

Synthesis and characterization of the metal-doped high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by mechanochemical process

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Abstract

The electrochemical performance of the high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was improved by doping the original material with the transition metal ion such as trivalent chromium, Cr^{3+} , which had larger bonding strength with oxygen and no Jahn–Teller effect. These high-voltage spinel compounds were prepared by the mechanochemical process, and the synthetic condition was optimized for the best electrochemical performance. It is believed that the high homogeneity of the mixture prepared by mechanical activation helps the synthesis of the phase-pure $\text{LiNi}_{0.5-x}\text{Mn}_{1.5-y}\text{M}_{x+y}\text{O}_4$ compound. The doping with the transition metal can enhance the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because the large bonding energy between the transition metal and the oxygen prevents the doped spinel from being oxygen-deficient during the high temperature synthesis process, leading to the structural and chemical stability in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The XRD patterns for the doped materials exhibited no impurity phase such as $\text{Li}_z\text{Ni}_{1-z}\text{O}$ commonly found in original $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ probably due to this structural stability of the doped materials. In addition, it is inferred that the improved cyclic performance is mainly attributed to the reduction of the Jahn–Teller distortion by substituting some portion of the high spin Mn^{3+} ions with other transition metal and less Mn dissolution of the doped spinel into the electrolyte, which effectively reduces the increase of impedance during the electrochemical cycling.

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1. Introduction

Recently, nickel-substituted manganese spinel, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been intensively studied as one of the most promising alternatives for the cathode materials of the fast-growing high-power lithium secondary batteries [1–11]. This material especially has attracted people's attention because it exhibits the highest practical 5 V capacity compared with other high-voltage class cathode materials such as spinel $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($M = \text{Cu}$ [12,13], Co [14,15], Fe [13,16]), inverse spinel LiNiVO_4 [17], olivine-structured LiCoPO_4 [18] and so on. The origin of the high voltage plateau of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_2$ type spinel compound was ascribed to the difference (~ 0.5 eV) in binding energy of the top valence band between nickel $\text{Ni}^{2+} 3d e_g (\uparrow\downarrow)$ and manganese $\text{Mn}^{3+} 3d e_g (\uparrow)$ level observed from the ultraviolet photoelectron spectroscopic study [3].

But, it has been reported that spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material shows a non-negligible capacity fading during the electrochemical cycling due to the structural and chemical instabilities resulting from the high spin Mn^{3+} ions, which is closely related with the oxygen deficiency of the spinel compound and the formation of impurity phases during the heat treatment process at the high temperatures [2,4,9]. In an ideal case, no Mn^{3+} ions should be present in the stoichiometric compound, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and all Mn^{3+} ions should be substituted by Ni^{2+} ions. However, small amount of Mn^{3+} is often observed in the compound after the high temperature heat-treatment, leading to the advent of nickel-oxide-like peaks in its X-ray diffraction (XRD) patterns and the existence of 4 V capacity in the cyclic voltammogram [2,4,5,9]. Past studies by some workers indicated that the extent of Ni substitution for Mn^{3+} in spinel $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ structure has a solubility limit around $x \approx 0.5$ and an extra amount of Ni beyond this limit could only exist as impurity phases such as $\text{Li}_z\text{Ni}_{1-z}\text{O}$ ($z \approx 0.2$) [4]. Other research group has noted that the manganese valence state in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is highly susceptible to the synthetic temperature range or the cooling rate of heat-treatment process [2]. They

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say that manganese ion is easy to be trivalent above a certain critical temperature level, and through a proper annealing process, small amount of Mn^{3+} ions, which is regarded to be greatly detrimental for the electrochemical and structural property, left in the compound can be completely transformed into Mn^{4+} .

In this study, we have optimized the synthetic conditions of metal-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through a mechanochemical process, and the structural and the electrochemical characteristics of the synthesized compound were investigated. It has been known that by introducing an appropriate doping element like chromium, which has large bond dissociation energy (or bond strength) with oxygen, the formation of impurity phases can be efficiently suppressed by relieving oxygen deficiency at the high temperature during the heat-treatment [4,9,13]. Besides, the effect of Jahn–Teller distortion of Mn^{3+} during the electrochemical cycling can be significantly mitigated by the substitution of trivalent Mn^{3+} with the other transition metal ion such as Cr^{3+} , which has only three electrons in its 3d energy level and therefore retains no Jahn–Teller distortion. The mechanochemical process or high-energy ball milling is a common method to prepare a highly homogenous mixture of powders of several species through mechanical activation [10,19–22]. It is believed that the frictional energy triggered by the movement of the balls and powders and the rotation of the bowl, promotes certain chemical reactions between the raw particles. The conventional solid-state method to synthesize the high-performance $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been reported unsuccessful so far due to the formation of nickel-oxide-like phases and the chemical instabilities of Mn^{3+} ions with electrolyte, resulting from the local inhomogeneity in the microchemistry and the large diffusion path between the particles during synthetic process [2,4,5].

2. Experimental procedure

The mechanochemical process was employed to synthesize the high-performance $\text{LiNi}_{0.5-x}\text{Mn}_{1.5-y}\text{M}_{x+y}\text{O}_4$ ($M = \text{Cr}, \text{Ti}, \text{Fe}, \text{Zn}$) cathode material, in which planetary-type ball mill was adopted for the mechanical activation of the starting materials. Proper amount of Li_2CO_3 , MnO_2 , $\text{Ni}(\text{OH})_2$ together with small amount of the doping materials such as Cr_2O_3 , TiO_2 , Fe_2O_3 , and ZnO was weighed and poured into 500 ml zirconia bowl at the same time. Considering ball to powder ratio (BPR) equal to 5:1, zirconia ball with \varnothing 10 mm, was weighed

and also put into the same bowl. After that, the powder was ball-milled at a speed of 400 rpm for 30 min. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed in the air atmosphere at a heating rate of $5^\circ\text{C}/\text{min}$ for the starting materials to determine a relevant heat schedule. After that, the ball-milled powder was collected and subjected to further two-step heat treatment at 600°C for 8 h in air and subsequently, at $800\text{--}900^\circ\text{C}$ for 12 h in the air or sometimes in the flowing oxygen atmosphere.

Structural properties of the synthesized compounds were studied by the X-ray diffraction technique (XRD). The surface and particle morphology of the synthesized materials were analyzed by scanning electron microscopy (SEM) images. The electrochemical cycling performance of the materials was studied by assembling coin-type cells (CR2032) and the cells were galvanostatically cycled at a 0.5 C rate ($1\text{C} = 147\text{ mA/g}$) between 3.5 and 5.0 V in a multi-channel battery tester. The cyclic voltammogram was obtained by scanning the cell at a slow rate of $20\ \mu\text{V/s}$. The synthesized cathode materials were mixed with 10% carbon black and 3% polyvinylidene fluoride (PVdF) as a binder, and made into a slurry using *N*-methylpyrrolidinone (NMP) as a solvent and coated onto aluminum foil which was used as a current collector. The typical loading rate of active materials was about 7.5 mg/cm^2 with $40\text{--}50\ \mu\text{m}$ thickness. The coated aluminum foil was allowed to dry in hot oven at 80°C and then it was roller pressed to better adhere the materials to the current collector. The cathodes were punched from the foil. The cells were assembled inside drying room using lithium metal as an anode, polypropylene (PP) film as a separator and a 1 M LiPF_6 in 1:1:1 ethylene carbonate (EC), ethylmethyl carbonate (EMC), dimethyl carbonate (DMC) co-solvent as an electrolyte.

3. Results and discussion

The thermogravimetric behavior of the starting materials for the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was shown in Fig. 1(a and b). The source materials for the major transition metal components Ni, Mn, dissociated rapidly at the relatively low temperature region, while lithium carbonate remained intact up to 700°C . The oxide doping materials such as Cr_2O_3 showed little weight gain or loss throughout the temperature scan, for which TG data were therefore left out here. However, it seems that the TG and DSC data for the mixed powder indicates that the major synthetic process occurs below 600°C and about 18% of the initial starting materials, is burned up during the firing, which is in good agreement with the mathematical calculation considering the weight loss between the initial and the final materials involved ($\text{Li}_2\text{CO}_3 + \text{MnO}_2 + \text{Ni}(\text{OH})_2 \rightarrow \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$). From Fig. 1a, it seems that quadrivalent manganese oxide MnO_2 dissociates abruptly around 550°C to become trivalent Mn_2O_3

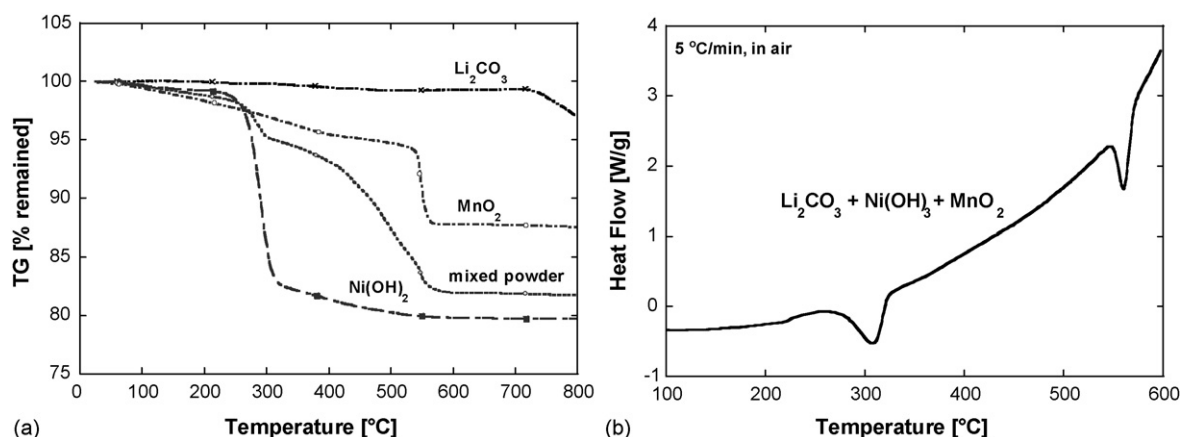


Fig. 1. (a) TGA results for the starting materials, Li_2CO_3 , $\text{Ni}(\text{OH})_2$, MnO_2 , and the mixed powder and (b) DSC results for the mixed powder.

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