Nano layered-spinel $0.8\text{Li}_2\text{MnO}_3 \cdot 0.2\text{LiMn}_2\text{O}_4$ as high-performance cathode for Li-ion batteries

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Abstract. The nano layered-spinel $0.8\text{Li}_2\text{MnO}_3 \cdot 0.2\text{LiMn}_2\text{O}_4$ cathode material has been synthesized by a simple solvothermal method. X-ray diffraction studies show that the as-prepared material has two compositions, including $\text{Li}_2\text{MnO}_3$ and $\text{LiMn}_2\text{O}_4$. Moreover, the surface morphology of the precursor and cathode material were characterized by scanning electron microscopy. Meanwhile, the EDS graph reflects homogeneous mixing of the two compositions due to the novel precursor synthesizing method. Consequently, as a cathode material for LIBs, the resulting nano layered-spinel $0.8\text{Li}_2\text{MnO}_3 \cdot 0.2\text{LiMn}_2\text{O}_4$ achieves a high discharge capacity of 248 mA h g$^{-1}$ at 25 mA g$^{-1}$ and 162 mA h g$^{-1}$ even at 1250 mA g$^{-1}$. In addition, the cathode material shows high reversible capability with 180 mA h g$^{-1}$ after 50 cycles, which delivers medium cycling performance.

1. Introduction

Nowadays, lithium ion batteries (LIB) have widely used in many areas closely related to our lives since it is commercialized by Sony corporation. However, there is ever-increasing demand for electronic device with high energy density and excellent cycle performance. Among all issues, cathode materials may be the key point, such as low capacity, inferior rate capability and so on. As common cathode material of LIB, LiCoO$_2$ has a high theoretical capacity of 274 mA h g$^{-1}$, but only half of it is available in the practical application.$^{[1]}$ Therefore, cathode materials for lithium ion batteries with high performance are urgently needed to be developed. Fortunately, lithium-rich manganese oxide materials are discovered to be the most promising candidates for cathode materials of lithium ion battery which can provide very large specific capacity more than 250 mA h g$^{-1}$ when charged over 4.6 V or higher, though it has several limits, such as relatively poor rate capability, low first cycle efficiency and significant voltage decay.$^{[2-9]}$

The research on lithium-rich manganese oxide cathode materials indicates that high
capacity benefits from the component of Li$_2$MnO$_3$ in the material and the ideal capacity of which can amount to 460 mA h g$^{-1}$.[10,11] However, pure Li$_2$MnO$_3$ is nearly inactive and has no reversible capacity. Therefore, additional components have been mixed in Li$_2$MnO$_3$, such as LiMnO$_2$, LiCoO$_2$, LiNiO$_2$, to improve it electrochemical activity. But this method decreases the ratio of Li$_2$MnO$_3$ which reduces the capacity correspondingly. We design another method by decreasing the size of Li$_2$MnO$_3$ particle to form nanoparticle of Li$_2$MnO$_3$ to improve the electrochemical activity.[12-15] At present, the preparation of the anode material by the solvothermal method can significantly reduce the path of the lithium ion insertion/deintercalation process. In addition, another problem to be resolved is poor rate capability. In previous studies, the spinel structure of LiMn$_2$O$_4$ has been used to improve the rate performance. In the crystal structure of LiMn$_2$O$_4$, Li ions locates on the tetrahedral sites, and the transition metal ions locates on the octahedral sites in an oxygen cubic close packed network. This structure provides fast 3D lithium diffusion frame which is useful to improve the rate capability. Up to now, many researches are focussed on mixing spinel LiMn$_2$O$_4$ into original cathode.[16,17] The original cathode may be LiMnO$_2$. But most don’t achieve expected goals of increasing rate performance. The reason could be spinel LiMn$_2$O$_4$ doesn’t mix into the original cathode material homogeneously. So we are expected to synthesize a homogeneous mixture of spinel LiMn$_2$O$_4$ and original material to improve the rate capability. However, conventionally, the original cathode is first synthesized and then enters the spinel LiMn$_2$O$_4$ in a specific manner, which usually causes uneven distribution of LiMn$_2$O$_4$. Herein, we propose a novel approach which put the step of mixing the two components forward to precursor preparation. By this method, a homogeneous precursor containing both components is first obtained, and then the final cathode material is obtained by annealing.[18-21]

To achieve the goal of high capacity and rate performance, we choice nanoscale Li$_2$MnO$_3$ as original cathode. In this work, we have successfully synthesized nano layered-spinel 0.8Li$_2$MnO$_3$·0.2LiMn$_2$O$_4$ by solvothermal method, which make spinel LiMn$_2$O$_4$ and layered Li$_2$MnO$_3$ mix homogeneously. In addition, characterization methods are utilized to characterize the morphology and crystal structure of the composite. Meanwhile, the electrochemical properties of the composites were investigated, including initial capacity, cycle performance and rate performance of the cathode material.

2. Experimental

2.1. Preparation of Sample

The precursor of 0.8Li$_2$MnO$_3$·0.2LiMn$_2$O$_4$ cathode material was synthesized by solvothermal method. Raw materials contain CH$_3$COOLi·2H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O and urea. Firstly, 1542.6 mg CH$_3$COOLi·2H$_2$O(5 mol% excesses), 2352.9 mg Mn(CH$_3$COO)$_2$·4H$_2$O and 2473.1 mg urea were dissolved in 70 mL ethanol at room temperature. After stirring for 2 hours, ethanol was added into the solution until the volume reached 80 mL. Then the solution was transferred into 100 mL autoclave and heated at 200 °C for 20 hours in muffle. After cooling to room temperature, the precursor was collected by using a centrifuge for 3 times. After sufficient drying, the precursor was calcined at 600 °C for 8 hours in the air. Finally, powder was washed several times with DI water and then dried at 80 °C for 10 hours to obtain final cathode materials.
2.2. Material Characterizations
The microstructures morphology and size of powders were characterized by scanning electron microscopy (SEM, Hitachi). The structure and phase composition of synthesized samples were characterized by X-ray diffraction (XRD, Rigaku RINT2000 with Cu-Kα radiation) in the range of 10°-90°(2θ) with a scan rate of 8 °min⁻¹.

2.3. Electrochemical Measurements
The electrochemical properties of the synthesized samples were tested using coin cells (CR2032). The positive electrode was prepared by mixing prepared active material (80 wt%), carbon conducting additive (Super 10 wt%) and poly(vinylidene fluoride) (PVDF 10 wt%) and dissolved them in N-methyl-2-pyrrolidone (NMP) then magnetic stirring over night. After that spread the uniformed mixture onto a smooth aluminum foil. The positive electrodes were dried at 75 °C for 3 h in the air and then at 120 °C for 10 h in a vacuum oven. Last diced the electrode to the needed size. Battery cells were then fabricated in an Ar-filled glove box with a lithium foil and porous polypropylene film(Celgard2400) as anode material and separator, and 1M LiPF₆ (EC+DMC, 1: 1 in volume) was used as the electrolyte respectively. The charge-discharge tests were performed in the voltage range of 2.0-4.8 V (1 C=250 mA g⁻¹).

3. Results and Discussion

3.1. Structure and morphology
The XRD patterns of the synthesized precursor and cathode material are shown in Figure 1. Peaks appearing in the precursor can be indexed to MnCO₃ and Li₂CO₃, implying that lithium element and manganese element have been mixed on precursor preparation. The pattern for cathode material has a number of peaks that can be well-indexed to Li₂MnO₃ (JCPDS no. 27-1252) and LiMn₂O₄ (JCPDS no. 35-0782), indicating that the materials synthesized have achieved our desired results.

Figure 1. XRD patterns of precursor and cathode material.

Morphology of precursor and final cathode were characterized by scanning electron microscopy (SEM). Figure 2 shows the SEM images of the precursor and final cathode samples. The SEM image of precursor shows spherical particle with appropriate interval each other on the magnification time of 2500. Meanwhile, the morphology of the particle shows perfectly spherical with little fragmentary on the magnification time of 10000. In addition, SEM imaging also showed essentially that the spherical particle is agglomerated by smaller secondary particles with a particle size of 30-100 nm about 80000 times magnification,
indicating the formation of nanoscale structure. Above all, homogeneous mixing is the key factor whether this cathode can demonstrate high rate capability. Moreover, the elemental contents of cathode material were analyzed through the energy-dispersive spectrometer in scanning electron microscopy (SEM-EDS). Figure 3 shows the EDS graph of the cathode. These results reveal that the ratio of Li and Mn in Li$_2$MnO$_3$ and LiMn$_2$O$_4$ has a distinct difference. Meanwhile, for the reason light atomic mass of Li that shows inferior effect on EDS, Mn is used to reflect the composition of Li$_2$MnO$_3$ and LiMn$_2$O$_4$. The content of Mn in Li$_2$MnO$_3$ and LiMn$_2$O$_4$ can be estimated to be 47 and 30.4 wt%, respectively. Additionally, the SEM-EDS result indicates the same brightness in the material which reflects homogeneous mixing of Li$_2$MnO$_3$ and LiMn$_2$O$_4$.

Figure 2. SEM of precursor and cathode material in different magnification. (a) precursor, 2.5k (b) precursor, 10k (c) precursor, 80k (d) cathode, 2.5k (e) cathode, 10k (f) cathode, 80k.

Figure 3. EDS graph of precursor. (a) and cathode material (b) on Mn element.

3.2. Electrochemical Performances

Figure 4 shows galvanostatic profiles of charge and discharge processes of 0.8Li$_2$MnO$_3$·0.2LiMn$_2$O$_4$ at 250 mA g$^{-1}$ in the potential range of 2.0-4.8 V vs. Li/Li$^+$ at room temperature. The cathode electrode delivers an initial charge specific capacity of 299 mA h g$^{-1}$ and a discharge specific capacity of 248 mA h g$^{-1}$, higher than that synthesized by conventional method. High capacity attributes to nano Li$_2$MnO$_3$ which activates by nanostructure. From the graph, we can see the first charge curve is different from subsequent cycles. There are two plateaus located at 3.7-4.3 V and above 4.5 V. The first plateau is attributed to lithium ion extraction from LiMn$_2$O$_4$ phase. The second plateau is considered to be the Li$_2$O taking off from the layered Li$_2$MnO$_3$ structure, which results in high irreversible charge capacity of the cathode during the initial charge process. The subsequent cycles only show one plateau correlated to LiMn$_2$O$_4$ phase.

The most desirable result is the elevation on rate performance. Figure 5 shows the rate performance of synthesized material at varied current densities ranging from 0.1 to 5.0 C. As can be seen, the discharge specific capacities of 0.8Li$_2$MnO$_3$·0.2LiMn$_2$O$_4$ are 248, 236, 220,
202, 177 and 162 mA h g$^{-1}$ at current densities of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C, respectively. These results indicate that active material structure of uniformly mixed Li$_2$MnO$_3$ and LiMn$_2$O$_4$ as cathode has significantly improved the rate performance. Meanwhile, the structure is decided by the preparation method. Acetate in the raw material is divided into two parts, one is acetic part which has strong alcohol-affinity, another is metal ions which are alcohol-resistant. Urea would decompose to CO$_2$ and NH$_3$ when the temperature reaches 130 °C. Therefore, there are many tiny bubbles existing in alcohol. Alcohol-resistant part metal ions reject alcohol and aggregate in the bubbles, however, the alcohol-affinity part dissolves in alcohol. Therefore, Li ions and Mn ions are aggregated together homogeneously in the bubbles. The metal ions react with CO$_2$ to generate MnCO$_3$ and Li$_2$CO$_3$ under 200 °C for 20 hours. From the SEM graph of precursor, we can see the spherical particles. Last, the precursor is annealing at 800 °C for 10 hours to generate the mixture of Li$_2$MnO$_3$ and LiMn$_2$O$_4$.

Figure 4. Charge/discharge curves for the initial three cycles of synthesized cathode under a current density of 25 mA g$^{-1}$.

Figure 5. Rate capability of synthesized cathode.

Figure 6. Cycling performance of synthesized cathode.

The cycling performance of 0.8Li$_2$MnO$_3$·0.2LiMn$_2$O$_4$ at a current density of 0.5C (125 mA g$^{-1}$) is shown in Figure 6. As a cathode material for LIBs, the reversible capacity attenuates 29 mA h g$^{-1}$ from the initial cycle to 30$^{th}$ cycle and maintains 180 mA h g$^{-1}$ after 50 cycles. The cycling performance doesn’t get the ideal effect. The reason may be the jahn-teller effect which leads to the structural distortion of LiMn$_2$O$_4$. We plan to solve this problem by doping and coating in the following research.

4. Conclusions

In summary, we have provided a novel method to fabricate layered-spinel cathode material for
lithium-ion battery. The nanoscale structure improves the activity of Li$_2$MnO$_3$ which is related to the capacity of the cathode. When tested as a cathode for LIBs, the $0.8\text{Li}_2\text{MnO}_3\cdot0.2\text{LiMn}_2\text{O}_4$ exhibited excellent specific capacity which could achieve 248 mA h g$^{-1}$. Meanwhile, the rate performance has been improved remarkably. The discharge capacity can surpass 200 mA h g$^{-1}$ even under a current density of 1 C. At a higher current density of 5C, the discharge capacity can also maintain 162 mA h g$^{-1}$. This work provides a successful material with combination property of high specific capacity and excellent rate capability for the development of cathode materials for LIBs, which shows broad prospects in future LIBs applications.

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