Process development and optimization for Li-ion battery production

Mareike Wolter, Diane Leiva, Marco Fritsch, Stefan Börner

Fraunhofer-Institut für Keramische Technologien und Systeme, Winterbergstraße 28, 01277 Dresden, Germany,
mareike.wolter@ikts.fraunhofer.de

Abstract

Li-ion Batteries with high power capability and high energy density have gained importance in the past years for automotive applications. Furthermore, the demands regarding cycle and calendar lifetime are much higher compared to portable applications where lithium technology is established since many years. Thus, manufacturing processes need optimization towards process stability, battery performance parameters and production costs. Recent results of process development for efficient battery manufacturing are presented.

Keywords: lithium battery, efficient production, material, electrode

1   Introduction

Lifetime requirements of ten years minimum and several thousands of cycles under harsh environmental and operational conditions define a major challenge which automotive lithium batteries have to meet. In addition, there are ambitious cost and energy density targets to achieve.

Existing manufacturing processes for small lithium batteries are not able to cover those demands. Our own investigations showed that consumer batteries have a typical lifetime of about 4 to 5 years including several hundreds of charge and discharge cycles. Afterwards significant degradation of the mechanical integrity of electrodes is observed.

To improve cell durability a deep understanding of material issues and the interaction with manufacturing conditions is necessary. As the conditions are very complex, the improvement of one battery parameter can adversely influence other performance parameters.

Figure1: Post mortem analysis of a commercial consumer battery.

Beginning with the cell raw materials (e.g. collector foils, active materials, separators, metal parts etc.) the production process includes many individual steps until the battery cells are ready for installation in a storage system. First, the anode and cathode slurries are produced by mixing active materials, binders, and additives with organic solvents under evacuated atmosphere. According to the applied procedures, the mixing takes several hours [1]. Afterwards, the slurries are applied to the current collector foils (commonly cathodes on aluminium foils and anodes on copper foils). In the

following step, the foils are dried in order to extract the solvents from the coating to result in porous electrode morphology [2]. Then the electrodes are calendered to achieve homogenous thickness of the active layers. Another aim is to establish an optimum electrical contact among the particles on the one hand, and between the coating and the current collectors on the other hand [3]. In a subsequent step, the continuously produced electrodes are cut into sheets to be stacked, or cut into strips which are wound to so-called jelly rolls [4]. After that, tabs and terminals are applied to the collector foils and the electrode bundles are inserted in the battery cell housing. Under vacuum or an inert gas atmosphere the electrolyte is filled into the cells. Sealing of cells is the last step of mechanical assembly followed by the end-of-line treatment including formation, aging, and electrical characterization. From that moment the cell is active and an electrical voltage exists between the positive (cathode) and negative (anode) terminal.

To investigate optimum process parameters related to battery durability and performance a consortium of research institutes and industrial partners is installing a pilot line for manufacturing of battery cells. The presented work shows some results of this collaboration.

2 Process development for efficient production

2.1 Development toward environmental friendly production – application of aqueous slurries

Commonly organic solvents like N-methylpyrrolidone (NMP) are used in electrode manufacturing process bearing potential health and safety risks. Thereby special investment and fabrication costs for safety arrangements, drying and recycling of the solvent are necessary. The switch to water based slurries can lead to a simplification and cost reduction of the electrode manufacturing process, as it is already realized for graphite based anode slurries. Thus, increased efforts are made to development water based $LiFePO_4$ cathode slurries as well.

Therefore, the dispersing process and the sedimentation stability of $LiFePO_4$ in dependence of the dispersant type and amount were investigated. Proper water compatible binder systems were evaluated with regard to the slurry's solid content, rheology and suitability for a continuous industry casting process. The electrode quality and properties were characterized both by analytical methods and electrical performance tests as well as measurement of water content after processing. Electrochemical properties like capacity and cycling stability can be compared to traditional NMP processed $LiFePO_4$-cathodes.

2.2 Comparison of mixing technologies for the preparation of slurries

The processing of active materials and preparation of slurries is a decisive process step for the coating of lithium battery electrodes.

Many performance properties of Li-ion cells can be attributed to the preparation of the active materials for the electrodes as dispersing time during mixing decides on homogenization or agglomeration In addition to the selection of materials and coating technology, the mixing of slurries is decisive. Therefore various mixing technologies were compared (intensive mixer, planetary mixer, dissolver, drum-mill) to determine the influences of mixing parameters on the slurries and evaluate the up-scaling potential.

Figure 2: Intensive mixer and planetary mixer used for mixing investigation.

In order to compare different mixing technologies the effect of the dispersion of the particles in suspension, the energy input into the system as well as the influence of parameter selection on the process times were investigated. The experiments were done on pilot scale and electrodes from the different slurry mixes were prepared.

For aqueous anode slurries the experiments showed that carboxymethyl cellulose (CMC) solution has to swell sufficiently in advance for appropriate viscosity. To ensure mechanically stable anodes the styrene-butadiene rubber (SBR) binder has to enclose the graphite particles.

Vacuum mixing process supports dispersing and reduces bubbles.
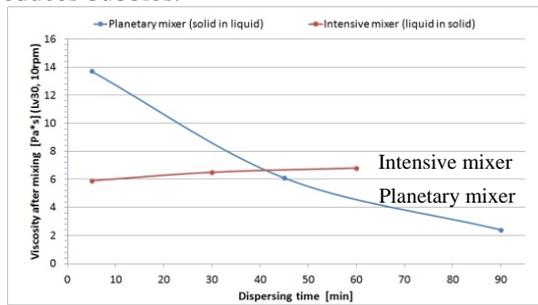
Figure 3: Viscosity of anode slurry at different dispersing times.

2.3 Effect of calendering on porosity and structural properties

Calendering is one of the fundamental issues regarding the electrode production to be mastered in order to achieve a high electrical performance and cyclability in large scale energy storage systems based on lithium ion battery technology [5]. Thus a systematic study was done on performance of $LiFePO_4$-cathodes depending on porosity and structural properties influenced by calendar parameters.

The porosity of the cathodes was varied by a systematic calendering with loads ranging from 0 to 667 N/mm. A combination of analytical methods such as FESEM, AFM and µ-Raman spectroscopy was used to study microstructural changes after compression. After that electrode performance tests consisting of C/5, C/2, 1C and 2C discharge cycles and accelerated aging experiments with 2C-cycles at 60°C were carried out on in-house assembled 2032 coin cells.

The results demonstrate a strong correlation between electrode porosity and gravimetric capacity, cycle stability as well as internal resistance (fig 4).
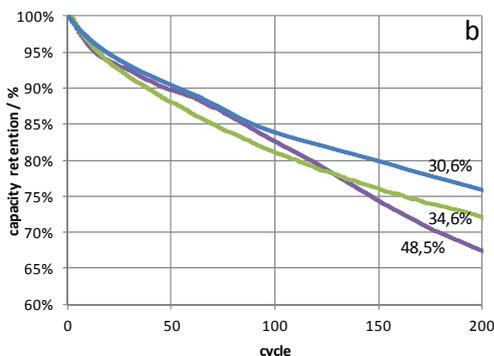
Figure 4: Influence of the $LiFePO_4$ cathode porosity on changes in capacity retention after 200 cycles at 60°C and 2C.

3 Addressing time and investment intensive process steps – formation and end of line test

Strongly related to electrode characterization are the production steps of formation and end-of-line testing which are significant bottlenecks in present production lines, as the charge/discharge rates and therefore the duration of the individual formation and test cycles strongly influence the number of necessary test circuits and test benches. Thus it is worthwhile to take a close look at the data obtained and extract as much information from these cycles in order to minimize the testing time.

In general, formation and end-of-line tests have to fulfill the following tasks:
- Build-up of a stable, but low resistive solid electrolyte interface
- Process control and feedback for quality management
- Performance check and verification of user requirements specifications

During the formation process, the battery is charged for its first time and along with Li intercalation and de-intercalation a solid electrolyte interphase (SEI), consisting of decomposition products of the electrolyte, builds up at the electrodes. Particularly in the case of graphite based anodes the SEI inhibits exfoliation [6, 7] of the active material through unintended solvent co-intercalation and, due to its insulating nature, also protects the electrolyte from being further decomposed. To achieve a high performance battery with a long lifetime at possibly low costs it is thus crucial to establish a formation process that delivers a stable and highly ion conductive SEI in a minimum amount of time.

Since the properties of the resulting SEI are determined by a complex interplay of many parameters such as temperature, electrolyte and electrode composition as well as current-voltage profile, formation optimization requires a high number of experimental data. To minimize time and effort, this topic is therefore addressed by statistical design of experiments (DOE) leading to a maximum of information at a minimum of experimental effort.
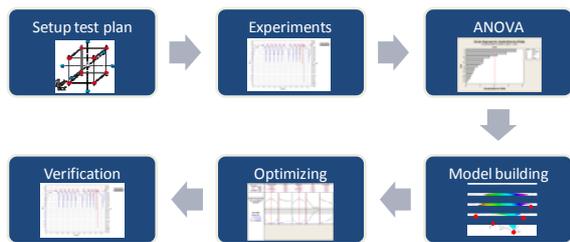
Figure 2: Formation optimization strategy by DOE.

3.1 Controlling anode quality during formation process

Since the SEI consists of electrochemically decomposed electrolyte components (solvent, salts and additives), this process consumes not only parts of the electrolyte, it also takes a certain percentage of the first charge-capacity for these side reactions. Therefore, the first discharge capacity is smaller than the first charge capacity and the ratio of both is thus a measure for the amount of SEI build-up. The difference in capacity is often referred to as irreversible first cycle capacity and its ratio as first cycle coulomb efficiency.

This allows for instance controlling the anode quality in production process.
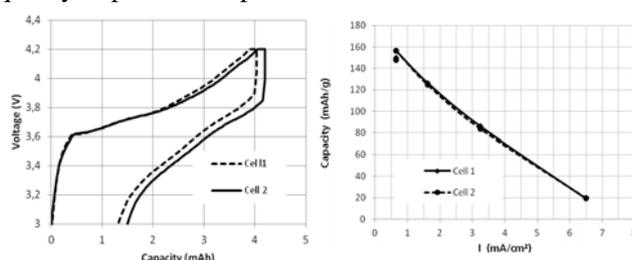
Figure 4: Rate-dependent capacity of two cells with NCA cathode material but differently sized anodes (anode of cell 2 is 14 % lighter than anode of cell 1) (left); C/10 formation charge/discharge cycle of the cells (right).

Since all other cell components were kept identical, the discrepancy in first cycle efficiency may be attributed to the weight difference of active anode mass, where cell 1 shows a capacity of 0,77 mAh and 10,2 mg/cm^2 for the anode where cell 2 has a capacity of 0,9 mAh related to the active anode mass of 11,9 mg/cm^2.

Thus, this example illustrates how data obtained during the formation cycle may be used to control quality of anodes.

3.2 End-of-line testing

After formation the cells are subjected to aging and end-of-line (EOL) test for final process control, i.e. performance check and verification of user requirements specifications. Again, the aim is to perform these processes in a possibly short amount of time and extract a maximum of information out of them. Thus, an intelligent data acquisition is necessary during aging and EOL-test to detect even slightest abnormal behaviour to deliver valuable feedback for quality management.

For instance cell's impedance is a crucial parameter that essentially determines the rate-dependant discharge performance. As formation is performed at very low C-rates, it is not suited to detect deviations from aimed-at cell impedance. To illustrate this, Fig. 5 (left) shows the formation cycle of two LiFePO$_4$/C cells with differently calendered cathodes. The cathode of cell 3 was calendered at 88 N/mm whereas the cathode of cell 4 was treated with 667 N/mm. Similar to the previous example a difference in anode size is detected and the first discharge capacity of both cells is 1.8 mAh. An influence of the calender force is thus not noticeable. However, a 'performance test', as shown in Fig. 5 (right), reveals a significant difference of both cells. Up to a C-rate of 1C the cells have almost identical capacities, but at an increased C-rate of 2C the difference becomes obvious and may be ascribed to a less dense and therefore less conductive coating of cell 3. This statement is further supported by the 10 Hz cell impedance which is 78 Ohm for cell 3 and 50 Ohm for cell 4.
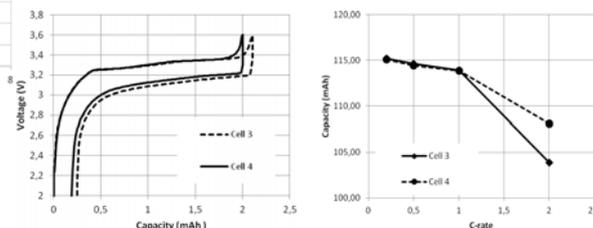
Figure 5: Formation cycle of two LiFePO$_4$/C button cells, whereby the cathode of cell 3 was calendared at 88 N/mm and the cathode of Cell 4 at 667 N/mm (left); rate-dependant discharge capacity of cell 3 and 4 (right).

The results discussed above show that a rigorous separation of formation and end-of-line testing is not reasonable since valuable information may be extracted from both procedures. By taking advantage of this, it is possible not only to reduce the overall testing time but also to give feedback information for controlling and optimizing the process quality of cell manufacture.

Acknowledgments

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Authors

Mareike Wolter is head of the 'energy storage systems' group and the battery lab at Fraunhofer IKTS. She graduated at the Technical University of Dresden in 1997. Following her work on sensors based on intrinsic conducting polymers at Department of Electro-chemistry she received a PhD grade in 2002. In 2003 Mareike Wolter joined the Fraunhofer-Institut für Verkehrs- und Infrastruktursysteme IVI, where she was responsible for the 'alternative propulsion systems' group. Since 2008, she is with the Fraunhofer-Institut für Keramische Technologien und Systeme IKTS.