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Modified structural characteristics and enhanced electrochemical properties of oxygen-deficient $Li_2MnO_{3-\delta}$ obtained from pristine Li_2MnO_3

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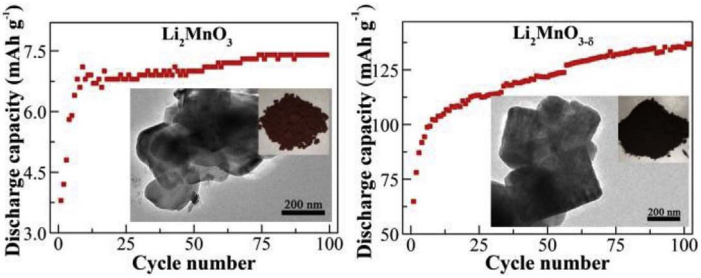
HIGHLIGHTS

- $Li_2MnO_{3-\delta}$ is obtained from Li_2MnO_3 by the $NaBH_4$-assisted heat-treatment at 380 °C.
- The modified structural properties of oxygen-deficient $Li_2MnO_{3-\delta}$ are obvious.
- The reversible capacity of $Li_2MnO_{3-\delta}$ is ca. 20 times as large as that of Li_2MnO_3.
- Gradual electrochemical activations of Li_2MnO_3 and $Li_2MnO_{3-\delta}$ are almost the same.
- A cationic-anionic redox mechanism explains the gradual activation of $Li_2MnO_{3-\delta}$.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-rich manganese(IV) oxide Li_2MnO_3 has hardly any activity as the cathode active substance of lithium-ion batteries (LIBs) but its reversible capacity can be greatly improved by introducing oxygen deficiencies. After the solid-state heat treatment of nanocrystalline Li_2MnO_3 by sodium borohydride ($NaBH_4$), the resulting $Li_2MnO_{3-\delta}$ crystallites comparatively acquire distinguishable appearances in color and shape and slight differences in surface composition and lattice structure. As a LIB cathode within the potential range of 2.5–4.7 V, at 20 mA g^{-1} pristine Li_2MnO_3 gives the specific discharge capacities of 3.3, 5.0 and 7.4 mAh·g^{-1} in the 1st, 10th and 100th cycles, while the derivative $Li_2MnO_{3-\delta}$ delivers the relatively high values of 64.8, 103.8 and 140.2 mAh·g^{-1} in the 1st, 10th and 120th cycles, respectively. Aside from the similar phenomenon of gradual electrochemical activation, substituting $Li_2MnO_{3-\delta}$ for Li_2MnO_3 means the great enhancements of charge-transfer ability and electrochemical performances. Especially, the cationic-anionic redox mechanisms of Li_2MnO_3 and $Li_2MnO_{3-\delta}$ are similar to each other, suggesting a possible solution to prepare high-performance $xLi_2MnO_{3-\delta}$·(1-x) $LiMO_2$ solid solutions for application purposes.

1. Introduction

Cathode materials with high capacity, low cost and long lifespan play an important role in their commercialization for lithium-ion batteries (LIBs) [1–3]. Ever since the demonstration of lithium-rich manganese-based layered oxides or solid solutions, xLi_2MnO_3·(1-x) $LiMO_2$ (e.g., M = $Ni_{1/3}Co_{1/3}Mn_{1/3}$), for next generation high-capacity LIB cathodes [4–6], their electrochemically "inert" constituent Li_2MnO_3, with a low reversible capacity and/or a poor long-term cycling, has been regarded as an ideal model to investigate structural and

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electrochemical properties of the lithium-rich layered compounds. This is simply due to the fact that, similar to the formula of "active" component $LiMO_2$, component Li_2MnO_3 can also be re-written as $Li[Li_{1/3}Mn_{2/3}]O_2$ to describe the additional lithium occupation in transition metal layers. However, this lithium arrangement can cause both phase transition and loss of reversible capacity during galvanostatic charge-discharge cycling. Therefore, if component Li_2MnO_3 merely functionalizes to stabilize lattice structure of the active component $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, with a theoretical capacity of ~280 mAh·g^{-1} for one-electron transfer, the well-known high-capacity feature of a solid solution $0.5Li_2MnO_3{\cdot}0.5Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, with an actual capacity higher than 200 mAh·g^{-1}, is extremely difficult to understand, especially at a cut-off voltage lower than 4.5 V.

Well-crystallized Li_2MnO_3 has a high theoretical capacity of 459 mAh·g^{-1} calculated according to a fictitious two-electron transfer mechanism. Considering the nearly "inert" nature of Li_2MnO_3 in practice, two well-recognized aspects should be mentioned: (i) further oxidation of Mn^{4+} in the octahedral coordination of Li_2MnO_3 could hardly proceed even within the electrochemical window of 2.5–4.8 V, and (ii) origin of the limited capacity of Li_2MnO_3 (i.e., < 30 mAh·g^{-1}) is still a controversial issue so far. Robertson and Bruce attribute the low electrochemical activity to the ion-exchanging of Li_2MnO_3-intercalated Li^+ with electrolyte-generated H^+, while Komaba et al. explain the limited capacity contribution using the electrochemical redox reaction of gaseous O_2 occurring at 4.5 V on Li_2MnO_3 electrode surface [7,8].

Comparing to Li_2MnO_3, LIB cathode material $Li_4Mn_2O_5$ possesses a high electrochemical activity and displays a discharge capacity as high as 355 mAh·g^{-1}, assigned to the combined contributions of Mn^{3+}/Mn^{4+}, Mn^{4+}/Mn^{5+} and O^{2-}/O^- redox couples [9]. In formula Li_2MnO_3, the partially replacing of Mn^{4+} with Ru^{4+} successfully induces the formation of oxygen deficiencies and thus the electrochemical redox reactions of Mn^{3+}/Mn^{4+}, Ru^{4+}/Ru^{5+} and O^{2-}/O^- couples could account for the high reversible capacity (i.e., 220 mAh·g^{-1}) of modified $Li_2Ru_{1-y}Mn_yO_3$ cathodes reasonably [10]. Similarly, Li_2MnO_3-like compounds such as $Li_2Ru_{1-y}Sn_yO_3$, $Li_2Ru_{1-y}Ti_yO_3$ and Li_2IrO_3 have been further proved to endow with both cationic M^{n+} and anionic O_2^{n-} redox activities for their high-capacity characteristics [11–13].

Differing with Tarascon's designs of Li_2MnO_3-like compounds [11–13], optimized synthesis or structural modification of pristine Li_2MnO_3 should be mentioned, which relates to the generation of a commonly defined Mn^{3+}-doping and oxygen-deficient form (i.e., $Li_2MnO_{3-\delta}$) for the improvement of electrochemical activity. For example, after a low-temperature treatment of pristine Li_2MnO_3 by metal hydride (i.e., CaH_2 or LiH), the resulting oxygen-deficient $Li_2MnO_{3-\delta}$ could deliver an extremely high initial discharge capacity of 388 mAh·g^{-1} at 10 mA g^{-1} but its improvement of the cycling stability was urgently needed [14]. Another example is the oxygen-deficient structure obtained via carbonthermal reduction, which presented a good cycling stability of the cathode $Li_2MnO_{3-\delta}$ but possessed a low specific capacity (e.g., 50th cycle, 60 mAh·g^{-1}, 10 mA g^{-1}) in each cycle therein [15].

Generally, introducing oxygen vacancies can intrinsically improve the electron/ion conductivity and electrochemical performance of transition metal oxides [16–21], and aroused by this, in this paper solid-state sodium tetrahydroborate ($NaBH_4$) was used as reducing agent to obtain the oxygen-deficient structure of $Li_2MnO_{3-\delta}$ from pristine Li_2MnO_3 via a thermal treatment route. Although acquiring a low discharge capacity of no more than 7.4 mAh·g^{-1} at 20 mA g^{-1}, the gradual electrochemical activation of pristine Li_2MnO_3 was detected. By comparison, the derived $Li_2MnO_{3-\delta}$ has almost the same increasing trend of electrochemical activation, and its high reversible capacity and superior cycling performance (e.g., 140.2 mAh·g^{-1}, 20 mA g^{-1}, 120th cycle) were investigated in detail in context.

2. Experimental

2.1. Syntheses of pristine Li_2MnO_3 and its derived $Li_2MnO_{3-\delta}$

All the chemicals are of analytical grade and were used without further purification. Ultrapure water (18.2 MΩ cm) was used throughout samples preparation.

Syntheses of pristine Li_2MnO_3 and its derived $Li_2MnO_{3-\delta}$ were described as below. Firstly, amorphous MnO_2 boxes were freshly prepared according to our previous results [22], which was used as a starting material to react with solid-state lithium carbonate Li_2CO_3 at the Li: Mn elemental molar ratio of 2.05: 1.00. Prior to the solid-state reaction, MnO_2 and Li_2CO_3 powders were mixed by mechanical milling in ethanol for 2 h and then dried at 80 °C overnight. Secondly, the admixtures of MnO_2 and Li_2CO_3 were heated under air-atmosphere at 800 °C for 8 h, resulting in pristine Li_2MnO_3. Thirdly, pristine Li_2MnO_3 was thoroughly mixed with powdered sodium tetrahydroborate ($NaBH_4$) at a mass ratio of 1: 2 by mechanical milling in ethanol for 2 h and dried at 80 °C overnight, and then placed into a nitrogen-atmosphere tube furnace at 380 °C for 6 h. After cooling down to room temperature naturally, the admixture was washed with methanol and water for the complete removal of impurities and then dried at 80 °C overnight, resulting in the oxygen-deficient sample referred to as a chemical formula of $Li_2MnO_{3-\delta}$.

2.2. Structural characterization

The chemical compositions of as-prepared Li_2MnO_3 and its derived $Li_2MnO_{3-\delta}$ were determined using an inductively coupled plasma/atomic emission spectrometer (ICP/AES). X-ray diffraction (XRD) measurements were performed on a Rigaku D/max-2400 powder X-ray diffractometer with Cu − Kα radiation (40 kV, 120 mA) and 2θ range of 10–80° (0.08° step per 25 s), and program Xpert HighScore Plus 3 was used for X-ray Rietveld analyses. Raman spectra were recorded on a LABRAM-HR confocal laser micro-Raman spectrometer employing a 20 mW laser at 632.8 nm. Scanning electron microscopy (SEM) observation was conducted on a Hitachi SU8010, fitted with a field emission source and operating at an accelerating voltage of 15 kV. Low- or high-resolution transmission electron microscopy (TEM or HR TEM) and selected area electron diffraction (SAED) measurements were performed on a JEM 2100 microscope (200 kV). X-ray photoelectron spectroscopy (XPS) analyses were carried out using a VG ESCALAB 220i-XL UHV surface analysis system with a monochromatic Al Kα X-ray source.

2.3. Electrochemical characterization

Working electrodes were freshly prepared, described as below. At first, admixture of active substance (i.e., Li_2MnO_3 or $Li_2MnO_{3-\delta}$; 70 wt %), acetylene black (20 wt%) and polyvinylidene fluoride (PVDF; 10 wt %) were ground, followed by the addition of N-methylpyrrolidone to form uniform slurry. Then, the resulting slurry was cast onto an aluminum foil and dried at 80 °C for 12 h in a vacuum desiccator. And then, the aluminum foil was cut into discs (12 mm in diameter) and used as LIB cathodes. CR2032-type coin cells were assembled in an argon-filled glovebox, using metallic lithium, nickel foam, Celgard 2300 microporous membrane and commercial LBC 305-01 $LiPF_6$ solution as counter electrode, current collector, separator and electrolyte, respectively.

All the electrochemical experiments were performed at 30 °C, and an electrochemical window of 2.5–4.7 V (vs. Li^+/Li and hereafter) was selected unless otherwise specified. Galvanostatic cycling tests were conducted on a LAND CT2001A battery system, and cyclic voltammetry (CV) tests were carried out on a LK 2005A electrochemical workstation at 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) tests were measured using an EG&G PAR 273A electrochemical workstation