Before lithiation

78 s lithiation

171 s lithiation

In-Situ TEM Observations of the Lithiation of Molybdenum Disulfide

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Abstract

The lithiation of molybdenum disulfide (MoS_2) has been directly studied in-situ in the TEM by observing specimens with the viewing direction parallel to the basal planes. The MoS_2 lamella were characterized by bright-field imaging during the lithiation, and both selected-area diffraction and high-resolution imaging before and after. An overall expansion of ~5% along the *c*-direction was observed with concurrent local contraction. The contraction can be related to the expulsion of Mo as Li reduces it to form Li_2S .

Keywords: intercalation compounds, layered structures, lithium-ion batteries, transmission electron microscopy (TEM), MoS_2 .

Research into new materials for energy storage is at an exciting stage with both new materials and well-known materials showing new physical phenomena [1-5]. Layered materials such as the transition metal dichalcogenides (TMDCs) are attracting renewed interest for battery applications [6] as a special example of insertion electrode materials that can take advantage of the intercalation mechanism [7, 8]. Work on the intercalation of alkali metals in TMDCs began in the 1970s [9-13], during which time many fundamental observations were made. For example, it was shown that the sodiated phase of NbSe₂ is orthorhombic with Na atoms occupying the octahedral sites in the van der Waals gap [9], and that the general stoichiometry of a fully-lithiated MX₂ compound (where M is a transition metal, usually in group 4B or 5B, and X is S, Se, or Te) is LiMX₂ except in the case of VSe₂, which formed Li₂VSe₂ [10].

Although bulk molybdenum disulfide (MoS₂) can exist with different structures the 2H (hexagonal) phase is the most stable and is the predominant phase that occurs in nature [14]. The orthorhombic 1T structure is commonly observed after exfoliation, which is achieved by lithiating the MoS₂ and reacting the lithiated material with water [15-17]. Transition metal clustering in this phase can lead to 2x1 (1T'), 2x2 (1T'') and other supercell variations [18]. However, if these materials are to be used commercially in batteries it is likely that they will be in the form of sheets that are rather thicker than those formed by the exfoliation process. The present study addresses the lithiation of such practical materials

While considerable understanding of these materials can be achieved by examining specimens after lithiation or after delithiation (i.e. ex-situ), observing the same specimens before, during and after lithiation has obvious advantages. In-situ TEM is the only technique that allows specific sites on the specimen to be monitored in this way with atomic resolution. The usual geometry used for such studies is to examine the layer materials with the beam normal to the layers since this orientation greatly simplifies specimen preparation (see, e.g., [9]). In the present report, a novel experimental geometry was used such that the electron beam was parallel to the (0001) planes. This geometry allowed direct observation of the Li intercalation process, in-situ in the TEM. Lamellae of single crystal MoS₂ have been examined in this way; this approach can easily be extended to other layer materials, and to special orientations or materials that do not cleave readily along a particular plane.

The MoS₂ lamella described here was prepared using an FEI Strata 400S dual-beam focused ion beam (FIB) instrument. Bulk, natural MoS₂ was oriented with the basal planes parallel to the sample holder surface, so that the lamella had the basal planes parallel to its surface normal. The lamella was lifted out in situ and placed on a Cu Omniprobe TEM half-grid. TEM analysis was carried out using an FEI Tecnai F30 instrument operating at 300 kV.

The holder used for the TEM experiment was a Nanofactory Instruments scanning-tunneling-microscopy (STM) model, which was originally intended to correlate TEM images with local density of states measurements. To this end, the TEM-STM holder accepts two inputs. The end nearest to the tip of the holder is fixed, and fits a piece of 0.013 inch-diameter wire, which was Al for this experiment; the Cu FIB grid with the MoS₂ lamella was affixed to the Al wire with a conductive Ag epoxy. The end closest to the base of the holder is ball-shaped, and fits into the socket of a so-called “top-hat” that holds the second electrode, typically mounted on a 0.01 inch-

diameter tungsten wire. This end is equipped with both mechanically- and piezo-driven motors for coarse and fine motion control in three dimensions (to nanometer precision) within the TEM. Li metal, which acted as the counter-electrode, was scraped onto the tip of the W wire and loaded into the holder in a He-filled glove box. During transfer from the glove box to the microscope, the Li metal was partially oxidized, and the Li_2O layer subsequently acts as the solid electrolyte.

Contact was made between the Li source and the MoS_2 lamella and a potential of -2.5 V was applied across the holder for 350 s; video was recorded throughout. The electrodes were then disconnected to allow for the acquisition of images and diffraction patterns, then reconnected and the -2.5 V potential reapplied while video was recorded. More images and diffraction data were collected after the electrodes were disconnected again.

Figure 1 shows frames of the video of the lamella at different stages of the experiment. In Figure 1a the MoS_2 is shown just before contact is made with the Li source, which is visible at the lower-right corner of the image; Figure 1 b-d show the progression of lithiation 26 s, 78 s, and 171 s after the -2.5 V potential was applied, respectively. The most striking feature of the lithiated material is the group of straight lines of lighter contrast running horizontally across the specimen. The first such line to appear is arrowed in Figure 1b. The extension of the lines increased from right to left during observation; Additional lines then appeared with the appearance of the lines proceeding sequentially from the bottom of the lamella, nearest to the Li source, to the top. Although the lines appear to be perfectly straight, they were actually observed to step abruptly from one basal plane to a parallel one. The stepping direction could be either up or down.

The low-magnification images shown in Figure 2 are bright-field images of the MoS_2 recorded before and after lithiation and clearly show the increase in size that this block of MoS_2 experiences.

Figure 3 shows high-magnification images of the MoS_2 before and after lithiation, each with the corresponding diffraction pattern. The average spacing of the (0002) planes in Figure 3a is 0.61 nm, which gives $c = 1.22$ nm; this value is in good agreement with the literature value of 1.2295 nm [19]. The FIB processing has clearly damaged this thin area of the specimen but it has not changed the spacing of the basal planes. The lighter lines in Figures 1-3 are actually typically 3-4 fringes thick.

Although the intuitive assumption when examining Figure 3b is that the lighter lines correspond to lithiated material (because they are lighter) and so should have a wider spacing, in fact the average spacing of the fringes inside these bands of lighter lines corresponds to $c = 1.14$ nm while the average spacing of the fringes in the rest of the image corresponds to $c = 1.28$ nm. The latter represents a 4.9% expansion in the [0001] direction relative to the initial spacing of the MoS_2 planes. These bands are thus proposed to be platelets of Mo-poor material (referred to as such to distinguish them from the MoS_2 lamella that is the TEM specimen).

Figure 3b also features one of the previously mentioned steps in the platelets. The planes are visibly distorted between the tips of the two lines in the center of the image, and the tips appear

to be complementary in shape, i.e., they are related by a 180° rotation normal to the image. All of these features terminate (i.e., change planes) in the same way. After stepping across 12 or more planes, the platelet continues with the same width suggesting that it is, indeed, a continuous defect, as expected from the in-situ observation.

The streak along the (0002) systematic row in the diffraction pattern in Figure 3d is due to these platelets. It appears as a streak rather than a series of very closely spaced spots because of the relatively large distance between the platelets, and because they are not quite evenly spaced.

Because the in-situ holder is only equipped with single-tilt capabilities, and in fact the nature of the in-situ experiment precludes tilting without significant risk to the specimen, extensive analysis using dark-field imaging could not be performed. However, initial dark-field imaging did confirm that there is no localized strain field associated with the platelet.

The initial lithiation of MoS_2 is proposed to involve a transformation from trigonal prismatic coordination of Mo by S to octahedral coordination [20]. The geometry used in the present study is not able to detect this transformation directly since the electron beam is parallel to the basal planes; the LiMoS_2 is proposed to have the 1T structure (rather than the 2H structure of the original MoS_2) [20]. However, the spacing of the basal-plane fringes in Figure 3b is particularly interesting. It is well-known that upon sufficient lithium insertion (after the initial structural changes within the basal planes), the Li begins to react with MoS_2 to form Li_2S according to

There does not appear to be any documentation of how this reaction proceeds or what happens to the Mo after the reaction occurs. The observations from the present study suggest that the observed contraction in the basal planes within the platelets is related to planar defects caused by the expulsion of Mo at the beginning of this reaction. The important observation is that the material remains crystalline even as the Mo is expelled. It is possible that the contraction is simply related to the occupancy of the Li atoms and the degree of lithiation in the platelets; DFT calculations have predicted c values ranging from 1.1999 nm to 1.42262 nm for partially lithiated material [21]. Ultimately the Mo does apparently form a separate phase in the in-situ experiment as will be reported elsewhere. A recent study found that the c lattice parameter increased by ~ 0.8 Å, $\sim 6.5\%$, after chemical lithiation [22] which is larger than the result obtained from the analysis of Figure 3b but actually quite close to the total expansion of the lamella in the vertical direction in Figure 2.

In discussing the expansion of TMDCs it is noted that an error in reporting the magnitude of the expansion in the c direction has developed over the years. For example, Li et al. [22] mention an expansion of 0.025 nm in their introduction, citing a 1994 paper on the diffusion of Li in MoS_2 [23]. However, Santa-Ana et al. obtained this value from a 1987 review paper by Friend and Yoffe [24]; in this and many other older papers on the subject of intercalation of TMDCs, the style was to report c as a multiple of the individual layer thickness. For example, c for MoS_2 is reported as 2×0.615 nm rather than 1.23 nm [24]. Therefore the cited 0.025 nm expansion is actually from 0.615 nm to 0.640 nm ($\sim 4.1\%$), while the two more recent papers might give the misleading impression that the expansion is only $\sim 2\%$, from 1.2295 nm to 1.2545 nm.

Figure 4 superimposes a drawing on the image of the defect stepping to clarify this special feature of Figure 3b. The basal-oriented platelets have been outlined by blue lines that are 4 basal planes wide; these two boxes are themselves connected by a set of green lines to suggest how the blue boxes are connected. The inset schematic then summarizes how the platelet steps between two basal segments. The platelet changes orientation from one basal plane onto an inclined plane and then back onto a parallel basal plane so that it is inclined to the electron beam where the step occurs. The inclined segment of the platelet could not be imaged directly (and hence the distortion, although visible, cannot be directly interpreted) since the Nanofactory holder used for the experiment is single-tilt, but it is interesting to note that the green box is not perpendicular to the basal plane. In fact it is never so aligned between any of the basal-oriented platelets, but always appears similar to the orientation outlined schematically in Figure 4, even if this involves stepping in the opposite direction of the Li motion as the defect propagates. The inclined platelet must therefore be faceting onto a pyramidal plane rather than a prismatic plane. Indeed, close examination of the (0002) and (000 $\bar{2}$) spots in Figure 3d reveals “relrods” (which refers to the distortion of the points in the reciprocal lattice due to the non-infinite dimensions of specimen features) protruding very slightly from the spots. While these features are small enough as to make measurements on them difficult, they suggest a characteristic angle for the steps between platelets in the range of 36° - 48°, which is consistent with the 38° angle between the bottom basal segment of the platelet and the step between the basal segments in Figures 3b and 4.

The lithiation of MoS₂ involves an expansion of the MoS₂ layers as the Li intercalates along the basal plane. In the early stages, the lithiation process involves an expansion of the basal planes as has been observed in this study and a subsequent macroscopic expansion normal to these planes. This process is facilitated by the formation of blocks of material (referred to as platelets in this report) that lie primarily on the basal plane but can step from one plane to a parallel one and have a smaller plane spacing. These platelets are interpreted as being the first stages of the expulsion of Mo metal from the structure. This expulsion is expected to be relatively easy, and does occur quite rapidly during in-situ observation, because the material remains crystalline during the process.

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Figure Captions

Figure 1. Frames from the video recorded during the lithiation experiment; the Li source is visible in the lower right corner. (a) before contact is made between the Li source and the MoS₂ lamella; (b) 26s after the potential of -2.5 V was applied; (c) 78 s after the potential was applied; and (d) 171 s after the potential was applied.

Figure 2. Low-magnification bright-field TEM images of the MoS₂ FIB lamella (a) before and (b) after lithiation, showing the location of the light bands (the platelets) and the expansion of this specimen of MoS₂ normal to the *c* planes.

Figure 3. High-magnification TEM images of the MoS₂ lamella (a) before and (b) after lithiation, with the corresponding selected-area diffraction patterns in (c) and (d). Damage caused by the FIB can be seen in ‘a’ but the basal plane spacing is not altered.

Figure 4 (color online). Schematic illustration of the features in Fig. 3b. The blue boxes outline two edge-on blocks of ~4 basal planes that are connected by another block in green that is inclined to the electron beam and to the *c*-axis of the MoS₂.

Figure 1
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Figure 2
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Figure 3
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Figure 4
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