Main aging mechanisms in Li ion batteries

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Abstract

Some of the aging mechanisms occurring in Li ion batteries, either on rest or on cycling, are described from long-term storage or cycling data. Generally, the most critical part of the cell is the negative electrode/electrolyte interface. Stability of the solid electrolyte interface (SEI), more generally of the passivating layer, must be insured by proper material choice and additives. Excessive growth induces with time a capacity loss corresponding to the lithium corrosion, and a reduction of power capability of the electrode, from the active surface area degradation. In a worst case, reduction of charge rate capability may lead to local lithium plating during cycling, strongly aggravating the capacity fading. When the SEI is correctly built, with low electronic conductivity, the negative electrode stability can be very stable, as described by long-term aging (more than 4 years) at higher temperature than ambient. Vinylen carbonate is confirmed as outstanding additive. At elevated temperature, high SOC induces side reactions at the positive interface, involving electrolyte components oxidation. The results are an increase of cell impedance, and possible slow CO_2 evolution. Presence of lithium carbonate greatly enhanced the gas formation. The observed impedance increase indicates a reduction of the active surface area, in agreement with solid deposit. When properly designed with an appropriate choice of active materials and electrolyte, the Li ion system can provide a very long service.
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1. Introduction

Aging of Li ion cells is being more and more a concern, because this electrochemical system is increasingly used in many demanding applications. Such uses like satellites, Ev or standby batteries require a very long life sometime exceeding 15 years. Therefore, the knowledge of the side reactions leading to either capacity or power loss is mandatory to make correct life predictions. Because of the relatively large variety of Li ion systems and technologies, it is difficult to give an exhaustive picture of all the aging reactions likely to occur in any battery design. The aim of this paper is to discuss some basic mechanisms, illustrated by some examples and data.

Basically, energy loss can result from active materials transformation in inactive phases so reducing the cell ca-

pacity at any rate, and/or from increasing of cell impedance, lowering the operating voltage. Power capability loss is directly related to impedance growth. Most of the time both effects are jointly observed. Two types of aging situation can be distinguished: during use (i.e., on cycling) and on storage. While aging on storage is due to side reactions resulting from thermodynamic instability of materials in presence, cycling adds kinetically induced effects, such as volume variations, or concentration gradients. As a general rule, these two aging mechanisms are often considered as additive, but interactions may definitely occur.

The critical area where the side reactions take place is the interface between electrolyte and electrodes. The most obvious is the lithiated carbon electrode that is thermodynamically unstable versus the organic solvents, and which passivation generates irreversible loss of lithium. The interfaces modification may also induce power loss, and

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by-products formed may impair the electrochemical reaction (solids deposit, gas formation, . . .).

Aging/transformation/reaction of non-active materials (binders, conductors, current collectors, . . .) with the other components can also lead to power or capacity loss. This paper mainly addresses the side reactions on electrodes interface.

2. Aging on cycling

Aging on cycling is often described as the result of degradation of active materials reversibility, especially the positive, coming from phase transformations during lithium insertion. This is beyond the scope of this paper to describe these mechanisms, which are extensively studied and published for many materials.

It is therefore assumed in the following that a very reversible positive material is used, such as $LiCoO_2$ or mixed $LiNi_xCo_yM_zO_2$ (M being Al, Mn, . . .). A usual curve representing capacity versus cycle number is shown in Fig. 1. This figure describes the usual behavior of Saft MP176065 cell, using $LiCoO_2$ positive electrode, blend of natural and artificial graphites negative and EC/DEC/DMC 1 M LiPF6 electrolyte. The capacity fade rate decreases with cycle number, resulting in stabilization with time of utilization. This is in good agreement with a continuation of the passivation layer growth, but consolidation of the SEI produces a more and more stable interface, thus reducing the corrosion rate. This is typically what is observed also on a long-range storage, as will be discussed in the next section.

In some cases, the fading rate may exhibit an inflexion point, where the capacity loss starts to increase, instead of decreasing. As an example, Fig. 1 illustrates this behavior, obtained with a different electrolyte composition (B), compared to the previous example. In drastic cases, such as shown in Fig. 2, the capacity may decline very rapidly after a first "normal" phase. The examples in Fig. 2 where obtained on "pouch" Li ion cells commercially available, i.e., conven-
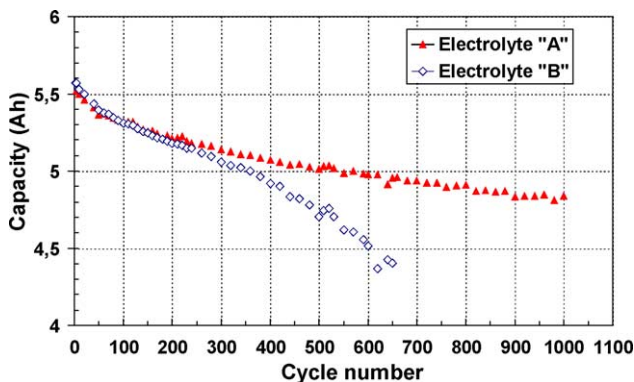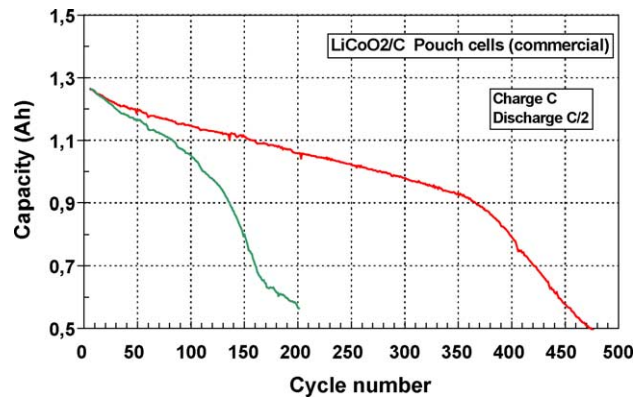

Fig. 2. Example of capacity evolutions during 100% DOD cycling. $LiCoO_2$/graphite pouch cells, charge at C, discharge at $C/2$, 20 °C).

tional Li ion chemistry built in soft package, also inappropriately classified as "polymer Li ion". The effect observed is not necessarily typical to this packaging design, but a weak mechanically soft case packaging may increase the risk of fading (Fig. 3).

When dismantling the cells described in Fig. 2 after cycling, a large deposit of Li metal was observed, which was the reason for rapid capacity decay. In the same time, a strong increase in cell resistance is observed (measured from a current pulse during 5 s at beginning of discharge) (Fig. 3). As it can be seen, there is a specific point exhibiting a change in the slope of the capacity or resistance curves, probably when Li starts to plate significantly.

Due to a reduction in charging capability of the cell, the degradation mechanism can be explained by the progressive clogging of the micropores of the negative electrode by the passivation layer growth. If this reaction is not stabilized enough, the reactions products (Li_2CO_3, alkyl-carbonates, polymers, . . .) will depose in the microposity, thus significantly reducing the active surface area. The current density (total current is imposed) increases on the remaining available surface of the larger pores, up to the point where the
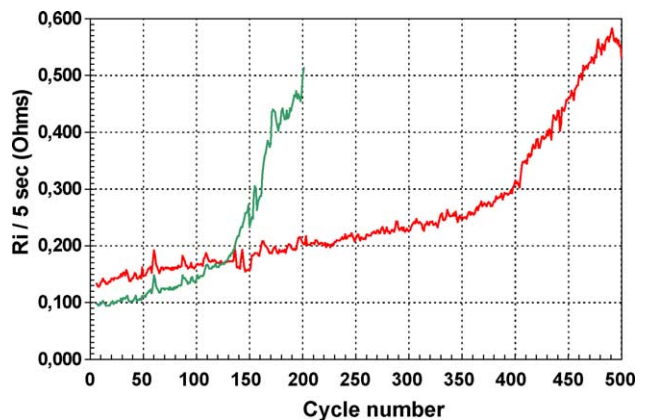

Fig. 1. Example of capacity evolutions during 100% DOD cycling. $LiCoO_2$/graphite Saft MP prismatic cells, charge at C, discharge at $C/2$, 20 °C).

Fig. 3. Example of resistance evolutions during 100% DOD cycling. $LiCoO_2$/graphite pouch cells, charge at C, discharge at $C/2$, 20 °C (see Fig. 2).
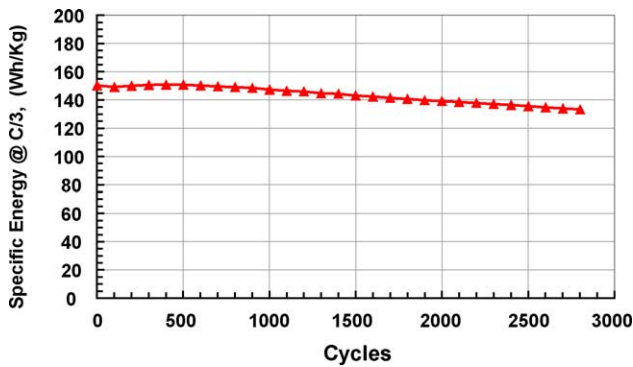
Fig. 4. Example of deep cycling (80% DOD, EV type) of Saft VLE 45 Ah Li ion cells Li-ion cells. 100% DOD *C*/3 diagnostic test every 100 cycles at 20 °C.

Fig. 5. Voltage profile at *C*/3 at 20 °C of VLE 45 Ah cells cycled at 80% DOD (see Fig. 4), at different cycle numbers.

reduction rate in these areas is larger than the maximum possible diffusion rate of Li in the graphite.

When induced, lithium plating itself will produce more deposit, and aggravates the phenomenon, which explains the increasing of capacity fading rate. Indeed, the electrode porosity is recognized as one of the first-order parameters controlling the capacity fade on cycling [1]. The charging rate has obviously a strong influence on this behavior. Temperature decrease would accelerate the fading rate, lowering the limit at which the Li plating will occur, and for the same reasons increasing temperature in some limits would be beneficial. This is a trade off effect between lithium corrosion rate, which accelerates reduction of active area (negative effect of temperature), and concentration gradients producing high local current density (positive effect of temperature).

Volume change of the carbon material during cycling results in partial degradation of the layer, and immediate "repairing" at the expense of the available lithium. To give a picture, a slight degradation at each cycle of 1% of the initial SEI that "costed" 10% of the capacity during the cell formation on first charge, would result in 10% capacity loss in only 100 cycles. For batteries, which are required to give more than 80% of the energy after 1000 cycles, this parameter must be extremely well controlled.

As an example, Fig. 4 describes a good energy retention obtained after almost 3000 deep cycles obtained from large Li ion cells (45 Ah) at 20 °C. The cell chemistry is based on a natural graphite negative, a $LiNi_xCo_yAl_zO_2$ positive and a PC/EC/DMC + VC additive, 1 M LiPF6 electrolyte. The cells are cycled following a "DST" cycling, reproducing a typical EV driving power profile, corresponding to an average of *C*/3 discharge rate to 80% DOD. Every 100 cycles, a complete 100% DOD diagnostic cycle at constant *C*/3 rate is performed down to a 2.7 V cut off voltage.

Fig. 5 reproduces some of the diagnostic curves recorded. An excellent stability of the discharge voltage profile is obtained, with a slight capacity reduction, associated to some limited resistance increase at the end of discharge. This effect is due to the positive electrode, as this electrode limits the cell capacity. Indeed, the incomplete efficiency of the
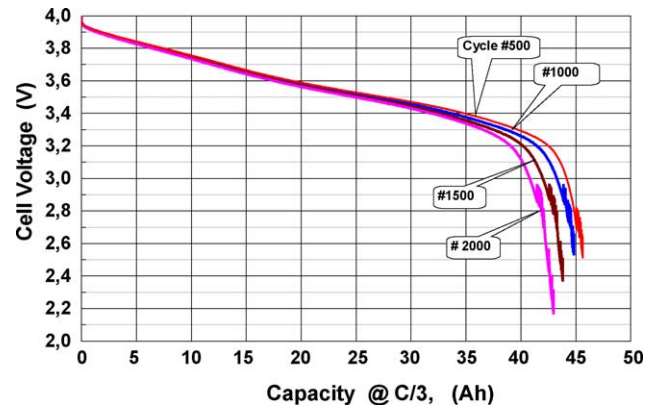
nickel-based material during the first charge (cell formation) produces an excess of lithium that is not totally consumed by passivation of the negative electrode and builds a "reserve" of lithium in the carbon, remaining at the end of discharge. In this particular design, the excess was initially about 15% of the initial capacity. When discharging the cell to lower voltage, the total amount of lithium can be utilized by further reduction of the positive electrode on a 1.5 V voltage plateau. As it can be seen in Fig. 6 representing the cycle #2804, a lithium excess of is still there, demonstrating a very low lithium corrosion rate resulting from the good stability of the SEI.

These data are the result of several factors: material choice, electrodes design and VC additive. In addition, the positive limited situation prevents a complete delithiation of the graphite, which is a good factor for SEI stability because the roughly 10% volume variation between graphite and LiC_6, occurs mostly during the first 20% of lithium insertion.

Providing a good choice of the active material, aging of the positive electrode during cycling may be due to volume variations, inducing loss of electrical contacts between some particles of active material (non-conductive) and the conductive additive network within the composite electrode.
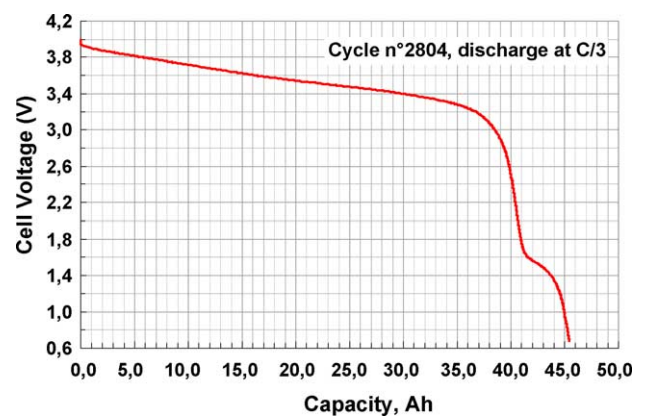

Fig. 6. Full discharge to 0.7 V of VLE 45 Ah cell after 2804 cycles at 80% DOD (see Fig. 4).

The electrode design and manufacturing process is therefore crucial, and sometimes published bad results attributed to a specific material are due to this important factor.

3. Aging on rest

3.1. Aging of negative electrode

When the cell is on rest, only thermodynamical stability of the components in presence will govern the aging.

The negative electrode stability is obviously the most critical, because of the strong reactivity of the organic electrolyte with any type of lithium electrode, including lithium ion. This situation gives paradoxically an outstanding longevity to lithium batteries, through the formation of an insoluble protective film, when the electrolyte has been correctly selected. This has been described long time ago by many authors, and Peled [2] proposed a concept now universally accepted of an solid electrolyte interface (SEI), through which lithium ions can move, but preventing the electrons to reach the molecules species of electrolyte susceptible of reduction. Any defect in the layer protection will result in lithium corrosion, and irreversible energy loss. Because of the high surface area of the porous negative electrode, this feature is more critical in Li ion batteries, and is a possible source of aging, either on cycling or on rest.

In reality, the layer in never totally "hermetic", and a low rate corrosion can be observed. Based on the assumption that SEI is not totally an electronic insulator, a lithium corrosion kinetic model has been proposed earlier [3] to account for the variation of capacity loss rate during accelerated aging on storage at high temperature. From this simple model, the corrosion rate is $dx/dt = k\chi s/e$, where x is the number of moles of Li being reacting, χ the specific electronic semi-conductivity of the layer, s the interface area and e is the SEI thickness.

By integration, a parabolic equation of time versus lithium loss can be established, which fits quite well with the experimental data: $t = A/(2k\chi s)x^2 + e_0/(k\chi s)x$, where A is a proportionality coefficient between the layer thickness and the amount of lost lithium and e_0 is the layer thickness at t_0, after cell formation. These data were obtained from storage tests at different temperature, which revealed an Arrhenius law dependence of the rate coefficient proportional to the electronic semi-conductivity of the SEI. The very strong influence of SEI pollution by metal ions is now well established, for example, Mn^{2+} solubility coming from Mn^{3+} containing positive materials. Increase in electronic conductivity of the SEI may result from metallic clusters produced by reduction of these metals, inducing large capacity loss and impedance increase, in accordance with the model proposed.

Although being probably too simple, this mechanism fits very well with the observed data, as shown in, for example, Fig. 7. This figure shows that the original fitting after about 1 year at 60 °C gave very similar results to those obtained 1 year later including new data, accredit-
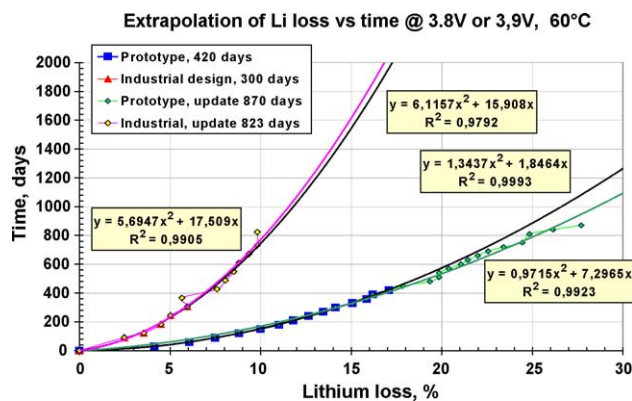

Fig. 7. Storage time on float at 60 °C vs. lithium loss. Saft Li ion Ni-based cells (Gen2 prototypes vs. Gen3 industrial).

ing the initial hypothesis and model parameters. The much better stability observed between the "industrial" (Gen3) and "prototype" (Gen2) design was mainly attributed to the use of VC additive [4,5] in the electrolyte, which improves drastically the "quality" of the SEI. Both cells use the $LiNi_xCo_yAl_zO_2$/graphite + PC/EC/DMC 1 M $LiPF_6$ chemistry.

Four years later, the data collected further confirm the model. Fig. 8 shows, for example, the data at 40 °C storage on the "industrial design" cells. Only less than 5% capacity loss is observed after 1500 days in these hot temperature conditions, as described in Fig. 9.

As long as the temperature is not too high, the effect of cell voltage, i.e., state of charge appears to have no impact on this mechanism, as well as on the impedance growth during storage, as shown, for example, in Fig. 10, obtained with an other group of cells. This is in agreement with the fact that the electrode reactivity, linked to its voltage, is not or few depending on negative electrode SOC. Like the capacity loss, the variation rate appears to reduce with time, to reach an almost steady state after less than 2 years. Indeed, the lithium corrosion result in solid deposit in the micropores, inducing a reduction of active surface area as described in the previous section, and increase of the polarization as observed. This effect is more pronounced during the first period, when
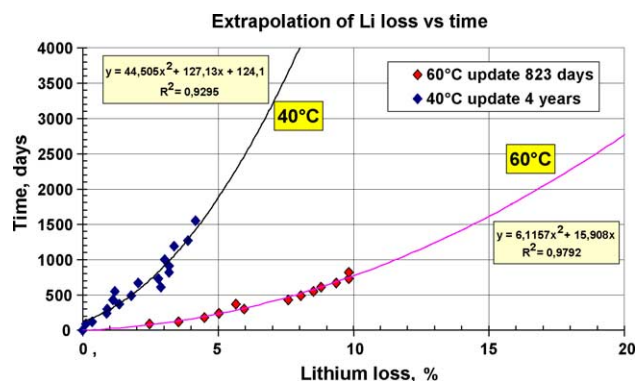

Fig. 8. Storage time on float (3.9 V) at 60 and 40 °C vs. lithium loss. Saft "Industrial" Li ion Ni-based cells.
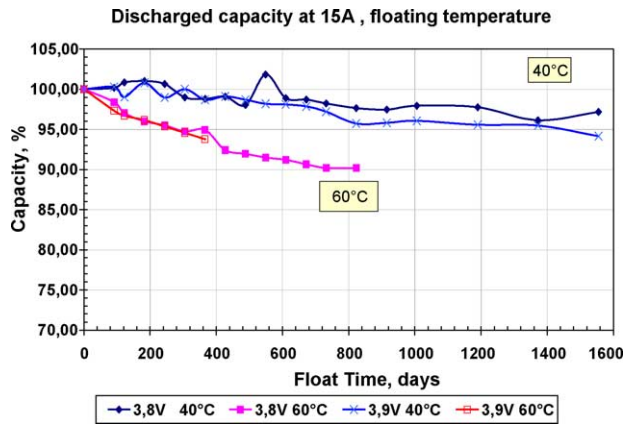
Fig. 9. Capacity at $C/8$ variation with storage time on float at 40 and 60 °C. Li ion Ni-based cells.

micropores are first filled, then stabilizes when the capacity loss rate becomes smaller, and available pores larger.

That does not apply for higher temperature and high SOC where a significant effect of cell voltage can be observed, indicating an impedance increase coming from the positive electrode [6].

3.2. Aging of positive electrode

When the temperature is increasing, the oxidizing properties of the positive electrodes against the electrolyte become to be the most important aging factor. Because this depends of the interface voltage, there is a significant influence of the state of charge. The most significant change is observed on cell power due to polarization increase, as described by several authors [7–9]. As an example, Fig. 11 describes the power evolution at 80% DOD (end of discharge) of 45 Ah high-energy cells (the same as shown in Fig. 4), after long period of storage at different temperatures from 20 to 60 °C, at 50% or 100% SOC. The cells are tested periodically to check the capacity and power evolution. From this figure, it can be seen that aging at 60 °C becomes important, and there is a large difference between 50% and 100% SOC, clearly
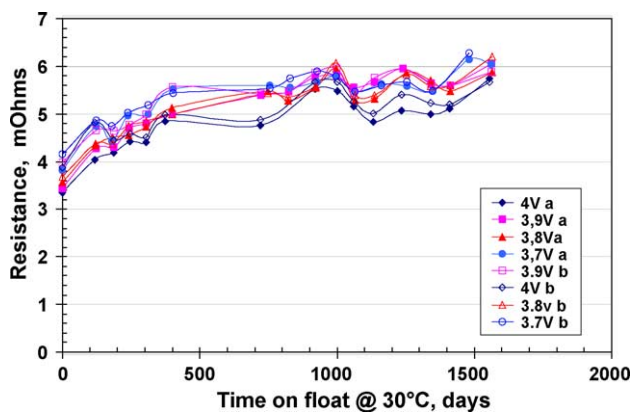

Fig. 10. Example of polarization resistance (from 5 min 25 A pulse) variation during storage at 30 °C, for several float (a) or rest (b) voltage.
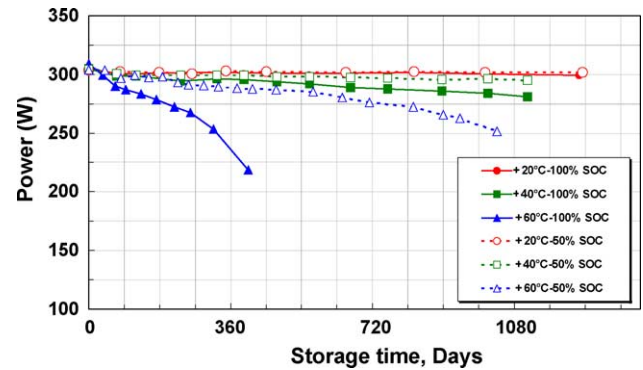

Fig. 11. VLE 45 Ah Li ion cells. Power evolution during storage at different temperatures from 20 to 60 °C at 50% SOC and 100% SOC.

showing the responsibility of the positive electrode. Fig. 12 shows the resistance variation as a function of DOD, after storage periods. Power at ambient or medium temperature such as 45 °C shows however a very good stability, even after more than 3 years.

As reported previously [10], laboratory cells using the same chemistry have been dismantled after aging, and samples of electrodes are used to build laboratory coin cells with a reference lithium electrode. The cells were aged 1 year at 60 °C, at 4 V (100% SOC). A drastic increase of the positive electrode polarization was observed, whereas the negative electrode remained fairly stable. In the same experiments, it was demonstrated that the structure of the positive material $LiNi_xCo_yAl_zO_2$ remained unchanged. Previous recent studies at Laurence Berkeley National Labs [11] showed by spectroscopic analysis of positive electrodes a loss of electronic conductivity of the surface, and solid deposits including polyphosphates.

In addition to impedance increase, high temperature and high voltage storage may induce CO_2 gas evolution. Resulting from electrolyte oxidation on positive electrode interface, it was found that the presence of Li_2CO_3 has a very strong effect on this phenomenon. Careful analysis [12] of the electrolyte decomposition in the presence of the cell components separately showed that both CO_2 and acidity (analyzed as HF) evolved, when in presence of charged positive material and lithiated graphite (much more than when charged positive only is present). That indicates an interaction between the two interfaces. Although the mechanism is not fully understood, it can be anticipated that partly soluble organic species formed by reduction on the negative electrode are diffusing to the positive electrode surface, where they are oxidized to produce protons and organic radicals that may polymerize. Reaction with Li_2CO_3 liberates CO_2, and protons can be slowly regenerated by the reaction of water with $LiPF_6$, following:

$$Li_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Li^+$$

and

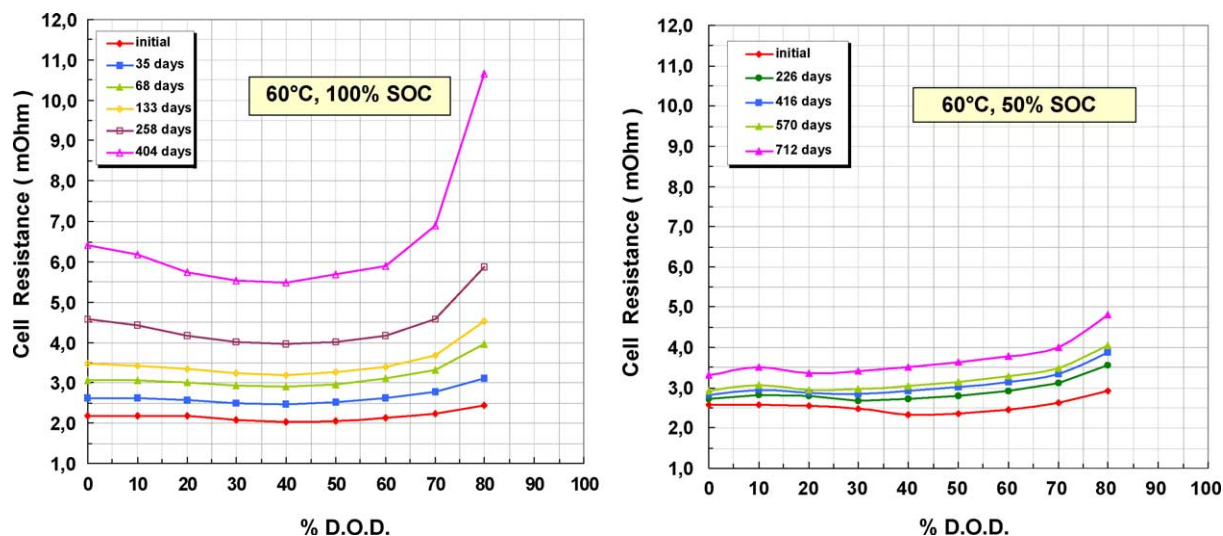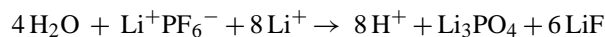$$H_2O + Li^+PF_6^- + 2Li^+ \rightarrow 2H^+ + LiPOF_4 + 2LiF$$
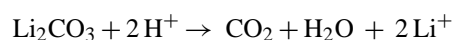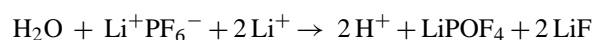
Fig. 12. Comparison of cell resistance evolution with DOD, between storage at 60 °C 100% SOC and 50% SOC (cells from Fig. 11).

Several other types of oxyfluorophosphates salts may be formed further by reaction with water, possibly up to the ultimate complete reaction:

$$4\,H_2O + Li^+PF_6^- + 8\,Li^+ \rightarrow 8\,H^+ + Li_3PO_4 + 6\,LiF$$

These insoluble salt deposits at the surface and within the positive electrode porosity, added to the organic species may be the cause of the polarization increase observed.

In detailed previous studies on aging on cycling, Aurbach et al. [13] described similar scenario. The authors concluded that surface reactions take place, depending on many factors. The initial active mass particles are usually covered by pristine surface films containing Li_2CO_3 as a major component, which is destroyed and replaced upon cycling by a variety of solution-related compounds including ROLi, $ROCO_2Li$, polycarbonates and salt reaction products. Acidic contaminants can catalyze polymerization of the alkyl-carbonate solvents to surface polycarbonate species. In $LiPF_6$ solution, contamination with HF plays a very important role, and the impedance strongly increases due to precipitation of LiF at the surface. Some recent NMR analysis on aged electrodes also confirmed the transformation of surface carbonates into other Li compounds eventually associated to organic species [14].

Gas evolution may be a life-limiting factor when the cells are maintained at high temperature, and high state of charge. Positive material nature and purity has been identified as critical factors. Fig. 13 shows, for example, pressure measurement within laboratory cells stored at high voltage and 60 °C, for several positive materials. As it can be seen, the nickel-based materials have a very different evolution profile compared to $LiCoO_2$. Although the pressure rises very quickly with Ni-based positives, the gas evolution leveled rapidly. On the contrary, the cobalt-based cells show a low initial but continuously increasing rate of pressure build up, demonstrating a different mechanism. This behavior is still under investiga-
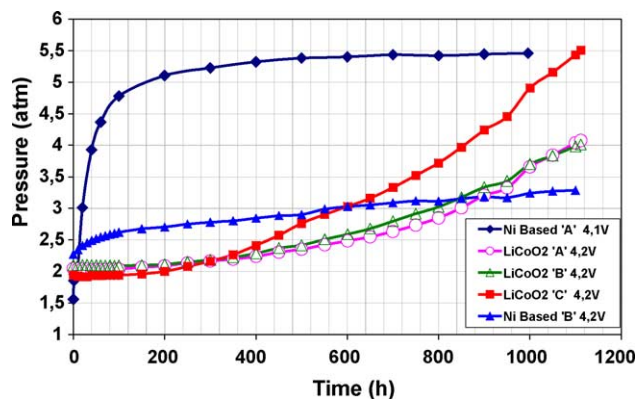

Fig. 13. Pressure evolution in laboratory cells stored at 60 °C, 100% SOC, for several positive materials.

tion. Fig. 14 displays a long-term evolution at full SOC with some cells using Ni-based material. The stabilization of the pressure at 60 °C after few months is here demonstrated over almost 2 years. The reaction rate at 40 °C is much lower, but
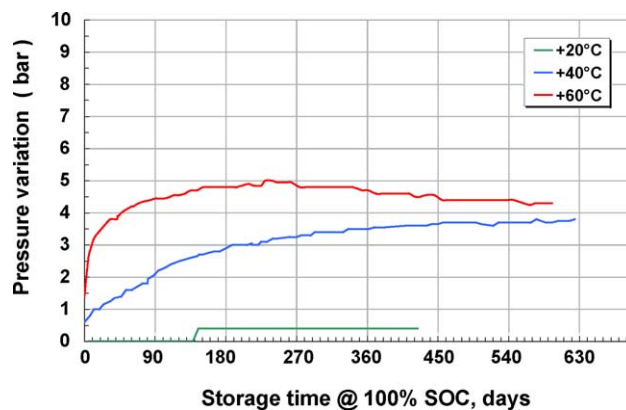

Fig. 14. Long-term pressure evolution of Li ion $LiNi_xCo_yAl_zO_2$/natural graphite cells at 100% SOC (4 V), for several temperatures.

evolves towards the same value. At ambient, no significant pressure variation is observed.

4. Conclusions

Although each Li ion chemistry may behave differently, there are few basic mechanisms, which may account for general aging phenomena in Li ion batteries. The most obvious is linked to the high reactivity of lithium from lithiated carbon, and stability of the passivating layer (SEI) is the key of the overall cell stability (electrolyte composition and purity, additives, . . .). Proper choice of carbon and electrolyte makes the negative electrode very stable, either on rest and cycling. This condition being fulfilled, the nature of positive electrode and its reactivity then determine the battery aging characteristics. Usual limitations at high temperature and high SOC come from impedance increase, and possibly gas formation. The layers formed on positive electrode seem not protective enough, and does not behave as an "SEI". In Ni-based chemistries, gas formation can be minimized/avoided through appropriate positive material purity. Good knowledge of aging mechanisms, and proper choice of materials in a good design can lead to provide Li ion batteries having very long expected life, for both power and energy, on rest or on cycling.

Acknowledgments

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