

Properties of large Li ion cells using a nickel based mixed oxide

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Abstract

The possible use of LiNiO₂ similar to LiCoO₂, as a positive material in rechargeable lithium batteries was recognized 20 years ago and starting 10 years later, many research studies led to material improvement through substitution of some of the nickel ions by other metallic ions. These modifications improve the thermal stability at high charge level or overcharge, as well as cycling and storage properties. Commercial material is now available at large industrial scale, which allows its use in big “industrial” Li ion batteries. Using low cost raw material (Ni), it is expected to be cost competitive with the manganese based systems usually mentioned as low cost on the total cell \$/Wh basis. Providing higher energy density, and demonstrating excellent behavior on storage and extended cycle life, LiNiO₂ has definite advantages over the manganese system. Thanks to their properties, these batteries have demonstrated their ability to be used in lot of applications, either for transportation or standby. Their light weight makes them attractive for powering satellites. Although safety improvements are always desirable for all non-aqueous batteries using flammable organic electrolytes, suitable battery designs allow the systems to reach the acceptable level of safety required by many users. Beside the largely distributed lead acid and nickel cadmium batteries, Li ion will found its place in the “industrial batteries” market, in a proportion directly linked to its future cost reduction.

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1. Introduction

Li ion batteries are now widely used in portable devices such as mobile phones and personal computers, but they are also able to fulfill a much wider range of applications, in large batteries for transportation and standby. Unlike the portable systems, they are expected to “live” reliably over a very long period of time (typically more than 10 years), and provide in some applications a very large number of cycles. From the electrochemical systems known today, nickel based LiNi_(1-x-y)Co_xAl_yO₂ appears to be the positive material best fitting these requirements. It is now available in large quantity from industrial suppliers, and its cost, already lower than LiCoO₂, will decrease with increasing production level. Indeed, cost is now the most important factor to allow this battery system to take a significant market share in the “industrial batteries” business. After being a pioneer in this system, SAFT is providing different types of these batteries

for various applications, built from industrial production lines.

2. From LiNiO₂ to LiNi_(1-x-y)Co_xAl_yO₂, a little bit of history

When the use of lithiated transition metal oxide was discovered 20 years ago [1], LiNiO₂ was already studied together with LiCoO₂. At this time, neither of these materials was commercially available. Studying these compounds as positive electrodes in Li metal rechargeable cells [2], and demonstrating the potential advantages of LiNiO₂ over LiCoO₂, the difficulty to prepare a “good” electro-active LiNiO₂ material was pointed out. It was found later that the tendency for Ni²⁺ to occupy sites in the Li⁺ layers introduces a structure distortion, which produces a drastic influence on its ability to de-insert/insert Li⁺ ions [3].

For this reason, and then because the material was found to be less stable when overcharged (mainly due to the fact that the compound was more delithiated), LiCoO₂ was chosen by almost all the battery manufacturers to start production of Li

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ion batteries for portable applications. Due to the huge growth of the portable phone and personal computers, this system is now established as a reference for Li ion.

However, continuous research has been done during years, driven by the potential cost interest versus cobalt, and very promising energy density due to its higher capability to liberate Li ion on oxidation. Indeed, lithiated nickel based mixed oxides are generally able to release up to 0.7 Li^+ /mole, at 4.1 V versus Li/Li^+ without performance degradation on cycling. That represents a potential specific capacity of around 200 Ah/kg , compared to 150 for LiCoO_2 and 120 for LiMn_2O_4 , while maintaining an average voltage of about 3.7 V versus the lithiated carbon anode.

Substitution by cobalt (ideally 20%) [4] was early identified as a solution to avoid the Ni^{2+} stabilization, allowing an easy manufacturing of the appropriate structural form.

Later on, many “doping” metallic ions were tested by a lot of laboratories, showing interesting specific properties [5]. Aluminum [6] was found to produce a significant stabilization of the delithiated form, inducing a better thermal stability, as shown by DSC experiments [7].

That discovery focused the research work, jointly with material manufacturers, ending with the definition of a mixed Co/Al material, which appears to exhibit excellent electrochemical properties, now recognized by more and more laboratories [8]. The exact composition used by SAFT is still proprietary, but the nickel to all total metals (excluding lithium) ratio is superior to 0.75 .

3. Impact of positive material specific properties on cell behavior

Unlike LiNiO_2 , $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2$ does not exhibit monoclinic/hexagonal phase transformations during cycling,

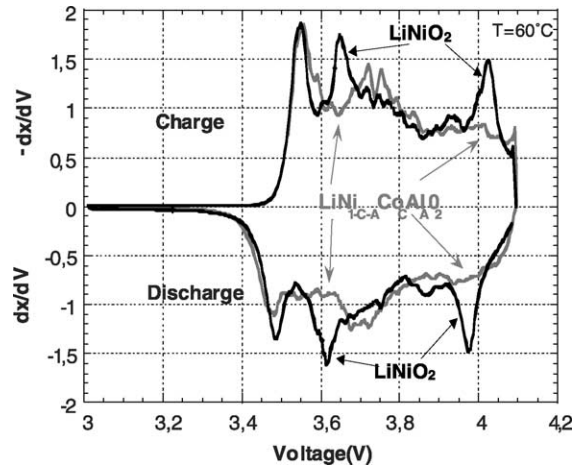


Fig. 1. Compared derived $x = f(V)$ curves for Li_xNiO_2 and $\text{Li}_x\text{Ni}_{(1-x-y)}\text{Co}_z\text{Al}_y\text{O}_2$ at low rate ($C/10$, 60°C).

as illustrated in Fig. 1, where no peaks are observed on the derived curve at 3.65 and 4 V , as for LiNiO_2 . This may at least partly explain the excellent stability on cycling, as described further.

The crystalline structure is very similar to LiCoO_2 , however, the charge and discharge curves are different, as shown in Fig. 2. Due to a small quantity of remaining Ni^{2+} , the first charge/discharge cycle is not totally reversible, although slightly better than LiNiO_2 . Therefore, the available capacity is slightly reduced, but still remains at the same level, or better than LiCoO_2 . This behavior induces an interesting consequence: as the total excess of lithium is not consumed by the carbon passivation, the positive electrode limits the cell capacity.

At the end of cell discharge at 2.5 V , about 15% of the Li capacity remains in the carbon electrode. If the cell is discharged beyond this voltage limit, a voltage plateau at

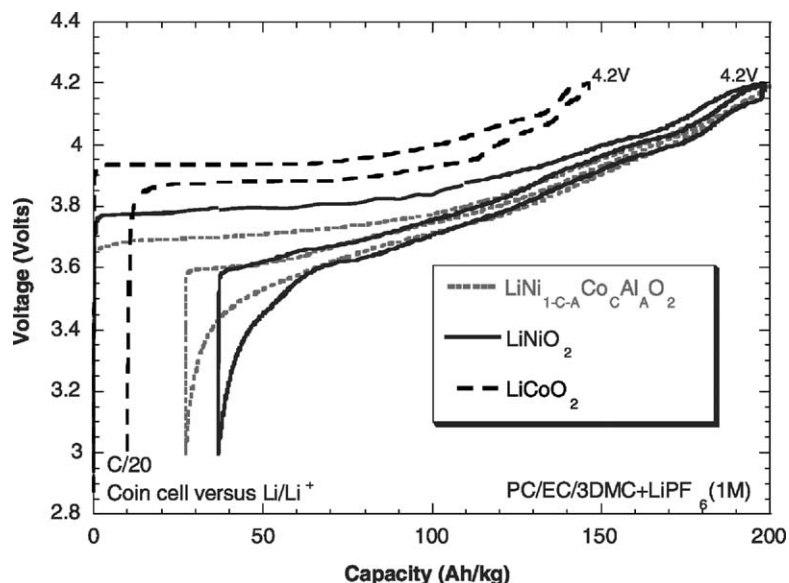


Fig. 2. Compared voltage profiles of several metal oxides at low rate ($C/10$, 25°C).

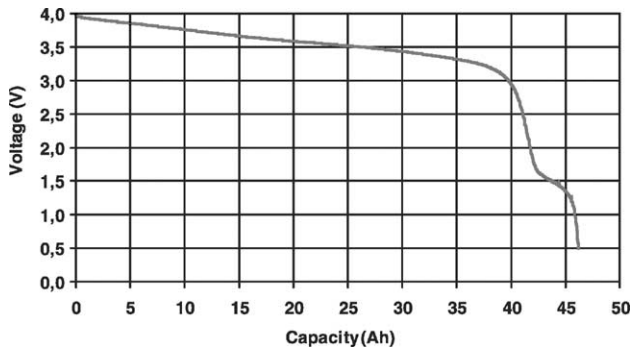


Fig. 3. Deep DOD voltage profile of $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2/\text{graphite}$ cell at low rate (C/10), ambient temperature.

about 1.5 V is obtained where the lithium is completely used up, as shown in Fig. 3 for a 40 Ah cell. This interesting feature gives the cell ability to be deeply discharged even to 0 V without risk of copper corrosion unlike other positive materials (in this case the negative electrode is only at about 1.5 V versus Li/Li^+). For the same reason, the cell can be stored for long periods from the complete discharged state of 2.5 V.

It should be noted that discharging the cell at elevated temperature of about 45 °C or more (depending on rate) allows the positive material to be totally reduced at high voltage, resulting in about 15% increase of the cell capacity in these conditions, but coming back then to a negative limited cell.

This particular feature has also a noticeable consequence on the cell shelf life. When the cell capacity is limited by the negative electrode, any loss of lithium directly impacts on the cell capacity, which is generally observed either on cycling, or extended storage at elevated temperature, because the passivating layer is not a full electronic insulator [9]. This induces also an outstanding cell energy stability on cycling or storage, as will be described further.

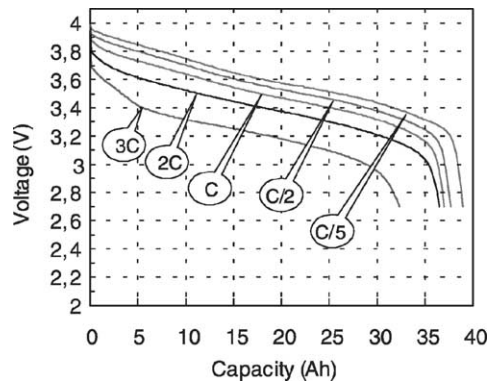


Fig. 4. Discharge profile of high energy cells $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2/\text{graphite}$ at different continuous rates, ambient temperature (EOCV = 4.0 0.25 > V).

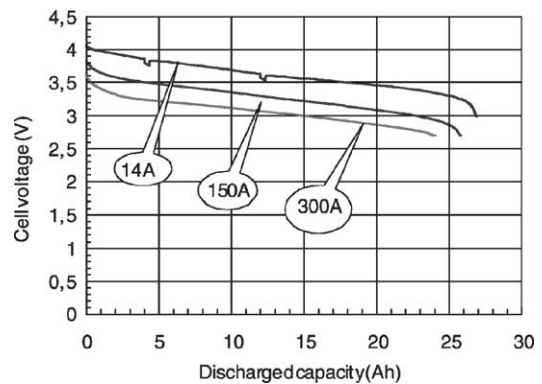


Fig. 5. Discharge profile at high rates of a medium range $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2/\text{graphite}$ high rate design. Discharge at 23 °C, after charge at 4.1 V EOCV.

Finally, the stabilizing property of Al ions on the positive electrode pushes significantly upwards (>about 100 °C) the temperature for the onset decomposition of the delithiated form, thus reducing the risk of thermal

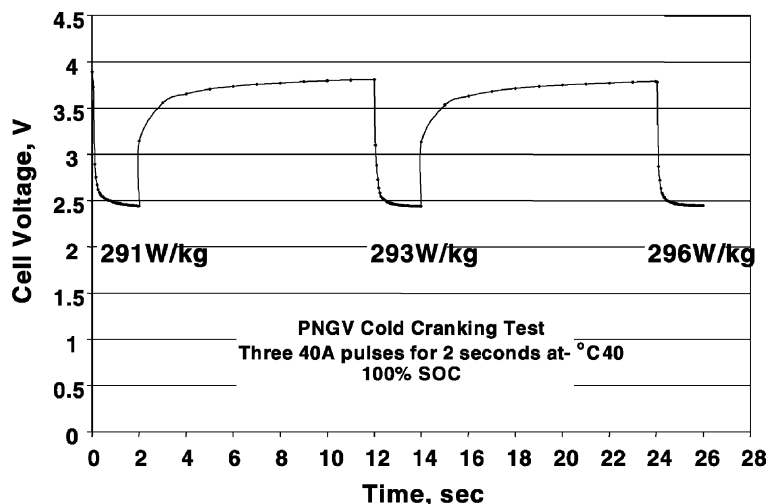


Fig. 6. Cold cranking test on HP8Ah cells, at -40 °C.

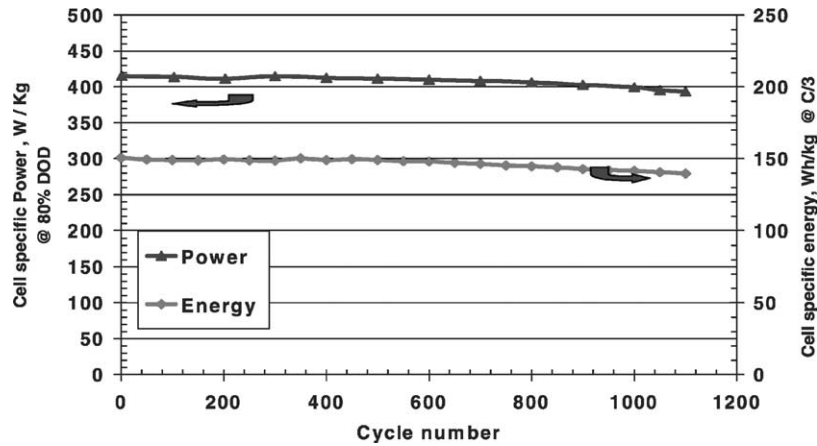


Fig. 7. Specific energy and power of HE cells during cycling at 80% DOD DST cycle. Every 50 cycles, energy measured at 100% DOD, C/3, power measured at 80% DOD, 300 A, –5 min pulse.

runaway in case of overcharge. In the same manner, the reactivity towards electrolyte is reduced, and that might be the reason for the excellent stability of cell impedance during storage, even at high temperature at high state of charge (floating). This behavior is indeed generally attributed to the electrolyte oxidation at the positive electrode interface [10]. This compares very favorably to pure LiNiO₂ or LiCoO₂, and is a big advantage over LiMn₂O₄, on which interaction with the electrolyte is still a major drawback.

4. Cell properties and applications

The Li ion cell technology is very well adapted to cover a complete spectrum of needs, from high energy to very high power. Using the general cell composition described hereunder, a complete range of products has been designed, in the usual spirally wound configuration, in cylindrical shape. The cell size proposed by SAFT ranges today from high energy 44 Ah to high power 8 Ah (1500 W/kg).

4.1. Cell general composition

Positive: LiNi_xCo_yAl_zO₂ + carbon + PVDF, on Al substrate (x > 0.75).

Negative: Artificial graphites blend + non-fluorinated binder on Cu substrate.

Electrolytes: Carbonates blend, function of cell type (energy, power, etc.) 1 M LiPF₆+vinylene carbonate.

Separator: PE/PP microporous.

4.2. Energy/power

Fig. 4 describes discharge curves of high energy cells at different discharge rates. It can be seen that even this high energy cell (145 Wh/kg) still sustain high discharge rates. Using an appropriate electrolyte, a “medium range” design (120 Wh/kg) can sustain extremely high continuous rate, as

shown in Fig. 5, describing a cell designed for military applications [11].

The lower energy (85 Wh/kg) HP8 high power cell for a hybrid electric vehicle is designed to deliver high power charge or discharge pulses (1500 W/kg) at the optimal

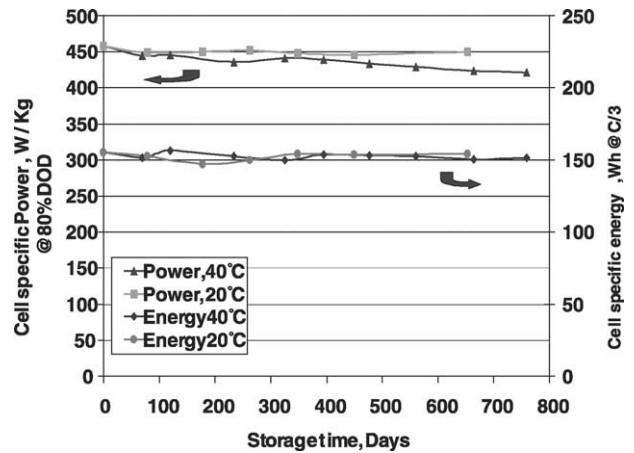


Fig. 8. High energy cells power and energy retention during floating at 4.0 V, at 20 or 40 °C.

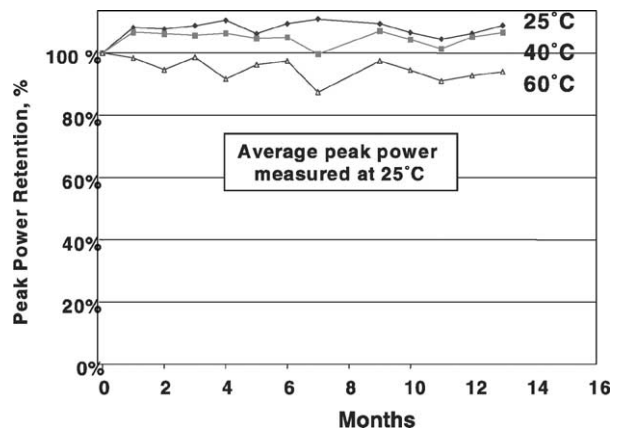


Fig. 9. Power retention on extended storage of high power cells at 50% SOC, at 25, 40 or 60 °C.

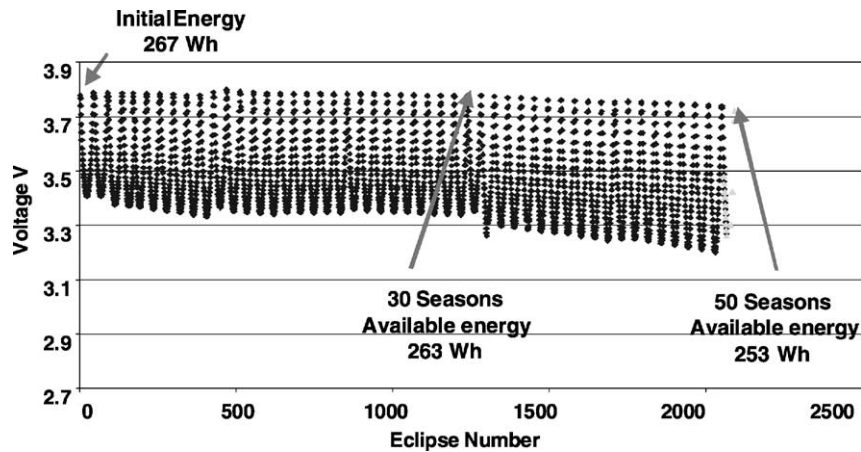


Fig. 10. VES 120 space cell. End of discharge voltage during GEO satellite cycling simulation.

operating SOC of 50%. At higher state of charge (90–100%), it can deliver even more power, such as >3 kW/kg during pulses of a few seconds. Even at very low temperature it can deliver very high peak power such as for cranking, as shown in Fig. 6, at -40 °C.

4.3. Cycling

The electric vehicle was the first application for which large Li ion cell development was initiated. Beside the obvious importance of specific energy and energy density, the cycling ability at deep DOD is of major importance, maintaining both energy and power capability over battery life. Fig. 7 shows the performance of high energy cells under cycling at 80% DOD in a “DST” profile, which includes charge (regeneration) and discharge peaks at various rates, corresponding to an average rate of about $C/3$.

The diagram describes the energy and power recovered during diagnostic 100% DOD cycles at $C/3$, made every 50 cycles. As can be seen, the energy remains remarkably stable during more than 1000 cycles, as well as the power ability, measured from a 300 A pulse at 80% DOD. These results illustrate the good behavior of the positive material, as well as the stability of the passivating layer on the carbon, preventing lithium loss. As a matter of fact, Fig. 3 describing the lithium excess has been recorded after 1000 cycles, which demonstrates the excellent stability of the layer, which we believe is due to the VC patented additive [12].

4.4. Calendar life

Due to both positive material chemical stability against electrolyte and passivating layer properties, the cells exhibit an outstanding shelf life characteristic. This is, for example, illustrated in Fig. 8, showing the energy and power retention of high energy cells, stored on a constant float voltage of 4.0 V, at 40 °C. After more than 2 years in this condition, both energy and power remains quite stable, similar to what is observed on storage at 20 °C.

In the same way, high power cells keep their power ability quite stable, even at 60 °C, as shown in Fig. 9.

This is definitely an advantage of this system, compared to what is currently obtained with LiCoO_2 cells, or even more, to LiMn_2O_4 systems.

4.5. Applications

Through these performances, the $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2/\text{graphite}$ cells have demonstrated their ability to be used in lot of applications, either for transportation or standby. Many demonstration programs have shown the interest of using Li ion system in automotive application, EV, HEV or 42 V uses [13]. Its light weight makes it definitely the best solution for space application, such as powering satellites [14]. As an example, Fig. 10 describes a geostationary satellite application simulation. Depth of cycling depends on the satellite illumination, and during the satellite life the battery is cycled following a complicated cycling profile following seasons. As can be seen, the goal of 30 seasons, representing 15 years of life, is largely superseded. In addition, the excellent demonstrated calendar life confirms the battery qualification for this mission.

The calendar life and reliability in severe environment are also the properties supporting the use of these cells in batteries for back up power sources, such as in outside cabinets for telecommunication uses.

5. Conclusions

Continuous research and development work on lithiated nickel oxides has allowed design and manufacture of large Li ion cells, used in large batteries for various applications, from high energy to high power. Industrial manufacturing equipment has been established to fulfill many requirements. The main specific features of these cells, using $\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Al}_y\text{O}_2$ and graphite in a conventional spirally wound cylindrical design, are an outstanding stability on cycling

and storage. At the same time, high specific energy density is maintained, depending on the required power, which can be also very high. The use of nickel instead of cobalt allows prediction of a lower cost, as production quantity increases. Manganese based oxides, for which final expected “cheap” cost will also depend on quantity, still suffer from significantly lower energy density, and lower chemical stability.

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