



Improvement of cycling performance in Ti substituted $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ through suppressing metal dissolution



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HIGHLIGHTS

- Ti substituted $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode was synthesized.
- Structural and electrochemical properties of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ were studied.
- Ti substituted cathode, $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.65}\text{Ti}_{0.10}\text{O}_{2.5}$, exhibits improved cycleability.
- Ti substitution has a significant impact on suppressing metal ions dissolution.

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ABSTRACT

Ti substituted $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode material with the composition of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ has been synthesized by spray pyrolysis method. A great variety of characterization methods have been applied to study the influence of Ti substitution for Mn on the structural, morphological and electrochemical performances of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$. X-ray diffraction (XRD) results of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ show that they exhibit similar XRD patterns as those of lithium-excess manganese metal oxide based cathode materials. It is confirmed from energy dispersive x-ray spectroscopy (EDX) data that Ti was homogeneously substituted for Mn and well distributed in the host structure. X-ray absorption near edge structure (XANES) spectra analysis reveals that oxidation state of Mn in $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ remains +4 while that of Ni changes from +2 to +4 during the initial activation process. Further investigation of the local structure of transition metal (TM) ions indicates that Ti has same coordination environment as that of Mn. Drastic capacity fade occurred in full cells with $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ cathode and graphite anode, while full cell with Ti substituted cathode shows high capacity retention after 100 cycles. Further examination of the amount of dissolved transition metal (TM) ions after long cycling test enable us to demonstrate that substitution of Mn with Ti in $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ has a significant impact on suppressing the TM ions dissolution and its deposition on both separator and anode thus leads to improved cycleability.

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1. Introduction

It is well known that lithium ion batteries (LIBs) has conquer share as powerful energy storage techniques in portable devices during the past several decades [1–3]. Besides lithium cobalt oxide LiCoO_2 [4,5] which has dominated the share of cathode materials market for LIBs for a quite long period due to its high electric conductivity and good reversible during lithium insertion/de-

insertion process, the ternary system $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [6] or $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [7–9] with improved electrochemical performance has also been widely used as cathode materials for LIBs. The increasing demand for LIBs definitely stimulates the development of novel electrode materials for LIBs. Furthermore, electrode materials with high energy density, high safety and low cost are required for the application in plug-in hybrid vehicle (PHEV) and electric vehicle (EV). Even though ternary $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material has the advantage of high energy density, the use of LiFePO_4 [10,11] and LiMn_2O_4 [12,13], should be more suitable since they have priority in safety and low cost due to their high thermal stability, environmentally benign, and inexpensive.

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Among various cathode materials for LIBs, Lithium-excess manganese metal oxide, denoted as $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ($M = \text{Ni, Co, Fe, Mn}$), have been a focus of studies and considered to be as next generation cathode materials because of the high working voltage and high specific capacity over 230 mAhg^{-1} [14–19]. Moreover, lithium and manganese rich metal oxide have the advantages of low cost due to the high content of manganese. However, these materials show large irreversible capacity at the initial cycle, resulting in a low first cycle efficiency and poor cycleability during cycling. The pre-cycling treatment demonstrated by Ito et al. is proved to be an effective approach to improve total coulombic efficiency and cycleability of lithium-excess manganese metal oxide based cathode material [20,21]. However, cycleability of lithium-excess manganese metal oxide is still far from perfect, especially in the case of full cell with carbon based anode material, extreme capacity fading has been observed.

As it had already well demonstrated in Mn-spinel cathode, the dissolution of Mn ions into electrolyte is the key reason for the capacity fade [22–25]. Similar observation has also been confirmed for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [26]. It can be expected that the dissolution of Ni as well as Mn ions into electrolyte will cause the reduction or deposition of transition metal ions on the graphite surface. In this work, the existence of insoluble deposits is proved to be the most significant reason of capacity fading in full cell with layered metal oxide cathode. Many efforts have been paid to suppress the transition metal ions dissolution or side reaction on the graphite surface [27–30]. Among them, surface protection seemed to be affective strategy [27,28] in LiMn_2O_4 spinel system. In these cases, it is hard to form uniform protection surface due to the difficulty in controlling the procedure. Consequently, the modification of the host structure would be easier and more effective for suppressing the dissolution of the transition metal ions.

In this study, we focus on the modification of the host structure of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ cathode through the partially substitution of Mn with Ti. Various analytical techniques have been employed to investigate the influence of Ti substitution for Mn on the structural and electrochemical properties of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ cathode. It was found that the concentration of dissolved TM ions after long cycling testing was drastically decreased for $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$. This study provide a facile approach to stabilize the structure of lithium-excess manganese metal oxide cathode and shed some light on the improvement of cell performance with these cathodes.

2. Experimental

2.1. Synthesis of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ ($x = 0, 0.10$)

Spray dry method was carried out with a spray drying instrument (pulvis mini-spray GB22, Yamato, Japan). The precursor solution was prepared by dissolving desirable amount of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ and Titanium citrate in water. The solution was then pumped into the spray dry instrument for reaction. The obtained precursor was heated at $200\text{ }^\circ\text{C}$ for 12 h and calcinated at $450\text{ }^\circ\text{C}$ for 12 h. The ground powder was ball-milled for 1 h and was subsequently calcinated at $900\text{ }^\circ\text{C}$ in air for 12 h to synthesize $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75-x}\text{Ti}_x\text{O}_{2.5}$ ($x = 0, 0.10$).

2.2. Instrumentation

The structure of the compounds was characterized by powder X-ray diffraction measurement (XRD) for 2θ value from 10° to 80° ($\text{CuK}\alpha$ radiation, SmartLab9kW, Rigaku). Nitrogen adsorption–desorption isotherm were carried out after the samples were

out-gassed and dehydrated (Mascorb1208, SHIMADZU). The specific surface area of each sample was calculated from the Brunauer-Emment-Teller (BET) method. Induced coupled plasma (ICP) analysis was used to determine the chemical composition of the obtained compounds (SPS-3520, SII NanoTechnology). The morphology of the compounds was observed by Field Emission Scanning Electron Microscope (FESEM, S-4700, Hitachi) and Transmission Electron Microscope (TEM, TecnaIG F20, FEI). The X-ray Absorption spectrum (XAS) experiments were performed at the Beam Line14B02 of the synchrotron radiation facility SPring-8 (JAPAN). The Mn–K, Ni–K edge and *in-situ* XAS measurement were performed with pouch cell. The REX2000 (Rigaku Corp.) and FEFF 8.2 software programs were used for the analysis of the XAS data.

2.3. Electrochemical characterization

Electrochemical characterization was performed using aluminum laminated cells. For the fabrication of positive electrodes, 88wt% of active material, 6 wt% of conductive agent, and 6 wt% of polyvinylidene difluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP). The formed slurry was cast by the doctor blade method onto aluminum foil and then dried. The total positive electrode loaded on the aluminum foil was 3.5 mg cm^{-2} . The obtained positive electrode was then punched from the cast to form cathodes. Negative electrodes were fabricated from 93 wt% of graphite, 1 wt% of conductive agent, and 6 wt% of PVDF in NMP. The obtained slurry was cast by the doctor blade method onto Cu foil and then dried to form negative electrode. The total negative electrode loaded on the Cu foil was 2.7 mg cm^{-2} . The area for cathode and anode in full cell were $24\text{ mm} \times 40\text{ mm}$ and $28\text{ mm} \times 45\text{ mm}$, respectively. The electrodes were separated by a porous polypropylene film (celgard 2500). The electrolyte was 1 mol dm^{-3} LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3:7 in volume). Lithium metal was used as the negative electrode (half cell) and also as the reference electrode.

The as-prepared electrodes were dehydrated at $130\text{ }^\circ\text{C}$ for 12 h and the cells were assembled in dry-room. The assembled cells were first cycled at a current rate of 20 mA g^{-1} between 2.0 V and 4.75 V at 0.1C (0.08 mA cm^{-2}) at $30\text{ }^\circ\text{C}$. In the following cycles, the cells were charged with CCCV between 2.0 V and 4.45 V at 1C and charged at various rates ($0.06\text{--}1.2\text{ mA cm}^{-2}$). For the evaluation of cycling performance, the cells were charged and discharged between 2.0 V and 4.45 V at 1C rate for 100 cycles.

3. Results and discussion

3.1. Investigation for the capacity fade of full cell with lithium-excess manganese metal oxide cathode

Fig. 1 shows the digital pictures and electrode cross-section SEM images of an aged full cell with $\text{Li}_{1.4}\text{Ni}_{0.3}\text{Mn}_{0.7}\text{O}_{2.4}$ ($0.4\text{Li}_2\text{MnO}_3\text{--}0.6\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$) cathode and graphite anode. The cell was cycled after 200 cycles and was then disassembled for SEM characterization. The obtained SEM images of cycled cathode, separator and anode are shown in Fig. 1 (a), (b) and (c), respectively. One can observe that deposits with a thickness of $5\text{--}10\text{ }\mu\text{m}$ formed between separator and anode.

Further characterization of the deposits by EDX shows TM were detected in deposits (Fig. 2). This reveals that transition metal, Ni and Mn, first dissolved from cathode, then diffused to anode side and finally deposited on separator and anode surface. It can be expected that the deposit accumulates on the anode surface which prevents lithium ion diffusion through. It is also confirmed that the formation of deposits on the anode surface occurred near the

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