

Short communication

Towards a high performing lithium polymer battery system (VARTA PoLiFlex™)

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Abstract

The design of a lithium polymer battery with excellent properties is presented. The focus is on cathode and anode active materials and their influence on cell properties like energy density and cycle behavior. Standard LiCoO_2 is compared with alternative cathode materials like Li-Co-Ni-Mn-O and high density LiCoO_2 . Furthermore, several natural graphites and their mixtures with synthetic graphite are discussed as potential anode active material as natural graphite is attractive concerning price. The good performance of VARTA Microbattery's PoLiFlex™ lithium polymer battery results from an adequate combination of cathode and anode formulations.

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1. Introduction

Advanced electronic consumer products such as GPRS and UMTS cellular phones, PDAs, and laptops demand mobile power supplies with high capacities. The optimization of a battery meeting these demands poses novel challenges concerning safety at normal and abusive operating conditions. However, these main objectives have to be reached in combination with long cycle life, good rate capability, high energy density and low self-discharge.

Recently, a new class of cathode materials, the Li-Co-Ni-Mn-O system (especially in its formulation $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$) has attracted widespread attention. These compounds are more attractive as the standard material LiCoO_2 due to lower price and ecological reasons. Moreover, they show a higher stability at elevated temperatures (during oven or overcharge tests) due to the presence of Mn^{4+} ions. These ions stabilize by electrostatic bonding the spinel structure formed during heating [1].

Furthermore, the presence of Ni^{2+} ions allows the deintercalation of 0.66 Li^+ (instead of 0.5 Li^+ for LiCoO_2) due to the formation of Ni^{4+} . The Co^{3+} ions stabilize the lamellar structure of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ during cycling. Shifting the stoichiometry to $\text{LiCo}_{0.1}\text{Ni}_{0.8}\text{Mn}_{0.1}\text{O}_2$ gives a huge capacity benefit in comparison to LiCoO_2 and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. But the high nickel content and the low manganese and cobalt quota could harm the excellent cycle and safety properties of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

The anode also contributes significantly to the performance of lithium polymer batteries. As the cathode, it should increase the energy density without jeopardizing the capacity retention. Moreover, the surface of the carbon particles of the anode material has to be as small as possible in order to avoid important capacity loss after SEI formation.

2. Experimental

VARTA Microbattery PoLiFlex™ cells are prepared according to the following steps. First, a slurry consisting of the electrode materials, conductive carbons and binders is mixed. This step is followed by the coating of anode and cathode films. The obtained electrodes are laminated on the current collectors. These laminates are cut in the appropriate form and size for the manufacturing of bi-cells. The bi-cells are stacked and after packaging, the obtained cell is activated with electrolyte, sealed

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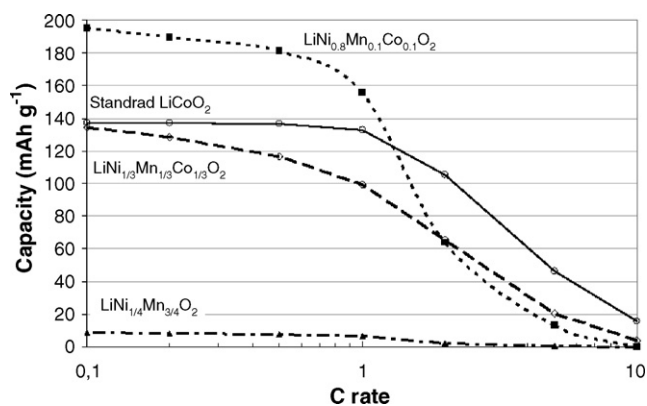


Fig. 1. Average of five signature curves for different cathode materials.

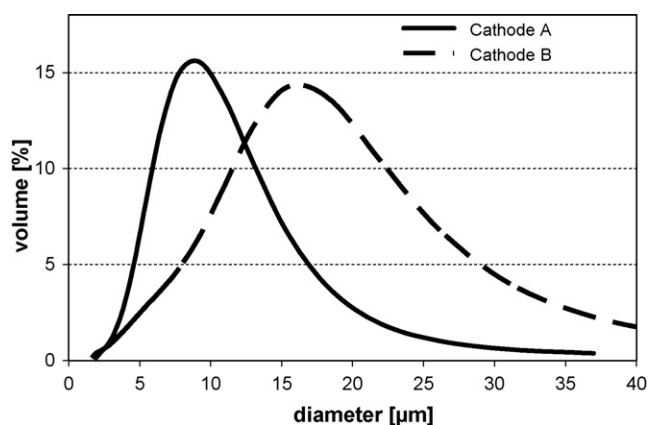


Fig. 2. Particle size distributions of Cathodes A and B.

and formatted. In this work, two PoLiFlexTM cell types are used for tests: PLF383562 (tests of cathode and anode materials) and PLF443441 (determination of the overall performance).

Swagelok[®] type cells are used as well. These cells are assembled in an argon-filled dry-box. The negative electrode is a disk of lithium metal foil. A Whatman[®] GF/D borosilicate glass fiber sheet, soaked with a 1 M LiPF₆ salt dissolved in EC/DMC solution (1:1), is placed between the two electrodes. The composite positive electrodes consist of films made in the same way as the ones of PoLiFlexTM cells. The typical loading of active material for each cell is 15–25 mg. The Swagelok[®] type cells are used for determining specific capacities at different C-rates for anode and cathode materials.

For both cell types, lithium intercalation and deintercalation was monitored with a “Maccor” cycling/data recording system with a potential window of 3.0–4.2 V for cathodes and PoLiFlexTM cells, and between 0.05 and 2.00 V for anodes, respectively. A typical signature curve is obtained in Swagelok[®] cells by charging the cell at C/10 and then discharging at different rates (with 30 min of relaxation between the different discharges).

3. Results and discussion

3.1. Since the safety of the PoLiFlexTM cells is one of our major topics, we are always looking for new materials improving it. But those materials should not compromise the good cyclability and energy density. A first test is usually performed in Swagelok[®] cells which need only small amounts of materials and give fast and accurate values for the rate capability. The signature curves, presented in Fig. 1, show that LiNi_{1/4}Mn_{3/4}O₂ has for all rates very poor capacities for our film formulation and in the potential window 3.0–4.2 V.

LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ shows a good capacity at low C-rates. Its disadvantage is the faster capacity fading in comparison to the reference LiCoO₂. This indicates either an insufficient intrinsic compartment or a non-appropriate film recipe. With a new formulation and thinner electrodes, a better behavior might be observed.

Among the materials we tested, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ seems to be the best candidate for replacing LiCoO₂ in terms of capacity if the other properties (e.g., no gassing at 80 °C storage in the fully charged state) that we still have to test, fulfill our requirements.

In order to take advantage of the good properties of these materials and to minimize their disadvantages, a blend could be taken into consideration. PoLiFlexTM cells will be built and the results concerning energy density, cycle data and safety will be submitted.

3.2. The energy density of a battery is beside its safety, the most important characteristic for the customer. To reach this target, the densification of the electrodes is indispensable, in particular of the cathode. For this reason, we densified the cathode using a lithium cobalt oxide with good compressibility.

It is well known that powders with a wide range of grain sizes can be densified easier than powders with a very narrow grain size distribution. This is due to the fact that the holes between the bigger particles can be filled with smaller ones. In our study, we compare two powders: Cathode A with a narrow (D5% 4 μm to D95% 17 μm) and Cathode B with a wide (D5% 4 μm to D95% 31 μm) grain size distribution (Fig. 2).

First we measured the tap densities of both lithium cobalt oxide powders. The tap density of Cathode B (2.70 g cm⁻³) is about 35% higher than the one of Cathode A (1.9–2.1 g cm⁻³). We coated cathodes with both lithium

Table 1
D5%/D95% values of the grain distribution; tap density of Cathodes A and B (pressed density of two cathode films with 500 kg cm⁻²)

LiCoO ₂	D5% (μm)	D95% (μm)	Tap density (g cm ⁻³)	Pressed density (g cm ⁻³)
Cathode A	4	17	1.90–2.10	2.85
Cathode B	4	31	2.70	3.10

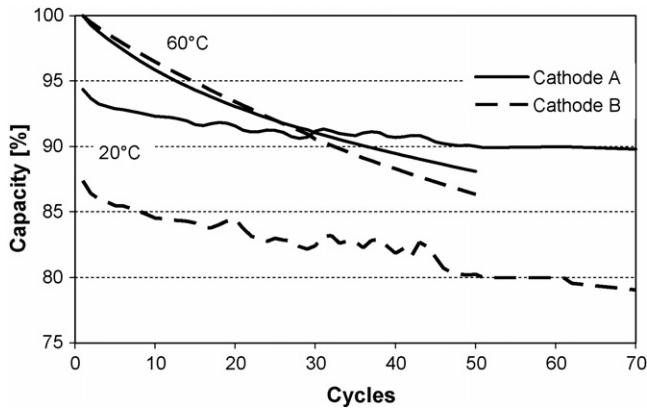


Fig. 3. Capacity retention at 20 and 60 °C of Cathodes A and B.

cobalt oxides and appropriate recipes directly on aluminum grid. After densifying these cathodes with 500 kg cm^{-2} , we determined a density of 2.85 g cm^{-3} for Cathode A and 3.10 g cm^{-3} for Cathode B (Table 1). This means an increase of the energy density for the cell of about 5%.

We built some Li-polymer cells with both electrodes to compare the electrochemical behavior of the low density (Cathode A) and the high density (Cathode B) lithium cobalt oxide. The cycling of the cells at 1 C at 20 °C and 60 °C (Fig. 3) showed big differences between Cathodes A and B. We want to focus especially on two phenomena:

- (a) For the first cycles, we see a great gap between the 1 C at 20 °C and 60 °C—curves in particular for the Cathode B. This means that Cathode B is more controlled by diffusion than Cathode A.
- (b) The cycling stability at 1 C at 20 °C over 70 cycles of Cathode B is much lower than the one of Cathode A due to diffusion limitations. In addition, Fig. 4 shows that at higher discharging rates, the difference between the two materials is even more significant. Cathode A is a candidate for further tests, whereas Cathode B is unusable for our cells.

Another possibility to increase the energy density is to modify the recipe of the film. By using the good active material presented above and reducing the binder and con-

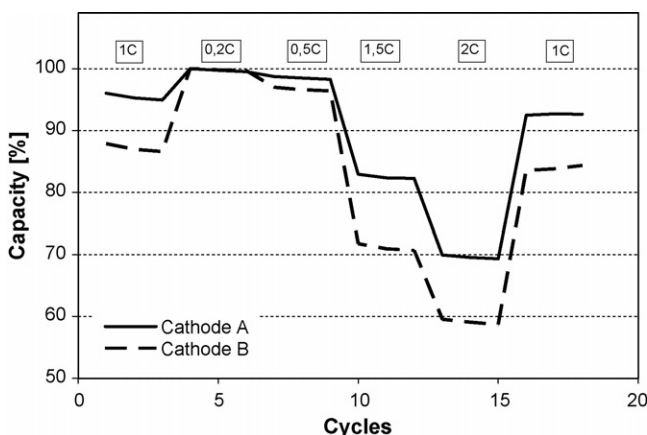


Fig. 4. Rate capability at 20 °C of Cathodes A and B.

Table 2
Physical properties of Graphite A and B

	Tap density (g cm^{-3})	Specific surface (BET) ($\text{m}^2 \text{g}^{-1}$)	D50 (μm)
Graphite A	0.915	<4.5	18.5
Graphite B	0.850	5.3	24.0

ductive carbon, a density greater than 3.2 g cm^{-3} can be reached while keeping the good cycling performance.

3.3. Another part of the cell that influences its energy density is the anode but it has less influence as the cathode. The anode material does not increase energy density, but a thinner anode film leads to more space for the cathode and thus a higher capacity. The film thickness can be reduced either by a higher carbon specific capacity or by a film densification.

In this work, we present the comparison of two natural graphites A and B (physical data, see Table 2). Comparable to the cathode materials, the graphite with higher particle size (Graphite B) possesses a higher tap density. However, the capacity of Graphite B is smaller than the one of graphite A, especially at high C rates (Fig. 5). Another disadvantage of Graphite B is the higher specific surface

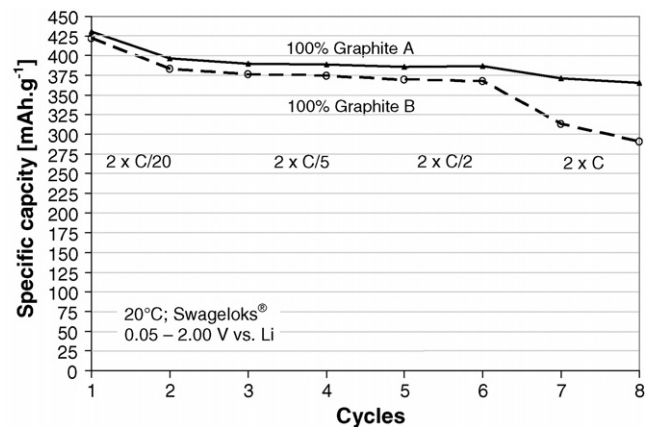


Fig. 5. Rate capability of Graphites A and B (average of five cells for each graphite).

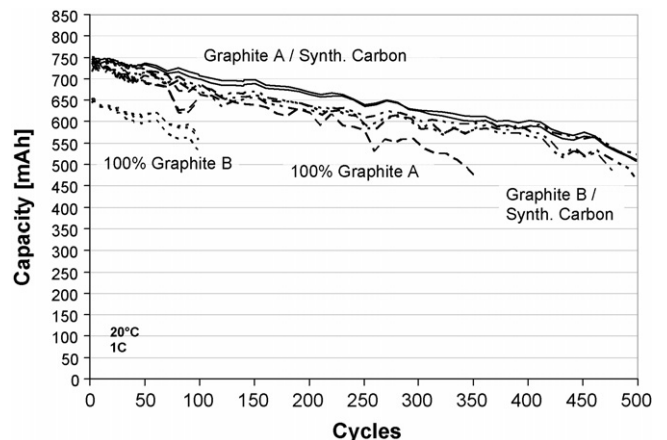


Fig. 6. PoLiFlex™ cells with standard cathode and different anodes cycled with 1 C at 20 °C.

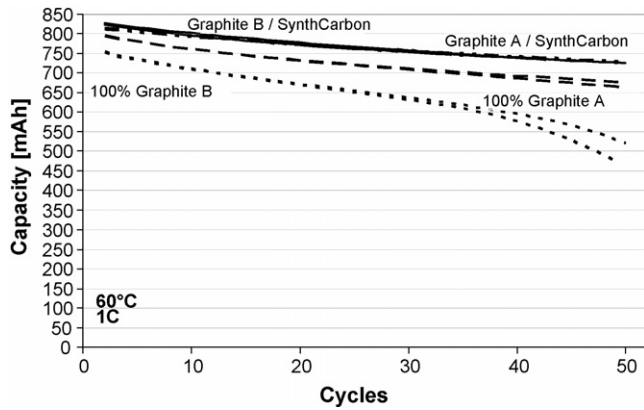


Fig. 7. PoLiFlex™ cells with standard cathode and different anodes cycled with 1 C at 60 °C.

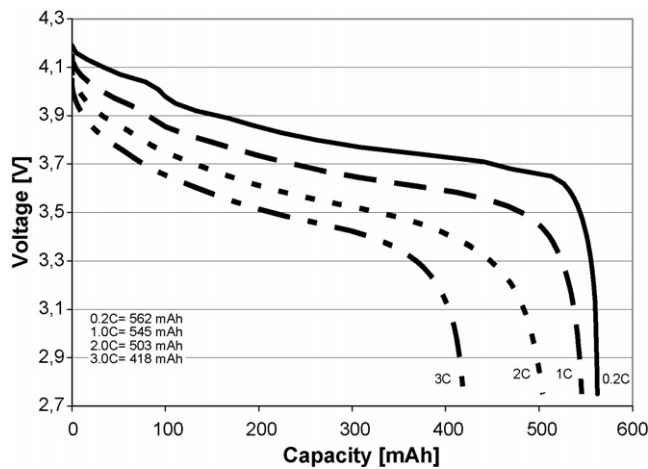


Fig. 8. Discharge profiles of a PLF443441 at different C rates (20 °C, 4.20–2.75 V).

which leads to a larger irreversible loss during the SEI formation.

The examined graphites in PoLiFlex™ cells show a strong capacity fading at 20 and 60 °C (Figs. 6 and 7). The measurements in PoLiFlex™ cells are in accordance with the results obtained with Swagelok® cells: Graphite B (650 mAh) has a smaller capacity (second cycle, 20 °C) than Graphite A (750 mAh, 20 °C) and a larger capacity fading at 60 °C (capacity retention at 60 °C after 50 cycles, A: 84%, B: 66%).

To improve the response at high rates and the capacity retention, both graphites are mixed with a synthetic active carbon. The initial capacity of PoLiFlex™ cells with Graphite A mixed with synthetic active carbon is the same as the one without, but the capacity retention is signifi-

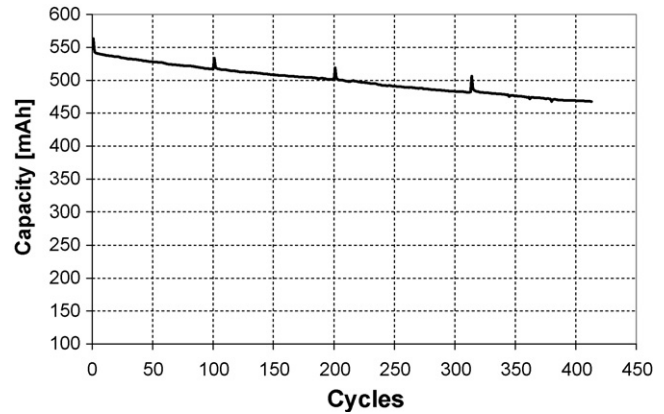


Fig. 9. Cycling behavior of a PLF443441 (1 C and each 100th cycle with 0.2 C; 20 °C, 4.20–2.75 V).

cantly improved: 95% instead of 88% after 100 cycles at 20 °C (Figs. 6 and 7). An improvement in capacity retention by mixing with synthetic active carbon can also be observed for Graphite B: 92% instead of 85% after 100 cycles at 20 °C. However, even this composite still does not reach the good properties of the Graphite A/synthetic carbon mix (Figs. 6 and 7).

3.4. The PoLiFlex™ cell realised with the improved cathode and anode films shows remarkable safety [2] and cycling properties. Fig. 8 displays the discharge curves of a lithium polymer cell (PLF443441) at different C rates (20 °C, 4.20–2.75 V). The cell has a capacity of 562 mAh at 0.2 C. Even at a 3 C the cell works very well (418 mAh).

In Fig. 9, the cycling behavior of a PLF443441 lithium polymer cell is depicted (with 1 C and each 100th cycle with 0.2 C; 20 °C). After 400 cycles, still more than 80% of the initial capacity is available. PoLiFlex™ cells work excellent in a temperature range of –20 to 60 °C.

4. Conclusion

In this publication, the way of choosing good anode and cathode materials for a polymer battery with excellent properties as VARTA PoLiFlex™ is described. Creating new recipes or mixing active materials with different properties are possible ways to implement novel compounds for electrodes.

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