

Lithium-ion batteries for electric vehicles: performances of 100 Ah cells

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Abstract

Among the new electrochemical systems, lithium ion using a liquid electrolyte appears to be one of the most promising technologies for the mid-term requirements of electric vehicles (EVs). Thanks to a dedicated research program over the past five years, SAFT is developing a complete EV battery system, including thermal management and electronic control system. Electrochemical cells of about 100 Ah, using LiNiO_2 and graphite, have been built and tested. They show performances of 125 Wh/kg and 265 Wh/l at the 1-h rate, at the beginning of life. Specific power obtained along the complete discharge fulfill the requirements for EV application. A 20 kWh 220 V assembly was built, including the associated electronic control equipment and air thermal regulation. © 1997 Published by Elsevier Science S.A.

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1. Requirements for electric-vehicle application

The first need for electric vehicles (EVs) is to increase the car autonomy, which can be achieved only by increasing the specific energy of the battery. Fig. 1 shows the calculated range of a mid-size car (800 kg), assuming a consumption of 135 Wh/(t km), as a function of battery weight, for several battery energy densities. About 300 kg is the maximum reasonable weight for the battery system of this type of car. As it can be seen, a 120 Wh/kg lithium-ion battery will guarantee a 250 km range, while a lead/acid battery of the same weight will give 25% of this value. The required peak power for such a car is about 40 kW/t, and increasing the specific power is associated with a specific energy increase, as the battery weight decreases for the same car range (or battery energy). Fig. 2 shows the calculation of the required specific peak power, as a function of the energy density, for several car ranges. A 20 to 30 kWh Li-ion battery (120 Wh/kg), for a 150 to 250 km range, requires about 200 W/kg specific peak power.

These performances being demonstrated, the battery must fulfill also the following two requirements: (i) low cost, which includes not only a suitable purchasing price, but associated with cycle life and reliability (i.e. cost of use, US \$/km), and (ii) safety.

As an example, the US Advanced Battery Consortium requirements for the mid- and long-term are given in Table 1.

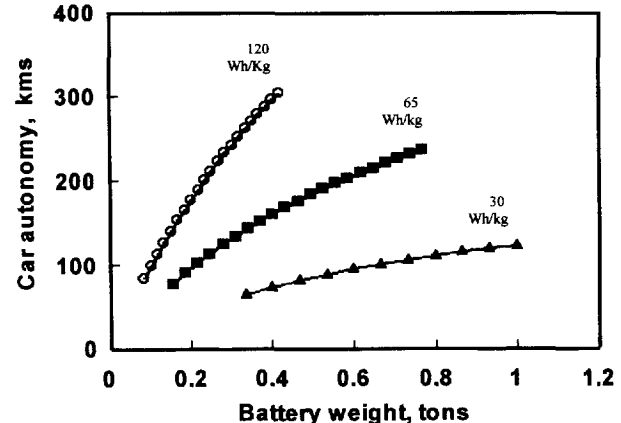


Fig. 1. Car autonomy as a function of battery weight, for various specific energies. Car consumption: 135 Wh/(t km), car weight: 800 kg.

2. Description of the electrochemical system

2.1. Negative electrode

Several types of carbon structure are being used for inserting lithium as the negative electrode in the Li-ion technology. A graphite material has been selected. The reasons for choice of this type of carbon are the low cost, good specific capacity (350 Ah/kg) with high first charge efficiency (> 80%), and electrode potential which keeps an almost constant value close to the metallic lithium one, all along its state-of-charge. This potential (100 to 200 mV) is however sufficiently dif-

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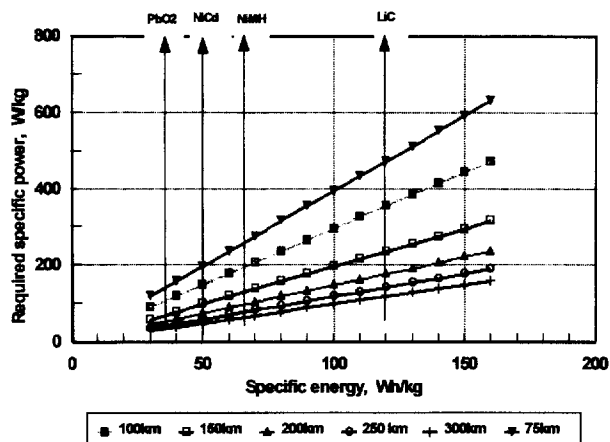


Fig. 2. Required specific peak power as a function of specific energy for various car ranges (battery size). Car consumption: 135 Wh/(t km), required power: 40 kW/t.

Table 1

Battery requirements for EV application (USABC)

	Mid-term	Long-term
Specific energy (Wh/kg)	> 100	200
Specific power (W/kg)	> 150	400
Cycle number (with <20% degradation)	> 600	> 600
Temperature range (°C)	-30 to +65	-40 to +85
Charging rate (h)	< 6	3 to 6
Life duration (year)	> 5	> 10
Cost/kWh (1000 units of 40 kWh) (US \$)	< 150	< 100

ferent from that of lithium to prevent metallic lithium deposition during charge.

Other carbon types of less-ordered structure may be used. However, the average potential versus lithium is markedly increased, resulting in a significant battery voltage drop, according to the state-of-charge, specially at the end of discharge. The end of charge of hard carbon at the usual rate, which occurs for a large part at 0 V versus lithium, is difficult to manage in order to avoid any lithium metal deposit.

An essential property of all the negative electrodes in the organic electrolyte media (liquid or polymer) is the build-up of a passivating surface layer, also called solid electrolyte interface (SEI), which insures the stability of the system. Produced by electrochemical reduction of the electrolyte, and so using a part of the initially available lithium (cycling efficiency at first cycle < 100%), the SEI prevents any further oxidation of lithium from lithiated carbon by the electrolyte. Its nature and suitable properties are greatly depending on type of carbon, surface area, and the composition of electrolyte. The stable layer built on the choosen graphite is obtained with a limited irreversible capacity loss at the first cycle (20%), resulting in improved cell energy density.

For a given design, the specific energy of a complete cell stack, including electrolyte, separator and current collectors, can be calculated as a function of carbon properties. Fig. 3

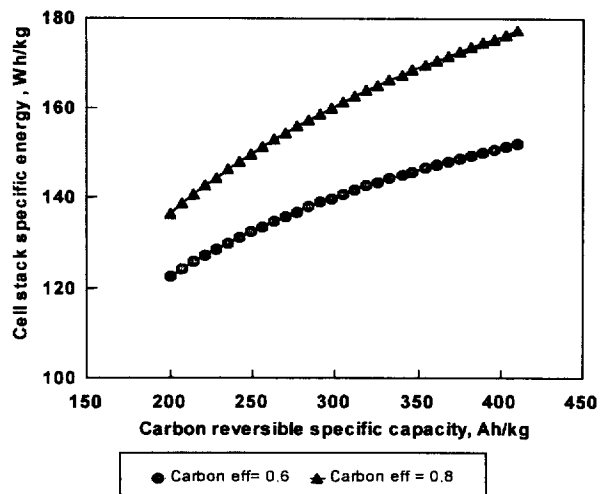


Fig. 3. Cell stack specific energy as a function of carbon reversible specific capacity: (·) 0.6 carbon efficiency, and (▲) 0.8 carbon efficiency. Positive material: LiNiO₂.

describes an example of such calculation as a function of specific capacity of carbon, for two efficiencies of carbon charge/discharge at the first cycle (SEI), using LiNiO₂ as the positive electrode.

2.2. Positive electrode

The main useful characteristic of the lithium insertion compound used as the positive material is the amount of lithium which can be reversibly extracted per mole, or mass unit.

A few materials have been proposed as possible candidates, mainly LiCoO₂, LiNiO₂ and LiMn₂O₄. The cobalt oxide is presently used in small portable batteries, but its high cost is an issue for EV application. They can be compared by the calculated cell stack energy density, as defined above, as a function of the extracted lithium per mole (X), using a graphite negative electrode (Fig. 4). In this figure, the arrows indicate the present status for each oxide. More lithium could be possibly extracted, with increasing charge voltage, however the stability of materials decreases on lowering the lithium content, and raising the average oxidation level of metallic

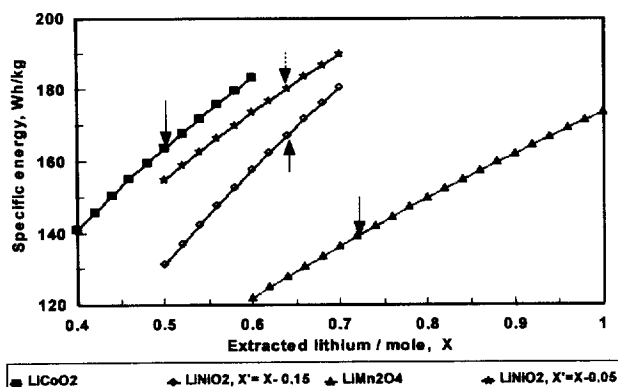


Fig. 4. Cell stack specific energy as a function of extracted Li/mole of positive material, carbon = 350 Ah/kg, first charge efficiency = 0.8. The arrows indicate the present situation.

ions. LiMn_2O_4 is expected to allow a complete de-lithiation to form $\lambda\text{-MnO}_2$, while nickel and cobalt oxides cannot reach this state, as neither CoO_2 nor NiO_2 have stable structures. However, the voltage needed is still quite high (>4.3 V), requiring more stable solvent than presently experienced for a complete chemical stability. More lithium might be used from nickel or cobalt oxides, providing suitable stabilizing modification of the structure such as doping with other metallic ions, as described in many papers in this volume.

In the case of LiNiO_2 , the amount of lithium which is re-inserted during the first discharge (X') is smaller than that extracted during the first charge (X). This amount is then reversibly involved during cycling. This is attributed to a slight departure from stoichiometry, as demonstrated in Ref. [1]. The compound close to stoichiometry can be prepared at laboratory level, and a scaling-up to industrial processes can be anticipated in the future. This is shown in Fig. 4, for a value $X - X'$ of 0.05, instead of 0.15 as currently produced today [2].

The presently chosen material is LiNiO_2 . This choice has been made considering the excellent electrochemical properties of this material (185 Ah/kg at 4.1 V during the first charge), and much lower cost compared with LiCoO_2 .

3. 100 Ah cell

3.1. Cell design

Prismatic prototypes were built, showing the nominal characteristics described in Table 2.

Electrodes are composed of active material, (LiNiO_2 and graphite), polyvinylidene fluoride binder, and carbon conductive agent, applied on a metallic current collector of aluminium and copper, respectively. A microporous polyolefin membrane is used as a separator, and the electrolyte 1 M LiPF_6 is dissolved in a proprietary solvent mixture [3].

3.2. Energy/power performances

After charge up to 4.0 V, these cells were tested at different discharge rates and temperatures. Fig. 5 shows discharge curves at rates ranging from $C/5$ to $2C$ at ambient temperature. Discharge at medium rate ($C/5$) delivered 115 Ah, representing 265 Wh/l and 125 Wh/kg. The capacity at $2C$ is still about 90% of that obtained at $C/5$. The cell behaviour at $C/2$, at temperatures from -10 to 20°C , is given in Fig. 6. In a climatic chamber, the cell temperature is regulated and there is no significant heating during discharge, the temperature of cell stack is kept close to -10°C . In these conditions, 80% of the capacity at 20°C is recovered. With good isolated cells, the coulombic efficiency was 93%, and the end of discharge temperature reached about 5°C .

Cell power capability has been evaluated by applying 150 A, 3 min pulses during a constant discharge rate at 50 A, see Fig. 7. From this test, the cell resistance can be calculated,

and the maximum peak power (30 s) can be extrapolated, for the maximum current, where a minimum voltage of 2.7 V is reached (Fig. 8). The impressive figure of almost 1000 W/kg is so calculated at the beginning of discharge. In fact, this calculation, based on a constant resistance independence of the intensity, gives a higher value than can be sustained by the system (that represents about 1000 A). With increasing depth-of-discharge (DOD), the calculated maximum peak power decreases while the resistance remains almost constant. This is due to decreasing of open-circuit voltage with state-of-charge, allowing a smaller voltage drop down to

Table 2
General characteristics of a new '100 Ah' prismatic cell

Weight (kg)	3, 30
Dimensions (mm)	137 × 53 × 216
Volume (l)	1.57
Nominal capacity (Ah)	115
Nominal energy (Wh)	415
Specific energy (Wh/kg)	125
Energy density (Wh/l)	265
Specific peak power at 90% DOD to 2.7 V, at 20°C (W/kg)	300
Temperature range ($^\circ\text{C}$)	-10 to $+50$

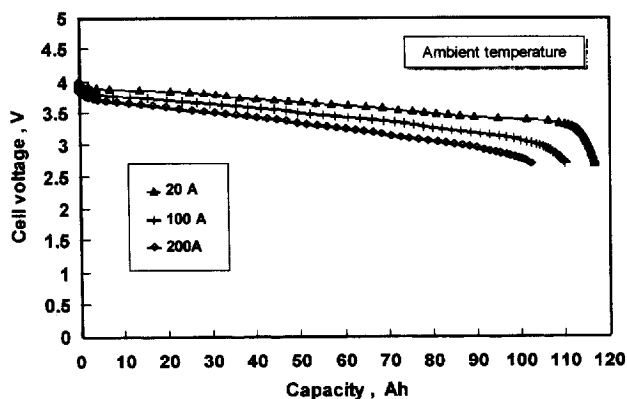


Fig. 5. Discharge curves at several constant rates of a 115 Ah LiNiO_2 /graphite cell, at ambient temperature.

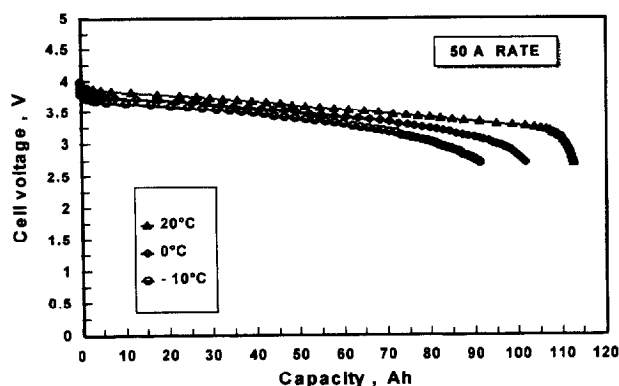


Fig. 6. Discharge curves at several temperatures of a 115 Ah LiNiO_2 /graphite cell at a $C/2$ rate.

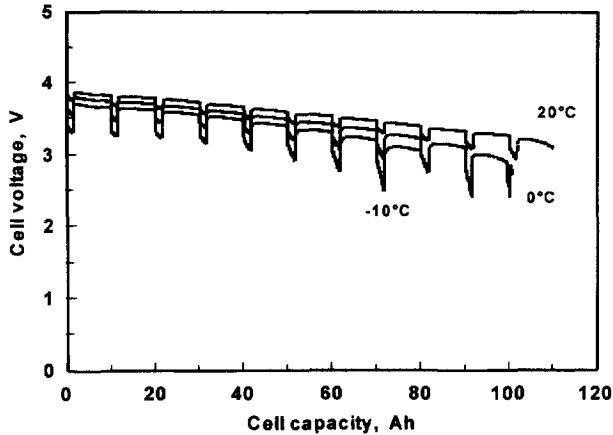


Fig. 7. Pulse discharge of a 115 Ah LiNiO₂/graphite cell at different temperatures. 150 A 3 min pulses, added to 50 A constant current.

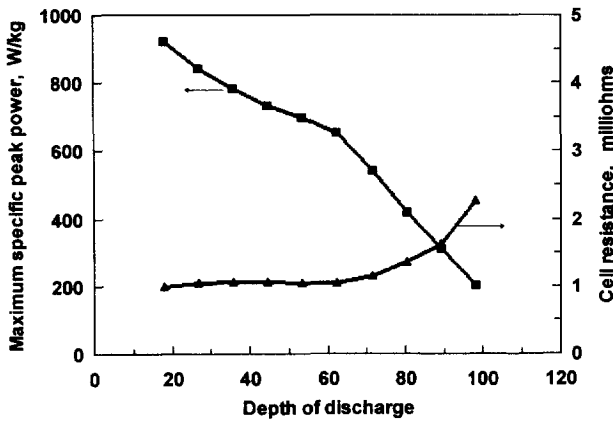


Fig. 8. Cell resistance and maximum peak power calculation as a function of DOD to a cut-off voltage of 2.7 V for a 115 Ah LiNiO₂/graphite cell at ambient temperature.

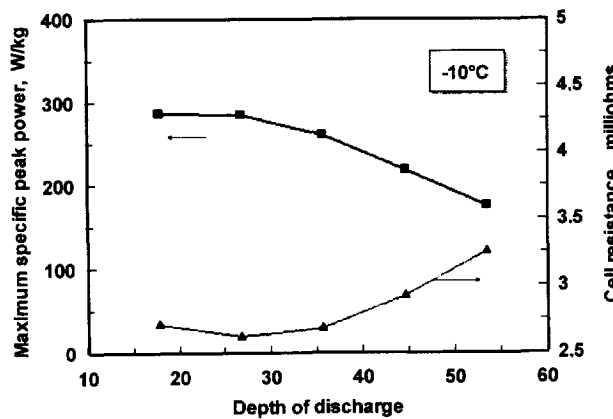


Fig. 9. Cell resistance and maximum peak power calculation as a function of DOD to a cut-off voltage of 2.7 V for a 115 Ah LiNiO₂/graphite cell at -10 °C.

cut-off voltage. The peak power actually obtained near the end of discharge (80%), is still about 400 W/kg, which is higher than requested by the EV application.

At low temperature the resistance increases resulting in lower power ability. However, the peak power remains higher than 200 W/kg up to 50% of DOD at -10 °C, see Fig. 9.

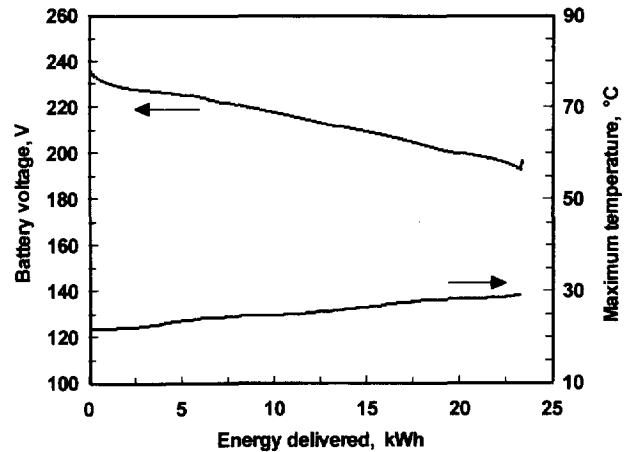


Fig. 10. Voltage and temperature profile as a function of delivered energy of a 20 kWh battery assembly, at C/2 rate on constant load at ambient temperature.

From these results, it can be concluded that the electrochemical system is totally able to fulfill the energy/power requirements for EV applications.

3.3. Cycle life

Despite a very good electrochemical reversibility of active materials, as demonstrated previously in Ref. [4], the electrode ageing may induce practical energy degradation upon cycling. Several phenomena may be involved in that process, and this is still a subject of investigation. Recent improvements were experienced with small laboratory cells. About 15% loss was obtained after 500 cycles (100% DOD). Further improvements should extend the practical cycle life to more than 1000 cycles.

4. Battery assembly

The described design was used to build a '20 kWh' series assembly of about 60 cells, to supply a voltage of 240 to 160 V. These cells were placed in a specifically designed structure, including an air thermal regulation. The complete electronic control circuitry, managing each cell end of charge or end of discharge voltage, as well as safety features were also installed and tested.

After a few cycles, the battery was discharged at different rates. Fig. 10 shows the C/2 rate, obtained on constant load. Nominal capacity (115 Ah) was obtained, delivering a total energy of 23 kWh.

5. Conclusions

The data obtained today with full-scale prototypes demonstrate that the Li-ion battery concept is suitable to reach the energy/power requirements for improved EVs. From first

Table 3
Targeted characteristics for module prototypes and complete battery systems

Characteristics	Module (3 kWh)	Battery system (30 kWh)
Specific energy (Wh/kg)	150	120
Energy density (Wh/l)	250	200
Specific peak power (W/kg)	300	230
Cycle life (deep discharge)	800	600
Capacity losses	<20%	<20%

results presented, using $\text{LiNiO}_2/\text{graphite}$, the targeted performances for optimized battery modules prototypes (3 kWh) and complete battery systems are given in Table 3. The two main goals for the present and future work are: (i) low serial costs, and (ii) safety in all abuse circumstances. These performances will lead to multiply by a factor four the autonomy of a car using the same weight of lead/acid batteries (250 km versus 60 km).

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