

Synthesis of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as 5V cathode material by carbonate co-precipitation method

Shiyu Li^{1, a}, Shan Geng^{1, b}

Lanzhou University of Technology, 730050, China

^a191348761@qq.com, ^b295647060@qq.com

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Abstract. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been synthesized by carbonate co-precipitation method in which we got the precursor that was pretreated with H_2O_2 (an oxidant), in order to oxidize part of Mn^{2+} to Mn^{4+} , results in a decrease of Mn^{3+} in the structure. Result in the average valence of Mn is approximately 4 in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structure, leading to an improved structural stability. The sample was characterized by XRD (X-ray diffraction) and SEM (Scanning Electron Microscope) test, respectively. The XRD results show that peaks of the sample are consistent with that of standard $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The SEM pattern shows that there are complete octahedron exists, the result indicate that material structure is an intact spinel structure. In addition, electrochemical properties have been tested. The first discharge capacity is 100.8mAh g^{-1} at 0.25 C. And cycling performance was tested, it is also preferable.

1. Introduction

Lithium-ion batteries are widely used in electronic products, which has many advantages, ratio of the energy, the weight is minor, without memory effect and so on [1-3]. In the future, lithium-ion batteries are also expected to be the technology of choice for electric vehicles and hybrid electric vehicles [4]. Therefore we need to study cathode materials with high voltage and with large battery capacity. At present, the location of the part of manganese has been displaced by transition metal cation. It can obtain $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}$), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has large battery capacity in these materials, which has been concerned [5]. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the cathode material has many superiority, low cost, environmental friendliness and high voltage ($\sim 4.7\text{ V}$). However, it suffers from poor cycling behavior that caused by excessive Mn^{3+} [6].

In this study, we obtained the precursor by carbonate co-precipitation method. The precursor was treated with H_2O_2 , it can oxidize part of Mn^{2+} to Mn^{4+} to avoid excessive Mn^{3+} in structure [7]. While lots of Mn^{4+} exist in structure, result in an improved structural stability. This feature prevents structural degradation by Jahn-Teller distortion [8]. The sample of precursor is treated with H_2O_2 Shows good performance in every respect. It has been observed that the standard octahedron in SEM, performing good cycle performance in the electrochemical tests.

2. Experimental

2.1 Synthesis. Three steps of the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. First, using analytical $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, analytical $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as the manganese source and nickel source, respectively. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 50mL distill water (1:3 by molar mass). Na_2CO_3 was dissolved in 100mL distill water then added into mixed solution of manganese source and nickel source with stirring at $90\text{ }^\circ\text{C}$ until sediment formed. H_2O_2 was added into the above solution after Na_2CO_3 had been added in 20 minutes for 3 h with stirring at $90\text{ }^\circ\text{C}$. Second, the complex after washing and drying was calcined at $600\text{ }^\circ\text{C}$ for 48 h in air. Then we obtain precursor. Third, The mixtures of the precursor and $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ with molar ratio of 2:1.05 (Mn: Li) was calcined at $850\text{ }^\circ\text{C}$ for 10h in air. Ultimately, we obtained spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

2.2 Cell preparation. The mixture of 80 wt. % of active material, 10 wt. % of acetylene black

and 10 wt. % of poly vinylidene fluoride (PVDF) was dispersed in 1-Methyl-2-pyrrolidinone (NMP) to prepare slurry. Aluminum foil was coated with the above slurry and dried at 120 °C for 12 h in vacuum and then we get the electrode. In an argon atmosphere glove box, the coin cell was assembled by using lithium wafer, the above electrode as the anode material and cathode material, respectively, using celgard 2400 as the separator material and 1M LiPF₆ in EC:DMC (1 : 1 by volume) as the electrolyte material.

2.3 Characterization. X-ray powder diffraction (XRD) design of the sample was analyzed on an X-ray diffractometer (Rigaku, D/Max-2400) with Cu-K α radiation (40 kV). The morphology of the materials was observed by scanning electron microscopy (SEM, JSM-5600, Japan). Electrochemical performance is tested by using a Landt cell test system (Landt CT2001A).

3. Results and Discussion

Fig.1. XRD (x-ray power diffraction) pattern of the spinel sample was obtained at 850 °C. Comparing with standard atlas, the peaks of surface of (111), (311), (400), and (440) are obvious which prove the sample is spinel structure. Also we found peak strength increases when the sample is calcined at 850 °C, which attest that a good crystal of the sample was obtained at high temperature. However, peaks at 37.5° and 63.1° are characteristic peak of impurity NiO [8]. Because with the increase of temperature, lock of oxygen will happen, it leads to produce impurity [9].

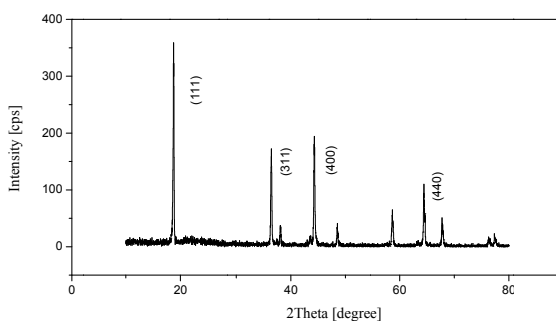


Fig.1. XRD (x-ray power diffraction) patterns of the spinel sample.

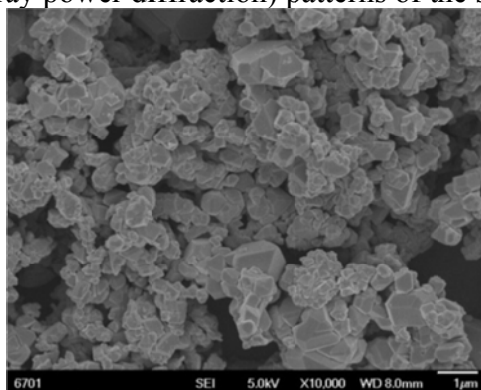


Fig.2. the SEM pattern of the sample

Fig.2 shows the SEM diagram of the sample. Sintering temperature has an influence on the morphology of material [10]. The octahedron can be seen in the figure. It is not hard to find that part of the particle size is bigger the reason is that high temperature promotes the growing of crystal nucleus when the sample has been calcined at 850 °C.

It can be seen that the first charge-discharge curves of LiNi_{0.5}Mn_{1.5}O₄ at 0.25 C in the range from 3.5 V to 5 V in Fig.3. The curves exhibit a large plateau in the 4.7 V region and a smaller plateau at about 4.1 V region. Plateau of 4.7 V is attributing to the Ni^{2+/4+} redox couple. Plateau of 4.1 V is due to the Mn^{3+/4+} redox couple [11]. It is clear that a few Mn³⁺ ions are present. As can be seen from the Fig.3, the discharge capacity of LiNi_{0.5}Mn_{1.5}O₄ is 100.8mAh g⁻¹ at 0.25 C.

Cycling performance is an important aspect of evaluating the electrochemical performance of electrode material. Fig.4 shows that the curve of cycling performance. The stability of the structure

decides cycling stability [12]. Using H_2O_2 to oxidize Mn^{2+} to Mn^{4+} can support structure. The above result indicates that the average valence of Mn is approximately 4 in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structure, which could avoid the J-T structural distortion, leading to an improved cycling performance.

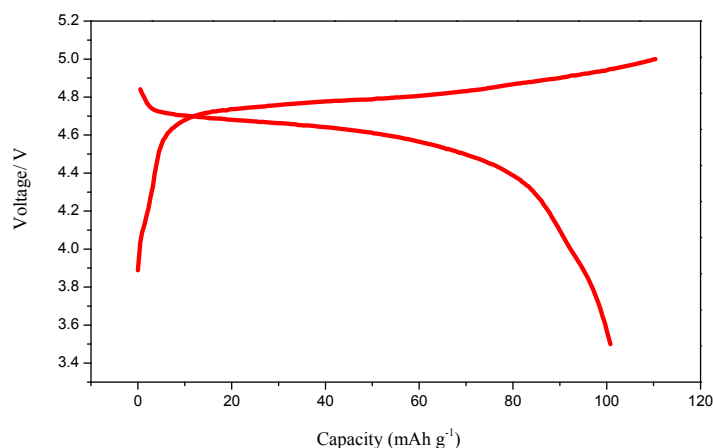


Fig.3. The first charge-discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 0.25 C in the range from 3.5 V to 5 V.

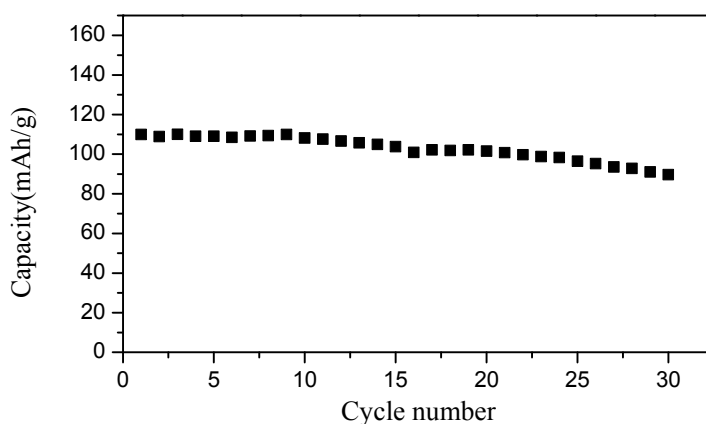


Fig.4. The curve of cycling performance.

4. Summary

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material has been synthesized by carbonate co-precipitation method. The peaks of the sample are cohering with peaks of standard $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. But lack of oxygen will happen when the sample was calcined at high temperature. Most crystals are regular octahedrons with crystal forms completely. The first discharge capacity is 100.8mAh/g at 0.25 C. And the sample also has a good cycling performance.

Acknowledgements

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