

LiMn_{2-y}M_yO₄ (M = Cr, Co) cathode materials synthesized by the microwave-induced combustion for lithium ion batteries

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Abstract

Spinel LiMn_{2-y}M_yO₄ (M = Cr and Co, where y = 0.0, 0.1, and 0.2) powders with narrow and uniformly sized particles were successfully synthesized by microwave-induced combustion, using lithium nitrate, manganese nitrate, chromium nitrate, cobalt nitrate, and urea as the starting materials. The LiMn_{2-y}M_yO₄ powders synthesized by microwave-induced combustion were investigated by thermogravimeter analyzer (TGA), X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The Cr and Co-substituted spinel samples were used as cathode materials for lithium-ion battery, whose discharge capacity and electrochemical characteristic properties in terms of cycle performance were also investigated.

The results revealed that the Li/LiMn_{2-y}M_yO₄ (M = Cr, Co) cells can be ranked in terms of initial capacity as follows: LiMn₂O₄ > LiMn_{1.9}Cr_{0.1}O₄ > LiMn_{1.9}Co_{0.1}O₄ > LiMn_{1.8}Cr_{0.2}O₄ > LiMn_{1.8}Co_{0.2}O₄. The Li/LiMn_{2-y}M_yO₄ (M = Cr, Co) cells showed lower fading rate than Li/LiMn₂O₄ cell during 30 cycles, while Cr-substituted spinel exhibited the lower fading rate than Co-substituted spinel. On the other hand, the fading rate of Li/LiMn_{2-y}M_yO₄ cells can be ranked as follows: LiMn₂O₄ > LiMn_{1.9}Co_{0.1}O₄ > LiMn_{1.8}Co_{0.2}O₄ > LiMn_{1.9}Cr_{0.1}O₄ > LiMn_{1.8}Cr_{0.2}O₄.

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1. Introduction

Spinel-type LiMn₂O₄ has recently become an attractive material for making the cathode of lithium ion rechargeable batteries because of its relative low cost and high capacity [1–3]. However, the capacity of LiMn₂O₄ fades during cycling for several reasons, such as an instability of an organic-base electrolyte in a high potential region [4], the dissolution of manganese into electrolyte [5,6], change in crystal lattice arrangement with cycling [7], and others. In order to overcome the capacity fading, the manganese atom was partially replaced by transition elements, such as Ni, Cr, and Co [8–10]. The conventional way to produce these materials involves the solid-state reaction of

mixing with oxides or carbonates containing lithium and manganese cations, and calcination at high temperature. However, the solid-state reaction requires a long heating time and followed by several grinding, annealing process, which has some inherent disadvantages including chemical inhomogeneity, coarser particle size, and introduction of impurities during ball milling. Several chemical methods such as co-precipitation, sol–gel technique, Pechini method and ultrasonic spray pyrolysis method have been developed to overcome the above-mentioned disadvantages, which synthesized by solid-state reaction. However, these chemical methods involved complicated steps such as precise control of pH, precipitation, etc., to obtain the correct stoichiometric compound.

In the current research, we used a new method called microwave-induced combustion synthesis to produce LiMn_{2-y}M_yO₄ (M = Cr and Co, where y = 0.0, 0.1, and 0.2) cathode materials. Microwave processing of materials is

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fundamentally different from the conventional processing in terms of the heat generation mechanism. In a microwave oven, heat is generated within the sample itself by the interaction of microwaves with the material. In a conventional heating, heat is generated by heating elements and then it is transferred to the surface of sample [11]. The microwave-induced combustion synthesis entails the dissolution of lithium nitrate, chromium nitrate, cobalt nitrate, manganese nitrate and urea in water, and then heating the resulting solution in a microwave oven. Urea and metal nitrate decompose and giving off flammable gases such as NH_3 , HNCO , O_2 , and NO . After the solution reaches the point of spontaneous combustion, it begins to burn in solid form above 1000°C . The combustion is not complete until all the flammable substances are all burnt out and it turns out to be a loose substance which shows voids, pores, and highly friable formed by the escaping gases during the combustion reaction [12]. The whole process takes only 30 min to yield $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) cathode materials.

2. Experimental

2.1. Preparation of $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) powders

The synthesis process of $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) powders involved the combustion of redox mixtures, in which metal nitrate acted as an oxidizing agent and urea as a reducing agent. The initial composition of the solution containing lithium nitrate, manganese nitrate, chromium nitrate, cobalt nitrate, and urea was based on the total oxidizing and reducing valences of the oxidizer and fuel using concepts in propellant chemistry [13].

Stoichiometric amounts of lithium nitrate [LiNO_3], manganese nitrate [$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], chromium nitrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], and urea [$\text{CO}(\text{NH}_2)_2$] were dissolved in 15 ml of water in a crucible. The crucible containing the solution was placed in a microwave oven (CEM, MDS 81D, 650 W). The microwave power of microwave oven operated at 100% (650 W) for 30 min. Initially, the solution boiled and underwent dehydration followed by decomposition with the evolution of large amount of gases (N_2 , NH_3 , and HNCO). After the solution reached the point of spontaneous combustion, it began to burn with the release of much heat, vaporized all the solution instantly and burnt in solid form above 1000°C . The entire combustion process for producing $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) powders in the microwave oven took only 30 min, and then the microwave-heated $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ powders were annealed at the temperature of 800°C for 8 h in air.

2.2. Analysis of $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) powders

Thermogravimetry (TG; Rigaku Thermalplus TG 8120) was used to study the weight loss of the microwave-heated LiMn_2O_4 powders. A heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C in air. The crystallography of samples were characterized using a computer-interface X-ray powder diffractometer (XRD; Rigaku D/Max-II) with $\text{Cu K}\alpha$ radiation. The lattice constants were calculated by iterative least square refinements using silicon as standard (10 wt.%). The particle morphology and size of the microwave-heated $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ powders and annealed at 800°C for 8 h were characterized using a scanning electron microscopy (SEM; Jeol JSM-6500F).

The total average valences of Mn ion were obtained by potential titration. Firstly, the $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) powders were dissolved in excess of FeSO_4 and once the Mn dissolved completely and then the excess FeSO_4 was back-titrated with 1N KMnO_4 solution. For the total Mn, both Mn^{3+} and Mn^{4+} in the samples were reduced to Mn^{2+} in a mixture solution of HCl and H_2SO_4 under heating. This solution was titrated with 1N KMnO_4 around pH 7. $\text{Na}_4\text{P}_2\text{O}_7$ was added to complex the oxidation product Mn^{3+} . The average oxidation state of Mn was calculated by above-mentioned method [14].

2.3. Electrochemical properties of $\text{Li}/\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) batteries

The charge and discharge characteristic of $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}, \text{Co}$) cathode were examined in laboratory cells. The cells consist of a cathode and a lithium metal anode separated by a micro-porous polypropylene separator. The electrolyte used 1 M LiPF_6 in a 50/50 vol.% mixture of EC/DMC. The positive electrode was consisted of a mixture of 83 wt.%, 10 wt.% of acetylene black, and 7 wt.% poly vinylidene flouride (PVDF). The mixture was pressed onto a stainless screen mesh at $250 \text{ kg}/\text{cm}^2$ and vacuum dried at 110°C for 12 h in an oven. The cells were cycled in the voltage range of 3.0–4.5 V with typical current density $0.1 \text{ mA}/\text{cm}^2$ at room temperature. Cyclic voltammetry was performed for the solid solution using a flooded three-electrode glass cell. The cyclic voltamograms were taken for a sweep rate of $0.05 \text{ mV}/\text{s}$ between 3.0 and 4.5 V. All assembling of the cell was carried out in a glove box filled with Ar gas.

3. Results and discussion

3.1. Properties of synthesized powders

Phase transformation of microwave-heated LiMn_2O_4 powders and the mixtures of the reactants LiCO_3 with MnCO_3 powders were studied using TG measurement. Fig. 1(a) shows the TG curve for the mixtures of the reactants LiCO_3 with MnCO_3 powders. There are three steps for the weight loss. The first steps from room temperature to 200°C may be attributed to the evaporation of residual water; the second step between 250 and 420°C corresponds to the crystallization of LiMn_2O_4 phase; the third step between 450 and 900°C , which indicates the weight loss of mixtures is about 3%. This was due to that the solid-state reaction forming LiMn_2O_4 is completed at this stage. Fig. 1(b) shows the TG trace for microwave-heated LiMn_2O_4 powders, which indicates the weight loss is about 5% during the whole heating process. This can be attribute to the most LiMn_2O_4 spinel phase have been formed during microwave-induced combustion process.

Fig. 2 shows the X-ray diffraction patterns of the microwave-heated $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ ($M = \text{Cr}$ and Co , where $y = 0.0, 0.1$, and 0.2) powders annealed at 800°C for 8 h. Evidently the microwave-heated $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ powders annealed at 800°C

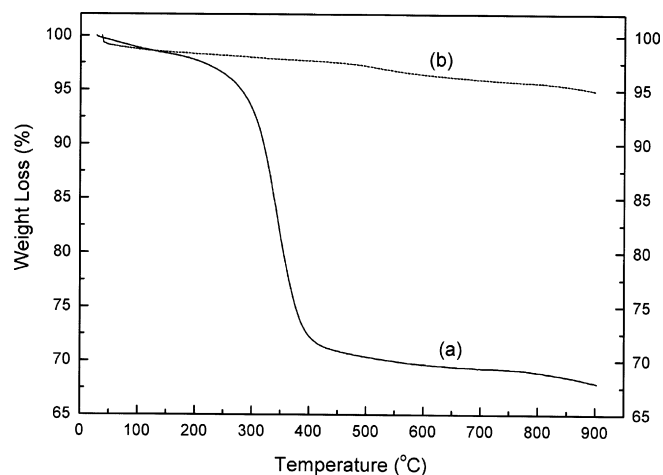


Fig. 1. The thermogravimetric analysis curves for: (a) the mixtures of the reactants LiCO_3 with MnCO_3 powders and (b) the microwave-heated LiMn_2O_4 powders.

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