



## Modification of the Solution Flameless Combustion Synthesis of Spinel $\text{LiMn}_2\text{O}_4$ by Nitric Acid

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In present work, the effect of auxiliary oxidant  $\text{HNO}_3$  with different amounts on structures and properties of spinel  $\text{LiMn}_2\text{O}_4$  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  $\text{LiMn}_2\text{O}_4$  were investigated using XRD, SEM and charge-discharge cycling, respectively. The results showed that the main phase of productions obtained was the  $\text{LiMn}_2\text{O}_4$  and the impurity phase was greatly affected by the amount of  $\text{HNO}_3$ , for instances, a  $\text{Mn}_2\text{O}_3$  impurity phase was detected at low  $\text{HNO}_3$  amount (below 1.0 for the  $\text{NO}_3^-/\text{CH}_3\text{COO}^-$  molar ratio), while a  $\text{Mn}_2\text{O}_3$  phase was observed at high  $\text{HNO}_3$  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  $\text{HNO}_3$ , indicating that the crystalline of  $\text{LiMn}_2\text{O}_4$  was forming and their particle size decreased gradually. After adding proper  $\text{HNO}_3$  into raw compounds, the  $\text{LiMn}_2\text{O}_4$  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:**  $\text{LiMn}_2\text{O}_4$ , 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 life<sup>1-3</sup>. 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 present<sup>1-3</sup>. For the commercial lithium-ion batteries, although  $\text{LiCoO}_2$  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 pollution<sup>4</sup>. After that, there are many substitutes of  $\text{LiCoO}_2$ , including layered<sup>5</sup>, spinel<sup>6</sup> and olivine-type<sup>7</sup>. The spinel (for example  $\text{LiMn}_2\text{O}_4$ ) has the advantages of safety, structural stability, wide raw material resources, cheap and environment friendly, hence it has become one of the major objects of cathode materials<sup>8</sup>.

There are many traditional methods to prepare  $\text{LiMn}_2\text{O}_4$ , such as microwave sintering<sup>9</sup>, high temperature solid<sup>10,11</sup>, sol-gel<sup>12</sup> and solution combustion synthesis<sup>13</sup>. 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  $\text{LiMn}_2\text{O}_4$  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  $\text{LiMn}_2\text{O}_4$  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  $2\theta$ -range of  $10$ - $70^\circ$  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  $\text{LiMn}_2\text{O}_4$ , acetylene black and polyvinylidene fluoride with the mass ratio of 8:1:1) onto an aluminum current collector and then drying at  $80^\circ\text{C}$  in an oven. All cells were assembled in an argon-filled glove box. The electrolyte was 1 M  $\text{LiPF}_6$  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 ( $V_{\text{HNO}_3}$ ) by solution flameless combustion at  $600^\circ\text{C}$ . It is seen that the main phase is  $\text{LiMn}_2\text{O}_4$  (JCPDS, No. 35-0782) and the impurity phase compositions are  $\text{Mn}_3\text{O}_4$  ( $V_{\text{HNO}_3} < 3.0$  mL, Fig. 1b-d and JCPDS No. 80-0382) or  $\text{Mn}_2\text{O}_3$  ( $V_{\text{HNO}_3} > 3.0$  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  $\text{LiMn}_2\text{O}_4$  X-ray diffraction peak broadened and the crystalline degree was increased.

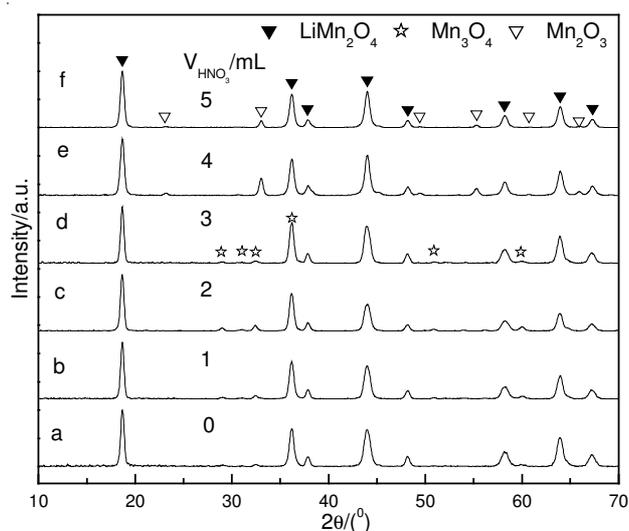


Fig. 1. XRD patterns of solution flameless combustion synthesized products prepared with nitric acid modification at  $600^\circ\text{C}$

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

$\text{HNO}_3$  was done and the XRD was presented in the Fig. 2. From this figure, the mixed impurity phases of  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  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  $\text{HNO}_3$  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  $\text{Mn}_3\text{O}_4$ , while above 1.0, he impurity phase abruptly transformed into  $\text{Mn}_2\text{O}_3$ . This result is consistent with the work of Choi and Manthiram<sup>14</sup>, which utilized nitrate as oxidant. The reason was during SFCS  $\text{CH}_3\text{COO}^-$  without oxidation by  $\text{NO}_3^-$  decomposed CO, which was a reducing agent to reduce the high quantivalence Mn, where the  $\text{Mn}_2\text{O}_3$  was reduced to  $\text{Mn}_3\text{O}_4$ .

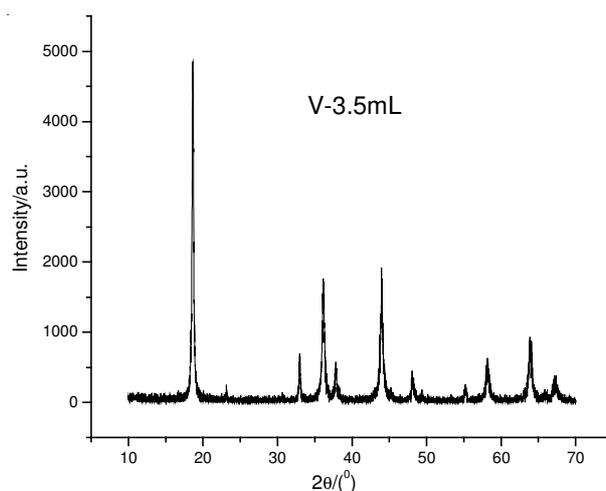


Fig. 2. XRD patterns of combustion synthesized products prepared with 3.5 mL nitric acid

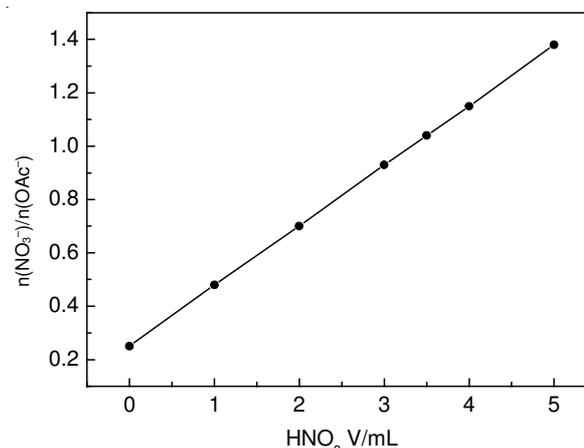


Fig. 3. Relationship between concentrated nitric acid content and the  $n(\text{NO}_3^-)/n(\text{OAc}^-)$  ratio

Fig. 4 presents the SEM morphologies of products with nitric acid (0-5.0mL) 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  $\mu\text{m}$  and the agglomeration

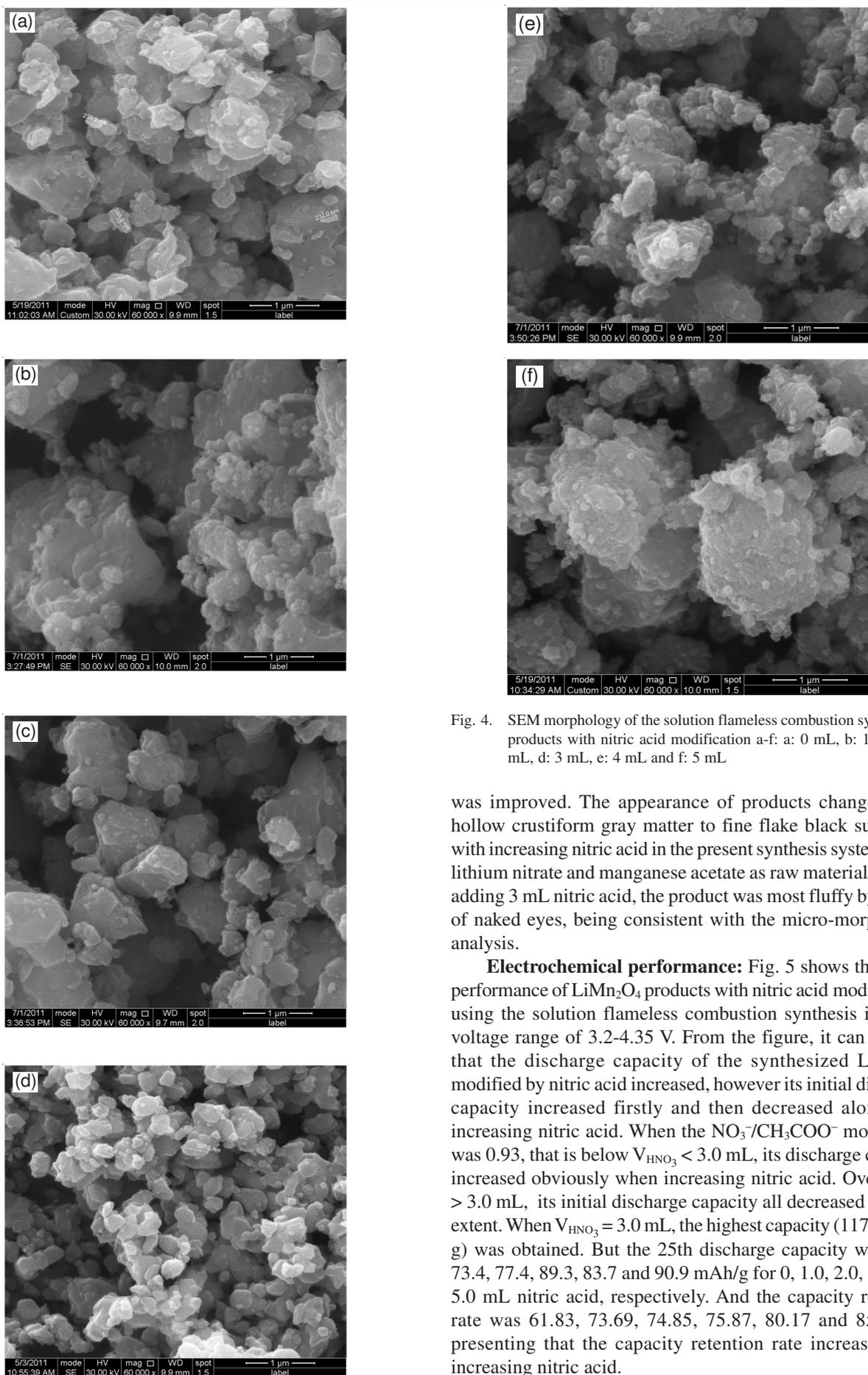


Fig. 4. SEM morphology of the solution flameless combustion synthesized products with nitric acid modification a-f: a: 0 mL, b: 1 mL, c: 2 mL, d: 3 mL, e: 4 mL and f: 5 mL

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  $\text{LiMn}_2\text{O}_4$  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  $\text{LiMn}_2\text{O}_4$  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.

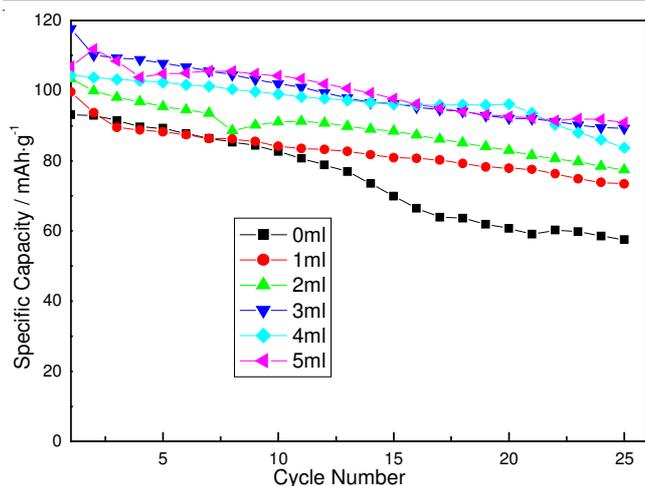


Fig. 5. Cyclic performance of the solution flameless combustion synthesized products prepared with nitric acid modification

## Conclusion

In summary, the nitric acid amount has a great effect on the synthesis of  $\text{LiMn}_2\text{O}_4$  using the solution flameless combustion method. Although for with or without nitric acid modified  $\text{LiMn}_2\text{O}_4$ , their main phase was all the spinel  $\text{LiMn}_2\text{O}_4$ . A  $\text{Mn}_3\text{O}_4$  impurity phase was detected at low  $\text{HNO}_3$  amount (below 1.0 for the  $\text{NO}_3^-/\text{CH}_3\text{COO}^-$  molar ratio), while a  $\text{Mn}_2\text{O}_3$  phase was observed at high  $\text{HNO}_3$  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  $\text{LiMn}_2\text{O}_4$  increased with increasing nitric acid amount added. The effect of nitric acid content on the morphology of the  $\text{LiMn}_2\text{O}_4$  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  $\text{LiMn}_2\text{O}_4$  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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