

Short communication

Structural and electrochemical properties of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ ($0 \leq x \leq 0.7$) cathode materials for lithium-ion batteries

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Received 3 July 2004; accepted 29 July 2004

Available online 18 October 2004

Abstract

A comparative analysis of the properties of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($0.2 \leq x \leq 0.7$) powders, obtained by the freeze drying method, was performed. Lattice parameters of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ decreased considerably with growing amounts of Li until $x = 0.3$; at $x > 0.5$ trace amounts of Li_2MnO_3 are observed by X-ray diffraction (XRD) patterns. X-ray photoelectron spectroscopy (XPS) analysis displayed an increase of $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio at $0.3 < x < 0.5$, while Mn 2p spectra were almost identical in all samples. Rechargeable capacity values ($V = 2.5\text{--}4.6\text{ V}$) increased systematically with x reaching its maximum ($185\text{--}190\text{ mAh g}^{-1}$) at $x = 0.5$. Samples with superstoichiometric lithium content also demonstrated good C rate characteristics.

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Keywords: Secondary Li batteries; Li–Ni–Mn oxides; Cation stoichiometry; Freeze drying; Capacity fade

1. Introduction

Due to high costs and insufficient capacity of LiCoO_2 , commonly used as a cathode material in Li-ion batteries, much effort has been dedicated to developing cheaper alternatives. Initially, LiNiO_2 and LiMnO_2 have been studied [1–3] but stoichiometric LiNiO_2 demands a complicated synthesis procedure while its multi-phase reactions during electrochemical cycling leads to structural degradation [1,2]. Layered LiMnO_2 has a significant disadvantage in its crystallographic transformation to spinel structure, during electrochemical cycling [4,5]. To overcome the disadvantages in LiNiO_2 , the substitution of Al [6] or Fe [7] for Ni has been investigated. Ammundsen et al. [8] have reported Al and Cr-doped monoclinic LiMnO_2 which showed sloping discharge curves from 4 to 2.5 V, with rechargeable capacity of more than 150 mAh g^{-1} .

Recently, a concept of a solid solution of LiNiO_2 and LiMnO_2 , $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$, was proposed by Ohzuku and Makimura [9], to overcome the disadvantages of LiNiO_2 and LiMnO_2 . $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ has been reported as having the hexagonal O_3 structure similar to $\alpha\text{-NaFeO}_2$ and LiCoO_2 [10,11]. The alternating-layer arrangement provides a very suitable two-dimensional conduction pathway for the Li^+ ions.

Most solid solutions in the Li–Ni–Mn–O system demonstrate several general features. First of all, it is relatively easy to substitute Li for Ni and Ni for Li in both A and B-positions of a hexagonal layered ABO_2 structure, due to the small difference in ionic radii between Li^+ and Ni^{2+} [12,13]. Ni ions placed at the Li position obstruct the two-dimensional diffusion of Li^+ ions and irreversible capacity fade during the initial charge.

In the case of LiCoO_2 , Levasseur et al. [14] first reported the existence of Co^{2+} and oxygen defects in Li_xCoO_2 ($x > 1$), using Li [7] nuclear magnetic resonance and neutron diffraction measurements. It was also found that monoclinic dis-

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tortion for $\text{Li}_{0.5}\text{CoO}_2$, during charge, can be prevented by adding extra lithium during synthesis [14,15]. Recent studies have also demonstrated the existence of single phase compounds, $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$, with hexagonal structures which can be considered as solid solutions of LiNiO_2 and Li_2MnO_3 [16–19]. Such compounds contain considerable amounts of lithium in B-positions of the ABO_2 lattice and demonstrate enhanced electrochemical performance. At the same time, the properties of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ -based compositions, containing superstoichiometric amounts of lithium, have not been studied until now.

2. Procedure

$\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ ($x = 0, 0.2, 0.3, 0.5, \text{ and } 0.7$) powder was prepared by the freeze drying method. Li acetate, Ni and Mn acetates were dissolved in water, in the stoichiometric ratio. The solution was frozen by liquid nitrogen spray, via a pneumatic nozzle, and freeze-dried at $P = 5 \times 10^{-2}$ mBar (Alpha 2–4, Christ) for 1–2 days. Thermal decomposition of precursor powders was obtained by the fast-heating of precursors to 500°C , followed by 8 h of dwell time. The products of thermal decomposition were pressed into pellets and placed, for 12 h, into a muffle furnace preheated to 900°C . The cooling of samples was performed by air quenching. $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ powder was obtained by grinding the quenched pellets.

X-ray diffraction (XRD; Geigerflex, Rigaku, $\text{Cu K}\alpha$) measurements were conducted in the range of diffraction angles from (2θ) $17\text{--}90^\circ$ at $0.5^\circ \text{min}^{-1}$. Silicon powder was used as an internal standard. The XRD patterns were indexed and lattice parameters were determined using least squares hexagonal fitting of all the diffraction lines. For X-ray photoelectron spectroscopy (XPS, PHI-5800), samples were spread over a polymeric adhesive tape and affixed to the sample holder. All spectra were recorded using an X-ray source ($\text{Al K}\alpha$ radiation) with a scan range of $1400\text{--}0$ eV of binding energy. The collected high-resolution XPS spectra were analyzed using an XPS peak software-fitting program. The energy scale was adjusted on the carbon peak in C1s spectra, at 284.6 eV. The micromorphology and crystallographic structure of powder particles were examined with a transmission electron microscope (TEM, Philips CM-30, $U = 200$ kV).

Electrochemical characterizations were obtained using a CR2032 coin-type cell with the following parameters: cut-off voltage $2.5\text{--}4.6$ V and $I = 5 \text{ mA g}^{-1}$ (0.03C), 25 mA g^{-1} (0.15C), and 50 mA g^{-1} (0.3C) at room temperature. The cathode was fabricated with 20 mg of accurately weighed active material ($\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$) and 12 mg of conductive binder (8 mg of teflonized acetylene black (TAB) and 4 mg graphite). It was pressed on 200 mm [2] of stainless steel mesh, used as the current collector, under 300 kg cm^{-2} of pressure and dried at 120°C for 24 h in a vacuum oven. The test cell was made of a cathode and an anode (lithium metal), separated by a porous polypropylene film (Celgard 3401).

The electrolyte used was a mixture of 1 M LiPF_6 -ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by vol., Merck).

3. Results and discussion

XRD patterns of the synthesized powder, $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$, is shown in Fig. 1. The value “ x ” refers to the amount of superstoichiometric lithium in $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$. The samples in the range of $0 < x < 0.3$ are single phase, with hexagonal structures of $\alpha\text{-NaFeO}_2$ -type (space group $R\bar{3}m$), similar to a high temperature polymorph of LiCoO_2 . Small additional peaks at $20\text{--}25^\circ$, which appeared at $x = 0.5$ and 0.7 , can be attributed to superstructure in hexagonal ABO_2 lattice [12] or to the Li_2MnO_3 [17]. In the last case, the appearance of Li_2MnO_3 could have been caused by the exceeding of the solid solution limit of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ at $x \geq 0.5$.

This conclusion correlates quite well with the lattice parameters plots versus the amount of superstoichiometric lithium (Fig. 2), demonstrating a considerable decrease of c , up to $x = 0.3$, with little or no further changes. The character of the lattice parameters variation with x , can also be seen at the

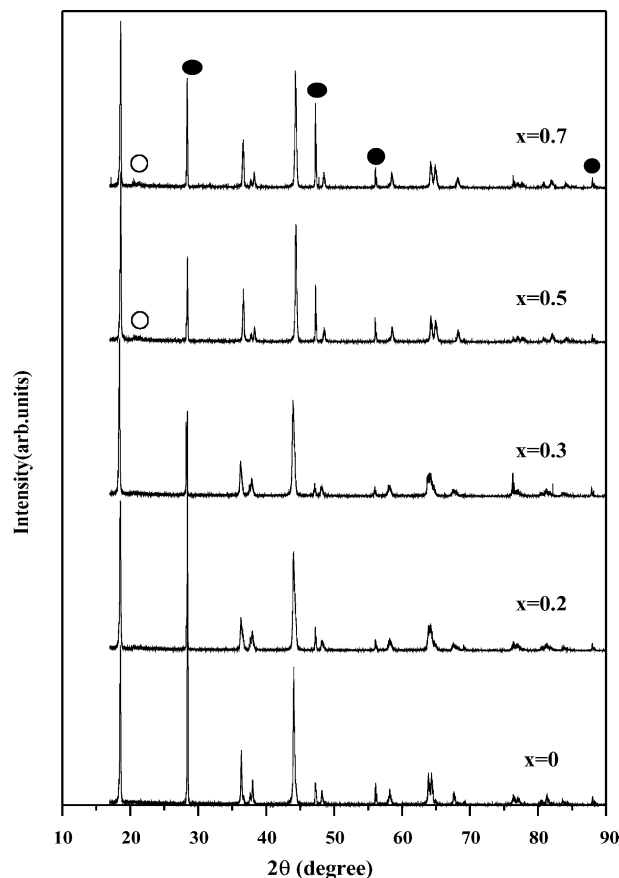


Fig. 1. XRD diffraction patterns of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{2+\delta}$ ($x = 0, 0.2, 0.3, 0.5, \text{ and } 0.7$). The closed circles indicate Si internal standard, and the open circles indicate Li_2MnO_3 .

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