

Improvement of electrochemical properties of $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{(0.4-x)}\text{Mg}_x]\text{O}_{2-y}\text{F}_y$ cathode materials at high voltage region

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Abstract

Spherical $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{(0.4-x)}\text{Mg}_x]\text{O}_{2-y}\text{F}_y$ ($x=0, 0.04, y=0, 0.08$) with phase-pure and well-ordered layered structure have been synthesized by heat-treatment of spherical $[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4-x}\text{Mg}_x]_3\text{O}_4$ precursors with $\text{LiOH}\cdot\text{H}_2\text{O}$ and LiF salts. The average particle size of the powders was about 10–15 μm and the size distribution was quite narrow due to the homogeneity of the metal carbonate, $[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{(0.4-x)}\text{Mg}_x]\text{CO}_3$ ($x=0, 0.04$) precursors. Although the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_{1.92}\text{F}_{0.08}$ delivered somewhat slightly lower initial discharge capacity, however, the capacity retention, interfacial resistance, and thermal stability were greatly enhanced comparing to the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_2$.

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1. Introduction

Layered LiCoO_2 has been the most widely used as positive electrode material in commercial lithium secondary batteries due to ease of preparation, high electronic conductivity, good rate capability, and excellent cycling performance. However, the LiCoO_2 still has some limitations due to its high cost, low capacity, toxicity, and instability at high potential windows (>4.3 V). For example, Li_xCoO_2 delivered a reversible capacity of around 140 mAh g^{-1} typically charged to 4.2 V ($x \approx 0.5$), which is much lower than its theoretical capacity of 274 mAh g^{-1} . Recently, $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ system such as $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ has been shown to be the most promising alternative to LiCoO_2 [1–3]. The chemistry of the material is quite interesting; $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ consists of Ni^{2+} , Co^{3+} , and Mn^{4+} . The Mn^{4+} is electrochemically inactive so that it provides necessary structural stability during electrochemical cycling while Ni^{2+} and Co^{3+} are electrochemically active in the forms of $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$ redox couple, respectively [4,5]. However, compared to LiCoO_2 , the $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ sys-

tem shows lower conductivity due to reduced cobalt content and exhibits unstable cycling performance, especially when cycled above 4.6 V [4,6]. One method to improve the electrochemical performance at high voltage is substituting fluorine for oxygen to stabilize the layered host structure [7,8].

In this paper, we report the effects of fluorine substitution for oxygen and magnesium for manganese on the structure, electrochemical behavior, and thermal stability of $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$. The structural, electrochemical, and thermal properties of this material are characterized by X-ray diffraction (XRD), galvanostatic charge/discharge cycling, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and electrochemical impedance spectroscopy (EIS), respectively.

2. Experimental

Spherical $(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{(0.4-x)}\text{Mg}_x)\text{CO}_3$ powders were prepared as follows. An aqueous solution of NiSO_4 , CoSO_4 , MnSO_4 , MgSO_4 (cationic ratio of $\text{Ni}:\text{Co}:\text{Mn}:\text{Mg}=0.4:0.2:0.4-x:x$) with a concentration of 2.0 mol dm^{-3} was pumped into a continuous stirred tank reactor (CSTR, capacity 4L) under CO_2 atmosphere. At the same time, Na_2CO_3 solution (aq.) of 2.0 mol dm^{-3} and desired amount

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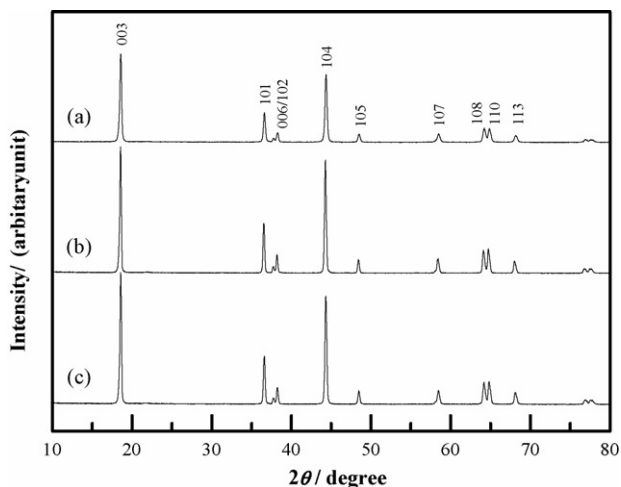


Fig. 1. Powder X-ray diffraction patterns (XRD) of: (a) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$, (b) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_2$, and (c) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_{1.92}\text{F}_{0.08}$.

of NH_4OH solution (aq.) as a chelating agent were also separately fed into the reactor. The concentration of the solution, pH, temperature, and stirring speed of the mixture in the reactor were carefully controlled. At the initial stage of the co-precipitation reaction, the irregular secondary particles were formed and the irregular particles changed gradually into spherical particles by vigorous stirring for 12 h in the reactor. Then, the spherical $(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4-x}\text{Mg}_x)\text{CO}_3$

particles were filtered and washed. The obtained spherical $(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4-x}\text{Mg}_x)\text{CO}_3$ powders were dried at 110°C and the carbonate was fired at 500°C for 5 h to decompose the carbonate into mixed oxide compounds. A mixture containing an excess amount of LiNO_3 and/or LiF , and the de-carbonated powder, $(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4-x}\text{Mg}_x)_3\text{O}_4$ (hereafter referred as precursor) were preheated at 300°C for 5 h, and finally calcined at 900°C for 20 h in air.

Charge–discharge tests were performed with a coin type cell (CR2032) with a current density of 20 mA g^{-1} at 30°C . The cell consisted of the positive and the lithium metal negative electrodes separated by porous polypropylene film. For the fabrication of the positive electrode, a mixture containing 20 mg of $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$, $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_{2-y}\text{F}_y$ ($y=0, 0.08$) powder and 5 mg of conducting binder (3.3 mg of teflonized acetylene black (TAB) and 1.7 mg of graphite) was pressed on a 2.0 cm^2 stainless screen at 500 kg cm^{-2} . The electrolyte was a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1M LiPF_6 by volume (Cheil Industries Inc., Korea).

Powder X-ray diffraction (Rigaku, Rint-2000) employing $\text{Cu K}\alpha$ radiation was used to identify the crystalline phase of the prepared powders. The prepared powders were also observed using scanning electron microscopy (SEM, JSM-6340F, JEOL). The chemical composition of the resulting powders was analyzed by atomic absorption spectroscopy (Vario 6, Analyticjena). AC impedance measurement were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from

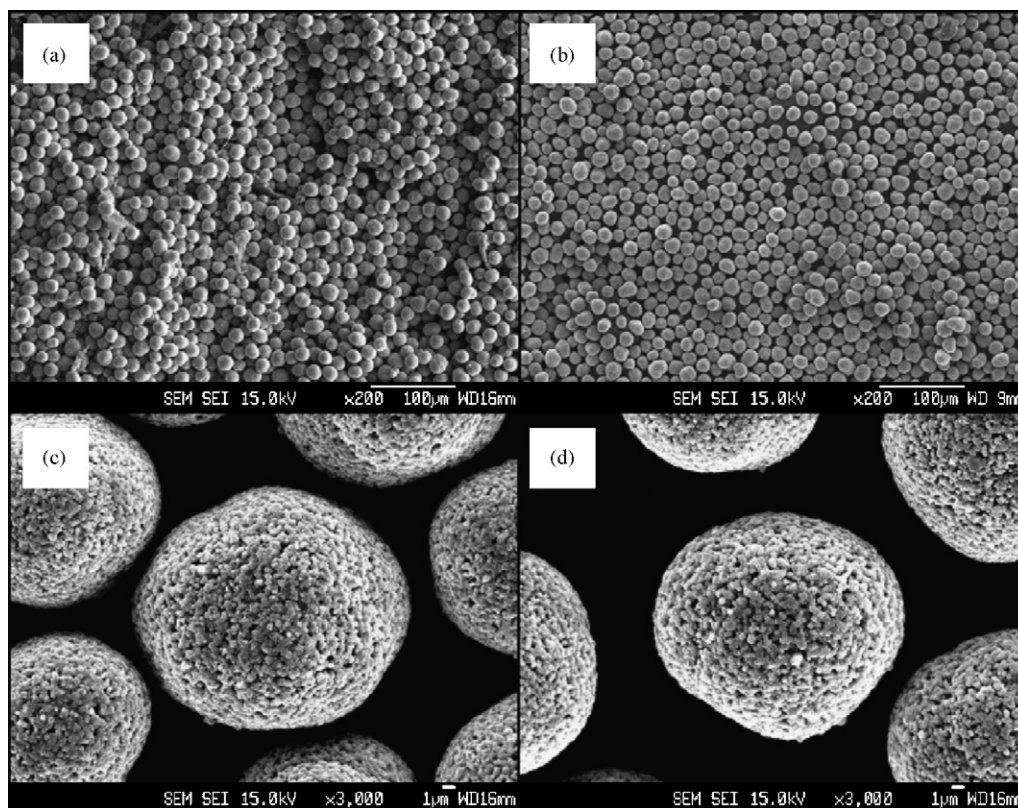


Fig. 2. Scanning electron microscope (SEM) images of the precursor of the: (a) $[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$, (b) $[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_2$, (c) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$, and (d) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.36}\text{Mg}_{0.04}]\text{O}_{1.92}\text{F}_{0.08}$.

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