

Review of In-situ and Ex-situ Techniques for Characterization of Li-ion Batteries

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Abstract—This paper describes the analytical techniques and sample preparation methods used in in-situ and ex-situ investigations of Li-ion batteries (LIBs). The introduction briefly describes the current state of Li-ion batteries and their aging mechanisms. The article is further divided into a description of ex-situ and in-situ techniques. Ex-situ techniques include a detailed description of sample preparation for repeatable results using Broad Ion Beam (BIB) polisher. In-situ techniques are described in the form of a report of selected published experiments. The paper is further extended with our experiments involving ex-situ analyses of cylindrical and flat cell types using BIB in planar mode and cross-section mode. In the case of in-situ experiments, the design of the cell inside the SEM chamber is described. Two experiments have been performed - on the surface of a MEMS chip, and also using a micromanipulator as a current collector of the investigated electrode.

Index Terms—Li-ion, SEM, FIB, EDS, BIB, battery, energy storage, in-situ, ex-situ, sample preparation, ionic liquid

I. INTRODUCTION

Depending on the application, we require from electrochemical current sources high energy density (gravimetric, volumetric), long lifetime (number of possible charges - cycle lifetime and service life), good resistance to external conditions (e.g. temperature), resistance to high loads (charging and discharging currents), low cost, environmental compatibility, safety, and others. Lithium-ion batteries (LIBs) meet these requirements for most of today's applications, making them the most widely used battery type. However, as time goes on, the demands on batteries are increasing. In the future, it is also necessary to take into account the limited supply of raw materials for battery production (mainly nickel and cobalt). Therefore, there is an effort to find new materials to respond to these challenges [1] [2] [3].

In the future, the use of materials such as sulfur or silicon, high-voltage spinels, and solid electrolytes are being considered. These technologies have been known for a long time, but have not been used commercially, mainly due to the instability of such a system and the very low cycle life. The aim is to understand the degradation mechanisms and propose solutions. In the manufacturing process, the aim is to prevent degradation and potentially hazardous conditions [3] [4] [5].

Since LIBs are secondary cells that can be recharged repeatedly, the reactions taking place during cycling are ideally

100 % reversible. In practice this is not the case, certain changes are irreversible, causing aging and irreversible loss of capacity and performance. This may occur not only during operation but also by improper storage in an inactive state [6].

The main mechanisms include aging due to phase transformations of the crystallographic structure of the electroactive materials, electrolyte decomposition, and Solid Electrolyte Interphase (SEI) formation. When the SEI layer is disrupted, a new layer is formed, which further consumes lithium, and lithium dendrite formation can also occur on the anode side. Transition metals may also dissolve from the cathode and migrate toward the anode. A number of techniques are available to analyze these processes. The most versatile is the use of scanning electron microscopy together with associated methods such as EDS [7].

This work continues with a description of sample preparation and an overview of the ex-situ and in-situ techniques used using SEM to characterize Li-ion battery systems. The individual parts are complemented by experience from our experiments.

II. EX-SITU TECHNIQUES

For comparable results, the battery must be analyzed under similar defined conditions. A common reference is the open-circuit voltage (OCV) and the depth of charge/discharge (SOC/SOD) derived from it. Since the OCV is also influenced by other factors (previous load), it is advisable to hold the defined voltage for several hours or to perform a certain number of identical cycles for all analyzed samples. From a safety point of view, it is recommended to discharge the battery as much as possible. On the other hand, the voltage should not leave the nominal values specified in the datasheet in order to avoid material changes not caused by cycling (e.g. dissolution of current collectors) [8] [9].

The battery contains materials highly sensitive to contact with air humidity, oxygen, and nitrogen. When exposed to air, the samples are visibly degraded within seconds. In addition, the frequently used lithium salt LiPF_6 reacts with air moisture to form HF. Therefore, it is necessary to open cells in a glovebox filled with inert gas with controlled levels of O_2 and

H₂O (ideally also N₂) or dry laboratory environments with ventilation [8] [10] [11].

It is preferable to avoid short-circuiting during disassembly. Therefore, non-conductive tools should be used and excessive pressure should be avoided. The standard procedure is to remove the housing and then separate the electrodes. In the case of whole battery modules in electric vehicles, the interconnected flat-type cells can be separated by using a nylon string. However, excessive mechanical stress must be avoided. Before disassembling an unknown cell type, the X-ray method can be used to determine the optimal location for the cut [10] [12].

Inspection of multilayered structures in the cross-section can be problematic. For cylindrical cells, a metal casing can be used as a fixation to hold the layers together during mechanical polishing. However, the pouch and prismatic cells need to be fixed with, for example, a clamp or embedded in epoxy resin [12].

Further sample preparation is often required before analysis. Grinding and polishing are common preparation techniques to remove roughness and obtain a smooth surface. However, these traditional mechanical techniques apply shear forces to the sample that may result in damage to the sample. The electrode layers may delaminate and grooves can be created on the surface. Broad ion beam (BIB) technology is therefore often used for final polishing. These systems sputter the sample material with noble gas ions (typically argon). No mechanical stress is applied, leaving extremely flat surfaces and cuts with minimal artifacts. BIB is typically used in two different modes - surface (planar) polishing and cross-section polishing. During polishing, the sample is heated, so it is necessary to ensure sufficient heat dissipation or to use cooling (typically a Peltier cell or liquid nitrogen) [12] [13] [14] [15].

In the case of surface polishing, the beam hits directly the rotating specimen. The surface is mechanically pre-polished and then only a few micrometers of material are sputtered. Figure 1 shows an example of a sample prepared in this way. It is a 18650 cylindrical Li-ion cell. It was discharged to 0.1 V, cut perpendicularly with a hacksaw, and mechanically pre-polished on SiC grinder paper. Isopropyl alcohol was used as the grinding medium. This was followed by final polishing using a two-ion gun BIB polisher Fishione Model 1061 Ion Mill with Cryo Cooling. SEM inspection of the prepared area provides information about the internal arrangement of the electrodes including defects on the current collector of the anode (red arrows) [16].

Thin materials up to 1 mm are suitable for cross-sections. The sample is placed behind the mask (hard-to-sputter material, e.g. titanium) in a slight overhang (overlap of the sample above the mask surface, usually tens of microns). The overlapping part is sputtered off and a sharp edge is created. The size of the overhang is a compromise between time and the certainty of removing the part containing the defects caused by shearing/cutting the material. The specimen is rotated alternately during the process (so-called rocking or oscillation), which ensures that the beam is always coming

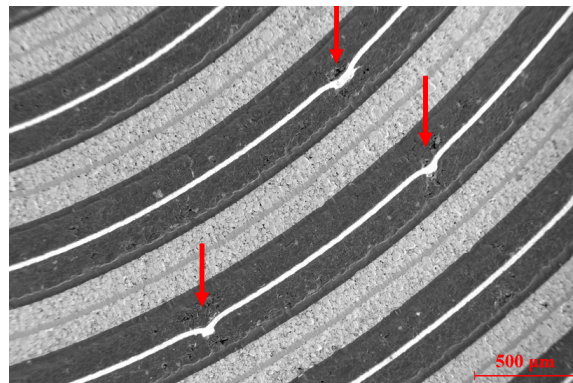


Fig. 1. Cross-section of whole 18650 cylindrical cell prepared using BIB in planar mode.

from a different angle. This enlarges the polished area and reduces artifacts.

Typically, individual electrodes or a separator are prepared in this way. Figure 2 is a comparison of the same area of the cathode before polishing (only cut with scissors) and after polishing. A BIB polisher Fishione Model 1061 Ion Mill was used for preparation in cross-section mode with an overhang of approx. 20 μm and an oscillation of ±30°.

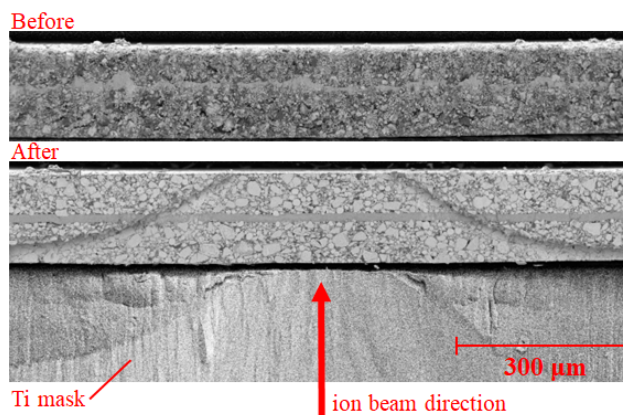


Fig. 2. Cross-section of battery cathode prepared using BIB. Comparison of the surface before and after polishing.

After shearing, the structure is damaged and only the current collector is hardly recognizable. After polishing, a region with a Gaussian profile (due to the beam intensity) is apparent where particles of electroactive material, binder, and current collector are recognizable. It can be determined that this is a blend of two electroactive materials, there is no significant grain cracking or delamination, the electrode has no surface coating (e.g. alumina layer) and there is no significant SEI layer.

III. IN-SITU TECHNIQUES

One of the first in-situ SEM experiments was published in 1988. The cell was prepared by deposition of thin layers of active material (FeS, TiS₂, V₆O₁₃) on current collectors

connected through a vacuum feedthrough outside the microscope. A solid-state electrolyte (polyether with ethylene oxide base and LiClO_4 salt) was used. Lithium metal was used as a counter electrode. The cell was assembled in a glove box and transported in a short time (about 30 s) to the SEM to reduce degradation in air. The cell was scanned from the side of the sandwich structure and was heated during cycling due to poor conductivity. A schematic drawing of the cell is shown in Fig. 3. No changes in the structure could be observed for the stable TiS_2 , V_6O_{13} showed small cracks, and FeS completely decayed [17].

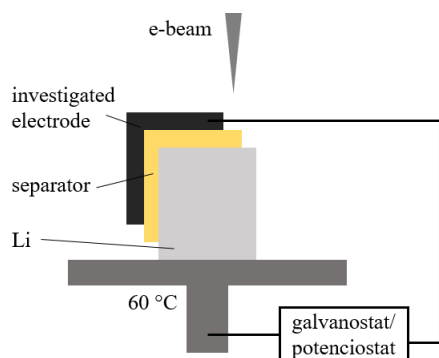


Fig. 3. Schematic drawing of the in-situ experiment – cell investigated from the side view.

Another approach is to observe from the top. In 2011, a paper was published in which the half-cell consisted of lithium metal placed on a stage connected to a microscope frame, with an ionic liquid in a separator (TFSI + LiTFSI) and SnO_2 pressed into a steel grid as the active material. The lithium and separator with electrolyte were transported from the glovebox in a hermetically insulated capsule, which was opened after pumping the SEM chamber by rotating the stage. The grid with the active material was then attached to the separator. The disadvantage of the arrangement is that the electrode is examined from the top, on the side opposite to the lithium. A schematic drawing of the cell is shown in Fig. 4. However, it was possible to observe the nanoscale structural changes in real time. Also, local charging and deposition of lithium were observed during scanning at locations far from the metal lattice (interaction with the electron beam) [18].

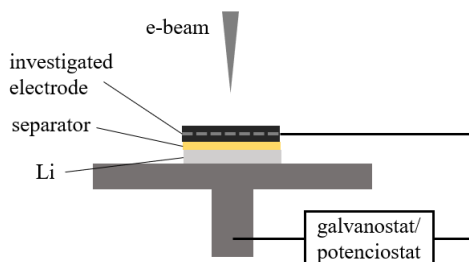


Fig. 4. Schematic drawing of the in-situ experiment – cell investigated from the top view.

Deposition of the electroactive material onto the grid can also be done electrophoretically without the need for a binder.

The 2016 work thus creates an electrode from silicon microplates in which lithium concentration could be observed by varying the contrast of the BSE image [19].

Another way of investigation is to fabricate the cell directly in the SEM chamber using FIB-SEM technology and a micromanipulation needle as a current collector (see Fig. 5 for a schematic drawing). A 2013 scientific paper describes an LTO/ionic liquid/NCA battery. A small piece of the NCA-containing electrode material was cut out using a focused ion beam (FIB), conductively and mechanically joined by assisted deposition with a micromanipulation needle, and dipped in ionic liquid. An inspection hole was cut in the middle of the electrode to observe changes during cycling [20].

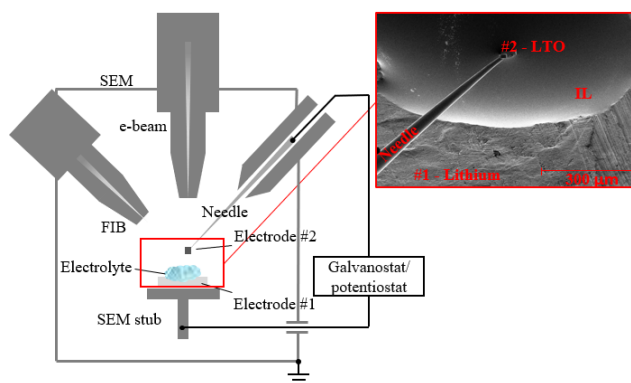


Fig. 5. Schematic drawing of the system using a micromanipulator as a current collector (left); SEM image taken during the experiment (right).

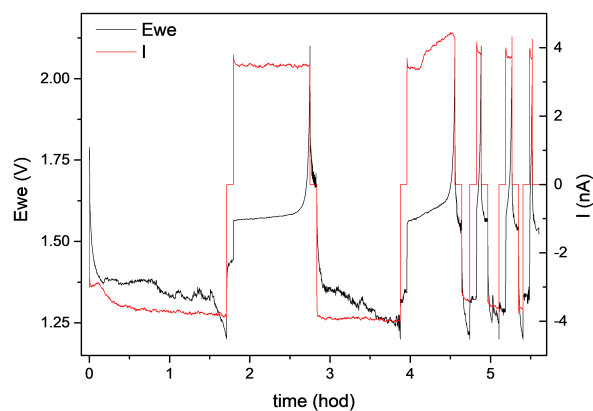


Fig. 6. Electrochemical cycling of the cell where a micromanipulator was used as a current collector. The graph shows that the capacitance decreases with each cycle.

We used this method for the construction of a lithium/ionic liquid/lithium titanate (LTO) half-cell [21]. For the experiment, we used a Scios 2 SEM (Thermo Fisher Scientific) equipped with an EasyLift micromanipulator, a gallium FIB, and a MultiChem Gas Delivery System. A piece of lithium was placed on the stub, which was electrically connected through a vacuum feedthrough to the potentiostat Biologic SP-150 as a shared reference and counter electrode. The lithium metal was placed on the stub and dropped with 1-Ethyl-3-

methylimidazolium tetrafluoroborate (EMIMBF) ionic liquid in a mixture with LiBF_6 salt in 0.5M concentration serving as the electrolyte. A chunk of LTO material was glued to the micromanipulation needle by assisted carbon deposition. The needle was modified, insulated from the microscope frame, and connected to the potentiostat as a working electrode. After dipping the LTO into the electrolyte, several cycles were successfully performed (see Fig. 6). The experiment was strongly affected by electromagnetic interference and side reactions of the lithium metal with the electrolyte. We are currently working on improvements.

The vacuum environment of SEM is convenient for the study of dendrite growth. The sample can be observed on the reaction side as a function of time without the necessity of opening the cell after cycling. Published results confirmed lithium deposition and dendrite growth at increased rates at higher currents for polymer and liquid electrolytes. In the case of sulfur-based solid-state cells, dendrite growth was also observed, although this was not predicted. However, the fact is that higher current densities can cause cracks in the solid electrolyte and hence subsequent inhomogeneous deposition of lithium [22] [23] [24].

To study dendrite growth, a special cell consisting of a pair of contacts on a wafer with deposited lithium, connected to a current source, was published in 2017 (see Fig. 7). This wafer is then attached to another wafer with a SiN_x inspection window transparent to electrons, preventing the evaporation of volatile electrolytes in a vacuum. A constant current flows through the cell and the interface between the lithium metal and the electrolyte was monitored. The effect of additives on enhancement or suppression of dendrite growth was described [28].



Fig. 7. Cell for the study of dendrite growth.

We used a similar setup for our first in-situ experiment [25]. The cell construction was performed on the surface of a MEMS chip (see Figure 8) [26]. This chip was designed for heating and biasing experiments in a SEM chamber (Thermo Fisher Scientific) [27]. The biasing contacts were used as current collectors for electroactive materials, directly connected to the potentiostat Biologic SP-150 via vacuum feedthrough. Chunks of approximately $30 \times 50 \times 20 \mu\text{m}$ were cut from the electroactive materials (metallic lithium and LTO) using FIB on Helios Hydra 5 UX DualBeam and Helios 5 UC DualBeam SEMs (Thermo Fisher Scientific). By assisted carbon deposition using the MultiChem Gas Delivery system, they were glued to an EasyLift micromanipulation needle, transferred and aligned with biasing contacts, and connected by assisted carbon deposition as well. EMIMBF ionic liquid

in a mixture with LiBF_6 salt in 0.5M concentration was used as an electrolyte, which was transferred to the area between the electrodes after their construction.

The system is very sensitive to surface contamination around the electrodes. Cell capacitance is at most tens of nAh, so even a very thin layer of redeposited material can short-circuit the battery. Care must also be taken with the amount of used electrolyte. Once the electrodes are flooded, it is no longer possible to disconnect the cell and if the electrolyte covers the investigated area, it cannot be removed and there is no possibility of further investigating this area. On the other hand, the preparation process can be well automated and have a high repeatability of results. Also, the preparation process can be managed in the SEM chamber without the need for air transfer. The heating area of the chip can also be used for the synthesis of electroactive materials which will be subsequently used for electrode preparation. We are currently dealing with this concept [25].

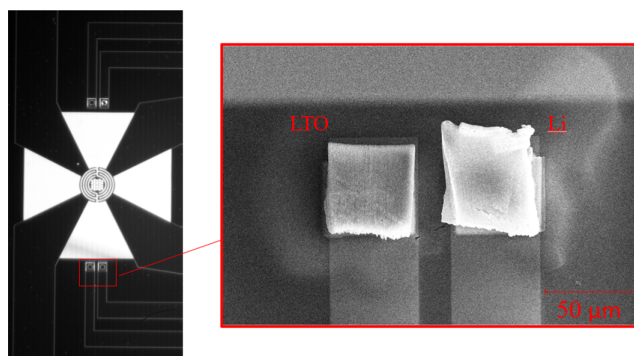


Fig. 8. MEMS chip used for the cell construction (left); Detail of the biasing contacts area with the electroactive material (right).

IV. CONCLUSION

Scanning electron microscopy provides high-resolution images of LIBs surface or cross-sections and is a powerful method for the study of most of the important processes taking place inside Li-ion batteries. It can be used both in adjusting the manufacturing process in the factory as well as in research in the laboratory.

However, the analysis has its specificities because LIBs contain sensitive materials. The vacuum environment of the SEM can limit the observation in their native state. Due to the low mechanical stability, the samples must be handled with care to distinguish preparation-induced defects from cycling-induced defects. Therefore, BIB technology is often used for sample preparation, especially for ex-situ analysis.

Although SEM alone provides detailed information on morphology and microstructure, it does not provide information about the associated electrochemical processes. For these purposes, in-situ experiments that allow SEM analysis and electrochemical cycling at the same time can be beneficial.

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