Surface Imaging by ABF-STEM: Lithium Ions in Diffusion Channel of LIB Electrode Materials

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Lithium ions in LiMn$_2$O$_4$ crystals have been shown observable by using an aberration corrected electron microscope (R005) which has achieved a sub-50 pm resolution. Based on the annular bright-field image of the observed image, surface imaging of a LiMn$_2$O$_4$ crystal is discussed through simulation. The present simulation showed that ABF images with large convergence angles are sensitive to the top surface profile. A vacancy located at the top surface of the lithium or manganese atomic columns can be observable with contrast reduced by 10-25% from the columns without vacancy. [DOI: 10.1380/ejssnt.2012.454]

Keywords: Surface structure, morphology, roughness, and topography; Scanning transmission electron microscopy (STEM); Energy technology

I. INTRODUCTION

Recent development of electric vehicles has required more powerful, stable and lighter batteries. Lithium ion battery (LIB) is the most promising power supply because of high energy density and stability of power [1–3]. But the short lifetime of present LIBs is one of important subjects to be improved [4]. The lifetime of LIB is known to be determined by the interface condition between electrode and electrolyte [5]. To improve the interface stability, surface controlling [6–8] and surface profiling methods have been devised. Surface XRD has revealed the surface structure change during battery performance [9]. AFM and SEM have given information about morphology change [10–12]. However, direct detecting of lithium ions had not been achieved.

Recent electron microscopy studies have suggested the possibility of direct observation of lithium ion diffusion. Lithium ions have been imaged in real space at atomic level by annular bright field (ABF) imaging of the aberration corrected scanning transmission electron microscope (AbC-STEM) [13, 14]. Furthermore, it has been reported that the number of lithium ions in a diffusion channel was countable in ABF images by quantitative STEM [15].

The modern AbC STEM give not only better spatial resolution, but also improved depth resolution due to a reduced depth of focus (DOF). With this advantage, annular dark field imaging of STEM has been applied to slice the sample optically to obtain 3D information of impurities in the sample [16, 17].

In this report, we studied characteristics of ABF imaging with a large convergence angle and the possibility of surface imaging, imaging of vacancies at the top surface of specimen. We show that lithium ions in a LiMn$_2$O$_4$ crystal are observable in ABF images by an AbC-STEM of a 50 pm resolution (R005) [18]. The observed images are reproducible by multi-slice simulation. For large convergence angles of the incident beam, focused on the top surface, the simulated images of LiMn$_2$O$_4$ surfaces show the image contrast sensitive to the vacancy at the top surface due to the shallow depth of focus (DOF): Lithium ion vacancy and manganese ion vacancy, locating at the top surface, give 20% and 25% reduction of the column contrast, respectively.

II. ABF IMAGE OF A LIMN$_2$O$_4$ CRYSTAL: SIMULATION AND EXPERIMENT

A. Atomic structure of a LiMn$_2$O$_4$ crystal

A LiMn$_2$O$_4$ crystal, a well-known positive electrode material of LIB, has a spinel structure (space group: Fd3m, a = 0.8245 nm [19]). Manganese ions are located in octahedral sites and lithium ions, tetrahedral sites in the cubic close packed (ccp) array of oxygen ions. Figure 1(a) shows the LiMn$_2$O$_4$ crystal viewed from the [110] direction. Each atomic column contains a single element. Manganese columns (blue sphere) are positioned on the side of rhombic unit, oxygen columns (grey sphere) are positioned at both sides of manganese columns. Lithium columns (red one) are positioned along the long diagonal of the rhombic unit. In this view, there are two kinds of manganese columns, Mnα and Mnβ: Mnα column has two manganese ions per 0.583 nm along the incident beam (001) direction.
FIG. 1: (a) Scheme of a LiMn$_2$O$_4$ crystal viewed from the [110] direction. Polyhedrons indicate MnO$_6$ units. Manganese, oxygen and lithium ions are displayed by spheres of different colors (manganese, blue; oxygen, gray; lithium, red). The rhombus indicates the unit area of a LiMn$_2$O$_4$ crystal, of which the short and long diagonal are 0.583 nm and 0.824 nm, respectively. (b) Perspective view of a LiMn$_2$O$_4$ crystal having ion vacancies at the top surface. The yellow circles indicate ion vacancies of manganese (blue dashed circle) and lithium (red).

direction, while Mn$\beta$ column has one. In an oxygen column, two oxygen ions are positioned per 0.583 nm along the incident beam direction and in a lithium column, one lithium ion. The lithium columns are known as the diffusion channel of ion conduction [20]; when a lithium ion diffuses out from the diffusion channel, a vacancy is created in the channel. Diffusion of lithium can induce displacement of manganese ions. The model structure of a LiMn$_2$O$_4$ crystal after creation of a vacancy is shown in Fig. 1(b).

Each ion vacancy is positioned at the top surface: dashed circles correspond a manganese vacancy and a lithium vacancy, respectively.

B. DOF of ABF image: experiment

A LiMn$_2$O$_4$ crystal was observed by ABF imaging, using an AbC-STEM (R005 electron microscope) [18]. The electron probe was accelerated at 300 kV and transmitted the LiMn$_2$O$_4$ sample along the [110] direction. A series of ABF images was obtained with a 2-nm defocus step in order to investigate the depth of focus. The convergence semi-angle ($\alpha$) of the incident electron probe was chosen to be 24 mrad and 30 mrad. The detector inner-outer semi-angle, $\beta$, was 12-24 mrad (for $\alpha = 24$ mrad) and 15-30 mrad (for $\alpha = 30$ mrad).

Figure 2(a) shows a through-focus series of ABF images observed from the [110] direction with the convergence angle of 24 mrad. All atomic columns including lithium columns appear as dark dots at over-focus ($0 \leq f \leq 4$ nm). Mn$\alpha$ columns are positioned at the corner of the rhombic unit marked by black lines. As the defocus goes into under-focus, column contrast changes from dark to bright. We defined the zero defocus (0 nm) as the defocus value where the probe is focused on the top surface of the specimen and the plus (+) defocus as the defocus value where the probe is focused over the top surface [21]. Within the defocus range of 0-4 nm, ABF images show clear contrast. Beyond that defocus range, images become blurred and atomic columns are not distinguished clearly. The defocus range, in which dark contrast of columns remains to be a half of the maximum contrast, is defined as the depth of focus (DOF) [22]. The ABF images obtained with the convergence angle of 30 mrad shows similar contrast change, but gives shallower DOF. As shown in Fig. 2(b), clear images were obtained for the defocus range of 0-2 nm. The observed DOF values for 24 and 30 mrad are plotted by triangles in Fig. 3(b) with error bar.

The observed images showed firstly that the optimum focus giving the maximum contrast is over-focus regime, which decreased as the convergence angle increased. Secondly, the ABF images at 24 and 30 mrad showed that the dark contrast of atomic columns was proportional to the number of atoms aligned in the column, as reported in the previous paper [15].
FIG. 3: (a) Defocus series of simulated image of a LiMn$_2$O$_4$ crystal for a convergence angle (α) of 24 and 30 mrad. The film thickness is 3 nm. The range of DOF is shown by white region. (b) The plot of DOF as a function of the convergence angle of the incident electron beam. Theoretical equation is referred from Ref. [16].

C. DOF of ABF image: simulation

The theoretical calculation of STEM image of a LiMn$_2$O$_4$ crystal was performed under the same imaging condition with the experiment. The simulated ABF images show coincidence with the experimental images. Following the accordance between the experiments and simulations, we calculated the ABF images of a large convergence angle to find imaging conditions for detection of a surface ion vacancy.

The calculation was performed with xHREM program [23] based on Multi-slice method. The detector semi-angle, β, was α/2 ≤ β ≤ α (α: the convergence semi-angle of the incident beam). The thermal diffusion scattering absorptive potential approximation was included with Weikenmeier-Kohl scattering factor. The Debye-Waller factors of manganese, oxygen, and lithium were assumed to be 0.84, 1.11, and 1.07 Å$^2$, respectively [19]. The slice thickness was 0.291 nm in the [110] direction. The cut-off scattering vector $\sin \theta_B/\lambda$ was 4.5 Å$^{-1}$, where $\theta_B$ is the Bragg-angle and $\lambda$ is the electron wavelength at 300 keV ($\lambda = 0.00197$ nm). The observed images were reproduced after convolving a Gaussian function to the calculated one. Gaussian function with a FWHM = 65 pm reproduced the experimental images of 24 mrad, and those of 30 mrad [24]. The Gaussian function, effective source size [24], represents the blur due to residual aberrations, chromatic aberration, statistic noise and instrumental noises.

The simulated images for α = 24, 30, 50, and 100 mrad are summarized in Fig. 3(a). The simulated images of α = 24 and 30 mrad reproduce the experimental images, where all atomic columns appear as dark dots at over-focuses. As the convergence angle of the probe increases, DOF of ABF images becomes shallower. Then, well-resolved ABF image can be obtained only for the probe focused at the top surface of specimen. It imposes that the ABF image with a large convergence angle, 50-100 mrad, is sensitive to the top surface profile.

III. SURFACE ABF-IMAGING OF LiMn$_2$O$_4$

A. Imaging manganese vacancy at surface

ABF images were calculated for large convergence angles of 50, 70, and 100 mrad. The defocus value was zero. Figure 4 shows simulated ABF images of manganese columns with and without one vacancy at the top surface. The upper panels of Figs. 4(a) and (b) are simulated images of the model structure illustrated in Fig. 1(b) with 100 mrad-convergence angle. In Fig. 4(a), oxygen and Mnβ columns in the rectangular area align alternatively from the left to the right. The second Mnβ column from the left has one vacancy at the top surface. Although the Mn columns with and without a vacancy appear dark contrast, the intensity profile shows that one vacancy reduces the column contrast by 25%.

The simulated image of a 5nm-thick model is shown in Fig. 4(b). The contrast of Mnβ with a vacancy decreases by roughly 25% from that without vacancy. For the case of one manganese vacancy positioned at the middle of the column or at the bottom surface, the column contrast reduced less than 3%. Thus, one vacancy only at the top surface reduces the column contrast regardless to the film thickness. A smaller convergence angle of 50 mrad gave the contrast decrease by 10%, which can also be useful for detecting manganese vacancy at the top surface.
FIG. 5: Simulated ABF images of one lithium vacancy at the top surface: (a) 2 nm-thick and (b) 5 nm-thick LiMn$_2$O$_4$ crystal. The convergence semi-angle of the incident beam is 100 mrad. The number in bracket is the number of ions in the lithium column without vacancy for given film thickness. Intensity profiles show image contrast of lithium columns in a red rectangle of each ABF image. Solid horizontal line in the profile is the image intensity of the columns without vacancy and, dashed line is the reference intensity.

B. Imaging lithium vacancy at surface

Figure 5 shows the simulated images of the model with one lithium vacancy in the lithium diffusion channel (Fig. 1(b)). The convergence angle of incident beam was 100 mrad. In the area of the red rectangle in Fig. 5(a), the lithium column at the left side has one lithium vacancy at the top surface. The other lithium column contains no vacancy (four lithium ions within the film thickness of 2 nm). The lithium column with a vacancy gives less contrast than the other (without vacancy), as seen in the line profile. One lithium vacancy at the top surface reduced the contrast by roughly 20%. Contrast decrease is the same amount for a 5 nm-thick model (Fig. 5(b)). For the case of one lithium vacancy positioned at middle of the column or at the bottom surface, the column contrast was not reduced more than 3%. Thus, a lithium vacancy at the top surface can be observed with a decreased column contrast. As the convergence angle became small, the contrast of the vacancy at the top surface reduced: 15% with 70 mrad and 20% for 100 mrad. This ABF imaging with the large convergence angle of the incident beam could provide the surface image of electrode materials of lithium ion batteries.

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IV. DISCUSSION

Surface imaging by ABF imaging with the large convergence angle is promising, although it needs further instrumental development: The convergence angle of 50 mrad at 300 kV had already been achieved [25].

Chromatic aberration gives image blurring because of energy spread of the cold emission source. The blurring is represented by convolution of Gaussian function. According to convolution theorem, Gaussian function does not alter the relative contrast relation (the ratio of the vacancy contrast to the non-vacancy column contrast) but absolute image intensity. By using monochromaterr [26, 27], and/or chromatic aberration corrector [28–30], the ABF image with high contrast can be obtained.

The optimum defocus of ABF image giving the maximum contrast is at over-focus regime, although annular dark field (ADF) image has optimum defocus at under-focus regime. Simultaneous ABF and ADF observation might give much information of the surface structure.

V. CONCLUSIONS

LiMn$_2$O$_4$ crystal was observed by ABF imaging with an aberration corrected STEM. In ABF images, all atomic columns including lithium columns are visible as dark dots at over-focuses. As the convergence angle increases, the optimum over-focus giving the maximum intensity approaches to zero-focus. The depth of focus (DOF) decreases, then, and ABF image becomes sensitive to the structure of the top surface: A manganese ion vacancy at the top surface gives the contrast reduction, 10% for 50 mrad, and 25% for 100 mrad of the convergence angle. A lithium ion vacancy gives the contrast reduction of 15% for 70 mrad, and 20% for 100 mrad. This ABF imaging with the large convergence angle of the incident beam could provide the surface image of electrode materials of lithium ion batteries.
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