Study on Synthesis and Electrochemical Properties of Nanophase Li-Mn-spinel

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Li-Mn-spinel was synthesized using the rheological phase reaction method. First, the precursor was prepared by rheological phase reaction. Then it was decomposed to form Li-Mn-spinel, which was characterized by X-ray diffraction analysis and IR spectra. The particle size of Li-Mn-spinel was determined by the method of the transmission electron microscopy. The synthesized materials are of nanometer size with 30—100 nm in the average diameter. The electrochemical properties of the Li-Mn-spinel were also studied. It proved that this method not only provided a simple practicable and effective route for the synthesis of Li-Mn-spinel, but also had many advantages such as lower sintering temperature, shorter sintering time, fine particles and particularly excellent electrochemical performances.

Keywords lithium-ion battery, lithium manganese oxide, spinel, reheological phase reaction

Introduction

Secondary lithium batteries have been studied for the past several decades because they exhibit the highest specific energy. Nevertheless, the safety and recharge ability associated with use of metallic lithium prevent its widespread acceptance in the market. To alleviate these problems, the "rocking-chair" or "lithium-ion" rechargeable batteries have been developed successfully and first commercialized by Sony energy technical Inc. in 1990. As lithium ion batteries have excellent performances such as the high voltage and capacity, no-memory effect, *etc.*, the projects on lithium ion batteries attracted a lot of chemists all over the world. Promising materials for cathode in "lithium ion" batteries are $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$, spinel-$Li_xMn_2O_4$, and so on. Among these cathode materials, spinel-$Li_xMn_2O_4$ exhibits several advantages and is one of the most promising candidates in terms of its low cost, easy preparation and no toxicity. Much study has been devoted to extracting the more excellent electrochemical properties from the material $Li_{1+x}Mn_2O_4$. It is greatly influenced by the particle size, crystal microstructure, the chemical composition, *etc.*, all of which mainly depend on the preparation methods and preparation conditions. It is therefore worthwhile to develop a novel preparation method and to control the preparation condition precisely.[1-6] The rheological phase reaction method has characteristic features as a preparation method. This method is a process of preparing compounds or materials from solid-liquid rheological mixture. That is, the solid reactants were fully mixed in a proper molar ratio, made up by adding a proper amount of water or other solvents to form a solid-liquid rheological mixture, in which the solid particles and liquid substance were uniformly distributed. Then it was allowed to form precursor under suitable conditions. By sintering the precursor, the end product can be formed. This method enables us to synthesize expected product at lower temperature and shorter sintering time than that of the conventional calcinations method. In addition, the particle size of end product is very fine and possesses some particular chemical properties.[7]

Experimental

Material preparation

Lithium acetate [$Li(OAc)\cdot 2H_2O$], manganese acetate [$Mn(OAc)_2\cdot 4H_2O$] and citric acid are analytical grade reagents. Lithium acetate, manganese acetate and citric acid were ground and fully mixed well in molar ratio of 1:2:3.0 with a little water in a reactor to form rheological state mixture. It was allowed to sufficiently react to form the precursor at 90—100 ℃ for 14 h. The precursor formed is light yellow solid. The Li-Mn-spinel was obtained by sintering the precursor at suitable temperature twice (preheated at 550 ℃ for 2 h and sintered at 680 ℃ for 4 to 6 h).

Material characterization

The process of their thermal decomposition was studied by differential thermal analysis (DTA) and thermogravimetry (TG) using a shimadizu model DT-40 instrument in air atmosphere at a heating rate 20 ℃ · min^{-1}, and platinum cups were used as holders of sample and reference. Alumina was

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used as a reference material. Infrared spectra were measured with a Nicolet 60-SXB spectrophotometer, and matrix material was KBr. XRD analysis of the samples was carried out on a Shimadzu XRD-600 diffractometer using Cu $K\alpha_1$ radiation. TEM was measured on a JEM-100cxII using the accelerated voltage (80 kV).

Electrochemical measurement

Test positive electrodes were prepared by mixing spinel powders (62.5 wt%), 25.0 wt% acetylene black and 12.5 wt% PTFE. 40 mg of this mixture was pressed onto a nickel grid, prior to use, the positive electrodes must be dried at 120 ℃ in a vacuum furnace for a period of 24 h, lithium foil was anode. The mode test cells were fitted together in a glove box under argon atmosphere. The electrolyte was a solution of 1 mol·L^{-1} $LiClO_4$ in EC-DMC (1∶1 mol%). The powder microelectrode was prepared by mixing spinel powder (50 wt%) and acetylene black (50 wt%). The electrochemical behaviors of the spinel materials were characterized by cyclic voltammetry. The experiments were carried out in a two electrodes glass cell. Metallic lithium was used as both a counter and reference electrode at the same time. The electrolyte was the same as above. The instrument was electrochemistry station made by Shanghai Chenghua Instrument Company.

Result and discussion

Thermal analysis of precursor

The thermogravimetric and differential thermal analysis curves of the precursor are shown in Fig. 1. It can be seen that the thermal decomposition of precursor proceeds in three stages. From Fig. 1, it can be seen that from 50 to 207 ℃, the precursor loses crystal water. From 207 to 296 ℃, the little acetic acid and acetic salt can volatilize and be decomposed. When temperature increased and was controlled between 300 and 370 ℃, the precursor burned violently, forming expected product Li-Mn-spinel. During this process, the citrate was oxidized to form CO_2 and H_2O, at the same time,

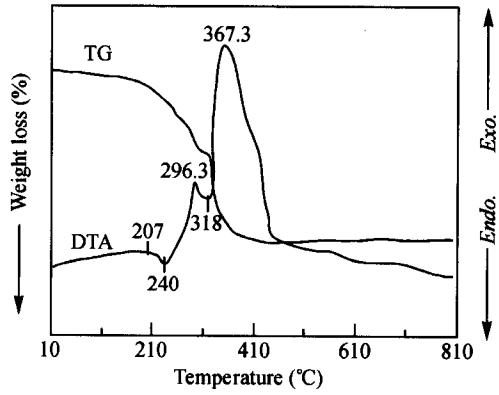

Fig. 1 TG-DTA curves of the precursor heated from 10 to 810 ℃ in flowing air.

the Mn(II) ions were oxidized to form Mn(III) and Mn(IV) ions in the Li-Mn-spinel.

IR *spectra*

The IR spectra of Li-Mn-spinel were examined and shown in Fig. 2. From Fig. 2, it can be seen that the band occurring at 619 and 501 cm^{-1} resulted from *anti*-symmetric vibration of Mn(IV)—O and Mn(III)—O in Li-Mn-spinel crystal [Mn(IV)O_6 and Mn(III)O_6 octahedron]. The band at 1124 cm^{-1} resulted from *anti*-symmetric stretching vibration of Li-O in spinel (LiO_4 Tetrahedron). It proved that the spinel $LiMn_2O_4$ had formed.[8]

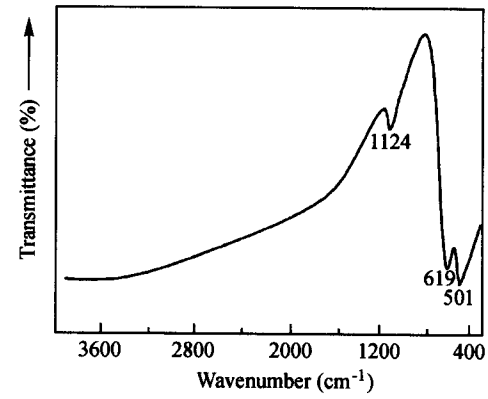

Fig. 2 Infrared spectra of Li-Mn-spinel ($LiMn_2O_4$) formed at 680 ℃.

XRD *data*

XRD measurement was carried out for the end product formed by this method. The correlation XRD patterns of the product are shown in Fig. 3. All diffraction lines can be indexed if assuming a cubic lattice. The cell parameter of $LiMn_2O_4$ was calculated from the XRD, $a = 0.8241$ nm. The experimental data are in agreement with those reported in the paper for Cubic spinel ($LiMn_2O_4$)[9]. The experiment exhibited that the end product was of pure spinel phase. The peaks of impurities such as Mn_2O_3, Li_2MnO_3 can not be detected.

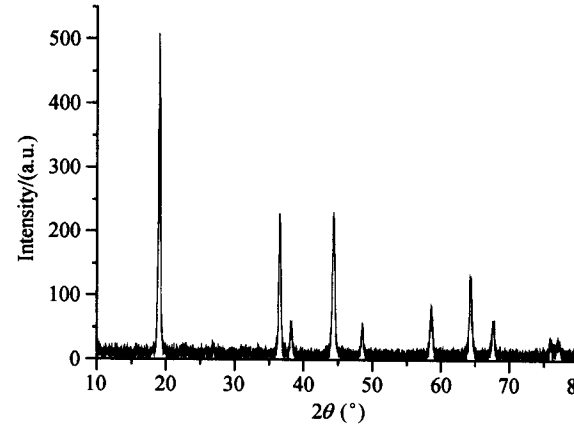

Fig. 3 XRD patterns of $LiMnO_4$ formed at 680 ℃.

Fig. 4 shows the TEM image of $LiMn_2O_4$ prepared by sintering the precursor twice at different temperatures (preheated at 550 ℃ and sintered at 680 ℃) in air. The single particle showed a characteristic crystal shape as quasi-globularity. The average diameter of the Li-Mn-Spinel was around 30—100 nm and showed nearly the same shape.

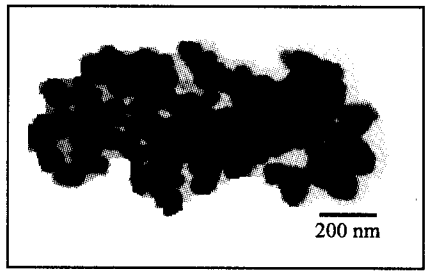

Fig. 4 Transmission electron micrographs of the Li-Mn-spinel powders ($LiMn_2O_4$) formed at 680 ℃.

Electrochemical properties

The electrochemical properties of $LiMn_2O_4$ were investigated with the Model test cells. The positive electrodes were made of a composite of 62.5 wt% Li-Mn-spinel, 25 wt% acetylene black and 12.5 wt% PTFE. The test electrode had an active area with 1 cm^2. The anode was a Li metal foil. The electrolyte was a solution of $LiClO_4$ (1 $mol \cdot L^{-1}$) in solution of EC and DMC (1 : 1 mol%), and micro-porous polypropylene carbonate film was used as a separator. A computer controlled 16-channel battery cycler was used to test charge and discharge characteristics of the cells. The cells were charged and discharged at a constant current density of 1 $mA \cdot cm^{-2}$ and cut-off voltages were 3.5 and 4.4 V. The capacities of $LiMn_2O_4$ are plotted as a function of cycle number in Fig. 5. The charge and discharge curves for the $LiMn_2O_4$/Li are shown in Fig. 6. The initial capacity can reach 126 $mAh \cdot g^{-1}$. The capacity loss after 50 cycles was about 12% of the initial capacity. It can maintain nearly its rechargeable capacities upon farther cycling.

In order to prove that this kind of cathode material has good cycle performance, the powder microelectrode was used to carry out cyclic voltammetry of the system [$Li/LiMn_2O_4$-EC-DMC (1:1)-$LiClO_4$]. The results are shown in Fig. 7, the $LiMn_2O_4$ in electrolyte solution (EC-DMC-$LiClO_4$) shows that two couples of redox peaks, the anodic peak voltages (oxidation potential) are 4.07 and 4.18 V, and that cathode peak voltages (reduction potential) are 3.98 and 4.11 V, the corresponding differences of two redox peak voltage are 0.09 and 0.07 V respectively. This suggested that the lithium ions are easy to extract and insert into the spinel phase by two steps. The presence of two peaks may originate from the fact that lithium ions are removed from the tetrahedral sites in which Li-Li interactions occur, and then lithium ions are removed from the other tetrahedral sites in which lithium ions do not have any nearest neighbor Li-Li-interactions.[2] From cycle voltammogram, we can judge that good reversible processes are showed. So the spinel ($LiMn_2O_4$) formed by this method has good reversible performances in extracted and inserted process.

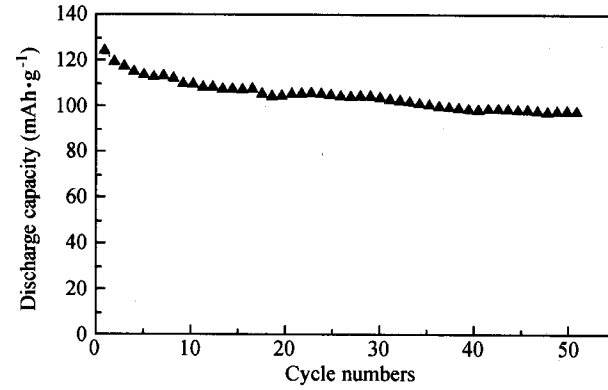

Fig. 5 Graph of discharge capacity vs. cycle number of $LiMn_2O_4$/Li cell (discharged at 1 $mA \cdot cm^{-2}$).

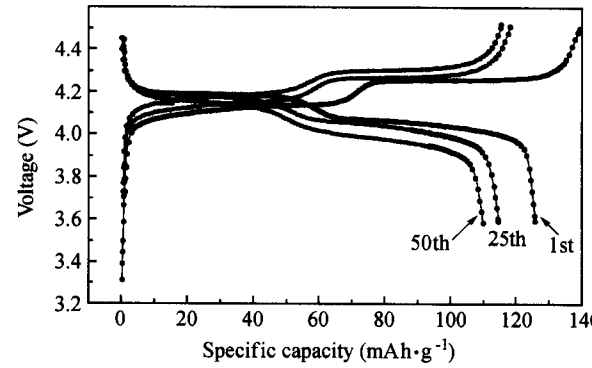

Fig. 6 Charge-discharge curves for $LiMn_2O_4$/Li cell in voltage range of 3.5—4.4 V.

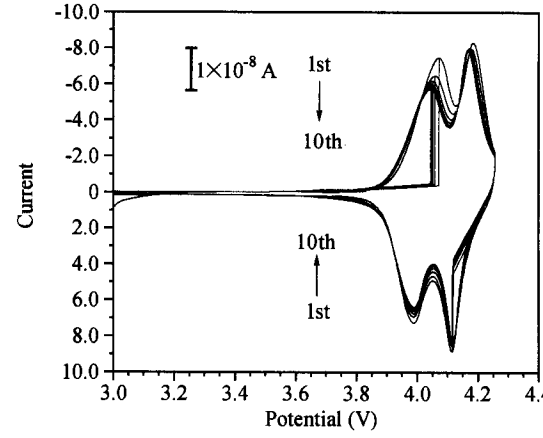

Fig. 7 Cyclic voltammagrams of $LiMn_2O_4$-EC-DMC-$LiClO_4$ system at 25 ℃. The potential was scanned at rate of 2 $mV \cdot min^{-1}$ (vs. Li/Li^+).

Conclusion

The Li-Mn-spinel was synthesized by rheological phase

reaction using citric acid as a chelating agent. The TG and DTA of the precursor indicated the thermal decomposition process of the precursor. The XRD and IR spectra of the end product showed that the light yellow precursor could be heated at suitable temperature to form the pure spinel phase ($LiMn_2O_4$), and the sintering time is much shorter than that of solid-state reaction. The spinel formed by this method takes on uniform particles distributing in the range of 30—100 nm. The initial discharge capacity of $Li/LiMn_2O_4$-EC-$LiClO_4$ cell between 4.3 and 3.5 V at 1 $mA \cdot cm^{-2}$ was 126 $mAh \cdot g^{-1}$. The capacity loss after 50 cycles was about 12%. This result is excellent if we take into account that we are working with a lithium metal anode and the well-known loss of battery performance resulting from poor reconstruction of lithium surface with cycling. The cell can maintain its good recharge ability upon further cycling. In this point, the voltammetry of the system has gone step further to prove it. Therefore the Li-Mn-spinel prepared by this method is suitable for lithium-ion battery applications.

References

1 Tarascon, J. M.; Guyomard, D. *J. Electrochem. Soc.* **1991**, *138*, 2859.

2 Xia, Y. Y.; Yoshio, M. *J. Electrochem. Soc.* **1997**, *144*, 4186.

3 Xia, Y. Y.; Zhou, Y. H.; Yoshio, M. *J. Electrochem. Soc.* **1997**, *144*, 2593.

4 Pistoia, G.; Rosati, R. *J. Power Sources* **1996**, *58*, 135.

5 Gao, Y.; Dahn, J. R. *J. Electrochem. Soc.* **1996**, *143*, 1783.

6 Tarascon, J. M.; Mckinnon, W. R.; Coowar, F.; Bowmer, T. N.; Amatucci, G.; Gayomard, D. *J. Electrochem. Soc.* **1994**, *141*, 1421.

7 Sun, J. T.; Wei, W.; Yuan, L. J.; Zhang, K. L.; Wang, Q. *Mater. Sci. Eng. B* **1999**, *64*, 157.

8 Peng, Z. S.; Ma, J.; Di. J.; Chu, Y. M. *Gongneng Cailiao* (*J. Functional Mater.*) **1999**, *34*, 379 (in Chinese).

9 Enders, P.; Fichs, B.; Kemmler-sack, S. *Solid State Lonics* **1996**, *89*, 221.

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