently chosen as the positive electrode.

In addition, lithiated nickel oxides materials are generally excellent regarding the electrochemical stability, leading to very good capacity retention figures on storage. Thanks to an almost linear variation of voltage profile vs. DOD, and unit cell voltage being less critical as the cells are generally assembled to give high-voltage batteries, a suitable working voltage window can be chosen to optimise the energy/safety properties [3].

Preparing mixed oxides with nickel and other metallic elements has been extensively studied, with the aim of improving properties like reversibility and thermal stability for safety. There are wide possibilities in this field [4], and we have selected combinations which lead to the best compromise. This is still a promising way of improvements, particular to nickel oxides structures compared to manganese ones.

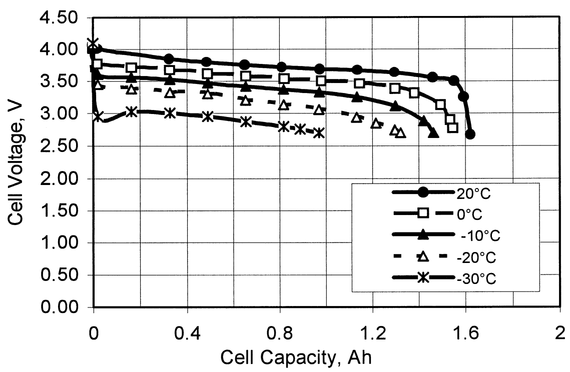

Fig. 1. Discharge curves of MP 144350 at various temperatures, at a $C/5$ continuous rate.

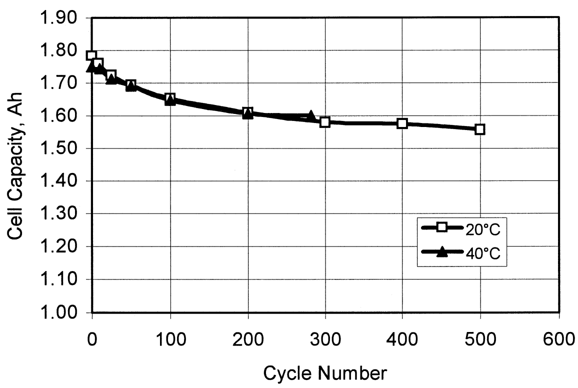

Fig. 2. Comparative cycling characteristics of a MP 144350 cell, at ambient and 40°C. 3 h charge at $C/2$ CC + 4.1 V CV, discharge at $C/5$ rate to 2.7 V COV.

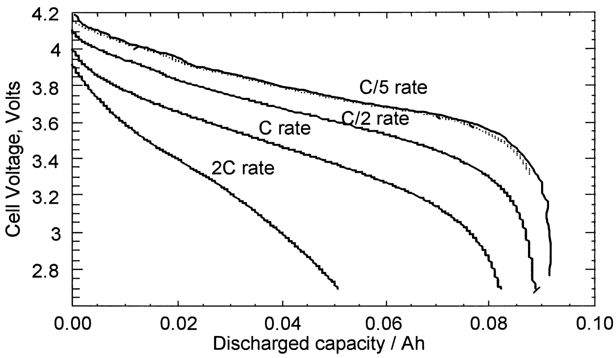

Fig. 3. Discharge characteristics of a Li Ion polymer cell @ ambient temperature.

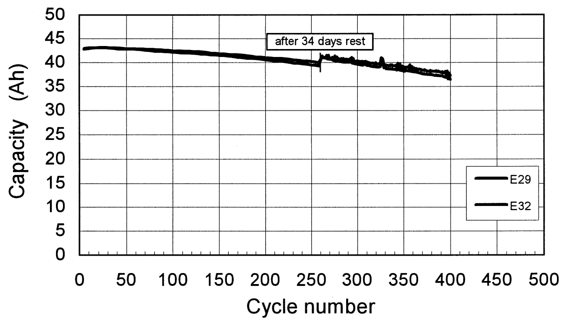

Fig. 4. Cycling properties of 44 Ah EV cells. Cycling conditions: ambient temperature, charge CC 18 A+4 V CV, discharge at 22 A, to 100% DOD at 2.7 V COV.

2.2. Electric vehicle

The most interesting properties of Li Ion in this application are the specific energy and energy density, to increase driving range, to more than 200 km. An optimised battery system will reach about 120 Wh/kg and 200 Wh/l. The EV program, initiated with the support of European Commission, French government agencies, in cooperation with car manufacturers, reaches the pilot production stage at the end of this year. Mass production of these batteries should start in the coming years, depending on the development of EV's.

The battery is built from 1 kWh modules, assembled to the customer's request on size and energy. Modules are made from cylindrical cells of about 40 Ah, which can be series/parallel connected to obtain the desired voltage/capacity. They contain an electronic control system, safety features, and liquid cooling circuit. Table 2 describes the present and future performances of such a module. Figs. 4 and 5 illustrate the performances of cells and modules, fulfilling the requirements for this application.

Safety is one of the major concerns for high energy density systems. Beside the choice of active materials, appropriate safety features and design, are the solutions to make these systems acceptable.

A complete battery management system has been developed, including an intelligent centralised electronic control system, high voltage unit, and thermal management. Several complete batteries are presently being tested on vehicles in partnership with car manufacturers and behave very satisfactorily.

2.3. Hybrid electric vehicle

In Hybrid Vehicles, the battery provides the peak power needed during starting or acceleration ('Power Assist type'), or as the sole power source during part of the time ('Dual Mode' type). In both case, the battery, which has a limited energy (few kWh), must supply enough power to move the car, and therefore should exhibits high power density and specific power, which may exceed 1000 W/kg. This can be also provided by the Li Ion technology. A development work was initiated in 1996 in US as part of the Partnership for a New Generation of Vehicle (PNGV) program, with the goal to demonstrate the feasibility of a complete battery satisfying the required performances, such as 1 kW/kg pulse, 46 Wh/kg, 75 Wh/l, and 120 K cycles at 3.3% DOD. Phase 1 of the program was successfully achieved, and 30-month phase 2 started early 1997, with the goal to develop a fully integrated 50 V battery module.

Cell chemistry is similar to the EV one, with an electrode design to achieve the required power. In spite of higher power, safety issues are not more critical than with EV design, as the energy density is somewhat reduced, due to the higher content on non active material per unit of cell volume. The cell prototypes provide acceptable behaviour under abuse conditions.

Modules of 0.3 to 0.5 kWh using high rate 6 Ah or 12 Ah cells have been designed, which deliver specific energies of about 60 Wh/kg (at *C*-rate), and can supply peak power of 1200 W/kg @ 50% DOD. Fig. 6 shows typical pulse specific power as a function of DOD, for discharge and regeneration phases. As the battery is continuously

Table 2
General performances of 1 kWh Li ion module for EV

	Present	Next generation
Specific energy, Wh/kg	138	147
Energy density, Wh/l	215	240
Specific power, W/kg (80% DOD, to 2.7 V/cell)	300	300
Cycling, *C*/2	13% loss after 400 cycles	$<$ 20% after 800 cycles

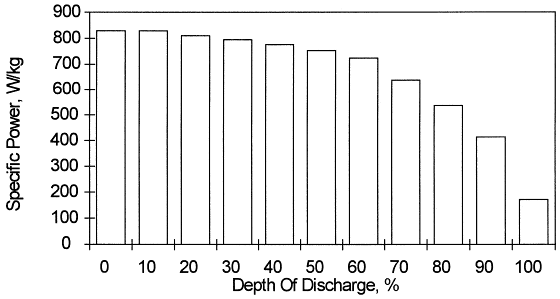

Fig. 5. Specific power vs. DOD of a 44 Ah EV cell, 30 s pulse, to a COV of 2.7 V @ ambient temperature.

cycling in small DOD conditions, the number of cycles has to be very high. To-date, the 6-Ah cells have demonstrated ability to be cycled during 150,000 cycles, at 3.3% DOD, under high rate conditions (peaks of various power up to > 1000 W/kg, representing actual use in car). They have lost about 5% of initial capacity (test still on-going).

2.4. Space applications

Specific energy and cycle life are also the very attractive properties which makes Li Ion the grade one battery for Space at the beginning of the 21st century. Based on the same electrochemistry, with some specific design particularities, batteries are being developed at SAFT for new programs of LEO, or GEO satellites.

Calendar life is expected to be very long, from the excellent electrochemical stability demonstrated to-date. An example of outstanding cycling properties of the electrochemical system is shown in Fig. 7, which describes the capacity retention and cell resistance of a small 0.7 Ah cylindrical cell during cycling at 10% DOD. Cell resistance is calculated from the voltage drop after a 18-s constant current pulse. A complete charge/discharge cycle

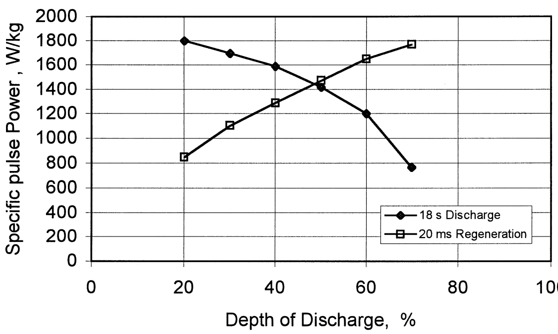

Fig. 6. Pulse power capability of a 12 Ah HEV Li ion cell, in function of depth of discharge.

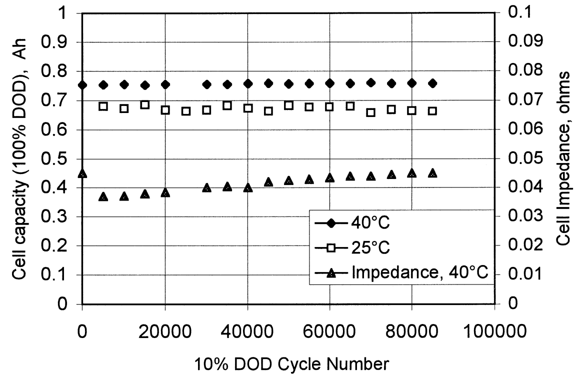

Fig. 7. Capacity and internal resistance (18 s pulse) of 0.7 Ah cell during cycling at 10% DOD, @ ambient temperature and 40°C. Cell diagnostic is made at 100% DOD to 2.7 V COV, at $C/5$ rate.

is made every 5000 cycles to check the cell characteristics. Neither cell capacity nor cell resistance has significantly changed over more than 85,000 cycles, representing about 0.9 year cycling. Even more important is the fact that during this test, still running, there is no detrimental effect of 40°C, compared to ambient temperature.

3. Conclusions

The results obtained in quite varied range of products show that the Li ion system, now widely used in small portable batteries, can bring real improvements to other applications. Beside the well established high energy density, power capability, long cycle life, can be turned to account in large 'industrial' batteries. Thanks to this experience, other uses of Li Ion are considered in a near future, for example in the field of stationary batteries for Telecom where lead acid batteries suffer from uncontrolled environmental conditions of utilisation and need expensive battery maintenance/replacements. The exceptional development of this new battery system allows to anticipate low manufacturing costs competitive with usual systems, as the quantities of the new materials which are used are drastically increasing.

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