

A soft chemical route to multicomponent lithium transition metal oxide nanowires as promising cathode materials for lithium secondary batteries

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Abstract

We have synthesized 1D nanowires of lithium nickel manganese oxides with two different crystal structures through the chemical oxidation reaction of solid-state precursor $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ under hydrothermal condition. According to X-ray diffraction and elemental analyses, the nanowires obtained by persulfate treatments at 65 and 120 °C crystallize with a hexagonal layered and an $\alpha\text{-MnO}_2$ -type structure, respectively, in which nickel and manganese ions exist in octahedral sites. Electron microscopic analyses reveal that the platelike crystallites of the precursor are changed into nanowires with the diameter of ~ 20 nm after the persulfate treatment. Thermal and infrared spectroscopic analyses clearly demonstrate that, in comparison with $\alpha\text{-MnO}_2$ -structured nanowires, the hexagonal layered nanowires contain less water molecules in the lattice, which makes them suitable for the application as electrode materials for lithium secondary batteries. According to electrochemical measurements, the hexagonal layered nanowires show a larger discharge capacity and an excellent cyclability with respect to repeated Li intercalation–disintercalation process. X-ray diffraction and electron microscopic analyses on the samples subjected to electrochemical analysis reveal that the layered structure and 1D morphology of the nanowires are still maintained after the electrochemical cyclings, which is responsible for their excellent electrochemical performances.

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Keywords: 1D nanowires; Chemical oxidation; Solid-state precursor; Lithium nickel manganese oxide; Hexagonal layered structure; Electrode materials

1. Introduction

Over the past decades, intense research efforts have been made to explore new efficient manganese-based cathode materials for lithium secondary batteries with a view to replacing currently commercialized LiCoO_2 compound. In particular, layered lithium manganese oxide has attracted special attention as an alternative electrode, since it possesses a large theoretical discharge capacity of more than 280 mA/g as well as economic and ecological merits [1–5]. However, the layered LiMnO_2 suffers from a detrimental phase transformation to a spinel-type structure during electrochemical cycle, resulting in the irreversible loss of discharge capacity. Recently the partial replacement of manganese with other transition metal ions like Cr, Co has been reported to improve the electrochemical performance of layered lithium manganate due to the enhancement of structural

stability [6]. In this context, layered $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ compound is of special importance as a promising cathode material for rechargeable lithium batteries [7,8]. This compound has been known to have a high structural stability, which is due to the fixed tetravalent oxidation state of manganese during electrochemical cycling [9–11]. On the other hand, nanocrystalline manganese oxides were reported to show superior electrochemical performances to the microcrystalline homologues [12,13]. However, there have been only a limited number of publications on the synthesis of 1D nanostructured manganates and related transition metal oxides [14–17]. Despite its promising electrode performance, the layered lithium nickel manganese oxide has never been obtained in the form of 1D nanostructure.

In this work, we were successful in synthesizing lithium nickel manganese oxide nanowires with two different structure types through a hydrothermal reaction of solid-state precursor. The crystal and electronic structures of the obtained nanowires were systematically investigated, along with the morphology of crystallites. We have also examined their electrochemical performance as a cathode material for lithium secondary batteries.

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2. Experimental

Pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ sample was prepared by sintering a stoichiometric mixture of NiMnO_3 and Li_2CO_3 at 1000°C in an oxygen atmosphere. The precursor NiMnO_3 was obtained by the heat-treatment of the equimolar mixture of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ at 450°C in air. Lithium nickel manganate nanowires were synthesized by chemical oxidation of the pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powder with 0.1–1 M aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution in a 50-mL autoclave with a Teflon liner. The autoclave was heated at 65 or 120°C for 30 h and then air-cooled to room temperature. The crystal structures of the resulting powders were examined by powder X-ray diffraction (XRD) using a Philips X'pert with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical composition, thermal behavior, and lattice vibration of the obtained powders were probed using atomic absorption–inductively coupled plasma (AA–ICP), thermal analysis, and infrared spectroscopy (IR). The crystal morphology and cationic composition of the oxidation products were probed using field emission-scanning electron microscopy/energy-dispersive spectroscopy (FE-SEM/EDS) with a Jeol JSM-6700F equipped with an energy-dispersive X-ray spectrometer. Also, high resolution-transmission electron microscopy/selected area electron diffraction (HR-TEM/SAED) analysis was carried out with Hitachi Model H-800 with an accelerating voltage 200 kV. Electrochemical measurements were performed in a CR2032 coin-type cell consisting of composite cathode, lithium metal anode, and porous polypropylene separator film. For the fabrication of the composite cathode, the mixture consisting of 20 mg powder of active material and 5 mg conducting binder (3.3 mg of teflonized acetylene black and 1.7 mg of graphite) was pressed on a 2.0 cm^2 stainless screen at 500 kg/cm^2 . The used electrolyte was 1 M LiPF_6 solution of ethylene carbonate:dimethyl carbonate (1:2 in volume ratio).

3. Results and discussion

The powder XRD patterns of the pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and its oxidized derivatives are presented in Fig. 1. The XRD patterns of the nanowires prepared at 65°C can be well indexed on the basis of a hexagonal layered structure. In addition to well-developed reflections, a weak reflection appears at $\sim 12^\circ$ corresponding to the (1 1 0) reflection of an $\alpha\text{-MnO}_2$ phase. The intensity of this peak becomes enhanced with increasing the

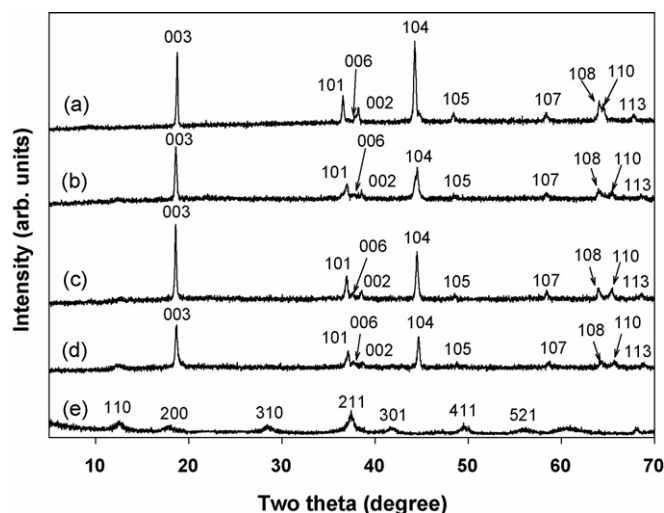


Fig. 1. Powder XRD patterns for (a) the pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and the corresponding nanowires after the oxidation reaction with (b) 0.1, (c) 0.5, (d) 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution at 65°C , and (e) 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution at 120°C .

concentration of persulfate solution, suggesting that a strong oxidation condition gives rise to the partial formation of $\alpha\text{-MnO}_2$. In this regard, we have also performed the 0.5 M persulfate treatment at 120°C , leading to the formation of pure $\alpha\text{-MnO}_2$ -type nanowires. The lattice parameters of the resulting nanowires were calculated from least squares fitting analysis, as listed in Table 1. All of the nanowires prepared at 65°C show similar lattice parameters that are almost the same as those of the pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, indicating the little change of crystal structure upon chemical oxidation reaction at low temperature. On the other hand, the lattice parameters of the nanowires prepared at 120°C match well with the previously reported values of $\alpha\text{-MnO}_2$ [18].

The effect of oxidation reaction on the morphology of the pristine compound was examined with FE-SEM measurement, see Fig. 2. The present FE-SEM images show that the plate-shaped crystallites of the precursor are changed into nanowires after the persulfate treatments at 65 and 120°C . For all the oxidation conditions presented here, the nanowires have a similar crystal dimension with the diameters of $\sim 20 \text{ nm}$ and the lengths of $\sim 1 \mu\text{m}$. The low magnification FE-SEM image (not shown here) provides strong evidence on the fact that the formation of the nanowires occurs in the whole part of the precursor with nearly complete conversion efficiency of more than 95%. As shown in Fig. 3, EDS analysis with an element mapping technique clari-

Table 1

Lattice parameters and crystal symmetries of the pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and the lithium nickel manganese oxide nanowires

| Sample | a (\AA) | c (\AA) | Crystal symmetry |
|--|----------------------|----------------------|------------------|
| Pristine $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ | 2.894 | 14.306 | Hexagonal |
| Nanowires prepared at 65°C with 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 2.858 | 14.400 | Hexagonal |
| Nanowires prepared at 65°C with 0.3 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 2.847 | 14.361 | Hexagonal |
| Nanowires prepared at 65°C with 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 2.848 | 14.373 | Hexagonal |
| Nanowires prepared at 65°C with 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 2.849 | 14.345 | Hexagonal |
| Nanowires prepared at 120°C with 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | 9.860 | 2.855 | Tetragonal |

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