

Atomic Structure of Li₂MnO₃ after Partial Delithiation and Re-Lithiation

Rui Wang, Xiaoqing He, Lunhua He, Fangwei Wang, Ruijuan Xiao, Lin Gu,* Hong Li,* and Liquan Chen

Li₂MnO₃ is the parent compound of the well-studied Li-rich Mn-based cathode materials xLi₂MnO₃·(1-x)LiMO₂ for high-energy-density Li-ion batteries. Li₂MnO₃ has a very high theoretical capacity of 458 mA h g⁻¹ for extracting 2 Li. However, the delithiation and lithiation behaviors and the corresponding structure evolution mechanism in both Li₂MnO₃ and Li-rich Mn-based cathode materials are still not very clear. In this research, the atomic structures of Li₂MnO₃ before and after partial delithiation and relithiation are observed with spherical aberration-corrected scanning transmission electron microscopy (STEM). All atoms in Li₂MnO₃ can be visualized directly in annular bright-field images. It is confirmed accordingly that the lithium can be extracted from the LiMn₂ planes and some manganese atoms can migrate into the Li layer after electrochemical delithiation. In addition, the manganese atoms can move reversibly in the (001) plane when ca. 18.6% lithium is extracted and 12.4% lithium is re-inserted. LiMnO₂ domains are also observed in some areas in Li1,63MnO3 at the first cycle. As for the position and occupancy of oxygen, no significant difference is found between Li_{1.63}MnO₃ and Li₂MnO₃.

1. Introduction

Lithium-ion batteries with high energy densities are highly desired.^[1,2] In 2001, Thackeray and Johnson proposed a material with composite structure in which a layered Li₂MnO₃ component is structurally integrated with either a layered Li*M*O₂ component or a spinel Li*M*₂O₄ component (M = Mn, Ni, etc.).^[3-12] It has been demonstrated that nearly 1 mol of lithium can be extracted from this kind of Li-rich Mn-based layered material, corresponding to capacities of 250–300 mAh g⁻¹.^[3,4] Based on the estimation, Li-ion batteries using this type of cathode could approach energy densities over 300 W h kg⁻¹, much higher than the 220 W h kg⁻¹ of the best Li-ion batteries using LiCoO₂ as cathode.^[3,13] This family of Li-rich Mn-based layered materials has attracted wide attention. In spite of their varied microstructure and composition, these materials have

R. Wang, Dr. X. Q. He, Dr. L. H. He, Prof. F. W. Wang, Dr. R. J. Xiao, Prof. L. Gu, Prof. H. Li, Prof. L. Q. Chen Institute of Physics Chinese Academy of Sciences Beijing 100190, P. R. China E-mail: l.gu@iphy.ac.cn; hli@iphy.ac.cn



DOI: 10.1002/aenm.201200842

a common and unique feature compared to previous layered compounds: a voltage plateau appears at 4.5 V vs. Li⁺/Li during initial charging, which is exactly similar to the delithiation behavior of standalone Li_2MnO_3 .^[14] Therefore, it is plausible that the parent compound Li_2MnO_3 plays a very important role and a clear understanding on its delithiation and lithiation mechanism should be helpful to clarify the complex behaviors of the Li-rich Mn-based layered materials and realize rational design.

The layered structure of Li₂MnO₃ is derived from rhombohedral α -NaFeO₂ with Li and Mn occupying the Na and Fe sites respectively. Unusually, one-third of the positions in the Mn-plane are replaced by Li to form an ordered LiMn₂ slab. The LiMn₂ stabs and the Li interslab layers stack into the C2/m structure, so that the chemical formula of Li₂MnO₃ can be written as $\{(Li_{1/2})_{2c}(Li_{1})_{4h}\}x_{interslab}$

{(Li_{1/2})_{2b}(Mn₁)_{4g}]_{slab}(O₁)_{4i}(O₂)_{8j}, in which the subscripts 2c, 4h, 2b, 4g, 4i, and 8j are the lattice sites occupied by the atoms in the round brackets.^[15–18] In earlier literature, the Li₂MnO₃ structure has been determined and the parameters of the cell are $a_{\rm mon.} = 4.937(1)$ Å, $b_{\rm mon.} = 8.532$ Å, $c_{\rm mon.} = 5.030(2)$ Å, and $\beta = 109.46(3)^{\circ}$. Lithium ions occupy the 2b (0, 1/2, 0), 2c (0, 0, 1/2), and 4h (0, 0.6606(3), 1/2) sites, manganese ions the 4g (0, 0.16708(2), 0) site, and oxygen ions the 4i (0.2189(2), 0, 0.2273(2)) and 8j (0.2540(1), 0.32119(7), 0.2233(1)) sites.^[17]

For LiMn₂O₄ and LiMnO₂, the electrochemical capacities and charge transfer originate from Mn³⁺/Mn⁴⁺ redox reactions. It is generally believed that Mn cannot be oxidized beyond +4 in an octahedral oxygen environment.^[19,20] In this sense, Li₂MnO₃, in which Mn has a valence of 4+, were considered electrochemically inert. However, Kalyani et al. demonstrated that Li₂MnO₃ could be activated electrochemically, rather than by acid treatment.^[21] The reported capacities of Li₂MnO₃ depend on synthesis conditions and test conditions.[14,21-24] Several mechanisms have been proposed to explain the unusual delithiation behavior of Li2MnO3, such as oxygen deficiency in the raw material,^[25] simultaneous removal of Li and O,^[26-28] Li⁺/H⁺ ion exchange,^[27,29] etc. The valence state of Mn is believed to remain 4+ during the charge process.^[14,27-29] All these proposed mechanisms are helpful to understand experimental phenomena. However, several questions about structure variation



and charge compensation need further clarification: i) can lithium in both the $LiMn_2$ and Li planes be extracted? ii) how does the lattice rearrange after lithium removal? iii) will the lattice vary irreversibly after the first delithiation? iv) by what is the charge compensated for the removed Li ions? and, v) at which depth of the delithiation process does the oxygen start to release? The first three questions are related to the variation of the crystal structure. The last two questions are related to the variation of the electronic structure.

Recently, spherical aberration-corrected scanning transmission electron microscopy (STEM) techniques have been greatly developed and direct observation of light atoms has become realistic.^[30-39] In particular, aberration-corrected annular-brightfield (ABF) transmission electron microscopy provides feasible access to the atomic structure at sub-angstrom resolution. In this technique, the contrast of the micrograph is proportional to $Z^{1/3}$ (Z is the atomic number.), which has an extra high sensitivity to light atoms, capable of resolving Li ions at atomic resolution. Detailed discussions on the mechanism and experimental conditions can be found elsewhere.^[33,37] Several groups have investigated the structure of Li₂MnO₃ by this kind of highresolution TEM experiment.^[15,16] However, to our knowledge, the atomic scale microstructural changes of Li₂MnO₃ after delithiation and re-lithiation have not been reported, which are essential to understanding the reaction mechanism.

In this work, pristine, partially delithiated, and re-lithiated samples of Li_2MnO_3 are investigated by spherical aberration-corrected scanning transmission electron microscopy (STEM) and neutron diffraction experiments, aiming to clarify questions i–iii above.

2. Experimental Section

Preparation and Characterization: Li₂MnO₃ powders were prepared by a solid-state reaction with LiOH \cdot H₂O (AR, Sinopharm Chemical Reagent Co., Ltd) and MnCO₃ (AR, Sinopharm Chemical Reagent Co., Ltd) as precursors. The starting materials were ball-milled in ethanol for 6 h and then dried. The resulting precursors were calcinated in air at a ramp rate of about 4 °C min⁻¹ to different final temperatures from 400 to 800 °C. Samples were brought back to room temperature by furnace cooling.

Two chemical delithiation methods were performed. The first method is to extract Li ions with H₂SO₄ under hydrothermal conditions. A Li₂MnO₃ sample (0.1 g) was added to an H₂SO₄ solution of a certain concentration. The added amount of H_2SO_4 correponds to mole ratios of H^+ in the solution to Li⁺ in the Li₂MnO₃ of 0.25, 0.5, 0.75, and 1.0. The mixtures were heated in an autoclave at 140 °C for 72 h. After hydrothermal treatment, the solids were filtered, washed with distilled water, and then dried at 80°C overnight. These samples were examined using STEM. The second method is to extract Li ions with nitronium tetrafluoroborate (NO₂BF₄). In a typical process, Li_2MnO_3 (150 mg) was immersed in a solution of NO₂BF₄ (50 mL) acetonitrile. The solution was stirred for 24 h with purified Ar gas bubbling at room temperature. The mixture was centrifuged and washed three times with acetonitrile before drying under vacuum. In our experiment, excess

ADVANCED ENERGY MATERIALS

NO₂BF₄ was used. The molar ratio of Li and Mn was detected with the inductively coupled plasma (ICP) method.

Powder X-ray diffraction data were collected on an X'Pert Pro MPD X-ray diffracter (Philips, Holland) using Cu Kα radiation ($\lambda = 1.5406$ Å). Aberration-corrected annular-bright-field scanning transmission electron microscopy was performed using a JEOL ARM 200F (JEOL, Tokyo, Japan) transmission electron microscope operated at 200 keV. The attainable resolution of the microscope is defined as 0.8 Å with the corresponding illumination and collection angles of 25 mrad and 12 to 25 mrad, respectively. The probe current was kept less than 10 pA; so that possible radiation damage can be well restricted. The contrast of the ABF micrograph is proportional to $Z^{1/3}$ (Z is the atomic number), which has an extra high sensitivity to light atoms, capable of resolving Li ions at atomic resolution. Detailed discussions on experimental conditions can be found elsewhere.^[33,37] Neutron powder diffraction experiments were peformed on the time-of-flight diffractometer POWGEN at the Oak Ridge National Laboratory, TN, USA. Samples were loaded in 6 mm vanadium cans and patterns were collected at room temperature with centre wavelengths 1.066 Å. Rietveld refinements employed the GSAS software with EXPGUI interface.

Electrochemical measurements were taken as follows. The Li_2MnO_3 powder electrodes were composed of the Li_2MnO_3 powder, carbon black, and PVDF at a weight ratio of 80:10:10. Al foil was used as current collector and the electrode area was 0.64 cm² (8 × 8 mm). The electrochemical experiments for the powder electrodes were performed using Swagelok-type two-electrode cells. The electrolyte was 1 \mbox{M} LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 (Shanghai Topsol Ltd., H₂O < 5 ppm). The cells were assembled in an argon-filled glove box and cycled using a Land automatic battery tester. After cycling, the cells were taken back into the glovebox and disassembled. TEM samples were prepared by dispersing the electrode materials on holey-carbon films. These films were sealed with a homemade bag and opened just before the TEM examination.

3. Results and Discussion

3.1. Characterization and Electrochemical Performances of ${\rm Li}_2{\rm MnO}_3$

XRD patterns of the Li₂MnO₃ powders calcinated at different temperatures are shown in **Figure 1**. All the reflections can be indexed in the monoclinic system using the space group C2/m. All the peaks become sharper when the preparation temperatures increase, indicating an improvement of the crystallinity. Li₂MnO₃ has a layered structure with alternating Li layers and transition metal (TM) layers separated by oxygen layers. Earlier reports have claimed that the superlattice peaks between 20° and 30° are related to the ordering of Li/Mn in the TM layers and the stacking faults.^[14,18,40] Compared with their results, there are more stacking faults in our samples because of the lower preparation temperatures. In this case, only some of the superlattice peaks can be seen. But it can still be observed that the samples prepared at lower temperatures have much broader





Figure 1. XRD patterns of the Li₂MnO₃ powders calcinated at different temperatures. The 2θ values are according to a Cu K α wavelength ($\lambda = 1.54$ Å).

superlattice peaks, which means there are more stacking faults perpendicular to the layered (001) direction.

The initial charging and discharging curves of Li_2MnO_3 synthesized at different temperatures in the range of 4.8–2 V are shown in **Figure 2**. All the electrodes were cycled with a rate of 10 mA g⁻¹ at room temperature. As can be seen, the charging and discharging profiles are similar, exhibiting a plateau at approximately 4.5 V on charging and then a sloping curve on discharging. However, the specific capacity depends strongly on the temperatures used to synthesize the Li_2MnO_3 samples. Li_2MnO_3 prepared at lower temperatures exhibit much higher charge and discharge capacities. Yu et al. proposed that this phenomenon may be related to the thermodynamic properties of materials. There are more stacking faults and other defects in the materials calcinated at lower temperatures, which would increase the energy state of the materials and lower the activation barrier for Li diffusion.^[14]

3.2. STEM Images of Li₂MnO₃ after Electrochemical Treatments

Since the Li₂MnO₃ prepared at 800 °C has the best crystallinity among all the five materials, it is favorable to obtain highquality images in the STEM experiments. It should be mentioned that the initial charge capacity of Li₂MnO₃ synthesized at this temperature is about 85 mA h g⁻¹, which corresponds to a nominal composition of Li_{1.63}MnO₃. The voltage profile of the samples prepared at different temperatures are actually very similar. Therefore, it is believed that, although the capacity and delithiation depth for the Li₂MnO₃ prepared at 800 °C are relatively low, the observed results should represent similar structure evolution mechanisms.

The primary particle size of this material ranges from several tens of nanometers to a hundred nanometers, and secondary particle size is about 400–500 nanometers. Figure 3 shows a typical ABF image of pristine Li_2MnO_3 annealed at 800 °C along the [110] orientation, and the inset picture illustrates the corresponding atomic arrangement in the unit cell. It can be seen clearly that the

www.MaterialsViews.com



Figure 2. The first cycle charging (delithiation) and discharging (lithiation) curves of Li_2MnO_3 prepared at different temperatures. The electrode area was 0.64 cm². Current: 10 mA g⁻¹.

sample shows a high degree of crystallization and shares a layered structure. The image shows a pattern of two darker columns followed by a brighter column. This pattern is the direct imaging of the LiMn₂ planes. In the Li₂MnO₃ crystallographic structure, the LiMn₂ planes have an ordering in the cation arrangement. When viewed along the [110] orientation, the LiMn₂ planes appear as a repeating sequence of two manganese columns and one lithium column and the expected intercolumnar distance is 0.14 nm, which is consistent with our results shown in the ABF image.

However, it should be mentioned that two different areas with different structures can be seen (marked as areas A and B). In area A, the stacking of the LiMn₂ planes are sequential



Figure 3. ABF electron micrograph of Li₂MnO₃ synthesized at 800 °C viewed along the [110] orientation (inset: illustration of the atomic configuration in a unit cell of Li₂MnO₃.).



Figure 4. a) ABF electron micrograph of Li₂MnO₃ charged to 4.8 V. b) The corresponding line profiles from the ABF images.

along the *c* direction, clearly revealing the C2/m structure. In area B, two successive planes connected by red lines are sequential, and these two planes constitute the elementary unit. However, there is a plane shift between every two units, which seems to form a superstructure. The XRD patterns in Figure 1 show that the observed superlattice peaks between 20° and 30° of the Li₂MnO₃ synthesized at 800 °C are still broad, implying that the crystallinity of this sample is yet not perfect. Obviously, the STEM images provide more detailed local structure information compared to the XRD pattern.

The structure of the B area can also be understood in another way. The structure of Li_2MnO_3 has been investigated by several groups.^[40,41] Based on their definitions, the C2/m structure Li_2MnO_3 can be described as a stacking sequence of A1B1C1. Obviously, the B area has a different stacking sequence. If we presume that the O atoms in the B area adopt cubic closepacking, transitional metal may have the stacking sequence A1B1C2A2B3C3. As a result, the symmetry has been changed and the space group has also been changed. We checked several different parts of the material and found that the B area structure appears more often than the A area. Nevertheless, we still call the material a C2/m structure with regular stacking faults. For each elementary unit, the two LiMn₂ planes still arrange with a C2/m configuration; between the two units, the LiMn₂ planes seem to have the reverse arrangement.

Figure 4a shows an ABF image of Li_2MnO_3 charged to 4.8 V, and Figure 4b depicts the corresponding line profiles

of LiMn₂ planes at different places. Line 3 reveals that nearly all the lithium of LiMn₂ planes remain; Line 2 reveals that some of the lithium atoms at this site have been extracted; Line 1 shows that all the lithium atoms at this site have been extracted. This result indicates that the delithiation occurs inhomogeneously even at different atomic columns at a scale of 1–2 nm. Since the sample for ex situ STEM investigation approached an equilibrium state, an inhomogeneous distribution of lithium within the Li_{1.63}MnO₃ lattice could be thermodynamic stable or at least metastable; this needs further theoretical clarification.

ABF electron micrographs of the Li_2MnO_3 at the initial state and after electrochemical treatments are compared in **Figure 5**. Figure 5b shows the atomic structure of Li_2MnO_3 after being charged to 4.8 V, and Figure 5c shows Li_2MnO_3 at the state of being discharged to 2 V after being charged to 4.8 V. Three phenomena can be deduced from these results.

Firstly, a new kind of stacking sequence (marked by the green arrows in Figure 5b and c) has appeared following the electrochemical reactions. Adopting this kind of stacking, consecutive LiMn₂ planes with the same positions perpendicular to *a*–*b* plane have appeared. Moreover, the stacking sequence has become irregular. Jarvis et al. indicated that the preferred shear direction is <110> in NaCl-like structures, so they introduced b/3[010] stacking faults to explain the stacking faults observed in their TEM images.^[42] Here, considering the A1B1C1 stacking, if the B1 layer has a stacking fault of –b/3[010], then



Figure 5. ABF electron micrographs of: a) initial Li₂MnO₃; b) Li₂MnO₃ charged to 4.8 V; and, c) Li₂MnO₃ discharged to 2 V after being charged to 4.8 V.

ENERG



www.MaterialsViews.com

it would appear like the B3 layer. When viewed along the [110] direction, it will look like a O1 stacking, just as the stacking sequence marked by green arrows.

Secondly, the spacing between consecutive LiMn₂ planes is decreased during the charging and increased in the discharging process (0.47 nm \rightarrow 0.46 nm \rightarrow 0.48 nm), which is clearly indicated by the red arrows between each picture in Figure 5. Actually, the STEM results obtained in this work verify previous XRD results.^[14] As is well known, in layered structure LiMO₂, the layer spacing along the *c*-axis will expand after lithium extraction due to repulsion of the closed oxygen layer. It is suggested that the contraction of Li₂MnO₃ along the *c*-axis and the expansion of the layered LiMO₂ after delithitation may cause structural breakdown or cracking of Li-rich materials, which is integrated by these two structure units.

The third discussion is related to the motions of lithium in Li₂MnO₃ in the charge and discharge process. In Li₂MnO₃, lithium at 2b sites makes up the LiMn₂ plane together with manganese. In pristine Li₂MnO₃, the line profiles of LiMn₂ plane (Line 1 in Figure 6a) show a repeating sequence of two heavy atoms and a light atom with different image contrast. This can be understood as the repeating sequence of two manganese columns and one lithium column and is consistent with the Li₂MnO₃ crystallographic structure viewed along the [110] orientation. After electrochemical delithiation, the line profiles of LiMn₂ planes only show the repeating sequence of two manganese columns (see Line 1 and 3 in Figure 6b). This means that the lithium at the 2b site has been extracted completely in these two lines at this state. Then, after discharge, the line profiles (Line 1 in Figure 6c) show the 2b site is again occupied by reinserted lithium. To sum up, lithium at the 2b site is extracted after the charge and re-inserted after the discharge.

Lithium atoms at the 2c and 4h sites in $\rm Li_2MnO_3$ constitute the Li planes. In Figure 6a, Line 2 taken along the lithium

plane clearly shows the existence of lithium. And the image contrast of the lithium are nearly the same, which means the occupation of lithium at these sites are uniform. After electrochemical delithiation, the image contrast profiles of Li layers become more complicated. As shown in Line 2 and Line 4 in Figure 6b, some grey spots remarked by blue circles appear. These spots are compared to or even more obvious than the O below and above. This can only be caused by the occupancy of Mn with strong contrast. The positions of these spots are just in the middle of the two consecutive Mn planes below and above. These sites are the octahedral sites previously occupied by Li. In pristine Li₂MnO₃, no such obvious spots are obsered. Therefore, Mn should migrate into these sites after electrochemical delithiation. Looking close to these Mn, it can be observed that they are arranged at regular intervals. And these arrangement may indicate the possibility for converting into the spinel phase. It is surprising to notice that the occupancy of Mn in lithium layer disappears in the electrochemically re-lithiated sample. As shown in Line 2 in Figure 6c, after the discharge, the contrast of profiles taken along the Li-plane is almost the same, which means all lithium has been restored. This implies that the cation mixing of Mn into Li layer seems reversible at this early stage. Li₃MnO₃ can be described as Li[Li_{0.33}Mn_{0.66}]O₂ and the delithiated sample Li_{1.63}MnO₃ can be also be described as Li[Li_{0.09}Mn_{0.66}]O₂. Here we show these notations because nominally there is still a significant amount of Li present in the transition metal planes. However, the delithiation process is not uniform, so some areas in which there is no lithium left in the transition-metal planes are observed. In order to understand the lithium extraction phenomena, we performed DFT simulations on this issue; the results are presented elsewhere.^[48] Based on the simulation results, both Li in the Li layers and the LiMn₂ layers are extractable during the charging process. The sequence of Li removal is suggested as



Figure 6. Pictures and corresponding line profile of changes of Li ions in Li_2MnO_3 after electrochemical lithiation and delithiation: a) pristine Li_2MnO_3 ; b) Li_2MnO_3 charged to 4.8 V; and, c) Li_2MnO_3 discharged to 2 V after being charged to 4.8 V.

ENERGY MATERIALS www.advenergymat.de



www.MaterialsViews.com

follows: Li at 4h (in Li layer) and 2b (in LiMn₂ layer) sites are extracted with a ratio of 2:1 until the formation of $Li_{1.25}MnO_3$, then all the remaining Li at the 2b sites are removed until a total of 1 mol Li is extracted.

In our discussion above, we have observed some Mn atoms migrated to the Li-layer after the initial charge. As to the a-b plane, we have also observed that the manganese atoms move in the (001) plane after charging and retreat to their pristine sites after discharging. As shown in **Figure 7**, in Li₂MnO₃, lithium and manganese are all arranged in the octahedral sites and oxygen planes are placed between Li and LiMn₂ planes. When viewed along the [110] orientation, oxygen columns can be seen above and below the lithium and manganese columns, approximately (see Figure 3a). This phenomenon can also be seen clearly in our ABF image. In Figure 7a and c, the blue dotted lines clearly show the positions of all the lithium, manganese

and oxygen coincide in the vertical direction. However, the situation changes for the sample charged to 4.8 V. In Figure 7b, the dotted lines drawn across the manganese vertically do not pass through the lithium and oxygen. This indicates the manganese atoms swing in the (001) plane after charging and then get back to their pristine sites after discharge.

In addition, some other phases have also been observed for the same sample; these are depicted in **Figure 8**. In the A area of Figure 8a, the layered transition metal LiMn₂ layer has a changed structure with a complete manganese layer. This means that the layered LiMnO₂ is also formed locally. In addition, some areas having different structure are also found. Details are shown in Figure 8b. The D area is the ideal delithiated Li₂MnO₃, but it is obvious that the C area nearby has a different structure, which we could not determine. It is obviously not Li₂MnO₃ or LiMnO₂, but somehow like LiMn₂O₄,



Figure 7. Line profiles of LiMn₂ plane, O plane, Li plane, O plane, and LiMn₂ plane in Li₂MnO₃ samples at three different states: a) pristine Li₂MnO₃; b) Li₂MnO₃ charged to 4.8 V; and, c) Li₂MnO₃ discharged to 2 V after being charged to 4.8 V.





Figure 8. ABF electron micrographs of Li_2MnO_3 charged to 4.8 V. Different structures can be seen in different areas.

since it appears to belong to an orthorhombic or cubic crystal system. Earlier literature has reported that Li₂MnO₃ may transform into LiMnO2 and LiMn2O4 after electrochemical cycles.^[14,23,43,44] In our results, some small areas with structures not belonging to Li2MnO3 are observed. It should be mentioned these domains are very localized, and could not be detected by bulk-level methods, such as XRD or neutron diffraction. But they may act as nucleation seeds for further growth during the electrochemical cycles. Both thermodynamic and kinetic calculations are needed to clarify this important issue. If the above local phase transition is driven by intrinsic thermodynamic factors and is irreversible, then the voltage fading problem for Li-rich Mn-based layered materials may not be solved easily. Comprehensive investigations still need to be done in this area, especially in the regions near the new structure areas, to understand the detailed evolution and nucleation of new phases in their early stages.

3.3. STEM Images of Li₂MnO₃ after Chemical Delithiation

Due to the poor electrode kinetic properties of Li_2MnO_3 synthesized at 800 °C, further chemical delithiation was also performed on this sample to extract more lithium. A sulfuric acid hydrothermal chemical delithiation method was applied following the report by Tang et al.^[45] This method has the limitation of proton exchange but can delithiate completely. ICP experiments were conducted to determine the chemical compositions of the samples. Four samples with different Li/Mn ratio were obtained: 1.5:1, 1.0:1, 0.5:1, and 0.07:1 for samples I, II, III, and IV, respectively. XRD patterns of the four samples are depicted in **Figure 9**. It can be seen clearly that the monoclinic structure of Li_2MnO_3 was preserved as a main phase of the samples I, II, and III. The main peak of Li_2MnO_3 (001) plane locates at d = 0.475 nm, but all the samples I, II,

www.MaterialsViews.com



Figure 9. XRD patterns of the Li₂MnO₃ powders with different chemical delithiation states. The 2 θ values are according to a Cu K α wavelength ($\lambda = 1.54$ Å).

and III have a strong peak at d = 0.460 nm. Tang et al. claimed that this peak can be ascribed to the monoclinic phase with small lattice parameters perpendicular to the (001) plane.^[45] As to sample IV, it can be seen clearly that the sample has a composite structure of α -MnO₂ (JCPDS card 44-0141) and γ -MnO₂ (JCPDS card 14-644). Earlier reports suggested that the full lithium extraction brings about a structural change from the monoclinic phase to hydrated α -MnO₂ or β -MnO₂-like phase or $\gamma MnO_2.^{[\bar{45}-47]} The samples I and IV are chosen for STEM$ experiments and their ABF images are shown in Figure 10 and 11, respectively. It can be seen clearly that the sample I still shares a layered structure. It can be recognized that at this extraction state of lithium ions, a large proportion of the Li ions at 2b sites have been extracted. This indicates further that absence of lithium in the LiMn₂ layer seems favorable, in contrast to an impression that the existence of Mn may block the extraction of lithium. A detailed theoretical discussion about the lithium extraction paths and corresponding energy barriers will be clarified elsewhere with the help of molecular dynamic simulations.^[48]

For sample IV, the situation is more complicated. Firstly, it is a composite of α -MnO₂ and γ -MnO₂, and, secondly, γ -MnO₂ itself has a complicated composite structure. De Wolff proposed that γ MnO₂ has a random intergrowth of the pyrolusite and ramsdellite structures.^[49] Chabre and Pannetier introduced the concept of microtwinning to better explain the characteristically broad and diffuse diffraction peaks in y-MnO2.[50] Later, Wu et al. found that \mathcal{YMnO}_2 hexagon-based structures were made of ε -MnO₂, β -MnO₂, and ramsdellite.^[51] In our ABF images, we do observe some different structures, although we are not able to distinguish and separate them, as shown in Figure 11. The structure shows a distorted hexagon phase. Three of the vertexes are darker dots; the other three and the central point are lighter dots. For the atomic arrangement, the (001) face of ε -MnO₂, the (010) face of β -MnO₂, and the (010) face of ramsdellite all show a structure like Figure Figure 11a. The distorted hexagon may result from microtwinning. In spite



Figure 10. a) ABF electron micrograph of the chemically dethiated sample with the Li/Mn ratio of 1.52:1. b) The corresponding line profiles from the ABF images.



Figure 11. a) Illustration of the atomic configuration of γ MnO₂ viewed in the direction of [010] b) ABF electron micrograph of the chemically delithiated sample with Li/Mn ratio of 0.07:1.



Figure 12. Neutron diffraction patterns of Li₂MnO₃ before and after chemical delithiation.

of the difficulty of distinguishing the phase, we did observe directly an MnO_2 phase in the chemically delithiated Li_2MnO_3 .

FULL PAPER

3.4. Neutron Diffraction Spectra of Chemically Delithiated Li₂MnO₃

STEM images provide local structure information. Neutron diffraction experiments were also performed to understand the structure of Li_{2-x} MnO₃ (*x* = 0, 0.25) at a bulk level. Figure 12 shows the observed and refined data of neutron diffraction pattern; the fitting pattern is statistically in agreement with the recorded one. In the refinement, we first deal with the scale factor, the background function, the diffractometer zero point, and the unit-cell parameters, then the profile function, the atomic coordinates, and the isotopic thermal factor, and, finally, the occupancy of Li ions. From the refined results (Table S1 in the Supporting Information), it can be seen that the lattice constants in the aand, b-directions increase after chemical delithiation, but that in the *c*-direction decreases. Overall, the volume of the unit cell almost stays constant for Li1,75MnO3 (corresponding to 64 mA h g⁻¹ charging capacity). It should be noted that for the delithiated compound Li_{1.75}MnO₃, even if the occupancies of all three Li ion sites are fixed to 1.0, the agreement between the computed and observed patterns is already good with $R_p = 7.2\%$ and $R_{\rm wp}$ = 4.4%. We released to refine all the Lisite occupancies, and found that the Li(2b) occupancy became over 1.0; therefore, this parameter is fixed in the final refinement.



With this treatment, the occupancies of lithium for the 2c and 4h sites are 0.7 (±0.3), and 0.9 (±0.1), respectively, resulting in a Li concentration of 1.75 (±0.27), consistent with the starting stoichiometric ratio. The *R*-factors improve slightly to $R_p = 6.9\%$ and $R_{wp} = 4.1\%$. Furthermore, for Li_{1.75}MnO₃, the isotropic thermal vibration factors of lithium atoms at the 2c, 4h, and 2b sites are considerably larger than Mn and O, implying a mobile characteristic of Li atoms. The thermal factor of Mn atoms is slightly larger than that of O atoms, which probably means that the Mn atoms are more mobile than O atoms. This simulation result is consistent with our results from the STEM images. More reliable data about the diffusion trajectory and the isotropic thermal vibration factors will be further checked by high-temperature neutron experiments in the near future.

4. Conclusion

In this paper, the structures of pristine, partially delithiated, and lithiated Li_2MnO_3 were studied mainly by ABF-STEM experiments. Based on the results, a number of conclusions can be drawn:

- i) Stacking faults exist in the initial Li₂MnO₃.
- ii) Lithium extraction is not uniform; lithium can be extracted from LiMn₂ planes and reinserted in localized regions.
- iii) Mn can be migrated into the Li layer after electrochemical delithiation and can swing reversibly in the (001) plane during delithiation and lithiation.
- iv) Oxygen seems to keep stable for delithiated sample of Li₁₆₃MnO₃.
- v) LiMnO₂ and some new domains are formed in some areas in delithiated sample of Li_{1.63}MnO₃ in the first cycle.
- vi) Li_2MnO_3 can be converted into MnO_2 after a complete chemical delithiation.

To summarize the relationship of the conclusions and the questions in the introduction part: conclusion ii answers questions i, and conclusions i, iii, and v answer questions ii and iii. The conclusions describe the structural changes of Li_2MnO_3 samples occurring at a relatively shallow electrochemical delithiation level. Further investigation on Li_2MnO_3 after deeper delithiation, where oxygen may be released from the lattice, will be more interesting and are planned in order to achieve a complete understanding of its crystal structure evolution mechanism.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support from CAS Innovation project (KJCX2-YW-W26) and "973" project (2010CB833102 and 2012CB932900) is acknowledged. This work was also supported by National Natural Science Foundation of China (NSFC) No. 11174334. LG acknowledges financial support from



www.MaterialsViews.com

the "Hundred Talents" program from the Chinese Academy of Sciences. The kind help of Dr. A. Huq of ORNL for neutron experiments and data analysis is appreciated.

> Received: October 19, 2012 Revised: February 14, 2013 Published online: June 6, 2013

- [1] J. B. Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587.
- [2] J. M. Tarascon, M. Armand, Nature 2001, 414, 359.
- [3] M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li, S. A. Hackney, J. Mater. Chem. 2005, 15, 2257.
- [4] C. S. Johnson, J. S. Kim, C. Lefief, N. Li, J. T. Vaughey, M. M. Thackeray, *Electrochem. Commun.* 2004, 6, 1085.
- [5] J. S. Kim, C. S. Johnson, J. T. Vaughey, M. M. Thackeray, S. A. Hackney, *Chem. Mater.* **2004**, *16*, 1996.
- [6] M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey, S. A. Hackney, *Electrochem. Commun.* 2006, 8, 1531.
- [7] M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, S. A. Hackney, J. Mater. Chem. 2007, 17, 3112.
- [8] Z. H. Lu, L. Y. Beaulieu, R. A. Donaberger, C. L. Thomas, J. R. Dahn, J. Electrochem. Soc. 2002, 149, A778.
- [9] K. Shizuka, T. Kobayashi, K. Okahara, K. Okamoto, S. Kanzaki, R. Kanno, J. Power Sources 2005, 146, 589.
- [10] Y. M. Todorov, K. Numata, Electrochim. Acta 2004, 50, 495.
- [11] N. Tran, L. Croguennec, C. Labrugere, C. Jordy, P. Biensan, C. Delmas, J. Electrochem. Soc. 2006, 153, A261.
- [12] C. S. Johnson, N. Li, J. T. Vaughey, S. A. Hackney, M. M. Thackeray, Electrochem. Commun. 2005, 7, 528.
- [13] C. X. Zu, H. Li, Energy Environ. Sci. 2011, 4, 2614.
- [14] D. Y. W. Yu, K. Yanagida, Y. Kato, H. Nakamura, J. Electrochem. Soc. 2009, 156, A417.
- [15] J. Bareno, C. H. Lei, J. G. Wen, S. H. Kang, I. Petrov, D. P. Abraham, Adv. Mater. 2010, 22, 1122.
- [16] C. H. Lei, J. G. Wen, M. Sardela, J. Bareno, I. Petrov, S. H. Kang, D. P. Abraham, J. Mater. Sci. 2009, 44, 5579.
- [17] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, Chem. Mater. 2009, 21, 4216.
- [18] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, Solid State Ionics 2010, 180, 1652.
- [19] B. Ammundsen, J. Paulsen, Adv. Mater. 2001, 13, 943.
- [20] J. A. Saint, M. M. Doeff, J. Reed, J. Power Sources 2007, 172, 189.
- [21] P. Kalyani, S. Chitra, T. Mohan, S. Gopukumar, J. Power Sources 1999, 80, 103.
- [22] J. K. Ngala, S. Alia, A. Dobley, V. M. B. Crisostomo, S. L. Suib, Chem. Mater. 2006, 19, 229.
- [23] S. H. Park, Y. Sato, J. K. Kim, Y.-S. Lee, Mater. Chem. Phys. 2007, 102, 225.
- [24] S. F. Amalraj, B. Markovsky, D. Sharon, M. Talianker, E. Zinigrad, R. Persky, O. Haik, J. Grinblat, J. Lampert, M. Schulz-Dobrick, A. Garsuch, L. Burlaka, D. Aurbach, *Electrochim. Acta* 2012, *78*, 32.
- [25] D. Pasero, L. J. Gillie, A. R. West, Electrochem. Solid-State Lett. 2005, 8, A392.
- [26] Z. Lu, J. R. Dahn, J. Electrochem. Soc. 2002, 149, A815.
- [27] A. R. Armstrong, A. D. Robertson, P. G. Bruce, J. Power Sources 2005, 146, 275.
- [28] A. R. Armstrong, M. Holzapfel, P. Novák, C. S. Johnson, S. H. Kang, M. M. Thackeray, P. G. Bruce, J. Am. Chem. Soc. 2006, 128, 8694.
- [29] A. D. Robertson, P. G. Bruce, Chem. Commun. 2002, 2790.
- [30] Y. Shao-Horn, L. Croguennec, C. Delmas, E. C. Nelson, M. A. O'Keefe, *Nat. Mater.* 2003, *2*, 464.
- [31] H. Hojo, T. Mizoguchi, H. Ohta, S. D. Findlay, N. Shibata, T. Yamamoto, Y. Ikuhara, *Nano Lett.* **2010**, *10*, 4668.







www.MaterialsViews.com

- [32] Y. Oshima, H. Sawada, F. Hosokawa, E. Okunishi, T. Kaneyama, Y. Kondo, S. Niitaka, H. Takagi, Y. Tanishiro, K. Takayanagi, J. Electron Microsc. 2010, 59, 457.
- [33] L. Gu, C. B. Zhu, H. Li, Y. Yu, C. L. Li, S. Tsukimoto, J. Maier, Y. Ikuhara, J. Am. Chem. Soc. 2011, 133, 4661.
- [34] R. Ishikawa, E. Okunishi, H. Sawada, Y. Kondo, F. Hosokawa, E. Abe, Nat. Mater. 2011, 10, 278.
- [35] X. Lu, Z. Jian, Z. Fang, L. Gu, Y.-S. Hu, W. Chen, Z. Wang, L. Chen, Energy Environ. Sci. 2011, 4, 2638.
- [36] R. Huang, T. Hitosugi, S. D. Findlay, C. A. J. Fisher, Y. H. Ikuhara, H. Moriwake, H. Oki, Y. Ikuhara, Appl. Phys. Lett. 2011, 98, 051913.
- [37] X. He, L. Gu, C. Zhu, Y. Yu, C. Li, Y.-S. Hu, H. Li, S. Tsukimoto, J. Maier, Y. Ikuhara, X. Duan, Mater. Express 2011, 1, 43.
- [38] S. D. Findlay, N. R. Lugg, N. Shibata, L. J. Allen, Y. Ikuhara, Ultramicroscopy 2011, 111, 1144.
- [39] S. D. Findlay, N. Shibata, H. Sawada, E. Okunishi, Y. Kondo, T. Yamamoto, Y. Ikuhara, Appl. Phys. Lett. 2009, 95, 191913.

- [40] J. Breger, M. Jiang, N. Dupre, Y. S. Meng, Y. Shao-Horn, G. Ceder, C. P. Grey, J. Solid State Chem. 2005, 178, 2575.
- [41] Y. S. Meng, G. Ceder, C. P. Grey, W. S. Yoon, M. Jiang, J. Breger, Y. Shao-Horn, Chem. Mater. 2005, 17, 2386.
- [42] K. A. Jarvis, Z. Deng, L. F. Allard, A. Manthiram, P. J. Ferreira, J. Mater. Chem. 2012, 22, 11550.
- [43] S. H. Park, H. S. Ahn, G. J. Park, J. Kim, Y. S. Lee, Mater. Chem. Phys. 2008, 112, 696.
- [44] A. D. Robertson, P. G. Bruce, Chem. Mater. 2003, 15, 1984.
- [45] W. P. Tang, H. F. Kanoh, X. J. Yang, K. Ooi, Chem. Mater. 2000, 12, 3271.
- [46] H. Kanoh, K. Ooi, Y. Miyai, S. Katoh, Langmuir 1991, 7, 1841.
- [47] H. Kanoh, W. P. Tang, Y. Makita, K. Ooi, Langmuir 1997, 13, 6845.
- [48] R. J. Xiao, H. Li, L. Q. Chen, Chem. Mater. 2012, 24, 4242.
- [49] P. M. De Wolff, Acta Crystallogr. 1959, 12, 341.
- [50] Y. Chabre, J. Pannetier, Prog. Solid State Chem. 1995, 23, 1.
- [51] C. Wu, W. Xie, M. Zhang, L. Bai, J. Yang, Y. Xie, Chem.-Eur. J. 2009, 15.492.