Effects of structural defects on the electrochemical activation of Li_2MnO_3

Liang Xiao,^{1,4} Jie Xiao,^{1,*} Xiqian Yu,² Pengfei Yan,³ Jianming Zheng,¹ Mark Engelhard,³ Priyanka Bhattacharya,¹ Chongmin Wang,³ Xiao-Qing Yang,² and Ji-Guang Zhang^{1,*}

¹ Dr. L. Xiao, Dr. J. Xiao, Dr. J. Zheng, Dr. P. Bhattacharya, Dr. J.-G. Zhang
Energy and Environment Directorate, Pacific Northwest National Laboratory, 902 Battelle Blvd.,
Richland, Washington 99352 USA
E-mail: Jiguang.zhang@pnnl.gov

² Dr. X. Yu, Dr. X-Q. Yang
Chemistry Department, Brookhaven National Laboratory, Upton, NY, 11973 USA

³ Dr. P. Yan, Mr. M. Engelhard, Dr. C.M. Wang
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 902
Battelle Blvd., Richland, Washington 99352 USA

⁴ Dr. L. Xiao
Department of Chemistry, School of Chemistry, Chemical Engineering and Life Sciences,
Wuhan University of Technology, Wuhan, Hubei 430070 China

Keywords: Li_2MnO_3 , structural defect, Mn^{3+} , lithium-rich, lithium-ion batteries

Abstract

Structural defects, e.g. Mn^{3+} /oxygen non-stoichiometry, largely affect the electrochemical performance of both Li_2MnO_3 and Lithium-rich Manganese-rich (LMR) layered oxides with Li_2MnO_3 as one of the key components. Herein, Li_2MnO_3 samples with different amount of structural defects of Mn^{3+} /oxygen non-stoichiometry are prepared. The results clearly demonstrate that the annealed Li_2MnO_3 (ALMO), quenched Li_2MnO_3 (QLMO), and quenched Li_2MnO_3 milled with Super P (MLMO) all show pure C2/m monoclinic phase with stacking faults. MLMO shows the largest amount of Mn^{3+} , followed by the QLMO and then the ALMO. The increased amount of Mn^{3+} in Li_2MnO_3 (such as sample MLMO) facilitates the activation of Li_2MnO_3 and leads to the highest initial discharge specific capacity of 167.7 mAh g^{-1} among the

samples investigated in this work. However, accelerated activation of Li_2MnO_3 also results in faster structural transformation to spinel-like phase, leading to rapid capacity degradation. Therefore, the amount of Mn^{3+} needs to be well controlled during synthesis of LMR cathode in order to reach a reasonable compromise between the initial activity and long-term cycling stability. The findings of this work could be widely applied to explain the effects of Mn^{3+} on different kinds of LMR cathodes.

Introduction

The lithium-ion battery is the most popular chemical energy storage system for mobile applications, such as portable electronics and electric vehicles (EVs). However, the energy density of current lithium-ion batteries still cannot meet the requirements of long-range EV applications due to the limited energy density of cathode materials such as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. [1,2] Therefore, much effort has been dedicated to seeking alternative cathode materials with higher energy density. Lithium-rich, manganese-rich (LMR) layered oxides, denoted as $x \text{Li}_2\text{MnO}_3 \cdot (1 - x) \text{LiMO}_2$ ($\text{M} = \text{Mn, Ni, Co, Fe, Cr, etc.}$) are attractive cathode candidates because of their high discharge capacity ($>250 \text{ mAh g}^{-1}$), high operating voltage ($>3.5 \text{ V vs. Li/Li}^+$) and low cost. [3-6] However, the long-term cycling stability of an LMR cathode, including its low conductivity, low initial Coulombic efficiency, and continuous voltage fade are closely correlated to the physicochemical properties of lithium-rich layered oxides containing Li_2MnO_3 component. [2,7]

Recently, the structural defects, especially oxygen non-stoichiometry and Mn^{3+} , of Li_2MnO_3 material have been studied regarding their influence on its electrochemical performance. [8-10] It is reported that oxygen non-stoichiometry leads to a significant enhancement in electronic

conductivity and electrochemical activity of Li_2MnO_3 in reversible intercalation of lithium.[10] Moreover, oxygen non-stoichiometry and Mn^{3+} in the Li_2MnO_3 component also have significant influence on the electrochemical performance of LMR layered cathode materials. It has been reported that a self-adjusted oxygen-partial-pressure approach could induce the formation of Mn^{3+} inside the $\text{Li}[\text{Li}_{0.14}\text{Mn}_{0.47}\text{Ni}_{0.25}\text{Co}_{0.14}]\text{O}_2$ crystal by simply varying the lithium sources.[11] The existence of Mn^{3+} ions was found to enhance the activation of the Li_2MnO_3 component and the electrochemical performance of the LMR materials.[11]

In the present work, we prepared Li_2MnO_3 samples with higher amounts of Mn^{3+} by several approaches, including annealing, quenching, and ball milling a quenched sample with Super P. The effects of the structural defects (oxygen non-stoichiometry/ Mn^{3+}) on the morphology, structure and electrochemical performance of Li_2MnO_3 prepared by different treatments were systematically investigated. A more fundamental understanding of the influences of Mn^{3+} on the Li_2MnO_3 -containing LMR cathode materials was obtained.

Sample Preparation

The Li_2MnO_3 samples were prepared by ball milling stoichiometric amounts of Li_2CO_3 and MnO_2 (both from Sigma-Aldrich) for 4 h using a SPEX SamplePrep 8000M Mixer/Mill, followed by heat treating at 900°C for 12 h in air and different cooling procedures. An excess of 5 mol% Li_2CO_3 was used to compensate for Li loss at high temperature. QLMO and ALMO correspond to samples prepared by quenching or annealing to room temperature, respectively. Some of the quenched Li_2MnO_3 was further milled (Retsch planetary mill model PM 100 CM) with 5 wt% Super P (from Timcal) for 4 h, which was labelled MLMO.

Characterization

Powder XRD data was collected on beamline X14A of the National Synchrotron Light Source at Brookhaven National Laboratory by a linear position-sensitive silicon detector ($\lambda = 0.779 \text{ \AA}$). The XRD patterns for the as-prepared Li_2MnO_3 samples were refined using the General Structure Analysis System (GSAS) program. The SEM images were obtained using an FEI Helios Nanolab 600 instrument at 5 kV that was equipped with an Everhart-Thornley detector for secondary electron imaging. All the three samples were characterized by HRTEM and SAED on an FEI Titan 80-300 transmission electron microscope at 300 kV. The microscope was equipped with an image Cs corrector that enables sub-angstrom resolution in HRTEM imaging. The XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA (Electron Spectroscopy for Chemical Analysis) Microprobe with a focused monochromatic Al $K\alpha$ X-ray (1486.7 eV) source and a spherical section analyzer.

Electrochemical Measurements

Electrodes were prepared by casting a slurry of the Li_2MnO_3 sample, Super P, and poly(vinylidene fluoride) (Kynar HSV 900, Arkema Inc.) in an N-methyl pyrrolidone (Sigma-Aldrich) solvent onto aluminum foil. The weight ratio of Li_2MnO_3 : Super P: PVDF was 80:10:10. After vacuum drying at 80°C , the electrodes were punched into disks 1.4 cm in diameter. The active material loading was $3\sim 4 \text{ mg cm}^{-2}$. R2032 coin cells with aluminum-clad cans were assembled in an argon-filled MBraun glove box using lithium foil, Celgard polyethylene film, and 1 M LiPF_6 in a mixture of ethylene methyl carbonate and ethylene carbonate at a 7:3 volume ratio as anode, separator and electrolyte, respectively. The electrochemical tests were performed on an Arbin BT-2000 battery tester at room temperature.

The cells were cycled between 2.0 and 4.8 V vs. Li^+/Li at a current density of 10 mA g^{-1} . All potentials refer to Li^+/Li throughout this work.

Results and discussion

Figure 1 shows scanning electron microscopy (SEM) images of Li_2MnO_3 samples prepared by different methods. Quenched Li_2MnO_3 (QLMO) (**Figure 1a** and **1b**) and annealed Li_2MnO_3 (ALMO) (**Figure 1e** and **1f**) exhibit agglomerated secondary particles that are composed of small primary particles with particle sizes of 100~200 nm. However, quenched Li_2MnO_3 that has been milled with Super P (MLMO) (**Figure 1c** and **1d**) shows larger secondary particles than either QLMO or ALMO samples due to the further agglomeration caused by planetary milling. On the other hand, some of the small particles in MLMO are smaller than those in QLMO, which means planetary milling breaks the primary particles of QLMO. The effect of this mechanical pulverization on the structure of Li_2MnO_3 will be discussed later.

Figure 2 shows the synchrotron X-ray diffraction (SXRD) patterns of prepared Li_2MnO_3 powders (QLMO, MLMO and ALMO). In the present work, no impurity phase is observed in any of the three samples, which means pure-phase Li_2MnO_3 has been successfully prepared. The observed diffraction peaks of all samples match well with the positions of reflections corresponding to the monoclinic (C2/m) Li_2MnO_3 phase. In particular, the super-lattice peaks between 10° and 15° are characteristic of LiMn_6 cation ordering that occurs in the transition metal (TM)-rich layers of the Li_2MnO_3 crystal lattice.[12,13] The diffraction peaks of MLMO all correspond to the C2/m Li_2MnO_3 phase, indicating that there is no detectable structural change after ball milling the QLMO with Super P. The refined lattice parameters are listed in **Table 1**, and are close to the values reported previously.[14,15] The lattice parameters *a* and *b*, which are

indications of the distances of Mn-Mn and Mn-Li in the TM slabs, increase in the order of ALMO, QLMO, and MLMO. Meanwhile, the unit cell volumes increase in a similar order. The results indicate a slight valence drop of Mn from Mn^{4+} ($r = 0.54 \text{ \AA}$) to Mn^{3+} ($r = 0.65 \text{ \AA}$) in QLMO and MLMO samples. It is possible that quenching leads to oxygen loss and Mn^{3+} , and ball milling with Super P gives rise to the slight reduction of Mn from Mn^{4+} to Mn^{3+} , resulting in the lengthening of Mn-Mn / Mn-Li bonds and the increase of cell volume.

To investigate the valence difference of Mn in the Li_2MnO_3 samples, the Mn 2p X-ray photoelectron spectroscopy (XPS) spectra of QLMO, MLMO and ALMO were collected and compared in **Figure 3**. There are multiplet splittings of Mn 2p XPS spectral peaks, which is consistent with a literature report.[16] Mn $2p_{3/2}$ XPS spectra of QLMO (**Figure 3a**) and ALMO (**Figure 3c**) can be fitted by five peaks with parameters (binding energy (B.E.), full width at half maximum (FWHM) and percentage) listed in **Table 2**. This means that the valence of Mn on the surfaces of QLMO and ALMO generally remains at +4. However, besides the five peaks corresponding to Mn^{4+} , fitting of Mn $2p_{3/2}$ XPS spectra of MLMO (**Figure 3b**) requires additional peak assignments at 639.9 and 640.6 eV to achieve a good fit. The binding energy of these two peaks is slightly lower than that of Mn^{4+} peaks. The XPS peaks at 639.9 and 640.6 eV could be ascribed to the presence of Mn^{2+} and Mn^{3+} , respectively. This result further substantiates that Super P slightly reduces the particle surface of Li_2MnO_3 during mechanical milling, consistent with the X-ray diffraction (XRD) characterization result. **Figure 4** shows [100] zone high-resolution transmission electron microscopy (HRTEM) images and corresponding selected area electron diffraction (SAED) patterns from each sample. They confirmed that all three samples adopt the monoclinic $C2/m$ layered structure with a high density of stacking faults between neighboring lamellar domains.[17,18] Due to the high density

stacking faults, the SAED patterns show strong streaks along (001) planes, as indicated by the red arrows in **Figure 4b**. Annealing cannot eliminate the stacking faults due to the synthesis route via solid-state reactions at high synthesis temperatures.[15,19] It has been reported that surface cubic spinels were found in Li-rich cathodes that are partially reduced by Super P upon heating treatment.[20] However, in the present work, there was no new phase formed and no phase separation found after mechanical milling with Super P. This implies that milling with Super P at room temperature does not induce the bulk structural change of Li_2MnO_3 , despite the slight reduction of Mn as confirmed by the XPS analysis.

Figure 5a shows the first charge-discharge profiles of the QLMO and ALMO samples. **Figure 5b** shows the details of differential capacity vs. voltage (dQ/dV) profiles during initial charge of QLMO and ALMO samples. These two samples exhibit similar charge/discharge capacities in the first cycle with almost the same lengths of voltage plateaus above 4.5 V. As compared to ALMO, QLMO shows slightly lower electrode polarization (indicated by arrow “n” in **Figure 5a**) during the charge process, implying a reduced energy barrier for activation of Li_2MnO_3 . This is consistent with the small de-intercalation peak for the QLMO sample at around 4.25 V in the dQ/dV curve (indicated by arrow “n” in **Figure 5b**). QLMO also exhibits a relatively sudden change in voltage profile at ~ 4.5 V, indicated by the arrow “m” in **Figure 5a**, which corresponds to a much sharper peak at ~ 4.5 V as indicated by arrow “m” in **Figure 5b**. This behavior indicates a faster activation of QLMO than of the annealed sample (ALMO). Generally, the extraction of lithium ions in the first charge will take place at a voltage higher than 4.5 V. The anodic reaction of QLMO at 4.25 V could be attributed to the lithium de-intercalation associated with the oxidation of Mn^{3+} to Mn^{4+} . This result suggests that a small quantity of Mn^{3+} already exists in the quenched sample, although it is difficult to determine the relative amount of Mn^{3+}

from the XPS fitting shown in Table 2. The result is reasonable and consistent with the XRD analysis since oxygen doesn't have enough time to diffuse into the bulk lattice during quench process and hence oxygen vacancies and Mn^{3+} defects remain in the bulk phase of QLMO. In contrast, Mn^{3+} on the surface of Li_2MnO_3 is easier to be oxidized to Mn^{4+} during quenching treatment.

Figure 5c shows the first charge-discharge profiles of all three samples (QLMO, MLMO, and ALMO) investigated in this work. The corresponding dQ/dV profiles during initial charge of these three samples are shown in **Figure 5d**. Because of the presence of a significant quantity of Mn^{3+} in the MLMO sample, the Li_2MnO_3 phase can be activated much more easily, and thus high charge/discharge capacities can be achieved. The charge and discharge capacities of MLMO are improved to 278.4 and 167.7 mAh g^{-1} , respectively, which are considerably higher than those of QLMO and ALMO. Consequently, greatly enhanced de-intercalation reaction peaks below 4.5 V are observed for MLMO in the dQ/dV curves shown in **Figure 5d**. The enhanced performance of MLMO samples can be attributed to several factors. First, it is reasonable that milling with conductive carbon would improve the conductivity of Li_2MnO_3 via addition of conductive agents and thus alleviate the electrode polarization. Another more important reason for the enhanced electrochemical activity of the MLMO sample is the presence of a significant quantity of Mn^{3+} , which has been demonstrated to be beneficial for enhancing the conductivity and facilitating the activation of Li_2MnO_3 , lithium-rich layered oxides, and high-voltage spinel.[8,11,21,22]

Figure 6 shows the evolution of charge/discharge voltage profiles during cycling and the cycling stability of different Li_2MnO_3 samples. Severe voltage decay and capacity fading are observed for all three samples in **Figure 6a**, **6b** and **6c**, indicating the structural instability of

Li_2MnO_3 during electrochemical activation and the subsequent cycling. In **Figure 6d**, the discharge capacities of both QLMO and ALMO gradually increase in the initial 10 cycles, which is related to a gradual activation process to utilize more lithium ions. It is clearly seen that the capacity increase of QLMO is faster than that of ALMO in the initial 10 cycles. The discharge capacity of QLMO reaches its maximum value of 140 mAh g^{-1} at 10th cycle, while the maximum discharge capacity of ALMO is only 114 mAh g^{-1} . The result further suggests that the small amount of Mn^{3+} associated with oxygen vacancies facilitates the electrochemical activation of QLMO as compared to ALMO.

As expected, MLMO shows the highest reversible capacities of about 160 mAh g^{-1} in the first 4 cycles among all the three samples, because of the presence of the highest content of Mn^{3+} /oxygen non-stoichiometry. However, Li_2MnO_3 is thermodynamically unstable after extraction of Li_2O , and an irreversible phase transformation occurs from layered to spinel-like structure.[23,24] Despite its enhanced electrochemical activation of Li_2MnO_3 during early-stage cycling, MLMO shows the fastest capacity degradation during cycling. This is because increased activation of Li_2MnO_3 is accompanied by the accelerated phase transformation from layered to spinel-like structure, resulting in voltage decay and capacity fading. All three samples degrade to almost the same capacities after 45 cycles, as shown in **Figure 6d**. This means that the Li_2MnO_3 samples with different amounts of Mn^{3+} are all structurally unstable and transform to a spinel-like structure, even though they experience a different activation rate.

Conclusions

In conclusion, Li_2MnO_3 samples with controlled amounts of structural defects of Mn^{3+} /oxygen non-stoichiometry have been systematically investigated. All the samples show pure C2/m

monoclinic phase with stacking faults. The existence of Mn^{3+} was found to facilitate the activation of Li_2MnO_3 phase. MLMO, with the largest amount of Mn^{3+} (9.7%), delivers the highest initial discharge specific capacity among all the three samples. However, accelerated activation of Li_2MnO_3 also gives rise to faster structural transformation from layered to spinel-like phase, leading to rapid capacity fading. The fundamental findings of this work provide a valuable guide for reaching a compromise between the initial activity and long-term cycling stability, by controlling the amount of Mn^{3+} in both Li_2MnO_3 and Li_2MnO_3 -containing LMR cathode materials.

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U. S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231, Subcontract No. 18769, under the Advanced Battery Materials Research program. The microscopic and XPS study described in this paper was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at PNNL. L. Xiao is grateful for a scholarship from the China Scholarship Council for overseas studies (No. 201208420238) and support from the Fundamental Research Funds for the Central Universities (No. 2014-Ia-031). P. Bhattacharya is grateful for support from a Linus Pauling Distinguished Postdoctoral Fellowship at PNNL. The work at Brookhaven National Laboratory was supported by the DOE Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies under Contract Nos. DE-AC02-98CH10886 and DE-SC0012704.

References

- [1] J. R. Croy, A. Abouimrane, Z. Zhang, *Mrs Bulletin* 39 (2014) 407-415.
- [2] H. Yu, H. Zhou, *J. Phys. Chem. Lett.* 4 (2013) 1268-1280.
- [3] J. Zheng, M. Gu, A. Genc, J. Xiao, P. Xu, X. Chen, Z. Zhu, W. Zhao, L. Pullan, C. Wang, J.-G. Zhang, *Nano Lett.* 14 (2014) 2628–2635.
- [4] J. Zheng, M. Gu, J. Xiao, B. J. Polzin, P. Yan, X. Chen, C. Wang, J.-G. Zhang, *Chem. Mater.* 26 (2014) 6320–6327.
- [5] M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li, S. A. Hackney, *J. Mater. Chem.* 15 (2005) 2257-2267.
- [6] M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, S. A. Hackney, *J. Mater. Chem.* 17 (2007) 3112-3125.
- [7] X. Yu, Y. Lyu, L. Gu, H. Wu, S.-M. Bak, Y. Zhou, K. Amine, S. N. Ehrlich, H. Li, K.-W. Nam, X.-Q. Yang, *Adv. Energy Mater.* 4 (2014) doi: 10.1002/aenm.201300950.
- [8] Y. Okamoto, *J. Electrochem. Soc.* 159 (2012) A152-A157.
- [9] K. Kubota, T. Kaneko, M. Hirayama, M. Yonemura, Y. Imanari, K. Nakane, R. Kanno, *J. Power Sources* 216 (2012) 249-255.
- [10] D. Pasero, V. McLaren, S. de Souza, A. R. West, *Chemistry of Materials* 17 (2005) 345-348.
- [11] X. Zhang, D. Luo, G. Li, J. Zheng, C. Yu, X. Guan, C. Fu, X. Huang, L. Li, *J. Mater. Chem. A* 1 (2013) 9721-9729.
- [12] J.-S. Kim, C. S. Johnson, J. T. Vaughey, M. M. Thackeray, S. A. Hackney, W. Yoon, C. P. Grey, *Chem. Mater.* 16 (2004) 1996-2006.
- [13] J. Zheng, W. Shi, M. Gu, J. Xiao, P. Zuo, C. Wang, J.-G. Zhang, *J. Electrochem. Soc.* 160 (2013) A2212-A2219.
- [14] S. F. Amalraj, L. Burlaka, C. M. Julien, A. Mauger, D. Kovacheva, M. Talianker, B. Markovsky, D. Aurbach, *Electrochim. Acta* 123 (2014) 395-404.
- [15] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, *Dalton Trans.* 41 (2012) 1574-1581.
- [16] H. W. Nesbitt, D. Banerjee, *American Mineralogist* 83 (1998) 305-315.
- [17] J. Bareño, C. H. Lei, J. G. Wen, S. H. Kang, I. Petrov, D. P. Abraham, *Adv. Mater.* 22 (2010) 1122-1127.
- [18] K. A. Jarvis, Z. Deng, L. F. Allard, A. Manthiram, P. J. Ferreira, *Chem. Mater.* 23 (2011) 3614-3621.
- [19] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, *Solid State Ionics* 180 (2010) 1652-1659.
- [20] B. Song, H. Liu, Z. Liu, P. Xiao, M. O. Lai, L. Lu, *Sci. Rep.* 3 (2013).
- [21] J. Xiao, X. Chen, P. V. Sushko, M. L. Sushko, L. Kovarik, J. Feng, Z. Deng, J. Zheng, G. L. Graff, Z. Nie, *Adv. Mater.* 24 (2012) 2109-2116.
- [22] J. Zheng, J. Xiao, X. Yu, L. Kovarik, M. Gu, F. Omenya, X. Chen, X.-Q. Yang, J. Liu, G. L. Graff, *Phys. Chem. Chem. Phys.* 14 (2012) 13515-13521.
- [23] P. Yan, L. Xiao, J. Zheng, Y. Zhou, Y. He, X.-T. Zu, S. X. Mao, J. Xiao, F. Gao, J.-G. Zhang, C. Wang, *Chem. Mater.* 27 (2015) 975–982.
- [24] J. Zheng, P. Xu, M. Gu, J. Xiao, N. D. Browning, P. Yan, C. Wang, J.-G. Zhang, *Chem. Mater.* 27 (2015) 1381-1390.

Table 1. Refined lattice parameters of prepared Li_2MnO_3 (QLMO, MLMO and ALMO) with monoclinic C2/m phase

Samples	a (Å)	b (Å)	c (Å)	$\beta / ^\circ$	cell volume (Å ³)
QLMO	4.932(6)	8.536(1)	5.025(6)	109.239(3)	199.785(8)
MLMO	4.938(0)	8.543(5)	5.028(6)	109.244(9)	200.290(6)
ALMO	4.932(4)	8.536(0)	5.025(1)	109.241(3)	199.753(0)

Table 2. Mn ($2p_{3/2}$) peak parameters for Mn in prepared Li_2MnO_3 samples (QLMO, MLMO and ALMO)

Sample	Peak	B.E.(eV)	FWHM* (eV)	Percent** (%)
QLMO	Mn^{4+}	641.4	1.2	46.0
	Mn^{4+}	642.3	1.2	29.4
	Mn^{4+}	642.9	1.2	15.8
	Mn^{4+}	643.8	1.2	6.8
	Mn^{4+}	644.6	1.2	2.0
MLMO	Mn^{3+}	640.6	1.2	9.7
	Mn^{4+}	641.6	1.2	38.8
	Mn^{4+}	642.4	1.2	19.4
	Mn^{4+}	643.0	1.2	19.8
	Mn^{4+}	644.0	1.2	7.7
	Mn^{4+}	645.1	1.2	2.7
ALMO	Mn^{4+}	641.4	1.2	44.9
	Mn^{4+}	642.4	1.2	31.1
	Mn^{4+}	643.1	1.2	14.7
	Mn^{4+}	643.9	1.2	7.2
	Mn^{4+}	644.8	1.2	2.1

*All peaks modelled as 70% Gaussian-30% Lorentzian.

**The percentage represents the contribution of each peak to the total number of counts under the Mn ($2p_{3/2}$) peak.

Figure 1. SEM images of (a, b) quenched Li_2MnO_3 (QLMO), (c, d) quenched Li_2MnO_3 milled with Super P (MLMO), and (e, f) annealed Li_2MnO_3 (ALMO).

Figure 2. SXR D patterns of prepared Li₂MnO₃ powders (QLMO, MLMO and ALMO) with $\lambda = 0.779 \text{ \AA}$.

Figure 3. Fitting results of Mn 2p XPS spectra of (a) QLMO, (b) MLMO and (c) ALMO.

Figure 4. [100] zone HRTEM images and SAED patterns of (a, b) QLMO, (c, d) MLMO and (e, f) ALMO samples. HRTEM images show high density of stacking faults between (001) planes (highlighted by blue lines in (a), (c) and (e)).

Figure 5. (a) Details of first charge-discharge profiles of QLMO and ALMO samples. (b) Details of dQ/dV profiles during initial charge of QLMO and ALMO samples. (c) First charge-discharge profiles of all three samples. (d) dQ/dV profiles during initial charge of all three samples.

Figure 6. Voltage profiles of (a) QLMO, (b) MLMO and (c) ALMO and (d) their discharge specific capacities, during cycling in the voltage range of 2.0–4.8 V.