A Review of the Li-ion Battery in-situ Experiments in Scanning Electron Microscope

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Abstract—This paper focuses on the description of in-situ experiments with lithium-ion batteries in a scanning electron microscope during cycling. With these experiments, we are able to better understand the working principles and internal processes of Li-ion batteries and improve their efficiency, reliability, and safety based on this knowledge. However, conducting these experiments poses several challenges, which are described in the paper, along with ways in which they can be partially mitigated.

Keywords—Li-ion, battery, in-situ, SEM, real-time observation

I. INTRODUCTION

Lithium-ion batteries, due to their high energy density and long cycle life, have become an essential component of modern technology, powering a wide range of devices, from smartphones to electric vehicles. Nevertheless, despite their widespread use, there are still challenges related to their efficiency, safety, and lifespan that need to be addressed [1], [2]. However, it is not only about improving currently known materials and optimizing them, but also about introducing new so-called advanced Li-ion batteries. These batteries are experiencing significant advancements in materials and design. Solid-state batteries, employing a solid electrolyte, promise improved safety and energy density [3]. High-energy cathodes, including nickel-rich and lithium-rich variants, enhance overall performance [4]. Silicon anodes are being explored to boost energy density, albeit with challenges like volume changes [5].

To further optimize and improve all these Li-ion systems, it is crucial to understand the internal processes and mechanisms of these batteries, which requires detailed characterization [6].

This is where scanning electron microscopy (SEM) can be used among many other characterization techniques. SEM, which uses a focused beam of electrons to create detailed images of materials at a microscopic level, provides valuable insights into the structure and composition of the battery materials [7].

Taking this a step further, in-situ SEM allows researchers to observe and study these batteries under operating conditions, providing real-time information about the dynamic processes occurring within the batteries. This has opened new opportunities for improving the performance and safety of lithium-ion batteries [8], [9].

Although SEM has proven to be an indispensable technique for characterization, there are several problems. Achieving high resolution during battery operation can be limited, and the introduction of experimental conditions may lead to sample artifacts that affect accuracy. The field of view is often constrained, making it challenging to capture a comprehensive picture of the entire battery system. Continuous exposure to the electron beam can result in sample damage, impacting the observed properties. Additionally, the complexity of in-situ experiments, the necessity for specialized equipment, and the requirement to closely mimic actual operating conditions pose practical challenges [8], [9]. Also, the interpretation of the results demands a deep understanding of both electrochemistry and electron microscopy.

This paper explores advancements, both recent and foundational, highlighting emerging technologies that show promise in overcoming in-situ SEM-related limitations. By examining the spectrum of progress in the field, from recent innovations to longstanding methodologies, we aim to provide a comprehensive perspective on the in-situ analysis of Li-ion batteries in SEM. Through this complex examination, we endeavor to contribute significantly to the ongoing discourse surrounding battery characterization, fostering dialogue and innovation aimed at enhancing efficiency, safety, and longevity.

II. ADVANTAGES OF THE IN-SITU TECHNIQUES

In the field of lithium-ion battery research, both ex-situ and in-situ techniques play crucial roles in unraveling the mysteries of battery behavior. Ex-situ techniques involve the removal of battery components for subsequent analysis, providing valuable insights into the composition, structure, and chemical properties of the materials [10]. While ex-situ methods have been instrumental in advancing our understanding of lithium-ion batteries, they lack the ability to capture dynamic processes occurring during actual battery operation [11]. Another problem is that sample preparation for ex-situ analysis usually must take place in a box with a protective atmosphere. This is because the batteries contain materials that are sensitive to humidity, oxygen, or nitrogen. During sample preparation (battery disassembly), samples may also be damaged or degraded due to improper handling or use of excessive force [12].
These limitations are where in-situ techniques shine and offer unique advantages that significantly enhance our understanding of Li-ion batteries. SEM provides exceptional temporal resolution, enabling researchers to precisely capture rapid electrochemical changes at the micro or nanoscale. This high-resolution imaging is crucial for real-time observations of dynamic processes, such as the lithiation and delithiation of electrodes, offering direct insights into the evolution of electrode materials and the formation of solid-electrolyte interfaces (SEI) [9], [13]. Additionally, SEM allows for the direct visualization of interfaces, providing detailed information on the structural and morphological changes critical for optimizing electrode materials and electrolytes. The application of in-situ SEM, with its ability to provide real-time, high-resolution imaging, empowers researchers to tailor battery designs and materials for improved efficiency, thereby addressing key challenges in the quest for advanced lithium-ion battery technologies [9], [8].

III. SEM INSTRUMENTATION FOR IN-SITU ANALYSIS

An electron microscope consists of several important parts. At its core, a SEM instrument consists of an electron gun that emits a focused beam generated via thermionic emission from a heated filament (W or LaB₆) or a field emission gun (FEG). The electron beam is then focused into a probe on the surface of the sample using an electromagnetic lens [7], [8]. The use of the FEG electron source proves more suitable for in-situ battery analyses due to its high brightness, coherence, and reduced chromatic aberration [7]. The improved stability and smaller probe size contribute to superior spatial resolution and detailed observations of dynamic processes during battery cycling [8].

Another essential part is the detectors. In addition to the classical Everhart–Thornley detector (ETD), it is advisable to use so-called in-lens detectors. These detectors are able to detect more electrons, but also electrons with lower energy, and thus improve the overall image obtained. Other necessary detectors include an EDS detector for energy dispersive spectroscopy and determining the exact material composition together with a quantitative data [7]. However, conventional EDS detectors are not capable of detecting materials with a proton number lower than 4. Therefore, if EDS analysis of lithium with a proton number of 3 is required, a special EDS detector, referred to as windowless, is needed [14]. Yet another detector that can be used for in-situ analysis of batteries is electron back scattered diffraction detector (EBSD). With this detector, phase changes and orientation changes in the material structure can be observed [8].

Other useful tools that can be used in SEM for in-situ analyses include various micromanipulators, which can be used to assemble an electrochemical cell directly in the microscope chamber or, in the case of suitable shielding and wiring, also as current and voltage probes [15]. There can also be various electrochemical probes to connect the battery to the potentiostat. For the investigation of mechanical properties, it is possible to use nanintenders [16]. Other useful tools and instrumentation for in-situ battery research include, e.g., heating or cooling stages [17], gas injection systems [18], or systems for sample transfer in a protective atmosphere [8].

All of the above equipment can be purchased from vendors and easily configured for the purpose of the experiment. However, special holders and electrochemical cells are also needed for in-situ battery analysis, which are not commonly sold, and scientists are usually left to construct them on their own. Configurations of these electrochemical cells can be divided into two groups: open cells and liquid cells (closed cells) [9].

The open cell configuration is easier to manufacture and assemble but has the disadvantage that the entire battery is exposed to the environmental conditions of the microscope. If a deep vacuum is used for imaging, the use of this cell precludes the use of conventional electrolytes, i.e., lithium salts in organic solvents, which would evaporate in the chamber. Thus, this open configuration is suitable for batteries with a solid-state electrolyte or batteries with an ionic liquid electrolyte that does not evaporate in a vacuum [9]. The main advantage of this configuration is the high resolution of the images. However, the high resolution decreases with the use of low-vac mode, or environmental scanning electron microscope (ESEM), which can be used to reduce sample charging or to get closer to the battery's real operational conditions [19], [20].

On the other hand, the completely closed and sealed design of the liquid cells allows the use of ether- and ester-based electrolytes. This can be used, e.g., to observe the formation and evolution of the SEI layer in these electrolytes or for in-situ analysis of the battery under the real conditions of the commonly used electrolytes. The observation itself is then performed through a silicon nitride (SiN) observation window. The main disadvantage of this configuration then lies in this observation window, which significantly reduces the spatial resolution [9]. This configuration is also more challenging to assemble accurately, and the electrochemical cell cannot be modified after sealing, which is done with a resin epoxy. Another practical problem lies in the electrolyte layer that can form just below the observation window, making it impossible to image the electrode structure itself and due to closed construction, the excess electrolyte cannot be removed [21].

IV. LI-ION IN-SITU EXPERIMENTS

The first in-situ observation of a Li-ion battery was conducted by Braudy and Armand [22] in 1987. The authors delineated the fundamental principles and procedures for sample preparation for in-situ observations. In their experiment, lithium metal served as the anode, and the cathode explored various materials, including titanium dioxide (TiO₂), vanadium oxide (V₂O₅), and iron(II) sulfide (FeS). A polymeric electrolyte, consisting of a polyether with an ethylene oxide base and lithium perchlorate (LiClO₄) salt, functioned as the separator. Assembling the battery in a drybox using the hot-pressing method, the authors then transferred it into the electron microscope chamber. The sample orientation enabled the side-view observation of the sandwich structure. The research yielded significant results, particularly in observing the phase changes of TiO₂ and V₂O₅ during cycling. It was observed that the TiO₂ structure remained remarkably stable, whereas the V₂O₅ structure exhibited cracking. The cathode containing FeS underwent significant changes during the cycling, resulting in a breakdown of its structure.
Some research teams have tried to solve the problem of electrolyte evaporation using the ESEM. One notable experiment from 2006, conducted by Rainmann et al. [23] in ESEM with Ar and pressure of 200 Pa. Authors aimed to observe volume changes and potential mechanical damage on the anode of a Li-ion battery. The anode was a mixture of Sn, Super P, and polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) as a binder. The whole mixture was coated on a stainless-steel grid to achieve better wetting and also to be able to observe the active material of the anode. Lithium metal served as the counter electrode. Between the electrodes was an unspecified type of separator soaked with electrolyte. Unfortunately, the exact electrolyte details were not specified. However, ethylene carbonate (EC) and propylene carbonate (PC) were mentioned as the used solvents due to their higher boiling points. The researchers designed a custom electrochemical cell made of polypropylene, which can be seen in Figure 1. The main feature is that the sample placed in the holder is covered with a mylar film, which has a very small hole for the passage of electrons. In this way, they combined the advantages of liquid and closed cells. They used electrolyte with common solvents and were also able to maintain high spatial resolution due to the small observing window. Another feature is the system for keeping any vapor from the electrolyte inside the cell from escaping through the viewing hole. Finally, the authors were able to observe high-resolution changes in the anode structure, proving the functionality of their cell design.

In 2019 Shi et al. [19] introduced interesting experiment. This time, the authors decided to build a half cell and used lithium metal as the counter electrode. A composite of Si, graphite, the conductive additive C65, and a carboxymethyl cellulose (CMC) binder coated on copper foil current collector was then used as the anode. The electrodes were separated by a Whatman glass separator that was soaked in ionic liquid electrolyte (10 wt.% bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM TFSI). The aim of the work was to compare two types of working electrodes, namely unstructured S/C composite and 3D-line structured Si/C composite, into which channels were made with a laser. Assembling the cells took place in a glove box with argon atmosphere, and the arrangement was placed in the microscope chamber for side-view observations as shown in Figure 3. The results showed that the 3D-structured S/C electrode is more suitable for several reasons, among the main being better mechanical resistance to prevent separation from the current collector. Moreover, the channels enlarged the contact area of the electrodes and improved the utilization of anode materials. This greatly increased the charge capacity of 3D-line-structured anodes.
Another paper from 2019 was published by Tsuda et al. [24]. Authors introduced another in-situ experiment with a different open-cell configuration. The experimental setup featured a glass plate as the foundation, upon which the cathode, lithium cobalt oxide (LiCoO₂), on an aluminum current collector was positioned. Two Whatman glass separators were then layered on the cathode, between which a Ni wire was used as a reference electrode. The cathode, composed of Si particles deposited on a copper grid through electrophoretic deposition (EPD), was subsequently added to the top of the prepared sample. Whole battery structure can be observed in Figure 4. An ionic liquid, [C2mim] [FSA] with 1.0 M Li [TFSA] and [Li(G4)] [TFSA], served as the electrolyte. This innovative three electrode design allowed for unique observations and insights into the behavior of the Li-ion battery components during cycling, even though only the anode could be observed from the top view. The authors were able to observe changes in the morphology and phase changes of Si nanoparticles, which they were able to contrast with the discharge and charge curves. They also presented the strength of the three-electrode in-situ battery measurement technique.

In 2020 Kaboli et al. [25] published a study in which they focused on detecting the cause of solid-state Li-ion battery failure. The electrolyte in this case was a solid polymer electrolyte (SPE), which consisted of polyethylene oxide (PEO) and LiTFSI in a molar ratio of 30:1. Lithium nickel manganese cobalt oxides (NMC 622) was used as the cathode, and lithium metal was used as the counter electrode. From the abovementioned components, an electrochemical cell was assembled in a dry room, as indicated in Figure 5. The sample was then enclosed in nonconductive resin. The publication also included an experiment to exclude reactions between the used resin and the electrochemical component at room temperature and at 50 °C. Their results showed that no chemical reactions occurred between the sample and the resin enclosure. After the resin had cured, the sample was transferred to a cryo-microtomy machine, where the cross section was prepared. During the preparation of the cross section and polishing, care was taken to ensure that the surface was not contaminated, and therefore it was constantly flushed with argon. The sample thus prepared was then placed in the chamber of the electron microscope. The sample then had to be fixed in the chamber using nonconducting plastic plates, which also set the pressure on the measured cell, which is important for batteries with SPE. The sample was then heated to 50 °C, and after 24 hours of tempering, electrochemical measurements began.

During a cycling, the authors were able to discover the main cause of the failures that occur with these types of batteries. The main cause is the gradual thinning of the electrolyte, which has thinned from the original 23 um to 5 um during the cycling. The authors also processed the same data for the NMC cathode and lithium metal. While NMC changed its thickness periodically depending on charging and discharging, the thickness of metallic lithium was almost constant during the whole cycling. [25]

V. CONCLUSION

In summary, lithium-ion batteries stand as indispensable components in modern technology, owing to their high energy density and prolonged cycle life. However, persistent challenges in efficiency, safety, and lifespan require ongoing exploration and innovation. The evolution toward Li-ion and advanced Li-ion batteries brings both promise and difficulty, requiring a complex understanding of internal mechanisms for meaningful progress.

This paper has delved into the critical role of in-situ scanning electron microscopy (SEM) in unraveling the complexity of lithium-ion batteries. Despite facing challenges like spatial resolution limitations and sample artifacts, in-situ SEM provides invaluable real-time insights into dynamic battery processes during operation. The discussion extends beyond challenges to highlight recent and foundational advancements, emphasizing emerging technologies that exhibit potential for overcoming these limitations.

Moreover, the suitability of individual SEM components for in-situ battery analyses has been evaluated, shedding light on the significance of additional equipment tailored for in-situ SEM analysis. A focal point is the electrochemical cell for in-situ SEM analysis and its configurations, with the open configuration emerging as the most common choice for its versatility in examining various materials with high spatial resolution. However, it's crucial to acknowledge the limitations of this configuration, particularly its inability to accommodate organic solvent-based electrolytes. For this reason, batteries with an ionic liquid or solid-state electrolyte are most often investigated in this type of cell.

This review also confirms that there is a continued need to actively discuss the improvement of these in-situ techniques in SEM and focus on the development of additional equipment for these analyses that could make them easier and more efficient. It is also necessary to develop new tools that can enable a whole new branch of experiments that can reveal more about the internal process of not only Li-ion batteries but also post-Li-ion batteries.
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REFERENCES


