

Short communication

Electrochemical characteristic of $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) cathode materials synthesized by the microwave-induced combustion method

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Available online 5 June 2006

Abstract

Spinel $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) powders with small and uniform particle size were successfully synthesized by microwave-induced combustion. The $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) samples were used as cathode materials for lithium-ion battery, which their discharge capacity and electrochemical characteristic properties were investigated in this study. The results revealed that The $\text{Li}/\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) cells showed lower capacity loss than $\text{Li}/\text{LiMn}_2\text{O}_4$ cell after 30 cycles. Moreover, Cr-substituted spinel exhibited a lower capacity loss than Co-substituted spinel. The initial capacity of LiMn_2O_4 and $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ cells can be ranked as follows: $\text{LiMn}_2\text{O}_4 > \text{LiMn}_{1.925}\text{Cr}_{0.075}\text{O}_4 > \text{LiMn}_{1.925}\text{Co}_{0.075}\text{O}_4$. © 2006 Elsevier B.V. All rights reserved.

Keywords: LiMn_2O_4 powder; Microwave-induced combustion; Lithium-ion battery

1. Introduction

Recently, the spinel-type LiMn_2O_4 is an attractive cathode material for lithium-ion rechargeable batteries with its relative low cost and high capacity [1–3]. However, LiMn_2O_4 exhibits several capacity fading on cycling due to 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 so on. In order to overcome the capacity fading, the manganese atom was partially replaced by transition elements, such as Ni [8,9], Cr [8,9], Co [10]. The conventional way of producing these materials by the solid-state reaction of mixing with oxides or carbonates containing lithium and manganese cations, and calcined 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 such as: chemical inhomogeneity, coarser particle size, and introduction of impurities during ball milling.

In the current research, we used a new method called microwave-induced combustion synthesis to produce $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) cathode materials.

$\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) cathode materials. Microwave processing of materials is fundamentally different from the conventional processing in terms of the heat generation mechanism [11–13]. 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 [14]. The whole process takes only 30 min to yield $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) cathode materials.

2. Experimental

The synthesis process of $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($\text{M} = \text{Cr}, \text{Co}$) 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

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of the oxidizer and fuel using concepts in propellant chemistry [15].

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. The solution contained metal nitrates and urea boiled and underwent dehydration followed by decomposition with the evolution of large amount of gases. The entire combustion process for producing $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($M=\text{Cr}, \text{Co}$) powders in the microwave oven took only 30 min, and then the microwave-heated $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ powders were annealed at the temperature of 800°C for 8 h in air.

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 $10^\circ\text{C min}^{-1}$ from room temperature to 1000°C in air. The charge and discharge characteristic of $\text{LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($M=\text{Cr}, \text{Co}$) 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, 10 wt.% of acetylene black, and 7 wt.% poly vinylidene flouoride (PVDF). The mixture was pressed onto a stainless screen mesh at 250 kg cm^{-2} and vacuum dried at 110°C for 12 h in a oven. The cells were cycled in the voltage range of 3.0–4.5 V with typical current density 0.1 and 0.3 mA cm^{-2} , respectively, at room temperature and high temperature (55°C). 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 mV/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

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 attributed to the most LiMn_2O_4 spinel phase have been formed during microwave-induced combustion process.

The relationships between the discharge capacity of the cathode and the cycle numbers of $\text{Li/LiMn}_2\text{O}_4$ and

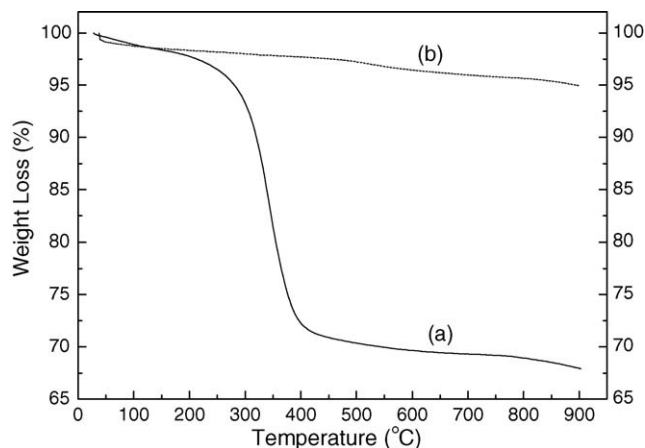


Fig. 1. The thermogravimetric analysis curves for (a) the mixtures of the reactants LiCO_3 with MnCO_3 powders, (b) the microwave-heated LiMn_2O_4 powders.

$\text{Li/LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($M=\text{Cr}, \text{Co}$) cells between 3.0 and 4.5 V at a current rate of 0.1 and 0.3 mA are shown in Fig. 2. It can be seen, the discharge capacity loss of the $\text{Li/LiMn}_2\text{O}_4$ cell at a current rate of 0.1 mA was the most severe among these cells inspite of the largest initial capacity. The capacity loss was calculated after the first thirty cycles, which capacity loss can be defined as $((C_1 - C_n)/C_1) \times 100\%$, here C_1 and C_n are the discharge capacity of first and n th cycle, n is the number of cycles. On the other hand, for $\text{Li/LiMn}_{1.925}\text{Cr}_{0.075}\text{O}_4$ cell, as increased the current rate from 0.1 to 0.3 mA, the initial capacity decreased from 124 to 121 mAh g^{-1} , however, the discharge capacity loss of $\text{Li/LiMn}_{1.925}\text{Cr}_{0.075}\text{O}_4$ cell also decreased from 6.2 to 4.1%. Similar tendency was also obtained in $\text{Li/LiMn}_{1.925}\text{Co}_{0.075}\text{O}_4$ cell. As increased the current rate from 0.1 to 0.3 mA, the initial capacity decreased from 116 to 114 mAh g^{-1} . Whereas, the discharge capacity loss of $\text{Li/LiMn}_{1.925}\text{Co}_{0.075}\text{O}_4$ cell also decreased from 7.7 to 7.0%. From the capacity loss at different current rates, we can obtain the result that Cr-substituted spinel showed lower capacity loss than Co-substituted spinel. These

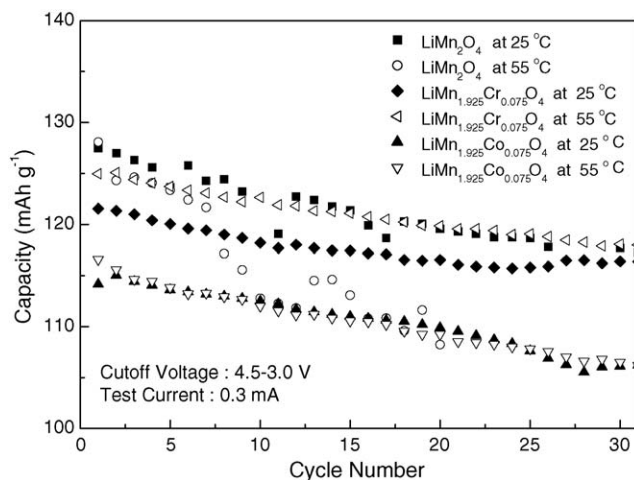


Fig. 2. Relationships between the discharge capacity of the cathode and the cycle numbers of $\text{Li/LiMn}_2\text{O}_4$ and $\text{Li/LiMn}_{1.925}\text{M}_{0.075}\text{O}_4$ ($M=\text{Cr}, \text{Co}$) cells between 3.0 and 4.5 V at various current rates at 25°C .

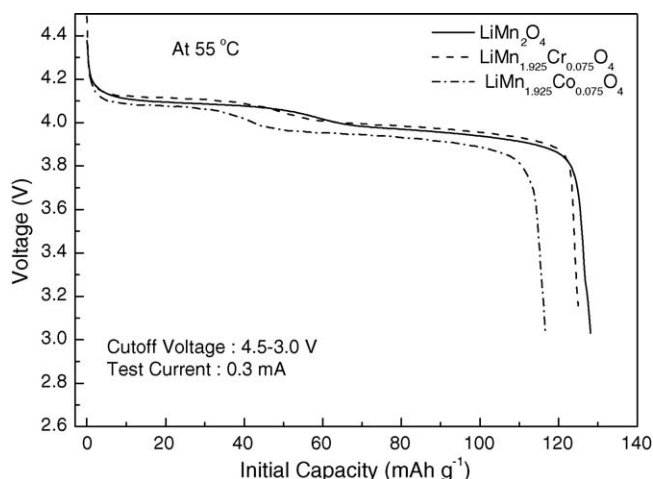


Fig. 3. The initial discharge curves between 3.0 and 4.5 V for Li/LiMn₂O₄ and Li/LiMn_{1.925}M_{0.075}O₄ (M=Cr, Co) cells at current rates of 0.3 mA at 55 °C.

results may be ascribed to the fact that Cr or Co-substituted spinels suppressed the Jahn–Teller distortion in the spinel structure. In addition, the bonding energy of Cr–O (1142 kJ mol⁻¹) and Co–O (1067 kJ mol⁻¹) are both stronger than that of the Mn–O (946 kJ mol⁻¹) bond, which results in the stability of the spinel structure.

Fig. 3 shows initial discharge curves for Li/LiMn₂O₄ and Li/LiMn_{1.925}M_{0.075}O₄ cells operated between 4.5 and 3.0 V at 55 °C. Two plateaus are clearly observed for all samples. The Li/LiMn₂O₄ cell provided an initial capacity of 128 mAh g⁻¹ and Cr and Co-substituted spinel provided a slightly lower initial capacity of 125 and 116 mAh g⁻¹, respectively, operated at 55 °C. In order to investigate the cycling performance at various operating temperature, we plotted the relation between the capacity and cycle number for Li/LiMn₂O₄ and Li/LiMn_{1.925}M_{0.075}O₄ cells at a current rate of 0.3 mA at 25 and 55 °C in Fig. 4. It indicates that the discharge capacity loss of the cells using Li/LiMn₂O₄ is a maximum than Cr and Co-substituted spinels at 55 °C. When the Li/LiMn_{1.925}M_{0.075}O₄

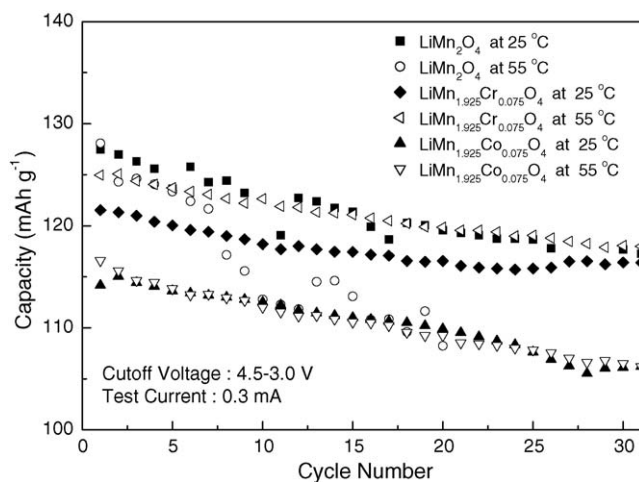


Fig. 4. Relationships between the capacity and cycle numbers of the Li/LiMn₂O₄ and Li/LiMn_{1.925}M_{0.075}O₄ (M=Cr, Co) cells between 3.0 and 4.5 V at a current rate of 0.3 mA at various temperatures.

cells with M=Cr, the capacity loss reached a minimum about 5.4% at 55 °C. Obviously, capacity loss at 55 °C is greater than 25 °C for all samples. This may be described to two reasons: (1) the high Mn species dissolve into the electrolyte solution leading to capacity fading. (2) the electrolyte solution decomposed at high temperature also leading to capacity fading.

4. Conclusions

Using lithium nitrite, manganese nitrate, chromium nitrate, cobalt nitrate, and urea as the starting materials, ultrafine LiMn_{1.925}M_{0.075}O₄ (M=Cr, Co) powders have been synthesized successfully by microwave-induced combustion. Results of this study show that substituted contents affect greatly the electrochemical properties of LiMn_{1.925}M_{0.075}O₄ samples for lithium-ion battery. The results revealed that the cycle performance of Li/LiMn_{2-y}M_yO₄ cells at higher temperature (55 °C) and higher current rate (0.3 mA) can be significantly improved by appropriate substituted with Cr or Co. This may be ascribed to Cr or Co-substituted suppressed the Jahn–Teller effect in spinel structure.

The conclusions for Li/LiMn₂O₄ and Li/LiMn_{1.925}M_{0.075}O₄ (M=Cr, Co) cells prepared by microwave-induced combustion method are the following:

- (1) The capacity loss at various current rates and at various temperatures can be ranked as follows: LiMn₂O₄ > LiMn_{1.925}Co_{0.075}O₄ > LiMn_{1.925}Cr_{0.075}O₄.
- (2) The initial capacity at various current rates and at various temperatures can be ranked as following: LiMn₂O₄ > LiMn_{1.925}Cr_{0.075}O₄ > LiMn_{1.925}Co_{0.075}O₄.
- (3) The cycle performance of Cr-substituted spinel is better than Co-substituted spinel at various current rates and at various temperatures.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 93-2622-E-259-004-CC3.

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