

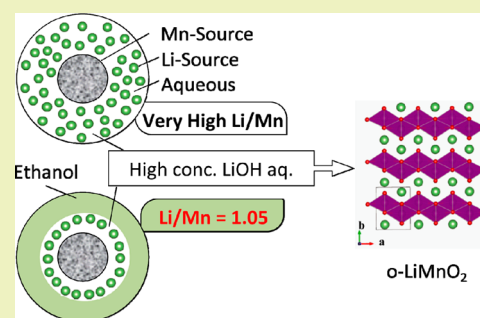
Strategy for Lowering Li Source Dosage While Keeping High Reactivity in Solvothermal Synthesis of LiMnO₂ Nanocrystals

Yi He,[†] Qi Feng,[‡] Siqu Zhang,[†] Qingli Zou,[†] Xianling Wu,[†] and Xiaojing Yang^{†,*}[†]Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China[‡]Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu 761-0396, Japan

S Supporting Information

ABSTRACT: The lithium resource is becoming increasingly scarce due to the increasing use of lithium ion secondary batteries. To obtain LiMnO₂, however, using a hydrothermal method, a high concentration of LiOH is required, namely, Li/Mn molar ratios in raw materials that are usually larger than 13. In this letter, we present a new strategy for drastically lowering the Li dosage based on the fact that the LiOH solubility is high in water but sparingly soluble in ethanol. Well-crystallized LiMnO₂ nanocrystals can be produced in miscible solvents with a Li/Mn molar ratio as low as 1.05. The results strongly suggest that a high Li⁺ concentration in the water phase would be beneficial for manganese oxides to form a layered structure, while the reactivity of Li⁺ accelerates its reaction with Mn₂O₃.

KEYWORDS: *o*-LiMnO₂, Solvothermal synthesis, Lithium dosage, Li/Mn molar ratio



INTRODUCTION

Abundant and low cost manganese resources make lithium manganese oxides one of the most promising cathode materials for lithium ion batteries. Because the theoretical capacity is as high as 285 mAh/g, twice that of the commercialized spinel type LiMn₂O₄,¹ layered-structural LiMnO₂ has attracted wide attention.^{2–5} LiMnO₂ has monoclinic and orthorhombic structures, noted as *m*- and *o*-LiMnO₂, respectively. The *m*-LiMnO₂ material, prepared through Na⁺/Li⁺ ion-exchange as reported early by Delmas⁶ and Armstrong,⁷ was considered very difficult to obtain,³ while many works focused on *o*-LiMnO₂. To prepare *o*-LiMnO₂, the solid-state reaction method^{8–14} is the most common. There are some shortcomings in this method, such as an inert atmosphere necessary for synthesis, the product's irregular morphology and big size at the micrometer level,^{11,13} and the easily generated impurity.¹² Chitrakar et al.¹⁵ reported a method to prepare *o*-LiMnO₂ using a solid-phase reaction under a steam atmosphere with an Li/Mn molar ratio of 1.05 at a low temperature (120 °C), but the crystallinity of the product was low. To overcome this, a hydrothermal method is good to use.^{16–19} However, a high Li/Mn molar ratio, such as 13:1,¹⁶ 16:1,¹⁷ 18:1,¹⁸ and 21:1¹⁹, in the aqueous solution is required to keep a high concentration of LiOH from 2.5 M to (over)saturation. A systematic study¹⁹ showed that the products were spinel-type lithium manganese oxide accompanying with Mn₂O₃, a layered salt-rock phase of Li₂MnO₃ and Mn₂O₃, and *o*-LiMnO₂ and Li₂MnO₃, as LiOH concentration ranged between 0.2 and 0.3 M, 0.4 and 0.8 M, and 0.8 to 6.4 M, respectively. Therefore, a high LiOH concentration is necessary to obtain layered structures. In a

microwave synthesis of LiMnO₂, a Li/Mn molar ratio can be decreased to 8:1,²⁰ but only 1/8 of the Li source is used for the formation of LiMnO₂ effectively.

The lithium resource is increasingly scarce due to the widespread use of lithium ion batteries. Therefore, it is urgent to find a way to reduce the residual Li in the reaction solution after the formation reaction of lithium manganese oxides. Because solubility of LiOH is as high as 12.8% in water,²¹ the reduction of residual Li in the reaction solution is not easy. Introducing ethanol to water could lower the LiOH dosage, while also keeping a high LiOH concentration in the water phase. Thus, this letter reports a new strategy to increase LiOH reactivity even at a low concentration by using a solvothermal reaction system, and then the product can be applied to the synthesis of well-crystallized *o*-LiMnO₂ nanocrystals. The result showed that the Li/Mn molar ratio can be lowered to 1.05:1, i.e., 95% of the Li⁺ ions in the Li source are utilized in the LiMnO₂-forming reaction.

EXPERIMENTAL SECTION

Raw material Mn₂O₃ was prepared from the decomposition of MnCO₃ by heating at 700 °C for 2 h in air. Keeping the Li/Mn molar ratio of 1.05:1, 2.5 g of LiOH·H₂O and Mn₂O₃ (4.5 g) were weighed. The powders were put into a mixture of water and ethanol with different proportions and then were heated in a 100 mL teflonlined autoclave. After cooling to room temperature, the product was filtered, washed

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with distilled water, and dried at 110 °C overnight. The samples were referred as W_xE_y, where *x* and *y* were the volume (mL) of water and ethanol, respectively.

RESULTS AND DISCUSSION

Figure 1 is the X-ray diffraction (XRD) patterns for the samples obtained at 170 °C for 72 h. As shown, all the peaks of W30E20

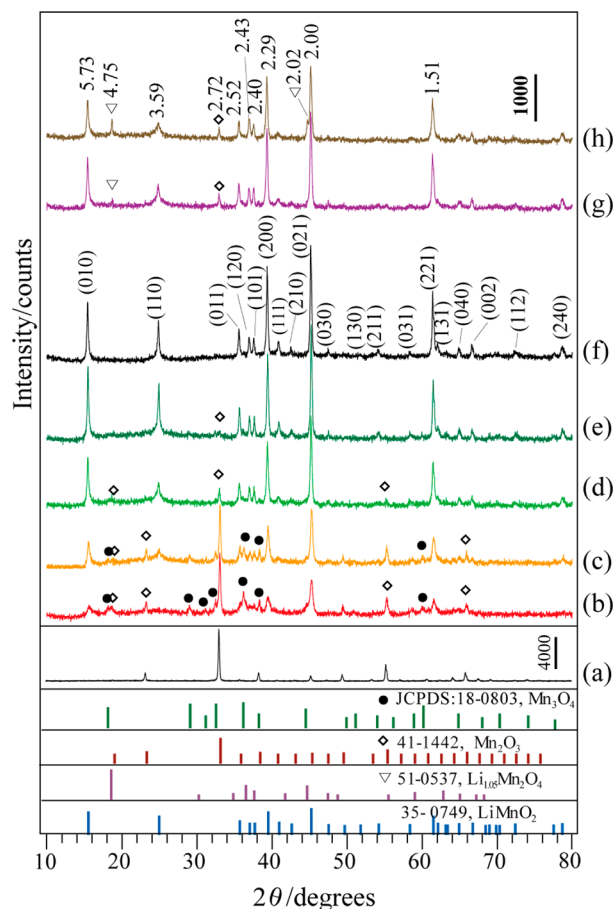


Figure 1. XRD patterns of (a) raw material Mn_2O_3 and the products (b) W0E50, (c) W5E45, (d) W10E40, (e) W20E30, (f) W30E20, (g) W40E10, and (h) W50E0 after solvothermally treated at 170 °C for 72 h. *d*-values, in Å.

can be indexed to the o- LiMnO_2 (JCPDS No. 35-0749, space group *Pmnm* (59), origin choice 2), exhibiting a pure phase obtained. The chemical analysis (Table 1) indicates that the composition of the sample was close to the stoichiometric one,

and the average oxidation state of manganese (Z_{Mn}) was 3.0. The morphology observation (Figure 2) showed that the

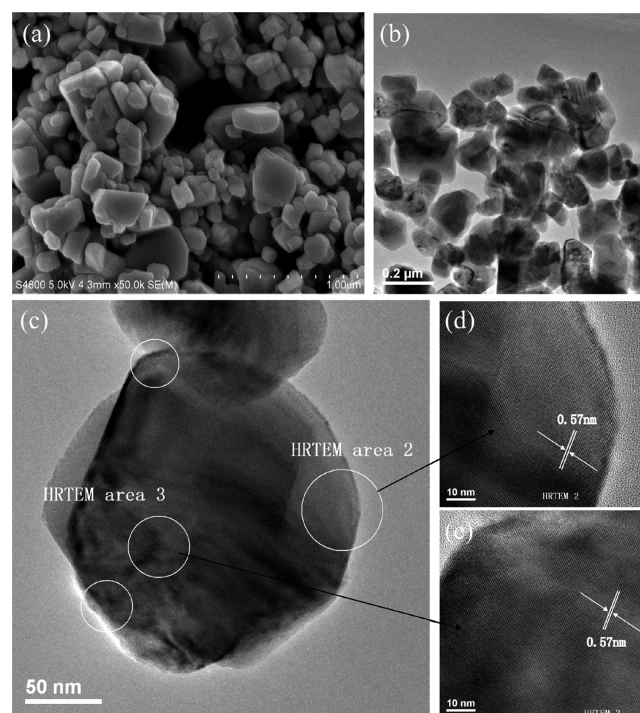


Figure 2. (a) SEM, (b, c) TEM, and (d, e) HRTEM images for W30E20 obtained at 170 °C for 72 h.

sample was typically comprised of particles 50–200 nm in size, and the larger ones had plate shapes with a thickness of ~50 nm and a length of ~200 nm. This morphology is different from that of the raw material Mn_2O_3 (Figure S1, Supporting Information), whose particles are secondary micrometer spheres accumulated with small regular particles. The lattice images of an o- LiMnO_2 particle (Figure 2d,e) indicate that the lattice fringe is 0.57 nm corresponding to (010) plane of o- LiMnO_2 . Furthermore, the particle was a single crystal because the lattice fringes were parallel among different observation areas.

As the aqueous solution and lower concentration of ethanol were used as the solvent (Figure 1h,g), the W50E0 and W40E10 samples had the main phase of o- LiMnO_2 , and other two phases can be also observed. One was unreacted Mn_2O_3 , which was frequently observed with low concentration of LiOH in an aqueous system.^{17,19} Another was a spinel phase, as the

Table 1. Chemical Analysis Results for Products Obtained at 170 °C for 72 h

sample	content calculated (found) ^a (wt %)		Li/Mn ^b	Z_{Mn} ^c	analyzed formula
	Li	Mn			
W0E50	3.48(3.75)	65.09(70.13)	0.42	2.8 ₉	$\text{Li}_{0.51}\text{Mn}_{1.21}\text{O}_2$
W5E45	4.56(4.75)	63.22(66.40)	0.57	2.9 ₄	$\text{Li}_{0.65}\text{Mn}_{1.14}\text{O}_2$
W10E40	6.23(6.31)	60.39(61.70)	0.81	2.9 ₉	$\text{Li}_{0.85}\text{Mn}_{1.05}\text{O}_2$
W20E30	6.68(6.70)	59.64(60.28)	0.88	3.0 ₀	$\text{Li}_{0.91}\text{Mn}_{1.03}\text{O}_2$
W30E20	6.62(6.83)	59.74(62.17)	0.87	3.0 ₀	$\text{Li}_{0.90}\text{Mn}_{1.03}\text{O}_2$
W40E10	6.77(7.17)	59.39(63.38)	0.89	3.0 ₂	$\text{Li}_{0.91}\text{Mn}_{1.02}\text{O}_2$
W50E0	7.21(7.60)	58.39(62.02)	0.97	3.0 ₈	$\text{Li}_{0.96}\text{Mn}_{0.99}\text{O}_2$

^aDetermined by inductively coupled plasma (ICP) atomic emission spectroscopy. ^bMolar ratio. ^cAverage oxidation state of manganese determined according to ref²³.

peaks of 4.75 and 2.02 Å could be assigned as $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$ (JCPDS 51-0537), and the SEM observation (Figure S1, Supporting Information) clearly indicated that the octahedra appeared as a specification of the spinel phase.²² Similar results (Figure S2, Supporting Information) were found for W20E0, for which a saturated LiOH aqueous solution with the Li/Mn molar ratio of 1.05:1 was used. The appearance of spinel phase was responsible for the Z_{Mn} value larger than 3 (Table 1).

On the other hand, as shown in Figure 1b, in the pure ethanol system, W0E50 had mainly the unreacted Mn_2O_3 (JCPDS 41-1442), which could be observed as the secondary spherical particles (Figure S1, Supporting Information), and the minor phases were Mn_3O_4 (JCPDS 18-0803) and o- LiMnO_2 . With increasing the water content, the peaks of o- LiMnO_2 became stronger, accompanying a decreasing in Mn_2O_3 and Mn_3O_4 phases, as illustrated in Figures 1c–e. The transformation from Mn^{3+} to Z_{Mn} with less than 3 in Mn_3O_4 was earlier reported in a hydrothermal reaction, and the hexagonal sheet-like particle (as illustrated in Figure S1, Supporting Information) was assignable to the latter phase.¹⁶ The Z_{Mn} value of 2.89 for W0E50 (Table 1) supports the existence of Mn^{2+} . For W30E20 heated at different times, Mn_3O_4 can be observed during o- LiMnO_2 formation (Figure S3, Supporting Information) corresponding to an increase in the Li/Mn molar ratio (Table S1, Supporting Information). However, for these samples, only less than 0.1 wt % Mn in the supernatant can be detected, showing that the amount of dissolved Mn^{2+} ions was very small, and they probably react with LiOH to form LiMnO_2 (Table S2, Supporting Information). Although the composition of W20E30 was almost the same as W30E20, the XRD pattern (Figure 1e) showed a small peak at $2\theta = 33^\circ$ arising from Mn_2O_3 . The result indicates that with a Li/Mn ratio as low as 1.05:1, pure o- LiMnO_2 could be produced in a mixture solvent with the appropriate proportion of water and ethanol, whereas the pure phase forms at a high concentration of LiOH in an aqueous system and hardly takes place in an ethanol system. This strongly suggests that the reactivity of Li^+ increases mostly due to an increase in its mobility that can accelerate its reaction with the Mn source to form lithium manganese oxides, while a high Li^+ concentration would be beneficial to form a layered structure. Both of reactivity and high concentration of Li^+ depend on the solubility of LiOH in different solvents. In water, LiOH is dissolved and ionized by water molecules, forming hydrous Li^+ and OH^- ions. The (hydrated) ions could be carried by ethanol molecules to the surface of the manganese source particles. If just considering the solubility of LiOH in water (12.8 wt % or 3.04 M) at room temperature while ignoring that it is sparingly soluble in ethanol,²¹ the effective concentration of LiOH in water for W20E30 and W30E20 is 3 and 2 M, respectively. In such a high concentration of LiOH, Mn_2O_3 can react to produce LiMnO_2 , which is the same situation as in a hydrothermal system. Accordingly, more water content would lessen the LiOH concentration, resulting against the formation of a layered structure. The effective concentration of LiOH in W40E10 and W50E0 was 1.5 and 1.2 M, respectively. The low concentration of LiOH would make less reactive Mn_2O_3 . In order to further clarify the roles of ethanol, a series of samples were synthesized with different amounts of ethanol on the base of W30E20. The XRD patterns (Figure S4, Supporting Information) indicated that (1) W30E0 and W30E5 had o- LiMnO_2 as main crystal phase, Mn_2O_3 , and a spinel of $\text{Li}_{1.05}\text{Mn}_2\text{O}_4$; (2) W30E10 and W30E15 had o- LiMnO_2 and Mn_2O_3 , while the spinel disappeared; and (3) the pure LiMnO_2

was obtained in W30E20, as also shown in Figure 1f. A large amount of ethanol can restrain the formation of spinel, i.e., the occurrence of Mn^{4+} , implying the reducing action of ethanol in the solvothermal condition. Therefore, ethanol contributes to the formation of LiMnO_2 by its reducing action besides improving the reactivity and high concentration of Li^+ .

In the case of low water contents, undissolved LiOH could continue dissolving in water during the reaction of $\text{Mn}_2\text{O}_3 + 2\text{LiOH} = 2\text{LiMnO}_2 + \text{H}_2\text{O}$, and the water molecules produced in the reaction would be helpful for the LiOH dissolution. Although the effective concentration (3 M) of LiOH in water for W10E40 is high enough to form the LiMnO_2 phase, the amount of LiOH dissolved in the solution is very low. Therefore, the diffusion rate of LiOH to the Mn_2O_3 solid would be very slow, which reduces the rate of formation of the LiMnO_2 phase and increases the reaction time, as observed, 96 h at 170 °C is necessary to obtain pure the LiMnO_2 phase for W10E40 (Figure S5, Supporting Information). The long reaction time helps with the formation of LiMnO_2 . The reactant species, dosages, temperatures, and so on are considerable factors that influence the reaction rate.^{16–19}

The electrochemical performance of the nanocrystals was examined using the W30E20 sample. The charge–discharge curves and cycle stability are presented in Figure 3. The

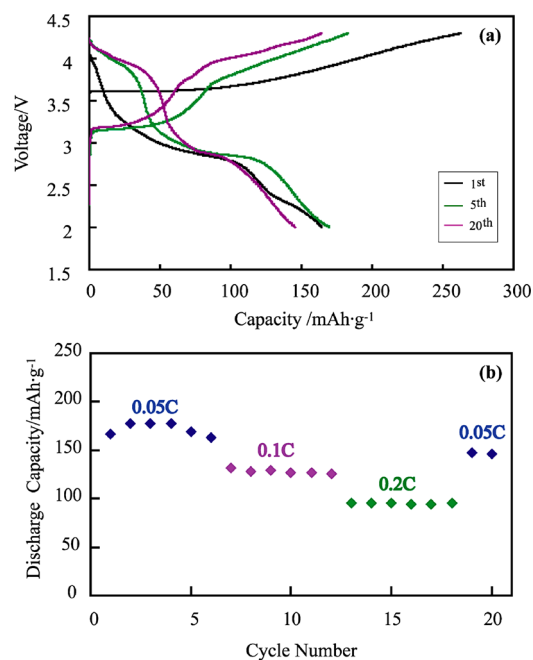


Figure 3. Electrochemical properties of W30E20: (a) charge and discharge curves and (b) the cycling performance of W30E20 at current densities of 0.05 C, 0.1 C, and 0.2 C.

capacity fading of o- LiMnO_2 materials is mainly presented by the loss in the 3 V region and extension of the 4 V plateau, as is related to the collective Jahn–Teller distortion of the cycle-induced spinel phase.¹³ As shown in Figure 3, the discharge capacity of the first cycle is about 166 mAh/g, which is larger than the reports used the solid-state method.^{12,14} The capacity was higher than 150 mAh/g after 6 cycles at 0.05C, indicating that the appearance of the spinel-like phase is not so fast. This can be observed in Figure 3a, where the 4 V plateau in the discharge curve of the fifth cycle was longer than that in the first cycle, whereas the 3 V plateau was not remarkably changed.

Although the discharge capacity decreased to 135 mAh/g at the higher current density (0.1C), stable capacities were well retained, similar to the behavior of the material obtained by a hydrothermal method.¹⁶ As the current density decreased from 0.2C to 0.05C, the discharge capacity can reach 150 mAh/g. The W30E20 sample exhibits a good cycle performance and high rate discharge ability.

CONCLUSION

In conclusion, a new strategy for lowering unreacted LiOH to 5% in a reaction solution while keeping a high reactivity for the formation of LiMnO₂ was successfully achieved. The solvent that has low polarity (ethanol in the present work as an example) and is miscible with water but undissolvable in LiOH takes on an important role to reduce the Li amount introduced to the reaction system.

ASSOCIATED CONTENT

Supporting Information

SEM images for samples of Mn₂O₃ used and the 72 h-heated sample, composition analysis results, and XRD patterns of samples heated at different times and for W20E0, W30E0, W30E5, W30E10, and W30E20. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-58802960. Fax: +86-10-58802075. E-mail: yang.xiaojing@bnu.edu.cn.

Notes

The authors declare no competing financial interest.

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