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Modification of the Solution Flameless Combustion Synthesis of Spinel LiMn_2O_4 by Nitric Acid

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In present work, the effect of auxiliary oxidant HNO_3 with different amounts on structures and properties of spinel LiMn_2O_4 using lithium nitrite and manganese acetate as raw materials by means of the solution flameless combustion synthesis method has been studied. The phase composition, microscopic morphology and electrochemical properties of the LiMn_2O_4 were investigated using XRD, SEM and charge-discharge cycling, respectively. The results showed that the main phase of productions obtained was the LiMn_2O_4 and the impurity phase was greatly affected by the amount of HNO_3 , for instances, a Mn_2O_3 impurity phase was detected at low HNO_3 amount (below 1.0 for the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio), while a Mn_2O_3 phase was observed at high HNO_3 amount (above 1.0 for the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio). From their XRD patterns, it can be seen that the diffraction peaks became sharper, with the increasing concentration of HNO_3 , indicating that the crystalline of LiMn_2O_4 was forming and their particle size decreased gradually. After adding proper HNO_3 into raw compounds, the LiMn_2O_4 nano-particles were the most uniform. Compared with the direct productions, the nitric acid modified productions possessed bigger capacity and better capacity retention rate. The discharge capacity of the product increased first and then decreased with increasing concentration of nitric acid.

Key Words: LiMn_2O_4 , Nitric acid, Solution flameless combustion synthesis, Cathode materials.

INTRODUCTION

The lithium-ion battery has an important position in today's new energy field for its advantages of high energy density, low self-discharge and long cycle life¹⁻³. The ability of storage lithium ions about anode and cathode materials determines the capacity of lithium-ion battery. Recently, the development of lithium ion cathode materials lags behind that of anode materials, to be a key restriction increasing the properties of Li-ion batteries. So the research on cathode material is a focus at present¹⁻³. For the commercial lithium-ion batteries, although LiCoO_2 is first used as a cathode material, it is difficult to meet the current needs of the green chemistry society for its limited resources, expensive and existing pollution⁴. After that, there are many substitutes of LiCoO_2 , including layered⁵, spinel⁶ and olivine-type⁷. The spinel (for example LiMn_2O_4) has the advantages of safety, structural stability, wide raw material resources, cheap and environment friendly, hence it has been become one of the major objects of cathode materials⁸.

There are many traditional methods to prepare LiMn_2O_4 , such as microwave sintering⁹, high temperature solid^{10,11}, sol-gel¹² and solution combustion synthesis¹³. But all of them

have some disadvantages, for instance, the solution combustion synthesis has too fast reaction rate to control the combustion reaction process, resulting in that the product is low purity and agglomerated nanocrystalline, consequently low capacity for Li-ion battery. In this paper, we added nitric acid as auxiliary oxidant into lithium nitrate and manganese (1:2) as raw material to control combustion reaction rate during the solution flameless combustion synthesis (SFCS) and obtain pure form of LiMn_2O_4 with nano-size particles. And the properties of the cathode material were studied in this paper.

EXPERIMENTAL

Calculate the raw material to obtain the target product LiMn_2O_4 ca. 3.0 g. Take lithium nitrate (AR, Shanghai Chemical Reagent Co. Ltd. Hanson) and manganese acetate tetrahydrate (AR, National Pharmaceutical Group Chemical Reagent Co. Ltd.) as raw materials were dissolved into distilled water in a crucible at room temperature. Then nitric acid (AR, Chengdu Joint Chemical Reagent Research Institute, 68 %) with different volumes was added into the above solution as auxiliary oxidant. Lastly, the crucible was put into a muffle furnace at 600 °C for 3 h, was taken out and cooled to room temperature in the air.

The morphologies were observed by scanning electron microscopy (FEI, Quanta 200). The phases and structures of products were analyzed by the X-ray diffraction (D/max-rB, Japan, $\text{CuK}\alpha$). X-Ray diffraction patterns were recorded using a D/max-rB diffractometer with $\text{CuK}\alpha$ radiation operating at 40 KV and 30 mA over 2θ -range of 10 – 70° with a scan speed of $4^\circ/\text{min}$.

The charge-discharge tests were conducted on a cell test instrument at land electric test system CT2001A (Wuhan Jinnuo Electronic Co. Ltd.) using cells 2025 with lithium metal as anode. And the cathodes were prepared by coating the slurry of a mixture (composed of prepared LiMn_2O_4 , acetylene black and polyvinylidene fluoride with the mass ratio of 8:1:1) onto an aluminum current collector and then drying at 80°C in an oven. All cells were assembled in an argon-filled glove box. The electrolyte was 1 M LiPF_6 in EC/DMC (1:1 in volume) and the Celgard 2320 film was used as separator. The cells were cycled in the voltage 3.2–4.35 V with 0.2C current density at room temperature.

RESULTS AND DISCUSSION

Phase compositions and structures: Fig. 1 shows a series of XRD patterns of productions synthesized with different nitric acid amount (V_{HNO_3}) by solution flameless combustion at 600°C . It is seen that the main phase is LiMn_2O_4 (JCPDS, No. 35-0782) and the impurity phase compositions are Mn_3O_4 ($V_{\text{HNO}_3} < 3.0$ mL, Fig. 1b–d and JCPDS No. 80-0382) or Mn_2O_3 ($V_{\text{HNO}_3} > 3.0$ mL, Fig. 1e–f and JCPDS, No. 24-0508). A reason should be the oxidant effect of nitric acid and the more nitric acid was added into, the more the manganese valence was higher. With the increasing nitric acid amount (0–5.0 mL), X-ray diffraction peak of the combustion synthesized product was sharp and corresponding FWHM decreases, indicating that the crystalline degree was increased. When $V_{\text{HNO}_3} > 4.0$ mL, the LiMn_2O_4 X-ray diffraction peak broadened and the crystalline degree was increased.

Fig. 1. XRD patterns of solution flameless combustion synthesized products prepared with nitric acid modification at 600°C

To corroborate that the concentrated nitric acid had effect on the impurity content, another experiment added 3.5 mL

HNO_3 was done and the XRD was presented in the Fig. 2. From this figure, the mixed impurity phases of Mn_3O_4 and Mn_2O_3 were not observed at all, implying that the impurity transformation was abrupt. The function of between the molar ratio of $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ and the HNO_3 amount was showed in the Fig. 3. The abrupt phase transformation of impurity may be occurred at the molar ratio of $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ being 1.0. For the ratio is below 1.0, the impurity was Mn_3O_4 , while above 1.0, the impurity phase abruptly transformed into Mn_2O_3 . This result is consistent with the work of Choi and Manthiram¹⁴, which utilized nitrate as oxidant. The reason was during SFCS CH_3COO^- without oxidation by NO_3^- decomposed CO, which was a reducing agent to reduce the high quantivalence Mn, where the Mn_2O_3 was reduced to Mn_3O_4 .

Fig. 2. XRD patterns of combustion synthesized products prepared with 3.5 mL nitric acid

Fig. 3. Relationship between concentrated nitric acid content and the $n(\text{NO}_3^-)/n(\text{OAc}^-)$ ratio

Fig. 4 presents the SEM morphologies of products with nitric acid (0–5.0 mL) modification by the solution flameless combustion synthesis from the figure, it can be seen that the nitric acid content has a great effect on the morphology of the products. With increasing nitric acid, the particle size was decreased. The reunite between the particles are all very serious as adding more or less nitric acid. When the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio was 0.93, namely adding 3.0 mL nitric acid, the particle size is uniform, 0.24–0.40 μm and the agglomeration

Fig. 4. SEM morphology of the solution flameless combustion synthesized products with nitric acid modification a-f: a: 0 mL, b: 1 mL, c: 2 mL, d: 3 mL, e: 4 mL and f: 5 mL

was improved. The appearance of products changes from hollow crustiform gray matter to fine flake black substance with increasing nitric acid in the present synthesis system using lithium nitrate and manganese acetate as raw materials. When adding 3 mL nitric acid, the product was most fluffy by means of naked eyes, being consistent with the micro-morphology analysis.

Electrochemical performance: Fig. 5 shows the cyclic performance of LiMn_2O_4 products with nitric acid modification using the solution flameless combustion synthesis is in the voltage range of 3.2–4.35 V. From the figure, it can be seen that the discharge capacity of the synthesized LiMn_2O_4 modified by nitric acid increased, however its initial discharge capacity increased firstly and then decreased along with increasing nitric acid. When the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio was 0.93, that is below $V_{\text{HNO}_3} < 3.0$ mL, its discharge capacity increased obviously when increasing nitric acid. Over $V_{\text{HNO}_3} > 3.0$ mL, its initial discharge capacity all decreased to some extent. When $V_{\text{HNO}_3} = 3.0$ mL, the highest capacity (117.7 mAh/g) was obtained. But the 25th discharge capacity was 57.5, 73.4, 77.4, 89.3, 83.7 and 90.9 mAh/g for 0, 1.0, 2.0, 3.0, 4.0, 5.0 mL nitric acid, respectively. And the capacity retention rate was 61.83, 73.69, 74.85, 75.87, 80.17 and 85.03 %, presenting that the capacity retention rate increased with increasing nitric acid.

Fig. 5. Cyclic performance of the solution flameless combustion synthesized products prepared with nitric acid modification

Conclusion

In summary, the nitric acid amount has a great effect on the synthesis of LiMn_2O_4 using the solution flameless combustion method. Although for with or without nitric acid modified LiMn_2O_4 , their main phase was all the spinel LiMn_2O_4 . A Mn_3O_4 impurity phase was detected at low HNO_3 amount (below 1.0 for the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio), while a Mn_2O_3 phase was observed at high HNO_3 amount (above 1 for the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio). When adding 3 mL nitric acid, the product obtained was purest. The crystalline degree of LiMn_2O_4 increased with increasing nitric acid amount added. The effect of nitric acid content on the morphology of the LiMn_2O_4 prepared was analyzed. Their particle size was decreased with increasing nitric acid. The particle reunite are very serious as adding more or less nitric acid. When the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio was 0.93, namely adding 3 mL nitric acid, the particle size was most uniform, but the agglomeration was also found. The discharge capacity increased after adding nitric acid and the

initial discharge capacity of the product increased firstly and then decreased with increasing nitric acid. But, the capacity retention rate increased with increasing nitric acid. When the $\text{NO}_3^-/\text{CH}_3\text{COO}^-$ molar ratio was 0.93, the highest initial discharge capacity of LiMn_2O_4 prepared was obtained was 117.7 mAh/g. But its capacity retention was not the best one and reduced to 75.87 % after 25 cycles.

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