

Full Length Research Paper

Nanometer complexes from explosives

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Lithium manganese oxides are of great interest as cathode materials for lithium-ion batteries. We describe here a new combustion method to synthesize lithium manganese oxides directly from lithium nitrate, manganese nitrate, ammonium nitrate and glycol. The resultant LiMn_2O_4 synthesized under the optimum synthesis conditions shows perfect spinel structure and uniform particle size distribution. The combustion products were characterized by scanning electron microscopy. And, powders X-ray diffraction and transmission electron microscopy were used to characterize the products. Lithium manganese oxides with approximately acrose crystal morphology of 100 - 200 nm length with 10 - 15 nm diameters and a variety of morphologies were found. The oxides produced by this cheap method affirmed the validity of combustion synthesis of fine powders. Lithium manganate with a fine structure different from that of the normal spinel is formed after combustion wave treatment due to the addition of ammonium nitrate. It might also provide a cheap large-scale synthesis method. Reagents combustion with the addition of ammonium nitrate is strongly nonequilibrium processes. Free metal atoms are first released with the decomposition of reagents, and then these metal and oxygen atoms are rearranged, coagulated and finally crystallized into lithium manganate during the expansion of combustion process.

Key words: Spinel phase LiMn_2O_4 , combustion method, ammonium nitrate, acrose crystal.

INTRODUCTION

The lithium manganese oxides synthesized by the conventional method has several disadvantages, such as inhomogeneity, irregular morphology, large particle size, broad particle size distribution, high synthesis temperature and repeated grinding. To overcome the disadvantages of solid-state reaction, several soft chemistry methods, such as hydrothermal method, sol-gel, solvothermal method, coprecipitation and pechini process have been developed. Among these methods, solvothermal method should use organic agents. It is toxic and unsafe. The sol-gel, coprecipitation and pechini process need further calcination and grinding. The hydrothermal synthesis is a powerful method to prepare various oxides. The advantage features of this method are to control the morphology, the particle size and the crystalline of products. However, most spinel Li-Mn-O products synthesized by the hydrothermal method reported in literature were powders with irregular shapes.

Liu et al. (2001) thought that the shock-induced chemical reactions leading to synthesis of compounds in powder mixtures occurred under conditions of the microsecond-scale duration of the high pressure, stress, strain-rate, and temperature states. Such high-rate chemical reactions can be advantageously utilized to synthesize materials with novel phases and unique microstructures, or to generate radically modified materials with physically interesting or technologically useful properties. Ma et al. (2004) reported that Spinel structure Li-Mn-O compounds are the most promising lithium ion insertion electrode materials for rechargeable lithium ion batteries because of a number of advantages over their alternatives, e.g., a lower cost compared with LiCoO_2 or LiNiO_2 , a high cell voltage, and a high environmental tolerance, etc. The excess of Li and substitution of Cr to Mn and small surface area impeded the occurrence of the split. The split is presumably considered relating to the disproportionation dissolution of stoichiometric spinel intensified by the elevated temperatures in slightly acidic electrolyte due to residual water impurity. LiMnO can selectively insert Li from an aqueous

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solution (Morcrette et al., 1998).

Tabuchi et al. (1997) introduced that the excess Li could substitute the Mn ion on the 16d site in the spinel structure. And they introduced that excellent cycling behavior for nonstoichiometric $\text{Li}_{1.0}\text{Mn}_{1.93}\text{O}_4$. Kim et al. (2001) investigated characteristics of charge/discharge cycling of LiMn_2O_4 .

Davidson et al. (1999) reported that using solid-state reactions method, however, the powder preparation route is also quite complicated, for example, several times calcination and subsequent physical grindings. Moreover, its electrochemical properties are greatly dependent on its crystalline particle size (Komaba et al., 2002). Liu et al. (2004) synthesized nanostructured spherical spinel lithium manganese oxide (Li-Mn-O) with about 200 nm in diameter for the first time by mild hydrothermal method, and studied systematically the influence of the reaction temperature and the time of formation of the nanostructures.

In this study, a combustion method has been developed to synthesize spinel phase lithium manganese oxides directly from lithium nitrate, manganese nitrate, ammonium nitrate and glycol. The resultant LiMn_2O_4 synthesized under the optimum synthesis condition shows perfect spinel structure. This synthesis method is inexpensive and simple.

EXPERIMENTAL

The new method is based on the phenomenon that nitrate can act rapidly with glycol $\text{C}_2\text{H}_4(\text{OH})_2$. The manipulation details are described as following:

LiNO_3 , NH_4NO_3 , $\text{Mn}(\text{NO}_3)_2$ (50 wt. % solution in water) and glycol were mixed in a desired proportions and stirred until a uniform solution was formed. The solution was poured into a crucible, and then the crucible was put into a furnace, which was preset at a high temperature. A rapid reaction of glycol with nitrate took place to form fine powder. Thus formed fine powders were heat-treated at 780°C for a period of time 12 h, and then cooled with furnace to room temperature. The spinel phase LiMn_2O_4 was thus obtained.

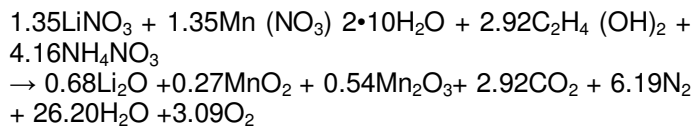
The solution was put into a ceramic crucible with an approximate 1800 kg/m^3 density and the mass was fixed at 0.002 kg. Then, they were annealed at 780°C for 18 h. All the final products were analyzed by XRD (X-ray diffractometry) [$\lambda\text{CuK}\alpha = 1.5418\text{ \AA}$] in the range of $10 - 80^\circ (2\theta)$. So for all the experiments, the combustion of slurry reagents synthesized a black powder containing mainly ultradispersed composite oxides of lithium manganate.

XRD analysis was carried out on an XRD-6000 Shimadzu diffractometer using $\text{Cu K}\alpha$ irradiation. The diffraction intensities were measured every step (0.028°) for 1 s in the 2θ range from 10 to 80° at room temperature (293K). Scanning electron microscopy (SEM) analysis was performed with JEOL JEM-1200EX for combustion synthesized lithium and manganate. The shape and size of the as-obtained particles were observed by transmission electron microscope (TEM, Tecnai G2 20 S-twin).

RESULTS AND DISCUSSION

The exact mechanism of the formation of such

nano-grains in the solution derived so far is poorly understood. The combustion reaction is violent.



We can figure out the combustion heat of 1 Kg reagents Q as follows

$$Q = 0.68 \times (-595.8) + 0.27 \times (-521.5) + 0.54 \times (-959.0) + 2.92 \times (-393.7) + 26.20 \times (-242.0) - 1.35 \times (-482.2) - 1.35 \times (-3432.6) - 2.92 \times (-452.3) - 4.16 \times (-340.0) \\ = -405.14 - 140.81 - 517.86 - 1149.60 - 6340.40 + 650.97 + 4634.01 + 1320.72 + 1414.40 \\ = -533.71 \text{ (KJ/Kg)}$$

The reaction equations at different temperatures are described as follows respectively.

When at 110°C , $\text{NH}_4\text{NO}_3 \rightarrow \text{HNO}_3 + \text{NH}_3 - 41.3\text{Kcal/mol}$ (endothermal).

When from 185 to 200°C , $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} + 10.2\text{Kcal/mol}$ (radiative).

When above 230°C , $2\text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O} + 30.7\text{Kcal/mol}$ (radiative, fast-breaking, and feebly gleamy).

When heated rapidly, $2\text{NH}_4\text{NO}_3 \rightarrow 2\text{NO} + \text{N}_2 + 4\text{H}_2\text{O} + 9.2\text{Kcal/mol}$.

When above 400°C , $4\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + 2\text{NO}_2 + 8\text{H}_2\text{O} + 29.5\text{Kcal/mol}$ (decompounding and exploding).

The general exploding reaction is as follows.



Figure 1 shows an XRD pattern of the dynamically synthesized lithium manganate. We obtained a nanosized texture containing lithium manganese oxides. It is obvious that the Bragg reflection peaks of the dynamically synthesized Lithium manganate are broadened, which may result from small grain size and/or presence of microstrain. Here the mean grain size for combustion synthesized lithium manganate refers to the mean size of crystallites of polycrystalline particles. XRD analyses were conducted at a fixed temperature in the present study; a precise determination of the structural parameters need more experiments including both high temperature and low temperature experiments. Reagents combustion is strongly nonequilibrium processes, generating a short duration of high pressure and high temperature.

A most intense LiMn_2O_4 line is seen on the x-ray pattern of these products. Berbenni and Marini (2003) reached the conclusion that LiMn_2O_4 forms directly and its formation is completed within 700°C and at $T > 820^\circ\text{C}$ LiMn_2O_4 reversibly decomposes to LiMnO_2 and Mn_3O_4

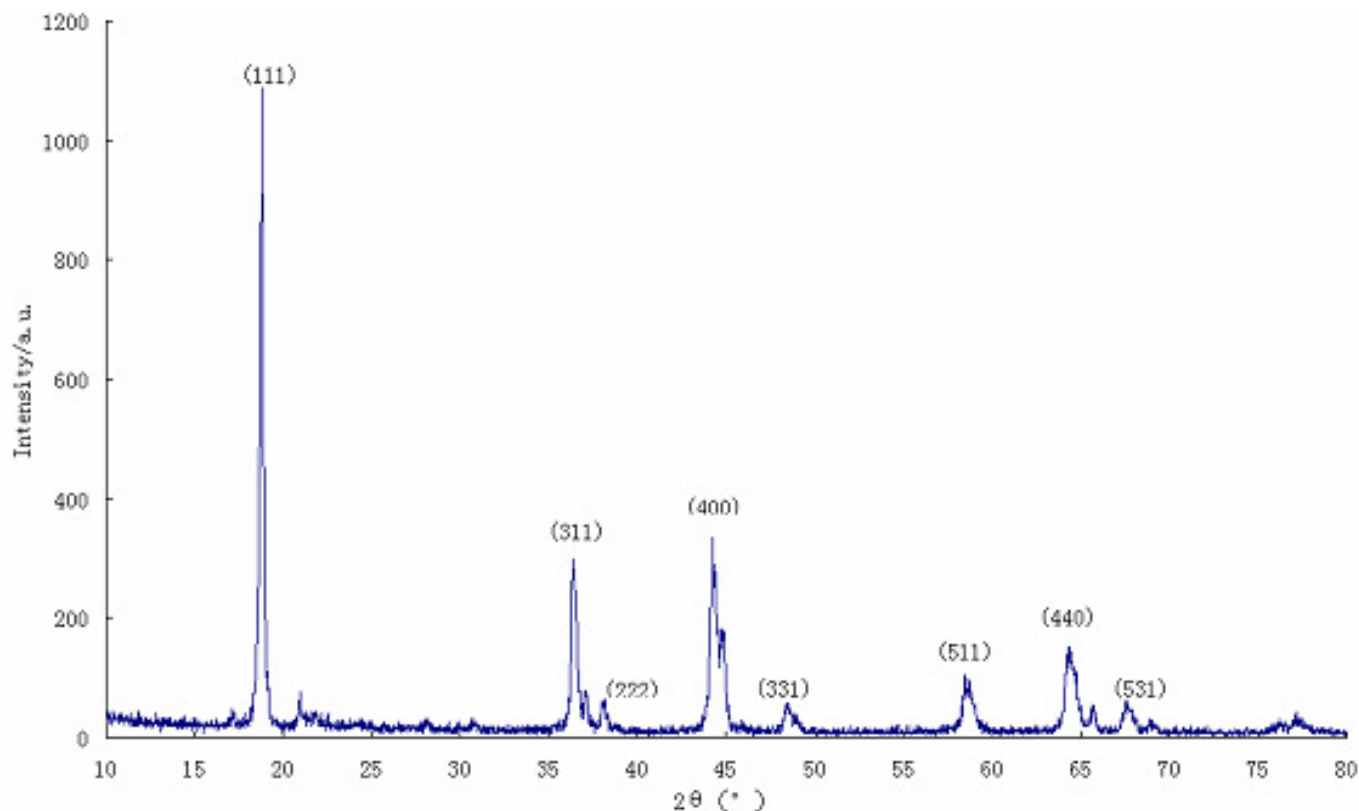


Figure 1. XRD pattern of lithium manganese oxides.

with an enthalpy of $30.05 \text{ kJ mol}^{-1}$ of LiMn_2O_4 .

The average grain size (D) was measured from the XRD peak using the Scherrer formula (Lin et al., 2001):

Where $\lambda=0.15418 \text{ nm}$, θ is the Bragg angle of the peak, and β is defined as the full width at half maximum.

The calculated mean grain sizes were 33.81 nm and the crystal constant $a = 0.8184 \text{ nm}$ for combustion synthesized lithium manganese oxides. The pattern represents the peak positions expected for $\text{Li}_{1.288}\text{Mn}_{1.716}\text{O}_{3.732}$ (JCPDS file n. 89-4604). Julien et al. 2003 concluded that spinel structure $\lambda\text{-LiMn}_2\text{O}_4$ is primarily characterized by structural groups as follows. (1) MnO_6 octahedra connected to one another in three dimensions by edge sharing; (2) LiO_4 tetrahedra sharing each of their four corners with a different MnO_6 unit but essentially isolated from one another; (3) a three-dimensional network of octahedral 16c and tetrahedral (primarily 8a) sites, through which lithium ions can move through the lattice. Lithium-/manganese-oxide spinels are, currently, of technologic interest as insertion electrodes for rechargeable 4-V lithium batteries.

Figures 2 and 3 are morphologies taken by SEM and TEM respectively. Lithium manganese oxides with approximately acerosic crystal morphology of $100 - 200 \text{ nm}$ length with $10 - 15 \text{ nm}$ diameters and a variety of morphologies were found.

Conclusions

Lithium manganate with a fine agglomeration structure different from that of the normal spinel is formed after combustion wave treatment through the addition of ammonium nitrate during the annealing process. It might also provide a cheap large-scale synthesis method. Lithium manganate with approximately $100 - 200 \text{ nm}$ acerosic crystal morphology and more uniform secondary particles, with smaller primary particles of diameters from 10 to 15 nm and a variety of morphologies were found. The oxides produced by this cheap method affirmed the validity of combustion synthesis of fine powders. Lithium manganate with a fine structure different from that of the normal spinel is formed after combustion wave treatment due to the addition of ammonium nitrate. It might also provide a cheap large-scale synthesis method. Reagents combustion with the addition of ammonium nitrate is strongly nonequilibrium processes. Free metal atoms are first released with the decomposition of reagents, and then these metal and oxygen atoms are rearranged, coagulated and finally crystallized into lithium manganate during the expansion of combustion process.

The simple and efficient approach employed for the nano-lithium manganese oxide products can be successfully used for the fabrication of LiMn_2O_4 . Indeed, the advantage of the ability to induce surface modification

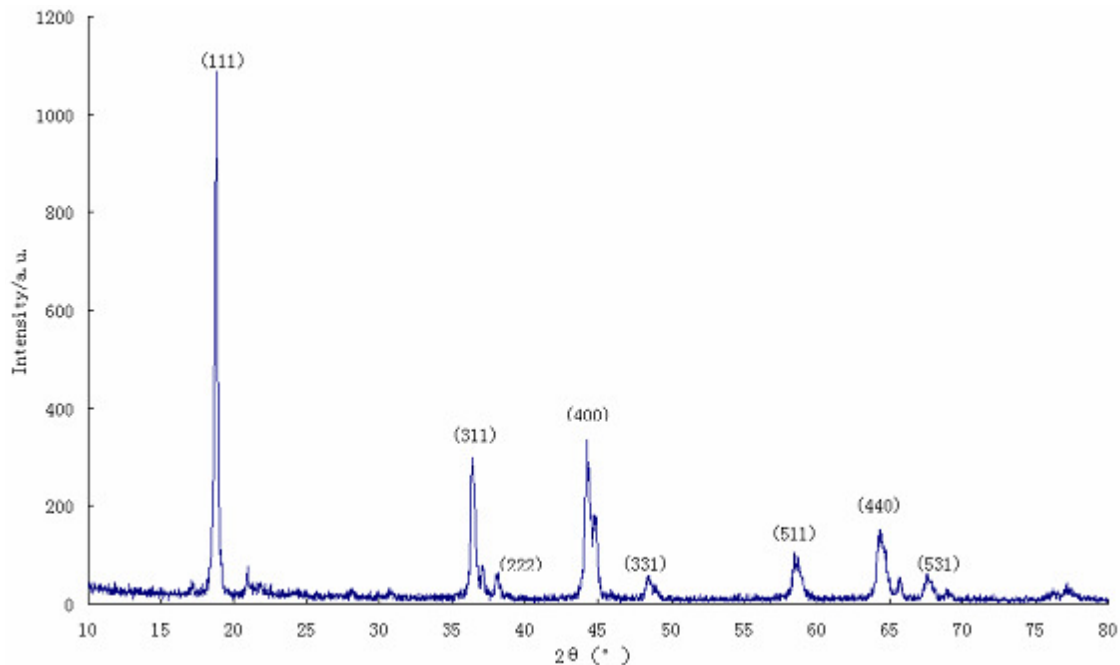


Figure 2. SEM image of combustion synthesized lithium manganese oxides.

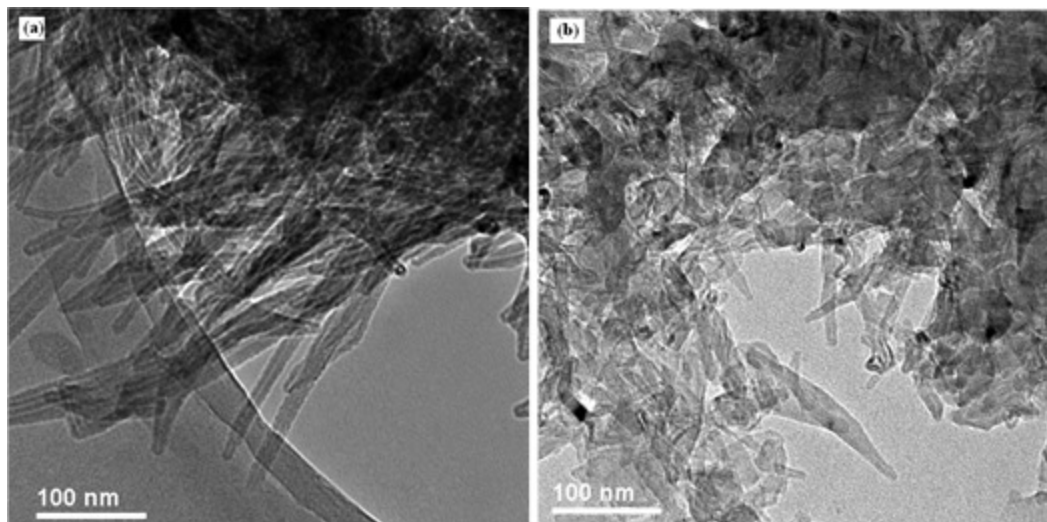


Figure 3. TEM image of combustion synthesized lithium manganese oxides.

of LiMn_2O_4 makes the method useful as well as usual high-technological methods. Further investigations of different cases may lead to new opportunity for the fabrication of LiMn_2O_4 powders with improved properties based on the simple method of combustion synthesis.

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