

Synthesis and characterization of spinel type high-power cathode materials $\text{Li M}_x\text{Mn}_{2-x}\text{O}_4$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cr}$)

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Abstract

The transition metal-doped spinel cathode materials, $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cr}$) were prepared by solid-state reaction. The structure and morphology of the samples were investigated by X-ray diffraction, Rietveld refinement and scanning electron microscopy (SEM). The diffraction peaks of all the samples corresponded to a single phase of cubic spinel structure with a space group $\text{Fd}\bar{3}\text{m}$. Field-emission SEM shows octahedron like shapes and the primary particles size was between 500 nm and 2 μm . Oxidation states of Ni, Co and Cr were found to be 2+, 2+ and 3+ as revealed by X-ray photoelectron spectroscopy. During discharging, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sample shows more than 130 mAh/g between 3.5 and 5.2 V at a current density of 0.65 mA/cm² and well developed plateau around 5 V, respectively.

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1. Introduction

Lithium ion rechargeable batteries, which employ lithium transition metal oxide cathodes and carbon anodes, have applications ranging in size from portable electronic devices to zero emission vehicles (ZEV) [1]. Recent developments include 4 V cathodes based on LiCoO_2 , LiNiO_2 and LiMn_2O_4 , [2] low temperature synthesis of cathode materials [3,4] and improved electrolytes [5] which have made it possible to explore the potential range to 5 V vs. Li/Li^+ . Among the cathodes materials studied, the spinel LiMn_2O_4 was considered as a suitable positive electrode in rechargeable lithium batteries because of its high discharge capacity, low cost and acceptable environmental aspects [6–8]. However, the spinel LiMn_2O_4 electrode suffers from rapid capacity fade during cycling. Many studies were done to minimize the capacity fade, which include substituting partially the Mn^{3+} ions by other transition metal ions [9–11]. Zhong et al. [12] recently suggested that all metal-doped spinels should be reinvestigated for the reversible intercalation of lithium in the high

voltage region (over 4.7 V). Cells with high operating voltage have been reported with cathodes based on spinel structure compounds, including 4.8 V for LiNiVO_4 [13] and $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ [14] and 4.7 V for $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ [15]. For some electrochemists, especially aiming to commercialize high-power ZEV, it has been a primary target to discover a cathode which works over 5 V, linked to high specific capacity and good cycling stability.

Even though the wet chemistry synthesis methods developed recently like sol–gel method can produce highly homogeneous submicron-sized particles with a narrow particle size distribution, they have some disadvantages such as high synthetic cost, which is about three times that of the solid-state method.

In the present study, we have prepared the metal ion-doped $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cr}$) spinel electrodes through the conventional solid-state reaction followed by ball milling. Mainly, we have focused our study to analyze the variation in the oxidation states of the transition metal ions in the $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cr}$) cathodes using the X-ray photoelectron microscopic measurements.

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2. Experimental

The powder was synthesized by conventional solid-state reaction. The precursors, such as lithium fluoride (LiF, Aldrich), lithium carbonate (Li_2CO_3 , Yakuri), tetramanganese trioxide (Mn_3O_4 , Daejung), manganese dioxide (MnO_2 , Daejung), cobalt hydroxide ($\text{Co}(\text{OH})_2$, Aldrich), nickel hydroxide ($\text{Ni}(\text{OH})_2$, Aldrich), chromium oxide (Cr_2O_3 , Fluka), were reacted to form the respected $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cr}$) spinel powders.

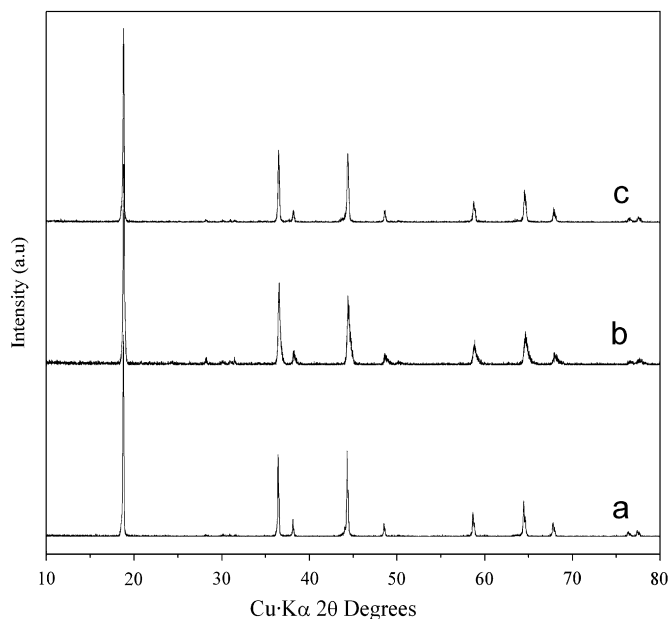


Fig. 1. X-ray powder diffraction patterns of (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and (c) $\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$, synthesized by solid-state reaction at 800°C .

Table 1
Lattice parameters of the $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cr}, \text{Co}$) samples synthesized by solid-state reaction

Sample	Lattice parameter (\AA)
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	8.14(9)
$\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$	8.15(8)
$\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$	8.19(8)

The precursors were weighted in air using a four-figure balance. The mixture was then blended and mixed in methanol in a ball mill for 24 h. It was then dried in the air for 1 day and to evaporate the moisture content the powders were dried in oven at 100°C for 2 h. The dried powders were ground using an agate mortar and pestle and calcined at 1000°C for 24 h in oxygen atmosphere. The calcined powder was then grinded and heated up to 700°C for 30 h to stabilize spinel like crystalline structure. The crystalline nature of the products was characterized by X-ray powder diffraction (XRD) using a D/MAX Ultima III diffractometer (Rigaku, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{\AA}$) and the lattice parameters were derived using the Rietveld method. The morphology of the samples was examined by field emission scanning electron microscopy (FESEM) using a Hitachi S4700 instrument. The cathode material underwent X-ray photoelectron spectroscopy (XPS) analysis to calculate the valence states of manganese and the substituted transition metal ions using Thermo VG Scientific instrument, Multilab 2000.

For electrochemical measurements, the 80% of cathode materials were mixed with 10% of carbon, and 10% of teflonated acetylene black. This mixture were pressed onto a stainless steel mesh and dried under vacuum at 180°C for 5 h. The cell consisted of a cathode and lithium metal anode separated by a glass fiber and separator. The electrolyte is a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M LiPF_6 . The coin type cells were assembled in a glove box under argon atmosphere and tested between 3.5 and 5.2 V vs. Li/Li^+ at 0.5 mA/cm^2 .

3. Results and discussions

3.1. Structural morphology

Fig. 1 shows the X-ray diffractions of the samples synthesized by conventional solid-state reaction. X-ray diffraction patterns were recorded after post heat treatment at 700°C for 30 h in oxygen atmosphere. The XRD analysis indicates that the samples prepared were identified as a single-phase spinel with a space group $\text{Fd}\bar{3}\text{m}$ in which lithium ions occupy the tetrahedral (8a) sites and the transition metal ions reside at the octahedral (16d) sites.

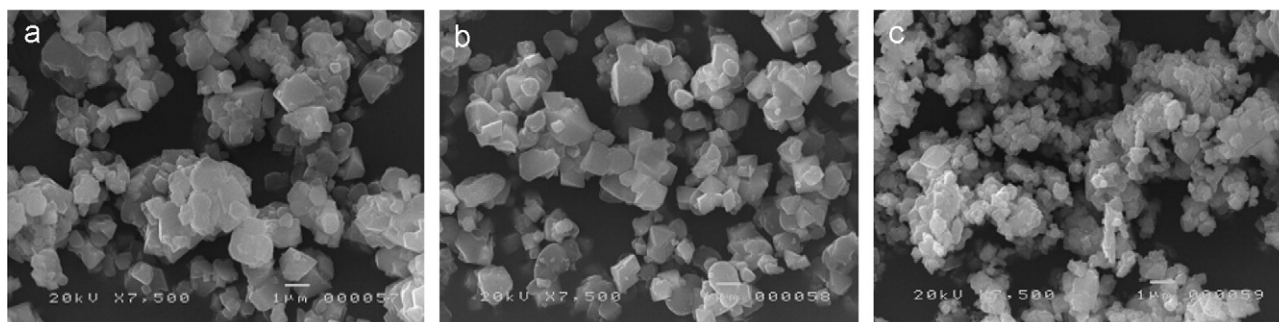


Fig. 2. Scanning electron microscope images of (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and (c) $\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The sharp (400) peak in the XRD patterns of all the compounds reveals that high-crystallized manganese oxides were synthesized. No additional peaks for other phases such as Li_2MnO_3 , LiMnO_2 or MnO_x were observed. The lattice parameters of the samples were calculated by Rietveld method and given in Table 1. The calculated parameters were found to be consistent with the reference data [10,16].

Fig. 2 shows the morphologies and particle size of the samples. From the observations of SEM results, it

was found that all samples show octahedron like shapes and the primary particles size was between 500 nm and 2 μm ranges. Also the SEM images show that the thermally treated samples possess small and unagglomerated particles.

3.2. X-ray photoelectron spectroscopic study

For the identification of oxidation states of transition metals in $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($M = \text{Ni}, \text{Co}, \text{Cr}$), XPS was

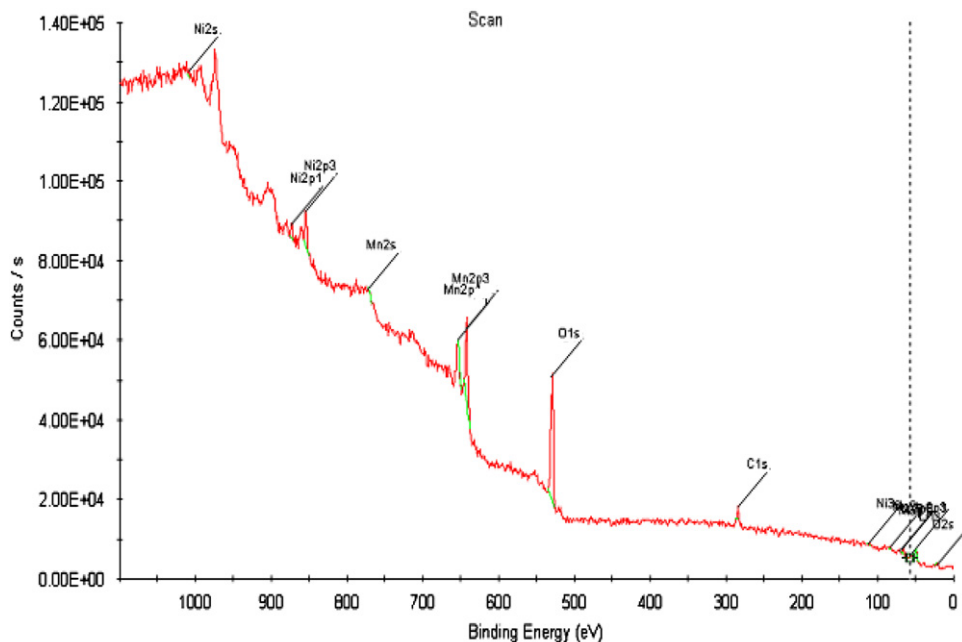


Fig. 3. XPS scan spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel cathode material.

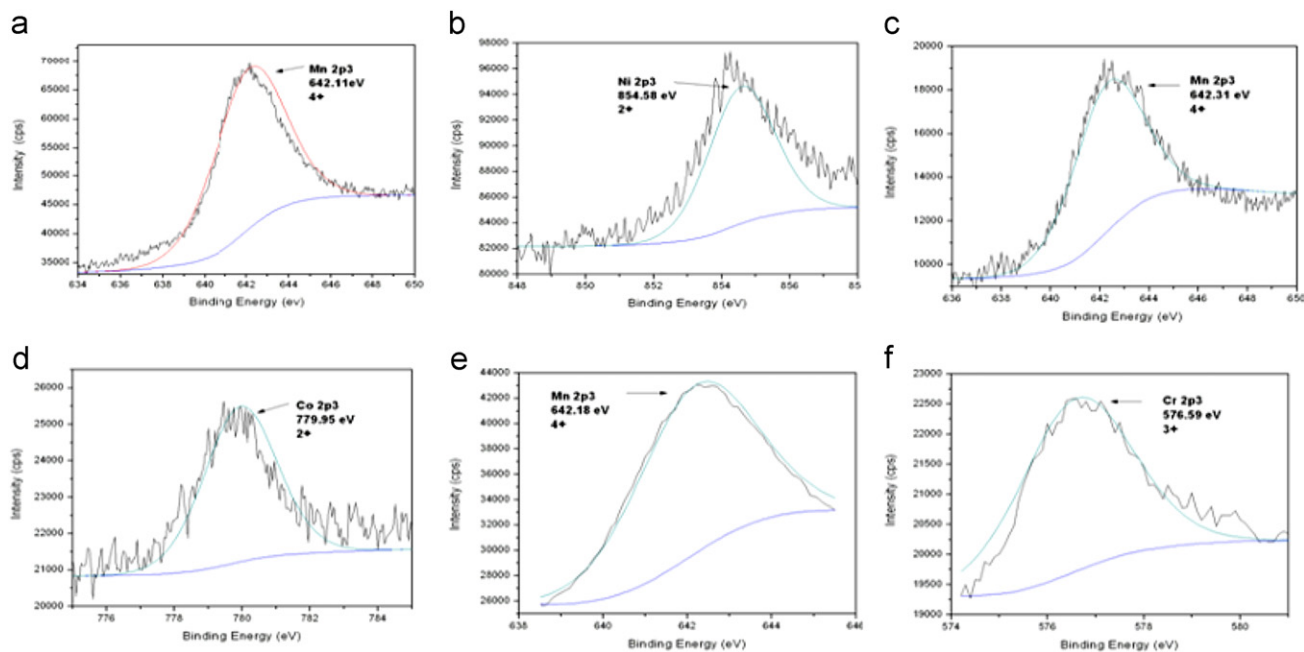


Fig. 4. XPS narrow scan spectra of (a) Mn 2p3 and (b) Ni 2p3, (c) Mn 2p3 and (d) Co 2p3, and (e) Mn 2p3 and (f) Cr 2p3 in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$, respectively.

performed with Al K α X-ray source. XPS result shows two types of data of survey scan and narrow scan. The survey scan data performed from 0 to 1100 eV in binding energy scale and include lots of quantitative and qualitative information, whereas the narrow scan focus on representative materials special spectra, so that accurate oxidation states of transition metals could be obtained. Fig. 3 shows the survey scan spectra of LiNi_{0.5}Mn_{1.5}O₄. According to this spectrum, we identified that Li, Mn and O presented in the sample and also identified their quantitative ratio, respectively.

Fig. 4(a)–(c) shows the narrow scan spectrum of Mn 2p_{3/2}, Ni 2p_{3/2}, Co 2p_{3/2}, and Cr 2p_{3/2} in LiM_{0.5}Mn_{1.5}O₄ (M = Ni, Co, Cr), respectively. In order to determine accurate oxidation states of transition metals, several scans were performed in selected binding energy range after survey scanning of entire range. According to the fitting results, the peak center of Mn 2p_{3/2}, Ni 2p_{3/2}, Co 2p_{3/2}, and Cr 2p_{3/2} were positioned at the binding energies of 642.11, 854.58, 779.95, and 576.59 eV. Therefore, we can suggest that the oxidation states of manganese, nickel, cobalt, and chromium in the LiM_{0.5}Mn_{1.5}O₄ (M = Ni, Co, Cr) were Mn⁴⁺, Ni²⁺, Co²⁺, and Cr³⁺, which were well fitted with the previous results by Amine et al. [15].

3.3. Electrochemical performance

Fig. 5 shows discharge capacities of LiM_xMn_{2-x}O₄ (M = Ni, Co, Cr) in the voltage range of 3.5–5.2 V at a current density of 0.65 mA/cm². From the discharge profiles, it can be seen obviously that all samples had two voltage plateaus approximately at 4 and 4.5 V. It can be suggested that the lithium ion was reversibly lithiated/delithiated through LiMn₂O₄ spinel framework. Usually, the spinel materials were characterized by two voltage plateaus in the discharge profile around 4 and 3 V. But in this present study, the characteristic voltage plateaus were shifted to higher voltage regions. As can be seen from the discharge profiles of all the samples, there are mainly two voltage plateau regions, which indicate the electrochemically active regions [11]. Region I around 4.0 V (3.5–4.3 V) is related to the Mn³⁺/Mn⁴⁺ couple. Region II around 4.4 V (4.4–5.0 V) is related to the redox reactions of the substituent transition metal ions. The initial discharge capacities of the LiNi_{0.5}Mn_{1.5}O₄, LiCo_{0.5}Mn_{1.5}O₄ and LiCr_{0.5}Mn_{1.5}O₄ were found to be around 123, 130 and 140 mAh/g, respectively. The capacity retention of the cathodes was found to be enhanced to compare with LiMn₂O₄ [17]. It may be due to two reasons. First, there may be a considerable decrease of the effect of Jahn–Teller distortion when substituting a small amount of Ni, Co and Cr for Mn in the spinel. This means that the concentration of Mn³⁺, which induces the Jahn–Teller distortion in the spinel is decreased. Second, there may be a reduction in spinel dissolution. It has already been established that the solvent oxidation potential plays an important role in the spinel dissolution [1,2].

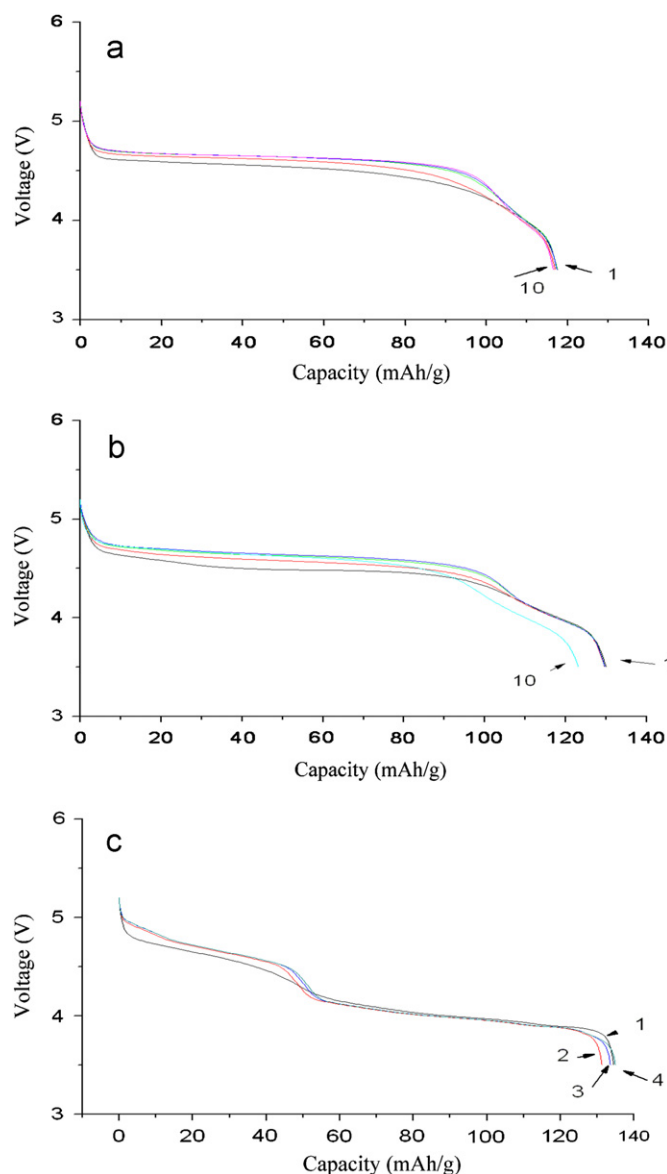


Fig. 5. Discharge capacities of (a) LiNi_{0.5}Mn_{1.5}O₄, (b) LiCo_{0.5}Mn_{1.5}O₄ and (c) LiCr_{0.5}Mn_{1.5}O₄ in the voltage range of 3.5–5.2 V at a current density of 0.65 mA/cm².

4. Conclusions

The high-voltage cathode materials, LiM_{0.5}Mn_{1.5}O₄ (M = Ni, Cr, Co) were synthesized via the conventional solid-state reaction. From the observations of SEM results, it was found that all the compounds studied in this work have particle sizes in the range of 500 nm and 2 μ m. The diffraction peaks of all the samples correspond to a single phase of cubic spinel structure with a space group Fd3m. Therefore, the normal spinel structure was preserved by doping metal ions, which occupy 16d octahedral sites. XPS results revealed that the substituents such as Ni, Co and Cr in LiMn₂O₄ exist in the 2+, 2+ and 3+ oxidation states. The electrochemical performances of the cathodes exhibited mainly two voltage plateau regions,

which indicate each transition metal ion's electrochemically active regions.

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