

Effect of annealing treatment on electrochemical property of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel

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Abstract: $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared under different cooling conditions. The electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared under different cooling conditions were investigated. The results show that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized with or without annealing treatment has similar X-ray diffraction patterns that can be indexed to cubic spinel structure. The mass loss occurring above 650 °C during the heating process can be mostly gained during the cooling process. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized with an annealing treatment exhibits almost one voltage plateau at around 4.7 V and higher capacity with a quick fading upon cycling, whereas $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized without annealing treatment shows two voltage plateaus at around 4.1 and 4.7 V and superior capacity retention upon cycling both at rates of 1/7C and 1C, though the capacity is not high.

Key words: lithium ion battery; cathode material; $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$; annealing treatment; electrochemical property

1 Introduction

The exponential growth in the electronics industry has led to an increasing demand for light mass power sources with high energy density and power capability[1]. This demand has been satisfied largely by the advent of rechargeable lithium-ion batteries[2–4]. LiCoO_2 is the first commercial cathode material for lithium ion batteries[5]. However, the poor resource and high-cost of cobalt has limited the application of LiCoO_2 as a cathode material for lithium ion batteries for electric vehicles. Among various cathode materials, LiMn_2O_4 is the most promising one and has attracted wide attention because of its low cost, nontoxicity and potential good electrochemical performance. However, its quick capacity loss on cycling becomes an obstruction to practical use, probably due to the structural transition and Mn^{3+} dissolution into the electrolyte, which destroy the structure and surface of the electrode[6–7]. A number of investigations have been involved in order to improve the cycleability of LiMn_2O_4 . Doping is often used[8–10].

Recently, many researches groups have investigated the transition-metal-substituted spinel materials ($\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$, $\text{M}=\text{Cr}, \text{Co}, \text{Fe}, \text{Ni}, \text{Cu}$) with high-voltage

plateaus above 4.5 V[11–15]. 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[13,16].

It is proved that the strategy of slowly cooling or annealing treatment at low temperature is very necessary to optimize the oxygen content of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because the oxygen loss of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurs when it is prepared at high temperature[14,16–17]. For example, OHZUKU et al[17] synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ employing an annealing treatment at 700 °C in air after the high-temperature calcination at temperature as high as 1 000 °C. WU et al[16] employed an annealing treatment at 600 °C to reduce oxygen loss from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared by sol-gel method. They have both proved that the annealing process can greatly suppress the voltage plateau at around 4.1 V and the capacity of the plateau at around 4.7 V is enhanced. But the effect of annealing treatment on the electrochemical property such as cyclic performance has not been investigated. In this paper, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was synthesized by solid-state reaction, and the effect of annealing treatment on the rate capability and cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was 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 calcined at 950°C for 12 h, one sample was directly cooled to room temperature, the other sample was followed by an annealing treatment at 600°C for 24 h in air.

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using $\text{Cu K}\alpha$ radiation was employed to identify the crystalline phase of the synthesized material. Thermal gravimetric analysis of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders was performed with a TA instrument (SDT Q600). The powders were heated and cooled at $2^\circ\text{C}/\text{min}$ in a constant flow of extra dry air.

The electrochemical characterizations were performed using CR2025 coin-type cell. For cathode fabrication, the prepared powders were mixed with 20% (mass fraction) of carbon black and 10% (mass fraction) of polyvinylidene fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the cathode was dried at 80°C for 1 d in vacuum. The test cell consisted of the cathode and lithium foil anode separated by a porous polypropylene film, and 1 mol/L LiPF_6 in EC:EMC:DMC (1:1:1 in volume) was used 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 from 3.5 to 4.9 V vs Li/Li^+ electrode at room temperature.

3 Results and discussion

Fig.1 shows the XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders. The patterns of both samples with and without

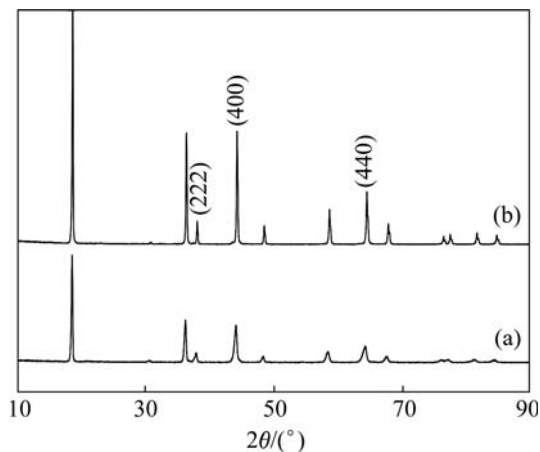
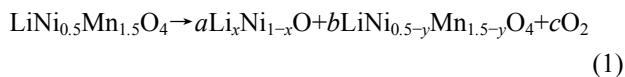


Fig.1 XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders calcined at 950°C : (a) Without annealing treatment; (b) With annealing treatment

annealing treatment are similar. All peaks can be indexed to the cubic spinel structure with a space group of $\text{Fd}3\text{m}$. In addition, relatively wide and weak peaks of the sample without annealing treatment are clearly observed in Fig.1(a), while sharp and intensive peaks of the sample with annealing treatment are seen in Fig.1(b).

The TG measurement of the sample calcined at 900°C for 12 h followed by an annealing treatment at 600°C for 24 h in temperature range from room temperature to 950°C is shown in Fig.2. It can be seen that the mass loss during heating process can be mostly gained during cooling process. This result is in good agreement with that in Ref.[14] where ZHONG et al reported that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ would lose oxygen and disproportionate to a spinel and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ when heated above 650°C , which can be written as



Furthermore, this reaction can be reversibly proceeded during the slow cooling or annealing process after high-temperature calcination. It is also clear that the mass loss occurred above 650°C and the mass gain stopped below 570°C , which suggest the annealing treatment temperature set at 600°C is suitable to optimize the oxygen content of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in our experiment.

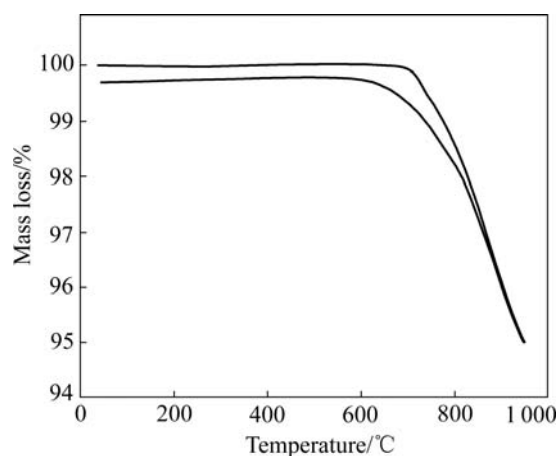


Fig.2 TG measurement on sample calcined at 900°C for 12 h followed by annealing treatment at 600°C for 24 h in air

Charge—discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cycled between 3.5 and 4.9 V at rates of $1/7C$ and $1C$ are shown in Fig.3. For the $1/7C$ rate, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was charged and discharged at the same rate of $1/7C$; in the case of the $1C$ rate, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was charged at the rate of $1/7C$ and discharged at the rate of $1C$. The annealing treatment has a significant effect on the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders. The sample synthesized with an annealing treatment almost exhibits one voltage plateau at around 4.7 V based on $\text{Ni}^{2+}/\text{Ni}^{4+}$

redox couple, whereas the sample synthesized without annealing treatment shows a plateau at around 4.1 V based on $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple in addition to the 4.7 V plateau, and delivers much smaller capacity, which is due to the oxygen loss at high temperature, leading to the appearance of impurity NiO or $\text{Li}_x\text{Ni}_{1-x}\text{O}$ and the decrease of manganese oxidation state from Mn^{4+} to Mn^{3+} [14, 18], as clearly seen in Fig.3. The peaks of impurity which are usually placed close to the lines (222), (400) and (440) of the spinel are not observed in Fig.1(a), which is probably due to the overlap of peaks of spinel phase and impurity because of widening of peaks. However, the sample without annealing treatment exhibits better rate capability than that of the sample with an annealing treatment. When the sample without annealing treatment is discharged at 1C, the voltage plateau and capacity are only little reduced, when the sample with an annealing treatment is discharged at 1C, the voltage plateau is greatly reduced, and the capacity is drastically decreased from 128 to 108 $\text{mA}\cdot\text{h}/\text{g}$. This observed behavior is probably attributed to higher conductivity of the sample without annealing treatment. The high electronic conductivity in oxides is most frequently observed in the mixed valency semiconductor [12,19]. For spinels such as Mn_3O_4 [19–20], NiMn_2O_4 [19] and LiMn_2O_4 [21], fast electronic transport is attained by thermally activated, small polaron hopping between Mn^{3+} and Mn^{4+} . In the case of the sample synthesized without annealing treatment, the oxygen loss results in the presence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ so as probably to improve its conductivity. Besides, the behavior may also be associated with different structures of the samples that are hard to be differentiated based on the XRD patterns. According to Ref.[22], the annealing treatment will result in the transformation of an disorder structure to an order structure for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and the disorder $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows better electrochemical performance, especially for the rate capability.

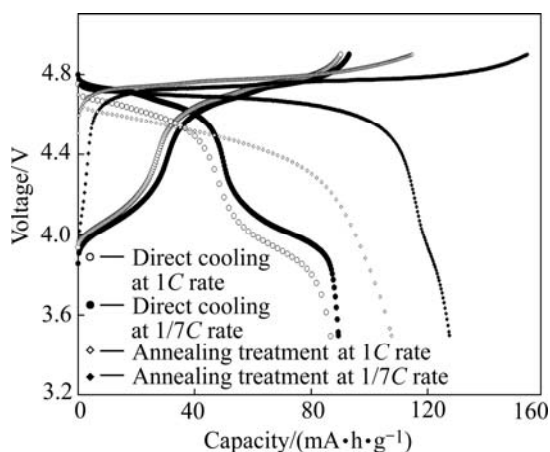


Fig.3 Charge—discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined at $950\text{ }^{\circ}\text{C}$ and rates of $1/7C$ and $1C$

Fig.4 shows the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cycled between 3.5 and 4.9 V. As seen in Fig.4, the sample synthesized with an annealing treatment delivers higher capacity but with a quick fading at both rates of $1/7C$ and $1C$. However, the sample synthesized without annealing treatment exhibits superior capacity retention upon cycling, though the capacity is low, and the discharge capacity remains invariable even after 47 cycles at the rate of $1/7C$. Furthermore, for the sample without annealing treatment which is cycled at the rate of $1C$ after 47 cycles, shows superior capacity retention, though a little decrease of the capacity when the rate increases.

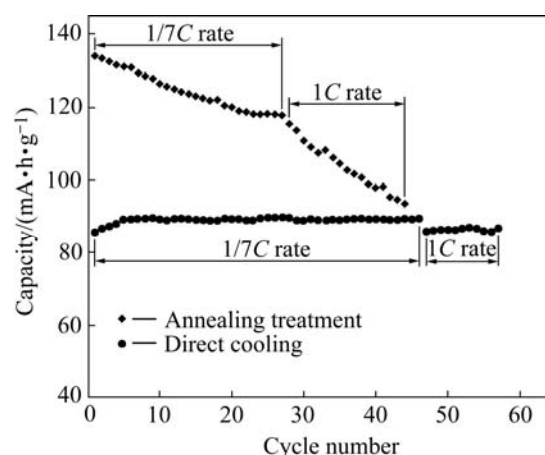


Fig.4 Electrochemical cycling performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined at $950\text{ }^{\circ}\text{C}$ and rates of $1/7C$ and then $1C$

From the above results, it can be concluded that direct cooling can improve the rate capability and cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, but reduce the capacity, especially the capacity of the voltage plateau at around 4.7 V because of the oxygen loss.

4 Conclusions

1) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is prepared under different cooling conditions. X-ray diffraction(XRD) patterns show that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized under different cooling conditions has the same crystal structure. TG measurement indicates that the mass loss occurring above $650\text{ }^{\circ}\text{C}$ during heating process can be mostly gained during cooling process.

2) The electrochemical property of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared under different cooling conditions is evaluated. The capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized without annealing treatment is better than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized with annealing treatment. Meanwhile, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized with annealing treatment exhibits higher capacity but with a quick fading upon cycling, whereas $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized without annealing treatment shows superior capacity retention

upon cycling both at rates of $1/7C$ and $1C$, though the capacity is not high and the 4.1 V plateau can be clearly seen.

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