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Visualization of Lithium Atoms in LiV_2O_4 by a Spherical Aberration Corrected Electron Microscope

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Rechargeable lithium-ion batteries have been pointed out to be a key component for portable electronic devices. It has been required to visualize lithium atom behavior in and around the host materials for battery performance, because lithium ions are inserted into or extracted from the host materials during the battery operation. Lithium atomic columns in $LiCoO_2$ crystals [1] or Al_3Li precipitates [2] were resolved by retrieving the exit wave phase of the specimen from a through focal series of high-resolution transmission electron microscope (TEM) images.

In this study, we detected lithium atomic columns in LiV_2O_4 crystal of a spinel structure (lattice constant of 0.824 nm) by using our developed spherical aberration corrected electron microscope (R005) [3]. A spinel structure whose space group is ***$F_{d\text{-}3m}$*** have been one of prospective candidates as positive electrodes of batteries, since they provide a three dimensional tunnel for lithium diffusion. We visualized lithium atomic columns by annular bright field (ABF) image using an annular detector located within the bright field region, which has been proposed to show both light and heavy elements simultaneously [4]. This is contrast to HAADF image, which does not show light element such as lithium simultaneously with heavy one.

The STEM probe has a current of 10 pA and was convergent with semi-angle of 30 mrad, within the range of which the electron beam was coherent. The ABF images were obtained by detecting electrons from 20 to 30 mrad in semi-angle. The detection angle was limited by experimental limitation. The specimen for observation was prepared by desiccating a drop of its suspension on holey carbon support films. We observed lithium, vanadium and oxygen columns by viewing the crystal from the [110] direction.

When viewing LiV_2O_4 crystal from the [110] direction (Fig. 1), vanadium columns are observed at two different sites: one (V_α) is located at the rhombic lattice site indicated by purple disks and another (V_β), at the middle (bridge) site of two neighboring rhombic lattice sites. The numbers of vanadium atoms along the [110] direction is two and one per a unit cell (0.58 nm) for V_α and V_β sites, respectively. Two lithium columns like a dumbbell are located between two neighboring oxygen columns along the [001] direction between the rhombic lattice sites. The lithium atom column is by 0.103 nm separated from the oxygen column and the number of lithium atom is one along the [110] direction per unit cell.

Figure 2 (a) is an enlarged raw ABF image. Along the [001] direction (horizontal axis), two weak troughs appear between two oxygen columns, corresponding to the sites of the lithium columns. Figure 2 (b) is an enlarged processed image at the same region as Fig. 2(a). It was obtained by applying radial difference filter and also frequency filter, which passes below $(80\ \text{pm})^{-1}$ with the edge smoothed from (80 pm)$^{-1}$ to (67 pm)$^{-1}$, to the raw image. In the radial difference filter, noisy background, which is estimated as a radial average of the Fourier transform of the whole image assuming that the contribution from statistical random noise varies slowly, was subtracted. In the process image, the lithium columns appear more clearly as dark troughs.

The ABF image of LiV_2O_4 crystal was simulated using multi-slice calculation to evaluate the experimental results. And the simulated image was convoluted with Gaussian function of 16 pm full-width-at-half-maximum, since the Gaussian-probe size was estimated to be 16 pm [5]. Figure 2(c) is the simulated ABF with 3 nm thickness and 1 nm defocus. This image reproduces the observed one well. Quantitatively, the intensity ratio of the lithium column to the vanadium one at site was almost the same between the observation and simulation.

In conclusion, we visualized the lithium columns in LiV_2O_4 crystal by annular bright field (ABF) image with a spherical aberration corrected electron microscope.

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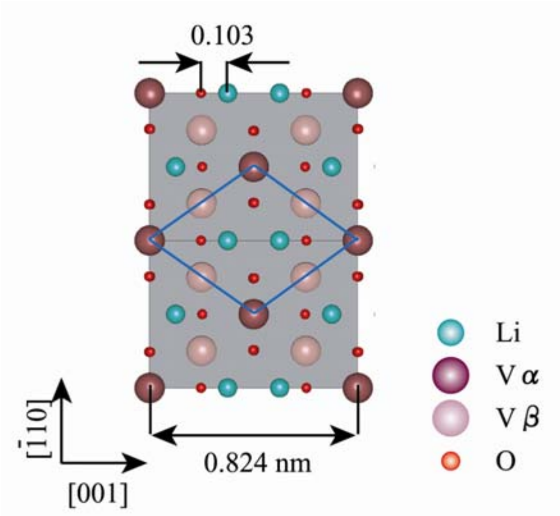

Fig. 1 Illustration of atomic structure of LiV_2O_4 crystal schematically viewing from the [110] direction. Vanadium columns are located either at the rhombic lattice site (purple disks, V_α) or at the middle (bridge) site of two neighboring rhombic lattice sites (light purple disks, V_β). Along the [001] direction, between two V_α sites, two lithium columns (green disks) are located between two neighboring oxygen columns (red ones).

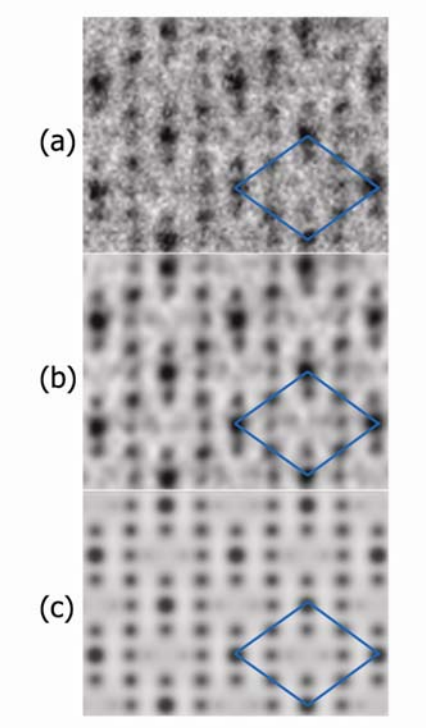

Fig. 2 Enlarged ABF images of LiV_2O_4 crystal viewing from the [110] direction. (a) A raw ABF image and (b) The processed ABF image. (c) The simulated ABF image. A unit of rhombic lattice is indicated by blue lines.