Synthesis and Characterization of \( \text{Li}_{1.05}\text{Co}_{0.3}\text{Ni}_{0.35}\text{Mn}_{0.3}\text{M}_{0.05}\text{O}_2 \) (\( \text{M}=\text{Ge},\text{Sn} \)) Cathode Materials for Lithium Ion Battery

CHEN Yuhong\(^1\), LI Yongzhen\(^1\), WANG Guizhen\(^1\), DI Qing\(^1\), SHEN Yushuang\(^1\)*, SUN Na\(^1\), TANG Zhiyuan\(^2\)

(1. Department of Chemical and Environmental Engineering, Hebei Chemical & Pharmaceutical Vocational Technology College, Shijiazhuang 050026, China; 2. School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China)

Abstract: In order to improve the electrochemical performance and thermal stability of \( \text{Li}_{1.05}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) materials, \( \text{Li}_{1.05}\text{Co}_{0.3}\text{Ni}_{0.35}\text{Mn}_{0.3}\text{M}_{0.05}\text{O}_2 \) (\( \text{M}=\text{Ge},\text{Sn} \)) cathode materials were synthesized via co-precipitation method. The structure, electrochemical performance and thermal stability were characterized by X-ray diffraction (XRD), charge/discharge cycling, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and differential scanning calorimetry (DSC). ESEM showed that Sn-doped and Ge-doped slightly increased the size of grains. XRD and CV showed that Sn-doped and Ge-doped powders were homogeneous and had the better layered structure than the bare one. Sn-doped and Ge-doped improved high rate discharge capacity and cycle-life performance. The reason of the better cycling performance of the doped one was the increasing of lithium-ion diffusion rate and charge transfer rate. Sn-doped and Ge-doped also improved the materials thermal stability.

Key words: lithium-ion batteries; cathode materials; Ge-doped; Sn-doped; co-precipitation

1 Introduction

Recently many researches have interested in \( \text{LiCo}_{x}\text{Ni}_{y}\text{Mn}_{(1-x-y)}\text{O}_2 \) layered cathode material for its higher capacity and better safety compared with \( \text{LiCoO}_2 \)[1-2]. However, this material had some problems, such as the lower rate capability arising from the lower electronic conductivity and tap density that should be resolved before it can replace \( \text{LiCoO}_2 \). One approach to improve the electrochemical performance was to partially substitute manganese cobalt nickel oxides for transition metals, such as iron[3], titanium[4], molybdenum[5] or chromium[6] and non-transition metals such as aluminum[6,7] or magnesium[4]. The doped element may participate in the redox processes or prevent unwanted reactions between cathode and electrolyte, so it stabilized the layered structure.

It was reported that cerium-doped made \( \text{LiNi}_{0.8-x}\text{Co}_{0.2}\text{Ce}_x\text{O}_2 \) cathode materials more regular and less cation mixing, so cerium-doped improved Cycling performance[8]. Stannum-doped could enhance the chemical diffusion coefficient of \( \text{D}_{\text{Li}} \) and improve the rate capability of \( \text{LiNi}_{3/8}\text{Co}_{2/8}\text{Mn}_{3/8}\text{O}_2 \)[9]. To the best of our knowledge, no studies on the electrochemical performance of Ge-doped and Sn-doped \( \text{Li}_{1.05}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{M}_{0.05}\text{O}_2 \) oxides had been published. So, we employed Ge and Sn as an additional dopant to synthesize a series of \( \text{Li}_{1.05}\text{Co}_{0.3}\text{Ni}_{0.35}\text{Mn}_{0.3}\text{M}_{0.05}\text{O}_2 \) (\( \text{M}=\text{Ge},\text{Sn} \)) materials prepared by a co-precipitation reaction. The structural and electrochemical performance of layered materials were studied.

2 Experimental

2.1 Materials synthesis

The molar ratio of cobalt/nickel/manganese sulfate was used as starting materials. The precursor \( \text{Co}_{0.3}\text{Ni}_{0.4-x}\text{Mn}_{0.3}(\text{OH})_2 \) was prepared by co-precipitation method. The particle size was controlled by the reaction time in order to enhance the BET surface area. A longer reaction time in the solution resulted in a larger particle size. \( \text{Co}_{0.3}\text{Ni}_{0.4-x}\text{Mn}_{0.3}(\text{OH})_2 \) continued to be rotated at 1000 r/min in the reactor at 45-50 °C. The pH value was maintained at 11-11.5 by controlling the amount of \( \text{NH}_3\text{OH} \). After filtration, rinsing, and drying, the \( \text{Li}_{1.05}\text{Co}_{0.3}\text{Ni}_{0.35}\text{Mn}_{0.3}\text{M}_{0.05}\text{O}_2 \) was prepared by mixing molar ratio amounts of 1.05 : 1 : 0.05 in \( \text{LiOH} \), \( \text{Co}_{0.3}\text{Ni}_{0.4-x}\text{Mn}_{0.3} \) (\( \text{OH}_2 \)) and \( \text{GeO}_2 \) or \( \text{SnO}_2 \) followed by a heat-treatment procedure at 900 °C for 20 h in a...
stream of dried air.

2.2 Preparation of test cells

Positive electrodes slurry for 2032 type simulated cells was prepared by thoroughly mixing active material(85%) with carbon black(10%) and polytetrafluoroethylene(5%) in ethanol. Electrodes with 0.5 cm\(^2\) in area and 0.02 mm in depth extruding onto aluminum foil were dried for 12 h at 120 °C under vacuum. 2032 type coin cells were then assembled in a argon filled dry box using foils of Li metal as counter electrodes and celgard 2400 as separators saturated with 1M LiPF6 in EC/EMC/DMC (1:1:1 in weight).

2.3 Morphology and structure tests

The surface morphology was observed by means of an environment scanning electron microscope(ESEM, Philips XL-30). Powder X-ray diffraction(XRD)(Philips X' Pert Pro MPD Co-K\(\alpha\)) was done to determine the material structure.

2.4 Electrochemical tests

The cyclic voltammograms(CV) and electrochemical impedance spectroscopy (EIS) were performed by electrochemistry working station (Gamry Instruments). The constant current and constant voltage charge(CCCV charge) was performed galvanostatic method at 0.2 C rate or 0.5 C rate and then potentiostatic methode at 4.3 V until the current dropped to less than 0.01 C and constant current discharge was enforced at different rate to 2.75 V.

2.5 DSC tests

For DSC experiments, the cells were finally fully charged to 4.3 V and opened in the Ar-filled dry box. After opening carefully, the electrode materials were removed from the current collector, the extra electrolyte was removed from the electrode surface and was rinsed by DMC. A aluminum sealed pan with a gold plated copper seal was used to collect 3–5 mg samples. The measurements were carried out in a differential scanning calorimeter (NETZSCH-204) using a temperature scan rate of 10 °C/min.

3 Results and discussion

3.1 Structural properties

The typical X-ray diffraction patterns recorded for \(\text{Li}_{1.05}\text{Co}_{0.3}\text{Ni}_{0.35}\text{Mn}_{0.3}\text{M}_{0.05}\text{O}_2\) (M=Ge,Sn) are shown in Fig.1. All of the patterns can be indexed to a signal phase of \(a\)-NaFeO\(_2\) type with space group \(R-3\ m\)\[10\]. The hexagonal unit cell parameter calculated using a least squares method were shown in table 1, \(\Delta\theta\) expressing the splitting between (0 0 6) and (1 0 2), \(\Delta\theta_1\) expressing the splitting between (1 0 8) and

![Fig.1 Power XRD profiles of Li\(_{1.05}\)Co\(_{0.3}\)Ni\(_{0.35}\)Mn\(_{0.3}\)M\(_{0.05}\)O\(_2\) compounds (a)No doped, (b)Ge-doped, and (c)Sn-doped](image)

<table>
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<th>Sample</th>
<th>c/Å</th>
<th>a/Å</th>
<th>c/a</th>
<th>Volume</th>
<th>R</th>
<th>(\Delta\theta)</th>
<th>(\Delta\theta_1)</th>
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<td>1.52</td>
<td>0.559</td>
<td>0.799</td>
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![Fig.2 ESEM images of Li\(_{1.05}\)Co\(_{0.3}\)Ni\(_{0.35}\)Mn\(_{0.3}\)M\(_{0.05}\)O\(_2\) (M=Ge,Sn) materials (a) no doped, (b) Ge-doped, and (c) Sn-doped](image)