TEM sample preparation for Li-ion secondary battery using ion slicer

JungSik Park (jspark@jeol.co.kr)
JEOL Korea https://orcid.org/0000-0002-7805-4282

Yoon-Jung Kang
Hanyang University Industry University Cooperation Foundation

SunEui Choi
Korea Electronics Technology Institute

YongNam Jo
Korea Electronics Technology Institute

Research Article

Keywords: Ion slicer, Lithium-ion secondary battery, Backside-ion milling, TEM sample preparation, Broad argon ion beam (BIB), High-resolution (HR) STEM

DOI: https://doi.org/10.21203/rs.3.rs-880065/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
TEM sample preparation for Li-ion secondary battery using ion slicer

JungSik Park¹*, Yoon-Jung Kang², SunEui Choi³ and YongNam Jo³

1 Product Application Support, JEOL Korea, Seoul 05355, Korea
2 Industry University Cooperation Foundation, Hanyang University, Seoul 04763, Korea
3 Korea Electronics Technology Institute, Gyeonggi-do 13509, Korea

*Correspondence: jspark@jeol.co.kr
Abstract
The main purpose in this paper is a sample preparation of transmission electron microscopy (TEM) for the lithium-ion secondary battery in the form of micro-sized powders. To avoid artefacts of the TEM sample preparation, the use of ion slicer milling for thinning and maintaining the intrinsic structure is described. Argon-ion milling techniques have been widely examined to make the optimized specimen, which makes TEM analysis more reliable. In the past few years, the correction of spherical aberration (Cs) in scanning transmission electron microscopy (STEM) has been developing rapidly, that results in the direct observation with the atomic level resolution not only for the high acceleration voltage but also its deaccelerated voltage as well. Especially, low-kV application has been markedly increased that needs the sufficient-transparent specimen without the structural distortion during the process of the sample preparation. In this study, the sample preparation for the high-resolution STEM observation has been greatly accomplished and investigations of its crystal integrity are carried out by Cs-corrected STEM.

Keywords: Ion slicer, Lithium-ion secondary battery, Backside-ion milling, TEM sample preparation, Broad argon ion beam (BIB), High-resolution (HR) STEM
Introduction

Lithium-ion secondary batteries comprising a positive electrode, a negative electrode, and an electrolyte have been the most revolutionary material as a type of rechargeable battery with the high capacity for the energy density per unit area. Generally, the negative electrode mainly consists of carbon, which is a theoretical capacity of 372mAh/g in the fully lithiated state (Shao, 2020). To further increase the gravimetric and volumetric capacity, silicon has been studied as one of the most promising negative electrode materials due to its higher theoretical capacity of 3579mAh/g (Obrovac, 2004; Key, 2009; Miao). Positive electrode materials including transition metals and lithium-ionic composites containing Li, Mn, Ni, Co, and O atoms play an important role in determining the performance and its cost. For that reason, it is essential to accurately identify the structural information of electrode materials at the atomic-level. Although many significant researches for the characterization of the lithium-ion battery have been contributed, but identifying materials for revealing the atomic-scale mechanism of the lithium-ion secondary battery has been rarely reported so far (Pender, 2020; Yamada, 2013; Miao, 2019; Nitta, 2015). The reason that I pointed out is because of the difficulty in preparing a homogeneous TEM specimen against the structural distortion. In general, lithium-ion secondary batteries are synthesized in the powder form with a size of several to tens micrometers, and it is not easy to make them as the uniform structure with a thickness of 100nm or less. If the powder has a size of 100nm or less, it can be easily dispersed in a solvent and placed on a grid to be sufficiently transmitted and observed in TEM, however, in the case of secondary batteries, due to the size restriction, it must be made thin enough by the cross-sectional operation to allow electrons to penetrate through the specimen. Generally, the epoxy molding method has been used for preparing powder samples, but there is a problem in processing of having resulted from the inhomogeneous phase/chemical distribution due to the
difference in the milling rate between epoxy and powder (Jiang, 2019). And the curtaining effect occurs due to thickness variation according to the powder shape, thereby, the condition of the sample in the local area could be severely deteriorated. In order to overcome these problems, the broad argon ion beam (hereinafter referred to as BIB) and the backside-ion milling by means of ion slicer were introduced (Kato, 2004). Current research focused on the practical aspects for the experimental analysis, due to the problem of beam damage caused by the high acceleration voltage in TEM analysis, the application fields of acceleration voltages of 100kV or less have greatly increased not only for secondary batteries, but also for 2D materials, semiconductor electronic circuit samples micronized to several nanometers, and so on. TEM analysis at a low acceleration voltage has a desirable thickness of 50nm or less by reason of the electron transmittance and the chromatic aberration (Sasaki, 2010). Another widely used technique to perform the TEM sample preparation called focused-ion beam (FIB) that enables the specimen to be thinned after obtaining cross-sectioned lamella by the raster scan on the bulk sample using gallium ions generated from liquid metal ion source (LMIS). Basically, it has a scanning electron microscope-based column, so it has a great advantage of targeting the region of interest (ROI) of the sample while observing the electron image, but it was often observed that artefacts such as sample alterations like the redeposition, the amorphization, vacancies and the gallium implantation from the reaction between the heavy gallium ions and the sample (Basnar, 2003; Roediger, 2011). In this study, lithium-ion secondary battery powders were preliminarily milled in the initial thinning and then finally milled in the backside-ion milling using the ion slicer and evaluate it with a spherical aberration corrected STEM. The ion slicer uses BIB and protects the surface by the inserted shield belt on the center of the area to be milled. Thinning was performed by sequentially irradiating both
sides with incident ions at a low angle and simultaneously controlling the stage to create a rocking beam. And because it is processed with mechanical polishing down to 100 micrometers-thickness (μmt), it can be easily handling and can prevent the deformation of the lattice structure caused by the mechanical polishing. Since the conventional ion milling method has been used with mechanical polishing down to 10μmt or less, consequently, artefacts were often appeared and making it difficult to observe in TEM.

**Experimental methods**

LiMn2O3 powders used staring in composite preparation was supplied by Hanyang university. Figure. 1 (a) shows a method for preparing an ion slicer sample of LiMn2O4 powders that mixed with the G2 epoxy resin/hardener in a ratio of 10:1 to make the powder/epoxy blend. This epoxy mixture was placed on the Si wafer and then the cover-glass was finally covered. The thickness of the cover-glass affects the milling time of the argon beam reaching to the resin/powder blend, which is the region of interest, so 100μmt of the cover-glass is recommended for the appropriate proceeding during the secondary operation of backside-ion milling. For the homogeneous milling, the internal porous structure should be avoided and it is also useful to use pressure tongs or decompression devices as a method of removing air bubbles in the blend, then, sufficiently harden it on the hot plate for about 20-30 minutes at temperature of 100°C. The sample thus obtained was cut into 2.8mm x 1mm x 500μm size using a diamond saw, then, polished until the 1mm-thick sample becomes the 100μm-thickness with a mechanical polisher using the diamond paper (abrasive grit size: 30μm) as shown in fig. 1(b). And the 100μmt-thinned sample was loaded on the holder stub of the ion slicer (JEOL, Japan) and the argon ion milling was proceeded after adjusting the shield belt to the center. A
preliminary milling in a large area by BIB was performed for about 3 hours under the following conditions; the acceleration voltage and the incident beam angle were 6kV and 0.4°, respectively. After that, the specimen holder turned upside down and mounted it in order to implement the backside-ion milling at 6kV and 4° for about 1 hour during the ion beam etching by being milled from the bottom of the cover-glass to the composite section. A post-milling in ensuring that powders with relatively high strength compared to resin can be homogeneously processed was sequentially performed at 3.5° and 3° for 20 minutes, respectively. The final milling step was performed under the acceleration voltage of 1kV for 10 minutes. For the STEM observation, the processed sample was carefully mounted in a reinforcement ring with a diameter of 3mm. Finally, the sample area in thin enough for the electron penetration was evaluated through a probe aberration corrected 200kV STEM with cold field emission (JEM-ARM200CF; JEOL, Japan) with 0.3eV energy resolution.

**Results and discussion**

Fig.3 shows high-angle annular dark field (HAADF)-STEM images at low magnification shown as the whole of the sample made by FIB and Ion slicer, respectively. The vertical curtaining effect generated by the surface roughness was observed with vertically parallel to the ion beam direction as shown in fig. 3(a). On the contrary, the HAADF STEM image of the specimen prepared by Ion slicer using BIB does not appear the curtaining effect inside the cross-sectional area, even in the same sample having a similar shape as shown in fig. 3(b). Fig. 4 is a high-resolution HAADF-STEM image taken to observe the structural state and information at the atomic-level. Fig. 4(a) is an image taken from the surface of the powder, and the surface side of the powder was milled sufficiently so that the atomic arrangement was
clearly observed, but it gradually deteriorates toward the inside. This was caused by the
difference in the milling rate of resin/powder, and has long been considered as an obstacle
problem in the TEM sample preparation for powder samples. On the other hand, In the case of
the sample processed by the BIB technique as shown in fig. 4(b), the cross-sectional ion milling
was processed cleanly and completely without any deformation or bending of the sample even
in the inner region. Ion slicer has a shield belt in the center of the area to be thinned, so it not
only protects the surface, but also enables that the curtaining effect does not occur because the
uniformly dispersed argon ion beam hits the area to be thinned. In addition, the phenomenon
caused by the milling rate difference in the powder/resin sample was significantly reduced. In
order to identify the curtaining effect generated in the FIB sample, high-resolution HAADF-
STEM images are obtained at high magnification. Fig. 5 sequentially shows the area where the
curtaining effect occurred and the internal atomic structure was observed while magnifying
from (a) to (f). It can be seen that the curtaining effect was severely occupied in the magnified
image of (b) contrary to the low magnification of (a). In the high-resolution images from fig.
7(d) to (f), it can be seen that the area where the curtaining effect occurred is relatively thin by
means of the dark-contrast in HAADF imaging. And the thickness deviation, and structural
defformation had been occurred due to the damage caused by the gallium ion beam. In practice,
this phenomenon poses problems for intrinsically interpreting the crystallographic structure.
To avoid the curtaining effect, a sample was processed using BIB and high-resolution HAADF-
STEM images and annular bright field (ABF)-STEM as shown in fig. 6(a) and fig. 6(b) were
obtained with the beam direction [311]. Based on the results, the curtaining effect was
significantly reduced, but the surface damage and the contamination were observed. In
particular, it can be seen that the atomic arrangement was not clearly observed in the ABF
image including the phase contrast. To solve this problem, the backside-ion milling was performed as a method of reducing the surface damage and the contamination. Hence, the conventional and backside-ion milling were compared and evaluated with high-resolution HAADF-STEM as shown in fig. 7. The backside-ion milling in which the structure was more clearly observed than the conventional ion milling. It can be seen that the surface was processed thinner as well as the difference in the surface damage and the contamination. Further, to observe the light element atomic column, HAADF and ABF STEM were simultaneously obtained to analyze the structure. Fig. 8(a) and (b) are high-resolution HAADF- and ABF-STEM images taken with the beam direction of [110], and the atomic modeling for the LiMn2O4 crystal structure is shown in fig. 8(c). Due to the Z-contrast, which is the scattering scales as approximately a $Z^2$ dependence for common scattering of the HAADF image, the distribution of Mn, which is as heavy element, can be easily recognized, but Li and O, which are light elements, are not observed (Pennycook, 1989). Therefore, when observing ABF image with relatively low atomic number dependence with the electron channeling effect, not only light elements but also heavy elements can be observed (Findlay, 2016). By directly comparing these two images, the column sites of Li and O were understood and it can be confirmed that they corresponded to the atomic model of the LiMn2O3 structure viewed from the spinel crystallographic orientation. Fig 9 shows the HR-HAADF (a) and HR-ABF (b) images viewed with the beam direction of [010]. The oxygen and manganese sites were all clearly visible on the lower left of its cropped images.

**Conclusions**

Through this study, the TEM sample preparation of the secondary battery powder which was
usually hard to handle was carried out using the backside-ion milling technique. It has been confirmed that this technique facilitates TEM specimen having thin and uniform. For the precise analysis, it is important to prepare the specimen containing the intrinsic state of materials. Furthermore, the ultra-thin TEM sample preparation technique has been gradually essential for various applications like the low-acceleration voltage analysis, electron energy-loss spectroscopy (EELS) analysis for the 0-500eV spectrum region containing vibrational (phonon) losses, etc.

Acknowledgements
No applicable.

Authors’ contributions
SEC and YNJ contributed to the success of sample preparation of Ion slicer. YJK performed the FIB work and helped organize the experiment for Cs-STEM. The author(s) read and approved the final manuscript.

Funding
No funding was received for this work.

Availability of data and materials
The data and materials described in this paper are available from the corresponding author on reasonable request.

Competing interests
No potential conflict of interest relevant to this article was reported.
References

Basnar B, Lugstein A, Wanzenboeck H, Langfischer H, Bertagnolli E, and Gornik E (2003) Focused ion beam induced surface amorphization and sputter processes. *J. Vac. Sci. Technol. B* **21** 927-930.

Findlay S D, Huang R, Ishikawa T, Shibata N, and Ikuhara Y (2016) Direct visualization of lithium via annular bright field scanning transmission electron microscopy: a review. *Microscopy* **66** 3-14.

Jiang R, Li M, Yao Y, Guan J, and Lu H (2019) Application of BIB polishing technology in cross-section preparation of porous, layered and powder materials: A review. *Front. Mater. Sci.* **13** 107-125.

Kato N I (2004) Reducing focused ion beam damage to transmission electron microscopy samples *J. Electron Microsc.* **53** 451-458.

Key B, Bhattacharyya R, Morcrette M, Seznec V, Tarascon J M, and Grey C P (2009) Real-Time NMR Investigations of Structural Changes in Silicon Electrodes for Lithium-Ion Batteries. *J. Am. Chem. Soc.* **131**, 9239-9249.

Miao Y, Hynan P, Jouanne A V, and Yokochi A (2019) Current Li-Ion Battery Technologies in Electric Vehicles and Opportunities for Advancements *Energies* **12** 1074.

Nitta N, Wu F, Lee J T, and Yushin G (2015) Li-ion battery materials: present and future. *Mater. Today* **18** 252-264.

Obrovac M N, and Christensen L (2004) Structural Changes in Silicon Anodes during Lithium Insertion/Extraction. *Electrochem. Solid-State Lett.* **7** A93.

Pender J P, Jha G, Youn D H, Ziegler J M, Andoni I, Choi E J, Heller A, Dunn B S, Weiss P S, Penner R M, and Mullins C B (2020) Electrode Degradation in Lithium-Ion Batteries. *ACS Nano* **14** 1243-1295.

Pennycook S J (1989) Z-contrast stem for materials science. *Ultramicroscopy* **30** 58-69.

Roediger P, Wanzenboeck H D, Waid S, Hochleitner, and Bertagnolli (2011) Focused-ion-beam-inflicted surface amorphization and gallium implantation—new insights and removal by focused-electro-beam-induced etching. *Nanotechnology* **22** 235302

Sasaki T, Sawada H, Hosokawa F, Kohno Y, Tomita T, Kaneyama T, Kondo Y, Kimoto K, Sato Y, and Suenaga K (2010) Performance of low-voltage STEM/TEM with delta corrector and cold field emission gun *J. electron Microsc.* **59** S7-S13.
Shao G, Hanaor D A, Wang J, Kober D, Li S, Wang X, Shen X, Bekheet M F, and Gurlo A (2020) Polymer-Derived SiOC Integrated with a Graphene Aerogel As a Highly Stable Li-Ion Battery Anode. *ACS Appl. Mater. Interfaces* **12** 46045-46056.

Yamada H, Suzuki, T S, Uchikoshi T, Hozumi M, Saito T, and Sakka Y (2013) Ideal design of textured LiCoO$_2$ sintered electrode for Li-ion secondary battery. *APL Materials* **1** 042110.
Figures

Figure 1. Schematic diagrams of the sample preparation showing a procedure for LiMn2O4 powder and epoxy mixture (a) and a conventional method for cutting before ion milling (b).

Figure 1

Schematic diagrams of the sample preparation showing a procedure for LiMn2O4 powder and epoxy mixture (a) and a conventional method for cutting before ion milling (b).
Fig. 2. A schematic diagram of the preliminary and backside-ion milling of the ion slicer.

Figure 2

A schematic diagram of the preliminary and backside ion milling of the ion slicer.

Fig. 3. High-angle annular dark field STEM images of LiMn2O4 powder which are milled by the focused ion beam (a) and the ion slicer (b), respectively.
Figure 3

High angle annular dark field STEM images of LiMn2O4 powder which are milled by the focused ion beam (a) and the ion slicer (b), respectively.

Fig. 4. High-resolution HAADF STEM images showing the edge surface of the LiMn2O4 powder prepared by the FIB milling (a) and the inner area prepared by the IS milling (b).

Figure 4

High resolution HAADF STEM images showing the edge surface of the LiMn2O4 powder prepared by the FIB milling (a) and the inner area prepared by the IS milling (b).
Fig. 5. HAADF STEM image at the low magnification of the FIB specimen (a) and enlarged HAADF STEM image from the red-dotted line box (b) and green- (c), blue- (d), orange- (e), and yellow– (f) are respectively magnified at each location.

Figure 5

HAADF STEM image at the low magnification of the FIB specimen (a) and enlarged HAADF STEM image from the red dotted line box (b) and green –(c), blue –(d), orange –(e), and yellow ––(f) are respectively magnified at each location.
Fig. 6. High resolution HAADF STEM image (a) and annular bright field STEM image (b). Those images are obtained with beam direction [311] as shown in the kikuchi image (c).

Figure 6

High resolution HAADF STEM image (a) and annular bright field STEM image (b). Those images are obtained with beam direction [311] as shown in the kikuchi image (c).

Fig. 7. High resolution HAADF STEM images of the backside-ion milled (left) and the conventional ion milled (right).
Figure 7

High resolution HAADF STEM images of the backside ion milled (left) and the conventional ion milled

![Image of HAADF STEM images](image)

Fig. 8. High resolution STEM image of the IS milled specimen shows the atomic arrangement in HAADF image (a) and light elements (Li, O) are clearly seen in ABF image (b). A schematic representation of LiMn2O4 crystal structure (c).

Figure 8

High resolution STEM image of the IS milled specimen shows the atomic arrangement in HAADF image (a) and light elements (Li, O) are clearly seen in ABF image (b). A schematic representation of LiMn2O4 crystal structure
Fig. 9. High resolution HAADF STEM image (a) and annular bright field image (b).

**Figure 9**

High resolution HAADF STEM image (a) and annular bright field image (b).