



Synthesis of high-capacity Ti- and/or Fe-substituted Li_2MnO_3 positive electrode materials with high initial cycle efficiency by application of the carbothermal reduction method

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HIGHLIGHTS

- ▶ High-capacity Fe- and/or Ti-substituted Li_2MnO_3 positive electrode materials were prepared.
- ▶ They had higher initial cycle efficiency than 70% and higher specific capacity than 200 mAh g^{-1} .
- ▶ Beneficial electrochemical performance was accomplished using carbothermal reduction.
- ▶ They are attractive for use as positive electrode materials in large-scale lithium-ion batteries.

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ABSTRACT

Carbothermal reduction using sucrose was applied to Fe- and/or Ti-substituted Li_2MnO_3 positive electrode materials to improve their poor initial cycle efficiency (<60%) of 2.0–4.8 V. The initial cycle efficiency was improved from 53% to 68% for $\text{Li}_{1+x}(\text{Ti}_{0.5}\text{Mn}_{0.5})_{1-x}\text{O}_2$, 63%–72% for $\text{Li}_{1+x}(\text{Fe}_{0.3}\text{Mn}_{0.7})_{1-x}\text{O}_2$, or 62%–78% for $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Ti}_{0.2}\text{Mn}_{0.6})_{1-x}\text{O}_2$ by application of the carbothermal reduction process. All samples belong to 3.2 V class positive electrode material with high initial discharge capacity higher than 220 mAh g^{-1} . The shape change of discharge curve with cycle progression was suppressed for all reduced samples. The compositional, transition metal valence state, and structural and powder property changes occurring before and after carbothermal reduction processing were examined to construct the material design concept of attractive Li_2MnO_3 -based positive electrode candidates using only naturally abundant and cheap elements (Ti and Fe) as constituent metals.

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1. Introduction

Among constituent materials of lithium-ion batteries, the positive electrode material is most important because its electrochemical properties dictate the operating voltage and capacity of the battery. With expansion of the applications of the lithium-ion batteries to vehicle installation for EV or PHEV and to energy storage for renewable energy, resource savings and cost reductions of the positive electrode material are necessary because material costs of positive electrode materials are higher than those of other

constituent materials, and because most positive electrode materials contain rare metal elements such as Co and Ni.

Even though many oxide-based positive electrodes ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, LiMn_2O_4) have been proposed for the application described above, Li-excess layered manganese oxide materials ($(1-\delta)\text{LiMO}_2-\delta\text{Li}_2\text{MnO}_3$, $0 < \delta < 1$, $M = \text{Ni}_{1/2}\text{Mn}_{1/2}$ or $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$) are attractive candidates showing specific capacity higher than 250 mAh g^{-1} within the wider voltage range from 2.0 to 4.8 V [1–3]. Among the various transition metal ratios, $\text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2$ has been known as an optimized composition showing high initial charge and discharge capacities (328 and 253 mAh g^{-1}) [4]. However, many problems (lack of initial reversibility, large capacity fading with cycle number, bad rate performance etc.) have been described in relation to practical use.

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The charge–discharge behavior of this material, which is rather complex, is mainly attributable to participation of the Li_2MnO_3 component as an electrochemically active material. While Li extraction and insertion reactions originating from the LiMO_2 component occurred between 3.5 and 4.4 V, Li_2O extraction from Li_2MnO_3 occurred at voltages higher than 4.5 V on charging. In addition, Li insertion to “ Li_2O -extracted MnO_2 ” component reactions occurred at voltages lower than 3.5 V on discharging [1,2,5]. The Li_2MnO_3 converts to spinel phase with increasing cycle number [6]. The thick passivation layer on the active material formed [7] and O_2 gas evolution occurred on initial charging at voltages higher than 4.5 V [8]. To optimize the electrochemical performance, setting Li_2MnO_3 content, δ in $(1-\delta)\text{LiMO}_2-\delta\text{Li}_2\text{MnO}_3$ solid solution is extremely important, as shown in Table 1 [2,3]. With increasing Li_2MnO_3 content, although the specific capacity increased drastically, other electrochemical characteristics became poor. In addition, special care is necessary for synthetic procedures because complete mixing of two or three transition metals is difficult by a simple solid-state reaction, and the discharge capacity of Li_2MnO_3 increased by reducing the primary particle size, which can be accomplished by lowering the calcination temperature [9]. These facts show that the material design concept to control electrochemical performance for the $(1-\delta)\text{LiMO}_2-\delta\text{Li}_2\text{MnO}_3$ remains under development.

From about ten years ago, we started to develop solid solutions of three kinds: Fe [10,11], Ti [12], and Fe and Ti [13] substituted Li_2MnO_3 -positive electrode materials. These materials are attractive candidates for use in large lithium-ion batteries because they contain only inexpensive and naturally abundant transition metal elements. However, they had poor electrochemical performance. Particularly, the initial cycle efficiency was less than ca. 74% and the average discharge voltage was around 3.0 V (1.5–4.8 V) at room temperature [14]. For practical use, the initial cycle efficiency must be greater than 80% under a narrower voltage range (2.0–4.8 V). While we proposed Fe- and Ni-substituted Li_2MnO_3 ($\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})_{1-x}\text{O}_2$) [15] as a new Co-free positive electrode material having high initial average discharge voltage 3.5 V at voltages of 2.0–4.8 V, a challenge to improve the poor electrochemical performance for the Fe- and/or Ti-substituted Li_2MnO_3 is necessary for the additional development of large-scale lithium-ion batteries.

As described in this paper, we sought to reduce the valence state of manganese using a carbothermal reduction method to obtain high initial cycle efficiency of greater than 80% in the voltage range of 2.0–4.8 V. The material design concept constructed from the change in valence state of manganese ion at the 1 cycled state; some manganese ions were reduced slightly from 4+ to 3+ state [1,2,5] and most Li_2MnO_3 -based positive electrode materials have high cycle efficiency of greater than 95% after the second cycle. As Table 1 shows, partial reduction of Mn^{4+} ion corresponds to a decrease in δ for $(1-\delta)\text{LiMO}_2-\delta\text{Li}_2\text{MnO}_3$ solid solution. Therefore we can expect to improve the cycle performance and raise the

average discharge voltage (>3 V). Even though a similar approach was described in previous reports in the literature [2,16,17], the reduction method and target material differed. The carbothermal reduction method was used mainly for improvement of the rate capability of various positive electrode materials [18–20].

2. Experimental

All samples (0.25 mol/batch) were synthesized using four-step processes comprising coprecipitation, hydrothermal reaction, calcination in air, and carbothermal reduction in an inert atmosphere. First, the mixed metal aqueous solution at a target transition metal ratio was prepared using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%; Wako Pure Chemical Industries), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99.0%; Wako Pure Chemical Industries), 30% $\text{Ti}(\text{SO}_4)_2$ solution (reagent grade; Wako Pure Chemical Industries), and distilled water (500 ml). The mixed metal solution was dropped into lithium hydroxide solution, which consists of 60 g of LiOH , and 1000 ml of distilled water to produce a mixed metal precipitate. The precipitate was aged by air bubbling treatment overnight.

After the aging process, the mixed metal precipitate was recovered by filtration process as a wet cake. The cake was mixed with 100 ml of distilled water, 50 g of $\text{LiOH} \cdot \text{H}_2\text{O}$, and 50 g of KClO_3 (oxidizer) into a PTFE beaker for hydrothermal treatment. The hydrothermal reaction time was 5 h at 220 °C into an autoclave. The product was washed repeatedly with distilled water to eliminate residual salts. Then the filtrated product was mixed with aqueous solution (100 ml) including 1/8 mol of $\text{LiOH} \cdot \text{H}_2\text{O}$ before drying at 100 °C overnight.

The dried mixture was calcined at 650 °C for 20 h in air after pulverization. The calcined product was dispersed in aqueous solution including sucrose. The amount of sucrose was adjusted to 0.1 M times of carbon per 1 batch. The dried mixture was calcined at 500 °C or 600 °C depending on the target metal ratio for 1 h under N_2 flow after pulverization (carbothermal reduction process). The products were purified by washing with distilled water, filtration, and drying at 100 °C for applying various characterization methods as well as electrochemical measurements. To examine the effects of carbothermal reduction, the reference samples were prepared separately by washing products with distilled water, filtration and by drying at 100 °C after the calcination described above at 650 °C in air.

The sample quality was checked using X-ray diffraction (XRD) measurements. For X-ray Rietveld analysis, Si powder (SRM 640c) was used as an external standard for calibrating the diffraction angle. The XRD data were collected between 10° and 125° of the 2θ angles under monochromatized $\text{CuK}\alpha$ radiation using an X-ray diffractometer (Rotaflex RU-200B/RINT; Rigaku). A split pseudo-Voigt profile function was selected for each XRD peak fitting. A computer program (RIETAN-2000 [21]) was used for X-ray Rietveld analysis. The Li, Ti, Fe, and Mn elemental analyzes were performed using inductively coupled plasma (ICP) emission spectroscopy and average valence state of transition metals except for Ti was analyzed through iodometric titration. The carbon content was estimated using a CS analyzer (EMIA-320V2; Horiba). The Brunauer–Emmett–Teller (BET) surface area was measured and used as specific surface area (SSA) data. The particle size distribution was collected for 0.5–350 μm (Aerotrak SPR7340; Nikkiso). The validity of the obtained particle size distribution was confirmed using a standard powder (GBM-20; The Association of Powder Process Industry & Engineering, Japan) with average particle size of $22 \pm 1.0 \mu\text{m}$.

The valence state analysis of Mn or Ti ions was conducted using corresponding metal K-edge X-ray absorption near edge structure (XANES) measurements. These spectra were obtained in

Table 1

Change in trends of the average valence state of constituent metals, and electrochemical data with increasing Li_2MnO_3 contents (δ) for $(1-\delta)\text{LiMO}_2-\delta\text{Li}_2\text{MnO}_3$ ($M = \text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$ [2] or $\text{Ni}_{1/2}\text{Mn}_{1/2}$ [3]) positive electrode materials reported previously.

Li_2MnO_3 content, δ	$\delta < 0.5$ (LiMO_2 at $\delta = 0$)	$\delta > 0.5$ (Li_2MnO_3 at $\delta = 1$)
Li content	Small	Large
Average valence state of constituent metals	Less than 3.5+	Greater than 3.5+
Specific capacity	150–200 mAh g^{-1}	250–300 mAh g^{-1}
Initial cycle efficiency	80–90%	50–60%
Average discharge voltage	>3.5 V	<3.5 V
Cycle performance	Good	Bad

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