

DEVELOPMENT OF $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ FOR LITHIUM BATTERIES VIA SOLID-STATE REDOX METHOD

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ABSTRACT

In this work, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which is a potential cathode active material in the 5 V-class, is prepared by the solid-state redox method. The precursor material was obtained when the mixture reactants were heated at 500°C for 10 hours and calcined at different temperatures in the range between 650°C and 950°C for 12 hours. The structures of the synthesized materials were verified with X-ray diffraction (XRD) measurements and Scanning Electron Microscope (SEM). The electrochemical properties i.e. the charge-discharge technique were determined using Solartron 1470.

INTRODUCTION

LiMn_2O_4 is a promising cathode material for lithium secondary battery since it is inexpensive and environmental friendly. $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ has a ca. 5 V plateau when part of the Mn-site is substituted for the 3d-transition metal (M=Cr, Co, Ni, Fe, Cu)[1]. The capacity and voltage plateau in Li/ $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ cells strongly depend on the kind of transition metal (M) used and their content [3].

In general, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ having *Fd3m* cubic structure can be prepared by a solid-state reaction, which requires pre-calcination and extended calcination time to form the highly ordered cubic spinel phase.

In this study, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a 5 V cathode material was synthesized by the solid state redox method, at different calcination temperatures. The aim of this work is to formulate new 5 V stable lithium battery in terms of cycle life with a high gravimetric capacity and a large energy storage capability.

EXPERIMENTAL DETAILS

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by the solid state redox method using the $\text{HLiO}\cdot\text{H}_2\text{O}$, Mn_2O_3 , and $\text{Ni}(\text{OH})_2$. The resulting solids were heated at 500°C for 10 hours in air, then calcined at 650, 750, 850 and 950°C for 12 hours in air.

The powder X-ray diffraction (XRD, Bruker) using $\text{K}\alpha$ radiation was performed at room temperature to identify the crystalline phase of the powders that were prepared with different calcination temperature. The peaks obtained were compared with the JCPDS data. The particle morphology of the samples was observed using FESEM (LEO 1525).

The method of assembling the cells is as follows: the cathodes consist of 20 mg of accurately weighed active material and sufficient amount of conductive binder. It was

pressed on a 100-mm² stainless steel mesh current collector. The electrode were pressed at 20 MPa, and dried at 100°C for an overnight in an oven. The electrolyte was 1M LiPF₆ in an ethylene carbonate/dimethyl carbonate (1:1) solution. All procedures were carried out in a Argon filled glove-box. Next, the specific capacities of the material were examined using Solartron 1470.

RESULTS

The X-ray diffraction patterns of the precursor material at 650, 750, 850 and 950°C for 12 hours are shown in Figure 1. The major Bragg diffraction peaks at $2\theta = 19^\circ$ and 36° were observed. Additional peaks were observed at 38° , 44° and 65° in the diffractogram of the precursor heated at 650°C as shown in Figure 1(a). When the precursor was heated at 750°C for 12 hours, the intensity of the peak at 36° and 44° is observed to increase and the peaks at 59° , 65° and 69° become more distinct. The materials experience structural changes where irregular polyhedral shapes at 750°C (Figure 2(b)) were transformed to single crystals of octahedral shape with well-developed [111] planes at 850°C (Figure 1(c) and 2(c)). Additional peaks were observed at 76° and 77° . The XRD pattern for the precursor heated at 850°C for 12 hours also showed the same number of peaks. This work agrees with the study carried out by J.-H. Kim *et al.* (2004) and our work previously (Mat, A. *et al.* (2005)) which showed that Li-Ni -Mn-O compound has all the peaks shown in Figure 1 (c). The Li-Ni-Mn-O compound began to form at around 750°C as indicated by the well-defined major peaks in the XRD pattern. The peaks of the compound heated at 750°C onwards are sharper than that heated at lower temperature showing better crystallinity. The presence of these peaks suggests that the lithiated material is LiNi_{0.5}Mn_{1.5}O₄. It was found that the JCPDS data as listed in Table 1 for LiNi_{0.5}Mn_{1.5}O₄ matches well with the XRD pattern of Figure 1(c).

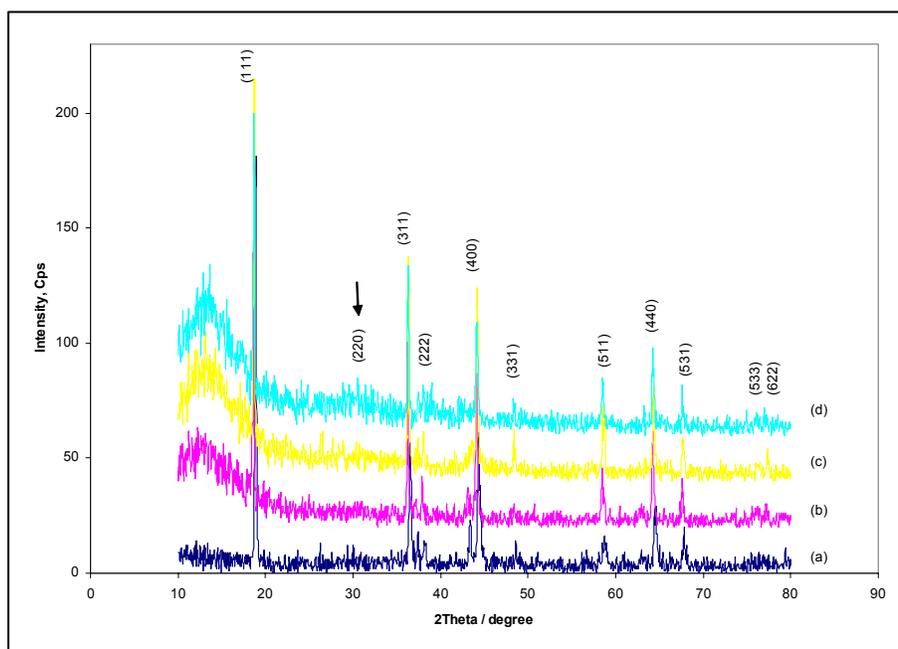


Figure 1: X-ray diffraction pattern of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders calcined at various temperature for 12 h: (a) 650°C ; (b) 750°C ; (c) 850°C ; (d) 950°C .

Sample	Observed values		JCPDS data	
	2 θ (degree)	Intensi ty	2 θ (degree)	Intensi ty
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursor heated at 850°C	19	127	18.8	100
	36	64	36.4	55
	44	66	44.3	60
	58	25	58.6	20
	64	32	64.4	35

Table 1: Comparison between data from XRD pattern for firing temperature at 850°C for 12 hours and data from JCPDS (Pattern N0. 32-0581).

It is expected that upon increasing the temperature above 850°C the peak at 19° should increase in intensity and if peaks are more defined, the noise level should further be reduced as the 2θ angle increases. Upon closer examination of the XRD pattern in Figure 1 for the precursor heated at 650°C to 950°C , the opposite effects were observed. Thus it is important to select the appropriate annealing temperature of the precursor material. The starting material used may also influence the appropriate temperature, but this is beyond the scope of the present study.

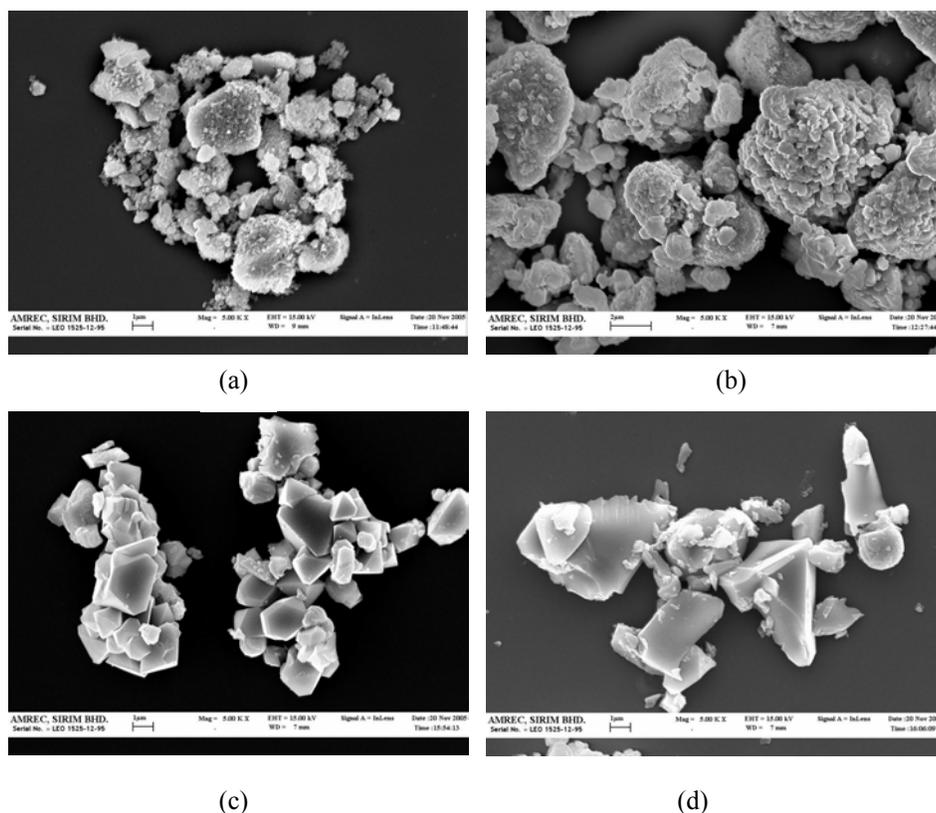


Figure 2: Micrograph of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined for 12 hours at different temperature: (a) 650°C; (b) 750°C; (c) 850°C; and (d) 950°C.

Figure 1 and 2 show the XRD patterns and SEM images for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders, respectively. As shown in Figure. 1(a)-(d), crystallization is accelerated with increasing calcination temperature up to 850°C. Morphological changes were clearly shown by the SEM images in Figure. 2. At temperature below 850°C, undeveloped crystallization and severe agglomeration were observed as shown in Figures. 2(a) and 2(b). As the calcination temperature increases, crystal growth proceeded and larger particles with clear octahedral shape were observed in Figure. 2(c). However, when heated up to 950°C, sudden structural and morphological changes were observed simultaneously in Figure. 1(d) and 2(d). In Figure. 1(d), the XRD pattern relatively becomes broad showing low peak intensities, and increased (2 2 0) peak (indicated by arrow) suggests that a part of transition metal ions is located at the 8a Li site. There was a report on Mn ion migration to the 8a Li site upon the decomposition of LiMn_2O_4 resulting in the development of the (2 2 0) peak in the XRD pattern [3]. Interestingly, as shown in Figure 2(d), morphological change was accompanied by structural decomposition at 950°C. The sharp edges of octahedrons at 850°C (Figure. 2(c)) were broken into pieces and irregular polyhedrons were formed at 950°C (Figure. 2(d)).

Figure. 3 shows voltage profiles of the three cycles of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder calcined at 850°C with constant current density of 20 mA/g at 25°C . As suggested by Ohzuku et al. [3], annealing after calcination of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder exhibits a flat voltage profile from the beginning of charge at about 4.7 V versus Li. A second plateau was observed around 4.0 V for this sample.

It is well known that ideal $\text{LiNi}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}\text{O}_4$ shows two distinct potential plateaus based on $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple [3]. With increasing calcination temperature, oxygen deficiency appears in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and this partly lowers Mn oxidation state from Mn^{4+} to Mn^{3+} . Provided that oxygen defect occurs during calcination, Mn^{3+} can be formed to satisfy the charge balance of the composition, leading to the appearance of the 4 V potential plateau from $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple [3].

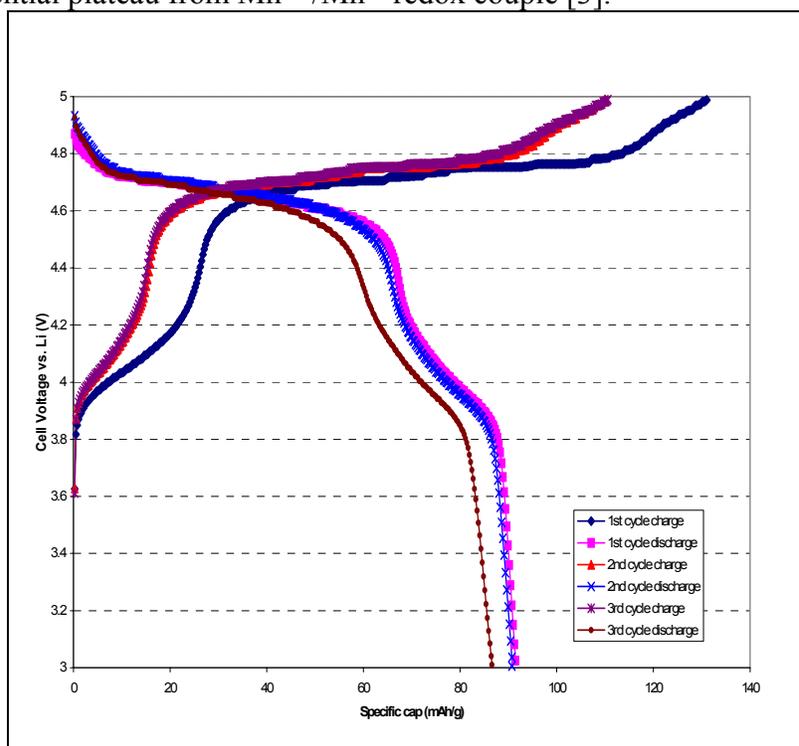


Figure 3: The charge-discharge curves of the Li/ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (850°C) cell at a constant current density of 20mA/g for three cycles.

CONCLUSION

We have shown that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a potential cathode material for 5V batteries. High crystalline $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was successfully synthesized via solid-state redox method. As calcination temperature increases, the well-ordered crystal growth oriented to [1 1 1] direction was observed showing the clear octahedral morphology, which is the characteristic of the typical cubic spinel. However, the well-ordered structure and morphology were degraded by calcination at 950°C . The optimum synthesis condition was to heat treat at 850°C as indicated by the XRD analysis.

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