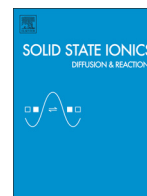




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High-pressure synthesis of lithium-rich layered rock-salt $\text{Li}_2(\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8})\text{O}_{3-x}$ for lithium battery cathodes

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ABSTRACT

A series of $\text{Li}_2\text{MO}_{3-x}$ ($M = \text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}$; $0 \leq x \leq 0.75$) in the Li_2MO_3 – Li_2MO_2 system was synthesized under high pressure, and their structures and electrochemical properties were investigated. X-ray diffraction measurements clarified the layered rock-salt-type structures in the composition range of $x = 0$ – 0.50 . The cell parameters continuously increased with x , which indicates the change in the oxygen content of the products. During the first charge process, $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_3$ showed an irreversible plateau region at 4.4 V, corresponding to electrochemical activation process. In contrast, the plateau region capacities drastically decreased with decreasing oxygen content. The oxygen-deficient phases are intrinsically electrochemically active without undergoing the activation process. The first discharge capacities increased with decreasing oxygen content from $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_3$ (100 mAh g^{-1}) to $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{2.57}$ (200 mAh g^{-1}). The oxygen deficiency significantly affects the initial electrochemical reactions and the charge/discharge capacities at the subsequent cycles for the lithium-rich layered cathodes.

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1. Introduction

Lithium-rich layered materials, $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ – LiMO_2 ($M = \text{Mn}$, Co , and Ni), are promising candidates as positive electrodes for next-generation lithium batteries because of their high charge–discharge capacity of over 250 mAh g^{-1} [1–4]. These electrodes are electrochemically activated to a high-capacity phase during the first charge process in the high-voltage region above 4.4 V (vs. Li^+/Li) [1–4]. The driving force for the change in composition and structure during the activation process is the extraction of lithium and oxygen from the layered rock-salt lattice [5–13]. The domains of the activated electrodes consist of several phases with different compositions and structures [14]; therefore, it is difficult to clarify the relationships between the compositions, structures, electrochemical properties. Recently, we have reported the direct synthesis of a single phase of electrochemically active $\text{Li}_2\text{MnO}_{3-\theta}$ by the chemical extraction of oxygen using LiH as a reduction agent [15]. However, it is still difficult to control the compositional ratios of lithium/transition metal/oxygen of the activated product by this method. It is therefore of technical importance to develop a new direct synthetic route for the production of electrochemically active lithium-rich layered positive electrodes.

High-pressure synthesis is a useful method to enclose starting materials into a reaction capsule for control of the product composition. In this report, we have attempted the synthesis of lithium-rich layered rock-salt with oxygen deficiency. Fig. 1 shows the phase diagram for

the Li_2MO_3 – Li_2MO_2 – LiMO_2 system. Li_2MO_3 ($M = \text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}$) was selected as a standard lithium-rich layered electrode with no oxygen deficiency. Cobalt and nickel were incorporated to stabilize the layered rock-salt structure under the high-pressure synthesis conditions above 1 GPa. Li_2MO_2 is the other end member of the Li_2MO_3 – Li_2MO_2 system and can be regarded as an oxygen-deficient phase with respect to Li_2MO_3 . $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ ($0 \leq x \leq 0.75$) were synthesized under high-pressure condition, and their structures and electrochemical properties were investigated using X-ray diffraction (XRD) and constant current charge/discharge measurements.

2. Experimental

Lithium-rich transition metal oxides $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ ($0 \leq x \leq 0.75$) were synthesized by high-pressure synthesis from starting materials of Li_2O_2 , Li_2O , Mn_2O_3 , CoO , and NiO . The oxygen content x in the mixture of starting materials was controlled according to the molar ratio of Li_2O_2 to Li_2O . These materials were ground in agate mortar for 30 min in an inert Ar atmosphere. The precursor was placed in a gold capsule under an Ar atmosphere in a glove box. The capsule was sintered at 950 °C for 30 min under a pressure of 1 GPa and then quenched to ambient pressure. The samples were washed with 1 mol dm^{-3} LiOH aqueous solution for 1 h to remove impurity phases and then dried under vacuum at 120 °C overnight.

The crystal structures of the samples were characterized using powder XRD measurements with $\text{Cu K}\alpha_1$ radiation using a powder diffractometer (Rigaku SmartLab). Lattice parameters were refined using the Rietveld analysis based on the structural model of the

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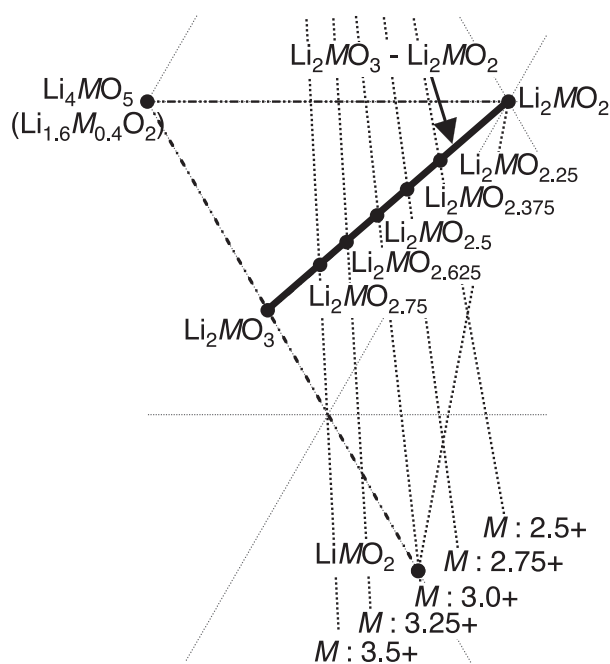


Fig. 1. Compositions of $(1-x)\text{Li}_2\text{MO}_3-x\text{Li}_2\text{MO}_2$ in the Li-O-M ternary phase diagram.

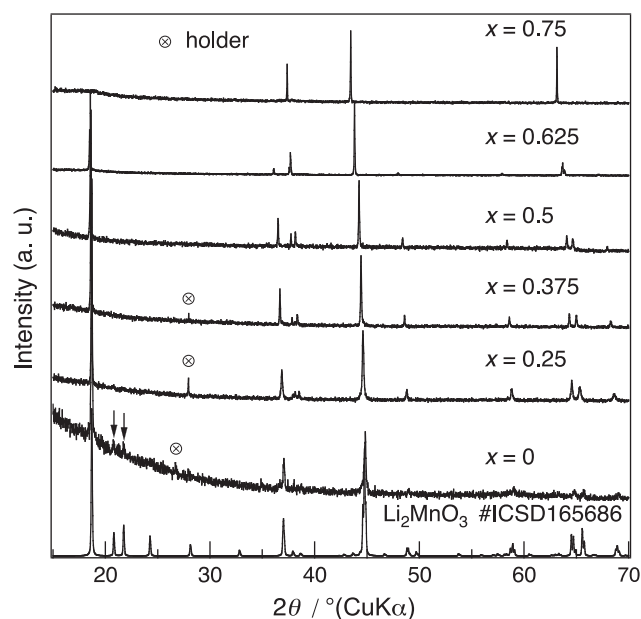


Fig. 2. XRD patterns for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ synthesized at 950 °C for 30 min under 1 GPa.

layered rock-salt structure with space group $R-3m$ using the Rietan-FP software [16].

Electrochemical properties were measured using 2032 coin-type cells. The cathode material consisted of the active material, Ketjen black, vapor grown carbon fiber (VGCF), and polyvinylidene fluoride (PVDF) at a gravimetric ratio of 80:8:2:10. Metallic lithium was used as the anode material. The electrolyte was 1 mol dm^{-3} LiPF_6 in a mixture of ethylene carbonate and diethyl carbonate (3:7 v/v). The voltage range was 2.0–4.6 V at a constant current rate of 5.5 mA g^{-1} .

3. Results and discussion

Fig. 2 shows XRD patterns for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$, where all diffraction peaks of $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_3$ ($x = 0$) can be assigned to the lithium-rich layered rock-salt structure with the space group $C2/m$. The diffraction peaks observed at 21° to 25° are attributed to the superlattice structure due to Li/cation ordering in the transition metal layer, which is often observed for lithium-rich layered materials [17]. No superlattice peaks were detected for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ in the composition range of $0.25 \leq x \leq 0.50$, but the peaks could be indexed according to the layered rock-salt structure with space group $R-3m$. The intensity of the diffraction peak around 18° was significantly decreased for the samples with $x \geq 0.625$, and no splitting was observed for the diffraction peaks around 37°. These results indicate a phase transition from the layered structure to a cubic-type structure in the highly oxygen-deficient compositions. Fig. 3 shows the lattice parameters for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ calculated using the rock-salt structure with space group $R-3m$. Both the a and c parameters increased proportionally with x in the range of 0–0.50, which indicates that the lattice expansion is dependent on the oxygen content. The c/a ratio is an indicator of the layered rock-salt structure stability. The c/a ratios for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ ($0 \leq x \leq 0.50$) were larger than 4.9, which also suggests the formation of the layered rock-salt phase [18].

Fig. 4 shows charge–discharge curves for $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ in the voltage range between 2.0 and 4.6 V. The first charge and discharge capacities of $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_3$ were 260 and 100 mAh g^{-1} , respectively. The large irreversible capacity of 160 mAh g^{-1} is attributed to an irreversible electrochemical reaction in the plateau region around 4.4 V at the first charge process. No plateau region was observed during

the charge process of following cycles. The plateau region observed at the first charge process is generally attributed to the electrochemical activation of the lithium-rich layered electrodes [5–13]. The charge/discharge capacities gradually increased from the second to eighth cycles. The discharge capacity and efficiency at the eighth cycle were 120 mAh g^{-1} and 91%, respectively. The oxygen-deficient $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$ ($0.25 \leq x \leq 0.50$) electrodes exhibited much higher first charge/discharge capacities than $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_3$.

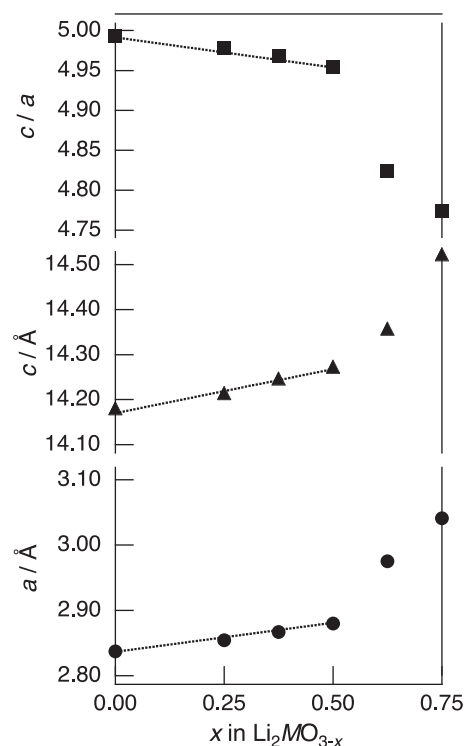


Fig. 3. Lattice parameters and c/a ratios as a function of x in $\text{Li}_2\text{Mn}_{3/8}\text{Co}_{1/4}\text{Ni}_{3/8}\text{O}_{3-x}$.

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