



# Investigation of aging mechanisms of high power Li-ion cells used for hybrid electric vehicles

Sandrine Bourlot\*, Philippe Blanchard, Stéphanie Robert

Johnson Controls – Saft Advanced Power Solutions, 111/113 boulevard Alfred Daney, 33074 Bordeaux Cedex, France

## ARTICLE INFO

### Article history:

Received 6 August 2010  
Received in revised form  
24 September 2010  
Accepted 29 September 2010  
Available online 8 October 2010

### Keywords:

Aging  
Post-life analyses  
Lithium-ion battery  
HEV

## ABSTRACT

High power lithium-ion batteries need to exhibit long service life to meet targets of automotive applications. This article describes the deep investigation of the so-called VL6P cells, high power lithium-ion cells mass produced by Johnson Controls – Saft (JC-S), in order to understand the root causes of their aging. Cells aged by calendar and cycle life are investigated here compared to fresh cells. Among the results of the different analyses, the most significant is that more active lithium is detected in negative electrode after aging. This tends to indicate that effect of aging is due to increase of positive electrode limitation. Results of this investigation will allow JC-S to continue to improve life of the lithium-ion cells.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

High power lithium-ion (Li-ion) cells are currently used in hybrid electric vehicles (HEVs). Besides other characteristics (high power capability, large operating temperature range) these batteries are requested to exhibit long service life, meaning high robustness versus aging processes.

The decrease of battery performance as a function of time is usually the consequence of two combined origins which are (i) operating conditions, via the influence of various parameters like regenerative and discharge pulses, delta SoC and total energy throughput, and (ii) engine-off storage conditions. During these “non operating” but “no cooling” time periods the battery continues to age because it is subjected to high temperature coming from the engine, the car body or even the parking ground. Main parameters included in this calendar life performance are time and temperature.

Degree of progression of battery aging processes or State of Health can be quantified by measuring key performance of cells like capacity and internal resistance. Following these parameters during tests, carried out using operating conditions and temperatures representative of real use, allows to make life projections.

In order to understand the root causes of this aging and further improve the life, a deep investigation of the cells has been carried out.

This study is reporting results obtained using the so-called VL6P cell used in mild hybrid operating conditions. This cell, a 7 Ah high power cylindrical design, is mass produced by Johnson Controls – Saft (JC-S). Important characteristics include NiCoAl (NCA) type cathode and graphite anode. Other general characteristics are indicated in Table 1. Aging tests which have been performed include calendar life tests at 60 °C, 60% SoC, and accelerated cycle life (20C, 10% delta SoC, room temperature). Performances of aged cells (variation of capacity and power compared to fresh state) are reported in Table 2.

## 2. Experimental

### 2.1. Samples studied

Three kinds of Li-ion VL6P cells are investigated in this study: (i) fresh cell, with no aging, for reference; (ii) cell aged by 1.5 years of storage at 60 °C, 60% SoC, to see the effect of calendar life; (iii) cell aged by 4200 operating hours of accelerated cycle life (20C, 10% delta SoC, room temperature), to see the effect of cycle life. This test lasted 1.5 years.

After the completion of the aging tests, complete tear down analysis of the cells is performed.

### 2.2. Procedure used for post-life analyses

After being fully discharged, cells are opened in an oil bath in order to recover gas and electrolyte. Then cells are dismantled inside a glove box, under inert atmosphere. Then electrodes and

\* Corresponding author. Tel.: +33 5 57 10 64 07; fax: +33 5 57 10 65 22.  
E-mail addresses: [sandrine.bourlot@saftbatteries.com](mailto:sandrine.bourlot@saftbatteries.com) (S. Bourlot),  
[philippe.blanchard@saftbatteries.com](mailto:philippe.blanchard@saftbatteries.com) (P. Blanchard).

**Table 1**  
General characteristics of Li-ion VL6P cells, mass-produced by JCS.

Capacity at C/3, 4 V, 25 °C (Ah)	7
Diameter (mm)	38
Length (mm)	145
Weight (kg)	0.36
Volume (dm <sup>3</sup> )	0.16
Energy (Wh)	25
Discharge power (W): 10 s, 50% SoC, 25 °C	
Voltage limit (2.5 V)	1000
Current limit (250 A)	730
Discharge power (W): 10 s, 50% SoC, -25 °C	180
Voltage limit (2.0 V)	

**Table 2**  
Performances of aged cells investigated.

Cell analysed	Performances: delta vs initial (irreversible losses)
Aged cell	-15% capacity
Calendar life (60 °C, 60% SoC): 1.5 years	-39% power (*)
Aged cell	-19% capacity
Cycle life (20C, 10% SoC): 4200 h	-12% power (*)

(\*) Voltage limit (2.5 V) discharge power (W): 10 s, 50% SOC, 25 °C.

separators are sampled on three lengthwise locations. These locations correspond to the external part of the cell (i.e. near the can), to the middle part, and to the internal part of the cylindrical cell (i.e. near the winding mandrel). This sampling allows to verify homogeneity of aging processes within the cell.

Different analyses are performed on electrodes like measurements of specific surface area (BET), micro-structural characterisation (SEM, XRD) and quantification of lithium content. On separator, observation by SEM, and DSC are performed.

### 2.3. Gas analysis

Gas is recovered from the cells, and volume is quantified. Then, analysis is performed by gas chromatography. As indicated in Table 3, no gas is recovered from fresh cell and from cell aged by

cycle life, and only very limited quantity is collected for cell aged by calendar life. This indicates that almost no pressure inside the cells was created by aging.

In the case of the cell aged by calendar life, mainly gasses formed during electrical formation are seen (carbon monoxide, methane), some carbon dioxide formation is noted. Oxygen and nitrogen observed come from the air of the dry room during cell manufacturing (before cell closing). In fact, gas creation is known to increase with voltage [1], and cells are tested here at 60% SoC as the application is hybrid vehicles. This explains the limited quantity formed.

### 2.4. Electrolyte analysis

Electrolyte is recovered from the cells and hydrofluoric acid (HF) content is determined by titration. As indicated in Table 3, a limited increase is observed for cell aged by calendar life, which remains <100 ppm. This indicates a very limited degradation of electrolyte, or compounds containing protons, like binder or separator.

### 2.5. Separator analysis

SEM observations of the separator (Fig. 1) show that after aging there's no pore clogging. And no difference is seen between the three different locations in the cells (external, middle and internal part).

DSC analyses were performed and they confirm that there's no evidence of separator degradation.

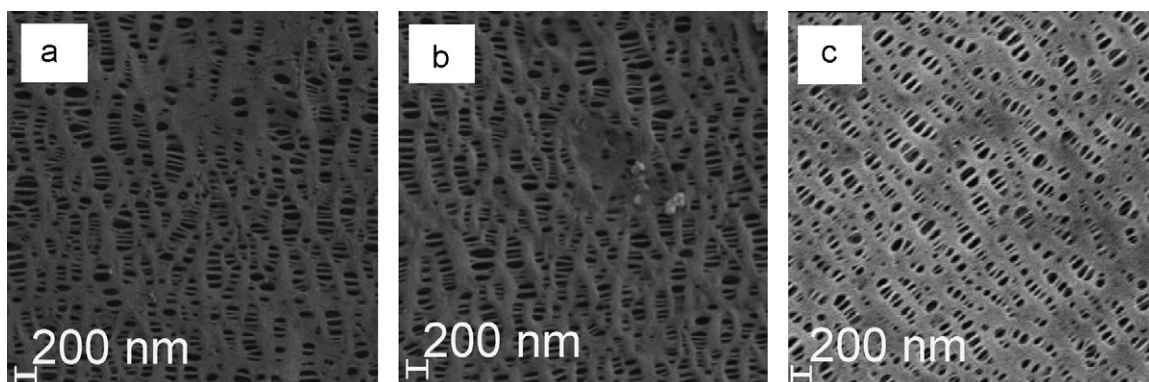
### 2.6. Electrodes analysis: specific surface area measurements (BET)

For positive electrode, the expected value is >30 m<sup>2</sup> g<sup>-1</sup>. Values found are around 6 m<sup>2</sup> g<sup>-1</sup> for fresh and aged cells (Fig. 2(a)). This means that the binder covers some surface, but as there's no increase in surface area, this indicates that there's no binder dissolution or no pulverization of active positive material. No difference is noticed in the three different locations in the cells.

For negative electrode, the expected value is around 5 m<sup>2</sup> g<sup>-1</sup> which is very close to values effectively found (Fig. 2(b)). This indicates that there's no carbon exfoliation inside the aged cells. Also here, no difference between the three locations in the cells is noticed.

### 2.7. Electrodes analysis: SEM observations

SEM observations of positive electrode show (Fig. 3) that after aging, no change in morphology of the positive electrode is evidenced. This indicates that there's no massive degradation of the



**Fig. 1.** SEM pictures of separators of (a) fresh cell (no aging), (b) cell aged by calendar life (60 °C, 60% SoC, 1.5 years), (c) cell aged by cycle life (20C, 10% delta SoC, 4200 h).

**Table 3**  
Gas and electrolyte analysis.

Cell analysed	Gas volume (mL)	Gas composition (%)						Electrolyte: HF (ppm)
		H <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO	
Fresh cell No aging	0	–	–	–	–	–	–	34
Aged cell Calendar life (60 °C, 60% SoC): 1.5 years	6	2.3	9.7	1.2	55.6	10.2	21	73
Aged cell Cycle life (20C, 10% SoC): 4200 h	0	–	–	–	–	–	–	25

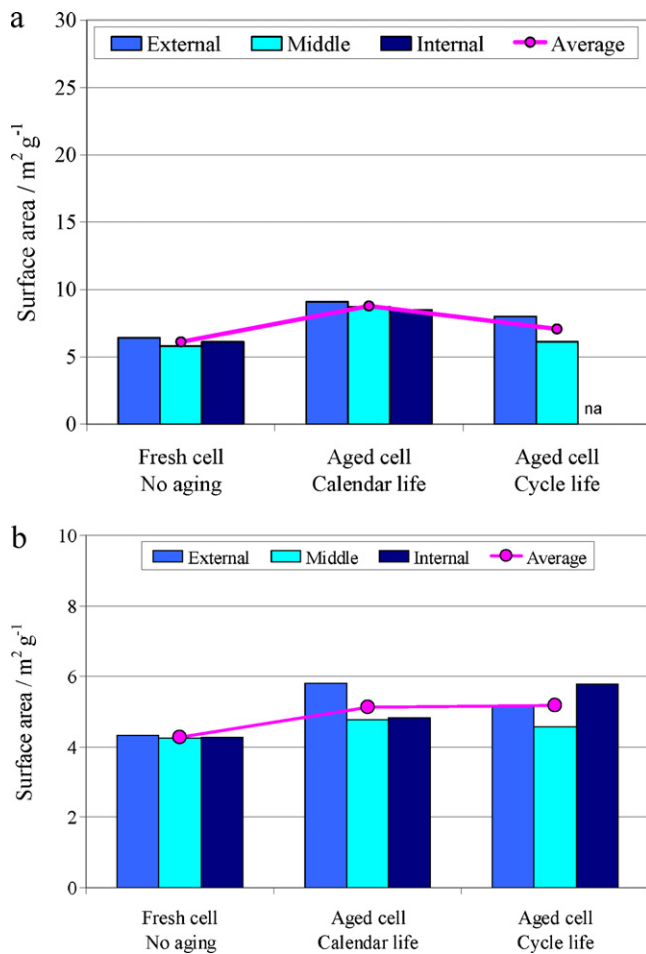
positive material at a scale observable by SEM. No difference is seen between the three different locations in the cells.

SEM observations of negative electrode show (Fig. 4) that after aging, no change in morphology of the negative electrode is evidenced. This means that there's no massive degradation of the negative material. Once again, no difference is seen between the three different locations in the cells.

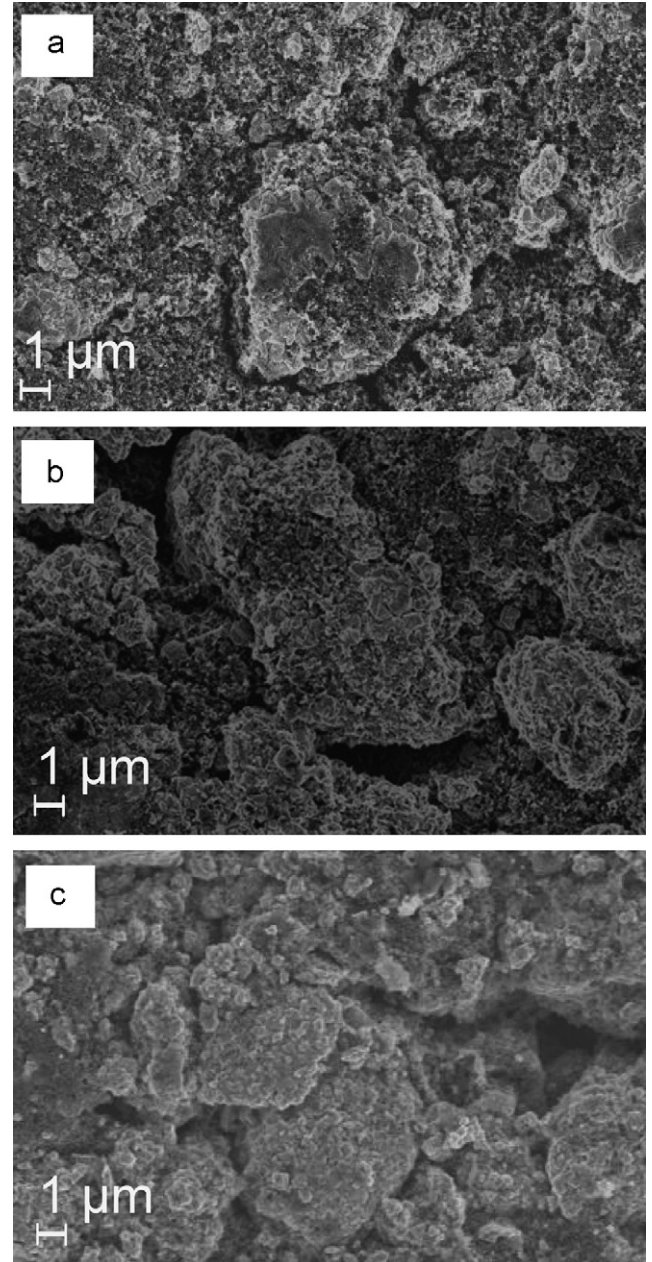
### 2.8. Positive electrode analysis: X-ray diffraction

X-ray diffraction analysis has been performed to determine if any new phase was present in the positive active material. Results are reported in Table 4.

The percentage of nickel in interslab position (cation exchange between lithium and nickel site) is slightly higher for cell aged



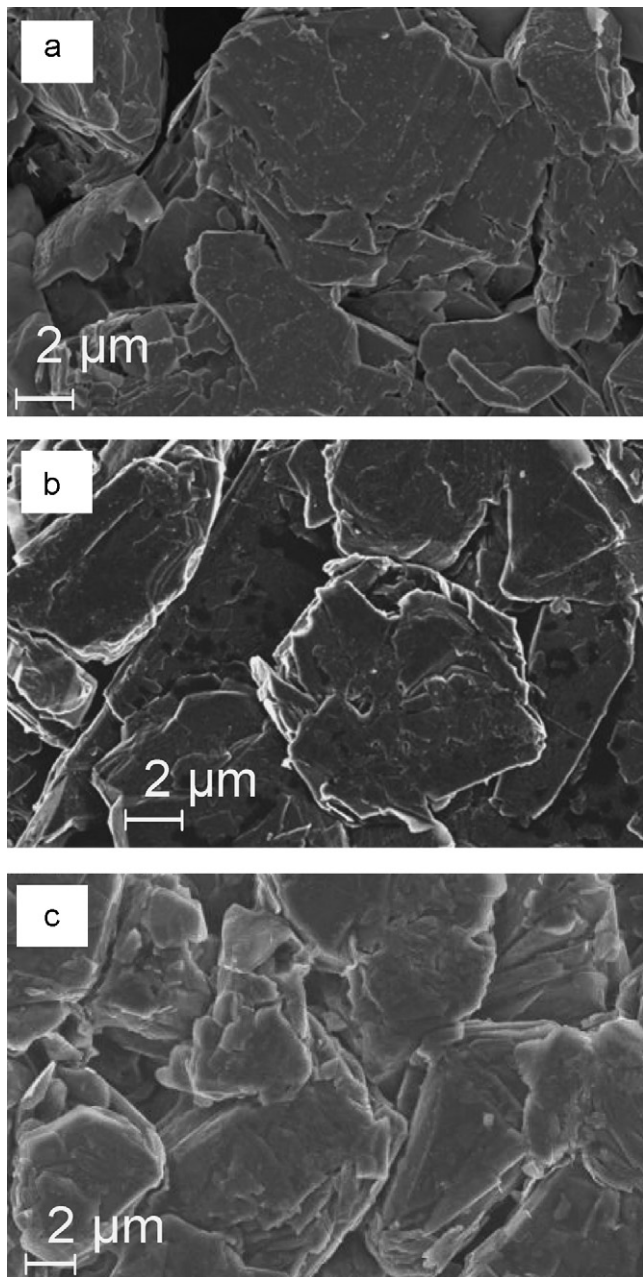
**Fig. 2.** Specific surface area measurements of (a) positive and (b) negative electrodes. For each kind of VL6P cell (fresh cell (no aging), cell aged by calendar life (60 °C, 60% SoC, 1.5 years), cell aged by cycle life (20C, 10% delta SoC, 4200 h)), value for the external part, middle part and internal part in the cell is reported.



**Fig. 3.** SEM pictures of positive electrodes of (a) fresh cell (no aging), (b) cell aged by calendar life (60 °C, 60% SoC, 1.5 years), (c) cell aged by cycle life (20C, 10% delta SoC, 4200 h).

**Table 4**  
X-ray diffraction analysis results of positive materials.

Cell analysed	Sample location	<i>a</i> (Å)	<i>c</i> (Å)	R-Bragg factor	% Ni (interslab)	Refinement with one phase
Fresh cell No aging	External	2.8593	14.224	1.389	0.2	Good
	Middle	2.8602	14.220	1.597	0.0	Good
	Internal	2.8606	14.216	2.047	0.0	Good
Aged cell Calendar life (60 °C, 60% SoC): 1.5 years	External	2.8591	14.228	1.524	0.7	Good
	Middle	2.8589	14.228	1.527	0.9	Good
	Internal	2.8593	14.228	1.346	1.3	Good
Aged cell Cycle life (20C, 10% SoC): 4200 h	External	2.856	14.246	1.278	0	Good
	Middle	2.853	14.267	1.401	0	2 phases:
		2.862	14.217	1.382	0.8	53–47%
	Internal	na	na	na	na	na



**Fig. 4.** SEM pictures of negative electrodes of (a) fresh cell (no aging), (b) cell aged by calendar life (60 °C, 60% SoC, 1.5 years), (c) cell aged by cycle life (20C, 10% delta SoC, 4200 h).

by calendar life. This tends to indicate that there's some aging of the material, even if it's limited (the percentage remains very low, around 1% only).

The Rietveld refinement for cell aged by cycle life indicates the existence of a second phase, which corresponds to the presence of non-homogeneous discharge states inside the material. This indicates that there's some aging of the material, more than in the case of cell aged by calendar life. Nevertheless, as this is not observed on all sample locations, this cannot be considered as a massive degradation.

#### 2.9. Electrodes analysis: quantification of lithium

The lithium content in the positive and negative electrodes has been quantified. The aim is to determine the location of lithium, and its form (active or passive).

##### 2.9.1. Quantification of lithium in positive electrode

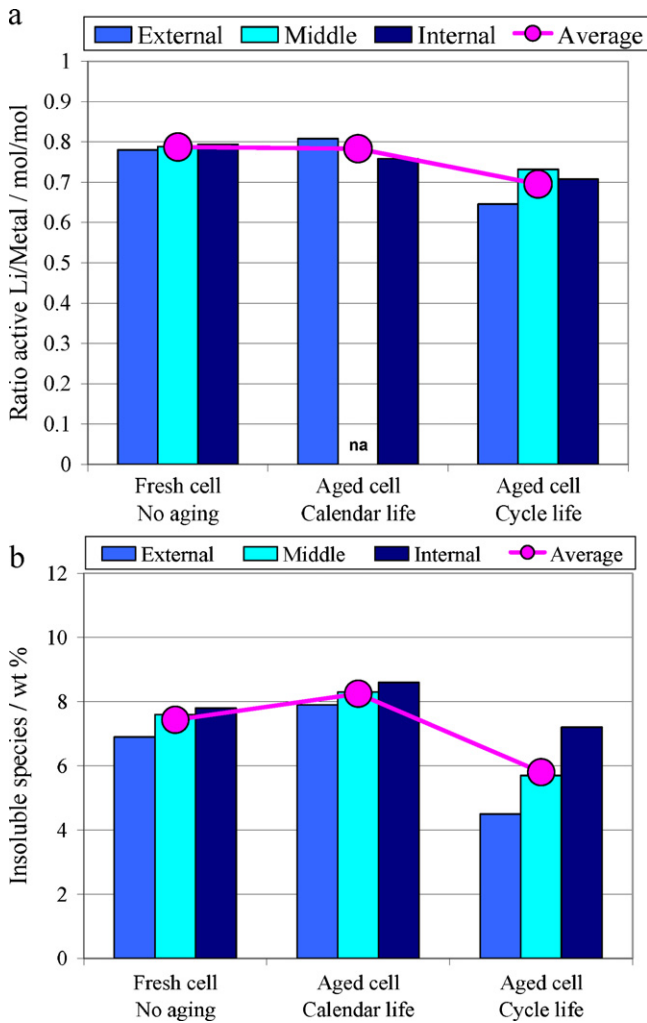
In order to identify all the lithium in the positive electrode, different steps have been followed. After the material of positive electrode is separated from the foil, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) is determined by pH titration with acid. Then, the same powder sample is dissolved in acid. The dried part represents the insoluble species (carbon and binder), as the filtrate is used to quantify total lithium and total nickel by atomic absorption. Active lithium is the difference between total lithium and lithium carbonate. Finally, material stoichiometry is determined by doing the ratio between active lithium and nickel. The ratio between active lithium and metal is determined by multiplying by the quantity of nickel in the alloy (by theory, ratio  $\text{Li}/\text{Me} = 1$ ).

The results show (Fig. 5(a)) that the ratio active  $\text{Li}/\text{Me}$  is smaller for the cell aged by accelerated cycle life which indicates that there's some loss of lithium in the positive. Moreover, on Fig. 5(b), it can be noticed that less insoluble species are observed for the cell aged by accelerated cycle life test which means that there's some binder dissolution. This is observed in a greater extent in the inner part of the cell. Nevertheless, no specific location has been put in evidence on the other analyses performed in this study, especially on negative electrode, that's why it cannot be stated that it's a significant trend observed here.

All these results tend to indicate that positive electrode shows some changes after accelerated cycle life: less active lithium in the material, and some binder or conductive carbon dissolution.

##### 2.9.2. Quantification of lithium in negative electrode

In order to identify all the lithium in the negative electrode, same procedure than for the positive electrode has been used. After recovering the material of negative electrode from the foil, water is added; in that way, active lithium reacts with water to form lithium hydroxide ( $\text{LiOH}$ ). A pH titration with acid allows to quantify lithium hydroxide ( $\text{LiOH}$ ) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ).



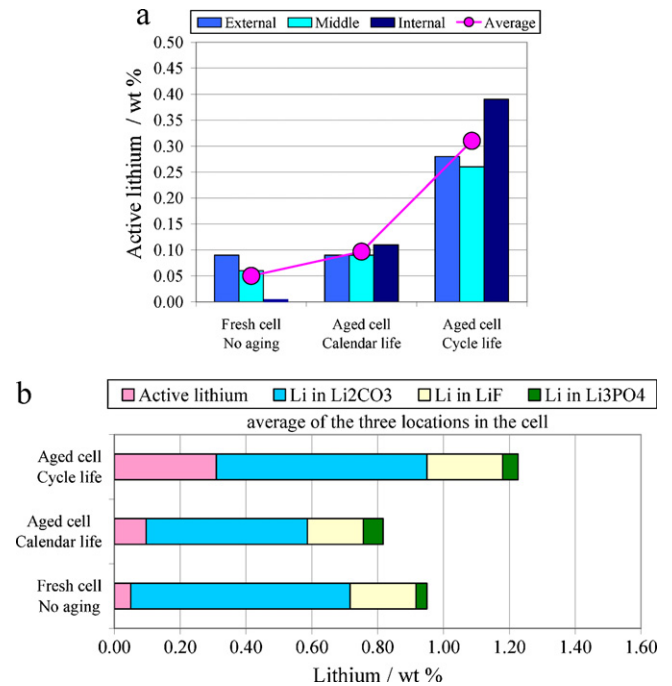
**Fig. 5.** Positive electrodes analyses: (a) ratio (mol/mol) between active lithium and metal, and (b) quantification of insoluble species (wt%). For each kind of VL6P cell (fresh cell (no aging), cell aged by calendar life (1.5 years at 60 °C, 60% SoC), cell aged by cycle life (20C, 10% delta SoC, 4200 h)), value for the external part, middle part and internal part in the cell is reported.

Then, the same powder sample is dissolved in acid. The filtrate is used to quantify total lithium by atomic absorption, and lithium in fluoride or phosphate compounds by ionic chromatography.

Before dismantling, cells were discharged at low rate down to 0.5 V (discharge at C/3 to 2.7 V, then C/10 to 0.5 V, at 20 °C) to measure the complete lithium capacity (extraction of all lithium from negative electrode). The quantification of lithium compounds in the negative electrode is reported in Fig. 6(a). The results show that there's more active lithium in the negative electrode for aged cells compared to fresh cells. The cell aged by accelerated cycle life test has more active lithium in the negative electrode than the cell aged by calendar life. It can be noted that even if active lithium is found, it's not lithium plating.

No specific location of active lithium in the cells analyzed is put in evidence (Fig. 6(a)). The dismantling of more aged cells would be needed to confirm the homogeneity of aging processes within the cell.

As regards the quantification of lithium compounds which compose the passivating layer ( $\text{Li}_2\text{CO}_3$ ,  $\text{LiF}$  and  $\text{Li}_3\text{PO}_4$ ), the expected value (1%) is effectively measured (Fig. 6(b)). This indicates that passivating layer stays stable during aging.



**Fig. 6.** Negative electrodes analyses: (a) quantification of active lithium (wt%). For each kind of VL6P cell (fresh cell (no aging), cell aged by calendar life (1.5 years at 60 °C, 60% SoC), cell aged by cycle life (20C, 10% delta SoC, 4200 h)), value for the external part, middle part and internal part in the cell is reported and (b) quantification of the different lithium species. Average values are reported.

### 2.9.3. Interpretation

No change is observed in the passivating layer of negative electrode which means that no increase of lithium is expected in this electrode. However, more active lithium is found in negative electrode of aged cells (especially in the cell aged by accelerated cycle life). Active lithium in the negative electrode corresponds to the lithium which is available for discharge if positive electrode is not limiting. Actually, for fresh cell, the discharge at low rate down to 0.5 V stops when there's no more lithium in negative electrode. That's why no active lithium is found in fresh cell (Fig. 6(a)). On the contrary, for aged cells, which are also discharged at low rate down to 0.5 V, active lithium is found in negative electrode. The only explanation for that is that positive electrode is limiting. The chemical analyses performed here allow to put in evidence this behaviour, especially for the cell which has the largest capacity fade (cell aged by accelerated cycle life) where this phenomena is more pronounced.

So this tends to indicate that effect of aging is due to positive electrode limitation. This means that the insertion process of lithium in the positive electrode is reduced because of a reduced capacity or a kinetic effect.

It can be noted that similar behaviour has been reported in other studies [1–4]: impedance measurements of the cell components clearly show that the positive electrode is mainly responsible for cell impedance increase.

Other studies have been focused on structural and electronic investigations of positive electrode material using TEM (transmission electron microscopy), XAS (X-ray absorption spectroscopy), and associated spectroscopic techniques [4–6] in order to understand how this degradation occurs (local chemical and structural changes). Further investigation of the cells used in this study would require these specific analysis techniques.

### 3. Conclusion

Three kinds of Li-ion VL6P cells were investigated in order to understand the root causes of their aging: (i) cell with no aging, (ii) cell stored at 60 °C (1.5 years at 60% SoC), (iii) and cell cycled according to accelerated profile (4200 operating hours according to 20C, 10% delta SOC, room temperature profile, which represents a test duration of 1.5 years).

On one hand, some observations of aged VL6P cells compared to fresh cells show: no gas generation inside the cells, no hydrofluoric acid creation in electrolyte, no pore clogging in separator, no massive degradation of the positive or negative materials (no change in specific surface area, no change in morphology (SEM)), stability of the passivating layer of negative electrode, homogeneity of aging processes within the cell.

On the other hand, some other observations indicate some aging of the positive material (by XRD) for aged cells, especially the cell aged by accelerated cycle life, even if it's not a massive degradation. Smaller ratio active Li/Metal in the positive electrode of the cell aged by accelerated cycle life is also put in evidence, and some binder dissolution is also observed. And more active lithium is detected in negative electrode after aging (and more in the cell aged by accelerated cycle life than by calendar life), which tends to indicate that effect of aging is due to increase of positive electrode limitation. So, it can be stated that aging comes from positive electrode.

Further investigation would require very specific analysis techniques in order to understand the aging mechanism on the positive electrode, like surface analysis techniques (TEM, XPS) to find out if positive solid-electrolyte interphase (SEI) is building up, and bulk analysis techniques in order to find out if some secondary or primary particles become inactive.

### Acknowledgements

Authors would like to thank the research team and the test laboratory in Bordeaux for their support in the different analyses performed (XRD, SEM, atomic absorption, chromatography, electric tests).

### References

- [1] M. Broussely, Ph. Biensan, F. Bonhomme, Ph. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz, J. Power Sources 146 (2005) 90–96.
- [2] F. Bonhomme, D. Germond, J.M. Lahuque, P. Biensan, J.C. Hall, Meeting Abstracts of IMLB, Biarritz, 2006 (Abstract 516).
- [3] D.P. Abraham, J.L. Knuth, D.W. Dees, I. Bloom, J.P. Christophersen, J. Power Sources 170 (2007) 465.
- [4] T. Sasaki, T. Nonaka, H. Oka, C. Okuda, Y. Itou, Y. Kondo, Y. Takeuchi, Y. Ukyo, K. Tatsumi, S. Muto, J. Electrochem. Soc. 156 (4) (2009) A289.
- [5] D.P. Abraham, R.D. Twisten, M. Balasubramanian, J. Kropf, D. Fischer, J. McBreen, I. Petrov, K. Amine, J. Electrochem. Soc. 150 (11) (2003) A1450.
- [6] S. Muto, Y. Sasano, K. Tatsumi, T. Sasaki, K. Horibuchi, Y. Takeuchi, Y. Ukyo, J. Electrochem. Soc. 156 (5) (2009) A371.