

Aging of lithium-ion batteries

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Abstract

Lithium-Ion (liquid electrolyte) batteries are considered as long life and reliable systems.

This paper:

- introduces discussion about aging and degradation mechanism both for storage and cycling,
- illustrates the proposed phenomena from results based on several years experimentation and obtained on scale one cells,
- shows the behaviour of several kinds of active materials,
- proposes some trends for life prediction.

Aging in Li-Ion cells may mainly come from:

- reactions of active materials with electrolyte at electrodes interfaces,
- self degradation of active materials structure on cycling,
- aging of non active components (ex: electrodes binders).

These phenomena lead to energy and/or power losses.

Reaction rates on depending on:

- type of materials and reactivity
- impurities
- manufacturing processes
- cell design
- type of application and profile of use.

On the negative electrode side the main parameters are passivation layer stability, the layer structure/composition (effect of additives in electrolyte and formation process), polluting agents.

On the positive electrode side key factors seem to be the material structure evolution and organic solvent oxidation.

These phenomena are highly dependent of voltage and temperature.

So far, according to experimentation for electric (EV) and hybrid (HV) vehicles applications, using scale 1 cells built with nickel based positive material the results show:

- more than 1 200 deep cycle (80% d.o.d. EV cycle) with only few percent of energy and power losses,
- more than 500 000 shallow cycles (3% d.o.d. HV cycle) with negligible power losses,
- 2 years of storage testing at full charge and various temperature (20 °C/40 °C/60 °C) leading to a life expectation of 10 years for EV applications and 15 years for HV applications.

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1. Introduction

Since 10 years lithium-ion cells (liquid electrolyte) and batteries have known a tremendous growth in the field

of consumer applications like mobile phone or portable computers and lithium-ion is currently number one on this market.

The new challenge for this technology is now to compete on standby, automotive or space and defence application with previous technologies (lead-acid, alkaline, etc.) and to replace them progressively. One main issue to succeed and to provide better life cycle cost is to show excellent life

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Table 1
SAFT product range

Cell type	High energy	Medium	High power
Key characteristics	45 Ah 150 Wh/kg 500–700 W/kg	25 Ah/40 Ah 120 Wh/kg 700–1000 W/kg	7 Ah/16 Ah 70–90 Wh/kg 1000–1800 W/kg
Potential applications	EV Telecom Space/defence	HEV (with ZEV autonomy)	HV 42 V systems UPS Defence

behavior on real configuration where cycling, floating, OCV storage, etc., are combined.

This paper shows results obtained up to now by Saft with a cell design based on lithiated nickel oxide for positive electrode. Some basic mechanisms to explain aging phenomena on negative and positive sides are briefly described.

2. Aging behavior of scale 1 cells

Since several years Saft has developed a range of lithium-ion cells and batteries to cover the full spectrum of applications.

Table 1 shows applications and main characteristics of these types of products composed of high energy (HE) cells high power (HP) cells and medium-range (MR) cells which give a compromise between power ability and energy content.

All these cells are built with the same standard active materials and components and the data shown below take benefits from the latest improvements made by Saft on the technology, including particularly the use of $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ as positive material, and vinylene carbonate as electrolyte additive.

Two types of aging situation has been selected:

- Operational use according to charge/discharge profile corresponding to the application;
- storage.

While cycling generally damages the materials reversibility, aging on storage is widely caused by interactions between electrolyte and active materials.

These conditions have been applied to the two main types of cells: high energy and high power.

2.1. Cycling behavior

Impact on energy (or capacity) and power are described on Figs. 1–3.

- The HE cell has been cycled according to typical electric vehicle profile (DST cycle) from full charge (4 V/cell) to 80% depth of discharge (DoD). The curves show after 1000 cycles negligible loss of energy and about 3% loss of power measured at 80% DoD under 30 s peak current of 150 A (Figs. 1 and 2).
- The HP cell was submitted to hybrid vehicle profile according to PNGV specifications with discharge (1.5% SoC) regeneration (1.5% SoC) around 50% SoC for the cell (Fig. 3).

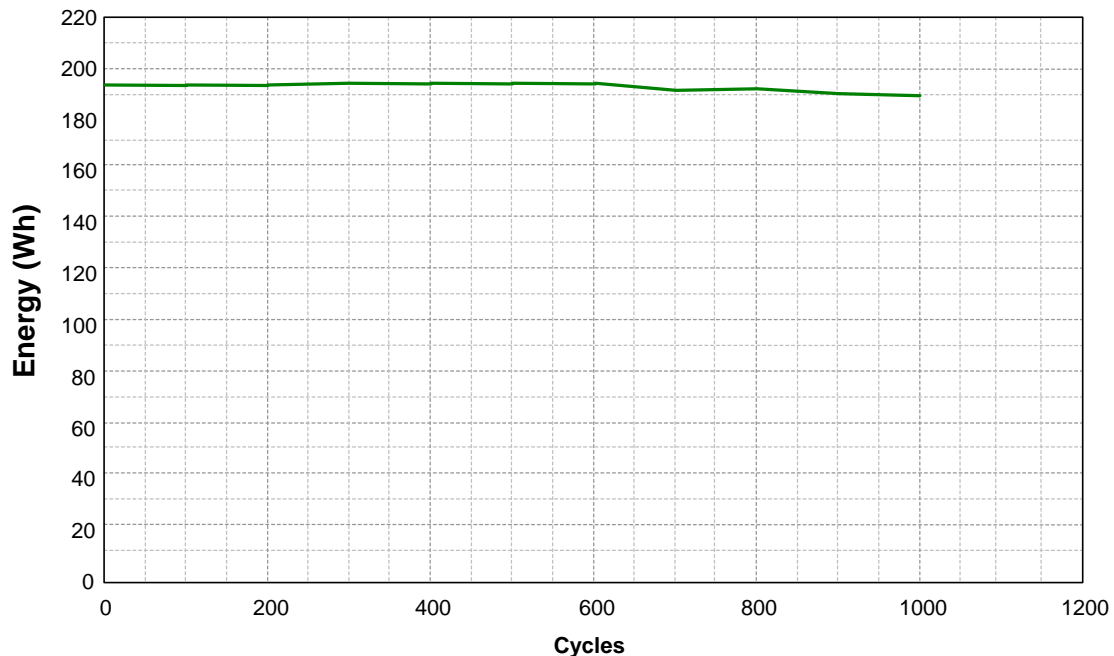


Fig. 1. DST cycling at 80% DoD, 20°C. High energy cell, energy evolution.

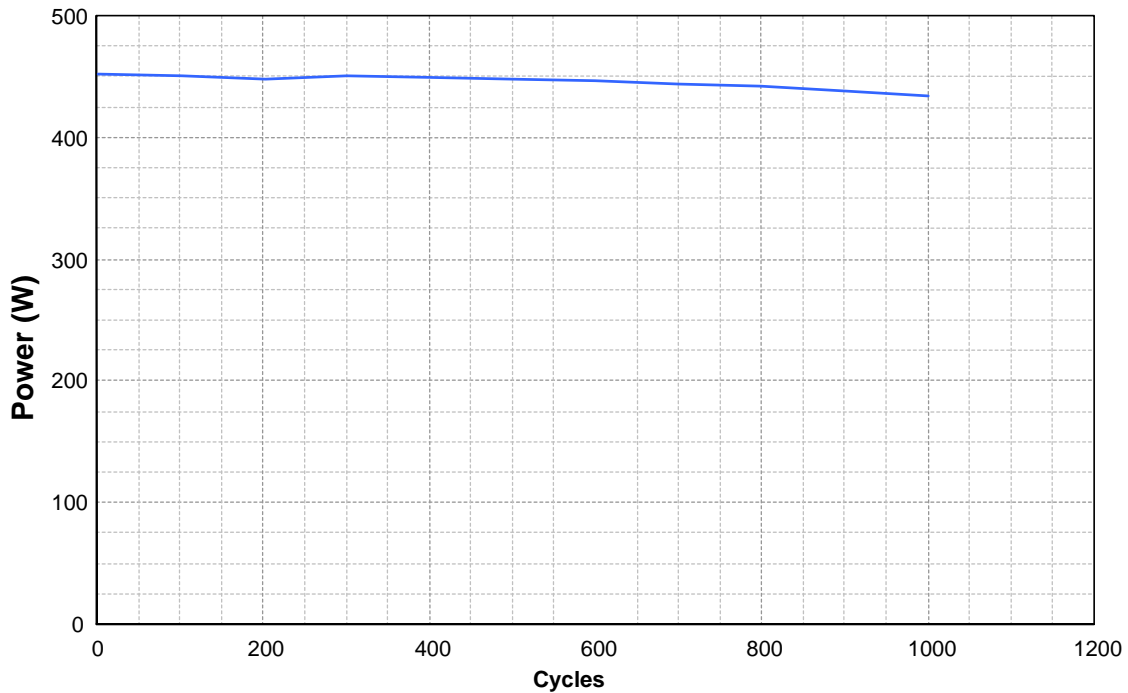


Fig. 2. DST cycling at 80% DoD, 20°C. High energy cell, power evolution.

After 350 000 cycles, capacity and power are still stable.

2.2. Storage behavior

Both HE and HP cells have been stored at different temperatures and voltages typical of the working state-of-charge (100% SoC for HE and 50% for HP).

After a period of 22 months on HE cell energy and power are quite stable at 20°C and show 4% losses at +40°C (Figs. 4 and 5).

After 1 year storage even at high temperature, HP cells provide the same performances as at the origin. Figs. 4–7 illustrate these characteristics (Figs. 6 and 7).

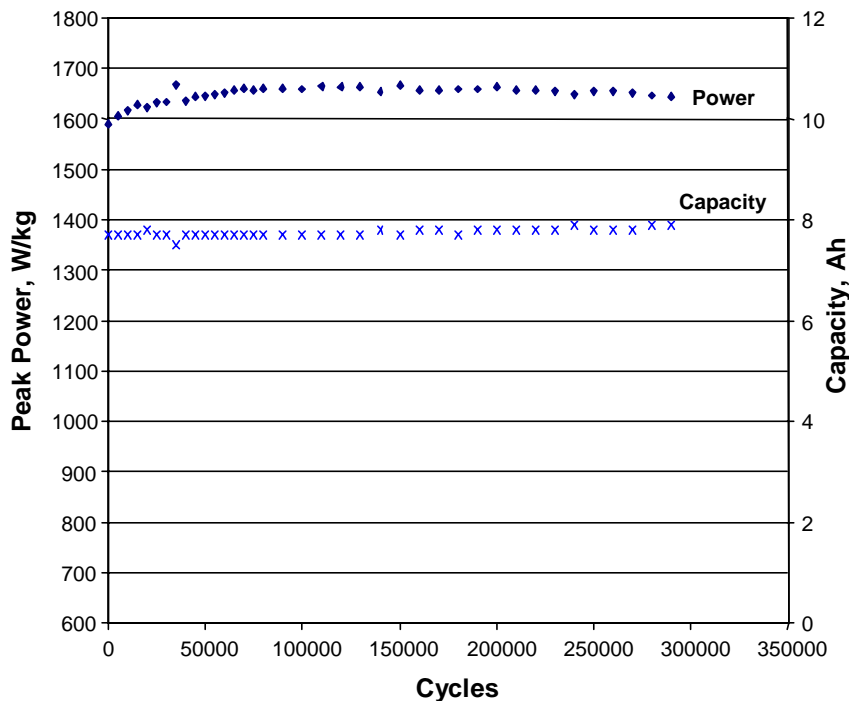


Fig. 3. Cycle life at 20°C. High power cell, capacity evolution. Discharge and charge 1.5% of capacity around a 50% SoC.

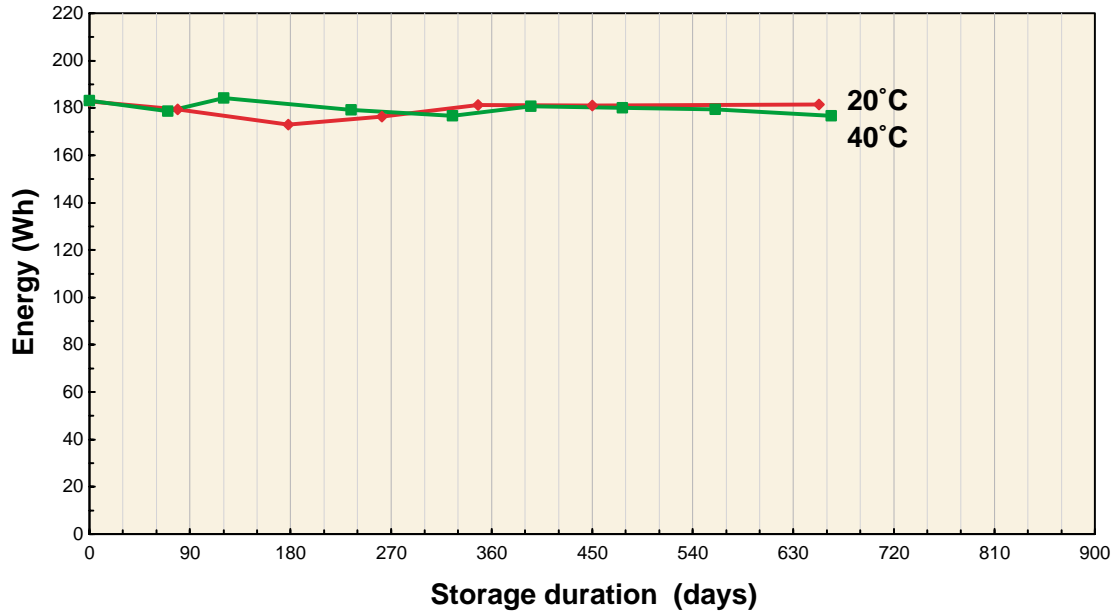


Fig. 4. Storage behavior 100% SoC at 20 and 40°C. High energy cell, energy evolution.

According to the results we can anticipate life duration summarized on Table 2 for several type of applications and conditions of use (SoC, DoD, charge rate).

Note that end of life is generally when properties (energy, power) are 80% of original. Last point illustrated by Fig. 8 is the influence of positive material on cycle life.

3. Aging phenomena

Aging in Li-ion cells comes from:

- reaction of active materials with electrolyte at electrodes interfaces;
- self degradation of active materials structure on cycling;
- aging of non active components.

These phenomena will result in capacity/energy and/or power losses.

Kinetics of reactions vary with the different types of Li-ion systems (nickel, cobalt, manganese ...) depending of:

- reactivity of materials and electrolyte;
- impurities;

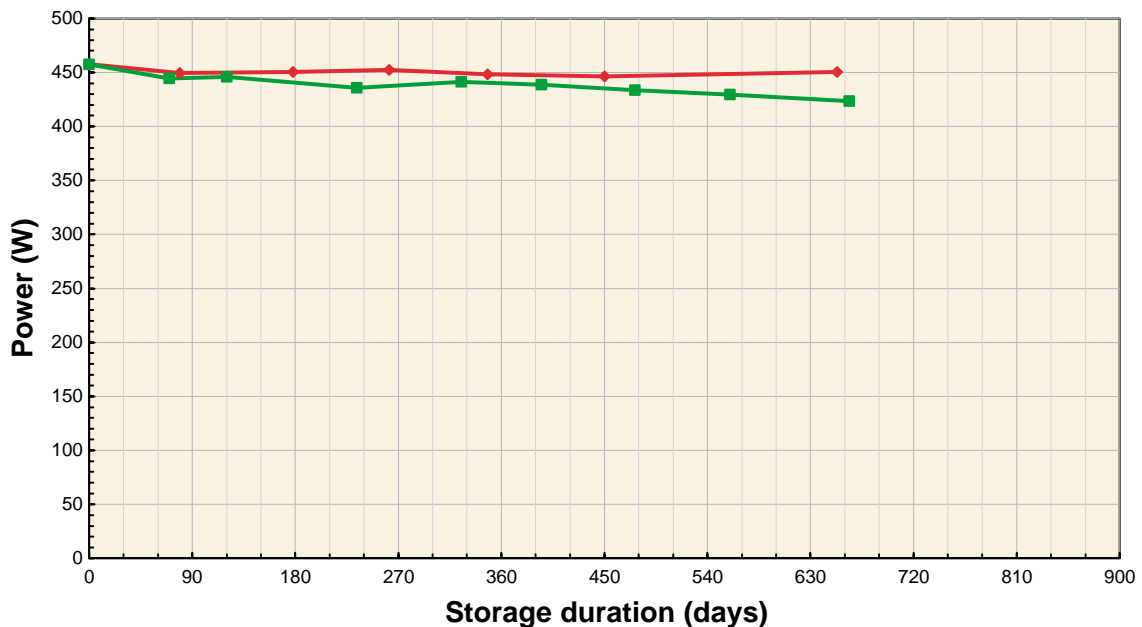


Fig. 5. Storage behavior 100% SoC at 20 and 40°C. High energy cell, power evolution.

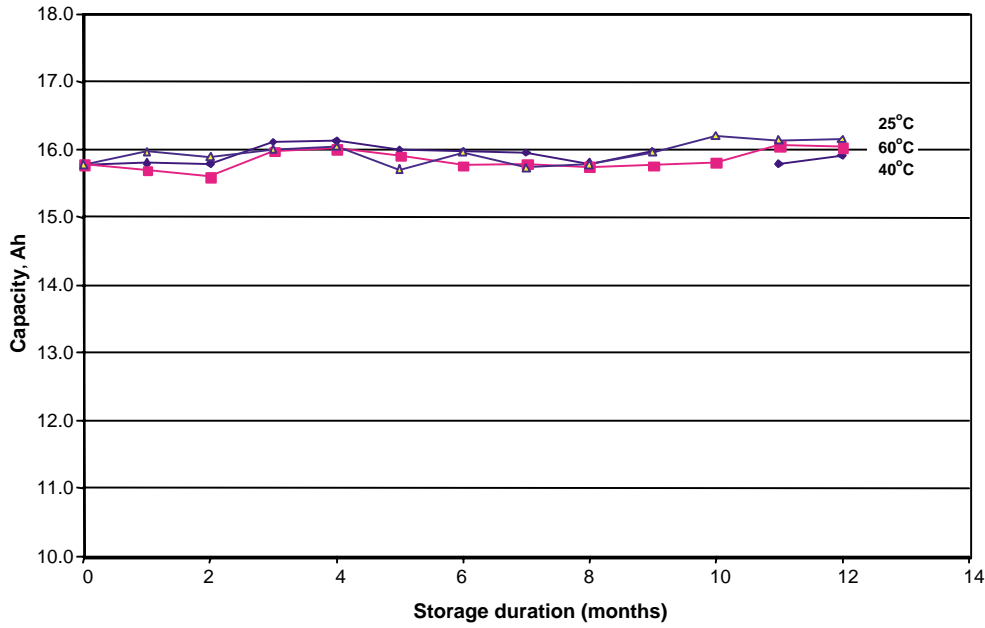


Fig. 6. Storage behavior at 50% SoC. High power cell, capacity evolution.

- manufacturing processes both for raw materials and cells;
- cell design;
- application and operating profile.

Globally, reaction rates are affected by state-of-charge and temperature.

So, we can consider reactions occurring on each electrode and the parameters influencing aging.

3.1. Negative side

A key issue is the stability of the passivation layer, built at the electrode/electrolyte interface and coming from the electrolyte reduction by lithium. A very low electronic conductivity should be maintained, while the ionic (Li^+) conductivity must be high to ensure sufficient discharge rate.

The film growth caused by electron tunneling through the layer is irreversibly consuming lithium (as during formation at the first charge), but is self-inhibiting due to the thickness increase. This behavior can be modeled for extrapolation as described on Fig. 9. Additives such as vinylene carbonate may have a beneficial impact on this property. Metallic impurities caused by reduction of soluble ions (for example Mn^{2+} ions) may have a very detrimental effect by increasing the electronic conductivity. This layer growth induces also a corresponding increase in the cell impedance.

3.2. Positive side

Unlike lithiated graphite electrode, the positive oxidation power is depending of state-of-charge. During aging at high

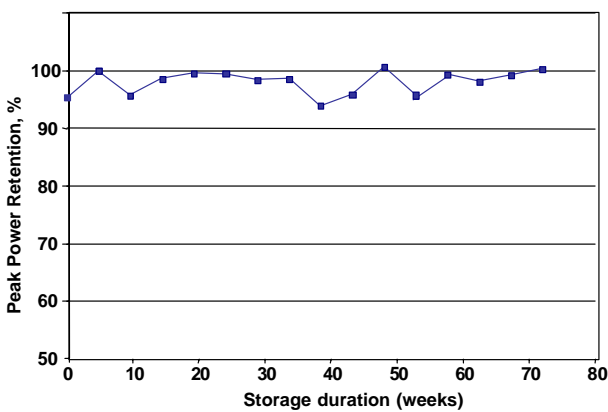


Fig. 7. Storage behavior at 40°C 50% SoC. High power cell, power retention evolution.

Table 2
Life prediction

Application	Average conditions				Life (years)
	SoC (%)	DoD cycling (%)	Temperature (°C)	Cycle numbers	
Automotive					
Hybrid	50	5	30	500000	15
Electric	100	80	30	1500	5
Stand-by					
Telecom, UPS ...	90	Variable	30	5000	15
Space					
GEO satellites	90	60	20	2500	20
LEO satellites	80	20	25	50000	8

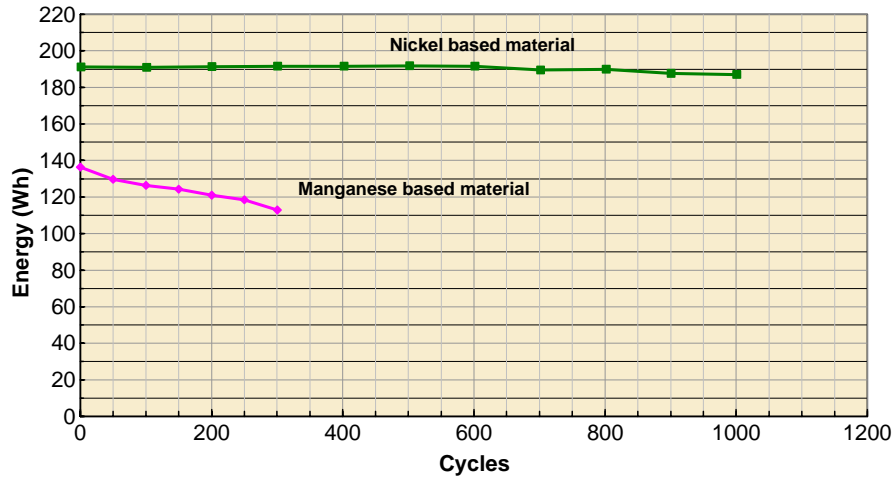


Fig. 8. Influence of positive material on cycle life. High energy cells DST (cycling at 80% DoD, 20 °C), energy evolution.

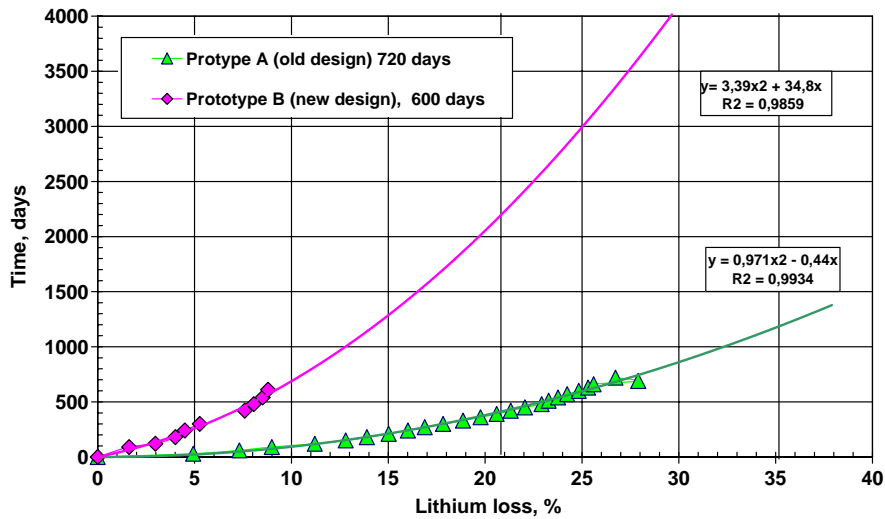


Fig. 9. Lithium loss vs. time @ 3.8 V, 60 °C according to electrolyte composition and cell design. Prototype B (new design) contains $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ positive electrode and VC additive in electrolyte.

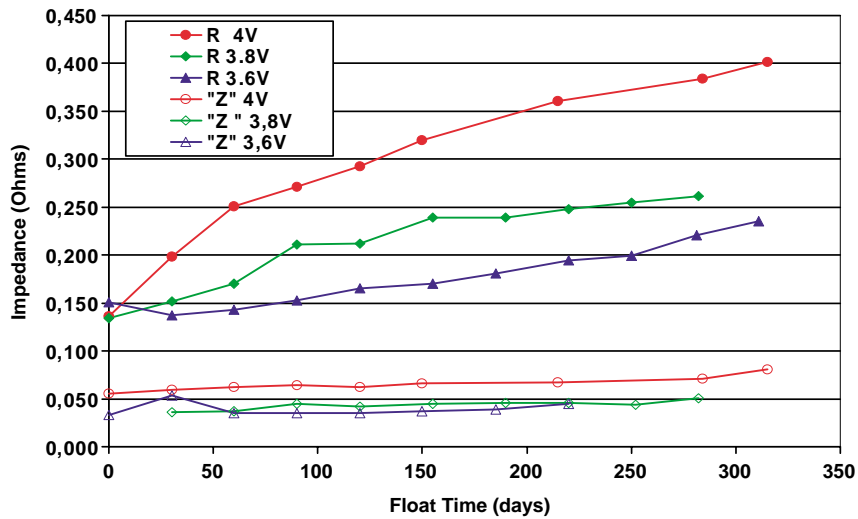


Fig. 10. Resistance evolution (C/5, 15 °C) of 18 650 prototypes using LiNiO_2 during floating at different voltages, at 60 °C. R is calculated from total relaxation after 5 min pulse, Z is calculated from 10 min pulse.

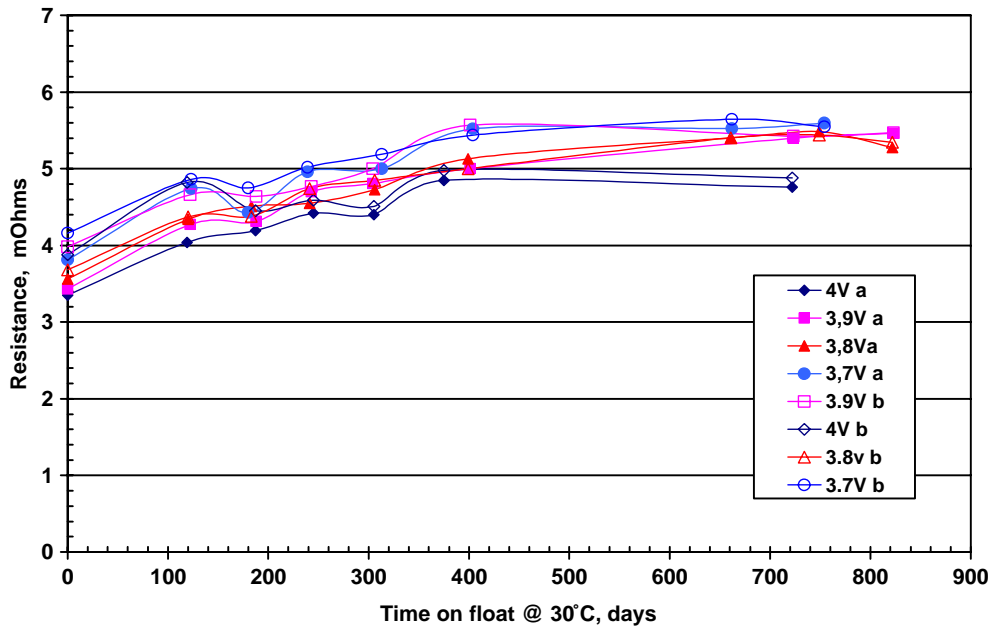


Fig. 11. High energy cells, using $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ as positive material. Resistance calculated from cell polarization after 5 min, from 25 A pulse at 25 °C, after floating at 30 °C. (a) and (b) represent two cells of same design.

voltage, oxidation of electrolyte components may induce insulating solid deposits which reduce the active surface thus increasing the actual reaction current density. This phenomenon is expected to be enhanced by temperature and to vary with the nature of positive material, electrolyte composition and impurities. The consequence is an increase of reaction impedance at the electrode interface while the high frequency impedance remains unchanged. This is illustrated by Fig. 10, on resistance evolution of prototypes 18 650 cells using LiNiO_2 .

Proper selection of positive material and electrode manufacturing process can alleviate this problem. Fig. 11 describes a 2 years continuous storage at 30 °C at different floating voltages with high energy cells containing LiNi_xCo_y

Al_zO_2 . There is no significant difference in impedance evolution as a function of SoC, which shows that the positive is not mainly involved in these storage conditions.

4. Conclusions

Based on actual results, the lithium-ion (liquid electrolyte) technology using a nickel-based positive material ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$) shows a reliable and long life behavior:

- more than one thousand deep cycles;
- several thousands shallow cycles;
- minimum life prediction of about 6–20 years according to application and operating profile.