Lithium polymer battery development for electric vehicle application

P. Baudry [a,*], S. Lascaud [a], H. Majastre [b], D. Bloch [c]

[a] EDF, R&D Department, Les Renardieres, route de Sens, BP 1, 77250 Moret-sur-Loing, France
[b] Bolloré Technologies, Odet, BP 607, 29551 Quimper Cedex, France
[c] CEA/CEREM, CENG-85X, 38041 Grenoble, France

Abstract

Bolloré Technologies, EDF and CEA/CEREM started in 1993 a program for the development of a lithium polymer battery technology with a first objective: producing reproducible 40 Ah single cells. A cell design was selected and a manufacturing process based on extrusion was built up. 40 Ah single cells were produced by this process and are undergoing tests. The cycleability obtained at 0.4 and 4 Ah is between 300 and 400 cycles, is still in progress, with a specific capacity around 150 mAh/g of cathodic vanadium oxide. Power tests, thermal modelling and specific energy projections based on the same electrochemical performances confirm the interest of the lithium polymer battery for electric vehicle application. © 1997 Published by Elsevier Science S.A.

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1. Introduction

The promotion of electric vehicles (EVS) requires the development of reliable, safe and low-cost large-scale energy storage systems. Among the different lithium systems, the all solid-state lithium polymer battery is considered as one of the promising technologies to fulfill the EV requirements. Bolloré Technologies, EDF and CEA/CEREM started in 1993 a program for the development of a lithium polymer battery technology [1]. The first objective is to manufacture reproducible 40 Ah single cells with processes offering a low potential cost at industrial scale and avoiding introduction of solvents.

2. Electrochemical system

2.1. Cell configuration

The metallic lithium anode, despite its high theoretical specific capacity, has not yet been commercially used for large-scale batteries with liquid or plasticized polymer electrolytes. Dendritic growth, electrolyte reaction with lithium and safety were the main problems unsolved. However, these drawbacks are strongly dependent on the cell configuration

and on the presence of solvent in the electrolyte. They can be reduced when a polymer electrolyte is used:

1. With the solventless solid-state polymer electrolyte, the lithium/electrolyte interface ageing is highly reduced [2]. A passivation film is observed, but it is permeable to lithium ions, and the correspondent impedance remains acceptable even after prolonged cycling.
2. The thin film configuration, associated with suitable selected conditions, prevents from short-circuit associated with dendritic growth [3]

2.2. Cathodic material

As discussed before [4], the all solid-state polymer battery requires a thermal management in order to maintain a temperature higer than 60 °C to obtain sufficient continuous power. With such an operating temperature, the use of 4 V/ lithium cathodic materials such as $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$ would enhance electrolyte degradation and possibly cathodic material irreversibility, specially at the end of recharge. Thus, 3 V/lithium cathodic materials fits better with the lithium polymer system. Although manganese oxide cathodes remain the most promising materials in term of environmental impact and cost, they suffer from capacity fading with cycling. Therefore, a vanadium oxide material (VO_x) has been preferred since its specific capacity and cycle life are higher.

* Corresponding author. Tel.. +331-60-73-68-20; Fax: +331-60-73-67-21.

2.3. Polymer electrolyte materials

A non-plastisized polyether, associated with a fluorinated lithium salt has been selected as the polymer electrolyte. This polymer has an enhanced mechanical strength compared with pure PEO. With the thin film configuration, the ionic conductivity, $\sim 6 \times 10^{-6}$ S/cm at 80 °C, is sufficient to give high specific power.

2.4. Energy density

Assuming a specific capacity of 200 mAh/g for VO_x, with an average voltage discharge of 2.5 V/Li, the theoretical specific energy for the cathodic material is 500 Wh/kg. Then, the actual energy density is obtained by the ratio between the amount of VO_x contained in the battery and the total weight. This ratio, without packaging and external current collectors, lays in the 0.20–0.35 range, depending on the cell configuration, which yields a battery specific energy of 100–175 Wh/kg.

3. Manufacturing process

Beyond the battery technical performances, an EV battery design requires the use, as far as possible, of cost-effective materials and manufacturing processes. Targets for this key issue are very demanding. As an example, mid-term and long-term USABC cost requirements are respectively 150 and 100 US$/kWh. Then, if we consider an EV powered by a lithium battery, the thinner the elementary stack, the larger the surface area that needs to be used. This represents between 500 and 2000 m^2 for thin film configurations, depending on the battery design and on the EV performance required. Therefore, the productivity of the film manufacturing process must be high with low investment cost.

Thermoplastic films are generally produced by extrusion. This process gives rise to very high productivities, around several hundreds of meters per minute for packaging or manufacturing of dielectric films. We selected this process to manufacture polymer batteries and the challenge was to adapt the manufacturing process to the performance requirements. A laboratory extrusion line was built and allowed the cathode and electrolyte thin films to be produced at a speed of 10 m/min; 0.4, 4 and 40 Ah elements are currently produced in order to select the suitable configurations and investigate the scaling-up effect.

4. Cycling results on 0.4, 4 and 40 Ah elements

The specific capacity obtained with 0.4 Ah single cells based on VO_x under cycling at 100% depth-of-discharge (DOD) and 80°C ($C/4$ rate on discharge and $C/8$ on recharge) is presented in Fig. 1. After a first decrease during the 50 first cycles, the capacity is stabilized at ~ 150 mAh/
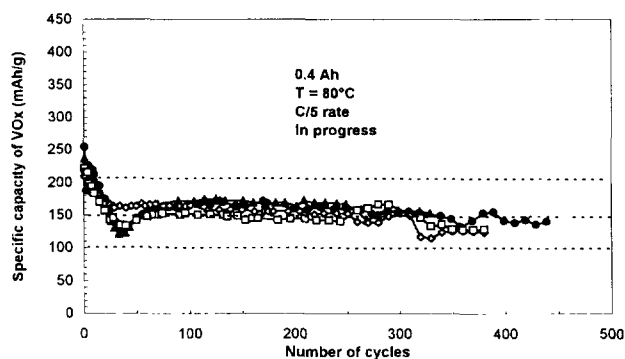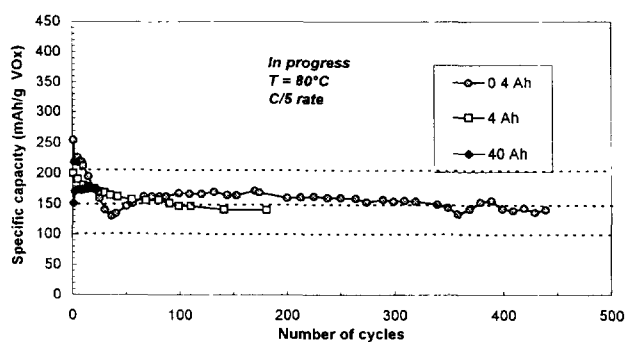

Fig. 1. Cycleability of 0.4 Ah single cells.

Fig. 2. Scaling-up effect for the especific capacity of VO_x on 0.4, 4 and 40 Ah single cells.

g; 300 to 400 cycles have been obtained, the cycling being still going on. The scaling-up effect, investigated by performing the same experiment on 4 and 40 Ah, is shown in Fig. 2. The performance of the specific capacity with 4 Ah elements is similar to that obtained on a 0.4 Ah one. Cycling tests on 40 Ah started recently and are presently in progress; their specific capacity fits correctly during the first 30 cycles.

These results need to be fully confirmed by long-term cycling of 40 Ah elements. Nevertheless, they suggest that no major problem relative to scaling-up has been identified. Our first objective is to obtain reproducibly 300 full cycles on 40 Ah elements at the end of this year. Then, the next cycleability target for the coming years will be 500 full cycles (for an urban EV having 200 km driving distance, this would represent 100 000 km for the battery life).

5. Specific power

Power tests of lithium polymer batteries reported in the literature frequently correspond to the beginning of cycling [5], and experiments performed after hundreds of cycles have shown a significant power loss [6].

The power/capacity relationship is here analysed in terms of obtained capacity when a sufficient power demand is applied continuously to the cells. After 150 cycles at 100% DOD, the capacity obtained at different rates at 80 °C on a 0.4 Ah element has been measured. A $C/2$ rate gives 100 mAh/g of vanadium oxide; additionnally, a $2C$ rate can be

Table 1
Evolution of the lithium battery performances

	Specific energy * (Wh/kg)	Specific power (80 °C) [a] (30 s, 80% DOD), (W/kg)	Specific power (90 °C) [a] (30 s, 80% DOD), (W/kg)
Present (single element)	110	130	195
Short-term (single element), <1 year	130	195	290
Mid-term (single element), 2–4 years	165	250	370
Mid-term (battery)	130	200	300

[a] Packaging, connectics and thermal management are not included for single elements. They are estimated at 20% of the total weight for a battery system. Theoretical VO_x specific capacity: 200 mAh/g.

sustained for several minutes, showing an excellent transient power ability. At 90 °C, instead of 80 °C, the power increase is 50%.

6. Electric and thermal modelling

Electric and thermal modelling has been performed for a 80 Ah element to assess the thermal behaviour for EV application. The simulation of the cross-sectionial temperature of this 80 Ah element at the end of a discharge at C rate is shown in Fig. 3. The heat exchange conditions are similar to those of an air-cooling system. The temperature rise during the discharge is 15 °C starting from 80 °C, and the maximum temperature dispersion within the element is less than 0.6 °C. This very good temperature homogeneity is due to an easy heat removal obtained with thin film configuration and a large anisotropy in thermal conduction.

7. Performance projections

Two different levels of performance projections can be proposed. The first one can be obtained directly by extrapo-

Fig. 3. Thermal modeling of a 80 Ah single cell cross section. Final temperature after a discharge at C rate; initial temperature: 353 K.

lation, just reducing the weight of electrochemically inactive materials which do not interact with the cell operation mode. Another evolution involves directly or indirectly the electrochemical cell operation, and is therefore more prospective. Present results, short-term and mid-term energy and power performances of the developed lithium polymer battery technology are listed in Table 1.

Some difference in characteristics with other EV batteries can be observed:

1. The presence of the lithium anode gives the highest specific energy for optimized configuration. With thin film configuration, the specific energy is very sensitive to nonactive material content, for example current collectors.
2. At 80 °C, the continuous power/energy ratio is 1.2–1.5 times lower than for lead/acid or Ni–Cd batteries. This stands in favour of an EV with a relatively large driving range, in the range of 200 km, the design should be power-driven (sustained speed criteria for instance) [7].
3. The power is very sensitive to temperature. At 90 °C, the transient power/energy ratio is higher than 2, and the EV manufacturer may like to select a lower driving distance with the objective of cost reduction.

8. Conclusions

After three years of R&D on the lithium polymer battery, 40 Ah single cells have been produced. The cycleability obtained with 0.4 Ah cells is promising and the performance at the beginning of cycling on 40 Ah cells is similar. The next year will be dedicated to the 40 Ah cycleability tests, reproducibility assessment and increase of specific energy and power. All these results confirm that the lithium polymer technology is a serious candidate as an advanced battery technology for EV application.

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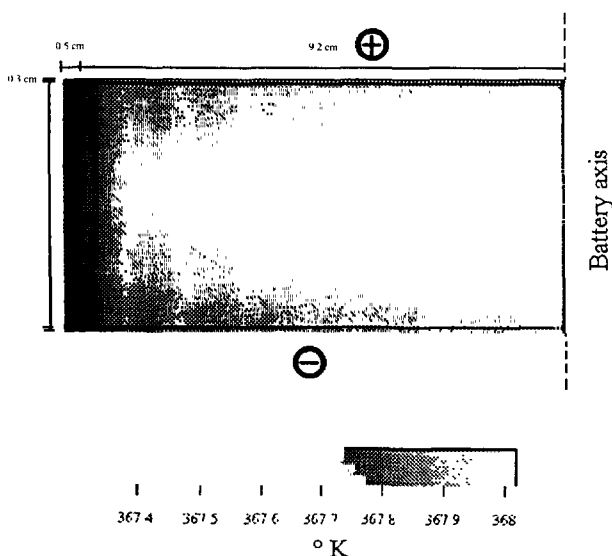[2] D. Fauteux, Electrochim. Acta, 38 (1993) 1199–1210.

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