

Short communication

Exploration of high capacity $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized by solid-state reaction

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Abstract

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by an improved solid-state reaction at high heating and cooling rates, the mixed precursors were initially heated up to 900 °C, then directly cooled down to 600 °C and heated for 24 h in air. X-ray diffraction (XRD) pattern shows that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has cubic spinel structure; scanning electron microscopic (SEM) image shows that the particle size is about 0.2 μm together with homogenous distribution. Electrochemical measurements show that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders delivered up to 143 mAh g⁻¹ with superior cycling performance at the rate of 5/7C.

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1. Introduction

Recently, several research groups have reported transition-metal-substituted spinel materials ($\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$; M: Cr, Co, Fe, Ni and Cu) with high-voltage plateaus above 4.5 V [1–5]. Among these materials, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is the most promising and attractive one because of its good cyclic property and relatively high capacity with a plateau at around 4.7 V [3,6].

So far, a variety of methods were used for preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, such as solid-state reaction [4,7,8], sol–gel [4,6], co-precipitation [9], emulsion drying [10], composite carbonate process [11], molten salt [12], combustion [13] and ultrasonic spray pyrolysis method [14]. When synthesized by different method, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had different property, so the synthesis method for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a key. There are few literatures on synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by solid-state method. Zhong et al. [4] have synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by heating three times at 750 °C with intermediate grinding, followed by a single heating at 800 °C. Idemoto et al. [7] reported

that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by preheating at 600 °C in air, then heating at 800 °C in O₂. Both prepared powders delivered low capacity (<120 mAh g⁻¹) and clearly exhibited a 4.1 V plateau, though reheating and regrinding or oxygen flow were applied to the synthetic process. On the other hand, Ohzuku et al. [8] have synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by firing at temperature as high as 1000 °C for 12 h followed by an annealing process at 700 °C for 48 h at relatively slow heating and cooling rates, and the resulting powders delivered flat voltage profiles at around 4.7 V with high capacity, but the temperature is so high and the synthetic time is too long. In this paper, we describe an improved preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by solid-state reaction in air, and the electrochemical properties of resulting powders were investigated.

2. Experimental

Appropriate amounts of Li_2CO_3 , NiO and electrolytic MnO_2 were initially ground in mortar, and then the mixture was thoroughly ball-milled. Subsequently, the mixed precursors were heated up to 900 °C, then directly cooled down to 600 °C and heated for 24 h in air. The heating

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and cooling rates were about $30\text{ }^{\circ}\text{C min}^{-1}$ and $10\text{ }^{\circ}\text{C min}^{-1}$, respectively.

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using Cu $K\alpha$ radiation was employed to identify the crystalline phase of the synthesized materials, recorded at room temperature. The particle size and morphology of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders was observed by scanning electron microscope (JEOL, JSM-5600LV) with an accelerating voltage of 20 kV.

The electrochemical characterizations were performed using CR2025 coin-type cell. For cathode fabrication, the prepared powders were mixed with 20 wt.% of carbon black and 10 wt.% of polyvinylidene fluoride in *N*-methyl pyrrolidone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at $80\text{ }^{\circ}\text{C}$ for 1 day in vacuum. The test cell consisted of the cathode and lithium foil anode separated by a porous polypropylene film, and 1 M LiPF_6 in EC:EMC:DMC (1:1:1, v/v/v) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 3.5–4.9 V versus Li/Li^+ electrode at room temperature. Cyclic voltammogram (CV) test was performed on a CHI660A Electrochemical Workstation over a voltage range of 3.5–5.2 V versus Li/Li^+ electrode at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

Fig. 1 shows the XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders. All fundamental peaks can be indexed to the cubic spinel structure. It has been reported [4] that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ losses oxygen and disproportionates to a spinel and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ when it is heated above $650\text{ }^{\circ}\text{C}$. Small $\text{Li}_x\text{Ni}_{1-x}\text{O}$ impurity peak placed close to the (400) line of the spinel denoted by asterisk is also observed in Fig. 1. Meanwhile, all fundamental peaks are sharp, which indicates $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were well crystallized. Scanning electron microscopic (SEM) image is shown in Fig. 2. Fine particles were observed, and the particle size was about $0.2\text{ }\mu\text{m}$ together with homogenous distribution, as is clear in Fig. 2.

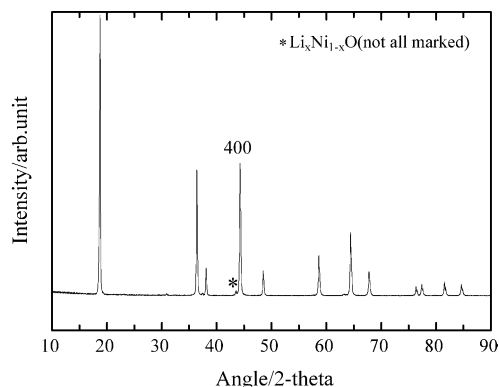


Fig. 1. Powder X-ray diffraction pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

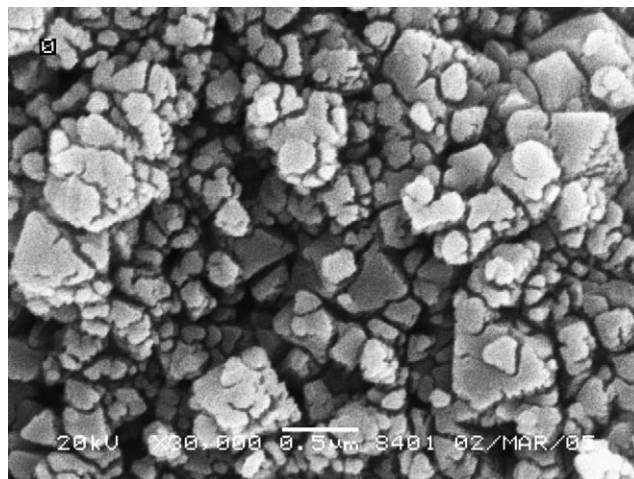


Fig. 2. SEM image of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The charge–discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cycled between 3.5 V and 4.9 V at the rate of $1/7C$ are shown in Fig. 3. The charge–discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders exhibit one plateau (formed of two very close steps [15]) at around 4.7 V, which is attributed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple [4], and the 4.1 V plateau has almost disappeared, as can be seen in Fig. 3. This observation is also supported by the cyclic voltammogram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, as shown in Fig. 4. The broad anodic and cathodic peaks (two peaks are overlapped because of very narrow potential gap between peaks and look like one broad peak [16]) correspond to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple. These peaks confirm the good reversibility of the lithium extraction/insertion reactions in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. When discharged at the rate of $1/7C$, the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered up to 143 mAh g^{-1} , which is, to our knowledge, the highest discharge capacity reported so far. Fig. 5 shows cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ charged at the rate of $1/7C$ and discharged at the rate of $5/7C$. The capacity remained invariable when the rate was increased from $1/7C$ to $5/7C$, and still retained 141 mAh g^{-1} after 30 cycles, which indicates the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has superior capacity retention upon cycling. These results are better than those reported by Zhong et al. [4] and Idemoto et al. [7], and

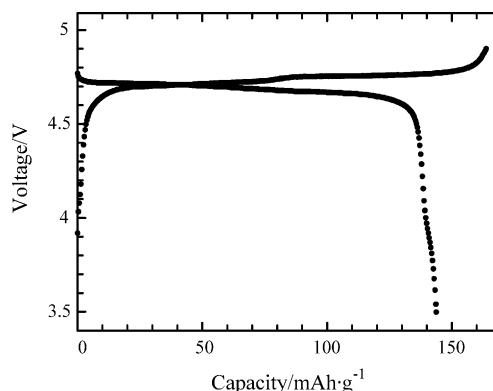


Fig. 3. The charge–discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at the rate of $1/7C$.

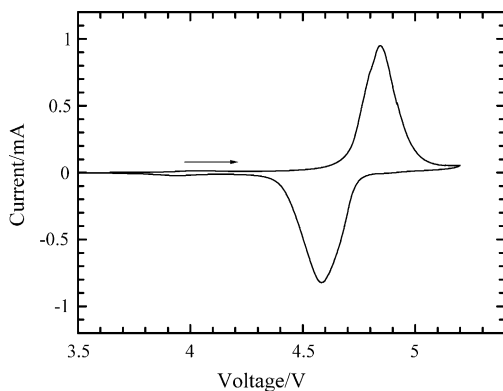


Fig. 4. Cyclic voltammogram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode scanned at 0.1 mV s^{-1} .

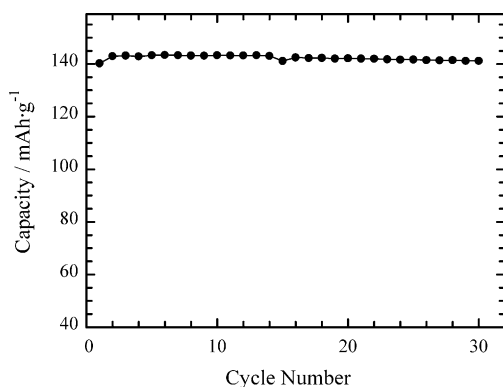


Fig. 5. Cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ charged at the rate of $1/7C$ and discharged at the rate of $5/7C$.

comparable to the results reported by Ohzuku et al. [8]. In addition, the heating and cooling rates are greatly enhanced, and the synthetic time was greatly reduced, compared to those reported by Ohzuku et al.

4. Conclusions

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been prepared by an improved solid-state reaction at high heating and cooling rate in air. X-ray diffraction pattern and scanning electron microscopic image

show that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has cubic spinel structure with homogenous particles. The prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders can deliver the capacity of 143 mAh g^{-1} with superior capacity retention upon cycling. The results demonstrate that the method described here is very suitable for synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and can improve its electrochemical performance.

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